NATURE OF THE RADICAL INTERMEDIATES IN A SUBSTITUTED CYCLOPROPYLCARBINYL--ALLYLCARBINYL SYSTEM

Thesis by

Thomas A. Halgren

In Partial Fulfillment of the Requirements
For the Degree of
Doctor of Philosophy

California Institute of Technology
Pasadena, California
1968
(Submitted February 2, 1968)

ACKNOWLEDGEMENTS

To Professor John D. Roberts, we express our sincere appreciation, both for his continuing interest in this research and for the liberal--and challenging--degree of freedom allowed us in major elements of the conception and execution of this work. Not to be overlooked has been his financial steadfastness in the waning days of this work.

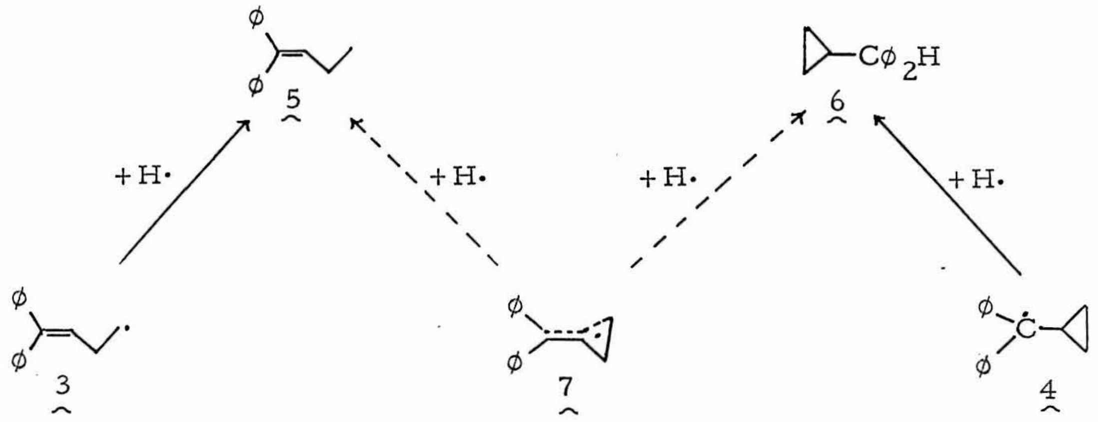
Thanks are also due many past and present members of the Roberts Group who allowed me to help in their work and who helped me in mine. Among these are Jack Firkins, Frank Weigert, Joe Dence, and Mel Winokur, and Drs. Joe Lambert, Gerhart Binsch, Adalbert Maercker, and Jim Magnuson.

Among other Faculty Members, admiration must be expressed for Dr. G. S. Hammond, who has maintained an interest in this work to the date of this writing. Had we only made more frequent use of his counsel!

Financial assistance in the form of scholarships, teaching assistantships, and research assistantships provided by the Institute is gratefully acknowledged.

ABSTRACT

We have sought to determine the nature of the free-radical precursors to ring-opened hydrocarbon 5 and ring-closed hydrocarbon 6. Reasonable alternative formulations involve the postulation of hydrogen abstraction (a) by a pair of rapidly equilibrating classical radicals (the ring-opened allylcarbinyl-type radical 3 and the ring-closed cyclopropylcarbinyl-type 4), or (b) by a nonclassical radical such as homoallylic radical 7.

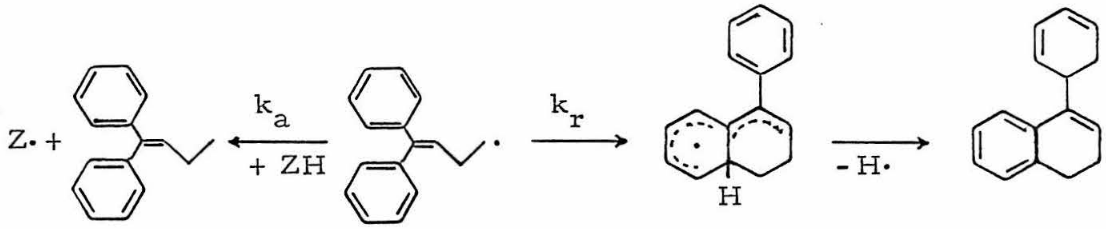


Entry to the radical system is gained via degassed thermal decomposition of peresters having the ring-opened and the ring-closed structures. The ratio of 6:5 is essentially independent of the hydrogen donor concentration for decomposition of the former at 125° in the presence of triethyltin hydride. A deuterium labeling study showed that the α and β methylene groups in 3 (or the equivalent) are rapidly interchanged under these conditions.

Existence of two (or more) product-forming intermediates is indicated (a) by dependence of the ratio 6:5 on the tin hydride concen-

tration for decomposition of the ring-closed perester at 10 and 35°, and (b) by formation of cage products having largely or wholly the structure (ring-opened or ring-closed) of the starting perester.

Relative rates of hydrogen abstraction by 3 could be inferred by comparison of ratios of rate constants for hydrogen abstraction and *ortho*-ring cyclization:



5 3 9 10

At 100° values of k_a/k_r are 0.14 for hydrogen abstraction from 1,4-cyclohexadiene and 7 for abstraction from triethyltin hydride. The ratio 6:5 at the same temperature is ~0.0035 for hydrogen abstraction from 1,4-cyclohexadiene, ~0.078 for abstraction from the tin hydride, and ≥ 5 for abstraction from cyclohexadienyl radicals. These data indicate that abstraction of hydrogen from triethyltin hydride is more rapid than from 1,4-cyclohexadiene by a factor of ~1000 for 4, but only ~50 for 3.

Measurements of product ratios at several temperatures allowed the construction of an approximate energy-level scheme. A major inference is that isomerization of 3 to 4 is exothermic by 8 ± 3 kcal/mole, in good agreement with expectations based on bond dissociation energies. Absolute rate-constant estimates are also given.

The results are nicely compatible with a classical-radical

mechanism, but attempted interpretation in terms of a nonclassical radical precursor of product ratios formed even from equilibrated radical intermediates leads, it is argued, to serious difficulties.

The roles played by hydrogen abstraction from 1,4-cyclohexadiene and from the derived cyclohexadienyl radicals were probed by fitting observed ratios of **6**:**5** and **5**:**10** in the sense of least-squares to expressions derived for a complex mechanistic scheme. Some 30 to 40 measurements on each product ratio, obtained under a variety of experimental conditions, could be fit with an average deviation of ~6%. Significant systematic deviations were found, but these could largely be redressed by assuming (a) that the rate constant for reaction of **4** with cyclohexadienyl radical is inversely proportional to the viscosity of the medium (i.e., is diffusion-controlled), and (b) that k_a/k_r for hydrogen abstraction from 1,4-cyclohexadiene depends slightly on the composition of the medium. An average deviation of 4.4% was thereby attained.

Degassed thermal decomposition of the ring-opened perester in the presence of the triethyltin hydride occurs primarily by attack on perester of triethyltin radicals, presumably at the –O–O– bond, even at 0.01 M tin hydride at 110 and 125°. Tin ester and tin ether are apparently formed in closely similar amounts under these conditions, but the tin ester predominates at room temperature in the companion air-induced decomposition, indicating that attack on perester to give the tin ether requires an activation energy approximately 5 kcal/mole in excess of that for the formation of tin ester.

TABLE OF CONTENTS

PART PAGE

PART PAGE

LIST OF TABLES

LIST OF FIGURES

LIST OF CHARTS

AN OVERVIEW

Theses, at least those recently submitted in Chemistry at this Institution, generally begin with an introduction in which the stage is set for the presentation of the current results and conclusions. That, however, is not the principal purpose of this section. To be sure, a liberal amount of stage-setting will be indulged, but generally at appropriate points later in the text.

As this thesis describes work in the field of free-radical rearrangements in small-ring compounds, an argument can be made for including a comprehensive introduction for the convenience of readers not reasonably conversant with the field. However, treatments of suitable length and scope are available in reasonably accessible sources, and this thesis is quite long enough as it is. I shall therefore simply list here available treatments and leave it to the reader to make whatever use of them he wishes.

The introductory section to a recent paper by Montgomery (1) conveys rather briefly (two and a half journal pages) the essential flavor of the field. Though structured to suit his particular uses, the discussion is appropriate here as well, for both Montgomery's work and mine emphasize rearrangements between cyclopropylcarbinyl radicals and their allylcarbinyl counterparts. The first and third subsections (about 25 pages) of the introduction to Rosen's 1964 thesis (2) discuss skeletal rearrangements of this particular type. The introduction (30 pages) to Schuster's 1961 thesis (3) covers much of the same ground, but includes as well a discussion of radical rearrangements in a number of other systems. Pryor's recent book "Free Radicals" (4) contains an easily readable chapter covering the literature on radical rearrangements through 1964. Finally, comprehensive literature reviews have been supplied by Walling (5) and by Freidlina (6).

1. Purpose of this Overview

The subject of this thesis is a complex one. In the spirit of the greatest possible clarity, no attempt will be made to use the detective-story mode of presentation. Indeed, the opposite will be attempted; to show the pattern of the results and their interpretation as early as possible and, in steadily increasing depth of rigor and sophistication, to demonstrate the validity of the interpretation. To this end, this section is intended to give a brief overview of the principal results obtained in this work and of the approach we shall take in seeking to interpret those results.

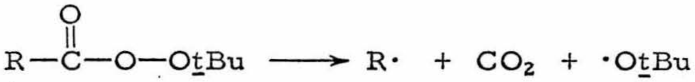
2. A Few Comments on Terminology

Some 28 compounds or intermediates not possessing conveniently short trivial names are discussed on multiple occasions in this thesis. Because it would be awkward to give, at each mention, the full chemical name, the various compounds have been assigned numbers in the order of their appearance in the text. I have been importuned to realize, however, that a total reliance on numerical designations places a severe strain on the reader unless a structure is indicated after any sizable gaps between the occasions that the associated number is used. A mixed system has therefore been employed. A numbered compound will be referenced by its number if the relationship between the number and the structure has been recently reinforced; or by a valid chemical name; or by use of an established synonym, generally in conjunction with the numerical designation. Synonyms may be contractions on the chemical name (e.g., diphenylbutene or the butene for 1,1-diphenyl-1-butene), but more commonly characterize some structural feature of the referenced compound (e.g., 'ring-opened hydrocarbon' and 'ring-closed hydrocarbon' for 1,1-diphenyl-1-butene and diphenylcyclopropylmethane, respectively).

The reader may find quite useful the listing of numbers and structures enclosed in a jacket on the inside back cover. A second copy has been placed preceding the list of references for use in microfilmed copies of this thesis.

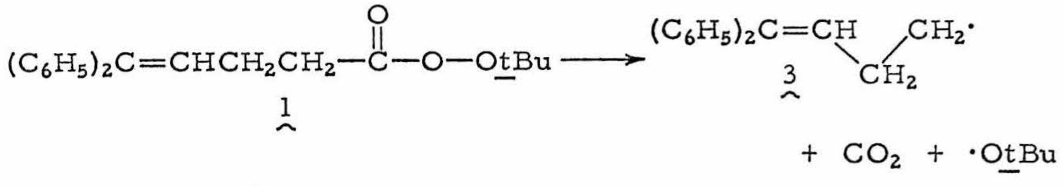
3. A Brief Overview of Principal Results and Conclusions

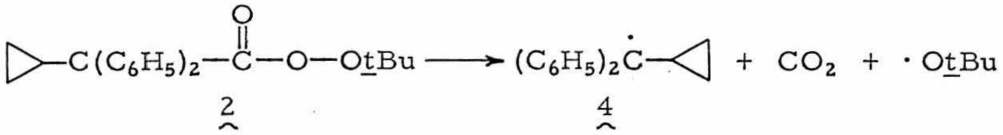
Nonacid-catalyzed thermal decomposition of *t*-butyl peresters appears to be a general means of generating alkyl or aryl free radicals of reasonably predetermined structure (7). For example, if one wished to study ethyl radicals, the perester of choice would be *t*-butyl perpropanoate, $\mathrm{CH_3CH_2CO_2O}\underline{\mathrm{t}}\mathrm{Bu}$. Similarly, a radical R· could be prepared by thermolysis of the structurally related perester, as below:



$$\mathrm{R{-}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{{-}O{-}O}\underline{\mathrm{t}}\mathrm{Bu} \longrightarrow \mathrm{R}\cdot + \mathrm{CO_2} + \cdot\mathrm{O}\underline{\mathrm{t}}\mathrm{Bu}$$

Thermal decomposition of the isomeric peresters **1** and **2** would then be expected to generate the radicals **3** and **4**, respectively. The principal goal of this research has been to characterize the chemical behavior of the 16-carbon radicals generated in this way. Perhaps the most interesting aspect of this problem arises from the possibility that radicals with ring-opened and ring-closed structures can interconvert. For example, attack of the radical center in ring-opened radical **3** on the nearer of the olefinic carbons produces the isomeric radical **4**. Similarly, **3** can be regenerated from **4** by the opening of one of the two equivalent cyclopropyl-ring bonds.

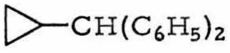




This suggests that products with both ring-opened and ring-closed structures might be formed whichever the perester employed. Such is indeed the case. In particular, the ring-opened hydrocarbon 1,1-diphenyl-1-butene (**5**) and the ring-closed diphenylcyclopropylmethane (**6**) are produced via abstraction of hydrogen from suitable hydrogen donors.

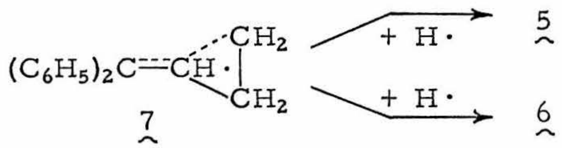
$(C_6H_5)_2C{=}CHCH_2CH_3$

5



6

The radical precursors of **5** and **6** might well be the ring-opened and ring-closed radicals **3** and **4**, each giving the structurally related hydrocarbon. However, the situation need not be so simple, for it is conceivable that a bridged "nonclassical" radical such as 7 (which represents a structural compromise between the limiting forms 3 and 4) might give rise upon hydrogen abstraction either to ring-opened or to ring-closed material. (A general definition of what might be meant by a nonclassical radical will be attempted in Section Three. For the present I shall assume familiarity with the concept as embodying attack of a reagent at more than one site and as possibly associated with unusually rapid rates of formation of intermediates.)



Thus, a principal purpose of the present account will be to marshal evidence on the nature of the radical intermediates which give rise to the isomeric hydrocarbons 5 and 6. As will become apparent, however, this thesis really has two stories to tell. The second will be to give a mechanistic description of the rather complicated sequence of reactions by which radicals generated as above are converted to the several stable products under a variety of experimental conditions.

In reality, the two stories are intimately related. Some of the observations and interpretations we shall find to be of great importance in deciding on the involvement of a species such as 7 do not leap unencumbered from the experimental data, but rather arise from a detailed characterization of the reaction mechanism. Moreover, for other cases in which interpretation of the data is *apparently* straightforward, our confidence in those interpretations will be greatly enhanced by the general success of the mechanistic formulation.

In a spirit of reciprocity, it might be asked whether the mechanistic study does not itself require assumptions concerning the nature of the intermediates which give rise to the isomeric hydrocarbons 5 and 6; and if so, whether such assumptions do not prejudice the interpretation of the data. In general, the answer is that such assumptions will frequently be made, but that the interpretation of the data is not prejudiced. The reason is that the intermediates giving rise to 5 and 6, whatever their nature, are generally in rapid equilibrium; and as every good kineticist knows, under such circumstances the form of derived equations is independent of which reactions are attributed to which of the equilibrated species. Alternative assignments change the interpretation of various parameters, but the matter of interpretation can be taken up after the values of the parameters have been extracted from the data.

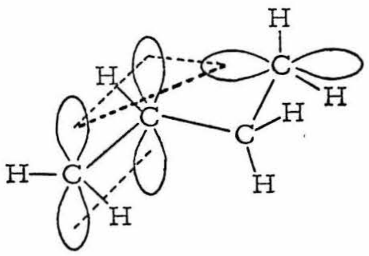
In the remaining pages of this Overview we shall make a start on each of the two stories. First we shall indicate why we have chosen to examine the present system for the intervention of a nonclassical radical such as 7 and we will give some examples of the types of information employed in that examination. Then we will survey the main features of the overall reaction mechanism and indicate the approach to be taken in giving a more complete description later in the thesis.

The nonclassical carbonium ion problem has commanded substantial interest over the past two decades. The *reprint collection*

"Nonclassical Ions" edited by Bartlett features many important papers in this field (8). As is well known, kinetic evidence points to very large driving forces in some systems for the bridging-with-charge-delocalization associated with the formation of the nonclassical ion. In contrast, there seem to be no analogous examples of nonclassical hydrocarbon free radicals (we exclude here bromine-bridged radicals (9)), even though the free-radical chemistry of several of the systems showing exotic behavior in carbonium ion reactions has been investigated. For example, formation of norbornyl or 5-norbornenyl radicals is unexceptional on kinetic grounds (10, 11). Moreover, the results of products studies on the 5-norbornenyl-nortricyclyl radical system are inconsistent with the sole intermediacy of a nonclassical radical capable of giving products of either structural form (12).

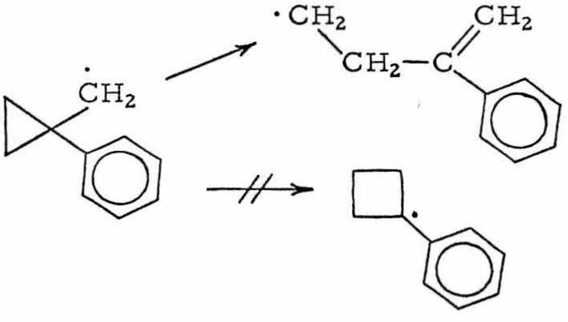
Apparently, in many cases the driving force for formation of a bridged intermediate in a carbonium ion system is wholly or entirely lost upon addition of the extra electron possessed by the analogously constituted free-radical system. It may be significant that semi-empirical molecular orbital calculations predict that this might be the case (13). Still, it is not yet clear that the diminished driving force will preclude altogether the formation of nonclassical radical intermediates. In attempting to resolve this uncertainty, it seems reasonable to carefully examine the free-radical chemistry of additional systems which apparently show substantial inclination toward formation of nonclassical intermediates in carbonium ion reactions; the present work is a case in point.

The facile interconversions of isomeric allylcarbinyl, cyclopropylcarbinyl, cyclobutyl systems in carbonium ion systems is well known and has been plausibly interpreted in terms of nonclassical bicyclobutonium ions (14). The sketch below indicates a proposed structure

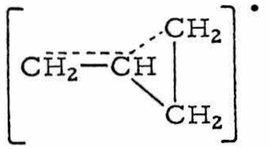


for the parent four-carbon bicyclobutonium ion (13a). Attack of solvent or an anion on the carbon at lower left leads to cyclopropylcarbinyl product. Similarly, attack at upper right gives allylcarbinyl product, and attack at the central carbon leads to cyclobutyl product.

One principal difference in the chemistry of analogously constituted radical intermediates is that allylcarbinyl and cyclopropylcarbinyl structures do not seem to be interconvertible with cyclobutyl structures (15). This generalization holds even where substitution should strongly promote just such an interconversion (15a):



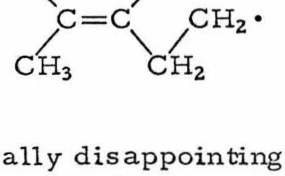
For this reason, speculation on nonclassical free-radical intermediates in this type of system has focused on structures of the so-called homoallylic type, as below:

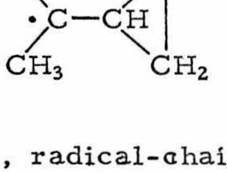


Free-radical studies on the parent 4-carbon system have been reported by several groups. Kinetic evidence indicates that the cyclopropylcarbinyl radical is formed substantially more easily than a typical primary radical (16). However, products studies have proved disappointing in that on hydrogen abstraction at best trace amounts of cyclopropylmethane are formed (17). Only in the chlorination of cyclopropylmethane have substantial amounts of the cyclopropylcarbinyl product been observed (16b, 18). These results have been reviewed by Rosen (2).

Evidently, if classical cyclopropylcarbinyl and allylcarbinyl radicals are involved, the former is less stable than the latter. Alternatively, if products are formed via a nonclassical species, that species probably closely resembles the allylcarbinyl radical. In either case, it seemed reasonable to try to effect closer competition by selectively stabilizing the cyclopropylcarbinyl form.

The ring-opened and ring-closed radicals for the dimethyl-substituted system are shown below. However, product studies here have

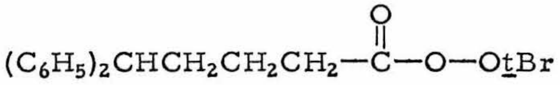




also been generally disappointing. Thus, radical-chain reduction of γ,γ-dimethylallylcarbinyl bromide by tri-*n*-butyltin hydride gave dimethylbutene with only a trace (less than 0.2%) of isopropylcyclopropane (19a). In contrast, decarbonylation of dimethylcyclopropylacetaldehyde did give 18% isopropylcyclopropane when carried out in the presence of approximately 3 M benzylmercaptan (19b). However, the reaction appears to be too complex to permit dilineation of the mechanistic pathways by which this material was formed (20).

Phenyl groups would be expected to be much more effective than methyl groups in increasing the stability of the ring-closed radicals. Accordingly, Howden (21) ran a preliminary investigation on the diphenyl-substituted system using perester 1 as a radical source. The most encouraging results were obtained when tri-*n*-butyltin hydride was employed as the hydrogen donor (see Table 12, p. 44). In particular, ring-opened hydrocarbon 5 and ring-closed hydrocarbon 6 are observed in proportions of about twenty to one for decomposition of 1 from 110 to 150° and 0.056 to 0.56 M in the initial tin hydride concentration. The lack of any substantial product dependence on the hydrogen donor concentration is consistent either with a mechanism in which both products are formed from a nonclassical radical such as 7, or with one in which the two classical radicals (3 and 4) are able to equilibrate rapidly with respect to hydrogen abstraction by either. Mechanisms involving both classical and nonclassical radicals are also possible, but for simplicity it seems desirable to restrict our attention, at least initially, to the two limiting possibilities.

Unlike the unsubstituted system discussed previously, the available kinetic evidence does not suggest that radical intermediates are formed more easily than might be expected from model compounds. Howden measured the rates of decomposition in chlorobenzene at 110° of ring-opened perester 1 and its saturated analogue 8. He found that the former decomposes only about 40% faster than the latter. Furthermore,



$$(C_6H_5)_2CHCH_2CH_2CH_2{-}\overset{O}{\overset{\|}{C}}{-}O{-}O\underline{t}Br$$

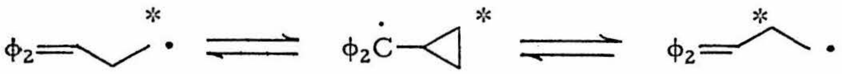
8

more, the rate constant for 1 is nearly the same as the rate constants observed by Trachtman and Miller for a series of peresters in which the R group is long-chain primary aliphatic (22). Half-lives for 1 and 8 and for two of the four cases studied by Trachtman and Miller are listed in Table 13, p. 51.

A detailed discussion of structure and reactivity of peresters is deferred until Section One. However, we can point out here that peresters giving phenyl-stabilized radicals decompose three and four orders of magnitude faster than primary aliphatic peresters (see Table 13). Thus, direct formation of a nonclassical radical from 1 should be accompanied by a large rate increase, unless the decrease in the energy of activation expected to be associated with any bridging in the decomposition transition state should happen to be largely balanced by the decrease in entropy associated with the greater restriction bridging implies. Activation parameters would be useful in this connection, but are unavailable.

We shall accept, with Howden (23), the implication that the classical ring-opened radical 3 is formed upon decomposition of perester 1. However, 3 might rapidly isomerize to 7, with that species then giving rise to the hydrocarbon products. To rule on that eventuality, we shall have to turn to studies on product composition.

One way in which the existence of a nonclassical radical such as 7 might be demonstrated is suggested by the elementary discussion of the interconversion of the classical radicals given on page 4. Because regeneration of the ring-opened radical 3 from 4 can be effected by the opening of either of two cyclopropyl-ring bonds, equilibration of the



3 4 3

classical radicals must exchange the methylene groups of the ring-opened radical; and the presence or absence of such an exchange can be detected by suitable labeling. Using deuterium labeling it has been found (p. 94–97) that the methylene-group exchange is rapid with respect to hydrogen abstraction from triethyltin hydride (1.3 M) at 125°.

We should note, however, that while the absence of exchange would point to the intermediacy of a nonclassical radical, the finding that the exchange proceeds does not suffice to disprove the intermediacy of such a species. If a nonclassical radical were only slightly more stable than the classical ring-closed radical, equilibrium between the two might be rapidly established, and this process would exchange the methylene groups.

In seeking to establish the nature of the radical intermediates, information on their number would be especially valuable. Such information can now be reported. Specifically, the ratio of ring-closed to ring-opened hydrocarbon for decomposition of the (more reactive) ring-closed perester 2 at 10 and 35° in the presence of triethyltin hydride is not independent of the tin hydride concentration, but increases in a linear fashion (Fig. 8, p. 100) as is predicted for selective trapping of a first-formed radical intermediate. That species might well be the classical ring-closed radical 4, but the actual observations do not demand this interpretation. What is established is that more than one radical intermediate gives rise to the isomeric hydrocarbons.

Information is also available concerning the dependence of the ratio of the two hydrocarbons on the reactivity of the hydrogen donor and on the reaction temperature.

The response of the radical system to the nature of the hydrogen donor has been probed using three hydrogen donors which cover a wide range in reactivity. The three are: 1,4-cyclohexadiene, possibly one of the most active of purely hydrocarbon donors; triethyltin hydride, indicated by several measures to be substantially more active than 1,4-cyclohexadiene; and the cyclohexadienyl radical, expected to be extremely reactive because it acts as a hydrogen donor in disproportionation-type reactions which are known to have high preexponential factors and minimal or nonexistent activation energies. The quantity of interest here is the ratio of ring-closed hydrocarbon 6 to ring-opened hydrocarbon 5 under conditions in which the radicals involved have sufficient time to reach equilibrium amongst themselves; we will call this quantity (which may not always be directly measurable) the *characteristic ratio*. Characteristic ratios at 100° are 0.0035 for 1,4-cyclohexadiene, 0.08 for triethyltin hydride, and greater (possibly by orders of magnitude) than 5 for the cyclohexadienyl radical.

Characteristic ratios will be temperature dependent unless the transition states for hydrogen abstraction leading to the two hydrocarbons (see Fig. 23, p. 333) happen to be of identical energy. If the transition state for formation of the ring-closed hydrocarbon lies below that for formation of the ring-opened isomer, the relative amount of the ring-closed isomer will be greater at lower reaction temperatures. This is the pattern observed experimentally for the hydrogen donors 1,4-cyclohexadiene and triethyltin hydride. Transition-state energy differences are found to be 1-2 kcal/mole for the former and 3 kcal/mole for the latter. In addition, a good argument can be made that the cyclohexadienyl radical conforms to the pattern with a difference of about 8 kcal/mole.

We shall find that such observations are easily explained if one assumes that only classical radicals are involved, but that a non-classical radical would have to behave very strangely indeed to reproduce the experimental observations.

Additional information which cannot be so directly stated is brought out in Sections One and Two of this thesis in the course of the detailed mechanistic treatment.

The reader may be curious to know how information on the characteristic ratio for hydrogen abstraction from cyclohexadienyl radicals was obtained. In general, one simply employs a hydrogen donor of interest as solvent. Such a course would clearly be impossible for a free-radical donor. It is possible, however, to generate cyclohexadienyl radicals *in situ* by allowing the peresters to decompose in the presence of 1,4-cyclohexadiene, whence some of the radicals abstract hydrogen from cyclohexadiene.

Because 1,4-cyclohexadiene and the derived cyclohexadienyl radicals can both serve as hydrogen donors, a mechanistic analysis is required to determine which products of interest result from hydrogen abstraction from which of these donors, and, indeed, to evaluate whether the observations can successfully be accounted for on any such basis. The mechanistic study of Section Two will focus primarily on results obtained for decomposition of the peresters (at various initial concentrations) in the presence of 1,4-cyclohexadiene (also at various initial concentrations) and at various reaction temperatures. However, it will also be instructive and reassuring to correlate in a similar manner the less extensive data for decomposition of the peresters in the presence of triethyltin hydride.

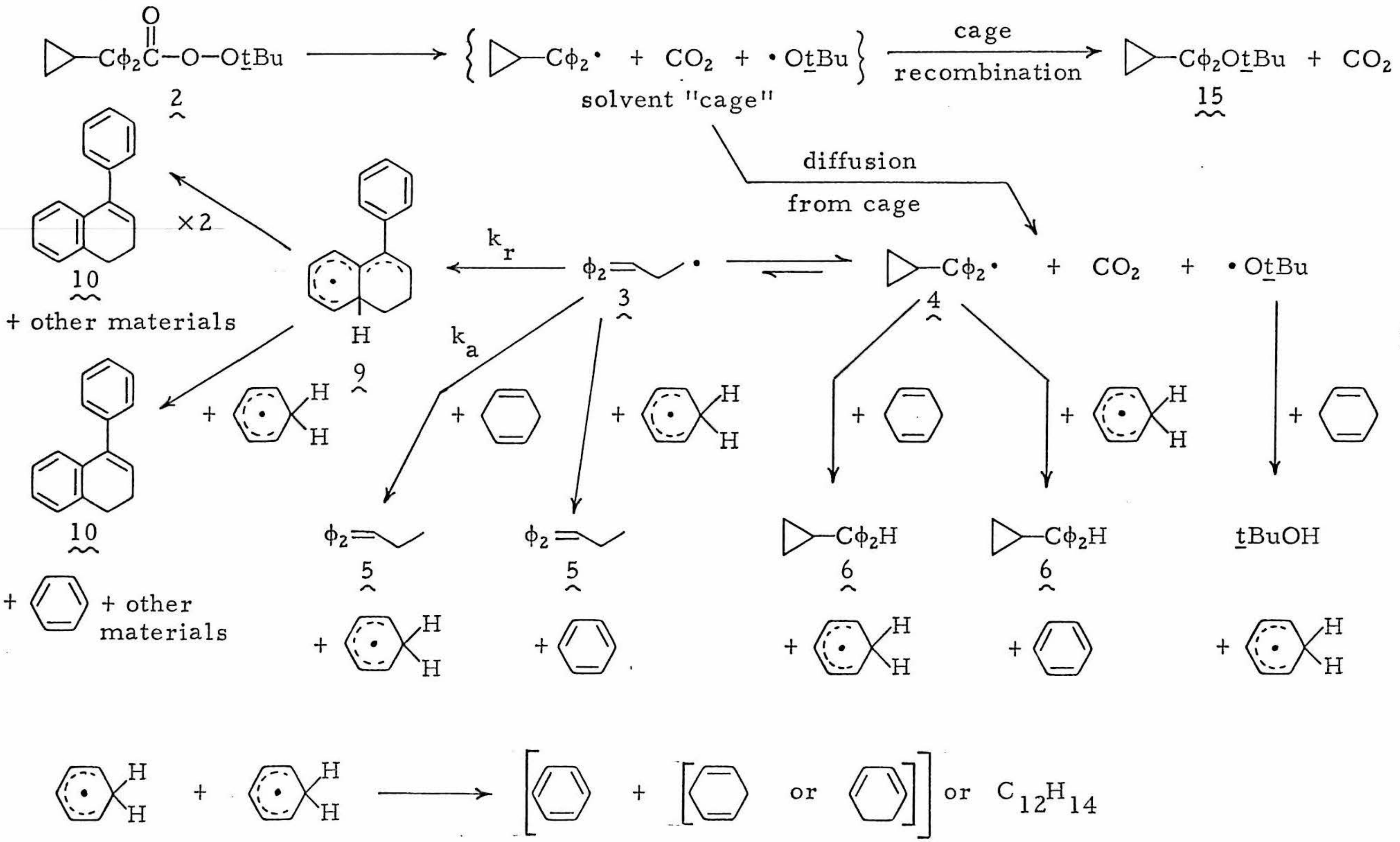
It will be helpful to subdivide the task of establishing a reaction mechanism. In the first part (Section One) we shall construct a mechanistic scheme to account for the dozen or so reaction products. In the second (Section Two) we shall derive and test mechanistic expressions based on that scheme.

To impart a workable measure of order to the construction of the trial mechanistic scheme, we shall follow in time the fate of a pair of free-radical intermediates produced simultaneously by decomposition of a perester molecule. This procedure is suggested by our observations which indicate that the major reaction steps fall into a number of classes associated with reasonably well-separated characteristic times. Time limits for some of the processes are given below. Because certain of the processes have appreciable activation energies the time limits will, of course, vary widely with the reaction temperature. The numbers cited below refer to a reaction temperature of 100°.

The reactions discussed here are depicted in Chart 1. For simplicity (vide infra), we shall consider the decomposition of the ring-closed perester 2 rather than that of the ring-opened perester 1. We start our clock at the moment a perester molecule fragments. The products of that fragmentation may be taken to be a ring-closed radical 4, a molecule of carbon dioxide, and a t-butoxy radical. Because the radical pair is initially separated by only a few angstroms, (re)-combination or disproportionation of the radical pair competes with diffusive separation. Such reactions, said to occur within an initial solvent cage (which is indicated by curly brackets in Chart 1), are probably important to times up to about 10^{-9} seconds; if reaction is not effected within this period, diffusion may be expected to have increased the separation of the radical pair to such an extent that subsequent reaction between the once-caged radicals will be improbable (24). Cage recombination to form the t-butyl ether 15 is illustrated in Chart 1; disproportionation to t-butyl alcohol and diphenylmethylenecyclopropane (16) apparently occurs as well.

We shall find that equilibration of the ring-opened and ring-closed radicals is inappreciable during the time in which nearly all of the cage product is formed, but appears to be nearly complete by 10^{-8} seconds after the fragmentation. The nature of the kinetics is

Chart 1. A Partial Mechanistic Scheme for Thermal Decomposition of t-Butyl Diphenylcyclopropylperacetate in the Presence of 1,4-Cyclohexadiene.



such that this figure would apply for decomposition at 100° of either perester. Only for triethyltin hydride can hydrogen abstraction compete with the establishment of the equilibrium. Even in this case, effective competition requires temperatures much lower than 100°; as remarked earlier, selective trapping of the first-formed intermediate is observed at 10 and 35°. Evidently, the processes which interconvert the radical intermediates slow more strongly as the reaction temperature is decreased than do the hydrogen abstraction processes when the hydrogen donor is triethyltin hydride.

Formation of the ring-opened and ring-closed hydrocarbons can proceed until about 10^{-4} sec after the fragmentation. The time limit of this case is established by the rate of *ortho*-ring-cyclization by (presumably) the ring-opened radical **3** to the so-called ring-cyclized radical **9** (see Chart 1). This process is an intramolecular analog of the addition of free radicals to aromatic systems which has been extensively investigated by Szwarc and co-workers (25).

Rate constants for the two processes are denoted by k_r for the ring-cyclization and k_a for hydrogen abstraction by the ring-opened radical from hydrogen donor ZH. The major product from the ring-cyclized radicals is 1-phenyl-3,4-dihydronaphthalene (**10**), formed principally by disproportionation of ring-cyclized radicals or by loss of a hydrogen atom to solvent radical Z· by **9**. As conversion of **9** to **10** is fairly efficient, we can write approximately

$$\frac{d(\mathbf{5})}{d(\mathbf{10})} \cong \frac{k_a(\mathrm{ZH})(\mathbf{3})}{k_r(\mathbf{3})} \quad ,$$

so that

$$\frac{k_a}{k_r} \cong \frac{\text{Yield of } 5}{\text{Yield of } 10 \times (\text{ZH})_{av}}$$

Values of k_a/k_r estimated for the hydrogen donors triethyltin hydride, 1,4-cyclohexadiene, and indene (taking approximately into account the inefficiency in the conversion of 9 to 10) are about 7, 014, and 0.03, respectively at 100°. All other solvents investigated (cyclohexane, ether, tetrahydrofuran, benzene, cumene, tetraethyltin) are so much less active as hydrogen donors that only trace amounts of the diphenylbutene 5 are formed. By this test, then, triethyltin hydride is clearly more active a hydrogen donor toward the ring-opened radical than is 1,4-cyclohexadiene, although both would be classed as relatively active hydrogen donors.

As mentioned above, conversion of the ring-cyclized radical 9 to the dihydronaphthalene 10 (and to other products such as tetrahydronaphthalenes and dimers) occurs principally via radical-radical termination reactions. Estimates of rate constants for such processes (*ca.* 10^9 M^{-1} sec^{-1}) indicate that under certain conditions a ring-cyclized radical might well still be around a second or more after the initial fragmentation.

Section Two - the section dealing with the evaluation of the mechanistic scheme - provides a considerable challenge because expressions for yields or ratios of products derived on the basis of a mechanism like that of Chart 1 are rather complex. In fact, no attempt was made to work out kinetic expressions until rather late in this work, for it was expected that the derived expressions would be so complex as to be essentially useless. For the most part, kinetic treatments in the chemical literature and in text books which are applicable to problems involving reactive intermediates are restricted to cases wherein some function of observables (such as yields and ratios of products, reagent concentrations, the reaction temperature, and so on) can be put in linear form. Such treatments allow the success of a proposed scheme to be evaluated graphically by noting the scatter of points about a best straight line. In the present situation, however, it seems quite safe to say that no such linear relationships can be written.

A more versatile approach is clearly called for, and that taken here can be summarized by the statement that if an expression cannot be tested graphically, it may still be possible to do it numerically. In the approach used (26), an initial set of estimates for the parameters involved is iteratively refined in the sense of least-squares. In mechanistic studies, the parameters will usually be preexponential factors or activation energies for individual rate constants or, more commonly, for such combinations of rate constants as appear together in the mechanistic equations. The success of a candidate mechanism can then be judged in part by how well it can fit the experimental data. In addition, both the numerical values and the standard deviations of the parameters, which are also obtained, can be useful in assessing the reasonableness of the overall mechanism or of individual mechanistic steps. And as remarked earlier in this Overview, values for some of the parameters will be important for our understanding of the nature of the radical intermediates leading to the isomeric ring-opened and ring-closed hydrocarbons.

A scientist's time is perhaps never better spent than in selecting systems for study, or in working out experimental procedures, which simplify matters to the extent possible. However, some things can be learned only in unavoidable complex situations, and in such cases numerical techniques can be indispensible. The computer exists, and the chemist should be prepared to use it. Perhaps publication of work such as this will help to acquaint others with the availability of numerical techniques for mechanistic studies.

In summary, the major part of this thesis will be concerned with the documentation of, and elaboration on, points raised in this Overview. In Section One we shall consider in detail the experimental observations and describe a possible mechanistic scheme. A general procedure for the numerical evaluation of a reaction mechanism will then be introduced in Section Two and applied to the present situation. Finally, the information on the behavior of the ring-opened and ring-closed radicals (or their equivalents) towards the hydrogen donors of interest will be drawn together in Section Three and discussed in the context of the general question of nonclassical free radical intermediates.

In view of the imposing length of this thesis, not at all accurately foreseen when the writing began, we have attempted to make the three Sections as independent as possible. We feel it should be possible for readers primarily interested in question of the nature of the radical intermediates to begin with Section Three, perhaps making use of the abundant references to earlier discussions provided there whenever a strong urge is felt to check up on the support for assertions made in Section Three. Similarly, readers who are primarily interested in the procedure for the least-squares analysis might similarly begin with Section Two; those interested mainly in the results of that analysis may find it sufficient to read the first subsection and the five page summary of the fourth subsection of Section Two.

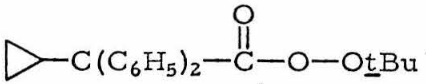
SECTION ONE: DEVELOPMENT OF A CANDIDATE REACTION MECHANISM

1. General Principles

In this section we shall develop a candidate reaction mechanism which assertedly can account in some detail for yields and ratios of reaction products observed for thermal decomposition under various conditions of t-butyl (γ, γ-diphenylallyl) peracetate (1) and t-butyl diphenylcyclopropylperacetate (2). Analysis of the quantitative success of the proposed mechanism in correlating relative yields of certain key products is undertaken in the next section.

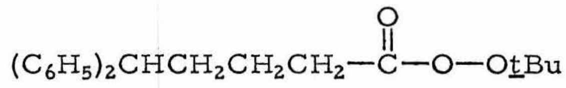
$(C_6H_5)_2C{=}CHCH_2CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}O\underline{t}Bu$

1



2

In addition, for reasons which will become apparent later, we will also be interested in the decomposition of 8, the saturated analog of 1.



$(C_6H_5)_2CHCH_2CH_2CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}O\underline{t}Bu$

8

Thermal decomposition of the peresters was chosen as the means by which to generate the radicals of interest in part for historical reasons (i. e., Howden (21) had previously employed 1) and in part for synthetic reasons (i. e., thanks to Maercker (69) and Bartlett (27), 2 could be made). Fortunately, this general method enjoys a substantial advantage over many of the other methods by which radicals of designated structure can be generated, such as the radical-chain decarbonylation of aldehydes, or the radical-chain reduction of halides by organotin hydrides. The advantage is that most of the main components defining the experimental conditions can be varied independently. For a given perester, those components can be taken to be (a) the identity and concentration of the hydrogen donor, (b) the reaction temperature, (c) the rate at which radicals are generated, and (d) the instantaneous perester concentration.

Of these, (a) has turned out to be perhaps the most important for this study. Changing the activity of the hydrogen donor enables one to study the pathways leading by hydrogen abstraction to product (as was stressed in the Overview for the relative formation of 1, 1-diphenyl-1-butene and diphenylcyclopropylmethane). Changing the concentration and/or the identity of the hydrogen donor may be used to study partitioning between hydrogen abstraction and other types of reaction for radicals of interest (such as the k_a and k_r processes shown in Chart 1).

The factors (b), (c), and (d) in perester decompositions cannot be varied independently, however, for the reason that the values specified for any two suffice to determine that for the third. In particular, the rate of radical generation is given by the product of the rate constant for the decomposition (which, except for solvent effects (66), is determined by the reaction temperature) and the instantaneous perester concentration. Nevertheless, it will be useful to consider briefly mechanistic applications of all three. This is done in the next three paragraphs.

Variation of the reaction temperature will alter kinetic relationships if various processes have different activation energies. If all rate constants can be described by the Arrhenius equation (67), product distributions will vary with temperature in a precise and ordered way, the details of which are fully determined by the assumptions made about the reaction mechanism. If the variations with temperature are found to hold to the expected pattern, the mechanism will be supported.

Of the many types of radical reactions, one which will always be present is bimolecular consumption of radical intermediates via disproportionation and/or combination reactions. Some products, then, will always be formed by reactions of pairs of radicals. If either member of a particular radical pair can be converted to product via pathways which do not involve a second free radical, the yield of the radical-radical product will depend on the steady-state radical concentrations. Formation of the ring-closed hydrocarbon, diphenylcyclopropylmethane, via disproportionation with cyclohexadienyl radicals (see Chart 1, page 17) is a case in point. Here, an alternative pathway for the ring-closed radicals is isomerization to ring-opened radicals, followed by the ortho-ring cyclization to the naphthalene series of products. Thus, we would expect that lower initial perester concentrations (which will lower the radical concentrations without changing temperature-dependent factors) should be associated with decreased yields of diphenylcyclopropylmethane. As Table 6 shows, such is indeed the case. On the other hand, if neither of the radical pair enjoys such options, a quite different result will be found; formation of the radical-radical product may take somewhat longer at lower steady-state radical concentrations, but will still get done. Thus, use of various initial perester allows one to probe for the existence of certain options for particular radical intermediates.

As noted above, for a series of reactions at a common temperature, the steady-state radical concentrations will depend very substantially on the initial perester concentration. However, variation of the initial perester concentration can affect observed product distributions in ways other than the one suggested in the preceding paragraph. Specifically, only in the ideal situation will each molecule of reaction product survive the reaction conditions. In real situations, once-formed products are almost always themselves susceptible to attack by radicals which one would hope could only mind their business of forming primary reaction products. As a result, serious divergencies may arise between the observed product distributions and those which would be observed if each product molecule could be removed, as formed, to a safe place pending a final audit. Such divergencies can cause serious complications in making mechanistic analyses. The problem can usually be minimized (if the destruction of products is in fact due to radical attack) by using initial perester concentrations sufficiently low and hydrogen-donor concentrations sufficiently high that radical intermediates vent their fury entirely on the hydrogen donor. However, this procedure may introduce problems of its own; minor impurities in, or developed by, the solvent can loom large for very low initial perester concentrations. (For a practical example, see below, p. 116.)

In summary, the experimental conditions for decomposition of a given perester can be defined in terms of the solvent composition, the reaction temperature, and the initial perester concentration. The effect of reasonably systematic variations in each of these factors has been investigated in this work.

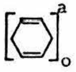
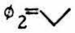
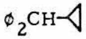
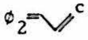
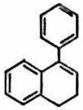
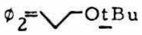
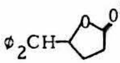
2. Yields and Ratios of Products

Nearly all of the experimental observations to be discussed in this thesis are summarized in the data tables which occupy the next several pages. For each table, the quantities defining the reaction conditions are given in the title and/or in the left-most columns. Observed yields of products are positioned toward the center, with product ratios, if displayed, toward the right. The tables are placed together, rather than being inserted as they are first referenced in the text, in order to make it easy for the reader to locate any given table and to most conveniently make comparisons between entries in different tables. In addition, some or all of the data has also been displayed graphically in Figures 1–4 which immediately follow Tables 1, 2, 3, and 10. Many readers will no doubt find the figures more instructive than the data tables.

A brief description of the general features of the experimental procedure is given in the following several paragraphs. Actually, there is no such thing as <u>the</u> experimental procedure. In view of this, additional information is recorded in the experimental section.

1. All reaction runs appearing in the tables were carried out on degassed samples in sealed tubes, immersed for ten or more half-lives in a bath containing an organic solvent of appropriate boiling point

Table 1. Thermal Decomposition of t-Butyl (γ, γ-Diphenylallyl)peracetate at Approximately 0.26 M[a] in Solutions of 1,4-Cyclohexadiene in Cyclohexane.

Bath Temp., °C	 M	Dimer[b,c] from 	yield, %  5	 6	 [c,d] 13	A[c,d,e]	B[c,d,f]	 10	 12	Sub-Total	 [g] 23	6/5	10 ×  [h] / 5
99	1.11	0.06	9.0	0.30	0.8	2.0	9.7	20.1	20	62	13	0.033	2.01
	2.03	0.09	11.8	0.24	1.0	1.9	7.6	15.6	17	55	12	0.020	2.42
	4.28	0.12	20.6	0.27	1.1	2.2	8.2	12.7	19	64	20	0.013	2.48
	4.28	0.11	19.7	0.26	1.3	2.6	8.4	13.8	17	63	--	0.013	2.86
	8.51	0.14	28.6	0.29	1.1	2.4	5.8	9.8	15	63	--	0.010	2.83
131	1.08	0.08	9.5	0.49	1.0	2.1	13.6	25.7	17	70	--	0.052	2.53
	1.98	0.09	14.4	0.40	1.1	2.3	12.1	21.8	19	71	18	0.028	2.74
	4.17	0.13	22.2	0.31	1.1	2.4	10.7	16.7	15	68	--	0.017	3.00
	8.28	0.17	30.4	0.33	1.3	2.8	9.5	11.6	15	71	--	0.011	3.14
150	1.06	0.06	8.1	0.41	0.9	1.9	12.2	24.6	15	63	13	0.051	2.74
	1.94	0.07	13.7	0.44	1.0	2.4	15.6	22.7	17	73	--	0.034	3.07
	4.08	0.10	21.7	0.43	1.2	2.3	11.5	17.5	12	67	12	0.020	3.16
	8.12	0.14	31.3	0.41	1.4	2.9	8.4	13.4	15	73	--	0.013	3.40
	8.12	--	31.5	--	1.0	2.6	10.0	13.5	13	71	--	--	3.41

[a] Assuming 12% volume expansion per 100° temperature rise.

[b] mmoles per mmole perester taken.

[c] Equal moles of this material and 5 assumed to give equal vpc peak areas.

[d] Total for these three accurately known; separation into components approximately effected by triangulation.

[e] May be benzophenone; see text, pp. 121, 122.

[f] Thought to consist of one or more isomeric 1-phenyltetrahydronaphthalenes; see pp. 77, 78.

[g] Tentatively identified; see Section One, subsection 6.

[h] From Table 17, p. 297.

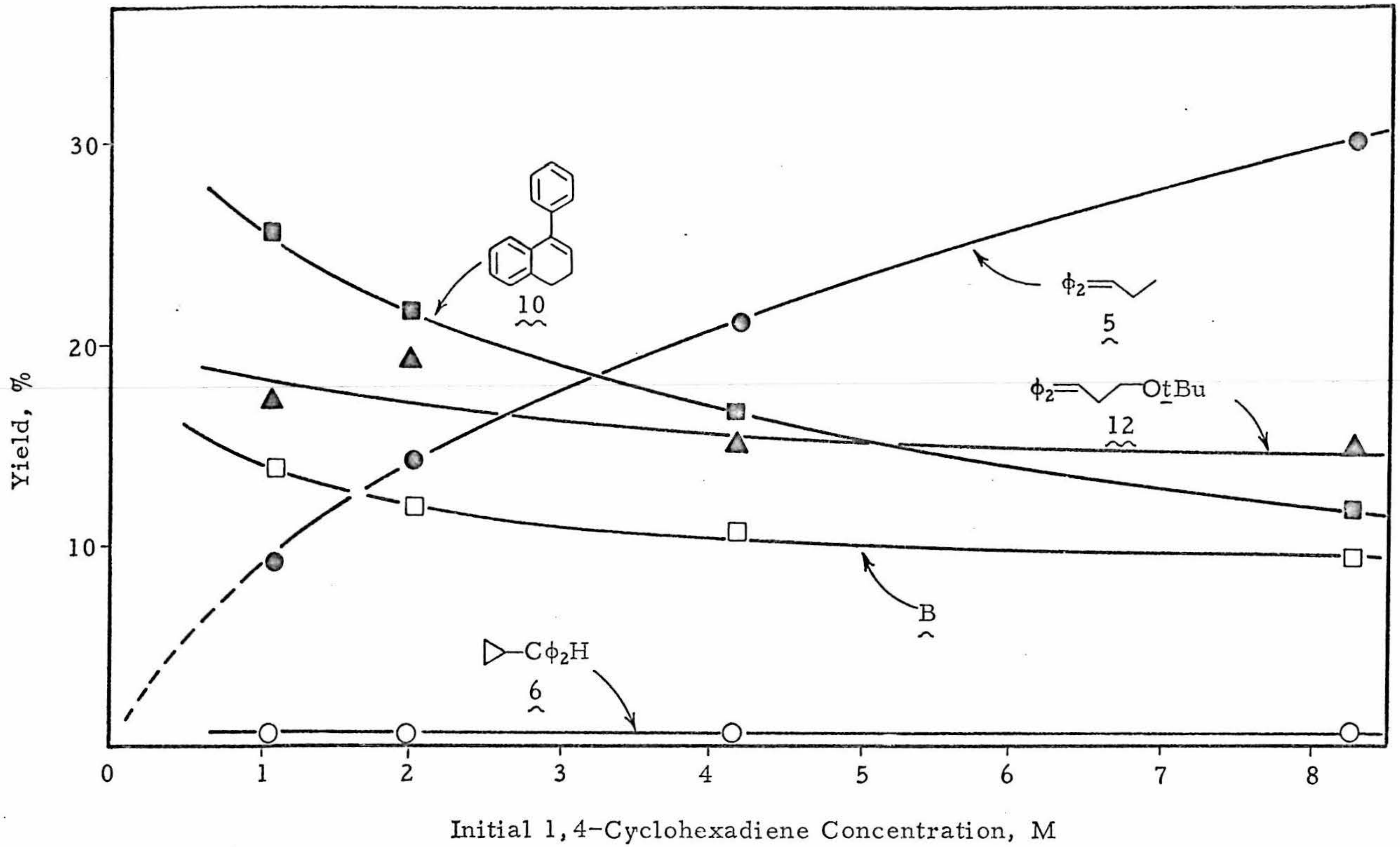
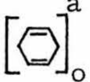
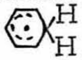
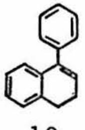
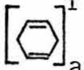


Figure 1. Thermal decomposition of t-butyl (γ,γ-diphenylallyl)peracetate (1) (0.26 M) at 131° in solutions of 1,4-cyclohexadiene in cyclohexane. Data from Table 1.

Table 2. Thermal Decomposition of t-Butyl Diphenylcyclopropylperacetate at 0.05 M[a] in Solutions of 1,4-Cyclohexadiene in Cyclohexane.

			Yield, %						
Bath Temp., °C	[a] M	Dimer[b] from 	$\phi_2{=}\vee$ 5	$\phi_2CH{-}\triangleleft$ 6	B[c,d]	 10	Total[e]	$\frac{6}{5}$	$\frac{10 \times [\;]_{av}}{5}$ [f]
0	2.95	0.10	18.9	13.5	40.0	12.0	84	0.715	1.87
	5.32	0.13	26.5	12.9	35.6	9.9	85	0.487	1.98
	7.97	0.16	33.7	13.2	35.5	9.6	92	0.392	2.27
	10.81	0.19	38.6	12.9	33.4	8.6	94	0.335	2.40
35	2.83	0.12	22.1	17.0	35.6	16.3	91	0.769	2.08
	5.11	0.15	31.1	16.1	30.9	13.6	92	0.518	2.23
	7.65	0.16	35.5	14.2	27.1	12.2	89	0.400	2.62
	10.38	--	45.0	14.6	28.0	11.0	97	0.325	2.54
70	2.72	0.12	19.8	15.1	31.0	20.4	86	0.763	2.79
	4.90	0.16	29.6	16.0	29.8	18.3	94	0.540	3.01
	7.34	0.13	35.8	14.5	26.0	14.4	91	0.405	2.95
	9.95	0.15	37.0	12.9	19.2	13.1	82	0.349	3.52

[a] Assuming 12% volume expansion per 100° temperature rise.

[b] mmoles per mmole perester taken.

[c] Equal moles of this material and 5 assumed to give equal vpc peak areas.

[d] Ring-closed ether 15 plus diphenylmethylenecyclopropane 16 plus a third material thought to be the same as B in Table 1; see Section One, subsection 5B.

[e] Does not include 1–2% of a product which may be ring-opened ether 12 or para-t-butoxy ether 17; see text, pp. 76, 77.

[f] From Table 17, p. 297.

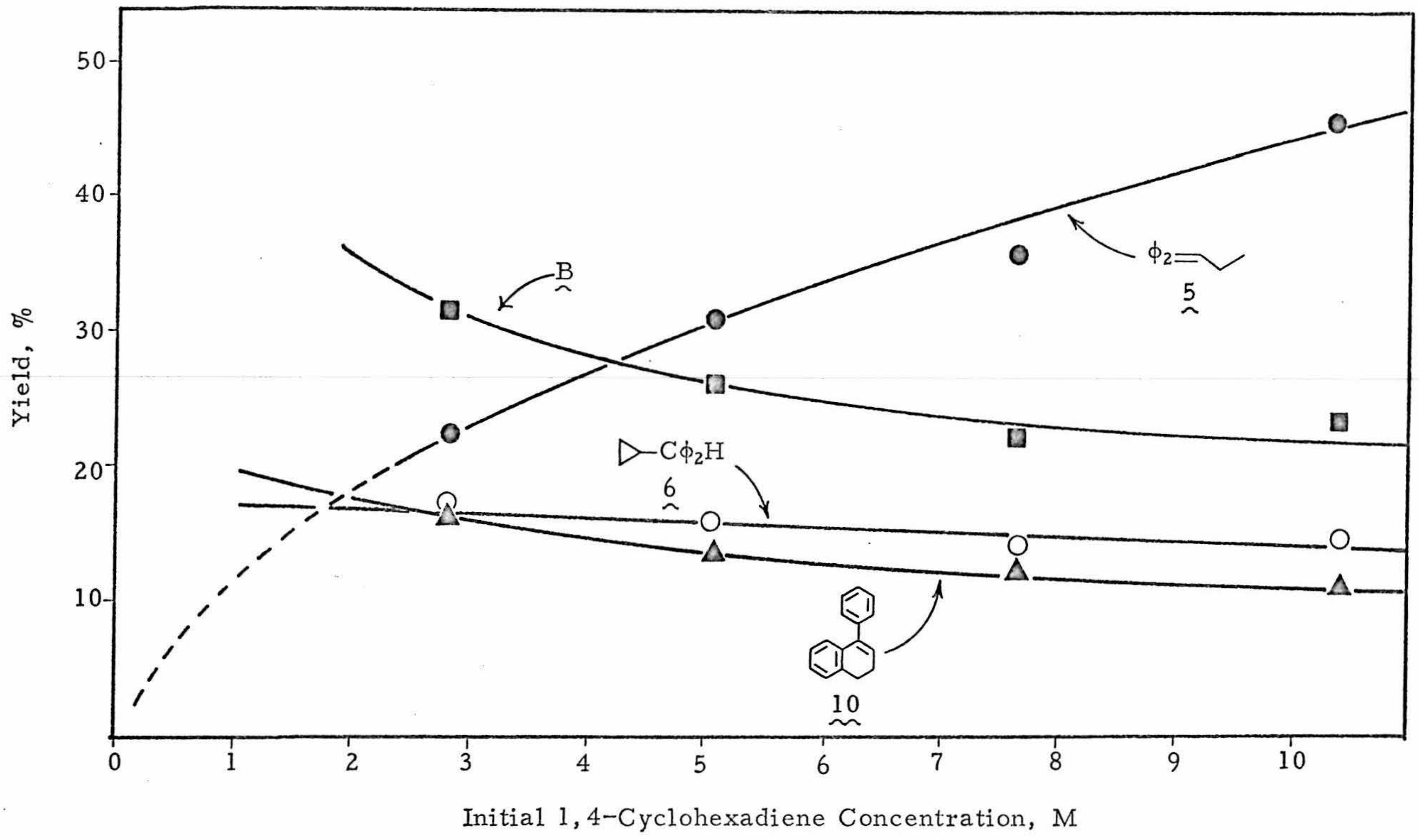
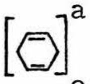
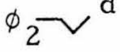
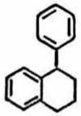
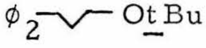
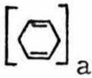


Figure 2. Thermal decomposition of t-butyl diphenylcyclopropylperacetate (2) (0.05 M) at 35° in solutions of 1,4-cyclohexadiene in cyclohexane. Data from Table 2.

Table 3. Thermal Decomposition at 152° of t-Butyl 5,5-Diphenylperpentanoate at Approximately 0.05 M in the Presence of 1,4-Cyclohexadiene and Cyclohexane.

		Yield, %[e]					
 [a] $_o$ M	Dimer from  [b]	 [d] 20	C[f]	 25	 18	Total	25 ×  $_{av}$ / 20
0[c]	---	5.1	4.1	19.6	20	49	---
1.8	0.13	58	13.6	6.9	21	100	0.214
4.5	0.16	64	7.6	3.2	19	94	0.225
7.2	0.18	70	5.5	2.04	18	96	0.210
9.0	0.19	69	4.3	1.60	16	91	0.209

[a] Assuming 12% volume expansion per 100° temperature rise. [b] mmoles per mmole perester taken.

[c] Concentration of cyclohexane is 7.8 M[a].

[d] Corrected for assumed 2.0% yield of 4,4-diphenyl-1-butene; see p. 82.

[e] Yields calculated assuming hydrocarbon products have same vpc sensitivity as 1,1-diphenyl-1-butene and that the ether 18 has the same sensitivity as the ether 12.

[f] See pp. 141-144 for composition of C.

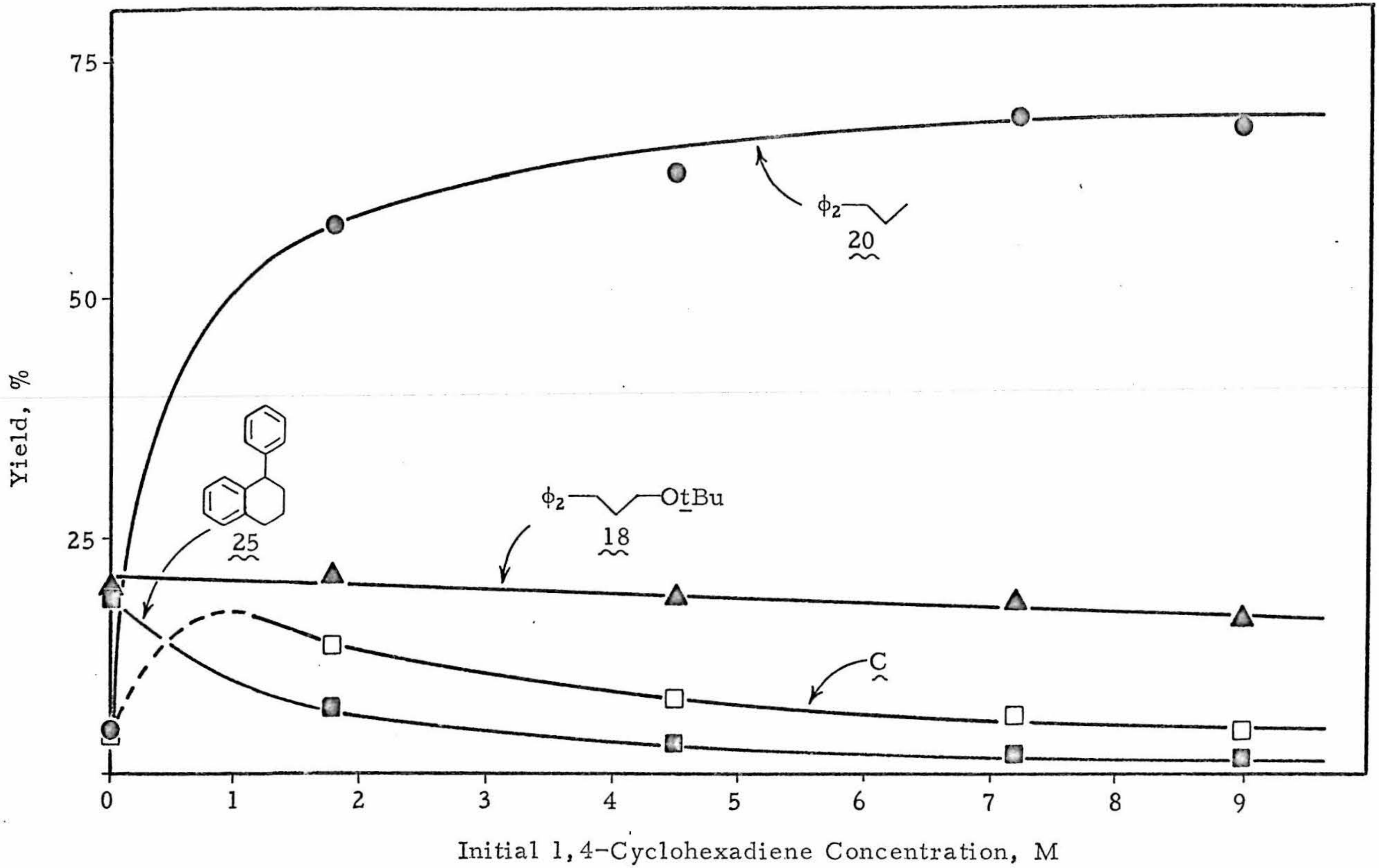
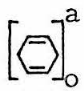
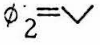
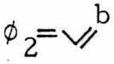
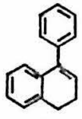
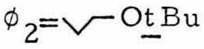
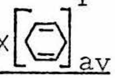


Figure 3. Thermal decomposition of t-butyl 5,5-diphenylperpropanoate (8) (0.05 M) at 152° in solutions of 1,4-cyclohexadiene in cyclohexane. Data from Table 3

Table 4. Thermal Decomposition at 110° of t-Butyl (γ,γ-Diphenylallyl)peracetate at Various Concentrations in Solutions of 1,4-Cyclohexadiene in Cyclohexane.

	Yield, %										
Initial[a] Perester Conc., M	[a] M	 5	 6	[b] 13	A[b,c]	B[b,d]	 10	 12	Total[e]	6 / 5	10 ×  av / 5 [f]
0.27	1.11	6.7	0.30	0.5	1.8	5.5	17.7	16	49	0.044	2.43
0.030	1.22	9.7	0.19	1.6	3.6	13.4	22.7	21	72	0.020	2.79
0.030	1.22	9.5	0.20	1.5	3.5	12.3	22.0	20	69	0.021	2.79
0.0051	1.23	8.2	0.10	1.8	2.7	11.9	18.7	17	60	0.012	2.79
0.0010	1.23	9.9	0.11	2.1	2.9	13.1	19.7	18	66	0.011	2.46

[a] Assuming 12% volume expansion per 100° temperature rise.

[b] Total for these three accurately known; separation into components approximately effected by triangulation assuming equal moles of these materials and equal moles of 5 give rise to equal vpc peak areas.

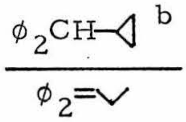
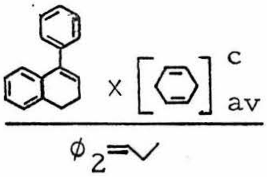
[c] May be benzophenone; see text, pp. 121, 122.

[d] Thought to be isomeric 1-phenyltrahydronaphthalenes; see text, pp. 77, 78.

[e] Also roughly 15-20% of a product at same retention time as that of material tentatively identified as lactone 23 in Table 1; see text, p. 85.

[f] From Table 17, p. 297. [g] Vessel packed with 100 mg glass wool in 2 ml of reaction mixture.

Table 5. Thermal Decomposition of t-Butyl (γ, γ-Diphenylallyl)-peracetate at Approximately 0.001 M in 1,4-Cyclohexadiene.

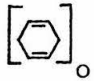
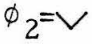
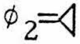
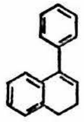
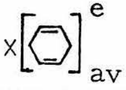
Bath Temperature °C	Initial[a] 1,4-Cyclohexadiene Conc., M	 [b]	 [c]
99	9.65	0.0040	2.35
110	9.45	0.0036	2.70
125	9.34	0.0038	2.83
144	9.20	0.0037	--

[a] Assuming 12% volume expansion per 100° temperature rise.

[b] See text, pp. 116-118, 273-275.

[c] From Table 17, p. 297.

Table 6. Thermal Decomposition at 35° of t-Butyl Diphenylcyclopropylperacetate at Various Concentrations in Solutions of 1,4-Cyclohexadiene in Cyclohexane.

Initial[a] Perester Conc., M	[a] M	 5	 6	[b] 16	B$_2$[b, c]	 10	Total[d]	$\frac{6}{5}$	10 × [e] — 5
		Yield, %							
0.101	2.45	17.9	21.0	6.7	7.1	15.7	68	1.17	2.12
0.022	2.52	22.0	14.1	7.1	7.1	20.2	71	0.64	2.31
0.0060	2.53	28.5	10.0	8.0	6.5	23.6	77	0.35	2.09
0.0010	2.53	26.9	4.4	7.3	5.9	24.2	69	0.165	2.28

[a] Assuming 12% volume expansion per 100° temperature rise.

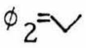
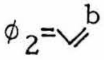
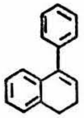
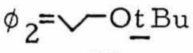
[b] Equal areas of this material and 5 assumed to give rise to equal vpc peak areas.

[c] Thought to be one or more isomeric 1-phenyltetrahydronaphthalenes; see text, pp. 77, 78.

[d] Does not include 1-2% of a product which may be ring-opened ether 12 or para-t-butoxy ether 17; see text, pp. 76, 77.

[e] From Table 17, p. 297.

Table 7. Thermal Decomposition of t-Butyl (γ, γ-Diphenylallyl)peracetate (1) and t-Butyl Diphenylcyclopropylperacetate (2) in Indene at Approximately 0.05 M.

Per-ester	Bath Temp., °C	Initial[a] Indene Conc., M	Yield, %								
			 5	 6	 13 [b]	A[b, c]	B[b]	 10	 12	Total	$\frac{10 \times [\text{Indene}]^{f}_{av}}{5}$
1	131	3.1[g]	6.2	≤ 0.06	≤ 0.1	0.2	0.4[d]	19.6	16	46	10
		7.5	10.7	≤ 0.02	≤ 0.1	0.3	0.5[d]	16.0	22	49	11
2	35	8.5	10.4	0.5	--	--	17.3[e]	11.2	--	39	9
			8.8	0.3	--	--	13.4[e]	12.7	--	37	12

[a] Assuming 12% volume expansion per 100° temperature rise.

[b] Equal moles of this material and 5 assumed to give equal vpc peak areas.

[c] May be benzophenone; see text, pp. 121,122.

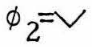
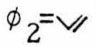
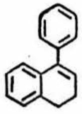
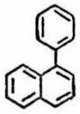
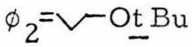
[d] Thought to be one or more isomeric 1-phenyltetrahydronaphthalenes; see text, pp. 77, 78.

[e] Thought to be ring-closed ether 15 plus diphenylmethylenecyclopropane 16 plus isomeric 1-phenyltetrahydronaphthalenes; see Section One, subsection 5B.

[f] Initial indene concentration less initial perester concentration.

[g] Cosolvent is n-octane.

Table 8. Thermal Decomposition of *t*-Butyl (γ,γ-Diphenylallyl)peracetate in Poorly Hydrogen-Donating Solvents and under Miscellaneous Conditions.

		Yield, %								
Solvent[g]	Temp., °C	 5	 6	 [d] 13	A[d,e]	B[d,f]	 10		 12	Total
Cyclohexane	131[a]	1.0	0.11	0.0	1.0	2.7	26.5	5	14	50
Diethyl ether	131[a]	1.1	≤ 0.6[i]	0.0	1.1	2.5	31.5	2	9	48
Tetrahydrofuran	131[a]	1.0	0.05	0.0	1.3	1.0	15.6	1	9	29
Cumene	150[a]	1.3	0.2	-	-	-	-	-	-	-
1,4-Cyclohexadiene, 0.2 M in *n*-octane	110[b]	2.4	0.12	1.4	2	7	24.3	-	13	49
1,4-Cyclohexadiene	150[a,j]	31.6	-	0.8	1.3	10.6	12.4	-	14	71
1,3-Cyclohexadiene, 0.6 M, in 1,4-Cyclohexadiene	150[a]	33.8	-	1.0	1.5	10.8	15.9	-	15	78
1,4-Cyclohexadiene, 0.85 M in Methanol	100[c]	0.7	0.1	0.03	0.1	0.3	2.9	-	1.1	5[h]

Footnotes for Table 8

[a] Initial perester concentration ca. 0.25 M.

[b] Initial perester concentration ca. 0.01 M.

[c] Initial perester concentration 0.11 M.

[d] Total for these three reasonably accurately known; separation into components approximately effected by triangulation assuming equal moles of these materials and equal moles of $\underset{\frown}{5}$ give rise to equal vpc areas.

[e] May be benzophenone; see text, pp. 121, 122.

[f] Thought to be isomeric 1-phenyltetrahydronaphthalenes; see text, pp. 77, 78.

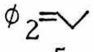
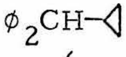
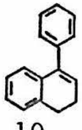
[g] Solvent concentrations quoted assume a volume expansion of 12% per 100° temperature rise.

[h] Also several new products; see Section One, subsection 6.

[i] See text, p. 130.

[j] Reaction time 6 hr.; analogous runs in Table 1 (i.e., rows 13 and 14) used reaction times of 2 hr.

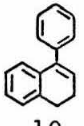
Table 9. Thermal Decomposition of t-Butyl Diphenylcycloproplyperacetate in Poorly Hydrogen-Donating Solvents.

			Yield, %						
Solvent	Bath Temp., °C	Initial Perester Conc., M	 5	 6	$B^{a,b}$	 10	Total	$\frac{6}{5}$	$\frac{5}{10}$
Cyclohexane	35	0.25	1.0	8.7	15	17.5	42	8.7	0.057
	35	0.05	1.1	7.5	27	23.5	59	6.8	0.047
	70	0.05	1.1	7.7	23	27.0	59	7.0	0.041
	35	0.01	0.5	3.4	19	17.3	40	6.8	0.029
Diethyl-ether	0	--	1.5	8.3	10	18.1	38	5.5	0.083
	35	0.05	2.0	9.5	15	28.0	55	4.7	0.071
	70	--	1.6	7.8	12	27.3	49	4.9	0.059
Benzene	35	0.2	0.4	9.1	8	9.4	28	25	0.04
		0.05	1.1	11.5	17	18.5	48	10	0.06
Et_4SnH	35	0.01	0.5	1.6	20	17	39	3.2	0.03

[a] Equal moles of this material and 5 assumed to give equal vpc peak areas.

[b] Thought to be ring-closed ether 15 plus diphenylmethylenecyclopropane 16 plus one or more isomeric 1-phenyltetrahydronaphthalenes; see Section One, subsection 5B.

Table 10. Thermal Decomposition of t-Butyl (γ, γ-Diphenylallyl)peracetate (0.002 M unless otherwise noted) in Solutions of Triethyltin Hydride in n-Octane.

		Yield, %									
Bath Temp., °C	$[Et_3SnH]_o^a$ M	ϕ_2=\/ 5	ϕ_2CH–◁ 6	B[b,c]	 10	Total Hydrocarbons	ϕ_2=\/–OtBu 12	Tin[d] Ester 14	Total	$\frac{5}{6}$	$\frac{10 \times [Et_3SnH]_{av}}{5}$
110	0.011	3.3	0.24	13	17.0	34	3.3	44	81	14	0.051
125	0.011	2.9	0.17	12	18.5	34	3.9	--	--	17	0.064
	0.044	11.1	0.76	(8)[i]	15.6	36	4.0	(49)[h]	(89)	15	0.059
	0.140	23.5	1.63	(4)[i]	10.0	39	2.0	--	--	15	0.059
	0.39	28.2	2.28	(2)[i]	3.6	36	0.7	(40)[h]	(86)	12	0.050
	0.94	30.7	2.85	--	1.4	35	$\leq$ 0.25	--	--	11	0.046
144	0.047	10.5	0.66	10	18.5	40	3.3	--	--	16	0.079
	0.141	16.8	0.97	4	10.1	32	1.9	--	--	17	0.083
	0.38	19.6	1.41	2	3.6	27	0.6	--	--	14	0.070
	0.93	11.2	1.33	--	0.3	13	< 0.2	--	--	9	0.024
125[e]	1.34	34.1	2.9	--	1.1	38	< 0.2	~50	~90	12	0.04
131[f]	1.89	34.3	2.2	--	0.6	37	< 0.2	--	--	17	0.03
110[g]	0.74							49			

[a] Assuming 12% volume expansion per 100° temperature rise.
[b] Thought to consist of one or more isomeric 1-phenyltetrahydronaphthalenes; see text, pp. 77, 78.
[c] Equal moles of this material and 5 assumed to give rise to equal vpc peak areas. [d] ϕ_2=\/–CO_2SnEt_3.
[e] Initial perester conc. 0.12 M. [f] Initial perester conc. 0.05 M.
[g] Initial perester conc. 0.02 M. [h] Measured at 110°. [i] See text, p. 134.

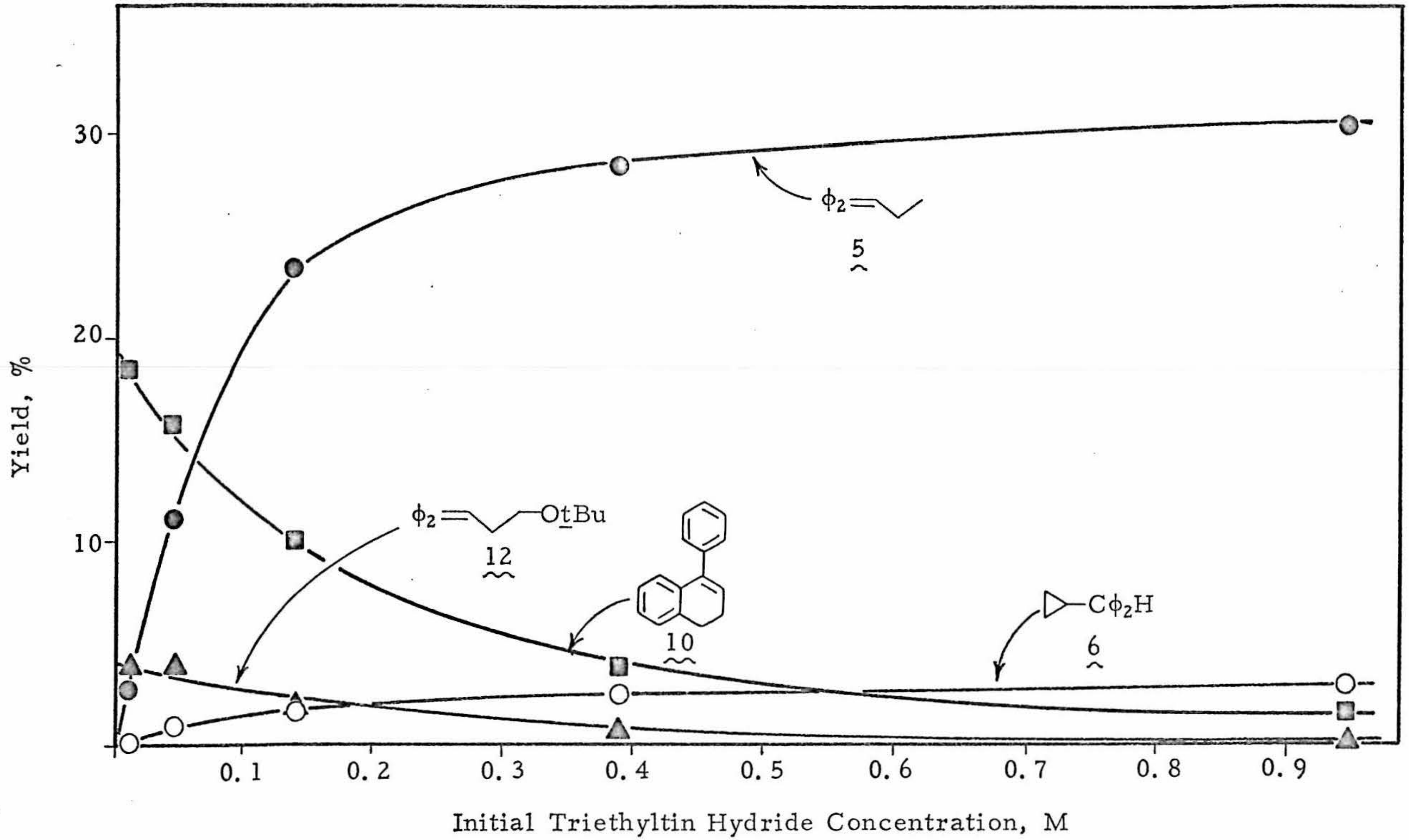
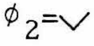
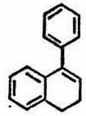


Figure 4. Thermal decomposition of *t*-butyl (γ, γ-diphenylallyl)peracetate (1) (0.002 M) at 125° in solutions of triethyltin hydride in *n*-octane. Data from Table 10.

Table 11. Thermal Decomposition of t-Butyl Diphenylcyclopropylperacetate in the Presence of Triethyltin Hydride.

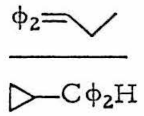
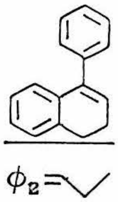
Bath Temp., °C	Initial Perester Conc., M	Initial Et_3SnH Conc., M	Yield, %					
			 5	 6	 10	Total[c]	$\frac{6}{5}$	$\frac{10 \times [Et_3SnH]_{av}^{d}}{5}$
10[a]	0.020	1.02	(Absolute Yields Not Determined)				0.39	0.037
		2.04					0.45	0.048
		3.06					0.54	0.074
		5.1					0.76	0.11
35[b]	0.010	0.25	62	10	4.4	76	0.16	0.017
		0.6	65	12	1.8	79	0.19	0.016
		1.8	68	16	1.0	85	0.24	0.026
		4.8	62	23	0.7	86	0.37	0.006

[a] Co-solvent is benzene. [b] Co-solvent is n-octane.

[c] Does not include any B that may be formed; see text, pp. 80, 81.

[d] Initial Et_3SnH concentration less initial perester concentration.

Table 12. Product Ratios Observed by Howden (21) for Thermal Decomposition of t-Butyl (γ, γ-Diphenylallyl)peracetate at 0.056 M in the Presence of Tri-n-butyltin Hydride

Bath Temp., °C	$[Bu_3SnH]$ M	Solvent	Weight[a] Fraction Hydrocarbon Isolated	Percent[b] CO_2 Evolved		 [c]
110	0.056	C_6H_5Cl	0.15	51	22	1.52
110	0.28	C_6H_5Cl	0.15	44	20	0.12
110	0.28	Cumene	0.50	36	17	0.12
110	0.56	C_6H_5Cl	0.33	73	17	0.06
130	0.28	Cumene	0.36	58	18	0.2
150	0.112	o-$C_6H_4Cl_2$	0.53	73	--	1.2
150	0.28	Cumene	0.41	80	20	0.12

[a] By distillation. [b] From total gas evolution assuming only carbon dioxide is evolved. [c] Obtained from Howden's vpc traces by triangulation assuming that a peak at the proper retention time for the dihydronaphthalene 10 is due to that material.

at reflux or otherwise subject to temperature control.

2. Yields and ratios of various products were obtained, except where noted, by vapor-phase chromatography (vpc) on a Perkin-Elmer Model 800 Gas Chromatograph equipped with a flame-ionization detector. Unless otherwise specified, the column employed was 6-12 ft. ($\frac{1}{8}$ in. o. d.) of aluminum tubing packed with 10% Ucon polar HB 5100 on 80-100 mesh HMDS treated Chromasorb W. In the usual procedure, area measurements relative to added internal standard (either diphenylmethane or 1-phenylnaphthalene) were made using a Perkin-Elmer Printing Integrator. However, triangulation, peak cut-out weights, or peak-height analysis were employed where baseline instability or inadequate resolution made the alternative procedures necessary or preferable. The relative areas were then converted to percentage yields for the various products from the weights of perester and internal standard taken and relative response factors, if known. Where the response factor is unknown (which is the case for several products not isolated in pure form), the assumption has been made that equal weights of 1, 1-diphenyl-1-butene (5) and of the product in question give rise to equal peak areas. Except for the runs at 10° in Table 11, the internal standard, if any, was added after completion of the thermal decomposition.

3. In most cases the vpc analysis was made on the crude reaction mixture (plus internal standard) itself. For reaction series featuring runs below about 0. 05 M initial perester concentration or in the presence of triethyltin hydride, however, it was necessary to concentrate the reaction mixture to prevent interference of the solvent peak

with the vpc analysis.

4. As will become evident, one or more spurious (i. e., incompletely characterized) factors seem to be operative in the decompositions of the ring-closed perester 2. Therefore, runs using 2 from common perester preparations will be so identified in the experimental section.

A few comments are now offered concerning the accuracy of the tabulated data. These comments should be taken into account in deciding whether observed trends are real or likely to be artifacts of the experimental procedure. We have previously discussed one reason--destruction of primary reaction products--that observed yields may not correspond precisely to amounts of products formed. Two others of experimental origin are: (a) error in the vpc area measurements. In most cases, reported yields are based on three or four vpc determinations. Nonetheless, relative observed yields or product ratios may be off by up to five percent even where no problems of resolution were encountered. Where such problems were encountered (see below), a much higher figure may be appropriate; and (b) in general, weights of perester, in the amount of about 20 mg, was weighed directly. If that weight is taken to be good to ± 1 mg, absolute yields will be uncertain to five percent over and above the uncertainty due to the relative-area measurements. In addition, uncertainty in the weight of internal standard taken can also often contribute an appreciable uncertainty in the product ratios. Note, however, that this weight-uncertainty factor does not effect ratios of products taken within a given run (such as the figures in the right-most columns of the data tables). For this reason, we will be on safer ground in working with these quantities, and it will be better to test a reaction mechanism by how well it reproduces ratios of products than by how well it does on absolute yields.

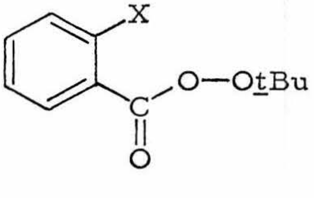
Consider, for example, the yields of the various products quoted in Table 2 for decomposition of the ring-opened perester **1** in the presence of 1,4-cyclohexadiene. For the three runs at about 1 M initial cyclohexadiene concentration, the one at the intermediate temperature (131°) gave the highest yield for all but one of the several products. It is no mean task to conceive of a mechanism which will reproduce such a pattern. In general, one would expect a monotonic variation with temperature, although a maximum yield at an intermediate temperature might be found for a given product if two or more mechanistic pathways to that product were properly combined or if product destructions had different temperature coefficients. In the case in question, however, the observed pattern is almost surely artificial.

The reader is advised that absolute yields are probably always reported to more precision than combined weight-uncertainty and area-uncertainty factors would support, in order to facilitate the calculation and comparison of product ratios.

3. Mechanisms of Perester Decompositions

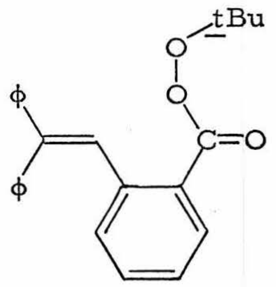
Unimolecular homolytic decomposition is the most common, but not the only, mechanism by which *t*-butyl peresters have been known to decompose. Alternative mechanisms include heterolytic decomposition, ionic decomposition catalyzed by strong acid, radical-induced decomposition, and molecule-induced decomposition. Rüchardt has supplied a comprehensive review of the mechanism of perester decompositions (7). Of the types listed above, homolytic, radical-induced, and molecule-induced decompositions have been observed in the present research.

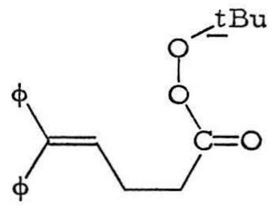
Let us take up these three mechanistic possibilities in reverse order. Molecule-induced decomposition (if intramolecular) is the free-radical analog of the neighboring-group participation in ionization which is so well known in carbonium ion chemistry (8, 28). The ortho-substituted t-butyl perbenzoate system employed by Martin and co-workers (29) is the free-radical system which seems to have been the most extensively studied. Although the immediate products of the induced decomposition are free radicals (a cyclized lactone radical and a t-butoxy radical), the large solvent effect on reaction rate observed by Martin indicates that the decomposition transition state apparently enjoys substantial ionic character.



$$X = \left\{ \begin{array}{l} -I \\ -CH{=}C(C_6H_5)_2 \\ -SC_6H_5 \\ -SCH_3 \end{array} \right\}$$

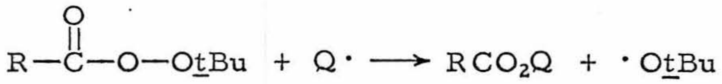
The case where X = diphenylvinyl is especially relevant here because of the strong structural similarity of that perester to the ring-opened perester 1.





1

Two types of radical-induced decompositions are known. One simply consists of attack by a radical ($Q\cdot$ in the below) at one of the peroxy oxygens. The process shown might be called "acyloxy-group



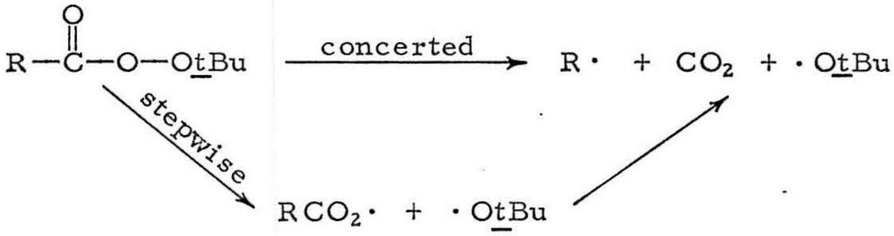
$$R-\overset{\overset{O}{\|}}{C}-O-O\underline{t}Bu + Q\cdot \longrightarrow RCO_2Q + \cdot O\underline{t}Bu$$

abstraction" to emphasize its formal similarity to the perhaps more familiar "hydrogen atom-abstraction" reaction. Radical attack on the other peroxy oxygen to give ether and an acyloxy radical, $RCO_2\cdot$, is also conceivable. The second type of radical-induced decomposition involves the establishment of a radical center within the perester molecule, usually via abstraction of a hydrogen atom from the perester (7); the newly established radical center may then intramolecularly attack the peroxy-oxygen linkage to give the cyclic ester and a *t*-butoxy radical (7).

Radical-induced decomposition is the predominant mechanism for decomposition of the ring-opened perester 1 (and possibly for the isomeric ring-closed perester 2) in the presence of triethyltin hydride under conditions employed in this work. This apparently is the first case in which a radical-induced perester decomposition involving attack on the peroxy functionality has been documented by product isolation as well as by kinetic evidence.

Under all other conditions investigated in this work, radical-induced decomposition appears to be negligible or absent.

Two mechanisms are conceivable for the normal homolytic decomposition. The two bonds broken in the overall process may cleave simultaneously with expulsion of carbon dioxide, or the weaker oxygen-oxygen bond may cleave first, followed by decarboxylation of the resulting acyloxy radical:



Bartlett and Hiatt (30) employed the following reasoning in attempting to distinguish in particular cases between the two possibilities. If the decomposition is concerted, the stability of the radical R· should strongly influence the rate of decomposition. On the other hand, the nature of the R group should have little effect on the stability of an acyloxy radical, and hence on the rate of decomposition, if the decomposition is stepwise. Table 13 lists half-lives at 110° for a series of peresters, many of which were studied by Bartlett and Hiatt. The variation in the ratio of the half-lives by a factor of 4×10^4 from the fastest to the slowest is a major change in most leagues, and can hardly mean other than that the decomposition is concerted, at least

Table 13. Half-Lives for Thermal Decomposition of Peresters, R-CO$_2$-O*t*Bu, in Chlorobenzene at 110°.

R-Group	Half-life, min.	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, e.u.	Ref.
CH_3-	230[c]	38	17	31
$(C_6H_5)_2CHCH_2CH_2CH_2$-	210	--	--	21
$(C_6H_5)_2C{=}CHCH_2CH_2$-	150	--	--	21
$CH_3(CH_2)_7CH_2$-[a]	139	35.3	14.0	22
$CH_3(CH_2)_{10}CH_2$-[a]	133	35.0	13.1	22
endo-norbornyl-	26	35.6	16.4	10
exo-norbornyl-	20	30.9	6.7	10
cyclohexyl-	14	31.3	8.6	10
$(CH_3)_2CH$-	135[b]	31.8	9.4	32
$C_6H_5CH_2$-	5.9[c]	28.7	4	33
$(CH_3)_3C$-	0.89[b]	30.0	11.1	33
$C_6H_5CH{=}CHCH_2$-	0.8[c]	23.5	- 6	30
$(C_6H_5)_2CH$-	0.18[c]	24.3	- 1	30
$C_6H_5(CH_3)_2C$-	0.06[c]	26.1	6	30
$(C_6H_5)_2CH_3C$-	0.04[c]	24.7	3	30
$C_6H_5(CH{=}CH)CH$-	0.025[c]	23.0	- 1	30
$(C_6H_5)_3C$-	0.006[c]	24.1	4.9	27

[a] Half-lives are for chlorobenzene but activation parameters are for nitrobenzene.

[b] Calculated by the Arrhenius relationship using authors' rate constants.

[c] Extrapolated (Eyring equation) from the half-life at 25 or 60° and enthalpy of activation quoted in the reference listed.

for those R-groups in the lower half of the table (30).

The interesting question is whether all of the peresters undergo concerted decomposition, or whether the slower ones decompose sequentially, with a change in mechanism occurring somewhere along the line; and if the latter is the case, where does the change occur?

To make a comparison between radical stabilities and decomposition rates we need some measure of the former. A reasonable procedure would be to use C-H bond-dissociation energies where these are available. Unfortunately, the requisite dissociation energies are available for only a few of the groups listed in Table 13. However, a scale can be constructed for the simple aliphatics; and the fact that the perester with R equals t-butyl decomposes about 250 times as rapidly as the parent perester with R equals methyl, suggests that the change in mechanism, if one occurs, will be found within that series. (For convenience we shall refer to a perester by giving the identity of the R-group.) Following Walling (34) we assign stabilization energies relative to methyl of: 4 kcal/mole for a primary radical; 8 kcal/mole for isopropyl or other unstrained secondary radical; and 12 kcal/mole for the t-butyl radical. Thus, the increment in stability is essentially constant in going from methyl to primary, from primary to secondary, and from secondary to tertiary.

If, then, all of the aliphatic peresters decompose concertedly, the half-lives should show a geometrical progression. That is, we should have approximately $(\text{ethyl}/\text{methyl})^3 = (\text{isopropyl}/\text{methyl})^2 = (\underline{\text{t}}\text{-butyl}/\text{methyl})$; or t-butyl/isopropyl = isopropyl/ethyl, etc. From Table 13 we see that t-butyl decomposes about 15 times as rapidly as isopropyl or cyclohexyl and that the unstrained secondary aliphatics decompose about 10 times as rapidly as those with primary R-groups. Thus, the decomposition is almost certainly concerted when R· is at least as stable as a secondary aliphatic radical.

However, the primary aliphatics decompose only about 50% faster than the parent perester, t-butyl peracetate. If we were quite certain that substitution of n-alkyl for methyl should not change the rate constant for simple oxygen-oxygen scission by more than some few percent, the slight rate acceleration observed could be taken as evidence that peresters with primary R-groups decompose partly by the concerted and partly by the sequential mechanism. Lacking that degree of confidence, we can only suggest here that a combination of concerted and stepwise processes is an attractive possibility for peresters such as ring-opened perester 1.

We might also mention another important factor in perester decompositions first identified by Bartlett and Hiatt (30). This factor concerns the lower entropies of activation observed where the radical R· can be stabilized by resonance. Effective resonance stabilization, as is well known, requires that the radical assume an optimal configuration with respect to rotation about one or more bonds. A partial freezing out of the same rotation(s) should be required if resonance stabilization of the incipient radical is to be available at the transition state, and the freezing out in the transition state of rotations allowed in the perester itself results in a lowered entropy of activation.

Bartlett and Hiatt pointed out that the trend is so well obeyed that the entropies of activation fall into a number of ranges associated with the number of frozen rotations (30). For isopropyl or _t_-butyl, where rotation about one bond must be fixed in developing the molecule of carbon dioxide, the entropy of activation is 9 e.u. or greater. For benzyl and cumyl, the orientation of the phenyl ring must also be properly set, and the entropies of activation are 4 and 6 e.u., respectively. Entropies of activation are 3 e.u. for diphenylethyl, −1 e.u. for diphenylmethyl, −1 e.u. for phenylvinylmethyl, and −6 e.u. for cinnamyl; all cases in which 3 bonds must be properly oriented at the transition state.

The one significant deviation from the pattern occurs for triphenylmethyl, whose activation parameters were only recently reported by Lorand and Bartlett (27). The reasoning employed above would suggest frozen rotations for 4 bonds in triphenylmethyl and a negative entropy of activation. The actual value, however, is about +5 e.u. The authors suggest that steric crowding in the 'tetrahedral' perester might be relieved as the triphenylmethyl group approaches the trigonal geometry of the radical; this factor would clearly tend to increase the entropy of activation. In addition, the steric congestion may orient the phenyl groups in the perester itself in a propeller configuration similar to that postulated for the triphenylmethyl radical (68). Thus, the increase in orientation at the transition state might be rather small.

This discussion is intended to convince (or to remind) the reader that the correlation of structure with activation parameters is sufficiently well advanced for perester decompositions to allow the estimation of activation parameters in new cases (e.g., the isomeric peresters 1 and 2). The reason is that activation parameters for the isomeric peresters will have to be specified in Section Two to quantitatively test the mechanism outlined in the present section, and those parameters have not been determined experimentally. As some rate information is available for each of the peresters, however, the procedure adopted is not thought to seriously compromise the mechanistic evaluation.

4. Cage-Reaction Processes - A general Discussion

Cage-reaction processes may occur when homolytic cleavage of one or more bonds creates a pair of reactive intermediates. If the reaction takes place in the gas phase at pressures of less than tens of atmospheres (35), the particles tend to diffuse apart so rapidly that there is no significantly greater chance that each will react with its original partner than with some species produced in a neighboring decomposition. In solution, however, the surrounding solvent molecules can greatly slow the separation of the radical pair. There is then in effect a solvent cage (36) about the particles which may allow a considerable number of radical-radical encounters before diffusion occurs to give separated radicals. In the course of their movements within the solvent cage, the original partners may (re)combine or disproportionate.

Cage reactions may be studied experimentally by determining the influence of added radical scavenger on the product distribution (24, 37). The idea is that reaction in the solvent cage is likely to take place very soon after the fragmentation, whereas products arising from reactions between radicals from separate decompositions are formed relatively later because of the requirements for diffusion. A scavenger of appropriate reactivity could then suppress the non-cage processes while leaving the cage processes essentially unaffected. And if the characteristic times for the two types of processes differ by several orders or magnitudes, a clean separation should be possible.

Moreover, experiments with very active scavengers have shown that at sufficiently high scavenger concentrations, the cage process itself can be interdicted (24, 37). In the present work, however, none of the solvents employed seems to react with any of the species directly produced by decomposition of either the peresters on a time scale as short as that which describes the cage processes, and no experiments with specially added radical scavengers have been carried out.

Just what is the time scale for cage processes observed in this work cannot be said with certainty. However, Noyes has suggested that in ordinary solvents the competition between cage reaction and diffusion will normally allow about 10^{-9} seconds for the former to be effected (24). Of course, the actual figure will vary with the nature of the caged particles, with the properties of the solvent, and with other factors, but Noyes' estimate should at least allow us to place upper limits on the rate constants for certain reaction steps.

5. Cage Processes in Decomposition of the Peresters

A. t-Butyl (γ, γ-Diphenylallyl)peracetate

Table 13 shows that the ring-opened perester 1 decomposes at 110° at a rate appropriate for a perester giving a primary radical. Moreover, the discussion in subsection 3 suggested that such peresters may decompose by a combination of concerted and stepwise pathways, as illustrated below for the ring-opened perester:

$$\begin{tikzcd}
1 \arrow[r, "\text{concerted}"] \arrow[dr, "\text{stepwise}"'] & \{(C_6H_5)_2C{=}CHCH_2CH_2\cdot \; + \; CO_2 \; + \; \cdot O\underline{t}Bu\} \\
 & \{(C_6H_5)_2C{=}CHCH_2CH_2CO_2\cdot \; + \; \cdot \; O\underline{t}Bu\} \arrow[u]
\end{tikzcd}$$

11

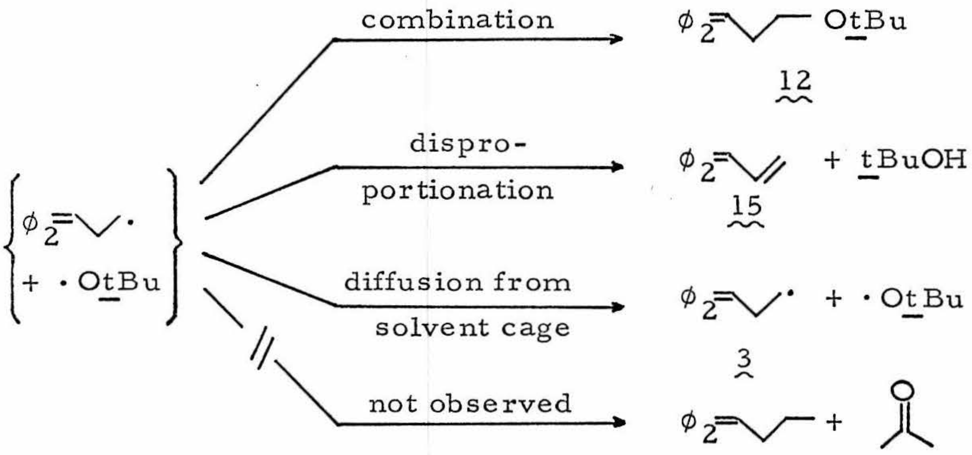
If the decomposition were entirely stepwise, the acyloxy radical would have to rapidly decarboxylate in the solvent cage to account for cage products observed and reported below. That this might well be possible is suggested by the work of Braun, Rajbenbach, and Eirich (38) who have shown that decarboxylation of acetoxy radicals (from the thermal decomposition of acetyl peroxide) is competitive with diffusion from the solvent cage. As acyloxy radicals have apparently not been trapped in this work, however, it will be sufficient to consider, for the present at least, that by some combination of the two pathways caged pairs consisting of a ring-opened radical 3 and a t-butoxy radical are generated.

We will consider first the formation of cage products in ether and hydrocarbon solvents. Then we will note how the pattern is changed in the presence of triethyltin hydride, where induced decomposition of 1 by triethyltin radicals competes with the normal process.

(1.) In Hydrocarbon and Ether Solvents

Of the several types of cage processes which might be considered, definite evidence was obtained for coupling to diphenylbutenyl *t*-butyl ether, 12, and disproportionation to 1,1-diphenyl-1,3-butadiene, 13, plus *t*-butyl alcohol. Because *t*-butoxy radicals undergo β-scission (to yield a methyl radical plus acetone), the disproportionation-type reaction shown lowermost below was considered, but ruled out when careful vpc analysis failed to detect 1,1-diphenyl-1-pentene for decomposition of 1 in 1,4-cyclohexadiene, cyclohexane, or diethyl ether.

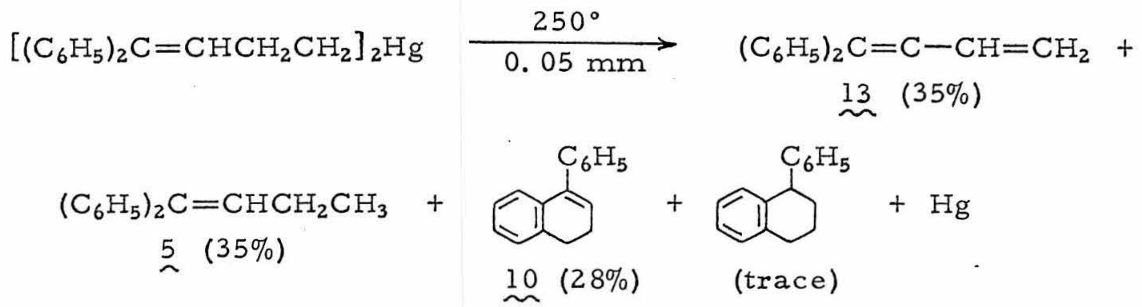
Chart 2. Cage Reactions in the Thermal Decomposition of *t*-Butyl (γ,γ-Diphenylallyl)peracetate.



The ether 12 was detected by vpc for decomposition of 1 in 1,4-

cyclohexadiene, cyclohexane, indene, diethylether, and tetrahydrofuran (Tables 1, 3, 7, 8). No assay was made for the run in cumene listed in Table 8. It can be separated conveniently from the other reaction products by elution chromatography on florisil or alumina. A separated sample from a run in the presence of 1,4-cyclohexadiene gave a nmr spectrum which agreed with that of the authentic material

The identification of the diene is somewhat less well established. Maercker and Roberts (69) found that the dialkylmercury compound shown below decomposed during attempted distillation under reduced



pressure to give a distillate containing metallic mercury and a 1:1 mixture of ring-opened hydrocarbon **5** and a compound which from its nmr spectrum was tentatively identified as the diene **13**. The retention time of the diene **13** relative to **5** on the standard Ucon Polar column appears to be the same as that of the peak attributed to **13** in this work. The diene **13** may well have been formed under Maercker's conditions by thermal decomposition of the mercury compound in the distillation pot followed by disproportionation of the caged diphenylbutenyl radicals. Dimerization would be expected as well, but only the monomeric products would have distilled.

Evidence that the ether **12** and the diene **13** are in fact cage products is offered in the next several paragraphs in the context of how one might in general attempt to distinguish cage products from products formed in other ways.

Yields of the ether 12 are given in Table 1 for decomposition of 1 at approximately 0.25 M in the presence of 1,4-cyclohexadiene. The major point to be noted is that the yield of the ether is substantially independent of the cyclohexadiene concentration. In this case, 1,4-cyclohexadiene scavenges radical pairs which escape the solvent cage. Thus, the constancy of the yield at any given temperature is consistent with a cage-reaction origin of 12. However, constancy of yield is not a sufficient criterion. For example, the yield of diphenylcyclopropylmethane, 6, also varies little with the 1,4-cyclohexadiene concentration (Table 1). Yields of the same material from the isomeric ring-closed perester 2 (see Table 2) show a similar constancy. Nevertheless, we shall see shortly that 6 is not in fact a cage product.

As was pointed out in subsection 1, yields of radical-radical products may in some cases depend strongly on the steady-state radical concentrations, which in turn can be rather uniformly varied by varying the initial perester concentration. However, the yields of cage products will not depend on the steady-state radical concentrations, for both radicals come from the decomposition of a single perester molecule. Some variation of yield with perester concentration may still be possible, however, for two reasons: (a) as also discussed in subsection 1, destruction of primary products will, if anything, be more important at higher perester concentrations; and (b) if induced decomposition (which gives no cage product) competes with the normal decomposition, the relative amount of the latter will usually be greater at lower perester concentrations (39).

The concentration study of Table 4 shows that the yield of the ether **12** is substantially independent of the initial perester concentration, although the data are rougher than one might like. Note, however, that the yield of the hydrocarbon **6** varies by a factor of four. A similar variation with perester concentration is seen in Table 6, where the perester employed is **2**. Thus, **6** cannot be a cage product.

Again, the lack of a concentration dependence is not a sufficient criterion. For example, the yield of the ring-cyclized hydrocarbon **10** (see Table 4 or Table 6) is not greatly dependent on the initial perester concentration, and even rises slightly at lower perester concentrations, as we have noted a cage product might. However, we can be sure that **10** is not a cage product because it fails the first test--invariance of the yield on the 1,4-cyclohexadiene concentration (see Table 1)--and because the ring-cyclization can be easily shown to be orders of magnitude too slow to compete with diffusion of the ring-opened radical from the solvent cage.

The ring-opened ether **12** passes both the scavenger-dependence and concentration-dependence tests. Certainly the use of the two together is far superior to reliance on either one alone. The reaction mechanism would have to be perverse or grossly simple to produce a product which passes both tests but is not a cage product. An example of the latter would be a reaction which gives only a single product; in such a case, isotopic labeling could be used to separate cage processes from non-cage processes.

Establishing a cage mechanism for formation of the butadiene 13 is more difficult because it does not seem to be very stable under the reaction conditions; addition of a radical to the terminal methylene group to give a highly stabilized phenylallyl radical apparently competes with attack on the bulk solvent. In the concentration study of Table 4, the observed yield of the diene is substantially higher for the lower initial perester concentrations. This can be attributed to diversion of attack of radicals from a diene to solvent as the ratio of solvent to diene is increased.

The higher yields of the diene at the higher 1,4-cyclohexadiene concentrations in Table 1 apparently reflect the fact that primary reaction products can also be protected by making the solvent more reactive. It seems significant that for decomposition of 1 in the relatively inert solvents cyclohexane, ether, and tetrahydrofuran (see Table 8) no diene is detected. The yield of the ether 12 also varies to some degree, but not so dramatically (see below).

Perhaps the best argument that the diene is a cage product is that other mechanistic possibilities predict that the yield of diene should decrease strongly on going to lower initial perester concentrations. For example, this is definitely the prediction for disproportionation of the ring-opened radical 3 with any species subsequent to diffusion from the solvent cage. The reason is that the ring-opened radicals have other options (e.g., ring-cyclization to the radical 9 or abstraction of hydrogen from solvent) and thus will be unable to wait out the longer time required for another radical species to make an appearance.

Taking the run in Table 4 at 0.001 M initial perester concentration as most likely to offer the best protection to once-formed diene and ether, our best guess for the disproportionation to combination ratio for a t-butoxy radical and a diphenylbutenyl radical under these cage-reaction conditions is 2.1/18 = 0.12.

Variation of the yield of the ether 12 with solvent composition might arise from radical-induced decomposition in some of the solvents, from subsequent radical attack on the ether, or might simply reflect physical differences among the various solvents in their ability to keep the caged particles long confined. If the latter is correct, we should expect the ether yields to correlate with properties of the solvent which reflect particle mobility. The success of one such correlation is explored in the following paragraphs.

Chandrasekar (40) has employed a generalized random-walk model to express the probability that a point particle which is at a certain point at time zero will be within a volume element centered at some second point at a later time t. Consider a situation in which the centers of two particles are initially separated by a distance r_0. If we assume that the probability per unit time that two particles in such a real system undergo cage reaction at time t is proportional to the probability that centers of the particles are arbitrarily close in the point-particle model system, then the integral overall time of Chandrasekar's eq. 107 (which expresses the latter probability) should be proportional to the net probability that cage reaction will take place. This treatment predicts that the cage efficiency will be proportional to $1/r_0D$, where D is the sum of the diffusion coefficients for the two particles.

Unfortunately, experimental data concerning diffusion coefficients are not sufficiently extensive to allow the prediction of diffusion coefficients for the two radicals of present interest. However, to judge how cage yields might vary from solvent to solvent, we need only estimate how the diffusion coefficients will *vary*, and for that we can employ a recent equation due to Houghton (70). The equation expresses self-diffusion coefficients (e. g., for diffusion of a cyclohexane molecule in cyclohexane solution, etc.) in terms of the quantity $T\rho/\eta$, where ρ is the density and η the viscosity of the medium in question. Unfortunately, a self-diffusion coefficient must depend on the type of molecule which is undergoing the diffusion as well as on the properties of the surrounding solvent. Thus, the relative diffusion coefficients of a third species in each of two solvents need not be very similar to the relative self-diffusion coefficients.

Still, we have little choice but to assume, if Chandrasekar's random flights treatment is applicable, that cage efficiencies will be proportional to reciprocal self-diffusion coefficients. Thus, in Fig. 5 the yield of the ring-opened ether **12** is plotted against the so-called kinematic viscosity, which is given by η/ρ, where η is in centapoise.

By this point, the reader should have accumulated a healthy respect for the approximations which have been made. In addition, in compiling the figure ether yields at 131° (where several have been measured) have had to be employed in connection with viscosities at 20° (where several are available and the others could be measured). Also, the yield of **12** in *n*-octane at 110° (Table 8) has been approximately corrected to 131° by assuming a temperature variation similar to that observed in cyclohexane – cyclohexadiene mixtures (Table 1). Finally, the directly measured cyclohexane value (14%, Table 8) has been discarded in favor of the value of 18% obtained from Table 1 by extrapolation to zero cyclohexane concentration, since the former value may in part be determined by subsequent radical attack on the ether in neat cyclohexane.

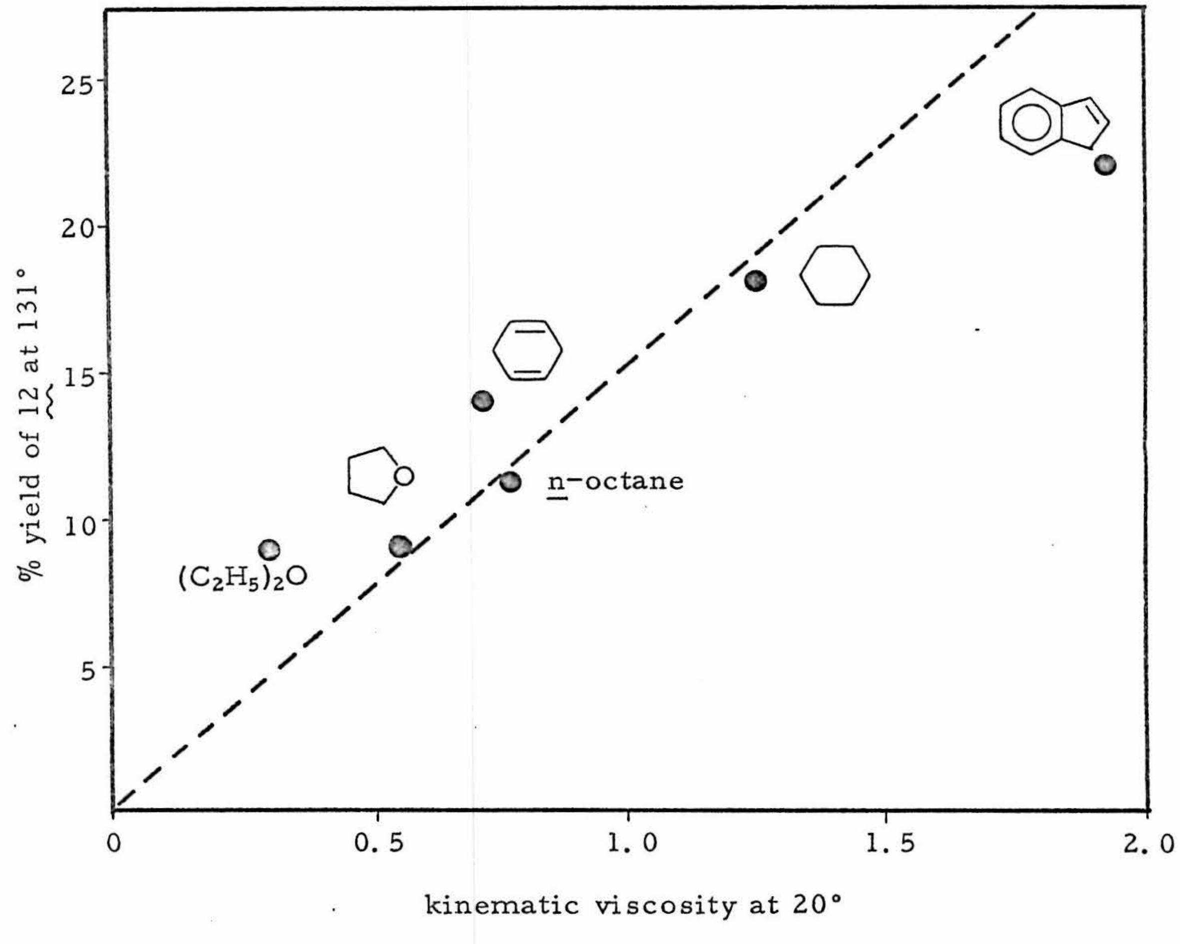


Figure 5. Variation in yield of the ether 12 with kinematic viscosity.

Although the 'theoretical' zero-intercept line does not give a fit of surpassing excellence, the trend is nevertheless roughly as expected. If anything, the points for the poorly hydrogen-donating solvents diethyl ether, tetrahydrofuran, and *n*-octane tend to be high. On this basis, it may be tentatively suggested that there is little or no radical-induced decomposition of the ring-opened perester 1 in any of the hydrocarbon or ether solvents studied. The low material balances for decomposition of the peresters in the poorly hydrogen-donating solvents would then be ascribed to inefficient conversion of the ring-cyclized radical 9 to the dihydronaphthalene 10.

(2.) In the Presence of Triethyltin Hydride

With yields of the ring-opened ether 12 in the ether and hydrocarbon solvents freshly in mind, the reader's attention is directed to Table 10, where yields of 12 for decomposition of 1 in solutions of triethyltin hydride in *n*-octane are listed (see also Fig. 4 which follows Table 10). The highest yield reported, about 4 percent, is far below the 16 to 20 observed for decomposition of 1 in the presence of 1,4-cyclohexadiene or the 13% in essentially neat *n*-octane. The most striking feature, however, is the major decrease in the observed yield of the ether 12 with increasing triethyltin hydride concentration.

That decrease might reasonably be due to any of three factors, or to a combination of the three: (a) a change in mechanism with radical-induced decomposition strongly predominating at the higher tin hydride concentrations; (b) formation --but subsequent destruction--of a normal amount of cage product, with the destruction--presumably via the known process of hydrostannation (41)--becoming increasingly efficient at the higher tin hydride concentrations; or (c) interdiction of the cage processes via facile abstraction of hydrogen from tin hydride by one or both of the caged species. The correct answer is alternative (a), though we will find that some contribution by the other possibilities cannot be ruled out at the higher tin hydride concentrations.

Note the clear kinetic implications of alternative (a): if the normal process makes only a small contribution, at each stage of the reaction, several perester molecules must fall by way of induced decomposition for each that dies of old age. Thus, if (a) is correct, unusually low yields of the ether must be associated with unusually high rates of decomposition.

Kinetic evidence reported in subsection 9 confirms this idea. For example, the half-life of 1 in chlorobenzene solution at 110° is about 150 minutes (21). For 0.01 M triethyltin hydride in *n*-octane, the half-life at 110° of an 0.002 M solution of 1 was found to be about 53 minutes. Moreover, in the presence of 0.4 M tin hydride under otherwise identical conditions, the half-life is only about 6 minutes.

It should be apparent that both kinetic measurements and yields of the cage ether 12 convey information concerning the relative amounts of normal and induced decomposition. Extraction of that information from the ether yields is straight-forward. The one additional piece of information we require is the yield of ether 12 for decomposition of 1 in *n*-octane alone. At 110° a yield of 13% was found for decomposition of 0.01 M perester in *n*-octane (with 0.2 M cyclohexadiene added to moderate the reaction and insure the survival of the ether (see row 5 of Table 8)). The yield of ether at higher temperatures should be similar, though somewhat smaller than at 110°, perhaps showing nearly the same temperature dependence as found for decomposition of **1** in the presence of 1,4-cyclohexadiene in cyclohexane (see Table 1). Thus, the fraction of normal decomposition for the runs in Table 10 at 125° can be estimated by dividing the observed yield of the ether by about 12.

Extraction of the same information from the kinetic measurements proceeds as follows: If the induced process is first order in perester--we will show in subsection 9 that it is for the runs of Table 10--the fraction of normal decomposition is simply given by the ratio of half-lives in the presence and in the absence of triethyltin hydride.

Thus, the compatibility of the two types of measurements can be tested. If no other factors were involved, that test would be made at this point. However, the fraction of normal decomposition can also be predicted from the stoichiometry of the reaction. This is most easily seen by noting that superposition of an induced decomposition on the normal process constitutes a chain reaction whose chain length is determined by the nature of the termination processes. Each induced decomposition consumes one triethyltin radical; if the chain is to be propagated without attenuation, the tin radical consumed must invariably be regenerated. Among the reaction products is the dihydronaphthalene **10**, whose formation requires the loss of a hydrogen atom by a ring-cyclized radical **9** to some second species. Thus, if the induced decomposition ultimately results in formation of the dihydronaphthalene, the tin radical will not be regenerated. Moreover, if the loss of the hydrogen atom by 9 occurs to a triethyltin radical, not just one, but two chains will be stopped. Incidentially, it is the predominant termination of chains in this manner which makes the induced decomposition first order in the perester concentration; chain termination by dimerization of triethyltin radicals would lead to three-halves order kinetics (39).

I should mention at this point, although it may already be clear to the reader, that relating the stoichiometry to the amounts of normal and induced decomposition presents greater difficulties than are involved in the implementation of the two other procedures. In fact, the process of obtaining agreement between the three approaches will enable us to determine more precisely than would otherwise be possible the relative rates of ring-cyclization and abstraction of hydrogen from triethyltin hydride by ring-opened radicals. These are important quantities because they are involved in elucidating the response of the radical system to the activity of the hydrogen donor.

To make best use of the stoichiometry approach, we shall need to know how the ring-cyclized radicals are consumed under less complicated circumstances, such as are found for decomposition of the peresters in the presence of 1,4-cyclohexadiene. This knowledge will help us to decide, where hypothesis is necessary, what reactions of the ring-cyclized radicals are most likely under the present circumstances. Therefore, we shall postpone the full discussion of the nature of the induced decomposition until subsection 9.

Before leaving this discussion entirely, I would like to clarify one point that was implicit in the above: triethyltin radicals attack the perester with about equal facility at each of the two peroxy oxygens (see Chart 6, p. 162). This conclusion appears to be required by the following line of reasoning. Hydrocarbon products are formed to the extent of 30 to 40 percent (except at the higher tin hydride concentrations at 144°, where extensive destruction of products via their hydrostannation and that of the perester itself evidently occurs). The significant point is that these hydrocarbons are major products even in circumstances where cage-ether yields indicate that induced decomposition strongly predominates. This fact requires that there be a way to form hydrocarbon products via the induced process. Presumably, attack of triethyltin radicals on the perester often affords _t_-butoxytriethyltin and the acyloxy radical 11, which then decarboxylates to give the ring-opened radical 3, etc.

The products of the alternative attack by the tin radicals are a _t_-butoxy radical and triethyltin (γ, γ-diphenylallyl)acetate, 14. Yields of the tin ester, where measured (by infrared absorbance or by weight)

$$(C_6H_5)_2C{=}CHCH_2CH_2CO_2Sn(C_2H_5)_3$$

14

are given in Table 10. I should caution, however, that the two values quoted in the bank of runs at 125° actually were determined for closely similar perester and tin hydride concentrations at 110°; they are listed in the 125° bank to conserve space and to allow an approximate accounting of material balances in the two runs in question.

Yields of the diene 13 have not been recorded in Table 10. The vpc traces allow, at most, yields of 0.2 percent, except for two or three cases in which appearance of a new material at slightly longer retention time would have obscured yields of up to 1 percent. Thus, quantitatively meaningful estimates of the diene yields cannot be extracted from the data. Moreover, from the disproportion to combination ratio of 0.12 estimated for the runs in 1,4-cyclohexadiene, it is clear that the diene yields here should be small. It is also probable that much of what little diene is formed is subsequently hydrostannated (41), and thus not observed.

B. t-Butyl Diphenylcyclopropylperacetate

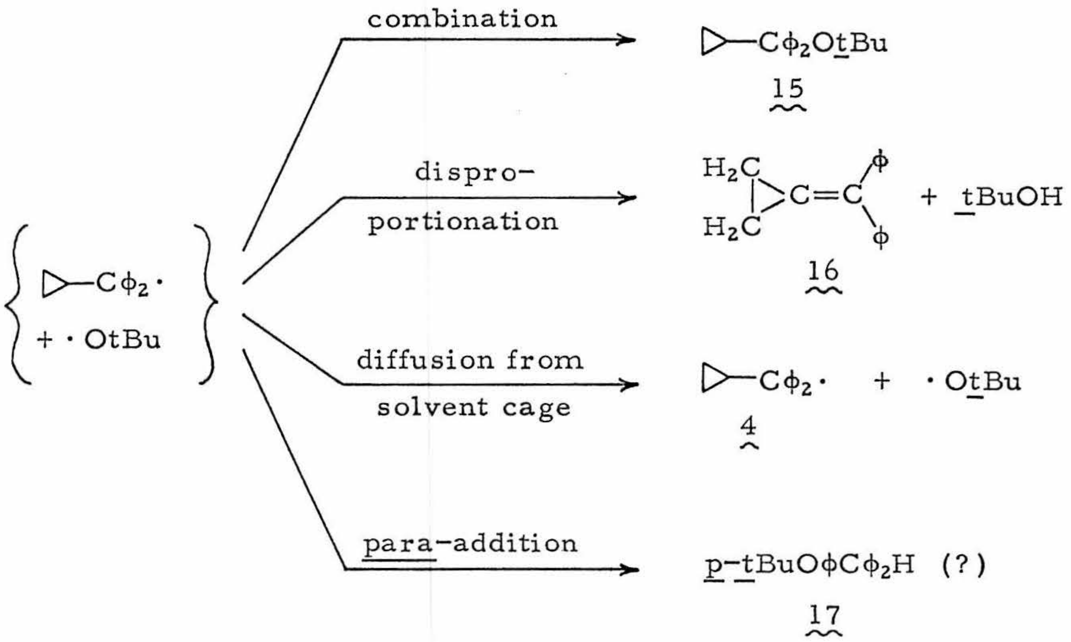
Decomposition of the ring-closed perester 2 is expected to produce, in the initial solvent cage, a ring-closed radical 4, a molecule of carbon dioxide, and a *t*-butoxy radical. As with the ring-opened perester, cage recombination and disproportion competes with diffusion. In this case, the products are the ring-closed ether 15 and the diphenylmethylenecyclopropane 16.

The ring-closed ether 15 and the methylenecyclopropane 16 have so closely similar retention times on Ucon polar that they are observed as a single peak. This curious[*] fact held up their identification for a considerable time while endeavors were directed to fitting nmr and UV

---

[*] One might have expected the greater molecular weight of 15 to lead to a retention time comparable to that observed for the ring-opened ether 12, which comes at about twice the retention time of 15 or 16. A possible explanation is that the steric congestion in 15 prevents strong interaction with the Ucon polar stationary phase.

Chart 3. Cage Reactions in the Thermal Decomposition of t-Butyl Diphenylcyclopropylperacetate.



data to a single compound. Another problem in the identification was the difficulty experienced in separating the material from other reaction products. In fact, no better than enriched samples were ever obtained, even this being possible only by choosing especially fortunate reaction conditions. Yields of the material we are discussing are listed in the data tables in the columns for substance B (see especially Tables 2 and 9 at this point).

The reader will note that the ratio of B to other products listed is relatively large for decomposition of perester 2 in cyclohexane. With this in mind, decomposition of 1 gram of perester 2 (rather than the usual 25 mg) was carried out in cyclohexane at 70°. Workup of the product mixture by elution with pentane on a Florisil column (no attempt being made to separate products) was followed by distillation three times in a bulb-to-bulb apparatus. Analysis of the resulting material by vpc revealed the presence of a number of products in the following relative amounts (by area): **B**, 32%; diphenylbutene **5**, 3%; diphenylcyclopropylmethane **6**, 15%; 1-phenyl-3,4-dihydronaphthalene **10**, 48%; and two minor products, 2%. The material was examined by nmr and a careful integration was made. A synthetic mixture with diphenylbutene, diphenylcyclopropylmethane, and the dihydronaphthalene in the same relative amounts as for the unknown was also prepared and investigated by vpc and nmr. This allowed accurate subtraction of the absorbances due to the three known components from the nmr spectrum of the reaction mixture.

The resulting residual spectrum is given (somewhat schematically) in Fig 6. Main features are the 39 units of phenyl absorbance, the 25 units comprising the 'doublet' at about 1.25 ppm, and the 8 units in a broad absorbance at about 0.3 ppm (indicative of secondary cyclopropyl protons). The 8 units remain from an original 17, only 9 of which could be attributed to the diphenylcyclopropylmethane known to be present. Of course, all the observed resonances do not necessarily correspond to the product **B**; some may be due to minor products which happen to be obscured in the vpc traces by some of the other products. Even so, only frustration was experienced in trying to divine a single structure which might account for even a major part of the observed resonances.

The critical clue in the resolution of the problem arose in another 'large-scale' run, this time in neat 1,4-cyclohexadiene. A nmr spec-

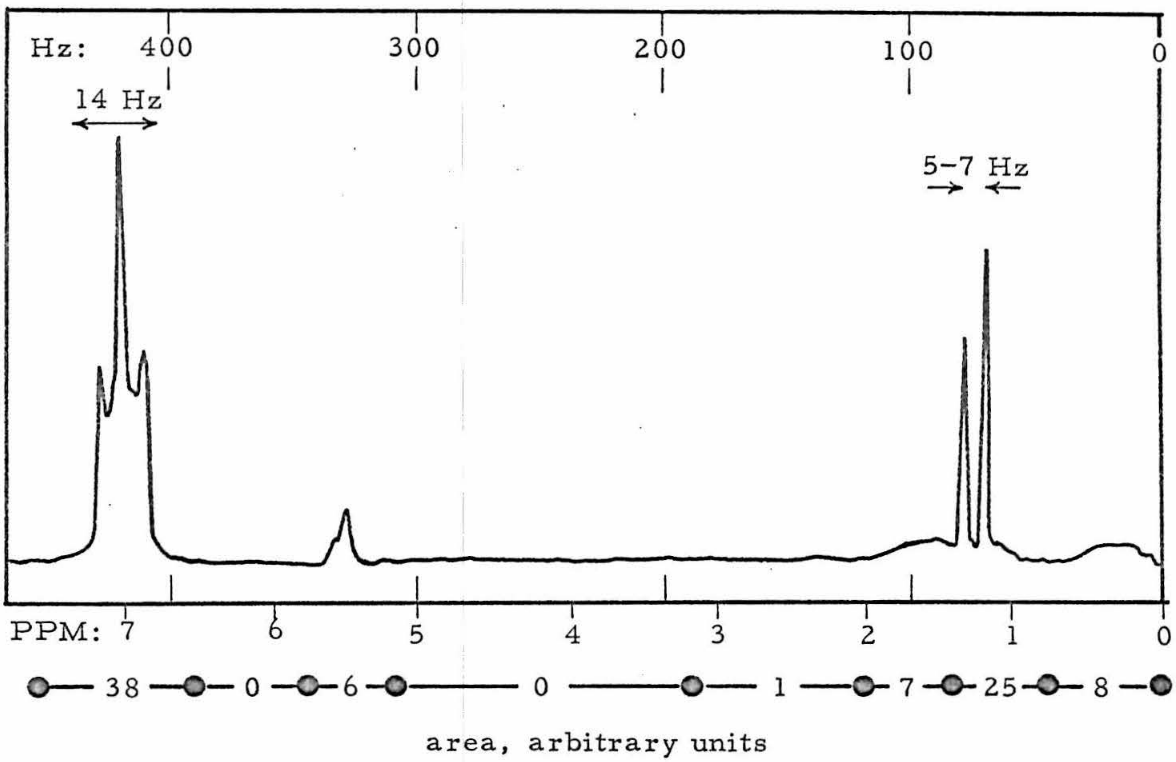


Figure 6. Residual nmr spectrum showing absorbance due to **B**

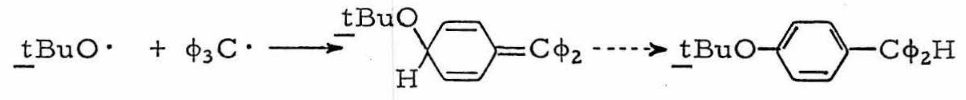
trum obtained on a distilled (but not chromatographed) sample again showed the upfield doublet, but the ratio of upfield to downfield peaks was about 6:1 rather than the 3:2 previously observed for decomposition in cyclohexane. Moreover, after careful chromatography on acid-washed alumina, the upfield peak disappeared entirely, though the downfield peak was apparently unaffected. Clearly, the components of the doublet are due to at least two substances. This inference allows an interpretation of Fig. 6. The 10 unit down-field peak is due to the methylenecyclopropane. The associated phenyl absorbance is 25 units. Thus the 15 unit upfield peak goes with about 13 units of phenyl absorbance, the 8 units of cyclopropyl-region absorbance, and possibly with some of the other absorbancies. The ring-closed ether **15** has 10 phenyl protons, 9 methyl protons, 4 secondary cyclopropyl protons, and one tertiary cyclopropyl proton. In view of the errors expected to be accumulated in obtaining the difference spectrum, the 10:9:4 agrees quite reasonably with the 13:15:8 inferred from Fig. 6.

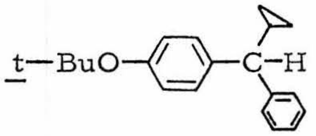
An independently prepared sample of the methylenecyclopropane was found to have the expected retention time on Ucon polar. Addition of a quantity of 16 to a reaction mixture containing a like amount of the candidate material was found to double the height of the 1.3 ppm singlet without detectably broadening it. This information would seem to establish the methylenecyclopropane as a reaction product.

The knowledge that it is also a cage product is due to a curious quirk of fate. The column used to obtain initial vpc traces for the concentration-study runs of Table 6 unexpectedly separated the product **B** into two peaks, one of which displayed the same retention time as the methylenecyclopropane on that column. That vpc column was prepared from a sample of Ucon polar carrying the same markings (50 HB 5100) as Ucon polar previously employed. However, a column made up from yet another sample of Ucon polar 50 HB 5100 caused the two peaks to again coalesce. Table 6 shows that the yield of the methylenecyclopropane varied little with the initial perester concentration. Because we know that the ring-cyclized radicals (from which the methylenecyclopropane must somehow be formed) have other options, the constancy of the yield indicates a cage-disproportionation origin.

Similarities to Lorand and Bartlett's study of *t*-butyl triphenylperacetate (27) must be noted here. Lorand and Bartlett found evidence that *t*-butyl triphenylmethyl ether is formed. As in this work, they were not able to isolate the ether, although nmr spectra of samples of the crude reaction mixture showed a peak at high field attributable to *t*-butyl protons. Upon chromatography on alumina, they obtained triphenylcarbinol, whose formation they attributed to cleavage of the ether on the column in view of the fact that infrared spectra showed that the carbinol was not present in the crude reaction mixture. Similarly, in this work the diphenylcyclopropylcarbinol was isolated in about the expected amount via careful chromatography on Florisil of the products of another 'large-scale' run. Finally, Lorand and Bartlett point out that *t*-butoxy triphenylmethyl ether is unknown; several attempts to prepare the ring-closed ether **15** in this work were uniformly unsuccessful.

Triphenylmethyl radicals, Lorand and Bartlett found, tend to do rather desperate things: evidently the space around the central carbon of the triphenylmethyl radical is so congested that the caged *t*-butoxy radical finds it about equally easy to attack a phenyl ring at the *para*-position to give a quinoid product, which is converted under the reaction conditions to *p*-*t*-butoxytriphenylmethane. The analogous product for this work, **17**, was shown by nmr to be present, if at all, in a yield of less than about 3 percent. However, an unidentified vpc peak which comes at approximately the retention time expected for the ring-opened





17

ether and whose area runs about 4-6% of that of the product **B** might well be due to that product. Of course, if the peak corresponded to ring-opened ether, and if the ring-opened material could be shown not to result simply from isomerization of the ring-closed ether, that result would be of interest in regard to possible formation of both ring-opened and ring-closed products from a common intermediate.

The reader will note that a product labeled **B** is listed in Table 1 for decomposition of the ring-opened perester. However, that material is not thought to be either the methylenecyclopropane **16** or the ring-closed ether **15**. The same designation has been used because a peak is also found at the retention time of '**B**' when the perester employed is **1**. My feeling is that the material designated **B** for decomposition of perester **1** is likely to be a 1-phenyltetrahydronaphthalene (or perhaps several isomeric 1-phenyltetrahydronaphthalenes (see Chart 4)). Its probable mechanism of formation is as follows: Ring-cyclized radicals are converted, somewhat inefficiently, to the dihydronaphthalene **10** via disproportionation reactions. If pairs of ring-cyclized radicals disproportionate, one of the products will be a tetrahydronaphthalene. Moreover, disproportionation of a ring-cyclized radical with a cyclohexadienyl radical can either produce dihydronaphthalene plus 1,3- or 1,4-cyclohexadiene, or a tetrahydronaphthalene plus benzene. In partial support of this identification, we can note that the be-

Chart 4. Possible Structures for Isomeric 1-Phenyltetrahydronaphthalenes.

havior of B as a function of the initial cyclohexadiene concentration in Table 1 is similar to that of the dihydronaphthalene 10. Further evidence will be considered later (pp. 129, 130, 281, 282).

If tetrahydronaphthalene is formed in the decomposition of the ring-opened perester, it should also be formed from the ring-closed perester. In fact, the product labeled B_1 in the Table 6 concentration study is likely to be tetrahydronaphthalene. Indeed, the unexplained absorbances in Fig. 6 could well be due to such a product(s). If this is correct, then what has happened to the ring-closed ether? We have already alluded to the instability of the ether on (acid-washed) alumina and to unsuccessful attempts to synthesize the ether. It is easy to imagine that acid-catalyzed cleavage might be a facile process. The perester 2 is prepared by the method of Lorand and Bartlett (27) from the acid chloride and sodium *t*-butylhydroperoxide; if the heterogeneous reaction is not carried to completion and the work up (by recrystallization from pentane at low temperature) does not eliminate all the acid chloride, the contaminated perester may develop HCl on decomposition.

Thus, the ring-closed ether might reasonably be observed or not depending on the purity of the perester. Examination of the yields of **B** suggests that the ether wholly or largely survived the reaction conditions for the runs of Table 2, for some of the runs of Table 9, and, fortunately, for the 'large-scale' decompositions referred to above; but not for the runs of Table 6, Table 7, or for other runs in Table 9.

If this interpretation is correct, we can use the results of Table 6 to divide as follows the 36% **B** reported in Table 2 for **2** in 2.8 M 1,4-cyclohexadiene at 35°: 7% is diphenylmethylenecyclopropane, a like amount is tetrahydronaphthalene, and the remainder, 21%, is ring-closed ether. Thus, the total amount of cage product is about 28% and the disporportionation to combination ratio is estimated to be about 7/21 = 0.33. Interestingly, the 6:1 nmr intensity ratio previously remarked for the large scale decomposition in 1,4-cyclohexadiene gives an estimate of 1/4:6/9 = 0.38, in rather decent agreement with the value inferred by vpc.

The reader will recall that for the ring-opened radical and the _t_-butoxy radical the disproportionation to combination ratio is about 0.12 (page 63). Considering that the ring-opened radical has two disproportionable hydrogens to one for the ring-closed radical and that the double bond in the methylenecyclopropane must be highly strained (71), that the disproportionation to combination ratio is substantially higher when the ring-closed radical is involved seems surprising. Perhaps the congestion about the radical center in the ring-closed radical is responsible for selectively disadvantaging its participation in combination reactions; the hydrogen atom removed by the _t_-butoxy radical in disproportionation is located a few angstroms from the center of greatest steric congestion.

Yet we note that as much or possibly even greater amounts of cage product are formed in decomposition of the ring-closed perester **2**. If the rate constant for combination of a ring-closed radical with a *t*-butoxy radical is appreciably less than that for combination of the ring-opened radical with the *t*-butoxy radical, why are the cage *efficiencies* in the inverse order? The lower decomposition temperatures for the ring-closed perester may be part of the answer, although the small temperature dependence of the cage processes for the ring-opened perester (see Table 1) suggests that this factor should not be large. The attractive explanation, it seems to me, is that most or all of the ring-opened perester decomposes by the stepwise pathway (see p. 51); the time necessary for decarboxylation of the acyloxy radical **11**, of course, decreases the potential cage efficiency. In contrast, decomposition of the ring-closed perester is expected to be concerted and the warring partners can have at it from the start.

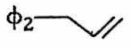
With the preliminary discussion of induced decomposition of the ring-opened perester in triethyltin hydride freshly in mind, we might ask whether induced decomposition can be inferred for the ring-closed perester as well (Table 11). Unfortunately, another product at nearly the same retention time as **B** is formed in those decompositions. Judging from peak areas found for some runs and from the high material balances quoted in Table 11, the new product does not contain the C_{16} fragment from the perester. That product might possibly be hexaethylditin. At any rate, the new material generally obscures the retention time region where the cage-products would be found.

Thus, while it is possible that induced decomposition occurs for the ring-closed perester, kinetic measurements would be needed to be sure. We can, however, say that, if induced decomposition is important, it must give principally *t*-butoxytriethyltin and the ring-closed acyloxy radical. For the ring-opened perester, as noted above (p. 70), triethyltin radicals attack either of the peroxy oxygens with comparable facility. Of course, the necessity to propose a different pattern for the ring-closed perester cannot be used as an argument against induced decomposition for **2**, for the steric congestion associated with the phenyl rings might well account for just such a shift in the position of attack.

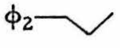
C. *t*-Butyl 4,4-Diphenylperpentanoate

Yields of the saturated ether **18** (Table 3) are remarkably similar to those for the ring-opened ether **12** (Table 1). As we shall document later on, the ring-closed radical strongly predominates in its equilibrium with the ring-opened radical at all temperatures studied. Thus, the similarity between yields of the ethers **12** and **18** strongly suggests that the isomerization of ring-opened radical to ring-closed radical does not take place on nearly as short a time scale as do the cage processes. Although the time scale for cage processes (24) is uncertain, this consideration would appear to set a maximum of about 10^8 to 10^9 for the rate constant describing the isomerization of ring-opened **3** to ring-closed **4**.

18



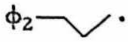
19



20

A product believed to be 1,1-diphenyl-3-butene (19) is found at slightly longer retention time than the saturated hydrocarbon 20. For decomposition in cyclohexane, its yield could be determined to be 2.0%. However, the massive yields of 20 formed in the presence of 1,4-cyclohexadiene made it impossible to independently observe the smaller peak. Therefore, I have assumed the figure of 2.0% is also correct in the other cases and have so corrected the total area for the two peaks in calculating yields for 20. The assumption that the mono-olefin 19 largely survives the reaction conditions in cyclohexane, whereas its unsaturated analog 13 does not, is not unreasonable in view of observations of Szwarc and co-workers (25) which show that methyl radicals add to butadiene or to 1,1-diphenylethylene about 50 times more rapidly than to ethylene.

Thus, the disproportionation to combination ratio for the saturated radical 21 and the *t*-butoxy radical may be taken to be greater than or equal to 2.0/20 = 0.1. That this quantity is nearly the same as for the unsaturated ring-opened radical with *t*-butoxy (0.12) implies that formation of the conjugated pi-electron system of the butadiene 13 does not greatly facilitate disproportionation. Such a result seems appropriate for a diffusion-controlled process, which, by virtue of successful competition with diffusion from the solvent cage, each cage reaction is.

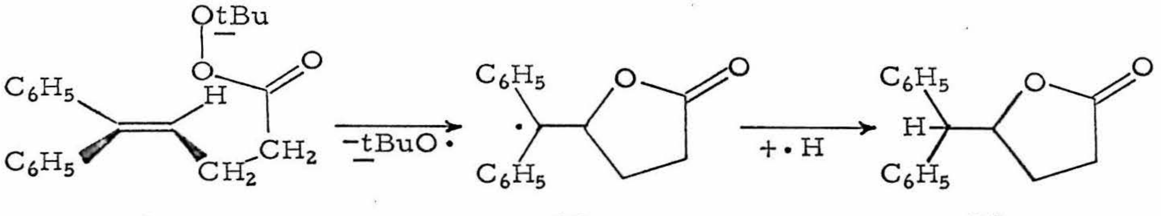


21

The regular decline in the yields of 18 as 1,4-cyclohexadiene replaces cyclohexane as solvent would appear to be a good example of the previously discussed dependence of cage yields on solvent viscosity.

6. Molecule-Induced Decomposition of t-Butyl (γ,γ-Diphenylallyl)peracetate

Of the three perester-decomposition mechanisms briefly surveyed in subsection 3, we have now covered normal homolytic decomposition and have made a start on radical-induced decomposition in triethyltin hydride. The third, molecule-induced decomposition, is possible in the ring-opened perester 1 because of the presence of the carbon-carbon double bond, but in the ring-closed perester 2 and the saturated perester 8 the necessary functionality is lacking. As stated in subsection 3, the essence of molecule-induced decomposition in 1 or in the closely related ortho-diphenylvinylperbenzoate system studied by Martin and co-workers (29) is attack of the double bond on the peroxy linkage to give a cyclic lactonyl radical and a t-butoxy radical. By analogy with Martin's system, the lactonyl radical may in part undergo



1 22 23

cage combination with the t-butoxy radical, but the dominant reaction is expected to be the one shown, hydrogen abstraction to give the lactone

23. Loss of a hydrogen atom by 22 to give the exocyclic unsaturated lactone may also occur.

Actually, the evidence for molecule-induced decomposition of 1 is only circumstantial in that no product arising via that mechanism (such as the lactone 23) has actually been isolated and subjected to analytical scrutiny. In truth, efforts to that end were begun only very late in the course of this research, and it was just not possible to spare sufficient time to carry through to that point. As circumstantial evidence goes, however, the evidence is rather good. Because the existence of molecule-induced decomposition affects the product ratios described in the quantitative mechanistic study of Section Two, it seems worthwhile to bring up the subject at this point.

The first significant observation is that a long retention-time product can be detected by vpc among the reaction products from the ring-opened perester 1 but not from the ring-closed 2. For short, let us call this material product X. The retention time of X is about 10 times that of the ring-opened *t*-butyl ether 12 on Ucon polar and 3 times that of 12 on silicone oil. These observations suggest (a) that X is not dimeric material formed from solvent radicals or hydrocarbon radicals derived from the peresters, since such a product should be formed both from 1 and 2, and (b) that the material is appreciably polar (this would nicely explain the difference in relative retention times of X and 12 on silicone oil and the more polar Ucon polar).

Yields of X for decomposition of 1 are shown in Table 1 as yields of the lactone 23 (which is what we shall conclude X is). There is no clear trend of yield with 1,4-cyclohexadiene concentration or with reaction temperature. The average yield is about 15%. The product was also detected in the concentration study reported in Table 4. Those observations have not been dignified by inclusion in Table 4, however, because the resolution on the particular silicone oil column employed allowed only semiquantitative accuracy. Nonetheless, a definitive result was obtained in the finding that X does not decrease in yield on going to lower initial perester concentration (the yield may actually increase by about a fourth). This clearly means that X cannot be a radical-induced product (such as a cyclohexadienyl ester of the ring-opened acid).

The possibilities excluded by the information presented above and the analogy to the benzoate system already combine to suggest that X is the lactone 23. Martin has reported that the rates of molecule-induced decomposition in his systems respond strongly to solvent polarity. For example, Martin's diphenylvinylperbenzoate decomposed 62 times as rapidly in methanol as in chlorobenzene (29a). With this in mind, decomposition of a sample of 1 of 10% 1,4-cyclohexadiene in methanol (v/v) was effected by maintaining the degassed reaction mixture at 100° for 100 hours (which is about 10 half-lives at the normal decomposition rate). First analyzed were the yields of the normal decomposition products (row 8 of Table 8). As expected, those yields are uniformly down by about a factor of 10. Were the yield of X also up from 15 to about 90%, the solvent change would be judged to have promoted the rate of the molecule-induced decomposition by about the factor of 60 expected by analogy to Martin's benzoate system.

This simple result, however, was not to be. Detected among the reaction products were the ring-opened acid (15%) and the methyl ester of the acid (also 25%) as well as **X** (still 15%). The acid was isolated by extraction with sodium bicarbonate and identified by its melting point and its infrared spectrum (carbonyl maximum 1710 cm^{-1}). The methyl ester was identified by its vpc retention time on silicone oil, by the presence of characteristic peaks in several nmr spectra, and by the position and intensity of its carbonyl maximum at 1740 cm^{-1}. The product **X** from this run had the same retention time on silicone oil as did that from a run in 1,4-cyclohexadiene analyzed at the same time. The formation of the methyl ester of the ring-opened acid can be attributed to direct methanolysis of the perester.* As regards the ring-opened acid, however, well, there could well have been stoichiometrically-sufficient water to account for its formation, but my understanding is that methanol is generally more nucleophilic than water; thus, on a kinetic basis, the formation of comparable amounts of the acid and the methyl ester is hard to rationalize. That only a 4% yield of the acid could be detected in the companion run in 1,4-cyclohexadiene

---

*Methanolysis of an anhydride would be expected to be rapid, while methanolysis of an ester would probably not be observed under the conditions employed. As the pK_a of *t*-butylhydroperoxide (12.8 (74)) lies between those of organic acids (about 5) and alcohols (about 17), methanolysis of **1** is perhaps not too surprising. A sample of the saturated perester 8 was treated similarly as regards solvent composition and reaction temperature. Again, the normal decomposition products were down in yield by approximately a factor of 10, and presumably methanolysis has occurred here also. A product at about the same retention time as the methyl ester of the ring-opened acid was detected by vpc and carbonyl bands at 1715 and 1745 cm^{-1} (appropriate for the saturated acid and its methyl ester, respectively) were observed in very nearly the same relative intensity as for methanolysis of **1**.

mentioned just above makes a free-radical mechanism highly improbable as the source of a 25% yield of the acid.

One possible difficulty in Martin's interpretation of his results (29a) should be mentioned here. The enhanced rate of decomposition in methanol was ascertained (a) by following the consumption of the perester by UV spectroscopy and (b) by following by UV the decolorization of an excess of the colored free-radical scavenger galvinoxyl (75). However, no product studies were cited for decomposition in methanol. The authors mention that the rate constant from the galvinoxyl decolorization is only semiquantitative because galvinoxyl slowly reacts with methanol at the temperature employed (90°). As *t*-butyl hydroperoxide, the expected by product of methanolysis, is an oxidizing agent and is substantially more acidic than methanol, it is at least possible that decolorization of galvinoxyl would also accompany methanolysis. Thus, whether the 62-fold rate enhancement in methanol is due entirely to the increased rate of molecule-induced decomposition must be regarded as uncertain.

After extraction with sodium bicarbonate, then, the reaction mixture contained a small amount of hydrocarbon products, the product **X** , the methyl ester, and possibly other products accounting for the difference between the material balance of about 75% computed from the yields quoted above and the theoretical 100%. A partial separation of the components was simply effected by repeatedly treating the residual oil obtained by stripping the solvent with small quantities of pentane. The hydrocarbon products dissolved first, followed by the methyl ester, and, more slowly yet, the product **X**. The process was stopped when the weight of the residue had been cut by four-fifths. The residue was then distilled in a small sublimation apparatus. The last few pentane extracts were then combined and similarly distilled. Obtained in this way were Fractions 1 and 2, respectively. The crude reaction mixture less the ring-opened acid (which we shall call Fraction 0) had previously been analyzed by vpc, nmr, and infrared spectroscopy, and Fractions 1 and 2 were now so analyzed. The combined data allow a test to be made of the supposition that the product **X** is the lactone **23**.

Specifically, the ratio of **X** to methyl ester could be inferred for each of the fractions by each of the three methods. If for each fraction the three methods give compatible results, then the structural features on which the nmr and infrared analyses are based may safely be attributed to the product **X**.

The nmr ratio was obtained from relative areas of a doublet (coupling constant about 7 Hz) at 4.2 δ attributable to the tertiary dibenzylic proton of **23** and the singlet methoxyl resonance at 3.8 δ due to the methyl protons of the methyl ester. For comparison, the dibenzylic protons of diphenylmethane were found 4 Hz upfield from the center of the doublet.

The infrared ratio was taken from the absorbancies of the carbonyl maxima at 1740 cm^{-1} (the methyl ester) and 1785 cm^{-1} (**X**). Bellamy (88) lists 1760–1780 cm^{-1} as the range expected for the carbonyl band of a saturated γ-lactone such as **23**. The ratios determined by infrared depend on the molar absorptivities assigned to the methyl ester and to **X**. These need not be the same; to effect something of a best fit, it has been assumed that the molar absorptivity of

X is 1.8 times that of the methyl ester.

Finally, vpc ratios were calculated assuming that **X** and the methyl ester have identical response characteristics.

The ratios obtained as above for the three cases are quoted in Table 14. Note that although the ratio varies significantly from sample to sample, the three analytical methods nonetheless give substantially the same results. This would seem to establish that (a) the product **X** is a carbonyl compound whose carbonyl frequency is approximately correct for a γ-lactone, and (b) the product **X** contains a single proton, split by only one other, which resonates at 4.2 δ, approximately the position expected for a dibenzylic proton. In addition, we also know that **X** is not a radical-induced product, is not acidic, is formed in the decomposition of the ring-opened perester **1** but not in that of the ring-closed perester **2**, is appreciably polar and has an appreciable vapor pressure at 105° (the bath temperature employed in the vacuum distilla-

Table 14. Ratios of **X** to Methyl (γ, γ-diphenylallyl)acetate According to VPC, NMR, and Infrared Spectroscopy

	Ratio		
Fraction[a]	VPC	NMR	IR
0	0.62	0.6	0.59
1	4.4	4.1	5.3
2	0.29	0.28	0.24

[a] See text for origin of the various fractions.

tions of Fractions 1 and 2). All of these properties admirably fit the lactone 23. In addition, evident in the nmr spectrum of Fraction 1 are absorbancies attributable to the phenyl protons, the four methylene protons, and the other tertiary proton of the lactone 23. I do not wish to leave the impression that sufficient definition was obtained in this low-concentration spectrum to attest to the correctness of the relative intensities of the various absorbancies, but at least it can be stated that absorbancies are present at the expected resonance positions.

Short of an analysis of an isolated sample, this, I feel, is pretty good evidence that X is the lactone 23.

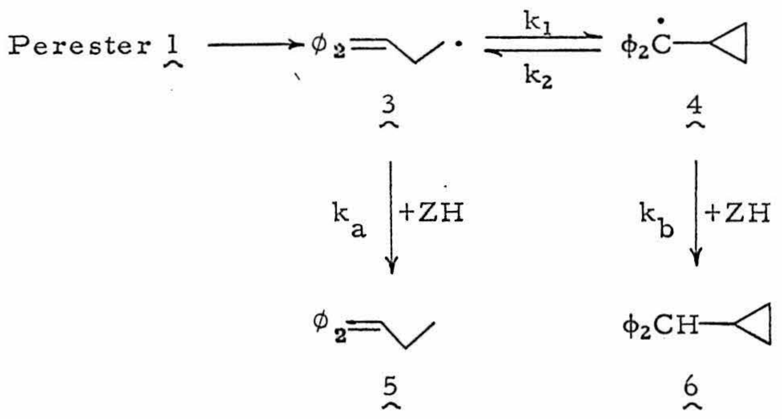
7. Equilibration of Radicals and Hydrogen Abstraction

We have seen that decomposition of each of the peresters can get under way via one or more initial steps. Of particular interest is what happens next for normal or radical-induced decomposition, the pathways leading to formation of the hydrocarbon products with which we are chiefly concerned.

In the usually dominant normal decomposition, the immediate reaction products, if cage combination or disproportionation is avoided, are the _t_-butoxy radical and a hydrocarbon radical. For the _t_-butoxy radical, hydrogen abstraction should follow quickly if 1,4-cyclohexadiene, indene, or triethyltin hydride are present. In the other solvents, β-scission to a methyl radical and acetone can be competitive with or even dominate any hydrogen abstraction from solvent, especially at the higher temperatures (42). If β-scission occurs, then the resultant methyl radical may attack the solvent; ring-cyclized radicals or solvent radicals; or products produced earlier in the decomposition, such as the isomeric hydrocarbons **5** and **6**, the dihydronaphthalene **10**, the butadiene **13** or, perhaps most likely, the phenyltetrahydronaphthalene(s).

No real attempt has been made to follow further the fate of the *t*-butoxy radical; its reactions have been so exhaustively investigated (42, 43) that further study here would not likely be of great value. Actually, the question of the fate of the *t*-butoxy radical is of real concern in this work only for decomposition of the peresters in the presence of 1, 4-cyclohexadiene and triethyltin hydride, where suppression of product destructions by the active hydrogen donors makes quantitative mechanistic treatments feasible. In these two cases, we shall simply assume that one solvent radical is formed per *t*-butoxy radical.

For the hydrocarbon radical, equilibration of the ring-opened and ring-closed forms is the next order of business. The nature of the cage products indicates that , at the time the *t*-butoxy radical takes its leave, the hydrocarbon radical nearly always will be ring-opened if the perester is ring-opened, or ring-closed if the perester is ring-closed. The radical equilibration may, of course, occur competitively with abstraction of hydrogen from the solvent. Such a situation is represented below starting from the ring-opened perester



We wish to work out an expression for the ratio of the isomeric hydrocarbons as a function of the rate constants and the concentration of the active hydrogen donor, ZH. We can proceed by writing

$$\frac{d(\mathbf{5})}{d(\mathbf{6})} = \frac{k_a(\mathbf{3})}{k_b(\mathbf{4})} .$$

Thus, we see that an expression for the ratio **3**:**4** is needed. This can be obtained from the rate law for (**4**),

$$\frac{d(\mathbf{4})}{dt} = k_1(\mathbf{3}) - (k_2 + k_b(\mathrm{ZH}))(\mathbf{4}),$$

by making the steady-state approximation, $d(\mathbf{4})/dt = 0$. Thus,

$$\frac{(\mathbf{3})}{(\mathbf{4})} = \frac{k_2 + k_b(\mathrm{ZH})}{k_1}$$

and

$$\frac{d(\mathbf{5})}{d(\mathbf{6})} = \frac{k_a k_2}{k_1 k_b} + \frac{k_a}{k_1}(\mathrm{ZH}). \qquad (1.7\text{-}1)$$

Eq. 1.7-1 can be integrated, if the concentration of ZH does not vary appreciably over the course of the reaction, simply by replacing (ZH) by its average value as determined from the reaction stoichiometry and initial concentrations.

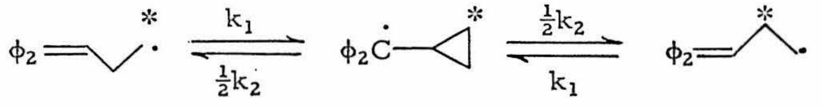
$$\frac{(5)}{(6)} = \frac{k_a k_2}{k_1 k_b} + \frac{k_a}{k_1}(\mathrm{ZH})_{av} \qquad (1.7\text{-}2)$$

According to eq. 1.7-2, competition between radical equilibration and hydrogen abstraction should result in a linear dependence of the ratio 5:6 on the hydrogen-donor concentration. As noted in the Overview (p. 10), Howden found no such dependence for decomposition of 1 in the presence of tri-*n*-butyltin hydride (Howden's observations are reproduced here in Table 12). More extensive studies in this work employing instead triethyltin hydride (to simplify analysis by vpc through the use of the lower molecular-weight solvent) corroborate Howden's findings. In fact, the ratios 5:6 given in Table 10 do not become larger at higher triethyltin hydride concentrations, but actually decrease. A similar decrease can be seen in the runs carried out by Howden at 110° (see Table 12). The reason for this behavior, which is quite unexpected, is uncertain. However, one might ascribe the trend to increasingly extensive hydrostannation (41) of the ring-opened hydrocarbon 5 at the higher tin hydride concentrations.

Whatever the reason, it seems unlikely that hydrogen abstraction competes with the radical equilibration for either of the tin hydrides at the relatively high temperatures employed. Of course, a marginal degree of competition could well be obscured by whatever is responsible for the observed trend.

An alternative interpretation to rapid radical equilibration would be that both hydrocarbons are formed from a common intermediate, such as the nonclassical radical 7. Because the nature of the cage products depends on the structure of the starting perester, it is obvious that a nonclassical radical cannot be formed directly from both peresters 1 and 2. Lack of dependence of product ratios on the tin hydride concentration--other than via product destructions, that is--would require that isomerization of the ring-opened radical 3 to the nonclassical radical 7 be fast compared to hydrogen abstraction by 3.

One possibility is that the nonclassical radical is much more stable than either of the classical radicals and abstracts hydrogen more rapidly than it is reconverted to either. Such an eventuality could be detected in the following way. Because the two nonequivalent methylene groups of the ring-opened radical 3 become equivalent in the ring-closed form 4,

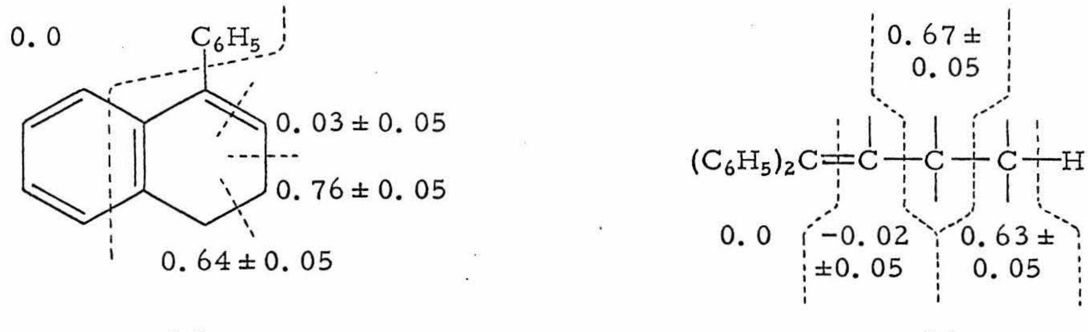


3-α labeled　　labeled 4　　3-β labeled

equilibration of the classical radicals must exchange the methylene groups. If isotopic labeling is used, the label will therefore be scrambled in the resultant products. On the other hand, because the methylene groups in the nonclassical radical 7 are nonequivalent, intervention of such a species provides a way of obtaining ring-closed hydrocarbon from ring-opened perester without making the methylene groups equivalent. If, therefore, the nonclassical radical **7** is formed irreversibly, the isotopic label would not be scrambled.

On the basis of these considerations, perester **1** was prepared with 1.4_2 g-atoms of deuterium in the α position. Following decomposition in cyclohexane at 125°, the distribution of the deuterium label in the ring-cyclized hydrocarbon **10**, which is by far the major product (see for example row 1, Table 8), was determined by nmr spectroscopy. The results are summarized in Fig. 7a.

It is clear that scrambling of the deuterium label in the radical intermediates is rapid with respect to isomerization of the ring-opened radical **3** (or its equivalent) to the ring-cyclized radical **9**. Here, the time during which exchange of the label may take place is limited only by the relatively slow rate at which the *ortho*-ring cyclization occurs.



(a) (b)

Figure 7. Distribution of the deuterium label as inferred by nmr spectroscopy in products from the decomposition of deuterium-labeled *t*-butyl (γ,γ-diphenylallyl)peracetate in (a) cyclohexane at 125°, and (b) 1.34 M triethyltin hydride in *n*-octane at 125°.

Decomposition of the labeled 1 in the presence of 1.34 M triethyltin hydride made it possible to reduce this time by approximately a factor of 8, according to the value of k_a/k_r quoted on page 135. Nonetheless, nmr analysis of the major product, the ring-opened hydrocarbon 3, showed that the processes exchanging the methylene groups are fast with respect to hydrogen abstraction from triethyltin hydride. A quantitative determination of the completeness of the exchange would require an evaluation of the secondary deuterium isotope effects which come with the method of labeling used. Indeed, if substitution of deuterium for hydrogen might be thought to constitute a major perturbation--if equilibration might correspond to a ratio of α- to β-deuterium substantially different from unity--considerable caution would have to be exercised in interpreting the data. However, the few secondary deuterium isotope effects which seem to have been reported are small, perhaps 10-15% per α-deuterium atom being a representative number at 125° (55).* In addition, the magnitude of the error limits indicated in the figure would render of doubtful value any attempt at a detailed analysis.

Thus, let us simply record that the equilibration is largely or wholly complete. This result is the first real test of the facility of the interconversion of ring-opened and ring-closed radicals which must be postulated to account for the ratios of the isomeric hydrocarbons in terms of classical radicals. The existence of the deuterium exchange

---

*The β-deuterium effect in radical reactions is smaller still. A representative number is 2% per β-deuterium (72).

does not, however, in and of itself make untenable the suggestion of *product control* via a nonclassical radical. Such a species might be able to exchange its methylene groups via the ring-closed radical (which might be an intermediate or simply a transition state) while yet being responsible for formation of the hydrocarbon products.

The failure of triethyltin hydride to interdict the radical equilibration came as something of a disappointment because the only significantly more reactive hydrogen donors which seem to be known, free radicals with easily abstractable hydrogen atoms, would be unlikely to do any better. This is because their very reactivity restrict such free radicals to rather small concentrations; and the important factor, after all, is the product of the rate constant for hydrogen abstraction with the hydrogen-donor concentration. Fortunately, it turns out that decreasing the reaction temperature slows the rate constants for the radical interconversions more strongly than the hydrogen abstraction rate constants. As noted previously, lower reaction temperatures may be employed with ring-closed perester 2 because extensive electron delocalization into the phenyl rings of the incipient ring-closed radical lowers the activation energy for the perester decomposition. Results are listed in Table 11 for decomposition of 2 at 10 and 35°.

We need here the complement to eq. 1.7-2 for entry to the radical system via the ring-closed perester. The new equation can be obtained from the old by noting that the roles played by the ring-opened and ring-closed radicals in the earlier derivation are simply interchanged. Thus, by interchanging 6 and 5, k_2 and k_1, and k_b and k_a, we obtain eq. 1.7-3.

$$\frac{(6)}{(5)} = \frac{k_1 k_b}{k_a k_2} + \frac{k_b}{k_2}(\mathrm{ZH})_{av} \qquad (1.7\text{-}3)$$

Before proceeding to interpret product ratios according to eq. 1.7-3, we must briefly consider whether the large variations in the observed ratios could reasonably arise other than by the selective trapping of first-formed intermediate embodied in that equation. This examination is especially pertinent in view of the fact that something other than selective trapping does cause ratio variations for decomposition of perester 1 in triethyltin hydride. However, the factor tentatively implicated in that case--hydrostannation of the ring-opened hydrocarbon 5--can easily be seen to be unimportant for the runs at 35°; the high meterial balances (76 to 86%) are inconsistent with destruction of the ring-opened hydrocarbon on the scale required to explain the ratio variations.* Note that there need be no inconsistency in invoking hydrostannation of products from decomposition of 1 but not from 2, for the reaction temperatures are quite different in the two cases. Key processes may well have appreciable activation energies.

Another possibility--formation of the isomeric hydrocarbons in

---

*Although yields are unavailable, a similar statement can be made for the runs at 10°. A quantity of 1-phenylnaphthalene, later realized not to have been recorded, was added to the solution of the perester from which aliquots were taken for the individual runs. Therefore, the 1-phenylnaphthalene provides a fixed, if unknown, point of reference; from the actual area measurements, it can be stated that the total yield of 5 + 6 + 10 varied even less than in the runs at 35°. One, of course, presumes that the total yields again were fairly high.

The assumption here that 6 will not be subject to hydrostannation is in accord with the ease of hydrostannation of olefinic materials and the corresponding lack of any indication that aromatic systems undergo hydrostannation (39).

part by hydrogen abstraction from some hydrogen donor other than triethyltin hydride--suffers from the apparent nonexistence of alternative hydrogen donors. Hydrogen abstraction from the ring-cyclized radical might occur, but the small yields of the ring-cyclized hydrocarbon 10 confirm the relative unimportance of such a pathway to the isomeric hydrocarbons.

Finally, the observed variations could arise from interpretation as ring-closed hydrocarbon of another product, uniquely formed under these reaction conditions, due to a fortuitous similarity in vpc retention times. Such an eventuality could have been ruled out by confirming a few of the ratios of 6:5 by nmr or by comparing retention times with those of the authentic materials on several vpc columns, but neither of these was done.

Plots at 10 and 35° of the ratio 6:5 against the average triethyltin hydride concentration (defined to be the initial tin hydride concentration less the initial perester concentration, since approximately two moles of tin hydride are used up per mole of perester taken) are given in Fig 8. The fit to a least-squares line is reasonable at each temperature.*

Two main features should be noted. The first is that the slope ($\equiv k_b/k_2$) at 10° is about twice that at 35°. The two values may be combined to give

---

*In weighting the points in the least-squares fit, it was assumed that the standard error in each could be taken to be 3 percent of value. The resultant fit at each temperature gave an average percent relative deviation of approximately 3 percent. The standard errors calculated for the parameters are shown in Fig 8.

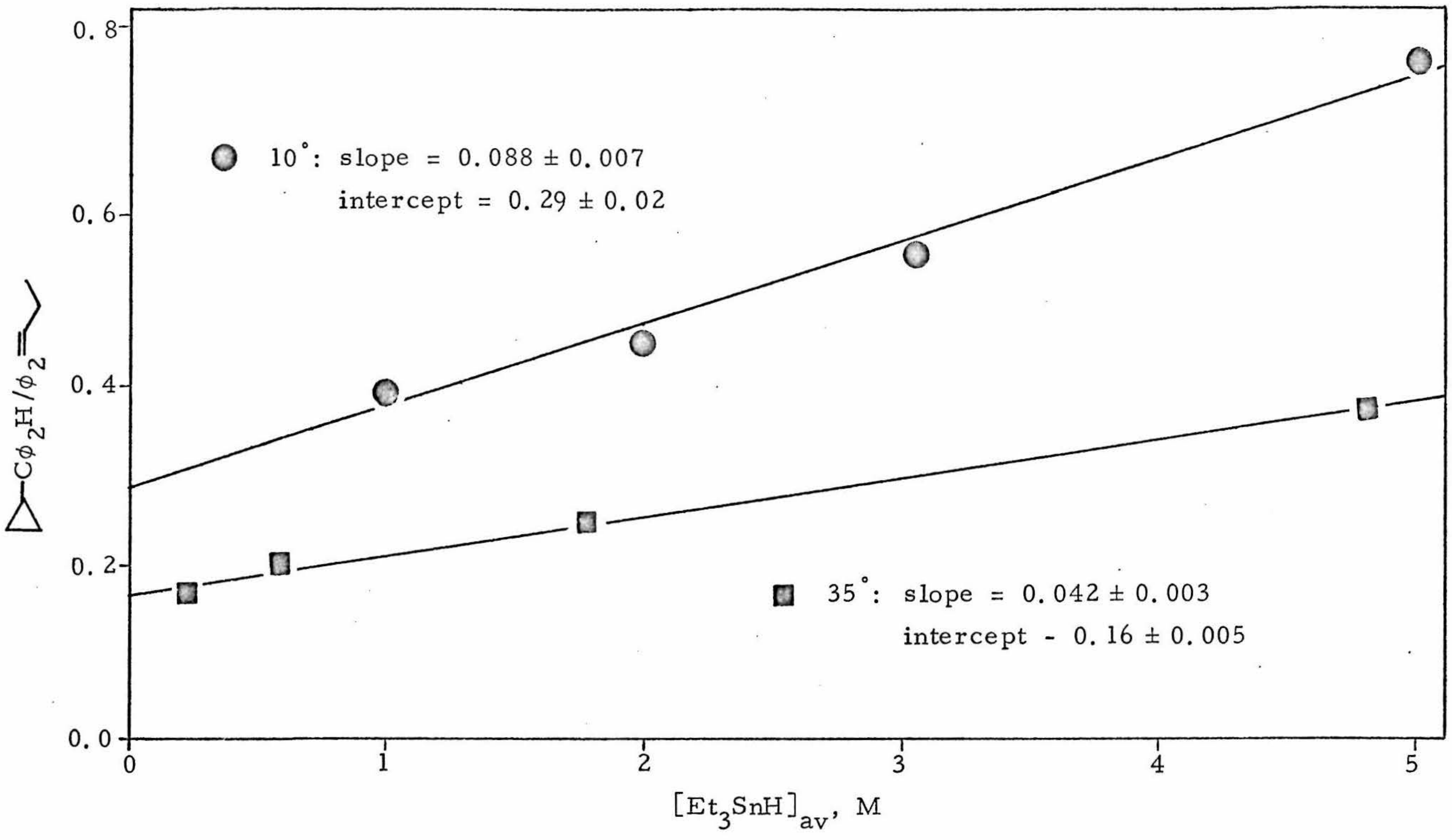


Figure 8. Variation in the ratio of ring-closed to ring-opened hydrocarbon with triethyltin hydride concentration at 10 and 35°. Error quantities are standard errors determined from the least squares fit.

$$k_b/k_2 = 2.4 \times 10^{-5} \exp(4.61/RT)^{*} \qquad (1.7\text{-}4)$$

Thus, we learn that the activation energy for abstraction of hydrogen by the ring-closed radical is about 5 kcal/mole less than that for isomerization to the ring-opened radical.

I must note here that the runs at 10 and 35° may not be strictly comparable because benzene was used as cosolvent for the runs at 10° whereas n-octane was employed at 35°. However, it seems unlikely that the solvent change itself is responsible for any significant variation in the trapping slopes; solvent effects in radical reactions are just not that large where electronegative atoms such as oxygen and chlorine are absent (66).

The second feature is that the intercept is also smaller at the higher temperature. If a linear extrapolation according to eq. 1.7-3 is valid, the intercept is simply the characteristic ratio mentioned in the Overview (p. 13)--the ratio of the isomeric hydrocarbons produced via hydrocarbon abstraction from a given hydrogen donor when all pertinent radical species are allowed first to equilibrate amongst themselves. As equilibration of the radical precursors of 5 and 6 is known to occur at the higher temperatures used for the decomposition of perester 1, ratios of ring-closed hydrocarbon to ring-opened hydrocarbon under those conditions should differ from intercepts observed here in a way which is consistent with a simple Arrhenius temperature dependence for the quantity k_1k_b/k_ak_2 of eq. 1.7-3.

---

[*] A standard error of 0.73 kcal/mole in the activation energy was calculated by propagation of errors from the standard errors in the slopes indicated in Fig. 8.

Of course, in implementing this test there is the additional problen of deciding which ratios in the higher temperature experiments are most likely to be unaffected by whatever causes the variation with tin hydride concentrations remarked earlier. For lack of a better procedure, I have selected from Table 10 the two runs at about 0.01 M triethyltin hydride (by far the lowest of the tin hydride concentrations employed). The characteristic ratios of ring-closed to ring-opened hydrocarbon for those two runs and as deduced at 10 and 35° from the intercepts in Fig. 8 are plotted according to the Arrhenius equation in Fig. 9.

The four points show some scatter about the least-squares lines drawn, but on the whole the fit is adequate. Selection of other runs from Table 10 would vary the equation for the line to some degree, but would leave uneffected the obvious trend to smaller ratios of **6**:**5** at higher temperatures.

The equation for the least-squares line is

$$k_1k_b/k_ak_2 = 1.5 \times 10^{-3} \exp(2.93/RT)^{*} \tag{1.7-5}$$

Dividing eq. 1.7-4 by eq. 1.7-5 we obtain

$$k_a/k_1 = 1.6 \times 10^{-2} \exp(1.68/RT)^{**} \tag{1.7-6}$$

---

[*] Standard errors in the intercepts employed in the least-squares treatment were taken from Fig. 8. For the two runs at the higher temperatures, standard errors of 0.01 have been assumed. The resultant standard error in the calculated activation energy is then found to be 0.30 kcal/mole.

[**] The standard error in the activation energy is calculated to be 0.79 kcal/mole by propagation of errors.

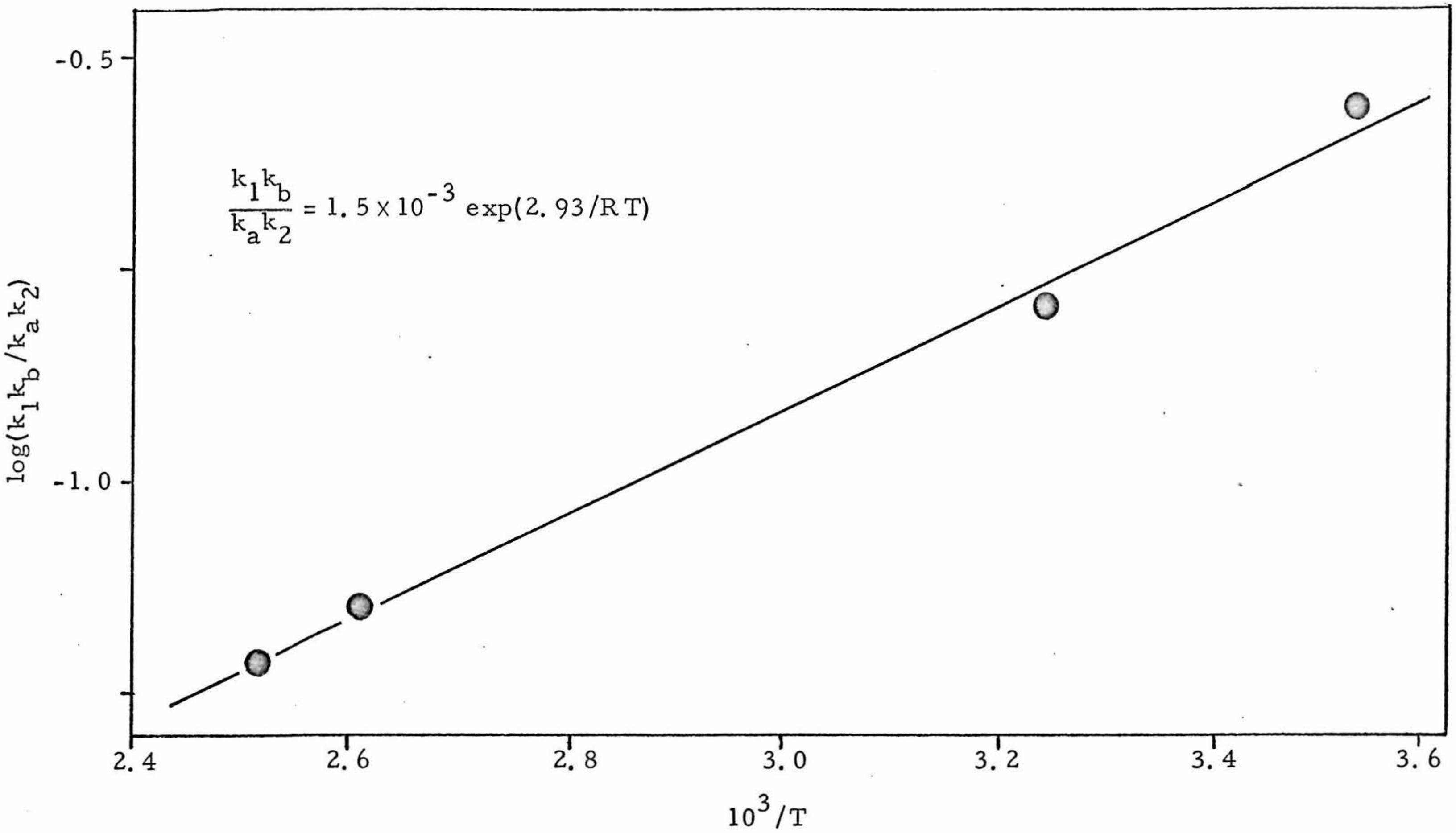


Figure 9. Arrhenius plot of characteristic ratios for hydrogen abstraction from triethyltin hydride.

The energies in the exponents of eqs. 1.7-4, -5, and -6 are related as sketched in Fig. 10. The 4.8 kcal/mole in eq. 1.7-4 is the height of the barrier for interconversion of the radicals (the center hump in Fig. 10) over that for hydrogen abstraction by the ring-closed radical (the left-most hump). Similarly, eq. 1.7-6 places the right-most barrier 2.0 kcal/mole below the radical-interconversion barrier. By subtraction, or from eq. 1.7-5, the transition state for formation of ring-closed hydrocarbon lies 4.8 - 2.0 = 2.8 kcal/mole below that for the formation of the ring-opened hydrocarbon.

The temperature dependence of the characteristic ratios thus gives us the relative positions of the two hydrogen-abstraction transition states. Placement of the transition state for interconversion of the radicals relative to the hydrogen-abstraction transition states was made possible by the measurement of product ratios under conditions where prior equilibration of the radicals does not occur. However, information derived from product ratios alone can not locate the wells for the two radicals; that requires the measurement or estimation of the activation energy for at least one reaction of each radical. Given that information, relative activation energies can be brought to bear.

The wells have been omitted in Fig. 10 to make clear what is known at this point and what is not. Later on, it will be possible not only to put in the wells, but also to include hydrogen-abstraction transition states for 1,4-cyclohexadiene and for cyclohexadienyl radicals. All but one piece of the necessary information will be developed in the present Section (i.e., Section One). Detail will gradually be added to the successors of Fig. 10 as it becomes available.

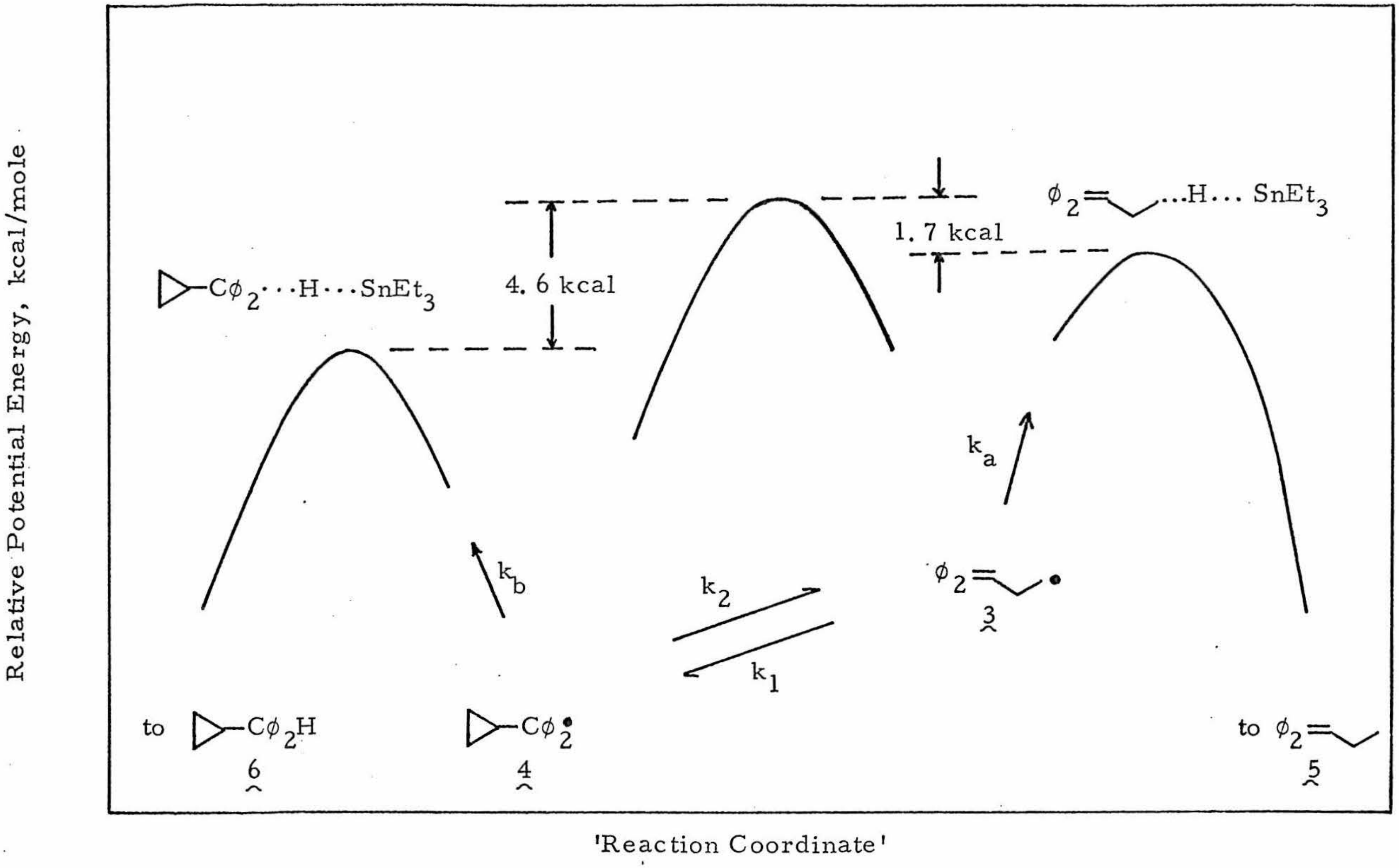


Figure 10. Relative energies of radical-interconversion and hydrogen-abstraction transition states for the ring-opened and ring-closed radicals in the presence of triethyltin hydride.

Part of Section Three will be given over to a quick review of the information by which the various levels are placed. At that time it will be possible to largely bypass embellishing arguments which must at some point be put forward, but which tend to suppress the continuity of the treatment.

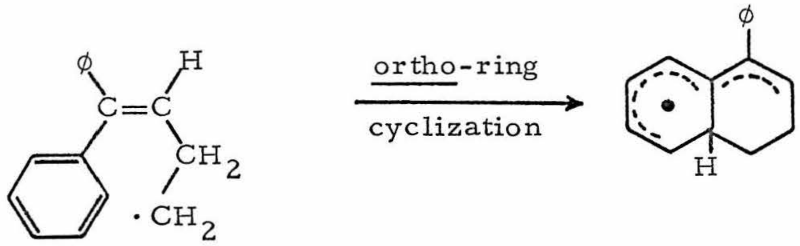
We should note, before leaving this subsection, that the present results do not rule out partial formation of both isomeric hydrocarbons from a single radical intermediate such as the nonclassical radical **7**; these results merely demonstrate that at least two radical intermediates lead to experimentally significant amounts of the isomeric hydrocarbons.

In principal, the various possibilities may be distinguished by trapping studies of the kind reported here. For example, at arbitrarily high hydrogen-donor concentration, the classical-radical mechanism predicts arbitrarily high ratios of **6**:**5** starting from **2**, but a mechanism involving **7** and **3** predicts a leveling off at the partitioning ratio for **7**. Of course, the problem is that arbitrarily high concentrations of triethyltin hydride can not be attained; the neat liquid is only about 5 M. Put another way, involvement of a nonclassical radical can lead to mechanistic expressions involving terms in the hydrogen-donor concentration of higher order than those which appear in eqs. 1.7-2 and 1.7-3. However, unless a hydrogen donor is available which permits much greater degrees of trapping than does triethyltin hydride, such terms may be expected to be dominated by the linear term. Thus, a linear relationship at low trapping does not preclude the existence of higher order terms which would signify a mechanism more complicated than one involving only the classical radicals **3** and **4**.

8. Hydrogen Abstraction, Ring Cyclization, and Conversion Reactions

Competition between equilibration of the ring-closed and ring-opened forms of the radical and abstraction of hydrogen from various hydrogen donors passes, at the next level of the reaction mechanism, to competition between hydrogen abstraction and *ortho*-ring cyclization to the radical 9.

There is no information as to what form(s) of the radical undergoes ring-cyclization, but it seems most reasonable to assume that the classical ring-opened radical is responsible; in this formulation, the ring-cyclization is simply an intramolecular example of the well-known addition of alkyl radicals to aromatic systems extensively studied by Szwarc (25).



3 9

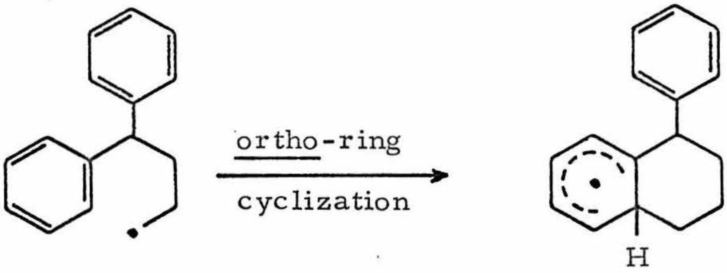
When the existence of the ring-cyclization process became apparent, that process seemed to offer only wholly lamentable mechanistic complications. Moreover, the high rate of ring-cyclization shortens radical lifetimes to such an extent that only a very few relatively active hydrogen donors can profitably be studied. However, existence of the ring-cyclization has turned out to be advantageous for two reasons. The first reason is that it provides a point of reference which makes possible the calculation of relative rates of hydrogen abstraction by ring-opened radicals from various hydrogen donors, especially 1,4-cyclohexadiene and triethyltin hydride. We noted earlier (p. 104) that activation energies for at least two rate constants are required to locate the energies of the ring-opened and ring-closed radicals with respect to the transition states indicated in Fig. 10. Measurement of actual rate constants for rapid reactions of steady-state free-radical intermediates is a ticklish problem which is far beyond the scope of instrumentation or techniques available in this research group (44). Therefore, we must rely on appropriate models for estimation of the necessary activation energies. Fortunately, a convenient model process is available for the ring-opened radical: Brown and James have reported an activation energy of 5.8 kcal/mole* for abstraction of hydrogen by ethyl radicals from 1,4-cyclohexadiene in the gas phase (45). Assuming, then, that the same value is appropriate for hydrogen abstraction from 1,4-cyclohexadiene by the ring-opened radical $\underset{\sim}{3}$ (which may behave very much like a typical primary radical), relative rates of hydrogen abstraction from 1,4-cyclohexadiene and triethyltin hydride

---

*Actually, this identification requires the assumption that combination and disproportionation of ethyl radicals require no activation energy; the quantity measured experimentally is the ratio of the hydrogen abstraction rate constant divided by the square root of the rate constant for pairwise consumption of ethyl radicals. While the experimental determination of the latter yields a value of 2 ± 1 kcal/mole (46), the reports that combinations of methyl radicals (47), isopropyl radicals (48), and t-butyl radicals (49) require no activation energy suggest that this value is likely to be in error.

at various temperatures suffice to locate the ring-opened radical on the reaction diagram.

The second reason is that comparison of relative rates of ring-cyclization and hydrogen abstraction for the ring-opened radical 3 and the saturated radical 21 (from the saturated perester 8) with appropriate model processes suggests that a common radical intermediate*



21 24

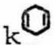
is responsible both for hydrogen abstraction to give 5 and for ring-cyclization. In view of the rather special conformation required for ring-cyclization and the presumption against formation of a nonclassical radical in a bicyclobutonium-type geometry (13), the radical most favorable for ring closure would presumably be the classical ring-opened radical.* Thus, the comparison argues against significant incursion of a species such as the homoallyl-type nonclassical radical 7 which would be capable of giving ring-opened hydrocarbon but not of undergoing ring-cyclization.

---

*One of course presumes that the conformations of 3 responsible for ring-cyclization and hydrogen abstraction may be different, but the same should be true in the saturated series.

We need now to consider how relative rate constants for hydrogen abstraction and ring-cyclization can be extracted from the data. If all the ring-opened hydrocarbon is formed from the ring-opened radical, then the rate equation for formation of ring-opened hydrocarbon is

$$d(\mathbf{5})/dt = k_a(ZH)(\mathbf{3}) \ . \qquad (1.8\text{-}1)$$

(We shall continue to use k_a for hydrogen abstraction by the ring-opened radical. When a particular hydrogen donor is intended, it will be indicated by a superscript, such as k_a^{SnH} for triethyltin hydride and k_a for 1,4-cyclohexadiene.) Similarly, the rate equation for *formation only* of the ring-cyclized radical is

$$d(\mathbf{9})/dt = k_r(\mathbf{3}) \ . \qquad (1.8\text{-}2)$$

Dividing eq. 1.8-1 by eq. 1.8-2 we get

$$d(\mathbf{5})/d(\mathbf{9}) = k_a(ZH)/k_r \ . \qquad (1.8\text{-}3)$$

If ring-cyclization is invariably followed by conversion to the ring-cyclized dihydronaphthalene **10**, we would also have

$$d(\mathbf{5})/d(\mathbf{10}) = k_a(ZH)/k_r \ . \qquad (1.8\text{-}4)$$

As with eq. 1.7-2, integration of eq. 1.8-4 can be effected by replacing ZH by its average value, provided ZH is substantially in excess. Then the *reduced ratio* R is given by*

---

*As quantities calculated according to eq. 5 will frequently be discussed in this thesis, economy and precision of language dictates the utilization of a special name.

$$R \equiv \frac{(\%\ \text{yield}\ 10) \times (\text{ZH})_{\text{av}}}{(\%\ \text{yield}\ 5)} \cong k_r/k_a \ . \qquad (1.8\text{-}5)$$

(The quantity R is of special interest because it does not include the explicit strong, but really not very interesting, dependence of the product ratio 10:5 on the hydrogen donor concentration. Thus, more subtle effects are made to stand out.)

However, the necessary condition for equating R with k_r/k_a--that ring-cyclized radical 9 always go on to give ring-cyclized hydrocarbon 10--seems never to be fulfilled experimentally. One possible problem--reversibility of the ring-cyclization--is shown below to be unimportant under conditions employed in this work. But another remains; in conversion to 10, the ring-cyclized radical 9 must lose a hydrogen atom through disproportionation in a radical-radical reaction. However, such reactions can also lead to combination; or may involve a disproportionation where the ring-cyclized radical *receives* the transferred hydrogen atom, leading to the tetrahydronaphthalenes 13 (see Chart 4, p. 78). Moreover, if each member of a radical pair is a ring-cyclized radical, no more than one of the two can end up as dihydronaphthalene.

Thus, the *conversion reactions* are expected to be inefficient. As a result, R will underestimate k_r/k_a. This assumes, of course, that neither 5 nor 10 is destroyed under the reaction conditions. Nonetheless, equating *reduced ratios* to k_r/k_a may still suffice for a rough guess for the latter.

To do better, we must in some manner estimate the relationship between the yield of the dihydronaphthalene and that of all naphthalenoid products. This can be done in most cases by direct vpc measurement of the yield of tetrahydronapthalenes and estimation of the amount of dimer likely to be present by consideration of material balances.

This discussion shows that we need to consider the whole of the reaction mechanism in order to extract values of k_r/k_a. The initial phases have been discussed in the subsections above. The remainder will be covered in this subsection on a solvent-by-solvent basis, with the exception of induced decomposition in the presence of triethyltin hydride, which is considered in subsection 9.

A. t-Butyl (γ, γ-Diphenylallyl)peracetate and t-Butyl Diphenylcyclopropylperacetate

(1.) In the Presence of 1, 4-Cyclohexadiene

Yields and ratios of products for decomposition of ring-opened perester 1 in the presence of 1, 4-cyclohexadiene are given in Table 1. The data at 131° is also shown graphically in Fig. 1. Note that, for runs at any one temperature, the yield of ring-opened hydrocarbon increases, and that of the ring-cyclized hydrocarbon decreases, with increasing cyclohexadiene concentration. The same sort of behavior is observed for decomposition of the ring-closed perester 2 (Table 2 and Fig. 2). The pattern is indicative of a partitioning in which one step (hydrogen abstraction by 3) depends on the cyclohexadiene concentration but the other (ring-cyclization) does not. The identification of 5 and 10 is based on (a) agreement of retention times for independently prepared samples with those of the candidate materials on Ucon polar, silicone oil, and Apiezon L; and (b) observation of distinctive nmr absorbances of the authentic materials in the nmr spectra of chromatographed and distilled reaction mixtures from 'large-scale' perester decompositions like those described on pp. 72-79.

The rightmost column of Tables 1 and 2 gives reduced ratios calculated from eq. 1. 8-5. If conversion of ring-cyclized radicals to dihydronaphthalene were 100% efficient, the numbers tabulated would simply be equal to $k_r/k_a^{⌬}$, a constant at each temperature. However, the numbers are not constant, but tend to increase with cyclohexadiene concentration within each reaction series. If the discussion following eq. 1. 8-5 is correct, the increase reflects an increasing efficiency of conversion of 9 to 10 at higher cyclohexadiene concentrations. The following interpretation is suggested. At higher cyclohexadiene concentrations, ring-opened radicals more frequently abstract hydrogen to give 5 plus a cyclohexadienyl radical, and less frequently undergo ring-cyclization. Therefore, an individual ring-cyclized radical is increasingly likely to meet a cyclohexadienyl radical rather than a second ring-cyclized radical at increased cyclohexadiene concentrations. The fact that the tabulated numbers increase with increasing cyclohexadiene concentration then implies that conversion of 9 to 10 is more likely if the second radical is cyclohexadienyl rather than ring-cyclized. Another possibility is that the rate-constant ratio $k_r/k_a^{⌬}$ is solvent dependent, increasing at higher cyclohexadiene concentrations (see pp. 259–265).

The essential irreversibility of the ring-cyclization can be seen from results given in Tables 4, 5, and 6. The rightmost column of each of these tables again gives reduced ratios calculated from eq. 1.8-5. In Table 4 (for decomposition of the ring-opened perester at 110°), the reduced ratios show little dependence on the initial perester concentration. As discussed in subsection 1, a shift to lower initial perester concentration results in smaller steady-state free-radical concentrations. If the ring-cyclization were reversible, there would then be a greater feed back of ring-cyclized radicals to ring-opened radicals at the lower perester concentrations. The reason is that whereas 'decyclization' is accomplished by a single radical, conversion to napthalenoid products requires a second radical, which will now be present in smaller concentration. As a result, if decyclization were competitive with conversion to naphthalenoid products at the highest perester concentrations in Tables 4 or 6, a substantial decrease would be seen (but is not) in the reduced ratios.

How large 'substantial' might be can be inferred from the variations of the ratio 6:5 with perester concentration in Tables 4 and 6. Like the dihydronaphthalene 10, the ring-closed hydrocarbon 6 is principally formed by disproportionation of the precursor radical with cyclohexadienyl radical. But unlike the ring-cyclized radical, formation of the ring-closed radical from the ring-opened radical is readily reversible. The ratio 6:5 decreases by a factor of 4 in Table 4 and by a factor of 7 in Table 6 as the initial perester concentration is decreased by factors of 300 and 100, respectively.

The lack of any similar variation in the ratio of 10 to 5 confirms the essential irreversibility of the ring-cyclization.* Of course, if we were to continue to decrease the initial perester concentration, and if the only options for ring-cyclized radicals were destruction in radical-radical reactions or decyclization, eventually a point would be reached at which there would be sufficient time for decyclization to occur.

The supposition that most of the ring-closed hydrocarbon is formed via abstraction of hydrogen by ring-closed radical from cyclohexadienyl radical can best be established by consideration of the quantitative accuracy with which the ratios **6**:**5** can be fit. That consideration is undertaken in Section Two, where it will be shown that the ratios **6**:**5** and **5**:**10** from Tables 1, 2, 4, 5, and 6 can be adequately correlated as described above, except that formation of small amounts of ring-closed hydrocarbon via hydrogen abstraction by ring-closed radicals from 1,4-cyclohexadiene must be included in the treatment. Note, for example, that the ratios **6**:**5** for 0.25 M ring-opened perester at about 9 M cyclohexadiene in Table 1 range from 0.010 to 0.013, while the same quantities (Table 5) at 0.001 M perester are only about 0.004. The significant factor here is the relative smallness of the decrease for the 260-fold variation in the initial perester concentration. It can be shown that at constant 1,4-cyclohexadiene concentration the contribution to the ratio **6**:**5** arising from formation of **6** via hydrogen abstraction from cyclohexadienyl radical should be very nearly exactly proportional to the square root of the initial perester concentration (which varies by a factor of 16).

---

*That decyclization is apparently much slower than ring-opening by the ring-closed radical can be shown to be in harmony with the greater exothermicity expected for the ring-cyclization. See the discussion on pp. 287-290.

These observations can be rationalized by the assumption that both hydrocarbons can be formed via hydrogen abstraction from 1,4-cyclohexadiene itself. Therefore, there is a value (equal to the characteristic ratio for hydrogen abstraction from 1,4-cyclohexadiene, see pp. 13, 101) below which the ratio **6**:**5** can not fall.

Actually, because some formation of **6** via hydrogen abstraction from cyclohexadienyl radical still occurs at 0.001 M perester, the characteristic ratio for 1,4-cyclohexadiene at 100° is about 0.0035, slightly lower than the observed **6**:**5** ratio of 0.040.

One experimental problem must be confessed here. The run at 99° listed in Table 5 gave a ratio **6**:**5** of approximately 0.1 when initially analyzed on the standard Ucon polar column. Note that this ratio is an order of magnitude higher than that quoted in Table 1 for 0.26 M ring-opened perester. However, the retention time of 'diphenylcyclopropylmethane' relative to diphenylbutene was about 4% lower than expected. On reinvestigation using a silicone oil column, the apparent ratio fell to 0.014. For good measure, the two columns were then joined together and the analysis repeated. The value quoted in Table 5 (0.0040) was now obtained, and the retention times of both candidate and authentic diphenylcyclopropylmethane were found to be 56.1 min. The other runs reported in Table 5 were analyzed only on the combined silicone oil--Ucon polar column.

Clearly, something is amiss. It was subsequently found that degassed samples of Aldrich 1,4-cyclohexadiene, whether taken from a newly opened bottle or one open for several weeks, and whether freshly distilled or not, develop upon heating one or more impurities which have very nearly the retention time of 6 on Ucon polar. From the retention time, the material(s) would seem to be trimeric, or C_{18}. Strangely, no other materials of comparable or longer retention time seem to be formed, and the yield of dimeric material is much smaller than that of the presumed trimer.

As Aldrich 1,4-cyclohexadiene routinely contains 1,3-cyclohexadiene in the amount of 0.01--0.1%, a possible mechanism for formation of the presumed trimer would be Diels-Alder addition of 1,4-cyclohexadiene to 1,3-cyclohexadiene, followed by addition of the adduct to a second molecule of 1,3-cyclohexadiene. However, no correlation between initial 1,3-cyclohexadiene concentration and yield of the presumed trimer was found for three samples (degassed; maintained at 135° for 25 hr) which were approximately 1%, 0.1%, and 0.02% 1,3-cyclohexadiene in 1,4-cyclohexadiene. The last of these samples was freshly distilled material. The concentrations of presumed trimer (assuming unexceptional vpc response characteristics) after heating were roughly 0.01 mg/ml, 0.022 mg/ml, and 0.008 mg/ml, respectively. These concentrations would be interpreted as yields of 6 of roughly 5%, 11%, and 4% for an initial concentration of ring-opened perester 1 of 0.001 M, but only 0.02%, 0.04%, and 0.015% for 0.26 M 1.

As yields of 6 for decomposition of 0.26 M 1 in neat 1,4-cyclohexadiene are 0.3--0.4%, apparent yields of 6 reported in Table 1 are probably not significantly distorted by any solvent-derived impurity which may be present. This is an important point because of the possibility the remaining small amounts of 6 detected by vpc analysis on the combined column for the runs of Table 5 might simply arise from an especially intelligent impurity. Fortunately, the calculations of Section Two (pp. 273-275) demonstrate that even for the runs of Table 1 a characteristic ratio of about 0.004 must be assumed for hydrogen abstraction from 1,4-cyclohexadiene to quantitatively reproduce the ratio data for 6:5.

Although the situation is a good deal muddier than one would like, we shall adopt the position that hydrogen abstraction from 1,4-cyclohexadiene to give ring-closed hydrocarbon 6 does occur to a measureable extent and has in fact been characterized experimentally.

The mechanistic evaluation of Section Two indicates that the characteristic ratio for 1,4-cyclohexadiene is slightly temperature dependent, lower temperatures corresponding to larger 6:5. This means that the transition state for formation of the ring-closed hydrocarbon lies below that for formation of the ring-opened hydrocarbon. Various new relationships are shown in Fig. 10, where the estimate of 5.8 kcal/mole for hydrogen abstraction by ring-opened radical from 1,4-cyclohexadiene (see p. 108) has been employed.

The much greater yields of the ring-closed hydrocarbon observed for decomposition of 2 (compare Tables 1 and 2 or Figures 1 and 2) comes about essentially as follows.

The half-life for decomposition of ring-opened perester 1 at 131° is about the same as that for 2 at 35°; therefore, because termination reactions of cyclohexadienyl radicals are expected to have little or no activation energy, the steady-state cyclohexadienyl radical concentration

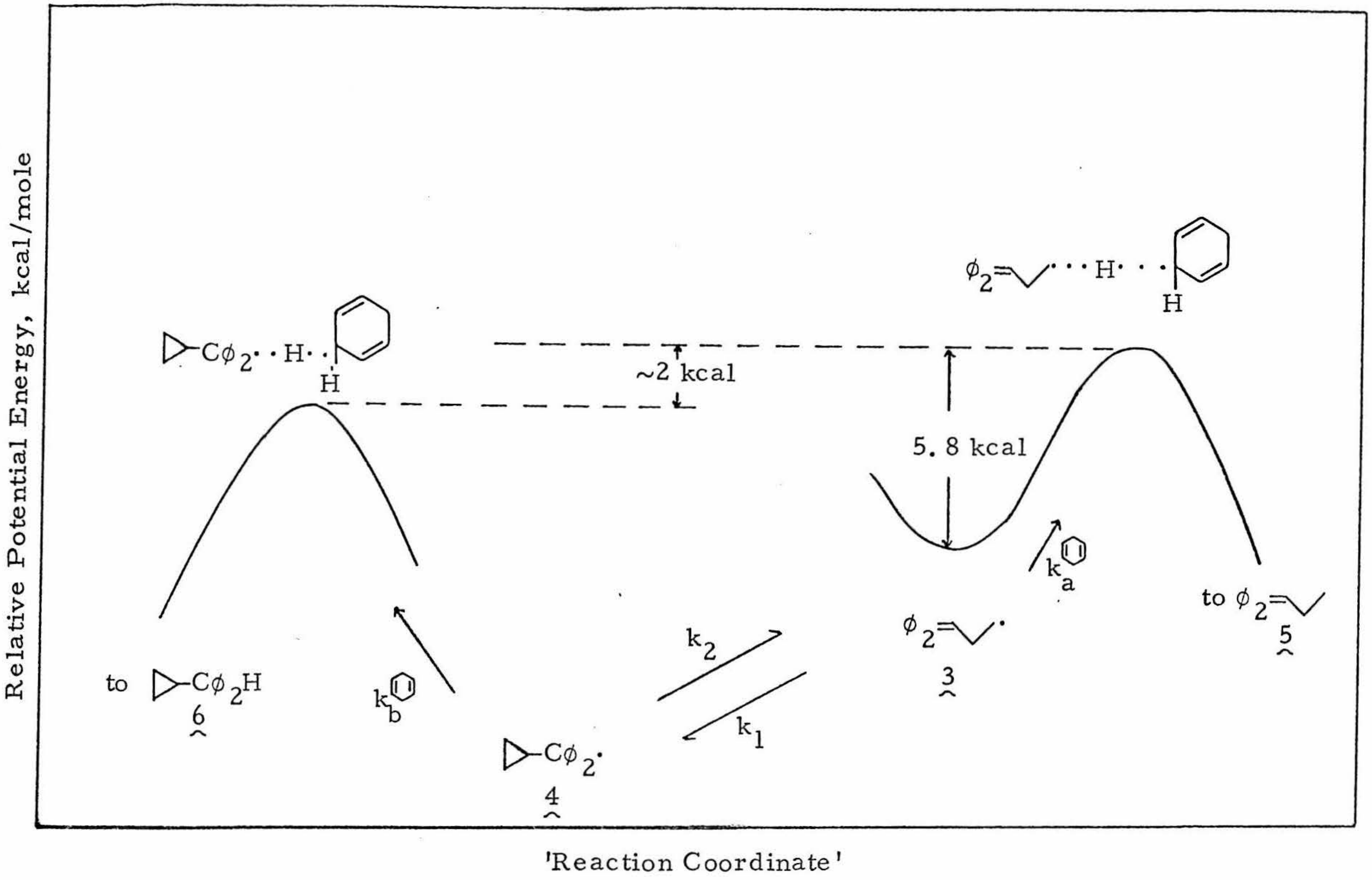


Figure 11. Some relative energies for hydrogen abstraction by the ring-opened and ring-closed radicals (3 and 4) from 1,4-cyclohexadiene.

goes roughly as the square root of the decomposition rate. However, the steady-state concentration of the ring-closed radical 4 will be quite different at the two temperatures. As 4 is more stable than the ring-opened 3 (see pp. 277-279), the ratio of 3 to 4 will be greater at the higher temperature. The rates of hydrogen abstraction from 1,4-cyclohexadiene to give 5 and ring-cyclization to give 9 will then be much faster at 131° due both to the temperature effect on $k_a^{⌬}$ and k_r and to the greater relative amount of 3. As a result, the steady-state concentration of ring-closed 4 will be much smaller at 131° than at 35°, and the amount of ring-closed hydrocarbon can be correspondingly less, even if the rate constant for hydrogen abstraction by 4 from cyclohexadienyl radical is somewhat greater at 131°.

Another important phenomenon--the almost nonexistent temperature dependence of the ratio 6:5 for closely similar cyclohexadiene concentrations (see Table 2)--comes about, broadly speaking, through the accidental cancellation of large changes in two of the factors involved in the discussion in the previous paragraph: increasing the temperature increases the rate of the perester decomposition (thus increasing the cyclohexadienyl radical concentration and favoring formation of 6 over 5); but decreases the ratio of ring-closed to ring-opened radical (thus favoring 5 over 6). Indeed, approximate dissection in Section Two of the overall effect into these two factors will make it possible to place the ring-closed radical on the reaction diagram with respect to the ring-opened radical and the various hydrogen-abstraction transition states.

To complete the description of the reaction mechanism for decomposition of the peresters 1 and 2 in 1,4-cyclohexadiene, we need to consider the products designated by letters, rather than by numbers and structures, in Tables 1, 2, 4, and 6. The product called B was previously considered when formation of cage products was under discussion (pp. 71-81). Little need be said here, except perhaps to remind the reader that B_1 of Table 6 (perester 2 at various concentrations), a part of B in Table 2, and most or all of B in Tables 1 and 4 was attributed to a tetrahydronaphthalene product or to isomeric tetrahydronaphthalenes (see Chart 4, p. 78). A principal reason for this assignment was that yields of B in Table 1 strongly parallel those of the dihydronaphthalene 10. Additional support for this assignment will be given later in the present subsection when we consider decomposition of the peresters in poorly hydrogen-donating solvents (pp. 126-131) and in Section Two, where yields of B will be calculated and compared with those measured experimentally (pp. 281, 282).

The product A may be benzophenone. The first suggestion that this might be so came about as the result of the following observations. If one takes a sample of 1 repeatedly recrystallized from pentane (and therefore presumably pure) and places it on a lab bench, uncovered or capped in a brown jar, in the course of one or two months the crystalline perester turns to a pale yellow slime, the principal constituent of which is benzophenone (identified by mass spectroscopy, infrared, and nmr). While the relevance of this observation to degassed thermal decomposition may be questionable, it does indicate that a mechanism exists for transforming the perester into benzophenone. What that mechanism is, I do not know, and offer here on speculation.

No attempt was made to isolate benzophenone from actual reaction mixtures, although it should not be difficult to do so. The evidence that A is benzophenone comes from vpc retention time measurements. On a column composed of a 12-ft. section of silicon oil followed by 6-ft. of Ucon polar, both benzophenone and a peak of about the correct area for A in the 110° run of Table 5 had retention times of 58.8 min. On Ucon polar alone, strong overlapping of the A and B peaks for the 0.27 M run of Table 4 made it impossible to determine with certainty the retention time of the A peak, but it is within 2% of that observed for benzophenone. Of course, benzophenone might have been a contaminant of the perester (presumably present in varying amounts), but arguing against this possibility is the fact that the 1.8% yield for 0.27 M 1 in 1.1 M 1,4-cyclohexadiene at 110° (Table 4) agrees well with the 2.0% yield from Table 1 for 0.28 M perester from another batch at 1.1 M 1,4-cyclohexadiene at 99°.

The average of the subtotal yields in Table 1 and the total yields in Table 4 is 66%. Adding to this figure 15% for the yield of the lactone 23 (see subsection 6) gives an average material balance of about 80% for decomposition of ring-opened perester in the presence of 1,4-cyclohexadiene. For the ring-closed perester, the average total yield for Table 2 is 90%. For Table 6, we have previously (p. 78) argued that, possibly due to an acid-producing impurity in the perester sample used, the anticipated 20 to 25% of ring-closed ether does not survive the reaction conditions. Taking this into account, the observed average total yield of about 69% should be corrected to about 90%. Thus, on the average, material balances are 80% for the ring-opened perester and 90% for the ring-closed perester. While the remainder need not be dimer containing napthalenoid residues from termination reactions of the ring-cyclized radicals,[*] these considerations would suggest that not more than 10 to 20% of unobserved dimeric products are produced. The average yield of dihydronaphthalene is about 17% and the average for tetrahydronaphthalene, judging from yields of $\underset{\frown}{B}$ in Tables 1 and 4 and of $\underset{\frown}{B}_1$ in Table 6, is about 9%. Thus, dihydronaphthalene probably accounts for about a third to a half of the ring-cyclized radicals.

Of course, the analysis given above is only approximately correct. An alternative approach--comparison on a run-by-run basis of the yield of the dihydronaphthalene with that measured for the tetrahydronaphthalene(s) and indicated by the material balance for dimeric products--is unattractive in view of the appreciable experimental error in product yields which is reflected by the magnitudes of largely random fluctuations in total yields from run to run. Unreliability of absolute yields arising from imprecise measurement of amounts of perester and internal standard taken has been mentioned previously (pp. 46-47); the procedure used here assumed that averaging absolute

---

[*] Addition of radicals to 1,4-cyclohexadiene might lead to materials which would not be observed by vpc. An indirect test of this possibility was made in a run in 1,4-cyclohexadiene to which 0.6 M 1,3-cyclohexadiene has been added (row 7, Table 8). Addition of methyl radicals to 1,3-cyclohexadiene proceeds possibly two orders of magnitude more rapidly than addition to the unconjugated 1,4-isomer (84). If, therefore, addition of hydrocarbon radicals to 1,4-cyclohexadiene occurs to any measurable extent, the material balance for the run in the presence of 1,3-cyclohexadiene should be noticeably low. Comparison with similar runs from Table 1 shows that this is not the case.

yields over large numbers of runs will tend to average errors arising from that source.

Detailed translation of these considerations of average efficiencies for conversion of ring-cyclized radicals to dihydronaphthalene to reliable estimates for $k_r/k_a^{⬡}$ will be undertaken in Section Two. It will be possible there to predict yields of tetrahydronaphthalene and of dimer as a function of parameters describing the conversion efficiency. Those parameters will then be chosen to reproduce tetrahydronaphthalene and dimer yields on the scale suggested by the above considerations.

Even at this point, however, we can get an approximate measure of the value of $k_r/k_a^{⬡}$. As calculated from eq. 1.8-5 (i.e., assuming 100% conversion of ring-cyclized radicals to dihydronaphthalene), the value of $k_r/k_a^{⬡}$ obtained by averaging over Tables 1, 2, 4, and 6 is about 2.6. If the average conversion efficiency is 40%, then the estimated value of $k_r/k_a^{⬡}$ near the middle of the temperature range (i.e., between 70 and 100°) becomes 6.5. In addition, $k_r/k_a^{⬡}$ is temperature dependent, as can be seen in the following way. According to eq. 1.8-5, the hydrogen-donor concentration at which the yields of the ring-opened and ring-cyclized hydrocarbons are equal is a measure of $k_r/k_a^{⬡}$. At 131°, that concentration (see Figure 1) is 2.6 M. At 35° (Figure 2), the yields cross at about 1.8 M. The initial 1,4-cyclohexadiene concentrations in each case must be corrected to average values with reference to the initial perester concentration and the reaction stoichiometry, but those corrections do not alter the apparent trend to higher values at higher reaction temperatures. Therefore, the activation energy for ring-cyclization is slightly greater than that for hydrogen abstraction from 1,4-cyclohexadiene by ring-opened radical.

We shall adopt here, from Section Two (p. 272), the relationship

k_r/k_a  $= 20\exp(-0.8/RT)$. (1.8-6)

(2.) In Indene

Results for decomposition of peresters 1 and 2 in indene are summarized in Table 7. Several major departures from the pattern of results with 1,4-cyclohexadiene may be noted. Yields of the ring-opened hydrocarbon are only about 10% for neat indene, in contrast to yields of 30--40% for neat 1,4-cyclohexadiene. This divergence in yields is reflected in the values of the reduced ratios calculated from eq. 1.8-5, which are approximately 10 in the presence of indene and 2.6 in the presence of 1,4-cyclohexadiene.

The overall yields are 46 and 49% for decomposition of 1, and 39 and 37% for decomposition of 2. Even adding a presumed 15% for the yield of the lactone 23 for decomposition of 1 and assuming that the low yields of B for the ring-closed perester result from at least partial destruction of the usual 20 to 25% of ring-closed ether, the resulting material balances of about 63% for 1 and 60% for 2 are rather low. If the difference between these quantities and 100% represents dimeric naphthalenoid products,* the efficiency of conversion of ring-cyclized radicals to dihydronaphthalene would be about 1/3, and the adjusted

---

*Higher molecular weight products may also be produced via addition of the ring-opened radical 3 to indene. For methyl radicals, addition to, and hydrogen abstraction from, indene occur with equal facility (85).

value of k_r/k_a^{indene} would be about 30, indicating that $k_a^{⌬}/k_a^{\text{indene}}$ is about 30/6.5 = 5.

Yields of the ring-closed hydrocarbon are much lower than for decomposition of the peresters in 1,4-cyclohexadiene. This is consistent with the supposition that most of the ring-closed hydrocarbon is produced in cyclohexadiene via abstraction of hydrogen by ring-closed radicals from cyclohexadienyl radical, for indenyl radicals can not function as hydrogen donors. The principal hydrogen donor for formation of the 0.3--0.5% 6 for decomposition of 2 in indene is likely to be the ring-cyclized radical. On this basis, the lesser amounts of 6 for decomposition of 1 arise much in the same way as the disparity in amounts of 6 for ring-opened and ring-closed perester in cyclohexadiene (pp. 118, 120).

(3.) In Poorly Hydrogen-Donating Solvents

By 'poorly hydrogen-donating solvents' is meant those in which ring-cyclization by the ring-opened radical is much faster than hydrogen abstraction from solvent. Data may be found in the upper bank of four runs in Table 8 for the ring-opened perester, and in Table 9 for the ring-closed perester. The solvents investigated are cyclohexane, diethyl ether, tetrahydrofuran, cumene, benzene, and tetraethyltin. Over this range of solvents, the yield of the ring-opened hydrocarbon 5 varies only from 0.4% for a benzene run to 2% for an ether run. Fully 7 of the 13 reported yields are either 1.0 or 1.1%.

This similarity in the yields of 5 requires some comment. Two possibilities are apparent: either all of the solvents employed happen to be nearly equally reactive toward the ring-opened radical; or materials developed in the course of the reaction (such as dihydro- and tetrahydronaphthalenes) are the active hydrogen donors. Estimation of k_r/k_a for some of the poorly hydrogen donating solvents would provide the most direct way of assessing the reasonableness of the first alternative.

We can proceed as follows for reaction in cyclohexane. From data given by Boddy and Steacie (54), we can calculate

$$k_{a'}^{\text{⬡}}/(k_t)^{\frac{1}{2}} = 10^{-7.2}\exp(-10.1/RT)(\text{cc-molecule}^{-1}\text{-sec}^{-1})^{\frac{1}{2}}\ , \qquad (1.8\text{-}7)$$

where $k_{a'}^{\text{⬡}}$ denotes the rate constant for abstraction of hydrogen by d_5-ethyl radicals from cyclohexane, and k_t denotes the rate constant for bimolecular combination plus disproportionation of the d_5-ethyl radicals. For hydrogen abstraction by (undeuterated) ethyl radicals from cyclohexadiene, Brown and James (45) give

$$k_{a'}^{\text{⌬}}/(k_t)^{\frac{1}{2}} = 10^{-7.3}\exp(-5.8/RT)(\text{cc molecule}^{-1}\ \text{sec}^{-1})^{\frac{1}{2}}\ . \qquad (1.8\text{-}8)$$

As only secondary deuterium isotope effects are involved, and as these should be small (55), approximate relative rates for hydrogen abstraction by ethyl radicals from 1,4-cyclohexadiene and cyclohexane can be obtained by dividing eq. 1.8-8 by eq. 1.8-7.

$$k_{a'}^{\text{⌬}}/k_{a'}^{\text{⬡}} = 0.8\exp(4.3/RT)\ . \qquad (1.8\text{-}9)$$

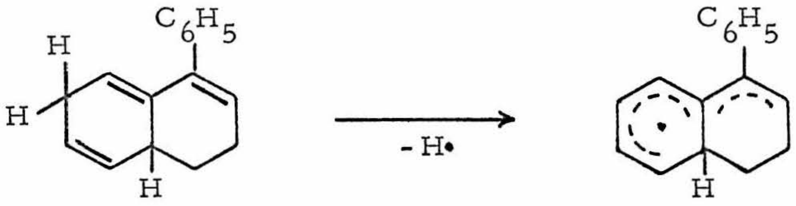
As ethyl-radical reactivities should be an excellent model for ring-opened radical reactivities, eqs. 1.8-6 and 1.8-9 can be combined to give

$$k_r/k_a^{\bigcirc} = 16\ \exp(3.5/RT)\ . \qquad (1.8\text{-}10)$$

Values of this quantity are 6×10^3 at 35° and 1.5×10^3 at 131°. Since neat cyclohexane is about 10 M, the total naphthalenoid products to ring-opened hydrocarbon is estimated to be 600:1 at 35° and 150:1 at 131°. Finally, if the total yield of naphthalenoid products plus ring-opened 5 is 60% at each temperature, yields of ring-opened hydrocarbon arising via abstraction of hydrogen from cyclohexane would be about 0.1% at 35° and 0.4% at 131°.

From Tables 8 and 9 we see that yields up to an order of magnitude greater are in fact found: 0.5 to 1.1% at 35°, depending on the initial perester concentration; and 1.0% at 131°. Two things may be said. Firstly, the estimated magnitudes of $k_r/k_a^{\bigcirc}$ suggest that only a part of the diphenylbutene observed can be attributed to abstraction of hydrogen from cyclohexane by 3. Secondly, even if the various approximations employed have introduced considerable error into the equation for $k_r/k_a^{\bigcirc}$, a major result--namely that $k_r/k_a^{\bigcirc}$ must be appreciably temperature dependent--should stand. Thus, hydrogen abstraction solely from cyclohexane would not be expected to give such similar yields of 5 at the two temperatures.

Both the observed yields and the lack of any appreciable temperature dependence therefore suggest the existence of alternative hydrogen donors. The ring-cyclized hydrocarbon 10 is a possible candidate. However, the 'best-looking' radical it could yield would presumably be endowed with less resonance stabilization than is possessed by the indenyl radical, for the radical from 10 would have an additional, conjugation-breaking methylene group. The (isomeric) tetrahydronaphthalenes (see Chart 4, p. 78) which could yield radicals with more extensive pi-systems, and therefore greater resonance stabilization, than cyclohexadienyl radicals, would seem to be more likely possibilities.



B (one possibility)

9

The situation may be rather similar in ether, tetrahydrofuran, cumene, and tetraethyltin. Model reactions involving methyl radicals (56) and phenyl radicals (86) suggest that cyclohexane, ether, and cumene should be of similar reactivity towards primary radicals. Tetrahydrofuran should be similar to diethyl ether for structural reasons, and tetraethyltin, having 8 secondary and 12 primary hydrogens, could well be similar in reactivity to cyclohexane. Benzene might be a special case, for radical addition yields a cyclohexadienyl-type radical which might give rise to ring-opened hydrocarbon through hydrogen donation, or might dimerize to give reactive cyclohexadienyl-type products.

Yields of B for decomposition of the ring-opened perester are 2.7% in cyclohexane, 2.5% in ether, and 1% in tetrahydrofuran. All of these yields are much lower than the 5 to 16% observed in the presence of 1, 4-cyclohexadiene. This disparity is at least qualitatively in agreement with the suggestion that B consists of tetrahydronaphthalenes (except for decomposition of perester 2, where the cage ring-closed ether 15 and methylenecyclopropane 16 contribute). Assuming that tetrahydronaphthalenes can still be formed (presumably via disproportionation of pairs of ring-cyclized radicals) under the conditions being surveyed, the high activity as hydrogen donors predicted above would ensure extensive destruction at the hands, especially, of *t*-butoxy radicals or their successors (methyl radicals or solvent radicals).

Yields of the ring-closed hydrocarbon 6 tend to be much larger in the decomposition of the ring-closed perester than in that of the ring-opened perester. This circumstance is reminiscent of results obtained in the presence of 1, 4-cyclohexadiene, and can be explained in a similar fashion. In this case, the role of the cyclohexadienyl radical would be played by the ring-cyclized radical or solvent radical, such as cyclohexyl, cumyl, and so on.

Yields quoted for 6 are 0. 2% or less for decomposition of 1, except for the run in ether (0. 6%). However, the higher apparent yield in ether does not necessarily indicate some special feature of ether which permits facile hydrogen donation to the ring-closed radical; while the relative retention time on Ucon polar of the vpc peaks attributed to 5 and 6 was correct, the spread between the peaks was about 3% greater on a silicone oil column (an easily observable difference) than that of the authentic materials. In contract, relative retention times were correct both on Ucon polar and on silicone oil for the run in cyclohexane, where a 'normal' yield of 6 is reported.

The much higher yields quoted for 6 in Table 9 were obtained by vpc analysis on Ucon polar, except for the first of the two runs in benzene, where a crude analysis by nmr gave roughly the same figure (87). Assuming that the quoted yields are correct, one important question which arises in Section Two needs to be investigated: do the comparable yields of 6 observed for decomposition of 2 in the presence of 1, 4-cyclohexadiene and in the poorly hydrogen-donating solvents indicate that disproportionation of the ring-closed radical 4 with the ring-cyclized radical 9 is an important reaction at the perester concentrations studied? Evidence that such a reaction is relatively unimportant has previously been considered in the results of decomposition of 2 in indene, where an alternative route for formation of 6--disproportionation of 4 with solvent radical--is disallowed because indenyl radicals can not function as hydrogen donors. As a result, the yield of 6 falls to only 0.3-0.5%. By inference, then, the appreciable amounts of 6 found for decomposition of 2 in cyclohexane, ether, etc., are principally due to hydrogen abstraction from solvent-derived radicals, such as cyclohexyl, etc.

(4.) In Triethyltin Hydride

The purpose of this subsection is to develop an equation for k_r/k_a^{SnH} for use (a) in conjunction with the analogous equation for 1, 4-cyclohexadiene to establish a bridge between the energy-level placements of Figs. 10 and 11, and (b) to help to predict the effect of the reaction stoichiometry on the competition between normal and induced decomposition of **1** in the presence of triethyltin hydrice (subsection 9).

Examination of entries in Tables 1 and 10, or of Figs. 1 and 4 which follow those tables, shows that the competition between ring-cyclization and hydrogen abstraction by ring-opened radicals is rather different in 1,4-cyclohexadiene and in triethyltin hydride. For example, the hydrogen-donor concentration at which rising yields of ring-opened hydrocarbon and falling yields of ring-cyclized hydrocarbon intersect is 3.2 M for 1,4-cyclohexadiene (Fig. 1) but only 0.06 M for triethyltin hydride (Fig. 4). This comparison indicates that triethyltin hydride is more active than 1,4-cyclohexadiene toward the ring-opened radical by approximately a factor of 50 at 125—131°. This calculation of course assumes that the efficiency of conversion of ring-cyclized radicals to dihydronaphthalene is the same in the two situations.

The greater activity of triethyltin hydride also shows up in the characteristic ratios (**6**:**5**), which are about 0.07 for triethyltin hydride and 0.0035 for 1,4-cyclohexadiene at 110°. Thus, the former is more reactive than the latter toward ring-closed radicals by roughly a factor of 20 x 50 = 1000. The pattern--larger response to increased hydrogen-donor activity by the less reactive radical--is as expected.

Extraction of reliable values of k_r/k_a^{SnH} requires some means of assessing the efficiency of conversion of ring-cyclized radicals to the ring-cyclized hydrocarbon. The procedure used for cyclohexadiene--averaging material balances over a large number of runs to take formation of dimers into account, etc.--can not be used here, in part because material balances are only rarely available. However, an additional factor comes to our aid: successful treatment of induced decomposition in triethyltin hydride from a mechanistic point of view requires the assumption that ring-cyclized radicals react only rarely with triethyltin radicals (see subsection 9). Thus, **10** must be formed mostly by reaction of pairs of ring-cyclized radicals, and because at most one of each pair can be converted to **10**, the maximum conversion efficiency is 50%. This explanation is largely substantiated by yields of **B** (see Chart 4, p. 78), although for some reason those yields do seem consistently smaller than those of **10** (see Table 10).

Because dimers apparently are formed in 1, 4-cyclohexadiene, where ring-cyclized radicals react either with cyclohexadienyl radicals or with other ring-cyclized radicals (which may be thought of as substituted cyclohexadienyl radicals), it seems likely that dimers are formed in triethyltin hydride as well. Thus, though the procedure is somewhat arbitrary, I have assumed in the following that the conversion efficiency of 35% is appropriate for reaction in the presence of triethyltin hydride.

The assumed 35% efficiency is in reasonable agreement with material balances. For the 110° run at 0.01 M tin hydride (row 1 of Table 10), the material balance is 81%. Apart from the possibility of experimental error, the discrepancy may be attributed to the yield of the lactone **23** and/or to the formation of naphthalenoid dimers. As explained earlier (p. 85) special conditions are necessary to observe the lactone **23**. Those conditions were not employed for the tin hydride runs. If, however, the suggestion is correct that **23** arises via molecule-induced decomposition (subsection 6), its yield would be expected to fall off with increasing incursion of radical-induced decomposition. From the observed yield of 3.3% for the cage ether **12**, the percent normal decomposition is only about 25% (see pp. 152–155). Thus the expected yield of **23** would be ~4%, rather than the 15% observed in 1,4-cyclohexadiene. That still leaves about 15% for the possible yield of dimers, from which the total yield of naphthalenoid products is 17 + 13 + 15 = 45%, and the conversion efficiency is 17/45 X 100 = 38%.

If yields of tin ester **14** for otherwise identical conditions are the same at 110 and 125°, the 0.01 M run at 125° also would support a conversion efficiency of about 35%. Further assuming that the yields of **B** will fall off at 125° as in the bank of runs at 144° (the vpc spectra for the four 125° runs were lost before yields of **B** had been extracted), the material balance for the 125° run at 0.044 M tin hydride is also consistent with a conversion efficiency of about 35%. However, the size of possible experimental error in individual runs is indicated by the results of a similar treatment of the 0.39 M tin hydride run at 125°; that treatment indicates a conversion efficiency of about 20%.

Thus, we will assume that k_r/k_a^{SnH} can be obtained by multiplying the reduced ratios calculated from eq. 1.8-5 (rightmost column of Table 10) by 1.0/0.35. However, one problem remains: as is clearly shown by the banks of runs at 125 and 144°, the reduced ratios decrease with increasing tin hydride concentration. This behavior might be due to preferential hydrostannation (41) of **10** or to a change in the pattern of the conversion reactions, as would for example be effected by increasing abstraction of hydrogen by ring-cyclized radicals from triethyltin hydride at the higher tin hydride concentrations. In fact, the latter explanation will be invoked in the subsequent mechanistic treatment of radical-induced decomposition in triethyltin hydride.

Whatever the perturbing factor, its influence would seem most likely to be minimal at low tin hydride concentrations. Accordingly, (linear) extrapolation to zero tin hydride concentration gives reduced ratios of 0.063 at 125° and 0.082 at 144°. The tin hydride concentration for the single run at 110° is so small (0.01 M) that no extrapolation would be needed. (In the extrapolation procedure at 125°, the run at 0.93 M tin hydride was neglected; the downturn in the yields of 5 and 6 between 0.38 M and 0.93 M indicates the emergence of a new factor, possibly involving hydrostannation of the perester itself as well as of various reaction products.)

Values of k_r/k_a^{SnH} calculated from these reduced ratios assuming a conversion efficiency of 35% (0.15 at 110°, 0.18 at 125°, and 0.23 at 144°) are plotted according to the Arrhenius equation in Fig. 12. The fourth point in that figure, the one at lower right, represents the k_r/k_a^{SnH} value at 35° obtained in the following way from the data of Table 11. Note, in Table 11, that the reduced ratios increase strongly with increasing triethyltin hydride concentration, rather than decreasing as in Table 10. A possible meaning of this trend can be inferred from the fact that the yields of 10 at 35° do not go to zero at the higher tin hydride concentrations as strongly as would be expected, but seem to level off at about 0.7%. Although absolute yields are unavailable at 10°, the reduced ratios again suggest that a similar thing is happening.

In making up the reaction tubes for the runs at 10 and 35°, the perester was first dissolved in benzene or *n*-octane. Aliquots of the resulting solution were then pipetted into reaction vessels which were then quickly cooled in Dry Ice-acetone. As the ring-closed perester is not readily soluble at the concentrations listed in either solvent, some time is required to effect solution. Judging from results in benzene or cyclohexane (Table 9), if 3% of the perester decomposed during the preparation and dispensing of the solution, a yield of about 0.7% of 10 would be accumulated. Since at room temperature (23°) the half-life of 2 is about 100 min (p. 237), a preparation time of about 6 minutes would thus explain the failure of 10 to go to zero yield at the higher tin hydride concentrations. No measure of the actual time was made, but it could well have been about that long.

This suggests that a constant amount be subtracted from observed yields of 10 at 35° and the reduced ratios be recalculated. Subtraction of 0.5% gives reasonably constant values of 0.015, 0.012, 0.013, and 0.015, for an average of 0.014. To convert the 0.014 to a k_r/k_a^{SnH} value, an estimation of the efficiency of conversion of ring-cyclized radicals to dihydronaphthalene 10 is again required. Since no experimental information on that efficiency is available for these conditions, the value of 35% inferred at higher temperature has again been employed to give k_r/k_a^{SnH} (35°) = 0.040, the value employed in Fig. 12.

The straight line in Fig. 12 is quite good. It is perhaps especially significant that the three points determined at 110 to 144° lie well on the line, in spite of the narrowness of that temperature range. The least-squares equation for the line is found to be*

---

*The standard error in the activation energy was calculated to be 0.7 kcal/mole. This result assumes that the conversion efficiency does not vary by more than 20% (relative) between 35 and 144°.

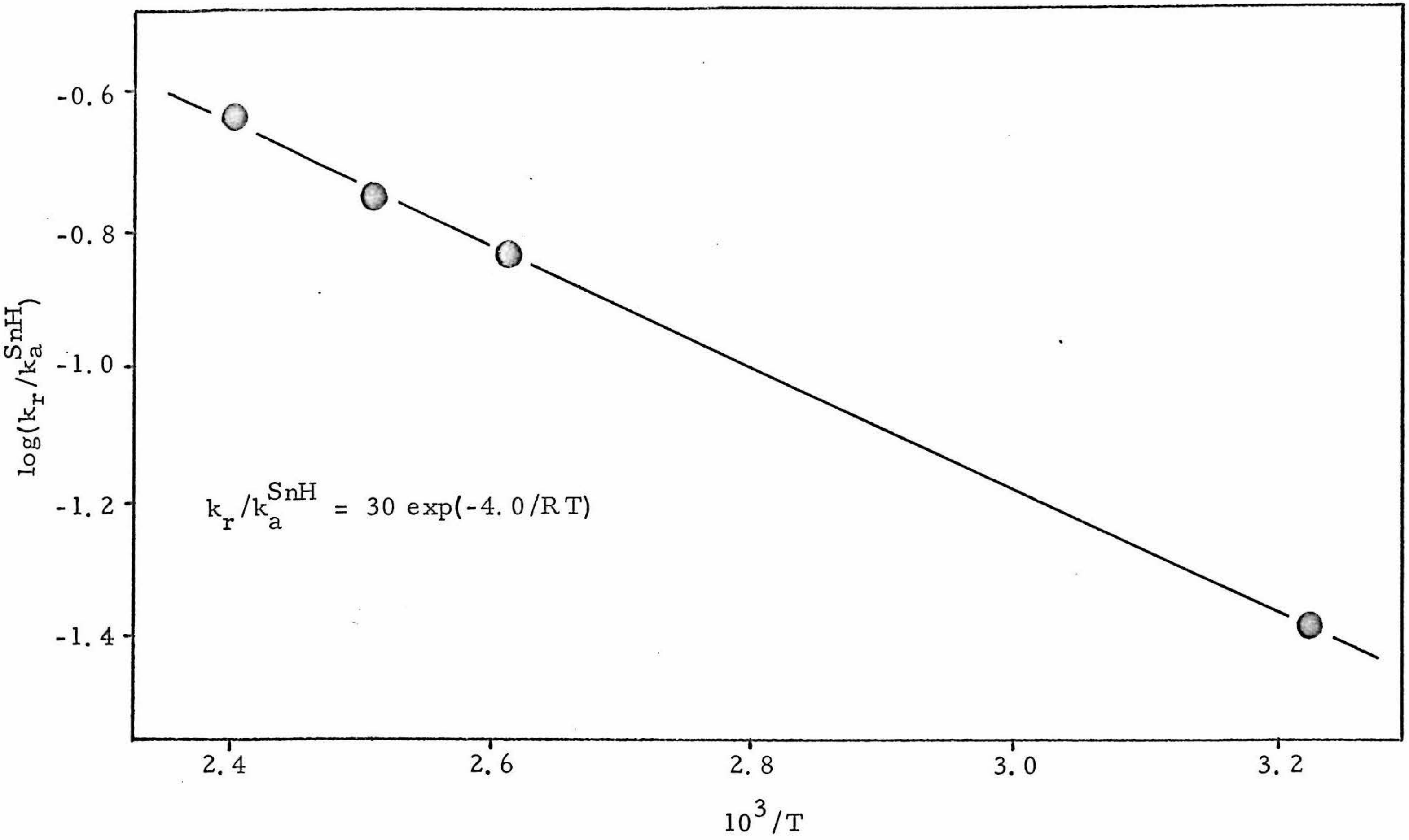


Figure 12. Arrhenius plot for k_r/k_a^{SnH}.

$$k_r/k_a^{\mathrm{SnH}} = 30\ \exp(-4.0/RT)\ . \qquad (1.8\text{-}11)$$

Combined with eq. 1.8-6 for $k_r/k_a^{⌬}$, we estimate

$$k_a^{\mathrm{SnH}}/k_a^{⌬} = 0.7\ \exp(+3.2/RT)\ , \qquad (1.8\text{-}12)$$

Thus, the activation energy for hydrogen abstraction from 1,4-cyclohexadiene by the ring-opened radical is about 3 kcal/mole greater than from triethyltin hydride. This information allows us to correctly superpose the reaction diagram figures 10 and 11. The result is Fig. 13 (where indicated energies have not yet been rounded to conform to reasonable estimates of experimental accuracy, this to encourage the reader to trace the implications of the superposition). We now can estimate that isomerization of the ring-opened radical to the ring-closed radical requires an activation energy of approximately 4 kcal/mole. In addition, the transition state for formation of the ring-closed hydrocarbon via hydrogen abstraction from triethyltin hydride is actually indicated to be lower in energy than the ring-opened radical itself; if the activation energy for that hydrogen abstraction process is 5--10 kcal/mole, the difference in energy of the two forms of the radical would be of similar magnitude.

B. *t*-Butyl 5,5-Diphenylperpropanoate

This perester differs structurally from the ring-opened perester in having a carbon-carbon single bond where the latter has a double bond. Reaction steps for processes in the decomposition of the

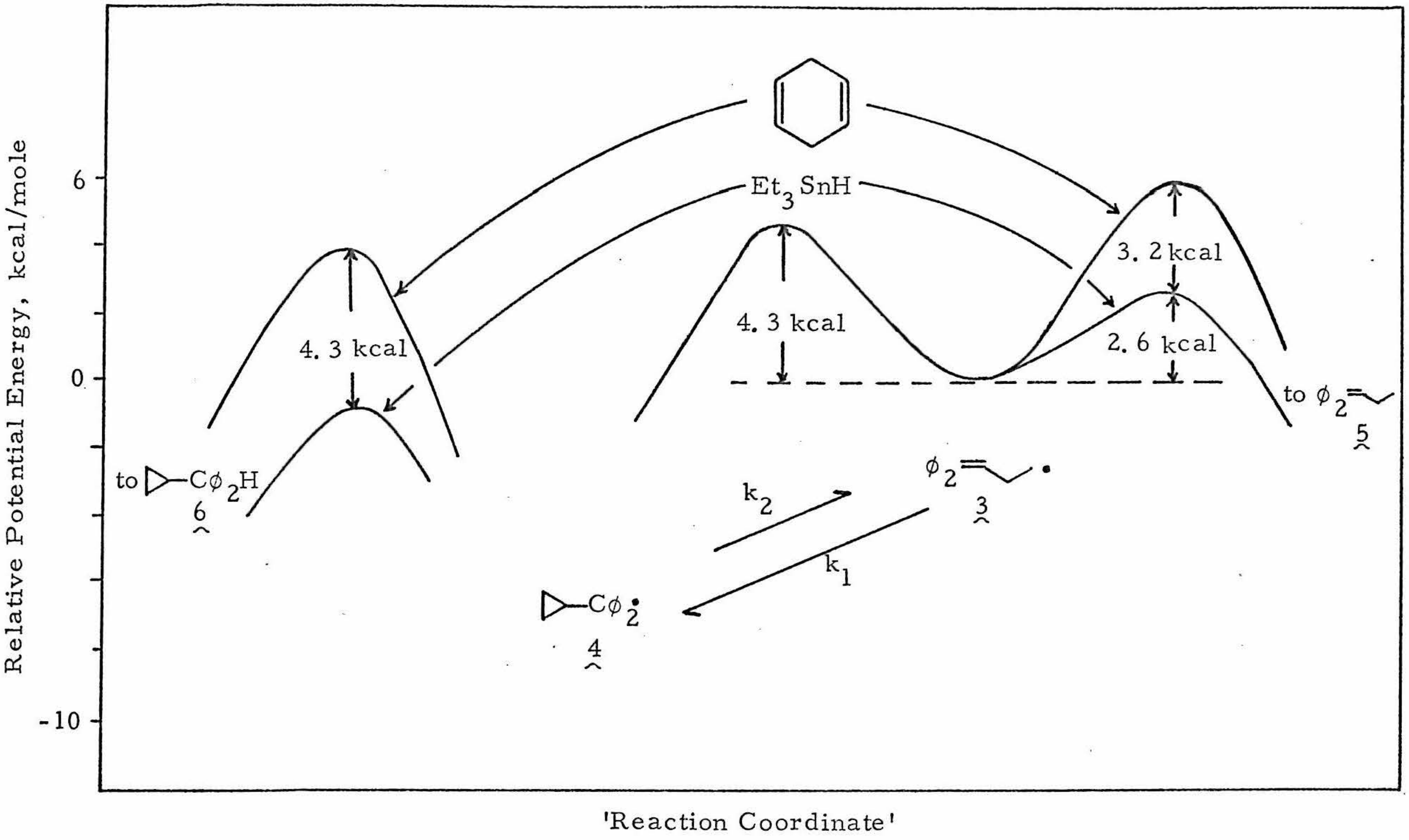
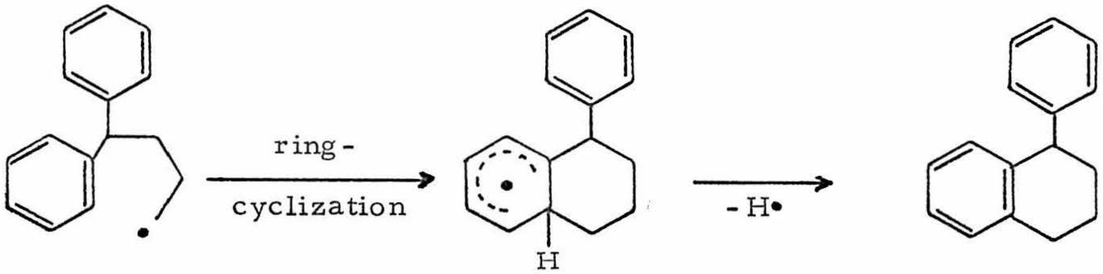


Figure 13. Reaction diagram obtained by superposition of Figs. 10 and 11 according to eq. 1. 8-12.

ring-opened perester which involve the double bond should have no counterparts in the decomposition of the so-called saturated perester (8), but others should; thus, comparison of results for the two peresters provides a kind of check on our understanding of the reaction mechanisms and, in particular, on the assessment of the role played by interactions having to do with the double bond.

Results for thermal decomposition of the saturated perester 8 are displayed in Table 3 and immediately following that table in Fig. 3.

Comparison of Figs. 1 and 3 shows that relatively large yields of the unrearranged hydrocarbon, in this case the saturated hydrocarbon 20, are realized and that those yields rise very abruptly with increasing 1,4-cyclohexadiene concentration. The average values, for runs at 152°, of the reduced ratios tabulated in the right-most columns of Tables 1 and 3 are 3.4 and 0.21, respectively. These numbers indicate that the rate of ring-cyclization relative to hydrogen abstraction is greater by a factor of approximately 16 in the unsaturated series.



21 24 25

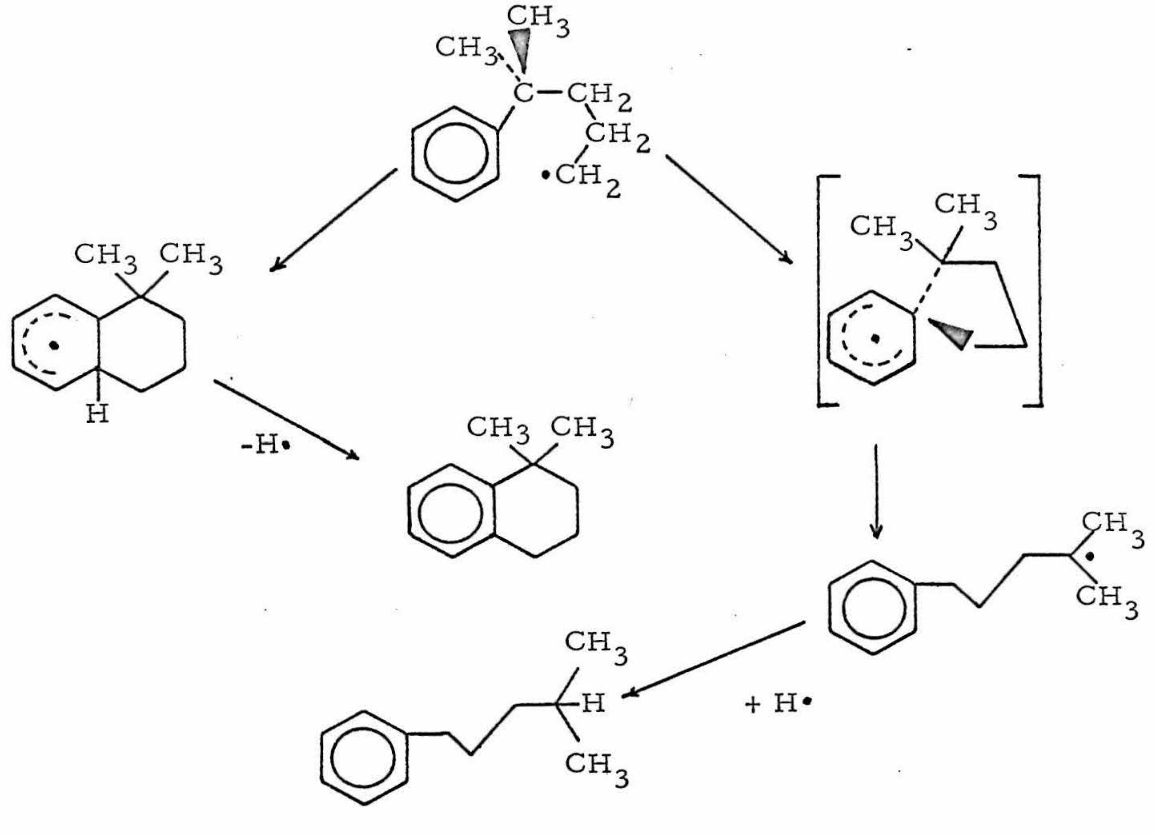
Of course, consideration of efficiencies for conversion of the ring-cyclized radicals 9 and 24 to the dihydronaphthalene 10 and the tetralin 25 might alter this factor to some degree, but would not upset the substantial difference which is evident. Possible reasons for a difference of this magnitude will be considered shortly.

The efficiency for conversion of the radical 24 to the tetralin 25 appears to be at most 50%. In particular, for a run at 100° in 3.2 M 1,4-cyclohexadiene in cyclohexane (not shown in Table 3), the peak corresponding to the C of Table 3 was found to be made up of nearly equal areas of a substance tentatively identified as the rearranged hydrocarbon 26 and a second material which might well be a hexahydronaphthalene. The latter would correspond to the tetrahydronaphthalenes implicated in the decomposition of the isomeric ring-opened and ring-closed peresters. As the yield of C is consistently 2--3 times that of the ring-cyclized hydrocarbon 25 when 1,4-cyclohexadiene is present, the yield of 25 evidently therefore accounts for not more than about half of the radicals 24 which are formed.

26

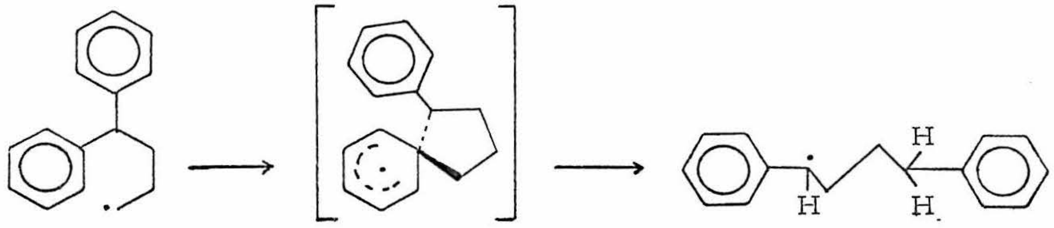
Identification of the ring-cyclized hydrocarbon 25 and the rearranged hydrocarbon 26 is based on a rather careful investigation of vpc retention times. On Ucon polar, the retention times of C and of 25 agreed within a reasonable experimental error of 2--3 tenths of a percent with those due to authentic 26 and 25. This was true both for the run at 3.2 M cyclohexadiene referred to above and for a run, also at 100°, in neat cyclohexane. On silicone oil, peaks for candidate and authentic 25 again agreed within 2--3 tenths of a percent. However, as noted above, the other peak in the Ucon polar trace was now split into two of about equal intensity in the case of 3.2 M cyclohexadiene run, one of which again agreed in retention time with authentic 26.

Precedent for formation of 26 can be cited in the work of Winstein and Lapporte (58) who investigated the radical-chain decarbonylation of 5-methyl-5-phenylpentanal (130° in chlorobenzene, initiated by di-t-butyl peroxide). They found that the phenyldimethylbutyl radical shown below cyclized both in the ortho- manner and to the 1-position on the phenyl ring. The ultimate products in the two cases, 1-1-dimethyltetralin and 1-phenyl-4-methylpentane, were detected by infrared in relative amounts of approximately 2.5:1. A point in question is whether the spiro-radical enclosed in square brackets is a discrete intermediate or merely the transition state for concerted phenyl-group migration.



Even if the former is the case, however, ring-opening to the tertiary radical should be highly favored over reversal to the primary radical. Thus, relative amounts of the two hydrocarbons should broadly reflect the relative rates of the two cyclizations.

In the present system, the analogous five-membered ring spiro radical (27) would also be expected to open to the more stable species, the rearranged radical 28. Assuming that yields of C quoted in Table 3 include hexahydronaphthalene in similar yield to the tetralin 25, relative amounts of 25 and C observed in the presence of 1,4-cyclohexadiene imply that ring-closure of 21 to 24 is favored over closure to 27 by approximately a factor of 1.5:1. Thus, relative ratios for the two cyclization pathways are similar in this system and in Winstein's.



21 27 28

While combined experimental ambiguities probably disallow quantitative comparison of the partitioning ratios for the two systems, we might note that reliable data on the effect of suitable substituents should indicate whether the phenyl migration is concerted or step-wise; one would expect the ability of the substituent to stabilize a radical center to profoundly influence the rate of the spiro-closure only if the original carbon-carbon bond is broken as the new bond is formed.

One oddity in Table 3, mentioned briefly above, is that the ratio **C**:**25** is ~ 2.5:1 in the presence of 1,4-cyclohexadiene, but only 0.2:1 in cyclohexane. This might at first seem inconcistent with our assertion that the spiro-closure product **26** constitutes about half of **C** for reaction in the presence of cyclohexadiene. The potential problem is that benzylic hydrogens such as those of **26** are no better than comparable in reactivity to cyclohexane towards simple primary radicals or t-butoxy radicals (57, 89). As any **26** formed should therefore not be destroyed under the reaction conditions, the expected facile attack of radicals on the hexahydronaphthalene (which we have said makes up the other half of **C** in 1,4-cyclohexadiene) might be expected to reduce the ratio **C**:**25** only to ~ 1. The explanation for the lower ratio actually found in cyclohexane is very possibly that little **26** is formed due to the lack of suitable hydrogen donors for conversion of **28** to **26**. While 1,4-cyclohexadiene would be expected to serve admirably, hydrogen abstraction from cyclohexane would be endothermic by approximately 10–15 kcal/mole. Therefore, in cyclohexane **28** may react largely with other radicals, and such reactions could frequently result in coupling rather than formation of **26**.

A value of 0.038 was obtained for the ratio **25**:**20** at 100° for 3.2 M 1,4-cyclohexadiene. Thus the reduced ratio is 0.12 at 100°, about 56% of the average of the values observed at 152°. In obtaining eq. 1.8-6 for k_r/k_a (p. 125), we have tacitly assumed that the efficiency of conversion of the ring-cyclized radical **9** to the dihydronaphthalene **10** is independent of the reaction temperature. On the same basis, the reduced ratios quoted here indicate that the activation energy for *ortho*-ring cyclization by the saturated radical 21 exceeds that for hydrogen abstraction from 1,4-cyclohexadiene by 3.5-4 kcal/mole. If we then assume that activation energies for hydrogen abstraction from cyclohexadiene are identical for the radicals 3 and 21, we conclude that the activation energy for *ortho*-ring cyclization by 21 exceeds that for cyclization by 3 by 2.5—3.0 kcal/mole.

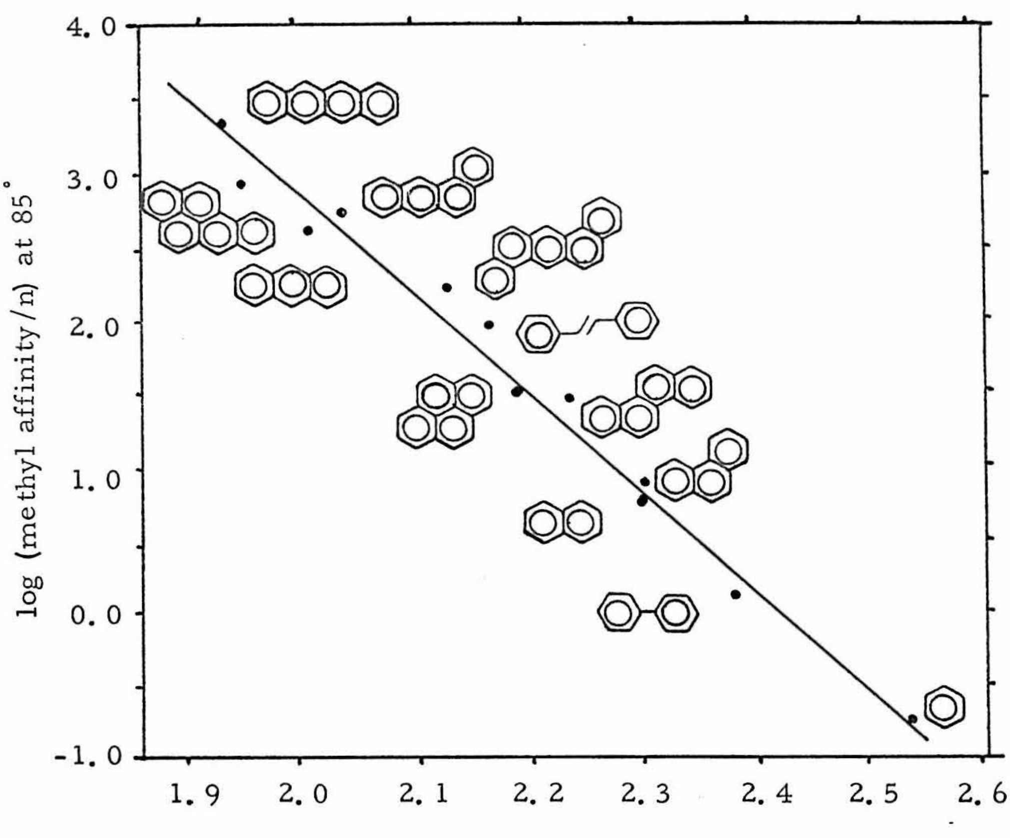
The question now is whether a difference of that magnitude can be rationalized under the assumption that only the classical radicals 3 and 4 need be invoked to account for formation of the isomeric hydrocarbons 5 and 6. This is the question addressed in the major part of the remaining pages of this subsection.

Szwarc and co-workers have carried out abundant experimental determinations of relative rates of addition of methyl radicals to aromatic and olefinic systems (25). Besides finding that strong correlations exist between relative rates of addition for methyl radicals and for ethyl radicals, propyl radicals, trichloromethyl radicals, and styryl radicals, their work is of interest here because relative rates of addition can also be correlated by quasi-theoretical treatments arising from simple Hückel molecular orbital theory (59).

Addition of a radical, anion, or cation to a particular carbon atom of a pi-electron system removes that center from the pi-system. Cyclization by the radicals 3 and 21 are intramolecular examples of such processes. This suggests that rates or activation energies of such addition processes might correlate with the energy necessary to 'localize' the appropriate number of pi-electrons (two for addition of a cation, one for a radical, and zero for an anion) at the center in question (62). Such a quantity (called the localization energy (61) can be obtained in HMO theory from the pi-electron energies of the initial and the localized systems.

There is some question as to the appropriateness of the localization picture when the resulting intermediate is actually more stable than the separated reactants (as can be shown to be the case for addition of simple alkyl radicals to aromatic systems). Moreover, there is substantial reason to suspect the validity of results obtained by HMO theory. However, the procedure outlined is found to be strikingly successful when applied to Szwarc's data (62, 25). One finds that log (methyl affinity/n), where n is the number of the most reactive positions in the substrate, is linearly related to the radical localization energy, as in Fig. 14 (63).

Leaving aside the question of why so crude a theoretical treatment is successful, the fact that it is, should permit its safe utilization in the problem under consideration. The localization energy for *ortho*-ring cyclization of the saturated radical 21 is identical in the HMO method to the value (2. 54 β) calculated for addition to benzene. For the unsaturated radical 3, however, an ambiguity arises concerning the values employed for the resonance integrals of bonds involving the two olefinic carbons. For aromatic carbon systems, an acceptable procedure (and that employed by Szwarc) is to assign all nearest-neighbor resonance integrals a common value of β, even though the minor variations in bond lengths found experimentally (or approximately predicted by bond orders) might be taken as cause for tying the resonance integral



Localization energy in units of β

Fig. 14. Correlation of methyl affinities with localization energies.

to the bond length (or to the bond order). For pi-electron systems in which bond lengths range between values close to those expected for classically single and classically double bonds, however, variable values of β must be used (50).

Accordingly, resonance integrals for the three interactions (or bonds) involving the carbon-carbon double bond of the ring-opened radical were obtained by the procedure employed by Szwarc in his companion study on methyl affinities for olefinic substrates (25). Using trial values of β, the mobile pi-bond orders (73) are calculated, bond lengths are inferred from Coulson's relationship (64), and new values of β corresponding to the calculated bond lengths are assigned from a table given by Roberts and Skinner (65). The cycle is carried to self consistency.* The calculated localization energy is 2.43 β, and the difference in localization energies for the two systems is 0.11 β. (For comparison, use of constant β results in a difference in localization energies of 0.15 β.)

Translation of this difference in localization energies into a difference in activation energies for ring-cyclization requires a further assumption, which we shall take (following the previous investigators) to be that the preexponential factors for addition of methyl radicals to specific centers on aromatic substrates are constant.# From the slope of the straight line in Fig. 14 one then obtains for any two substrates

$$\Delta E_{act} = 11.2\ \Delta L.E. \qquad (1.8\text{-}13)$$

As ethyl affinities and methyl affinities show apparently identical sensitivity to structural variations in the aromatic substrate (25), eq. 1.8-13 should be applicable to such differences in activation energy

---

*Final resonance integrals (in units of β for $r = 1.393$ Å) were 0.86 for the two carbon to phenyl-ring bonds and 1.09 for the carbon-carbon double bond.

#Use of the Arrhenius equation is assumed here. While some positions in polynuclear aromatics 'look' appreciably more hindered than a position in benzene, my experience with many of the systems of Fig. 14 suggests that the positions of minimum localization energy tend to be those which are least stericly congested.

for *ortho*-ring cyclization by **3** and by **21** as arise from the more extensive pi-system involved in cyclization of the former. The calculated activation energy difference of 1.2 kcal/mole is somewhat less than half the observed value but is at least of the correct sign.

Other factors may of course contribute to the activation energy difference. In particular, there may be specific conformational effects arising from the intramolecular nature of the ring-cyclization. Examination of Dreiding models indeed suggests that the hydrogen atoms on the two methylene groups in **21** *may* have to become eclipsed in the cyclization. No such unfavorable interaction arises in ring-cyclization by the ring-opened radical **3**. A reasonable guess for the extra energy of an eclipsed ethane-like fragment would be 3 kcal/mole, which is the barrier to internal rotation in ethane (90) and is also close to the barriers in many substituted ethanes (90). Thus, a partial eclipsing in cyclization of **21** could well account for the remaining portion of the activation energy difference.

The arguments given above should suffice to show that no contradiction arises, in consideration of activation energies, from the assumption that the classical radicals **3** and **4** account for formation of the isomeric hydrocarbons **5** and **6** as well as for ring-cyclization. We still need to inquire what type of results might signify the intermediacy of a nonclassical radical such as **7**. The question is difficult to answer in terms of the activation-energy differences discussed above, but becomes more tractable if relative rates of ring-cyclization and hydrocarbon formation for the saturated and unsaturated systems are considered. As quoted on page 140, that ratio is greater by a factor of approximately 16 in the unsaturated system.

Let us consider that both the nonclassical radical 7 and the classical radical 3 give rise to ring-opened hydrocarbon 5. In view of the lack of interconversion of cyclobutyl and allylcarbinyl-cyclopropylcarbinyl skeletons in free-radical reactions (see pp. 8, 9), it seems likely that the molecular orbital proscription against a bicyclobutyl-type (p. 8) nonclassical free radical in favor of a homoallyltic structure (such as 7) is valid (13). For geometrical reasons, then, we can assume that only the classical radical 3 undergoes the ring-cyclization. It follows that formation of substantial amounts of ring-opened hydrocarbon from the nonclassical radical 7 should lead to a rate of ring-cyclization relative to hydrocarbon formation which is anomalously low by comparison to the saturated model.

The question, then, is whether the factor of 16 is 'anomalously low'. As discussed above in terms of activation energies, the more extensive pi-system in the unsaturated system should favor ring-cyclization by 3 over ring-cyclization by 21. The 1.2 kcal/mole inferred from the localization energies is equivalent, at 152°, to approximately a factor of 4. This leaves a factor of 4 to be accounted for in other ways. In 21, the radical center can cyclize to either of two phenyl rings, while in 3, the geometry about the double-bond renders only one of the rings accessible. However, this factor may be more than offset by the existence of the additional carbon-carbon single bond in 21, which would seem to allow the radical center of 21 to explore many more regions of space quite remote from the phenyl rings than are permitted the ring-opened radical 3.

Additional factors are the eclipsing which *may* be required for ring-cyclization by 21 and, according to Dreiding models, the greater distance of minimum approach (without stretching bonds) between radical center and *ortho*-carbon in the unsaturated series.

Clearly, a quantitative assessment of all the relevant factors is quite impossible. Still, it is possible to say that there is no compelling reason to suspect that a mechanistic formulation involving only classical radicals is defective. On balance, this constitutes yet another occasion in which a nonclassical radical, if it exists, might have made its presence felt, but failed to do so.

Consideration of localization energies is useful in answering the potentially troubling question of whether 3 might be able to undergo a spiro-closure similar to that inferred for 21. The problem is that the assumption that B is comprised of isomeric tetrahydronaphthalenes is crucial to the estimation of efficiencies of conversion of 9 to 10, and thus to the indirect comparison we have made through eqs. 1.8-6 and 1.8-11 of relative rates of attack of 3 on 1,4-cyclohexadiene and triethyltin hydride. To show that spiro-closure by 3 is not an attractive process, we have calculated the localization energy for that process. The result, 2.82 β is 0.39 β higher than that for *ortho*-ring cyclization. According to eq. 1.8-13, this difference is equivalent to an activation energy difference of 4.4 kcal/mole, which in turn implies a rate difference of ~ 350 at 100°. As spiro-closure and ring-cyclization by 21 occur at comparable rates, and as the localization energies for the two processes are identical in the HMO method, the implication is that ring-cyclization by 3 should be favored over spiro-closure by a factor of ~350.

The same conclusion can perhaps be reached less esoterically by noting that 3 is a much more stable radical than the vinylic radical which would result from the alternative opening of the unsaturated analog of spiro radical 27.

9. Radical-induced Decomposition in Triethyltin Hydride

In the preliminary discussion in subsection 5A, we noted that under certain assumptions (survival of the cage ether; no interdiction of cage processes via rapid abstraction of hydrogen from triethyltin hydride by any of the caged species), the fraction of normal decomposition of perester 1 in triethyltin hydride is given by the ratio of the yield of cage ether 12 to that which would be observed in the absence of induced decomposition. As we have no way of suspending the radical-induced decomposition at the relatively high (ca. 1 M) triethyltin hydride concentrations where radical-induced decomposition predominates, we can not of course know with absolute certainty what the efficiency of production of the ether 12 would be under those circumstances: and either the physical or the chemical properties of the tin hydride could, in principal, occasion a substantial drift in the yield of 12 with the hydride concentration, even if no question of radical-induced decomposition arose.

It was also shown in subsection 5A that physical properties of the solvent can markedly affect the efficiency of cage ether formation. In particular, the so-called kinematic viscosity--the ratio of viscosity to specific gravity--seemed to be a useable measure of the ability of a solvent to keep the caged particles long confined, and thus to promote cage recombination or other cage reaction. At 20° the viscosity and kinematic viscosity of n-octane are 0.54 and 0.78, respectively (91). The analogous quantities are not known for triethyltin hydride, but I have investigated tetraethyltin; its viscosity at 20° is 0.63, its specific gravity is reported to be 1.19 (92), and thus its kinematic viscosity is 0.53. The figures for triethyltin hydride are expected to be rather similar. As the highest tin hydride concentration investigated (0.94 M) is still 80% n-octane by volume, the kinematic viscosity of the solution is not likely to differ substantially from that of n-octane itself. Thus, competition between cage recombination and diffusive separation of the caged particles may safely be taken to be substantially independent of tin hydride concentration for the relatively dilute solutions investigated in this work.

The chemical properties of triethyltin hydride are cause for somewhat greater concern. Specifically, hydrogen abstraction from triethyltin hydride by t-butoxy radical might compete with cage recombination and with diffusion from the solvent cage, at least at the higher tin hydride concentrations. That hydrogen abstraction reaction is expected to be exothermic by roughly 40 kcal/mole. Moreover, attractive polar contributing structures can be written for the transition state in question. These considerations suggest a reaction of low activation energy, if it is not actually diffusion-controlled. Moreover, scavenging of precursor acyloxy radicals by the tin hydride could in principle also affect the yield of the ether 12. However, this possibility can be discounted on the basis of the study reported by Neumann, Rubsamen, and Sommer on radical-induced decomposition of diacylperoxides in triethyl- and tri-n-butyltin hydride (93). They found that 0.5—1 M tin hydride efficiently traps relatively stable benzoyloxy radicals, but that even at room temperature decarboxylation of acetoxy and lauryloxy radicals ($CH_3(CH_2)_{10}CO_2\cdot$) is more than competitive with hydrogen abstraction from the tin hydride. Their results suggest that at the much higher temperatures employed in this work, scavenging of simple acyloxy radicals should be negligible.

In any case, evidence to be presented shortly strongly suggests that the yield of ring-opened ether 12 is not measureably affected by scavenging of caged radicals by triethyltin hydride.

Thus, the major source of uncertainty in any conclusions drawn from observed yields of the ether 12 would appear to arise from error in the measurements of the ether yields. The yield of 12 for 100% normal homolytic decomposition in n-octane solution can be inferred from the run shown in row 5 of Table 8. As previously noted, 0.2 M 1,4-cyclohexadiene (2% by volume) was employed in that run to moderate the reaction and thus to insure the survival of the cage ether. The fact that a rather normal 1.4% yield of the sensitive butadiene 13 survives the decomposition confirms the efficacy of the small cyclohexadiene concentration employed. Thus, the expected yield of 12 for 100% normal decomposition (hereafter abbreviated 100% n) at 110° is 12%. A reasonable estimate of the uncertainty in this value is ± 1%. As the viscosity of the reaction mixture will be somewhat less at 125° than at 110°, the yield of **12** is expected to be slightly less, as is in fact observed (Table 1) for decomposition of **1** in cyclohexane-cyclohexadiene mixtures. We shall adopt a value of 11 ± 1% for use at 125°. The principal uncertainty, however, is that in the determination of the ether yields for the decompositions in the presence of the tin hydride. For the four runs at 125° from 0.044 to 0.94 M triethyltin hydride, 1-phenylnaphthalene, which has a retention time about 10% less than that for the ether **12** (Ucon polar), was used as the internal standard in relatively large amounts. As a result, the ether appears as a relatively small peak on the tail of the 1-phenylnaphthalene, and those yields are probably good to not better than ± 20% relative. In contrast, the two 0.01 M tin hydride runs were subsequently carried out with extraction of the ether yields as the primary goal, and those ether yields should be good to ± 5%.

Percents of normal decomposition and standard errors calculated by propagation of errors from the quoted uncertainties in the ether yields are given in column 5 of Table 15 (p. 172). The sixth column of that table contains the fractions of normal decomposition calculated in a second way--from reaction rates measured at 110°. The numbers quoted are derived from ratios of rate constants for perester disappearance taken with respect to Howden's value of 0.0046 min^{-1} for chlorobenzene solution at 110° (see eq. 1.9-2).

Actually, the derived rate constants (see Figs. 15-18) were not obtained by following the decreasing perester concentration with time, but rather by following the increasing concentration of tin ester **14**;

the former course of action is rendered impractical (for triethyltin hydride--perester concentration ratios larger than about 5) by the strong, broad absorbance (Sn - H stretching) of the tin hydride at 1813 cm^{-1} which obscures the only strong perester absorbance, the carbonyl band at about 1785 cm^{-1}.

Figs. 15-18 are plots of absorbance of tin ester at the carbonyl maximum of 1651 cm^{-1} against time for degassed thermal decomposition. The perester disappears with a total rate constant, k_T, which is related to the rate constant for normal decomposition, k_o, according to eq. 1. 8-1, where the concentration of perester $\underset{\sim}{1}$ is denoted by (P), of triethyltin radicals by (Sn·), and the rate constant for attack of Sn· on P is denoted by k_1.

$$-d(P)/dt = k_o(P) + k_1(Sn\cdot)(P) = k_T(P) \quad . \qquad (1.9\text{-}1)$$

The fraction of induced decomposition is given by

$$k_o/k_T = (1 + k_1(Sn\cdot)/k_o)^{-1} \quad . \qquad (1.9\text{-}2)$$

Because the induced decomposition is very nearly first order in perester,* the tin ester absorbance, which is proportional to the tin ester concentration, is proportional to the concentration of perester which has undergone decomposition. As such, the rate constant extracted from the dependence of absorption on time is k_T. The equation ($A(t)$ is absorbance at time t; A_o, at $t = 0$; and A_∞, at $t = \infty$)

---

*This statement will be justified later in this subsection. Perhaps we should point out that this fact justifies our taking k_T to be constant in the treatment of the kinetic data given here.

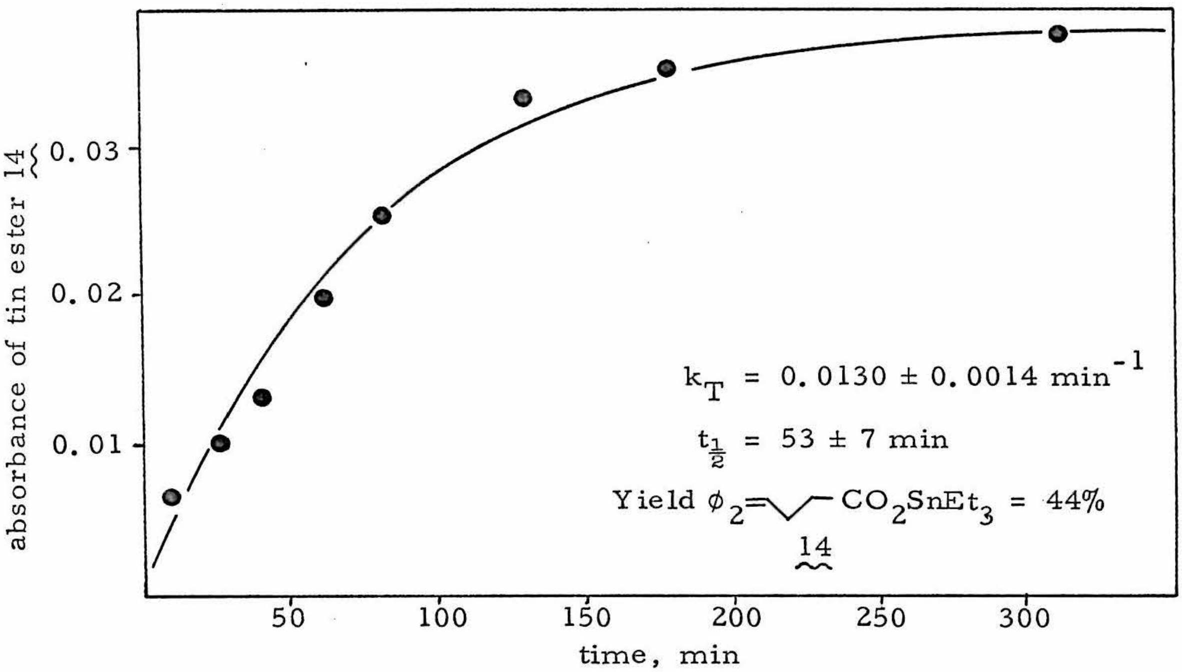


Figure 15. Decomposition of 0.002 M t-butyl (γ, γ-diphenylallyl)peracetate in 0.010 M triethyltin hydride in n-octane at 110°; not shown is a measurement at 550 min, absorbance = 0.0373.

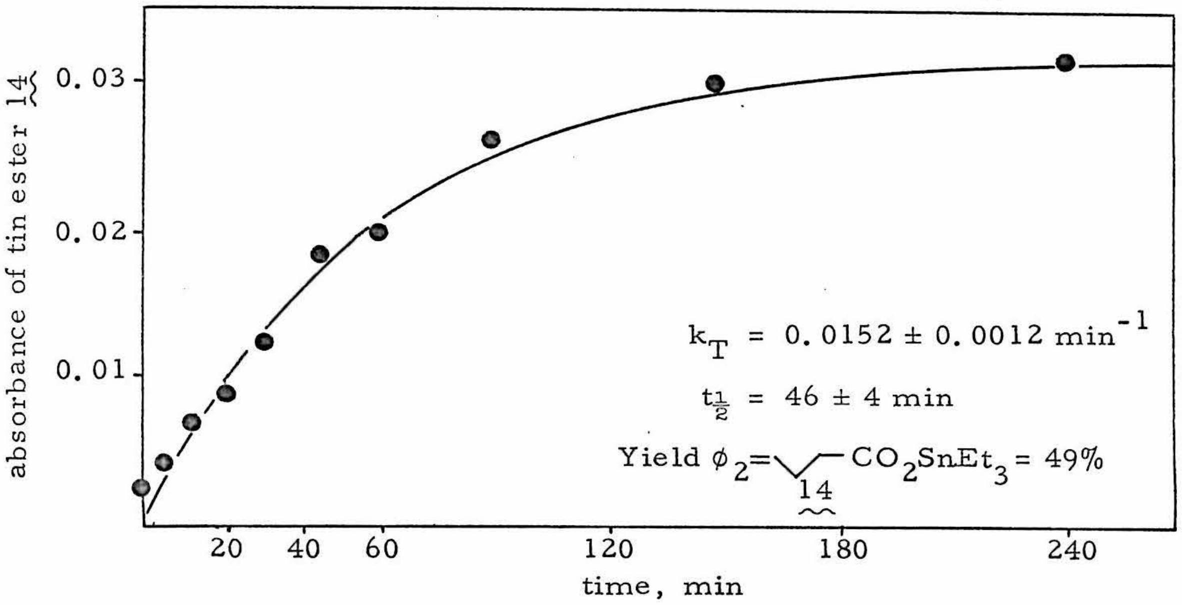


Figure 16. Decomposition of 0.002 M t-butyl (γ, γ-diphenylallyl)peracetate in 0.044 M triethyltin hydride in n-octane at 110°.

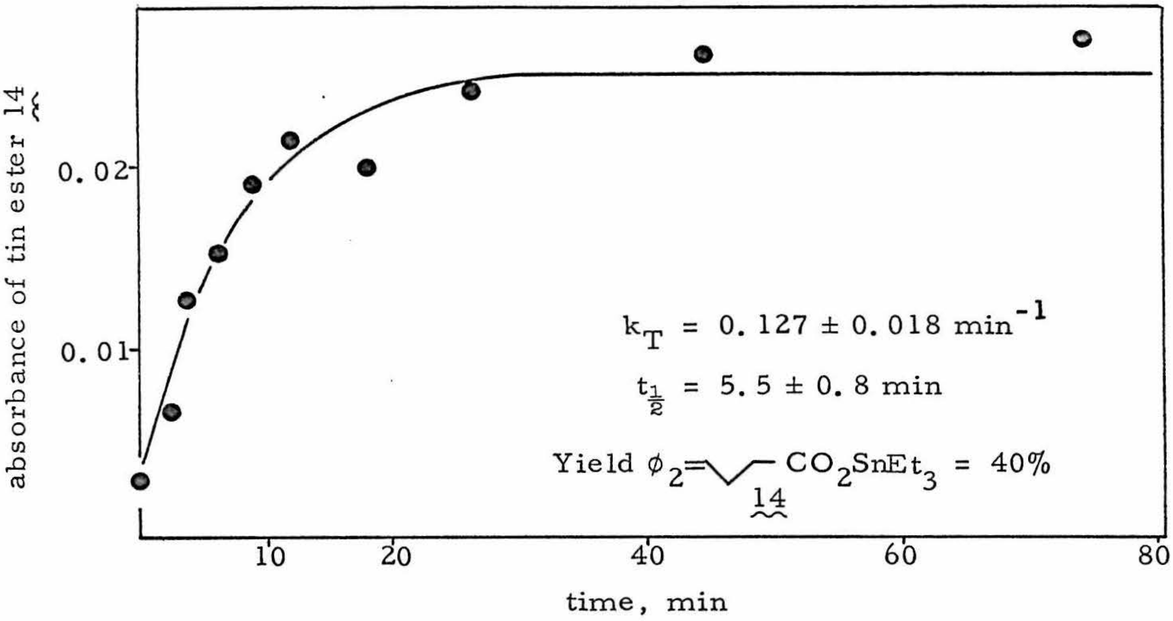


Figure 17. Decomposition of 0.002 M t-butyl (γ, γ-diphenylallyl)peracetate in 0.41 M triethyltin hydride in n-octane at 110°.

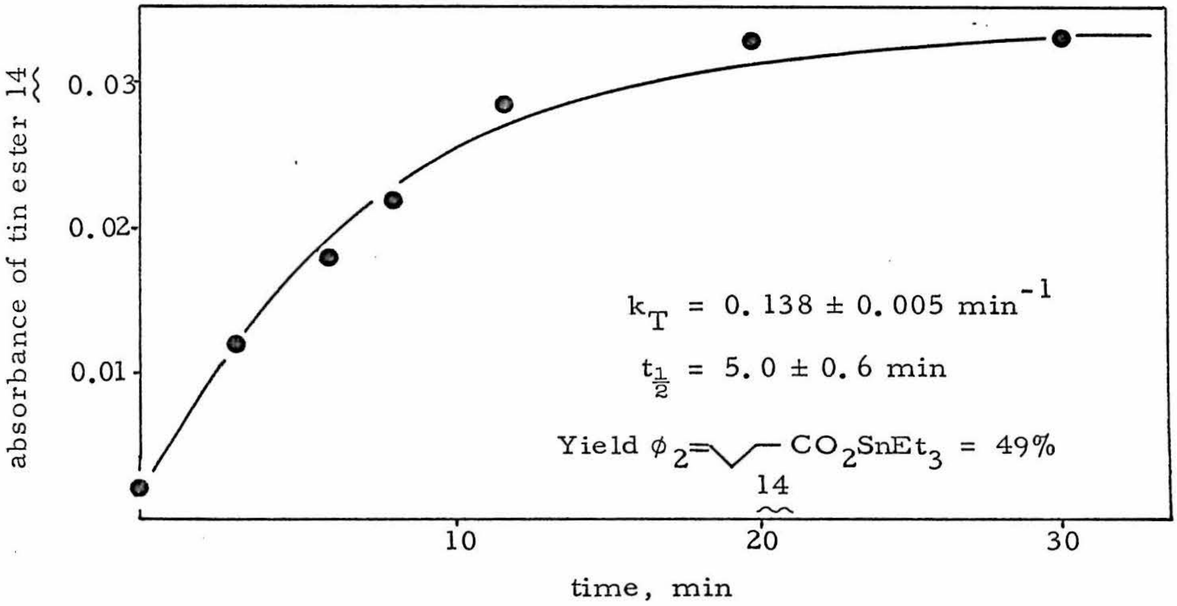


Figure 18. Decomposition of 0.02 M t-butyl (γ, γ-diphenylallyl)peracetate in 0.67 M triethyltin hydride in n-octane at 110°; not shown is a measurement at 112 min, absorbance = 0.0313.

$$A(t) = A_\infty - (A_\infty - A_o) \exp(-k_T t) \qquad (1.9\text{-}3)$$

is obtained. Rearranging and taking logarithms gives the more commonly used logarithm form:

$$\ln (A_\infty - A(t))/(A_\infty - A_o) = -k_T t \qquad (1.9\text{-}4)$$

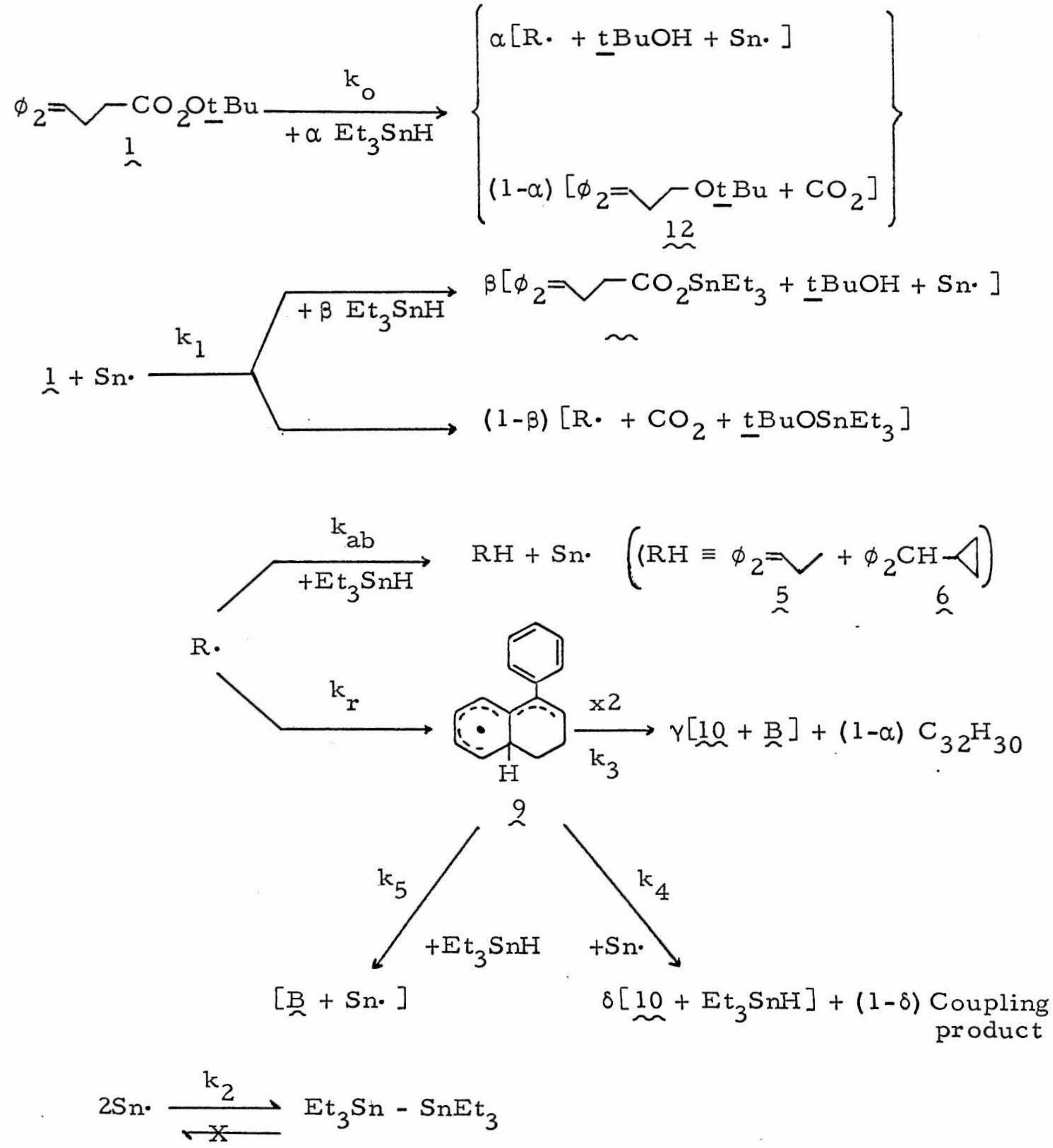
The absorbance data have not been exhibited in logarithmic form, as is usually done, however, because the nature of the experimental errors would make such a treatment highly misleading with the present data. The principal error, that in the absorbance reading, is expected to be fairly constant (and of substantial magnitude) throughout the run. For relatively long times, when A(t) approaches A_∞, the relative error in A_∞ - A(t) can become very large. As a result, a linear plot according to eq. 1.9-4 would have to feature error brackets which increase enormously at long times to keep in perspective the significance of deviations from the line. Under these circumstances, it seems better to plot absorbance vs. time, where deviations from the calculated least-squares lines are expected to be independent of time.

Extraction of rate constants and standard deviations was carried out using the formalism put forth in Section Two. Incidentally, a particular advantage of that formalism is that the results are independent of which form of a relationship (e.g., eq. 1.9-3 or eq. 1.9-4) is used (76).

Examination of Figs. 15-18 indicates a generally satisfactory fit to the lines drawn. The obviously sizable experimental errors in the absorbance measurements arise from the necessity of using extreme conditions (1-mm path length, 90 to 100% transmission range on a Beckman IR-7) in order to investigate initial perester concentrations (about 0.002 M) similar to those which previously had been employed in the product studies. Lack of any significant systematic errors (early points low, later points high, or vice-versa) would seem to confirm the applicability of first-order kinetics.

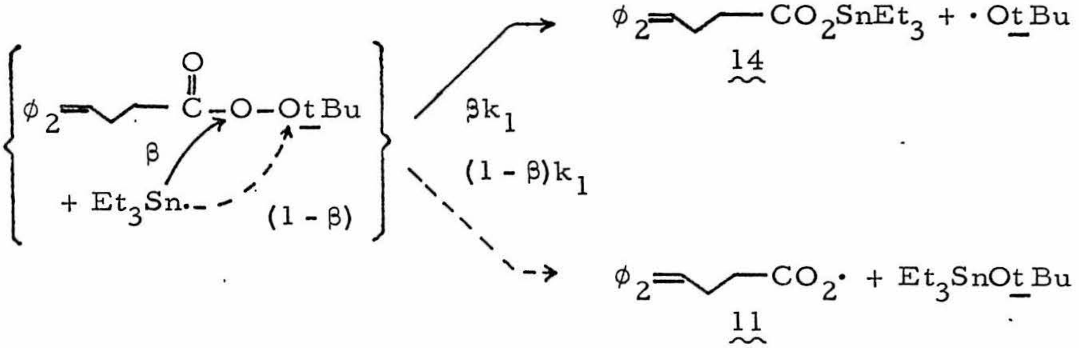
The real evidence that the induced decomposition is essentially first order in perester comes, however, from calculations based on the reaction stoichiometry. In this, the third approach, for calculating the balance between normal homolytic and radical-induced decomposition, we shall derive an expression for (Sn·) for substitution into eq. 1.9-2. As mentioned previously, inefficiency in the replacement of the triethyltin radical consumed in induced decomposition constitutes a mechanism for chain termination. The reaction steps we shall consider are depicted in Chart 5. Brackets which appear in the chart confine products which are produced together in particular reaction steps. The normal perester decomposition produces cage ether and carbon dioxide with an efficiency of $(1 - \alpha) = 0.13$ at 110°, and a pair of radicals with an efficiency of α. (The symbol R· represents both ring-opened and ring-closed radicals in a general sense as explained below.) I have written the species produced along with R· as t-butyl alcohol and a triethyltin radical; under the assumption that the t-butoxy radical invariably and rapidly abstracts hydrogen from triethyltin hydride, that formulation is kineticly equivalent, within the framework of steady-state kinetics, to presenting the t-butoxy radical as a discrete intermediate. The coupling of t-butyl alcohol and triethyltin radical in the

Chart 5. Mechanistic Scheme for Radical-Induced Decomposition of *t*-Butyl (γ, γ-Diphenylallyl) peracetate in Triethyltin Hydride.



following line is similarly motivated. That reaction--actually, it is shown as the upper branch of two--represents radical-induced decomposition involving attack of a triethyltin radical on the carbonyl peroxy oxygen of the ring-opened perester. We shall let β stand for the probability that the radical-induced decomposition takes this pathway. The tin radical might also attack the ether peroxy oxygen, as shown in Chart 6. The probability that induced decomposition will take the latter course is then 1 - β.*

Chart 6. Radical-Induced Decomposition of t-Butyl (γ, γ-Diphenylallyl)-peracetate by Triethyltin Radical.



The formulation depicted in Chart 5 is meant to draw attention to the different mechanistic consequences of the two modes of induced decomposition: in the ester-forming reaction, replacement of the attacking triethyltin radical is virtually guaranteed, whereas, if the tin

---

[*] A third possibility--attack by tin radical on the doubly-bonded carbonyl oxygen itself--can probably be excluded on the basis of the report (77) that the triethyltin radical attacks benzoyl peroxide, to within experimental error, only at peroxy oxygen and not at carbonyl oxygen.

ether* is formed, the probability of replacement of the tin radical depends on a number of factors. The radical R· may abstract hydrogen from the tin hydride, but may undergo ring-cyclization, whence replacement of the tin radical becomes doubtful. Three ways in which ring-cyclized radicals may be consumed are shown in Chart 4. To the right is depicted the reaction of a pair of ring-cyclized radicals to form the dihydronaphthalene 10. The conversion efficiency for this reaction must of necessity be less than or equal to 50% (i. e., $\gamma \leq 1$). Next we have transfer of a hydrogen atom from a ring-cyclized radical to a triethyltin radical or coupling of the two radicals. Finally, hydrogen abstraction by ring-cyclized radical from the tin hydride is the only one of the three <u>conversion reactions</u> which enables the chain to be propagated. Not considered is the possibility of reversal of the ring-cyclization. Its inclusion would greatly complicate the kinetic analysis. Fortunately, the evidence that little or no decyclization occurs in 1,4-cyclohexadiene, even at 0.001 M ring-opened perester (pp. 114, 115, 287-290) justifies its neglect here. Significant hydrogen abstraction by ring-cyclized radicals from solvent was not observed in

---

*Direct evidence for formation of t-butoxytriethyltin has neither been obtained nor seriously pursued. However, formation of tin ester in yields of only about 50% where other evidence (see Table 15) points to nearly exclusive radical-induced decomposition leaves little room for doubt as to the existence of two modes for the induced decomposition. Kuivila cites a personal communication from Sawyer to the effect that trialkylalkoxytin compounds react with excess tin hydride to yield the alcohol plus the hexaalkylditin (80). Thus, the tin ether may well not survive the reaction. This would be of interest for our purposes only if reaction of the tin ether with the tin hydride were to involve free-radical intermediates; and this is not known, although it is Kuivila's guess that free-radical intermediates are not involved (81).

1,4-cyclohexadiene (it would have lead to symptoms of the same type expected for decyclization), but as triethyltin hydride has been shown to be a much more active hydrogen donor than 1,4-cyclohexadiene (p. 132), the possibility can not be excluded here.

We can now give a kinetic treatment which will serve to illustrate several main features. This treatment will leave open the precise connection between a certain probability function g and the rate constants for reactions of ring-cyclized radicals; that connection will be developed in Appendix A and simply referenced here. The reason for the adoption of this seemingly round-about procedure is that giving the complete analysis here would be less instructive and would seriously risk hopelessly entangling the discussion in mere algebraic manipulation.

From eqs. 1.9-1 and 1.9-2, we see that prediction of the fraction of induced decomposition requires the development of an expression for $k_1(\text{Sn}\cdot)/k_o$. We proceed by writing down (in somewhat novel form) the rate law for (Sn·):

$$d(\text{Sn}\cdot)/dt = \alpha k_o(P)f + \alpha k_o(P) - k_1(\text{Sn}\cdot)(P) + \beta k_1(\text{Sn}\cdot)(P) + (1-\beta)k_1(\text{Sn}\cdot)(P)f - 2k_2(\text{Sn}\cdot)^2 \quad (1.9\text{-}5)$$

The function f which appears in the above is defined to be the probability that a tin radical will be generated as a radical R· is rapidly converted to product; if ring-cyclization did not occur, and R· invariably abstracted hydrogen from triethyltin hydride, f would be 1.*

---

*Perhaps the term 'probability' is inappropriate, for the range of f is not 0 to 1, but -1 to 1: if all radicals R· ring-cyclize and are subsequently converted to product by <u>consuming</u> a triethyltin radical, f would be -1.

Thus, the first term on the right-hand side represents the rate of formation of tin radicals, through the intermediacy of R·, due to normal decomposition of the perester. The second term describes the formation of the tin radical shown in the top line of Chart 5. The third term describes the consumption of tin radicals in the induced decomposition. The fourth indicates the 'immediate' replacement of a tin radical for that fraction, β, of the induced decompositions which give tin ester. The fifth is motivated similarly to the first: it describes the rate at which tin radicals are generated via induced decomposition giving tin ether and a hydrocarbon radical. The last term describes pairwise destruction of tin radicals.

The usual procedure, invoking the steady-state approximation $d(Sn\cdot)/dt = 0$, will allow us to solve for the Sn· concentration. Before doing so, it is interesting to note what would happen if f were equal to 1: the second, third, and fourth terms would add out, giving

$$(Sn\cdot) = [\alpha k_o(P)/k_2]^{\frac{1}{2}} \quad . \qquad (1.9\text{-}6)$$

Then, according to eq. 1.9-1, the induced decomposition would be 3/2 order in perester. However, because f must be less than 1 to account for formation of the dihydronaphthalene **10**, the three terms can not add out, but when summed are--like the last term--negative. This provides an alternative mechanism for chain termination. Thus, reaction of pairs of triethytin radicals can be negligible even though there be no cosmological prohibition against such reaction.

Termination by coupling of triethyltin radicals should be more important the closer f is unity, which means the higher is the triethyltin hydride concentration. For a 3/2 order induced decomposition under conditions where little normal decomposition occurs, the rate 'constant' k_T would then go as the square root of the perester concentration. The first-order kinetic analyses described earlier gave $k_T = 0.127\ \text{min}^{-1}$ for 0.002 M perester in 0.4 M tin hydride at 110° (see Fig. 17). If the induced decomposition were really 3/2 order, data for the same hydride concentration and reaction temperature, but for 0.02 M perester also erroneously treated by first-order kinetics would give an apparent k_T about $\sqrt{10} \cong 3$ times larger. This particular experiment was not carried out, but we do have one for 0.02 M perester and 0.67 M hydride (see Fig. 18). Because the higher tin hydride concentration should lead to more efficient chain propagation (if it had any effect), the 'first-order' rate constant for that run would be more than three times that for the run of Fig. 17 if induced decomposition were 3/2 order. Instead, the value found, $0.138\ \text{min}^{-1}$, is only about 10% greater. It is in larger part this comparison which disallows significant pairwise reaction of tin radicals for any reaction conditions considered. Thus, the k_2 reaction may be dropped from the reaction scheme. Incidentally, neglect of the back reaction (see Chart 5) is based on experimental evidence which demonstrates that hexaalkylditins do not dissociate at temperatures under 200° (78).

Setting $d(\text{Sn}\cdot)/dt = 0$ after dropping the last term in eq. 1.9-5 gives the expression we have been seeking:

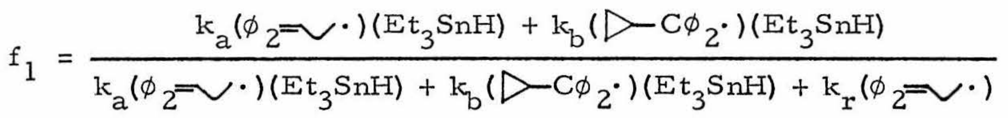
$$\frac{k_1(\text{Sn}\cdot)}{k_o} = \frac{\alpha}{(1-\beta)}\,\frac{(1+f)}{(1-f)} \quad . \tag{1.9-7}$$

The probability function f can be expressed as the sum of two probabilities:

$$f = f_1 + (1 - f_1)g \quad . \tag{1.9-8}$$

The symbol f_1 in eq. 1.9-8 denotes the probability that R· abstracts hydrogen from triethyltin hydride. Therefore, $1 - f_1$ is the probability that ring-cyclization occurs. Finally, g stands for the probability that conversion of a ring-cyclized radical 9 to product will occur so as to *generate* a triethyltin radical. Of course, conversion of 9 to product might also *consume* a tin radical; if this were invariably to happen, we would have $g = -1$.

By the definitions given above, f_1 is simply the rate of formation of ring-opened plus ring-closed hydrocarbon divided by the sum of those rates plus the rate at which ring-cyclization proceeds. Using rate constants previously defined (pp. 92, 110),



(1.9-9)

Because the ring-opened and ring-closed radicals rapidly equilibrate at temperatures employed for decomposition of the ring-opened perester (subsection 7, pp. 90-97), the concentration of ring-closed radical can be replaced by that of the ring-opened radical times the equilibrium constant k_1/k_2. This allows the cancellation of the radical concentrations in eq. 1.9-9. With the definition

$$k_{ab} = k_a + (k_1/k_2)k_b = k_a(1 + k_1k_b/k_ak_2) \quad , \tag{1.9-10}$$

eq. 1.9-9 can be rewritten as

$$f_1 = k_{ab}(Et_3SnH)/(k_{ab}(Et_3SnH) + k_r) \quad .$$

The ratio k_1k_b/k_ak_2 will be recognized (p. 93) as defining the characteristic ratio for hydrogen abstraction from triethyltin hydride. Its value is about 0.07 at 110 or 125°. Thus, $k_{ab} = 1.07\ k_a$, and (no longer suppressing the superscript SnH on k_a) we have

$$f_1 = 1.07(k_a^{SnH}/k_r)(Et_3SnH)/\left[1.07(k_a^{SnH}/k_r)(Et_3SnH) + 1\right] \quad (1.9\text{-}11)$$

It should be clear from subsection 8 that any uncertainty in the factor of 1.07 will be dwarfed by that in k_a^{SnH}/k_r.

Substituting eq. 1.9-11 into eq. 1.9-8 and substituting the result into eq. 1.9-3 gives eq. 1.9-12.

$$\frac{k_T}{k_o} = 1 + \frac{k_1(Sn\cdot)}{k_o}$$

$$= 1 + \frac{\alpha}{1-\beta}\left\{\left(\frac{2}{1-g}\right)(1.07\ k_a^{SnH}/k_r)(Et_3SnH) + \frac{1+g}{1-g}\right\} \quad . \quad (1.9\text{-}12)$$

The percent of normal decomposition (% n) is simply given by 100 times the reciprocal of eq. 1.9-12.

Because the function g is undefined except in a general sense, eq. 1.9-12 is only of limited usefulness. Nonetheless, certain limiting cases can be treated. As noted above, we could force g to be +1 under all reaction conditions studied by selecting a sufficiently large value for k_5 (see Chart 5). However, the fact that dihydronaphthalene is always observed means that g must always be less than 1. This is just as well, for eq. 1.9-12 is singular for g = 1. This result of course arises from our earlier neglect of the pairwise reaction of triethyltin radicals, the alternative mechanism for chain termination.

An interesting special case is g = 0; this can be arranged by agreeing to let ring-cyclized radicals react only with each other. Indeed, this was the basis on which the expression for k_r/k_a^{SnH} (eq. 1.8-11) was evaluated. Setting g = 0 in eq. 1.9-12, and using eq. 1.8-11, gives

$$\%\ n = 100\left[1 + \frac{\alpha}{1-\beta}\left\{0.028\ \exp(4.3/RT)(Et_3SnH) + 1\right\}\right]^{-1}. \quad (1.9\text{-}13)$$

Provided that α and β can be evaluated, eq. 1.9-13 is nice, clean, and readily testable. The parameter α is simply (1 - the cage efficiency), or 0.87 at 110° and 0.88 at 125°. β is the fraction of induced decompositions yielding the tin ester; its value is somewhat uncertain, but is clearly close to 0.5, as can be seen from yields of tin ester reported in Table 10. One puzzling fact must be admitted here: since the percent of induced decomposition increases with increasing tin hydride concentration, one would expect the yield of the tin ester to be greater at the higher tin hydride concentrations. However, the trend in Table 10 is, if anything, in the opposite direction. Perhaps this is partly due to experimental error of the same sort which lead to relatively large standard deviations in the rate constants for the kinetic measurements at 110° (from which the yields of tin ester were also calculated). The value $\beta = 0.55$ (which blames deviations about equally on all the experimental determinations) will be used.

Calculation 1 of Table 15 lists values of % n given by eq. 1.9-13.[*]

The special case g = -1 can be arranged by postulating a sufficiently high value for the rate constant for reaction of a ring-cyclized radical with a triethyltin radical. Equation 1.9-12 then leads to

$$\% n = 100 \left[1 + \frac{\alpha}{1-\beta} \left\{ 1.07\, k_a^{SnH} (Et_3SnH)/k_r \right\} \right]^{-1} . \qquad (1.9\text{-}14)$$

For this case, the conversion of ring-cyclized radicals to the dihydronaphthalene could be much more efficient than was previously assumed in deriving eq. 1.8-11 for k_r/k_a^{SnH}. We can put the efficiency at 100%[**] by dividing eq. 1.8-11 by a factor of 0.325 = 0.5 γ. Then eq. 1.9-14 becomes

$$\% n = 100 \left[1 + \frac{\alpha}{1-\beta} \left\{ 0.086 \exp(+4.3/RT)(Et_3SnH) \right\} \right]^{-1} . \qquad (1.9\text{-}15)$$

---

[*] Actually, values of k_a^{SnH}/k_r employed at 110 and 125° were chosen in all calculations listed in Table 15 to exactly reproduce the reduced ratios R (see eq. 1.9-19) obtained experimentally in the 0.011 M triethyltin hydride run at each temperature. If the two central points in Fig. 12 (p. 137) lay precisely on the best fit line, these values would be identical to those contained in eqs. 1.9-13 and 1.9-15.

Error limits in the 10 calculations listed in Table 15 were calculated according to eq. 2.2-19(p. 218) assuming the following standard errors in the various parameters: 0.02 for α; 0.03 for β; and 20% of value for k_a^{SnH}/k_r. The latter uncertainty arises from that in the assumed conversion efficiency as well as experimental uncertainty in the values of the reduced ratio R to which values of k_a^{SnH}/k_r have been fit.

[**] This corresponds to putting δ (Chart 5) = 1.0 and assuming that ring-cyclized radicals react solely with triethyltin radicals.

Values calculated from eq. 1.9-15 are given as Calculation 2 of Table 15.

We can now examine the agreement of the $g = 0$ and $g = -1$ mechanistic treatments with predictions from yields of the cage ether $\underset{\sim}{12}$ and reaction rates recorded in columns five and six of Table 15. With the exception of the 110° run at 0.002 M perester and 0.4 M tin hydride, the $g = 0$ predictions agree rather well with those from ether yields and reaction rates. The similar amounts of normal decomposition at 0.01 and 0.04 M tin hydride indicated both by the ether yield and reaction-rate criteria arises naturally for $g = 0$: if induced decomposition leads to ring-cyclization, that chain, but only that chain, is stopped; for $g = -1$, however, the same circumstance leads to interdiction of two chains. As a result, for perester concentrations as high as those employed (i.e., where pairwise destruction of triethyltin radicals is insignificant), % n goes to 100 at zero tin hydride concentration for $g = -1$, but for $g = 0$ must stay below about $100[1+\alpha/(1-\beta)]^{-1} = 35$ (compare eqs. 1.9-13 and 1.9-15).

The unsatisfactory fit using $g = -1$ can not be repaired by choosing a conversion efficiency of less than 100% for evaluation of k_a^{SnH}/k_r; if this were done, the value of k_a^{SnH}/k_r would be smaller and, according to eq. 1.9-14, the values of % n would be found to lie consistently above than those of Calculation 2.

Both treatments assume a constant conversion efficiency for formation of the dihydronaphthalene $\underset{\sim}{10}$. As such, they fail to account for the drift in the reduced ratios R (calculated from eq. 1.8-5, p. 111) listed in the right-most column of Table 10 and reproduced here as

Table 15. Radical-Induced Decomposition of t-Butyl (γ, γ-Diphenylallyl)peracetate in the Presence of Triethyltin Hydride. Correlation of Percent Normal Decomposition (% n) and Reduced Ratios (R) (From Eq. 1.8-5) Predicted in Various Ways.

Temp. °C	Initial Perester Conc. M	$[\mathrm{Et_3SnH}]_o$ M	R	From Ether Yields % n	From Reaction Rates % n	From Mechanistic Treatment			
						% n	R	% n	R
110	0.002	0.010	0.051	25.4 ± 2.4	35.4 ± 7.7	31.3 ± 1.6	0.051	71.1 ± 4.4	0.051
	0.002	0.044	--	--	30.3 ± 3.9	24.4 ± 1.9	--	35.9 ± 4.9	--
	0.002	0.41	--	--	3.6 ± 0.8	7.3 ± 1.2	--	5.7 ± 1.1	--
	0.02	0.67	--	--	3.3 ± 0.6	4.9 ± 0.9	--	3.6 ± 0.7	--
125	0.002	0.010	0.065	32.5 ± 3.2	--	31.6 ± 1.6	0.063	75.8 ± 3.9	0.063
	0.002	0.044	0.059	33.3 ± 7.2	--	25.9 ± 1.8	0.063	41.8 ± 5.2	0.063
	0.002	0.014	0.059	16.6 ± 3.6	--	16.9 ± 2.0	0.063	17.9 ± 3.1	0.063
	0.002	0.39	0.050	5.8 ± 1.9	--	8.8 ± 1.4	0.063	7.2 ± 1.4	0.063
	0.002	0.94	0.043	≤ 3.0	--	4.3 ± 0.8	0.063	3.1 ± 0.6	0.063

Calculation No.		1	2
(k_a^{SnH}/k_r)	110°	6.37	19.60
	125°	5.16	15.87
A(110°)		0.0	∞
B(110°)		0.0	--
γ		0.65	--
δ		--	1.0

Table 15 (Cont.)

	From Mechanistic Treatment							
	% n	R	% n	R	% n	R	% n	R
	30.9 ± 1.2	0.051	30.6 ± 1.2	0.051	33.8 ± 1.4	0.051	34.2 ± 1.4	0.051
	23.3 ± 1.2	--	22.2 ± 1.1	--	26.4 ± 1.5	--	27.3 ± 1.5	--
	5.2 ± 0.5	--	4.1 ± 0.4	--	8.6 ± 1.0	--	9.4 ± 1.0	--
	4.0 ± 0.4	--	3.5 ± 0.4	--	5.2 ± 0.7	--	5.8 ± 0.7	--
	31.3 ± 1.3	0.063	31.1 ± 1.2	0.063	35.0 ± 1.3	0.063	35.3 ± 1.3	0.063
	25.0 ± 1.2	0.061	24.1 ± 1.1	0.060	28.6 ± 1.4	0.067	29.6 ± 1.4	0.063
	15.1 ± 1.0	0.057	13.7 ± 0.9	0.053	18.9 ± 1.4	0.075	20.3 ± 1.4	0.063
	6.8 ± 0.6	0.049	5.6 ± 0.5	0.041	10.5 ± 1.1	0.089	11.6 ± 1.2	0.063
	2.6 ± 0.3	0.038	1.9 ± 0.2	0.028	5.6 ± 0.7	0.106	6.3 ± 0.8	0.063
Calculation No.	3		4		5		6	
$(k_a^{SnH}/k_r$ 110°	6.32		6.27		7.21		6.37	
125°	5.13		5.10		6.02		5.16	
A(110°)	0.0		0.0		0.01		0.01	
B(110°)	0.05		0.10		0.0		0.0	
γ	0.65		0.65		0.65		0.65	
δ	--		--		1.0		0.325	

Table 15 (Cont.)

	From Mechanistic Treatment							
	% n	R	% n	R	% n	R	% n	R
	34.2 ± 1.4	0.051	31.6 ± 1.2	0.051	32.7 ± 1.2	0.051	37.8 ± 1.2	0.051
	27.4 ± 1.5	--	23.0 ± 1.2	--	23.1 ± 1.2	--	26.1 ± 1.5	--
	9.5 ± 1.0	--	4.6 ± 0.5	--	4.2 ± 0.5	--	4.2 ± 0.5	--
	5.8 ± 0.7	--	3.6 ± 0.4	--	3.4 ± 0.4	--	3.4 ± 0.5	--
	35.3 ± 1.3	0.063	32.5 ± 1.2	0.063	34.1 ± 1.2	0.063	40.2 ± 1.2	0.063
	29.7 ± 1.4	0.063	25.3 ± 1.2	0.062	25.8 ± 1.2	0.062	30.2 ± 1.6	0.068
	20.5 ± 1.4	0.062	14.6 ± 1.1	0.059	14.4 ± 1.1	0.060	16.0 ± 1.5	0.068
	11.8 ± 1.2	0.060	6.2 ± 0.6	0.052	5.9 ± 0.6	0.053	6.0 ± 0.7	0.057
	6.4 ± 0.8	0.058	2.3 ± 0.3	0.042	2.1 ± 0.3	0.041	2.0 ± 0.3	0.042
Calculation No.	7		8		9		10	
$(k_a^{SnH}/k_r$ 110°	6.28		6.60		7.05		8.98	
125°	5.06		5.46		5.92		7.63	
A(110°)	0.01		0.003		0.01		0.01	
B(110°)	0.0		0.10		0.15		0.23	
γ	0.65		0.65		0.65		0.65	
δ	0.25		1.0		1.0		1.0	

column 4 of Table 15. Thus, we need to employ the full mechanistic treatment to handle situations close to $g = 0$, but with some role played by the k_4 and k_5 reactions shown in Chart 5. The definition of g developed in Appendix A is

$$g = \frac{X + B(Et_3SnH)\sqrt{X/(1)} - \underset{\wedge}{1}}{X + B(Et_3SnH)\sqrt{X/(1)} + \underset{\wedge}{1}} , \qquad (1.9\text{-}16)$$

where $A = (k_4/k_1)(\alpha k_o/k_3)^{\frac{1}{2}}$, $B = k_5/(\alpha k_o k_3)^{\frac{1}{2}}$, and X is a (positive, real) root* of the nonlinear equation

$$X\left[1 + \frac{1.07(k_a^{SnH}/k_r)(Et_3SnH)}{(1-\beta)} A\sqrt{X/(\underset{\wedge}{1})}\left\{1 + \frac{B(Et_3SnH)}{\sqrt{X(\underset{\wedge}{1})}}\right\}\right] + \frac{1.07(k_a^{SnH}/k_r)(Et_3SnH)}{(1-\beta)} A\sqrt{X/(\underset{\wedge}{1})} = 1 \qquad (1.9\text{-}17)$$

The limiting cases discussed above can be seen rather easily. The case of $g = 0$ implies small k_4 and/or large k_1 (i.e., $A = 0$) and small k_5 (i.e., $B = 0$); with these choices, eq. 1.9-17 gives $X = 1$, whence eq. 1.9-16 gives $g = 0$, as expected. The case $g = -1$ requires large k_4 (i.e., A very large);** that choice forces X to approach 0, and eq. 1.9-16 gives $g = -1$.

---

[*] When cleared of radicals, eq. 1.9-17 is found to be cubic in X, and thus has three roots. While I have been unable to show that only one of the roots will be real and positive, for all cases investigated that has been the case. Since eq. 1.9-17 is physically motivated, there should be no more ambiguity as to which root is to be taken than occurs for situations in which quadratic equations are involved.

[**] In practice, this works out to $A \geq 1$.

It is convenient to substitute the general expression for g into eq. 1.9-17 rather than first to explicitly work out numerical values for g for each situation of interest. The resulting expression (which is derived by conventional means in the Appendix, thus confirming the correctness of the treatment given here) is

$$\begin{aligned} \%\,n = 100\Big[1 + \frac{\alpha}{1-\beta}\Big\{&1.07(k_a^{SnH}/k_r)(Et_3SnH) \\ &\times\left[1 + X + B(Et_3SnH)\sqrt{X/(\mathbf{1})}\right] \\ &+ X + B(Et_3SnH)\sqrt{X/(\mathbf{1})}\Big\}\Big]^{-1} . \end{aligned} \tag{1.9-18}$$

Finally, the equation for the reduced ratio R is found to be

$$\begin{aligned} R &\equiv \frac{(\text{Yield of } \mathbf{10})\,(Et_3SnH)_{av}}{(\text{Yield of } \mathbf{5})} \\ &= \left(\frac{k_r}{k_a^{SnH}}\right)\left[\frac{\gamma X + \delta(1-X)}{1 + X + B(Et_3SnH)\sqrt{X/(\mathbf{1})}}\right] . \end{aligned} \tag{1.9-19}$$

where the term in square brackets expresses the efficiency of the conversion of ring-cyclized radicals to dihydronaphthalene. For the two cases $g = 0$ and $g = -1$, the conversion efficiencies are simply $\gamma/2$ and δ, respectively.

Because the concentration of ring-opened perester **1** appears in eqs. 1.9-16–1.9-19, it is clear that the previous claim--that the induced decomposition is first-order in the perester concentration--is not strictly correct. However, the perester concentration comes in only implicitly; not at all for the combinations $A = 0$, $B = 0$, and A large, B = 0; and only weakly for many intermediate cases.[*]

The fact that the perester concentration can have some effect, however, will enable us to repair the greatest single discrepancy between the g = 0 predictions and those from ether yields or reaction rates--the high calculated value of % n for the 110° run at 0.4 M tin hydride and 0.002 M perester. If A equals zero, then X simply is unity, and the effect of finite B can clearly be seen from eq. 1.9-18: % n will decrease more rapidly with increasing tin hydride concentration than is the case for g = 0. Thus, agreement for the 0.4 M run can be improved. Note, however, that g = 0 gives a % n at 0.67 M hydride and 0.02 M perester only slightly greater than that deduced from the reaction rate. If, then, a particular value of B were to decrease the predicted % n to the same degree for both the higher hydride concentration runs at 110°, we would have accomplished little more than a sharing of the blame. However, eq. 1.9-18 shows that the new effect is less pronounced at higher perester concentrations, and the already acceptable agreement for the run at 0.02 M initial perester concentration might not be sacrificed.

Calculations 3 and 4 were carried out for values of B (at 110°)[**] of 0.05 and 0.10, respectively. The drift in the values of R is in the

---

[*] In these calculations, eq. 1.9-18 has been numerically integrated over the course of the reaction using the three point Gaussian quadrature formula (94). The only moderate variation of the three instantaneous % n values for all calculations carried out confirms the adequacy of the three point integration formula.

[**] The value of B at 125° has been taken in all calculations to be that employed at 110° divided by a factor of 1.3. Justification of this procedure will be given shortly.

proper direction, though of too large a magnitude for the larger value of B. At the same time, the agreement of calculated and "observed" values of % n is distinctly improved for the two highest tin hydride concentrations at 110° and also for the 0.94 M tin hydride run at 125°.

Calculations 5, 6, and 7 explore the consequences of allowing A to be slightly greater than zero.* This corresponds to allowing some ring-cyclized radicals to react with triethyltin radicals. The effect on the conversion efficiency, and thus on the calculated values of the reduced ratio R, depends on whether δ is taken to be greater than, equal to, or less than $\frac{1}{2}\gamma$ ($\gamma = 0.65$ in all calculations). In Calculation 5 we have assumed that all reactions of ring-cyclized radicals with tin radicals give rise to the disproportionation products, the dihydronaphthalene 10 and triethyltin hydride (i.e., $\delta = 1$). All predicted % n values are found to be larger than the g = 0 values, with by far the greatest proportionate rise at the higher triethyltin hydride concentrations.**

---

*The value of A (110°) employed here is 0.01. In these and other calculations, the value of A employed at 125° has been taken to be 1.5 times the value given in Table 15 for 110°. The justification for this procedure will be given shortly.

**Calculations 5-7 for small A may at first glance seem inconsistent with results for large A (g = -1) obtained in Calculation 2. The connection between Calculations 2 and 5 comes about as follows. As A is increased, g moves from zero toward -1. However, the progression is not uniform, but rather is substantially more advanced at high tin hydride concentration. For example, for 0.94 M tin hydride at 125°, g = -0.5 in Calculation 5, but is scarcely different from zero for the 0.01 M runs. The result is that the values of k_a^{SnH}/k_r which give the desired values of R for the 0.01 M tin hydride runs are substantially the same as those calculated for g = 0. As A continues to be increased, eventually all values of g become substantially negative, and k_a^{SnH}/k_r rises abruptly. The result is to bring together again the values of R at high and low triethyltin hydride concentration and to greatly reduce the calculated values of % n at high tin hydride concentration.

Moreover, the predicted dependence of R on tin hydride concentration is opposite to that observed experimentally. For $\delta = \frac{1}{2}\gamma$ (Calculation 6), the values of R are independent of the tin hydride concentration, but the rise compared to g = 0 in the calculated values of % n is stronger than for $\delta = 1.0$. The trend continues; for $\delta = 0.25$ (Calculation 7), the quantities R show qualitatively the correct behavior, but the agreement between the calculated and "observed" % n values has further decayed. Clearly, there is no future, in seeking a good fit to the data, in continuing this particular line of exploration.

Comparison of Calculations 4 and 5 with Calculation 1 shows that the effects of increasing A and of increasing B on %n and on R are of opposing natures for $\delta > \frac{1}{2}\gamma$. This suggests that it may be possible to increase both A and B concurrently to a far greater extent than is possible singly. Calculations 8, 9, and 10 explore the consequences of this line of reasoning. For B = 0.10, A need only be increased to 0.003 to repair the excessive drift in R with triethyltin hydride concentration reported in Calculation 4. Calculation 9 extends this matching of opposite tendencies to B = 0.15, A = 0.01. The results are gratifying: the drift in R is just right, the % n values for the two higher tin hydride concentration runs at 110° have been moved together as observed experimentally, and the calculated % n for the 0.94 M tin hydride run at 125° remains under the limit set by the yield of the ether 12. However, the vein is soon exhausted; for A = 0.10, and B = 0.23, the overall drift in R is satisfactory, but the values are now incorrectly predicted to increase with increasing tin hydride concentration before finally turning strongly downward.

On balance, Calculation 9 yields the best agreement between calculated and "observed" values of % n. Certain features--the abrupt drop in the yields of the ether **12** with increasing tin hydride concentration and the similar rate constants obtained in the runs featured in Figs. 17 and 18--are well explained. The improvement over the limiting results for $g = 0$ is substantial. However, it is doubtful that we can take the values of A and B employed in this calculation to have been reliably established. In point of fact, the pairings of initial perester and initial tin hydride which happened to be chanced upon in this work exert insufficient leverage to permit reliable extraction of values for these parameters.

We can, however, tentatively assume that the values of A and B employed in Calculation 9 are reasonable ones and proceed to explore the consequences of this assumption. For each of these two parameters, estimates for all but one of the constituent rate constants can be made with some degree of confidence. This allows approximate values to be derived for the single rate constant in each (k_1 for A and k_5 for B) which is least subject to prediction. Still, it is possible to make a judgement on whether the derived values of k_1 and k_5 are physically realistic. If either is judged to be unrealistic, we would conclude that use has been made of a certain flexibility in our equations, but that no underlying mechanistic significance is to be inferred. On the other hand, an additional measure of confidence in the correctness of the mechanistic treatment would be in order should those estimates prove to be reasonable ones.

In the definition $B = k_5/(\alpha k_o k_3)^{\frac{1}{2}}$, the value of k_o has been found by Howden (21) to be 7.7×10^{-5} M^{-1} sec^{-1} at 110°. The value of the parameter α is about 0.87. The value of the rate constant k_3 for pairwise reaction of ring-cyclized radicals is unknown, but a guess can be formulated from radical-radical termination rate constants reported in the literature. Rate constants quoted by Walling (79) for chain termination in free-radical polymerizations are generally on the order of 10^7 M^{-1} sec^{-1}, although the value listed for vinyl chloride polymerization is 10^{10} M^{-1} sec^{-1}. For small molecule terminations, however, Walling has inferred a value of $\sim 10^9$ for coupling of *t*-butoxy radicals (82), and preliminary determinations by Weiner (83) for bimolecular reaction of *t*-butoxy radicals, of α-cyanoisopropyl radicals, and of α-cyanocyclohexyl radicals are all $\sim 3 \times 10^9$ M^{-1} sec^{-1}. We shall adopt a value of 10^8 M^{-1} sec^{-1} for k_3. We therefore find for $B = 0.15$ that $k_5 = 13$ M^{-1} sec^{-1} at 110°. Eq. 1.8-12 shows that preexponential factors for hydrogen abstraction by ring-opened radical **3** from 1,4-cyclohexadiene and from triethyltin hydride are nearly the same. This justifies taking the preexponential factor in k_5 to be 10^8, which value is typical for hydrogen abstraction from hydrocarbons. Then the derived value of k_5 at 110° implies an activation energy of approximately 12 kcal/mole.

The question now becomes: is this a reasonable value for the activation energy? Although little is known about activation energies for hydrogen abstraction from organotin hydrides, the following argument can be offered. When all is said and done, our estimate for the activation energy for hydrogen abstraction by the ring-closed radical **4** from triethyltin hydride will be approximately 8 kcal/mole (p. 349). By analogy with reported C–H bond dissociation energies of 72 kcal/mole for diphenylmethane and 75 kcal/mole and triphenylmethane (51), the bond dissociation energy for the dibenzylic C–H bond in the ring-closed hydrocarbon 6 can be estimated to lie in the lower or middle seventies. The Sn–H bond dissociation energy in trialkyltin hydrides is not known, but chemical experience is capable of yielding some information. In his 1963 review article, Kuivila suggests a value of approximately 70 kcal/mole for organotin hydrides (41). The C–H bond dissociation energy of the methylene hydrogens in 1,4-cyclohexadiene is reported to be 70 kcal/mole (52). That for the bond formed on converting the ring-cyclized radical 9 to the dihydronaphthalene 10 is expected to be a few kcal/mole less than this value by virtue of the more extensive delocalization in 9 as compared to the cyclohexadienyl radical; perhaps 67 kcal/mole is a reasonable estimate.

Thus we see that abstraction of hydrogen from a given donor by 9 is expected to be less exothermic by approximately 5–10 kcal/mole than is hydrogen abstraction by 4. For hydrocarbon donors, a good correlation exists between the activation energy and the heat of reaction for hydrogen abstraction by alkyl free radicals. For the degenerate (and thus thermoneutral) exchange reaction

$$CH_3\cdot + CH_4 \longrightarrow CH_4 + CH_3\cdot$$

the activation energy is 14 kcal/mole (95), but drops to 9 kcal/mole for abstraction of the tertiary hydrogen of isobutane by methyl radical; the latter reaction is exothermic by approximately 12 kcal/mole (34).

Similar relationships hold for a wide variety of radical-abstraction reactions (53), and such a relationship likely holds for hydrogen abstraction from triethyltin hydride as well. If so, the increased exothermicity for hydrogen abstraction by **4** over that for **9** is expected to confer on the former process a lower activation energy for hydrogen abstraction from the tin hydride; precisely this behavior is reflected in the independently obtained estimates of 8 and 12 kcal/mole, respectively. Not only is the order of the activation energy estimates correct, but the magnitude of their difference is also reasonable. Finally, the difference of about 5 kcal/mole in the activation energies for hydrogen abstraction by **4** from 1,4-cyclohexadiene and from triethyltin hydride (see Fig. 13) is consistent with a Sn–H bond dissociation energy smaller than the 70 kcal/mole C–H bond dissociation energy of 1,4-cyclohexadiene, perhaps on the order of 65 kcal/mole. Thus, hydrogen abstraction by **9** is expected to be very nearly thermoneutral, and in this light even the absolute value of 12 kcal/mole estimated for the activation energy of that reaction seems reasonable.

Of the points argued above, the suggested Sn–H bond dissociation energy of 65 kcal/mole rests on the weakest ground, for the tacit assumption that a tin hydride will behave in hydrogen donation like a hydrocarbon donor of equivalent C–H bond dissociation energy is unproven. In many other respects, tin and carbon differ greatly. Specifically, the greater polarizability of the large tin atom may reduce the activation energy characteristic of a thermoneutral abstraction reaction. If this is the case, the activation-energy relationships considered above could be rationalized on the basis of an Sn–H bond dissociation energy of 70 or even 75 kcal/mole. Conversely, if that quantity were found to be approximately 65 kcal/mole, the assumption of the similarity of carbon and tin in hydrogen abstraction would be supported.

The temperature dependence of B employed in the calculations was derived as follows. The activation energy for B is simply the activation energy of k_5 less one-half the sum of the activation energies of k_o and k_3. By analogy with activation parameters for perester decomposition given in Table 13, that for the normal decomposition of the ring-opened perester is expected to be about 34 kcal/mole. Activation energies for rapid radical-radical reactions tend to run about 2 kcal/mole (96). The origin of this token value is presumably the more rapid diffusion of particles at the lower solution viscosities which are associated with higher reaction temperatures. Thus, the predicted composite activation energy for B is -6 kcal/mole, and the value of B at 125° is that at 110° divided by 1.3.

The rate constants k_o and k_3 also appear in $A = (k_4/k_1)(\alpha k_o/k_3)^{\frac{1}{2}}$, where the rate constant for bimolecular reaction (disproportionation or coupling) of $\underset{\sim}{9}$ with a triethyltin radical is denoted by k_4, and that for attack of tin radical on the perester is denoted by k_1. If we take k_o and k_3 as before and arbitrarily set $k_4 = k_3$, we find that $A = 0.010$ implies $k_1 = 10^4\ M^{-1}\ sec^{-1}$ at 110°. As k_1 is an abstraction reaction, we will perhaps not be too seriously in error if we assign as its pre-exponential factor a value of 10^8 motivated by experience with hydrogen atom abstraction reactions. The associated activation energy is easily found to be 7 kcal/mole.* This already is an encouraging result: if the value found for A were of no mechanistic significance, a physically impossible estimate of the activation energy for k_1, such as a negative value, might have resulted. The activation energy of 7 kcal/mole and the rather large value estimated for k_1 seem respectable, however, when we recall that triethyltin radicals are in fact diverted to attack on perester, whereas hydrocarbon radicals (such as cyclohexadienyl radical) enjoy the more leisurely hunting up of a secone free radical for the purpose of mutual annihilation.

The explanation for the divergent behavior of tin and hydrocarbon radicals is apparently to be found in a consideration of bond dissociation energies. If we consider that the choice faced by either type of radical is between formation of a bond to hydrogen (disproportionation with $\underset{\sim}{9}$) or a bond to oxygen, the following comparison is relevant. The C–H bond dissociation energy in methane is 102 kcal/mole, whereas the C–O bond dissociation energy in methanol is given by Cottrell as approximately 90 kcal/mole (97). Thus, for alkyl radicals formation of a C–O bond is less exothermic than formation of a C–H bond by about 12 kcal/mole. This order is reversed for tin radicals; the dissociation energy of the Sn–O bond of trimethyltin

---

*This value leads to a composite activation energy of 9 kcal/mole for A. In Calculations 5–10 of Table 15 the value of A at 125° has been taken to be that at 110° times 1.6, where the factor of 1.6 arises from the 9 kcal/mole composite activation energy.

benzoate is roughly 115–120 kcal/mole,* whereas the Sn–H bond dissociation energy, according to our previous discussion, is only about 65 kcal/mole. Thus we see that formation of a Sn–O bond is approximately 50 kcal/mole *more* exothermic than formation of a Sn–H bond, and the difference between tin and carbon in this respect is fully 60 kcal/mole.

Although induced decomposition is exothermic both for carbon and for tin radical, this large thermochemical difference surely provides a driving force for making induced decomposition decidedly more attractive in the case of the latter.

The following experimental observations are of interest in regard to the effect of temperature on the relative facility of formation of tin ester and tin ether upon attack of triethyltin radicals on the ring-opened perester 1. Experiments thus far reported apply to degassed reaction mixtures heated to 110–125°. However, in the presence of air, decomposition of 1 in solutions containing triethyltin hydride proceeds at measurable rates even at room temperature. For example, the half-life of perester at room temperature (about 23°) of a solution 0.72 M in triethyltin hydride and 0.02 M in 1 was found to be roughly 3 hours. Solutions 0.002 M in 1 and 0.4 M or 0.048 M in tin hydride

---

*The experimental observation is that the thermochemical Sn–O bond energy, as obtained from heats of formation and of atomization, is 95 kcal/mole (98). However, Yergey and Lampe have recently shown that the actual bond dissociation energies for Sn–X bonds (X = Br, I, alkyl, aryl) are 20–21 kcal/mole higher than the thermochemical bond energies (99). They attribute the difference to a reorganization energy for the tin radical. I have added this correction to the thermochemical Sn–O bond energy to obtain the bond dissociation energy quoted.

displayed half-lives of about 6 and 50 hours, respectively. Presumably the agent initiating the induced decomposition is oxygen from the air (which is known to readily attack organotin hydrides): a sample of the run 0.72 M in triethyltin hydride maintained for 3 hours at about 10^{-4} mm showed negligible or nonexistent buildup of tin ester.

Interestingly, the yields of tin ester in these air-induced decompositions were on the order of 90%. This figure is to be compared to yields of 55% (i.e., $\beta = 0.55$) at 110 to 125°. Thus, the partitioning between radical attack leading to formation of tin ester and that leading to formation of tin ether must be appreciably temperature dependent, with the latter process having the higher activation energy.

Unfortunately, several factors conspired to make impossible the precise determination of the yield tin ester in the air-induced experiments. It turns out that the tin hydride has sufficient absorbance at 1651 cm^{-1} (the carbonyl maximum for the tin ester) to require that corrections be made to absorbances measured there. The application of these corrections is complicated by the fact that the concentration of tin hydride can easily be diminished (through air oxidation) by a factor of two or more before sufficient time has elapsed to permit taking the yield of ester to represent the limiting yield. In addition, tin hydrides do add to olefins (such as the tin ester **14**). Thus, the yield of tin ester may well pass through a maximum which lies below the true limiting yield of tin ester as controlled by relative amounts of the two kinds of attack on perester. Indeed, the true limiting yield may easily be as low as 85% or as high as 95%. In assessing the difference in activation energies for the two modes of radical attack, an uncertainty of this magnitude is quite significant. The estimate of 90% implies that the activation energy for attack on perester to give tin ether is 4.7 kcal/mole greater than that for attack to give tin esther. A limiting yield of 95% at room temperature would imply an activation energy difference of 6.3 kcal/mole.

APPENDIX A. Kinetic Treatment of Induced Decomposition in the Presence of Triethyltin Hydride

The purpose of this appendix is to derive eqs. 1.9-16--1.9-19 via conventional steady-state kinetics. All rate processes considered here are depicted in Chart 5, p. 161. We begin by writing down the rate law expressions for the steady-state free-radical intermediates Sn·, R·, and R'·. The latter symbol denotes the ring-cyclized radical 9, and, as in the earlier treatment, P stands for the ring-opened perester 1.

$$\begin{aligned} d(\mathrm{Sn}\cdot)/dt = {} & \alpha k_o(P) - (1-\beta)k_1(\mathrm{Sn}\cdot)(P) + k_{ab}(R\cdot)(\mathrm{Et_3SnH}) \\ & + k_5(R'\cdot)(\mathrm{Et_3SnH}) - k_4(\mathrm{Sn}\cdot)(R'\cdot) = 0 \end{aligned} \tag{A1}$$

$$\begin{aligned} d(R\cdot)/dt = {} & \alpha k_o(P) + (1-\beta)k_1(\mathrm{Sn}\cdot)(P) - k_{ab}(R\cdot)(\mathrm{Et_3SnH}) \\ & - k_r(R\cdot) = 0 \end{aligned} \tag{A2}$$

$$\begin{aligned} d(R'\cdot)/dt = {} & k_r(R\cdot) - k_5(\mathrm{Et_3SnH})(R'\cdot) - 2k_3(R'\cdot)^2 \\ & - k_4(\mathrm{Sn}\cdot)(R'\cdot) = 0 \end{aligned} \tag{A3}$$

The term $k_2(\mathrm{Sn}\cdot)^2$ has been omitted in eq. 1 for reasons discussed in subsection 9.

We now add together eqs. 1, 2, and 3, and solve for (Sn·):

$$(\mathrm{Sn}\cdot) = \frac{\alpha k_o(P) - k_3(R'\cdot)^2}{k_4(R'\cdot)} \tag{A4}$$

Note that eq. 4 involves Sn· and R'·, but not R·. We can obtain a second equation in Sn· and R'· by solving each of eqs. 2 and 3 for (R·) and equating the resulting expressions:

$$\alpha k_o(P) + (1-\beta)k_1(Sn\cdot)(P) = \left(1 + E(Et_3SnH)\right)\left\{k_5(Et_3SnH)(R'\cdot) + 2k_3(R'\cdot)^2 + k_4(Sn\cdot)(R'\cdot)\right\} \tag{A5}$$

where $E = k_{ab}/k_r$ (k_{ab} is defined in eq. 1.9-10).

Eq. 4 is now substituted into eq. 5 to eliminate (Sn·). Rearrangement of the resulting equation leads to:

$$\frac{k_3(R'\cdot)^2}{\alpha k_o(P)}\left[1 + \frac{(1+E(Et_3SnH))}{(1-\beta)k_1(P)}k_4(R'\cdot)\left\{1 + \frac{k_5(Et_3SnH)}{k_3(R'\cdot)}\right\}\right] + \frac{E(Et_3SnH)k_4(R'\cdot)}{(1-\beta)k_1(P)} = 1 \tag{A6}$$

We now make the following definitions:

$$X = \frac{k_3(R'\cdot)^2}{\alpha k_o(P)}\;; \qquad A = \frac{k_4}{k_1}\left(\frac{\alpha k_o}{k_3}\right)^{\frac{1}{2}}\;; \qquad B = \frac{k_5}{(\alpha k_o k_3)^{\frac{1}{2}}}\;.$$

Substitution of these quantities in eq. 6 is readily seen to give eq. 1.9-17 (p. 175).

The probability function g introduced in subsection 9 is defined to be the probability that conversion of ring-cyclized radical 9 to product occurs with the generation of a triethyltin radical. As noted previously, the term probability is not completely accurate, for we mean to account as well for the possibility that conversion of 9 to product consumes a triethyltin radical. That is, $-1 \leq g \leq 1$. In terms of rate constants defined in Chart 1, we must have

$$g = \frac{k_5(Et_3SnH)(R'\cdot) - k_4(Sn\cdot)(R'\cdot)}{2k_3(R'\cdot)^2 + k_5(Et_3SnH)(R'\cdot) + k_4(Sn\cdot)(R'\cdot)} \tag{A7}$$

inasmuch as the k_3, k_4, and k_5 processes are assumed to be the only reaction steps open to ring-cyclized radicals. Substituting for (Sn·) from eq. 4 and rearranging gives

$$g = 1 - 2\left[1 + \frac{k_3(R'\cdot)^2}{\alpha k_o(P)} + \frac{k_3(Et_3SnH)(R'\cdot)}{\alpha k_o(P)}\right]^{-1} . \tag{A8}$$

At first glance eq. 8 does not seem to be much of an improvement on eq. 7, but it indeed turns out that application of the definitions of X, A, and B reduces eq. 8 to a relatively simple form:

$$g = \frac{X + B(Et_3SnH)\sqrt{X/(P)} - 1}{X + B(Et_3SnH)\sqrt{X/(P)} + 1} \tag{A9}$$

Eq. 9 is identical to eq. 1.9-16.

As noted in subsection 9, eq. 1.9-18 (which relates % n directly to quantities developed in this Appendix) can be obtained by substituting 9 into an expression previously derived by a rather unconventional treatment which was drawn in terms of the probabilities that the reaction takes certain paths leading from two key branch points. We wish to show here that the treatment given previously was indeed a valid one. This will be done by deriving eq. 1.9-18 directly, According to eq. 1.9-2, the percent normal decomposition is given by

$$\% \text{ n} = 100\left[1 + k_1(\text{Sn}\cdot)/k_o\right]^{-1} \quad , \tag{A10}$$

where this expression is to be averaged over the course of the reaction if (Sn·) is not independent of (P). Eq. 4 can be rewritten in terms on the quantities A and X in the form

$$(\text{Sn}\cdot) = \frac{\alpha k_o(\text{P})}{k_1}\left[\frac{1 - \text{X}}{\text{A}\sqrt{\text{X}/(\text{P})}}\right] \quad . \tag{A11}$$

Eq. 11 is of limited usefulness, however, because we are interested in situations in which A is equal, or nearly equal, to zero, and both the numerator and the denominator of the term in square brackets vanish at A = 0. However, eq. 1.9-17 (or eq. 6) can be rearranged to the form

$$\frac{(1 - \text{X})}{\text{A}\sqrt{\text{X}/(\text{P})}} = \frac{1}{(1-\beta)}\left\{\text{E}(\text{Et}_3\text{SnH})\left[1 + \text{X} + \text{B}(\text{Et}_3\text{SnH})\sqrt{\text{X}/(\text{P})}\right] + \text{X} + \text{B}(\text{Et}_3\text{SnH})\sqrt{\text{X}/(\text{P})}\right\} \; . \tag{A12}$$

in which the right-hand side is well behaved. Thus, we can substitute from eq. 12 for the term in square brackets in eq. 11 and put the resulting expression into eq. 10. The equation thereby obtained is identical with eq. 1.9-18:

$$\% \ n = 100\left[1 + \frac{\alpha}{(1-\beta)}\left\{E(Et_3SnH)\left[1 + X + B(Et_3SnH)\sqrt{X/(P)}\right]\right.\right.$$
$$\left.\left. + X + B)Et_3SnH)\sqrt{X/(P)}\right\}\right]^{-1} \qquad (A13)$$

Next, the reduced ratio R is given by

$$R = \frac{(\text{Yield of } \mathbf{10})(Et_3SnH)_{av}}{(\text{Yield of } \mathbf{5})}$$
$$= \left(\frac{k_r}{k_a^{SnH}}\right)\left[\frac{\gamma k_3(R'\cdot)^2 + \delta k_4(Sn\cdot)(R'\cdot)}{2k_3(R'\cdot)^2 + k_5(Et_3SnH)(R'\cdot) + k_4(Sn\cdot)(R'\cdot)}\right] \qquad (A14)$$

As with eq. 7, the original equation for the probability function g, the denominator of the term in square brackets expresses the totality of the reactions open to ring-cyclized radicals under our mechanistic assumptions, and the numerator is comprised of those reactions which lead to the desired result, in this case conversion of ring-cyclized **9** to the dihydronaphthalene **10**. Therefore, the term in square brackets represents the efficiency of conversion of **9** to **10**. Introduction of the quantities A, B, and X puts eq. 14 into the form*

$$R = \left(\frac{k_r}{k_a^{SnH}}\right)\left[\frac{\gamma X + \delta(1-X)}{1 + X + B(Et_3SnH)\sqrt{X/(P)}}\right] . \qquad (A15)$$

---

*Conceptually, the approach taken here is incorrect. We really ought to have developed expressions for the yields of **5** and of **10**, integrated these expressions numerically, and then taken the ratio of the resulting numbers as in eq. 1.8-5; this is the approach taken in Section Two. However, as the quantity R does not vary greatly with perester concentration, the error in the treatment employed here is negligible.

Finally, we shall show that decyclization of ring-cyclized radical **9** to ring-opened radical **3** (rate constant k_{-r}) is mechanistically unimportant under the present conditions. Inclusion of this step would modify eqs. 2 and 3 by addition of the term $k_{-r}(R'\cdot)$ to the former and subtraction of the same term from the latter, so that eq. 4, the sum of eqs. 1, 2, and 3, would be unchanged. Eqs. 5 and 6 would differ, but the resulting equation for the variable X (eq. 1.9-17) would be unchanged if we make the definition

$$B \equiv \frac{k_5}{(\alpha k_o k_3)^{\frac{1}{2}}} + \frac{E}{1 + E(\mathrm{Et_3SnH})}\left(\frac{k_{-r}}{k_3^{\frac{1}{2}}}\right)\left(\frac{1}{\alpha k_o}\right)^{\frac{1}{2}} .$$

As eq. 6 was used directly in obtaining eq. 13, this definition of B is also appropriate for calculation of % n values.

The new term on the right-hand side is evaluated as follows. For satisfactory calculations in Table 15, $k_a^{\mathrm{SnH}}/k_r \cong E$ is about 7 liters/mole. The factor of $k_{-r}/k_3^{\frac{1}{2}}$ arises in the mechanistic treatment of Section Two, where an upper limit of 5×10^{-5} (liter-sec/mole)$^{-\frac{1}{2}}$ at 100° is inferred (heading Q, p. 287). The analogous value at 110° is 10^{-4} according to the assumed composite activation energy of 18 kcal/mole quoted there. The value of k_o at 110° is 7.7×10^{-5} sec^{-1} (21). Thus, we find with $\alpha \cong 0.9$ that the new term has a value of ≤ 0.08 for zero triethyltin hydride concentration. As the discussion under heading Q indicates that $k_{-r}/k_3^{\frac{1}{2}}$ and $k_o^{\frac{1}{2}}$ must have almost identical activation energies, this value is appropriate at 125° as well. Although this value is similar to values of B employed in various calculations in Table 15, this will not of itself much affect the calculations because the calculations are sensitive to values of B in the range employed only for the higher tin hydride concentrations; the important factor is the product $B(Et_3SnH)$. And the value of 0.01 for the new term at 0.94 M tin hydride, the highest hydride concentration employed, is easily neglectable with respect to values of B employed in the calculations.

For the reduced ratio R, one again finds that allowance for the decyclization may be made by redefining the parameter B, but this time we require

$$B(Et_3SnH) \equiv \frac{k_5(Et_3SnH)}{(\alpha k_o k_3)^{\frac{1}{2}}} + \left(\frac{k_{-r}}{k_3^{\frac{1}{2}}}\right)\left(\frac{1}{\alpha k_o}\right)^{\frac{1}{2}} \quad .$$

The value of the second term on the right-hand side is ≤ 0.01 according to estimates quoted above. The results for calculations displayed in Table 15 show that for values of B of about 0.1, the reduced ratios are strongly affected only for the higher tin hydride concentrations, or for values of about 0.1 for the product $B(Et_3SnH)$. Thus, the correction term is insignificant. Even if data considered in Section two permitted the ratio $k_{-r}/k_3^{\frac{1}{2}}$ to be an order of magnitude larger than was found to be the case, however, the revised definition shows that decyclization would not cause the reduced ratios to vary significantly with the hydride concentration, but would instead rather uniformly increase the denominator in eq. 15 and thus simply distort values of k_r/k_a^{SnH} inferred by fitting reduced ratios to eq. 15.

SECTION TWO: NUMERICAL EVALUATION OF THE REACTION MECHANISM

The purpose of this section is to give a quantitative mechanistic description of a complex set of processes which occurs when either of the peresters t-butyl (γ, γ-diphenylallyl)peracetate (1) or t-butyl diphenylcyclopropylperacetate (2) is allowed to decompose thermally in the presence of 1, 4-cyclohexadiene. The relevant experimental observations are listed in Tables 1, 2, 4, 5, and 6. Those observations have been discussed qualitatively in Section One, principally in subsection 8A. The present quantitative description will allow us to firmly establish a number of points which could be postulated, though not proven, on the basis of qualitative reasoning and to suggest the existence of other factors which may be detected only by examining the adequacy of mechanistic expressions derived with and without their inclusion.

We begin by introducing the reaction steps to be considered and presenting appropriate mechanistic expressions in subsection 1. The derivation of the mechanistic expressions is handled in Appendix B. A formalism for fitting expressions of arbitrary form in the sense of least squares is then described in subsection 2 and applied to the case at hand in subsection 3. Finally, results of the mechanistic treatment are presented in subsection 4.

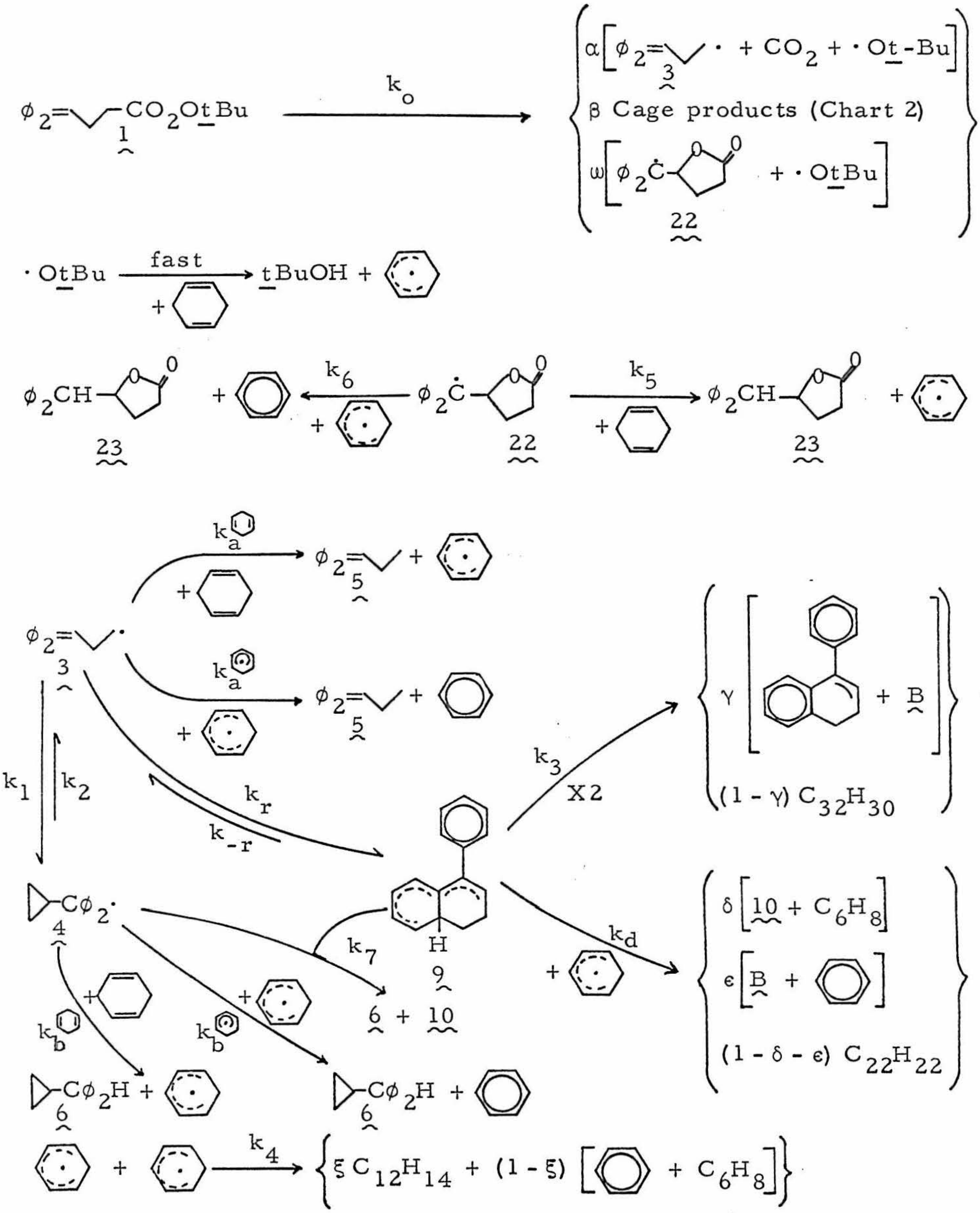
It is to be expected that many readers will be *presently* unconcerned with the details of the least-squares adjustment. Such readers may wish to read subsection 1 and then go directly to the presentation of results in subsection 4. Moreover, a five page summary of the principal conclusions of subsection 4 (pp. 290–295) has been provided. Some may wish to read that summary and refer to the original treatment only for points which seem especially interesting. Subsection 4 itself has been heavily indexed to ensure a sense of direction and to allow readers to pick and choose among areas to be examined.

1. Expressions for Yields and Ratios of Three Key Products

All of the types of reaction steps we shall consider are depicted in Chart 7. That chart assumes that the starting perester is the ring-opened perester **1**, but only upper portion would be different for decomposition of the ring-closed perester **2**.

Decomposition of the perester is shown at the top of the chart. A certain variable fraction α of such events leads to a kinetically free radical pair composed of ring-opened radical **3** and a t-butoxy radical. Another fraction β represents those events which result in formation of cage-reaction products, in this case the ring-opened ether **12** and the butadiene **13** of Chart 2, p. 58; here we are not interested in the identity of the cage products, but merely seek to take the fact of their formation into account. Lastly, we take molecule-induced decomposition (Section One, subsection 6) to make up a fraction w of the decomposition events, where $\alpha + \beta + \omega = 1$. For decomposition of ring-closed perester **2**, we would have $\omega = 0$ and the hydrocarbon radical formed with probability α would be the ring-closed radical **4**.

Chart 7. Mechanistic scheme for decomposition of t-butyl (γ, γ-diphenylallyl)peracetate in the presence of 1, 4-cyclohexadiene.



As rapid equilibration of **3** and **4** has already been established for decomposition of the peresters in 1,4-cyclohexadiene (see also p. 253), the identity of the first-formed hydrocarbon radical is immaterial.

We dispense with further consideration of the *t*-butoxy radical by postulating its rapid and certain abstraction of hydrogen from 1,4-cyclohexadiene.*

The nest process shown is conversion of the lactonyl radical **22** to the lactone **23**. Two pathways are provided; abstraction of hydrogen from 1,4-cyclohexadiene or from cyclohexadienyl radical.** The reason for postulating a radical-radical reaction here but not for consumption of *t*-butoxy radical (or methyl radical) is that whereas hydrogen abstraction from cyclohexadiene by the latter is exothermic by more than 30 kcal/mole, the analogous process for the dibenzylic lactonyl radical **22** is expected to be very nearly thermoneutral, and thus will sport a much smaller rate constant. However, the rates of the radical-radical processes are expected to be rather similar. The level of radical concentrations which can be predicted thus allow neglect of the radical-radical process in the case of the *t*-butoxy radical,

---

*Actually, β-scission may also occur--and because of the remarkable augmentation of that process noted in olefinic solvents (42, 43), might be significant. But then the resulting methyl radical would effect the hydrogen abstraction. The assumption is that one cyclohexadienyl radical results for each kinetically free *t*-butoxy radical produced in the decomposition of the perester, but how this comes about is not of interest.

**This description is only approximate in that lactonyl radicals undoubtedly react with radicals other than cyclohexadienyl. However, cyclohexadienyl radicals are expected to be the most prevalent, and are the logical choice for inclusion in an approximate treatment (which is all that is really needed).

but not in the case of the lactonyl radical. This is a matter of potential importance, since the product ratios of interest (<u>vide infra</u>) depend on the concentration of cyclohexadienyl radicals, which concentration can be augmented or diminished depending on the pathway chosen by the lactonyl radicals.

We now come to a block of interconnecting reactions which are intended to account for formation of three key hydrocarbons: the ring-opened $\underset{\frown}{5}$; the ring-closed $\underset{\frown}{6}$; and the ring-cyclized $\underset{\frown}{10}$. The rate constants k_1 and k_2 relate to the interconversion of the ring-opened and ring-closed radicals $\underset{\frown}{3}$ and $\underset{\frown}{4}$. Lengths of the arrows indicate the position of equilibrium which, according to arguments given earlier (p. 138), lies on the ring-closed side (see also heading K, p. 277). Each of the radicals may abstract hydrogen either from 1,4-cyclohexadiene (the k_a and k_b processes) or from cyclohexadienyl radical (the k_a and k_b processes). From subsection 8A of Section One we know that $\underset{\frown}{3}$ employs mainly the first type of process and $\underset{\frown}{4}$, mainly the second.

We have assumed that ring-opened radical $\underset{\frown}{3}$ is the species which undergoes <u>ortho</u>-ring cyclization to ring-cyclized $\underset{\frown}{9}$.

Because interconversion of $\underset{\frown}{3}$ and $\underset{\frown}{4}$ is much faster than any other processes of which they partake, our final equations and results will be interpretable in terms of alternative formulations in which a species such as the nonclassical homoallylic radical $\underset{\frown}{7}$ plays a part. However, we shall assume in the present section that the radicals $\underset{\frown}{3}$ and $\underset{\frown}{4}$ play the roles assigned them in Chart 7; other possibilities will be briefly considered in Section Three.

The rate constant for ring-cyclization is denoted by k_r and that for decyclization, by k_{-r}. Again, the lengths of the arrows are suggestive; we have already shown that decyclization is not an important reaction under the present conditions (pp. 114, 115). The reason for its inclusion here is to allow us to determine just how small k_{-r} must be, this by way of fully justifying the omission of decyclization in the mechanistic treatment given earlier of radical-induced decomposition in triethyltin hydride.

Several ways by which ring-cyclized radicals might be converted to non-radical products are included in this mechanistic treatment. Reaction of a pair of ring-cyclized radicals may lead to disproportionation (probability = γ) or to dimerization (probability = $1 - \gamma$). Similarly, reaction of a ring-cyclized radical with a cyclohexadienyl radical (rate constant k_d) may lead to disproportionation or to coupling, but now the disproportionation may occur in two ways, one leading to dihydronaphthalene 10 (probability = δ) and the other to one of the tetrahydronaphthalenes B (see Chart 4, p. 78) (probability = ϵ). The probability of coupling, then, is $1 - \delta - \epsilon$. Finally, disproportionation of 9 with the relatively stable ring-closed radical 4 (rate constant k_7) has been included by way of accounting for formation of small amounts of 6 in indene (Table 7) where solvent-derived radicals can not supply the necessary hydrogen atom and there is a good reason to think that hydrogen abstraction from indene itself would not be effective.

Lastly, the rate constant for pairwise reaction of cyclohexadienyl radicals is denoted by k_4.

The mechanistic scheme makes no provision for the possibility that the coupling products indicated by empirical formulas in Chart 7 might redissociate on the time scale of the perester decompositions. As ring-cyclized radicals and cyclohexadienyl radicals are relatively stable radicals, this assumption requires some justification. Fortunately, observed yields of cyclohexadienyl radical dimer appear to provide the desired justification (see subsection 4, p. 285).

As in the earlier treatment of induced decomposition in the presence of triethyltin hydride, the tough job--the actual algebraic manipulation of equations resulting from the processes of Chart 7--will be handled in an appendix (Appendix B). We will give here only the resulting mechanistic equations. Even these, however, can be pretty awesome.

We will be primarily interested in expressions for the product ratios R1 ≡ % yield 5/% yield 10 and R2 ≡ % yield 6/% yield 5. Expressions for the three product yields are given in eqs. 2.1-1, -2, and -3. Each takes the form of an integral over the course of the reaction, the integration variable $z \equiv (P)/(P)_o$ being the ratio of perester concentration part way through the reaction period to the initial concentration.

$$\%\ \text{yield}\ 5 = 100\alpha \int_0^1 \left\{ E{\ast}(ZH) + (G/H){\ast}\left(\frac{\alpha k_o (P)_o z}{2X}\right)^{\frac{1}{2}} \right\} W{\ast}dz \qquad (2.1\text{-}1)$$

$$\%\ \text{yield}\ 6 = 100\alpha \int_0^1 \left\{ E{\ast}I{\ast}(ZH) \right.$$

$$\left. + \; G\left(\frac{\alpha k_o (P)_o z}{2X}\right)^{\frac{1}{2}} \left[1 + \frac{4C{\ast}W}{S(1+T)}\right] \right\} W{\ast}dz \qquad (2.1\text{-}2)$$

$$\% \text{ yield } \underset{\sim}{10} = 100\alpha \int_0^1 \frac{2}{S(1+T)} \left\{ \delta + \frac{4W^*X^*\gamma}{S(1+T)} + G^*C^*W \sqrt{2\alpha k_o (P)_o z X} \right\} W^* dz \quad (2.\,1\text{-}3)$$

Aside from the integration variable z, four types of quantities appear in the above equations and in other mechanistic equations recorded below or in Appendix B. As it will be necessary to distinguish between the four classes in the least-squares analysis, we shall give them names.

First we have the adjustable parameters. These are the independent quantities which may be varied to effect the best possible agreement between calculated and observed product ratios. These include the arabic letters A through I and the Greek letters γ and δ. The arabic letters represent combinations of rate constants from Chart 7 which appear together in the mechanistic equations:

$$A = \frac{\omega}{\alpha} \qquad D = \frac{k_{-r}}{k_3^{\frac{1}{2}}} \qquad G = \frac{k_1 k_b^{\text{⌬}} k_3^{\frac{1}{2}}}{k_2 k_r k_d}$$

$$B = \frac{k_5 k_d}{k_6 k_3^{\frac{1}{2}}} \qquad E = \frac{k_a^{\text{⬡}}}{k_r} \qquad H = \frac{k_1 k_b^{\text{⌬}}}{k_2 k_a^{\text{⌬}}} \qquad (2.\,1\text{-}4)$$

$$C = \frac{k_7 k_d}{k_b^{\text{⌬}} k_3} \qquad F = \frac{k_3 k_4}{k_d^{\,2}} \qquad I = \frac{k_1 k_b^{\text{⬡}}}{k_2 k_2^{\text{⬡}}}$$

For purposes of orientation, it will be helpful to quickly run through a description of the roles played by the arabic-letter parameters:

A	measures the extent of molecule-induced decomposition of perester 1.
B	controls the competition between hydrogen abstraction by lactonyl radicals 22 from 1,4-cyclohexadiene and from cyclohexadienyl radical.
C	measures the facility of reaction of 4 with 9 with respect to the more important reaction of 4 with cyclohexadienyl radical.
D	provides for the possibility of decyclization.
E	is the rate-constant ratio which together with the 1,4-cyclohexadiene concentration, controls the partitioning of ring-opened radicals between hydrogen abstraction and ring-cyclization.
F	measures the respective tendencies toward self- and cross termination in a system containing ring-cyclized radicals and cyclohexadienyl radicals. It has a statistical value (100) of 0.25.
G	is composed of rate constants which determine the rate of formation of ring-closed hydrocarbon 6 from 4 plus cyclohexadienyl radical relative to the rate of formation of 9 via the *ortho*-ring cyclization process. Thus 6/E is an important determinant of the product ratio R2.
H	is the characteristic ratio 6:5 (p. 13) arising via hydrogen abstraction from cyclohexadienyl radicals by 3 and by 4.
I	is the analogous quantity for hydrogen abstraction from 1,4-cyclohexadiene.

The *observables* are those quantities which can be measured or inferred experimentally. Examples are: $(ZH)_o$, the initial concentration of the active hydrogen donor, 1,4-cyclohexadiene; and k_o and $(P)_o$ which denote the rate constant for thermal decomposition of the starting perester and the initial concentration of that perester. Other observables include the reaction temperature (not the 'T' in the above equations) and the experimentally measured values of the ratios R1 and R2 and of the yield of 5.

The third category is comprised of the variables X and W. As with the 'X' of the kinetic treatment of induced decomposition in triethyltin hydride, these arise from the steady-state equations describing the formation and destruction of radical intermediates. Their definitions will be given shortly.

The fourth and last category is made up of the quantities S and T; these are merely shorthand symbols for subexpressions constructed from the first three types of quantities:

$$S \equiv 1 + D*\left(\frac{\alpha k_o(P)}{2X}\right)^{-\frac{1}{2}} + G*C*W(2\alpha k_o(P)*X)^{\frac{1}{2}} \qquad (2.1\text{-}5)$$

$$T \equiv \{1 + 16W*X/S^2\}^{\frac{1}{2}} \qquad (2.1\text{-}6)$$

In Appendix A for induced decomposition in triethyltin hydride, we were able to obtain from the steady-state rate equations an equation involving the concentration of a single one of the several free-radical intermediates. At that point it became convenient to define a dimensionless variable X by grouping certain key rate constants with the concentration of the free radical in question. That gave a nonlinear equation in X, and the desired mechanistic equations were expressed in terms of a particular root of the 'X equation'.

The situation in Appendix B is similar, except that we come down to a system of two simultaneous nonlinear equations in the concentrations of a pair of radical intermediates. Our results are therefore expressed in terms of the dimensionless variables W and X,

$$W \equiv k_r(\underset{\sim}{3})/\{\alpha k_o(P)\} \qquad (2.1\text{-}7)$$

$$X \equiv \alpha k_o(P)k_3/\{2k_d{}^2(Z\cdot)^2\} \qquad (2.1\text{-}8)$$

where (Z·) is the concentration of cyclohexadienyl radicals. The two equations which W and X must simultaneously satisfy are:

$$\frac{1 + \dfrac{2W{*}D}{S(1+T)}\left(\dfrac{\alpha k_o(P)}{2X}\right)^{-\frac{1}{2}}}{1 + E{*}(1+I){*}(ZH) + G{*}(1+1/H){*}\left(\dfrac{\alpha k_o(P)}{2X}\right)^{\frac{1}{2}} + \dfrac{2G{*}C{*}W(2\alpha k_o(P)X)^{\frac{1}{2}}}{S(1+T)}} \qquad (2.1\text{-}9)$$

$$- W = 0$$

$$1 + W{*}\left\{E{*}(1+I)(ZH) + G{*}(1+1/H){*}\left(\frac{\alpha k_o(P)}{2X}\right)^{\frac{1}{2}}\right\} \qquad (2.1\text{-}10)$$

$$+ 2A{*}\left\{\frac{B{*}(ZH){*}\left(\dfrac{\alpha k_o(P)}{2X}\right)^{-\frac{1}{2}}}{1 + B{*}(ZH){*}\left(\dfrac{\alpha k_o(P)}{2X}\right)^{-\frac{1}{2}}}\right\} - \frac{2}{S(1+T)} - F/X = 0$$

Values of the variables W and X are extracted using a generalization of the Newton-Raphson method (101) starting from approximate values obtained from empirical relationships.

Finally, because 1,4-cyclohexadiene is consumed in the reaction, the (ZH) appearing in eqs. 2.1-1— -10 will not be the same as the initial concentrations recorded in the data tables. The procedure employed for making the necessary corrections is explained in Appendix B.

A computer program is rather obviously required to handle eqs. 2.1-1–2.1-10. Several approaches are conceivable. One would be to perform the calculations for several sets of values of the unknown parameters and to examine the results to determine which sets give a good fit to the observed product ratios. This was the general approach taken for induced decomposition in triethyltin hydride. Here, however, such an approach would result in utter confusion because of the large number of parameters involved.

The other extreme would be to include all of the parameters in the least-squares optimization. However, this would be improper because the least-squares criteria concern only the product ratios R1 and R2, whereas some consideration of actual yields must be provided. We shall do this by restricting γ and δ to values which lead to yields of the ring-opened hydrocarbon 5 which are of the correct magnitude on the average.* In addition, the parameter A must be chosen to reproduce yields of the lactone 23 rather than to best fit the product ratios R1 and R2.

The procedure actually employed is thus a compromise between two extremes. The arabic letter parameters E through I will be automatically optimized; the others will be set manually. As a result, some 20 calculations will be discussed in subsection 4.

---

*The parameter E, not γ and δ, essentially determines the % yield 5. However, if γ and δ are varied, E must follow in order to get % yield 5/% yield 10 right.

2. Generalized Least-Squares Adjustment

A. The Normal Equations

Let us suppose that we have obtained N measurements of a quantity R, perhaps the ratio of two products of interest. These may all involve separate experimental conditions, or may include replicative measurements. Let us further suppose that a suggested description of the problem leads to a theoretical expression for R which is a function of three unknown parameters (a, b, and c) and of the reaction temperature T. Thus we have three parameters and two sets of observables (R_i^{obs} and T_i). We might wish to minimize the sum of the squares of the differences between calculated and observed values of R. The criterion would then be

$$S(a,b,c) = \sum_{i=1}^{N} \left\{ R_i^{calc}(T_i, a, b, c) - R_i^{obs} \right\}^2 , \quad \text{a minimum} \qquad (2.2\text{-}1)$$

However, this formulation is reasonable only if errors in R_i^{obs} are expected to be constant, rather than proportional to R_i^{obs}. The latter will probably more often be the better approximation. Suppose, for example, that R is a product ratio (like our R1 and R2) which is obtained as a ratio of peak areas measured by vpc. If resolution is adequate, we should expect that the probable errors in the peak area measurements will be some small, but reasonably constant, fraction of the peak areas. If this is so, the probable errors in R will be proportional to R, and we should really seek to minimize the sum of the squares of the relative differences in observed and calculated values of R:

$$S(a,b,c) = \sum_{i=1}^{N} \left\{ \frac{R_i^{calc}(T_i, a, b, c) - R_i^{obs}}{R_i^{obs}} \right\}^2 , \quad \text{a minimum} \qquad (2.2\text{-}2)$$

Minimizing the function S(a, b, c) (S, for short) means finding values of a, b, and c which simultaneously satisfy eqs. 2.2-3.

$$\frac{\partial S}{\partial a} = 0 \; ; \qquad \frac{\partial S}{\partial b} = 0 \; ; \qquad \frac{\partial S}{\partial c} = 0 \; ; \qquad (2.2\text{-}3)$$

If we knew the analytic dependence of S on the parameters a, b, and c, finding these values would be trivial. Not in general having that information, we proceed to do the next best thing, which is to expand S in a Taylor series, truncated where required for mathematical tractability. Let us suppose that we have a set of estimates a^o, b^o, c^o of the desired parameters a, b, and c. Then expanding S to second order about the known point, we have

$$\begin{aligned} S(a,b,c) = {} & S(a^o, b^o, c^o) - \Delta a\, S_a - \Delta b\, S_b - \Delta c\, S_c \\ & + \tfrac{1}{2}(\Delta a)^2 S_{aa} + \tfrac{1}{2}(\Delta b)^2 S_{bb} + \tfrac{1}{2}(\Delta c)^2 S_{cc} \qquad (2.2\text{-}4) \\ & + \Delta a \Delta b\, S_{ab} + \Delta a \Delta c\, S_{ac} + \Delta b \Delta c\, S_{bc} \quad , \end{aligned}$$

where, for example,

$$\Delta a \equiv a^o - a \; ; \quad S_a \equiv \left(\frac{\partial S}{\partial a}\right)\Big|_{(a^o, b^o, c^o)} \; ; \quad S_{ab} \equiv \left(\frac{\partial^2 S}{\partial a \partial b}\right)\Big|_{(a^o, b^o, c^o)} \; .$$

All but the delta quantities in eq. 2. 2-4 are simply numbers evaluated at the point (a^o, b^o, c^o). Differentiating eq. 2. 2-4 with respect to a, b, and c, and recalling eq. 2. 2-3, we see that the unknown quantities Δa, Δb, Δc must be chosen to simultaneously satisfy eqs. 2. 2-5:

$$\left.\begin{aligned} \frac{\partial S}{\partial a} &= S_a - \Delta a\, S_{aa} - \Delta b\, S_{ab} - \Delta c\, S_{ac} = 0 \\ \frac{\partial S}{\partial b} &= S_b - \Delta a\, S_{ba} - \Delta b\, S_{bb} - \Delta c\, S_{bc} = 0 \\ \frac{\partial S}{\partial c} &= S_c - \Delta a\, S_{ca} - \Delta b\, S_{cb} - \Delta c\, S_{cc} = 0 \end{aligned}\right\} \qquad (2.\,2\text{-}5)$$

Our immediate problem thus reduces to the solution of three simultaneous linear equations. This solution can be effected in several ways, one of which is discussed below. When the values of the delta equations have been found, they are combined with the estimates (a^o, b^o, c^o) to obtain new values of the parameter, viz.:

$$\begin{aligned} a &= a^o - \Delta a \\ b &= b^o - \Delta b \\ c &= c^o - \Delta c \end{aligned} \qquad (2.\,2\text{-}6)$$

If the (a^o, b^o, c^o) are sufficiently good that negligible error is made at (a, b, c) in taking the Taylor series expansion of S about (a^o, b^o, c^o) only to second order, the (a, b, c) will be the least-squares estimates of the parameters. Generally, however, this will not be the case, and one must take the (a, b, c) as a new initial approximation (a^o, b^o, c^o). Of course, the iteration may diverge if the initial approximation (a^o, b^o, c^o) is not good enough. Then one must select a new trial set (a^o, b^o, c^o) and try again.

Let us now examine how the first and second derivatives of S can be calculated. At a very preliminary and restricted stage of calculations of the type reported in this Section, the derivatives were obtained numerically. This was done by writing a control routine to feed the variations of the initial parameter set (with all combinations of zero, one, or two parameters incremented or decremented by predetermined amounts) to the main program which assembled S. Then the derivatives were calculated by finite differences. The minimum number of sets of calculations of S required to assemble the necessary derivatives is $2n^2 + 1$, where n is the number of parameters. Clearly, the computer time required for calculating the derivatives in this way increases more strongly with the number of parameters than one would like. In addition, the approximation of using finite differences can lead to severe problems of numerical stability. However, for situations involving exceedingly complicated expressions of a small number of parameters, numerical differentiation may be the method of choice.

In general, we can do better by evaluating the derivatives analytically. We begin by rewriting eq. 2.2-2 in the form

$$S = \sum_{i=1}^{N} \frac{(F_i^o)^2}{(R_i^{obs})^2} \qquad (2.2\text{-}7)$$

where $F_i^o \equiv R_i^{calc} - R_i^{obs}$. Differentiating eq. 2.2-7 with respect to the parameter a gives

$$S_a = 2 \sum_{i=1}^{N} \frac{F_i^{\,o} F_{a_i}}{(R_i^{\,obs})^2} \quad , \tag{2.2-8}$$

where

$$F_{a_i} = \left(\frac{\partial F_i^{\,o}}{\partial a}\right)\Big|_{(a^o,b^o,c^o)} = \left(\frac{\partial R_i^{\,calc}}{\partial a}\right)\Big|_{(a^o,b^o,c^o)} \quad . \tag{2.2-9}$$

Differentiation of eq. 2.2-8 with respect to a second parameter, say c, gives

$$S_{ac} = S_{ca} = 2 \sum_{i=1}^{N} \left\{ \frac{F_{a_i} F_{c_i} - F_i^{\,o} F_{ac_i}}{(R_i^{\,obs})^2} \right\} \quad . \tag{2.2-10}$$

Thus we see that to take advantage of the presumed accuracy of an expansion of S through second order, we require all of the first and second derivatives of R_i^{calc} with respect to the parameters. For a case of 10 parameters (the number we shall employ in the least-squares treatment of the ratios R1 and R2 of subsection 2), this would amount to 10 first derivatives of R^{calc} plus 55 second derivatives (all those on or above the diagonal of a 10 × 10 matrix). However, we can generally make do with only the first derivatives of R^{calc}. The reason is that the second derivative terms (F_{ac_i} in eq. 2.2-10) are multiplied by $F_i^{\,o}$, which for a refined fit will sometimes be positive and sometimes negative. The result is a tendency to cancel when summed over the data points. We shall likely be left with a slower rate of convergence and perhaps a smaller radius of convergence, but in many cases this is a small price to pay. The fit to the product ratios R1 and R2 described in this Section is one such case; because of implicit dependencies, the first derivatives of the product-ratio expressions are difficult enough to work out.

If we further define

$$L_i = (R_i^{obs})^2 \quad , \tag{2. 2-11}$$

for reasons which will shortly be apparent, the system of equations (eqs. 2. 2-5) becomes:

$$\begin{aligned}
\Sigma \frac{F_{a_i} F_{a_i}}{L_i} \Delta a + \Sigma \frac{F_{a_i} F_{b_i}}{L_i} \Delta b + \Sigma \frac{F_{a_i} F_{c_i}}{L_i} \Delta c &= \Sigma \frac{F_{a_i} F_i^{o}}{L_i} \\
\Sigma \frac{F_{b_i} F_{a_i}}{L_i} \Delta a + \Sigma \frac{F_{b_i} F_{b_i}}{L_i} \Delta b + \Sigma \frac{F_{b_i} F_{c_i}}{L_i} \Delta c &= \Sigma \frac{F_{b_i} F_i^{o}}{L_i} \\
\Sigma \frac{F_{c_i} F_{a_i}}{L_i} \Delta a + \Sigma \frac{F_{c_i} F_{b_i}}{L_i} \Delta b + \Sigma \frac{F_{c_i} F_{c_i}}{L_i} \Delta c &= \Sigma \frac{F_{c_i} F_i^{o}}{L_i}
\end{aligned} \tag{2. 2-12}$$

where the summations go from 1 to N as usual.

These are the so-called normal equations. They are rigorously derived in many places, notably in Deming's 'Statistical Adjustment of Data' (26a). Deming's derivation is recapitulated, with examples of chemical interest, by Wentworth in the Journal of Chemical Education (26b). That derivation begins with the assumption that the errors in the observables (here, the product ratios R_i^{obs} and the reaction temperature T_i) are random and belong to a Gaussian distribution. In the minimization procedure, which is set up in quite different form from the approach given here, one performs a set of constrained variations. As is commonly done, Lagrange multipliers are invoked to handle the constraints. One then works out what the Lagrange multipliers must be and comes out with eqs. 2.2-12, where the factors L_i are found to be given by a sum containing a term of the form $\left(F_{x_i}\right)^2/W_{x_i}$ for each of the observables. F_{x_i} is the derivative of $F_i^{\,o}$ with respect to the observable x and W_{x_i} is the weight of observable x for the i-th observation. Specifically,

$$W_{x_i} = \left(\frac{\sigma_o}{\sigma_{x_i}}\right)^2 , \qquad (2.2\text{-}13)$$

where σ_{x_i} is the standard error in the i-th measurement of the observable x and σ_o is an arbitrary constant* of convenient magnitude.

For our product-ratio example, then, L_i will have two terms:

$$\begin{aligned} L_i &= \left(\frac{\partial F_i^{\,o}}{\partial R^{obs}}\right)^2 \left(\frac{\sigma_{R_i}{}^{obs}}{\sigma_o}\right)^2 + \left(\frac{\partial F_i^{\,o}}{\partial T}\right)^2 \left(\frac{\sigma_{T_i}}{\sigma_o}\right)^2 \\ &= \left(\frac{\sigma_{R_i}{}^{obs}}{\sigma_o}\right)^2 + \left(\frac{\partial R_i^{\,calc}}{\partial T}\right)^2 \left(\frac{\sigma_{T_i}}{\sigma_o}\right)^2 \end{aligned} \qquad (2.2\text{-}14)$$

---

*Note that σ_o will affect each of the terms in eqs. 2.2-12 equally. Therefore, the values of the delta quantities do not depend on the choice of σ_o.

If the errors in R_i^{obs} are assumed to be proportional to R_i^{obs} where the proportionality factor is 0.05 (i.e., $\sigma_{R_i^{obs}} = 0.05\, R_i^{obs}$) and σ_o is taken to be 0.05, we have that

$$L_i = R_i^{obs\;2} + \left(\frac{\partial R_i^{calc}}{\partial T}\right)^2 \left(\frac{\sigma_{T_i}}{0.05}\right)^2 . \qquad (2.2\text{-}15)$$

Comparison with eq. 2.2-11 shows that we were only approximately correct in originally defining S in terms of eq. 2.2-2: we accounted for errors in R_i^{obs} arising from our hypothetical vpc area measurements, but failed to account for the possibility that deviations between observed and predicted values of R_i might also arise from inaccuracy in the measurement of the reaction temperatures T_i. The second term in eq. 2.2-14 tells us, very reasonably, that the importance of errors in the latter is to be judged according to how sensitive R_i is to the reaction temperature and how uncertain is our measurement of that temperature. For many cases, however, including that of the real product ratios R1 and R2 of this Section, the dominant uncertainty is usually that in the measurement of the product ratio, rather than that in the measurement of the reaction temperature (or other observables, such as the hydrogen-donor concentration).

The normal equations are quite general, and we see that a simple recipe exists for setting them up. First one defines an expression F_i^o involving the observables and the unknown parameters which would be zero for each measurement i if the true values of the parameters <u>and</u>

of the observables could be employed. In the present example, $R_i^{calc} - R_i^{obs} = 0$ under such conditions. The factors L_i are then evaluated in terms of the derivatives of F_i^o with respect to the observables and assumed or statistically inferred standard errors in the measurements of the observables. Then F_i^o and its derivatives with respect to each of the unknown parameters are evaluated for the current approximations to those parameters. The normal equations then compiled as in eqs. 2.2-12. Finally, the set of simultaneous linear equations is solved (see below) for the difference quantities and the estimates of the parameters are updated. If necessary, the process is repeated.

We have not actually derived the normal equations here, although the present treatment would have constituted a derivation if we had started out with the correct form of S, namely

$$S = \sum_{i=1}^{N} \frac{(F_i^o)^2}{L_i} \quad . \tag{2.2-16}$$

However, rigorously obtaining the definition of L_i is not a trivial matter for one unschooled in probability theory. We have preferred simply to invoke the definition with a few comments on its reasonability.

Alternatively, Deming's derivation could have been recounted. However, its reliance on faintly mystical Lagrange multipliers might well serve to elicit a feeling of beauty on the part of the mathematical purist, but of confusion on the part of the chemist (the latter, at least, was its effect on this chemist). Better, we have therefore thought, to employ the present approach, where the criterion for minimization--the simultaneous vanishing of all the first derivatives of S--and the use of the familiar Taylor series expansion should provide a solid physical basis for understanding how the normal equations come to take their peculiar form.

B. The Reciprocal Solution

We still have several matters to transact to complete the description of least-squares adjustment. For example, we have yet to consider how the normal equations may be solved for the difference quantities. Especially convenient, if a digital computer is available, is the so-called reciprocal solution (26). This method of solution involves the recognition that the left-hand sides of eqs. 2.2-12 can jointly be expressed as the product of a square matrix $\underset{\approx}{S2}$ (for second derivatives of S--3 × 3 in the example considered here) with a column vector $\underset{\sim}{D}$ (for delta quantities; e.g., $\underset{\sim}{D}_a = \Delta a$). The result is a column vector $\underset{\sim}{S1}$ (for first derivatives of S with respect to the parameters):

$$\underset{\approx}{S2} \times \underset{\sim}{D} = \underset{\sim}{S1} \qquad (2.2\text{-}16)$$

If we then find the inverse of $\underset{\approx}{S2}$ ($\equiv \underset{\approx}{S2}^{-1}$) and left-multiply it into eq. 2.2-16, we obtain

$$(\underset{\approx}{S2}^{-1} \times \underset{\approx}{S2}) \times \underset{\sim}{D} = \underset{\approx}{S2}^{-1} \times \underset{\sim}{S1} = \underset{\sim}{D} \quad ,$$

and the difference quantities have been found.

The importance of this method of solution derives from the fact that the elements of $\underset{\sim}{S2}^{-1}$ are simply related to the standard errors in the parameters (26). For the case of three parameters, the elements of the so-called covariance matrix are:*

$$\begin{aligned} \sigma_a^2 &= \underset{\sim}{S2}^{-1}_{aa}\,\sigma_o^2 & \sigma_{ab} &= \underset{\sim}{S2}^{-1}_{ab}\,\sigma_o^2 \\ \sigma_b^2 &= \underset{\sim}{S2}^{-1}_{bb}\,\sigma_o^2 & \sigma_{ac} &= \underset{\sim}{S2}^{-1}_{ac}\,\sigma_o^2 \\ \sigma_c^2 &= \underset{\sim}{S2}^{-1}_{cc}\,\sigma_o^2 & \sigma_{bc} &= \underset{\sim}{S2}^{-1}_{bc}\,\sigma_o^2 \end{aligned} \qquad (2.\,2\text{-}17)$$

The standard deviation, or standard error, in the parameter a is just σ_a, while the variance in a is σ_a^2. In many cases, estimates of the standard deviations of the parameters is as important as estimates of the parameters themselves. The former information, as Wentworth says, is impossible to obtain from a graphical solution and is one of its most limiting features (26b).

Knowledge of the covariance matrix also enables one to calculate the variance of any function of the parameters (26). Suppose we have a function

$$g = G(a, b, c) \quad . \qquad (2.\,2\text{-}18)$$

Then the variance of g is given by

$$\begin{aligned} \sigma_g^2 = {} & G_a^2\sigma_a^2 + G_b^2\sigma_b^2 + G_c^2\sigma_c^2 \\ & + 2G_aG_b\sigma_{ab} + 2G_aG_c\sigma_{ac} + 2G_bG_c\sigma_{bc} \end{aligned} \qquad (2.\,2\text{-}19)$$

---

*In spite of appearances, eqs. 2.2-17 do not say that the uncertainties in the parameters depend on σ_o; this formulation merely neutralizes the effect of having allowed σ_o to be chosen arbitrarily.

where the usual notation for differentiation has been used; e.g.,

$$G_a = \left(\frac{\partial G}{\partial a}\right) \quad .$$

The cross terms (covariance terms) in eq. 2.2-19 can be very important if the values taken by the parameters are highly interdependent. An example in which this happens to be the case is given in part D below.

C. Covergence

Criteria for convergence will depend on what one wishes to get out of the calculation. A simple minded approach, and that used in this work, is to iterate until no significant improvement is made. This could be done by comparing the change in S between iterations j and j+1 with a suitably chosen convergence parameter to decide whether to perform iteration j+2. However, we can write

$$S(j+1) - S(j) \cong - S_a \Delta a - S_b \Delta b - S_c \Delta c$$

by dropping the second-order terms in eq. 2.2-4. Thus, we can instead make the comparison at the end of iteration j.

It may, of course, happen that the iteration diverges. In such cases, S(j+1) - S(j) as obtained above will become positive. The computer can be directed to terminate the current set of iterations if this happens. We should note, however, that in difficult problems, such as the fit to the R1 and R2 product-ratio data, a temporary increase in S may occasionally be necessary to make ultimately beneficial adjustments in the parameters, so one would want S(j+1) - S(j) to be larger than a predetermined quantity before allowing the termination of the iteration.

In fitting the R1 and R2 product-ratio data, we have included only eight of the most sensitive parameters in the iterative optimization (see p. 207). Unfortunately, stability problems, as partially explained in part D below, were sufficiently severe that it was not in general possible to begin by optimizing all eight simultaneously. We therefore worked with smaller sets of parameters until the fit was fairly refined. This was done by preparing a series of control cards, each specifying a set of parameters to be optimized, the maximum number of iterations to be done on that set (typically five) and a convergence parameter. When we had $0 > S(j+1) - S(j) >$ convergence parameter, the computer was instructed to discontinue the current set of iterations and read in the next control card, if any. But if S(j+1) - S(j) became 'large' and positive, the run was aborted. This procedure allowed us to gradually work up to iterations on the full parameter set without committing ourselves to an unnecessarily lengthy and time-consuming series of iterations.

D. An Example Concerning Parameterization

Perhaps it will be helpful to go through an example illustrating the implementation of the least-squares formalism. The example chosen will also enable us to make a point of potential interest concerning the parameterization of the Arrhenius equation.

Suppose we have obtained a series of N measurements of a rate constant k at various temperatures which we wish to fit to the Arrhenius equation:

$$k_i = ae^{-b/RT_i}, \quad i = 1,N \tag{2.2-20}$$

If we take a^o and b^o as initial approximations to the parameters, we can write*

$$F_i^o \equiv k_i - a^o e^{-b^o/RT_i} .$$

The derivatives with respect to the parameters are:

$$F_{a_i} = -e^{-b^o/RT_i} ; \qquad F_{b_i} = \frac{a^o}{RT_i} e^{-b^o/RT_i} ;$$

and those with respect to the observables are:

$$F_{k_i} = 1 ; \qquad F_{T_i} = -\frac{a^o b^o}{RT_i^2} e^{-b^o/RT_i} .$$

Let us further suppose that the measurements of k_i are uncertain by ± 10 percent and that our constant temperature bath is good to ± 0.1°. If we then choose $\sigma_o = 0.1$, we have that

$$L_i = k_i^2 + (F_{T_i})^2 .$$

---

[*] We could of course have taken F_i^o to be the negative of that given here.

These quantities may then be assembled according to the recipe of eqs. 2.2-12.

As a 2 x 2 matrix is trivial to invert, let's carry the solution through symbolically. Using the notation of part B above, the inverse matrix is

$$\underset{\sim}{S2}^{-1} = \begin{pmatrix} \underset{\sim}{S2}_{bb}/\Delta & -\underset{\sim}{S2}_{ba}/\Delta \\ -\underset{\sim}{S2}_{ab}/\Delta & \underset{\sim}{S2}_{aa}/\Delta \end{pmatrix} ,$$

where

$$\Delta = (\underset{\sim}{S2}_{aa})\,(\underset{\sim}{S2}_{bb}) - (\underset{\sim}{S2}_{ab})^2 \quad . \qquad (2.2\text{-}21)$$

(Remember that by symmetry $\underset{\sim}{S2}_{ab} = \underset{\sim}{S2}_{ba}$). The correction quantities are then found to be:

$$\begin{aligned} \Delta a &= \frac{(\underset{\sim}{S2}_{bb})(\underset{\sim}{S1}_{a}) - (\underset{\sim}{S2}_{ab})(\underset{\sim}{S1}_{b})}{\Delta} \\ \Delta b &= \frac{(\underset{\sim}{S2}_{aa})(\underset{\sim}{S1}_{b}) - (\underset{\sim}{S2}_{ab})(\underset{\sim}{S1}_{a})}{\Delta} \end{aligned} \qquad (2.2\text{-}22)$$

The interesting point about this result is that the parameters in the Arrhenius equation are such that

$$(\underset{\sim}{S2}_{ab})^2 \approx (\underset{\sim}{S2}_{aa})(\underset{\sim}{S2}_{bb}) \quad .$$

That is, the quantity Δ very nearly vanishes.

The near vanishing of Δ arises from the strong coupling between the two parameters of the Arrhenius equation. The existence of this coupling means that in trying to improve a given set of parameters, it simply will not do to optimize the fit with respect to one, while holding the other constant, then to optimize the second, and so on; one must adjust both parameters simultaneously by making properly correlated changes.

To see the correctness of this reasoning, suppose that the parameters are uncorrelated--that $(\underset{\sim}{S2}_{aa})(\underset{\sim}{S2}_{bb}) >> (\underset{\sim}{S2}_{ab})^2$. Eqs. 2. 2-22 would then simplify to

$$\Delta a = \underset{\sim}{S1}_{a}/\underset{\sim}{S2}_{aa} \;;$$

$$\Delta b = \underset{\sim}{S1}_{b}/\underset{\sim}{S2}_{bb} \;;$$

and it would be possible to optimize the parameters sequentially.

The reason this subject interests us is that, in problems of any size, strong correlation between various parameters will lead to near cancellation of terms involved in the matrix inversion and thus will aggravate any problems of numerical stability. As a result, a series of iterations which is apparently converging smoothly may simply 'jump the tracks' and become hopelessly lost. Each of the arabic-letter parameters for the product ratios R1 and R2 (see eqs. 2. 1-4, p. 203) can be described in terms of a composite activation energy and a composite preexponential factor. When such a description was used in the early stages of the mechanistic calculations, convergence was at best highly erratic. Fortunately, a simple way was found to rewrite the Arrhenius equation with 'decoupled' parameters, whereupon smooth convergence was generally obtained (see part C above). The computationally preferred form of the Arrhenius equation for a rate constant k is

$$k = a' e^{-b(1/RT - 1/R\overline{T})} , \qquad (2.2\text{-}23)$$

where $\overline{T}$ is a value of T near the middle of the range of temperatures investigated experimentally, a' is the least-squares estimate of k at $T = \overline{T}$, and b is again the Arrhenius activation energy.

It should be noted that the least-squares treatment of the unmodified Arrhenius equation (eq. 2.2-20) outlined in this subsection is perfectly adequate for that simple two-parameter problem. Thesis equations 1.7-5 and 1.8-11 were determined in that way. For the many-parameter problem of the present Section, however, the parameterization employed in eq. 2.2-23 had to be used.

We can show very simply that the new parameters are at most weakly coupled with the aid of Fig. 19, in which hypothetical rate-constant data are plotted against 1/T according to the well-known logarithmic form of the Arrhenius equation. The parameter b is of course related to the slope of the best straight line through the data, while a is related to the left-intercept.

The reader at this point is to play the role of a digital computer in attempting to correct an initial approximation (e.g., the straight line of Fig. 19) by adjusting one parameter at a time. The test is then this: if an initial, rather poor, approximation can be substantially improved in this manner, the parameters are only weakly coupled; otherwise, strong coupling is indicated.

Let us begin with the Arrhenius equation as it is usually written. The reader, presumably employing a clear plastic rule, is directed to adjust the initial line so as to reduce the sum of the squares of the deviations by changing the slope while keeping the intercept constant, or vice-versa.

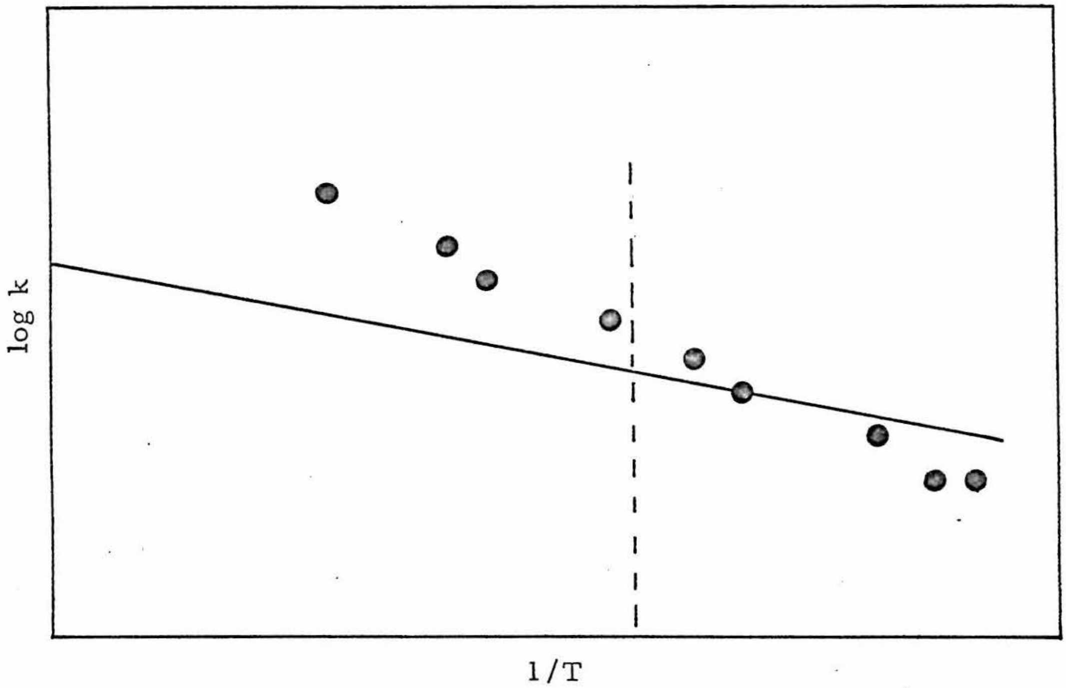


Figure 19. Hypothetical rate data illustrating correlation of parameters in the Arrhenius equation.

The reader will quickly notice that whether the slope or the intercept is varied first, the fit is improved at least to the extent that the new line intersects the data near the center of the temperature range. On attempting to adjust the other parameter, however, things get a little sticky; no clear improvement can be made.

A more complicated operation consisting of a simultaneously varying slope and left-intercept is clearly needed.

Let's try now with the modified Arrhenius equation, eq. 2. 2-23. The parameters are now effectively the slope and the intercept of the straight line with the vertical dotted line (which marks the approximate center of the temperature range). Note that the solid line moves in the same way in varying this intercept as it did in varying the left-intercept. On varying the slope, however, we now pivot about the intercept with the dotted line instead of about the left-intercept; and this makes all the difference in the world. Optimizing the new parameters sequentially leads to smooth convergence to a line which fits the data well. That is, the new parameters are substantially uncorrelated.

Accordingly, arabic-letter parameters arising in the mechanistic description of this Section have been described according to eq. 2. 2-23 rather than eq. 2. 2-20, where $\overline{T}$ has uniformly been taken to be 100° C.

The fact that the normal Arrhenius equation parameters are strongly correlated leads to a result well known to chemical kineticists, namely, that the standard deviations in the preexponential factor and the activation energy one estimates from a given set of data are quite large compared to the uncertainty in the rate measurements themselves. This again reflects the near vanishing of the quantity Δ of eq. 2. 2-21 and the corresponding importance of the covariance term σ_{ab} of eqs. 2. 2-17 in expressions based on eq. 2. 2-19.

3. Application of the Least-Squares Formalism to Thermal Decomposition of the Peresters in 1,4-Cyclohexadiene

The formalism of subsection 2 dealt with a situation in which N observations on a single product ratio were to be fit to a theoretical expression. In this work, we are interested in simultaneously fitting N observations on each of two product ratios, R1 ≡ % yield **5**/% yield **10** and R2 ≡ % yield **6**/% yield **5**.

Therefore we generalize eq. 2.2-16 to

$$S = \sum_{i=1}^{N} \left\{ \frac{(F1_i^{o})^2}{L1_i} + \frac{(F2_i^{o})^2}{L2_i} \right\} \qquad (2.3\text{-}1)$$

where $L1_i$ and $L2_i$ are the weighting factors for the various observations (see below) and

$$\begin{aligned} F1_i^{o} &= R1_i^{calc} - R1_1^{obs} \ ; \\ F2_i^{o} &= R2_i^{calc} - R2_i^{obs} \ . \end{aligned} \qquad (2.3\text{-}2)$$

Each summation in eqs. 2.2-12 (the normal equations) will contain two components, one for R1 and the other for R2.

Evaluation of the necessary derivatives of $F1^{o}$ and $F2^{o}$ with respect to the parameters consists of working out expressions for the derivatives of $R1^{calc}$ and $R2^{calc}$. As was previously noted, we shall include in the optimization procedure only the arabic-letter parameters E--I of eqs. 2.1-4. Each of these, however, requires two parameters for description via a modified Arrhenius equation (eq. 2.2-23). Thus, if E2 is the activation energy for the composite parameter E, we need an expression for $(\partial R1^{calc}/\partial E2)$. As E2 does not appear explicitly in any of our mechanistic equations, we can write

$$\begin{aligned}\left(\frac{\partial R1^{calc}}{\partial E2}\right) &= \left(\frac{\partial R1^{calc}}{\partial E}\right)\left(\frac{\partial E}{\partial E2}\right)\\ &= \left\{\left(\frac{\partial Y5}{\partial E}\right)/Y10 - R1^{calc}\left(\frac{\partial Y10}{\partial E}\right)/Y10\right\}\left(\frac{\partial E}{\partial E2}\right) ,\end{aligned} \tag{2.3-3}$$

where Y5 represents the theoretical expression for % yield of ring-opened hydrocarbon $\underset{\frown}{5}$ (i.e., eq. 2.1-1).

Thus, we need to work out expressions for the derivatives of eqs. 2.1-1—2.1-3 with respect to the arabic-letter parameters, E, F, G, H, and I. Because of the complexity of those equations, this task is not trivial. The principal complication arises from the appearance of the variables W and X in the product-yield expressions. Thus, the variation of an arabic-letter parameter will cause changes in the calculated product yields not only in accordance with the incorporation of a parameter into the product yield expressions, but also through the effect of changes in that parameter on the values of the variables W and X.

For example, the expression for $(\partial Y5/\partial E)$ involves the following terms:

$$\begin{aligned}\left(\frac{\partial Y5}{\partial E}\right)_{O,P'} = \left(\frac{\partial Y5}{\partial E}\right)_{O,P',V} &+ \left(\frac{\partial Y5}{\partial W}\right)_{O,P,V'}\left(\frac{\partial W}{\partial E}\right)_{O,P',V}\\ &+ \left(\frac{\partial Y5}{\partial X}\right)_{O,P,V'}\left(\frac{\partial X}{\partial E}\right)_{O,P',V}\end{aligned} \tag{2.3-4}$$

The subscripts indicate quantities held constant in the partial differentiations, according to the following pattern: the subscript O to each partial means that all the observables (the reaction temperature, the perester concentration, the 1,4-cyclohexadiene concentration) are held constant; P refers to the parameters, P' meaning that all parameters are held constant except the one by which differentiation is indicated; similarly, V refers to the variables W and X. Thus, the $(\partial Y5/\partial E)$ on the left-hand side is the quantity desired for substitution into eq. 2.3-3, whereas that on the right-hand side is obtained from eq. 2.1-1 on the assumption that W and X are independent of E; its value is $100\alpha \int_0^1 W{*}(ZH)\,dz$.

The terms $(\partial Y5/\partial W)$ and $(\partial Y5/\partial X)$ are similarly obtained by differentiation of eq. 2.1-1. More difficult to come by are the partials $(\partial W/\partial E)$ and $(\partial X/\partial E)$. As we do not have explicit expressions for W and X we must employ implicit differentiation. For convenience, let us call eq. 2.1-9 the W equation, or WEQ, and eq. 2.1-10, XEQ. Differentiating WEQ by E we again get three terms:

$$\left(\frac{\partial WEQ}{\partial E}\right)_{O,P'} = \left(\frac{\partial WEQ}{\partial E}\right)_{O,P',V} + \left(\frac{\partial WEQ}{\partial W}\right)_{O,P,V'}\left(\frac{\partial W}{\partial E}\right)_{O,P',V} + \left(\frac{\partial WEQ}{\partial X}\right)_{O,P,V'}\left(\frac{\partial X}{\partial E}\right)_{O,P',V} = 0 \qquad (2.3\text{-}5)$$

This equation is similar in form to eq. 2.3-4 for $(\partial Y5/\partial E)$, except that we know the sum of the terms to be zero because we originally had WEQ = 0. The partials $(\partial WEQ/\partial E)_{O,P',V}$, $(\partial WEQ/\partial W)$ and $(\partial WEQ/\partial X)$ simply come out to be numbers when current values of the various kinds of quantities are plugged into the derived expressions; $(\partial W/\partial E)$ and $(\partial X/\partial E)$ are unknown. Differentiating XEQ by E gives a second equation which is also linear in the unknowns $(\partial W/\partial E)$ and $(\partial X/\partial E)$. Combination of the two equations then yields the values of the unknowns which are to be substituted into eq. 2.3-4 and a host of sister equations which concern other product yields and other parameters.

We also require deviatives of $F1^o$ and $F2^o$ with respect to the observables in order to form the weighting factors L1 and L2. By analogy to eq. 2.2-14, we have

$$L1_i = (1/\sigma_o)^2 \left\{ \left(\sigma_{R1_i^{obs}}\right)^2 + \left(\frac{\partial R1_i^{calc}}{\partial ZH}\right)^2 \sigma_{ZH_i}^{\;2} + \left(\frac{\partial R1_i^{calc}}{\partial T}\right)^2 \sigma_{T_i}^{\;2} \right\} , \tag{2.3-6}$$

and similarly for $L2_i$. As noted previously, σ_o is to be chosen purely for numerical convenience; here we have taken it to be 0.05.

We have assumed that $\sigma_{R1_i^{obs}}$ and $\sigma_{R2_i^{obs}}$ are given by equations such as eq. 2.3-7,

$$\sigma_{R1_i^{obs}} = s_i(R1_i^{obs}) \tag{2.3-7}$$

where s_i expresses the relative uncertainty in $R1_i^{obs}$. For the R1 ratios, we have taken $s_i = 0.05$.

For the R2 ratios, however, a range of s_i values has been adopted as appropriate to varying conditions of vpc resolution. For runs in which the perester employed is the ring-closed 2, $R2^{obs}$ is not greatly different from unity. The result is that relative areas of the neighboring peaks due to ring-opened 5 and ring-closed 6 (the latter at 1.25 x the retention time of the former) could be measured with considerably better precision than the well-separated peaks due to 5 and 10 (relative retention time ~ 2.4) that determine the R1 ratios; for these runs, s_i was taken to be 0.03. On the other hand, the $R2^{obs}$ starting from ring-opened perester 1 are typically on the order of 0.02. An attenuation change following the appearance of the peak due to 5 was therefore required to give measureable peak heights for 6. The result, for the data of Table 1, was that triangulation had to be used rather than electronic integration. Even this was compromised by uncertainty as to the location of the base line caused by the presence of a peak attributed to the diphenylbutadiene 13 immediately following the peak due to 6. Thus, for these runs we have taken $s_i = 0.075$. In contrast, the use of retention times for 5 and 6 for the $R2^{obs}$ of Tables 4 and 5 about an order of magnitude longer than those employed in Table 1 (~40 min vs. 4 min) allowed unambiguous determination of the base line for computation of areas due to 6: for these runs, we have taken $s_i = 0.05$.

Uncertainty in 1,4-cyclohexadiene concentrations also can cause calculated product ratios to deviate from the observed quantities. This source of error is taken into account through the second term in braces in eq. 2.3-6, where we have taken*

$$\sigma_{ZH_i} = 0.05 + 0.1(P)_{o_i} \text{ (molar)} \quad . \qquad (2.3\text{-}8)$$

The motivation for the assumed dependence on the initial perester concentrations is that lack of precise knowledge of the quantity of 1,4-cyclohexadiene consumed in the reaction will make the instantaneous ZH concentrations employed in the mechanistic equations uncertain over and above the uncertainty incurred in making up the reaction mixtures.

Reaction temperatures were assumed to be good to ± 1° (i.e., $\sigma_{T_i} = 1.0$) except for runs at 70° for perester 2 (Table 2) and 150° for perester 1 (Table 1) where warm-up times of ~1 min are comparable to reaction half-lives calculated from activation parameters for perester decomposition discussed below (p. 235). In the latter cases, we have taken $\sigma_{T_i} = 3$. However, the actual calculations showed that in no case did the assumed uncertainty in the reaction temperature play a significant role.

For completeness, eq. 2.3-6 should also include a term arising from uncertainty in the initial perester concentration. The omission was originally an oversight. Fortunately, this is not a serious matter;

---

*Because thermal expansion of reaction mixtures has been taken into account approximately, true initial 1,4-cyclohexadiene concentrations may differ from those listed in Tables 1, 2, 4, 5, and 6 by considerably more than 0.05 M. But this would be a systematic error which would simply serve to slightly distort the calculated value for the parameter E, which multiplies the cyclohexadiene concentrations; this circumstance should not be allowed to play havoc with the relative weights of the various product-ratio observations.

if the initial perester concentrations are assumed to be good to at least ± 10%, one can easily show that the $L2_i$ would be increased by not more than 10% for initial conditions investigated in this work, and that the correction to the $L1_i$ would be infinitesimal.

According to eq. 2.3-6, we also need expressions such as $(\partial R1^{calc}/\partial ZH)$ and $(\partial R1^{calc}/\partial T)$. Derivatives with respect to the cyclohexadiene concentration were obtained by the approach outlined in eqs. 2.3-4 and 2.3-5. The reaction temperature comes into our mechanistic equations implicitly through the arabic-letter parameters A–I and through k_o, the rate constant for perester decomposition. We already have available the derivatives of $R1^{calc}$ and $R2^{calc}$ with respect to the parameters E–I. This information, plus derivatives with respect to k_o, allows us to assemble $(\partial R1_i^{calc}/\partial T)$ and $(\partial R2_i^{calc}/\partial T)$; the product ratios are sufficiently insensitive to the parameters A–D that the dependence on these quantities need not be included.

In view of the complexity of the starting eqs. 2.1-1 through 2.1-10, working out expressions for all the required partial derivatives would have been a prodigious undertaking. For example, the quantity of interest is in one case buried in the denominator of one component of a term to the one-half power which is in the denominator of a term which is in the denominator of the main expression. Fortunately, however, there is available a computer system known as FORMAC (for formula manipulation compiler) which is capable of performing a useful variety of operations on symbolic expressions (102). In this work, FORMAC's differentiation capability was employed to generate expressions for the desired partial derivatives.

The procedure essentially involved writing a control program containing instructions to read in expressions from punched cards, to differentiate those expressions with respect to a given variable, and to print out and punch out the results. The expressions read in were the integrands of eqs. 2.1-1—2.1-3, eqs. 2.1-5 and 2.1-6 for S and T, and the W and X equations, eqs. 2.1-9 and 2.1-10. Our job was then essentially reduced to seeing that numerical values for the component expressions were properly combined, as in eqs. 3.2-3—3.2-5, in the main product-ratio program.

Unfortunately, FORMAC puts out results in a form which seems calculated to require the maximum execution time on the computer. For example, A/B comes out as $A*B^{-1}$, and the latter takes ~ 20 times as long to execute on the IBM 7094. Therefore, it was necessary to recode the expressions generated by FORMAC, during which frequently recurring subexpressions were given symbolic names so as to be calculated only once (per integration mesh point, per data point, per iteration). The recoding reduced the execution time from ~ 25 sec to 4–5 sec per iteration.

The necessity of recoding the FORMAC-generated expressions is a minor objection, however; certainly the availability of FORMAC was the determining factor in the decision to pursue the mechanistic description to the present level of sophistication.

4. Results and Conclusions of the Least-Squares Optimization

A. Selection of Activation Parameters for Perester Decomposition

We now must settle on values to be used for the rate constants for thermal decomposition of the peresters **1** and **2**. As noted previously, only a single rate-constant value is available for each of the peresters. Therefore, we shall have to make use of the relationship of structure to activation parameters for perester decomposition discussed in subsection 3 of Section One.

In a careful infrared study, Howden found the rate constant for thermal decomposition of ring-opened perester **1** in chlorobenzene at 109.7° to be 7.71×10^{-5} sec^{-1}. This result is the average of two determinations which differed by only 2%. The solutions were 0.1 M in perester and 0.25 M in iodine (added to prevent radical-induced decomposition). Although first-order kinetics was observed in each of the two runs for somewhat less than two half-lives (after which the rate of decomposition substantially increased), the initial first-order behavior appears to reflect simple thermal decomposition of the perester.

The half-life of 150 min computed from Howden's rate constant agrees well with those of other primary peresters quoted in Table 13, p. 51. It seems reasonable to assume that the enthalpy of activation for normal homolytic decomposition of **1** is similar to the values of 35.3 and 35.0 kcal/mole quoted in Table 13 for two long-chain primary peresters. However, we must remember that k_o for perester **1** also includes the rate of molecule-induced decomposition (Section One, subsection 6). From reported enthalpies of activation for Koenig and Martin's *ortho*-diphenylvinyl perbenzoate, 26.4 kcal/mole, and for *t*-butyl perbenzoate itself, 34.2 kcal/mole, we expect the rate of molecule-induced decomposition of 1 to increase less rapidly with increasing temperature than the rate of normal homolytic decomposition. The difference of ~8 kcal/mole in the enthalpies of activation of the model perbenzoates would suggest, if applicable here, that the fraction of molecule-induced decomposition at 150° should be only about one-third that at 99°. This prediction appears to be too extreme to be compatible with the scattered (though admittedly not very accurate) determinations of the yield of the lactone 23 reported in Table 1, p. 28.

We have therefore assumed enthalpies of activation of 35.2 kcal/mole for normal homolytic decomposition of 1 and 31.2 kcal/mole for molecule-induced decomposition. A compromise value of 34.3 kcal/mole is then dictated by the relative importance of the two kinds of processes in the temperature range of interest and an entropy of activation of 11.70 e.u. is required to fit the half-life of 150 min at 110°. These values have been employed in the calculations reported below.

For the ring-closed perester 2, only a rough rate determination is available. The absorbance data plotted in Fig. 20 were obtained on a cumene solution which was initially 0.10 M in 2 and which was open to the air and was maintained at approximately 23° C in a thermostated room. The absorbance measurements were obtained by intermittantly scanning a region containing the carbonyl stretching band of 2 using a Perkin-Elmer Infracord Model 237.

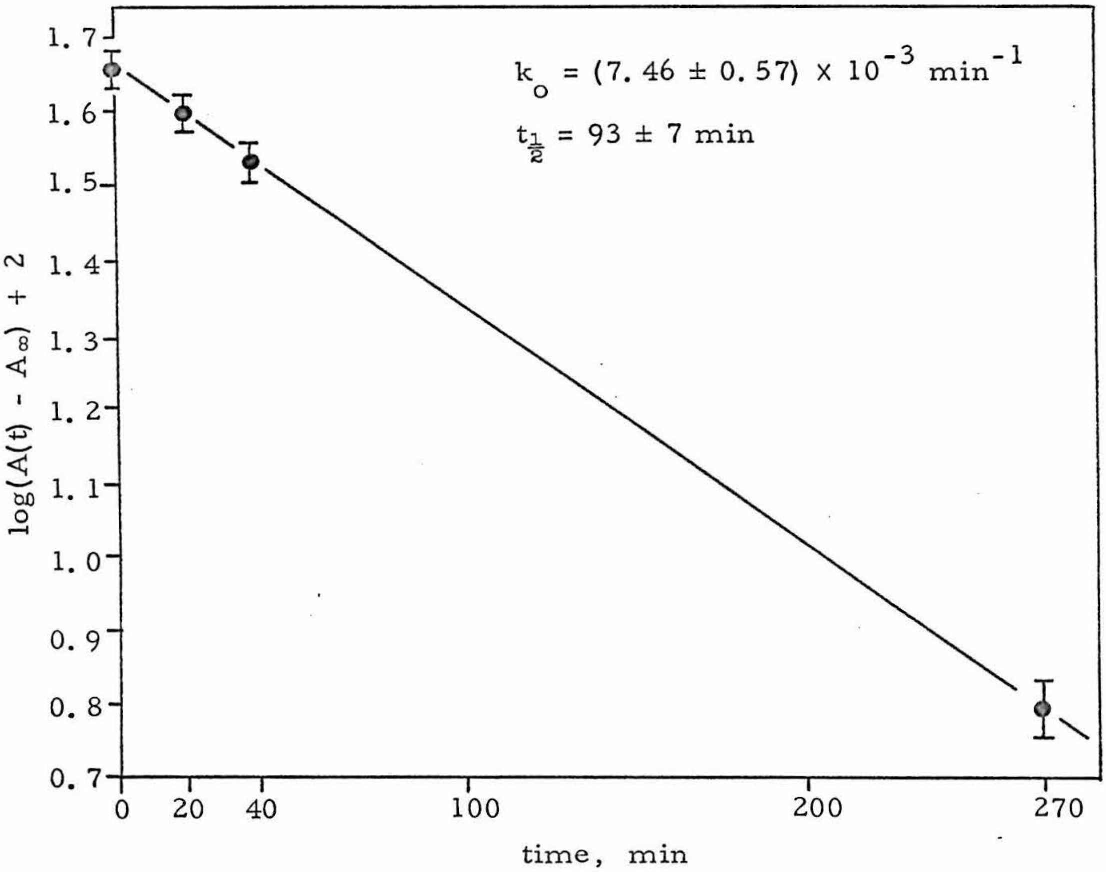


Figure 20. Decomposition of t-butyl diphenylcyclopropylacetate (0.10 M) in cumene at 23 ± 1° in the presence of air; A_∞, obtained for 18 hr reaction time, was 0.024.

Veteran observers will recognize that the conditions described here are more appropriate for an order-of-magnitude estimation than for the careful determination of a rate constant needed for quantitative analysis of experimental data. Indeed, the purpose of the rate measurement was simply to enable us to estimate reaction times corresponding to approximately 10 perester-decomposition half-lives for use in the degassed thermal decompositions reported in Tables 2 and 6.

A least-squares treatment gives $k_o = 1.24 \times 10^{-4}$ sec^{-1} and $t_{\frac{1}{2}} = 93 \pm 7$ min at 23°. The estimated uncertainty in the half-life reflects assumed uncertainties of 5–10% in the absorbance data, as indicated by error bars in Fig. 20. For comparison, extrapolated half-lives at 23° are 90 min for *t*-butyl triphenylperacetate and 4100 min for *t*-butyl diphenylperacetate. Activation parameters for these peresters are 24.1 and 25.0 kcal/mole, respectively (see Table 13). Clearly, the rate of decomposition of **2** is very similar to that of *t*-butyl triphenylperacetate. If we take the enthalpy of activation for decomposition of **2** to be 24.5 kcal/mole, the half-life of 93 min at 23° requires an entropy of activation of 6.38 e.u.

Actually, we are not rigorously wedded to the half-life estimate of 93 min, for the uncertainty of ± 7 min which comes out of the least-squares treatment is only part of the story. For example, the true reaction temperature might have been one degree higher or lower than was read off the wall thermostat; the associated error in the half-life at 23° would be ± 15%. Moreover, solvent effects on the rate of decomposition are conceivable, though of uncertain magnitude. Finally, the spacing of the absorbance measurements in time is unfortunate. It is not unusual to have first-order kinetic plots depart from linearity well before three half-lives have been reached; Howden's rate determinations on perester **1** constitute one such example. Thus, it would be dangerous to rely heavily on the measurement at 270 min. On repetition of the least-squares analysis using only the first three points, a half-life of 115 ± 43 min was found. We take this to mean that we are not likely to be off by orders of magnitude in perester-decomposition half-life, but that the 93 ± 7 min may be a bit too restrictive.

A possible experimental objection, the presence of air during the decomposition, is probably unimportant. Oxygen would be expected to influence the disposition of radical intermediates, but not the rate of their formation in the absence of radical-chain processes.

As a result of these considerations, a preliminary series of least-squares calculations was carried out employing a range of decomposition half-lives for **2** at 23°. The average deviations between calculated and observed product ratios R1 and R2 were found to be 7.4%, 7.0%, 6.9%, and 7.2% for assumed decomposition half-lives of 75, 93, 112, and 137 min, respectively.* Thus, (a) the quality of the fit to the ratio data is reasonably insensitive to the half-life of **2** at 23° and (b) the value which optimizes the preliminary fit is not very different from that determined experimentally.

Especially encouraging, as we shall see in detail below, is that the reaction mechanism is able to account for the observation that the ratios **6**:**5** are typically 0.5 starting from **2** (Table 2), but only about 0.02 starting from **1** (Table 1) and for a variation of a factor of 300 between maximum and minimum values. Thus, the basically satisfactory character of the fit frees us from any real worries as to the basic adequacy of the assumed reaction mechanism. Our main concern will therefore be to see whether the product ratios can universally be correlated within reasonable experimental error or whether the presence of systematic deviations between calculated and observed product ratios points to areas in which the reaction mechanism is not fully

---

*The quantity cited here is AVDEV, eq. 2.4-3, p. 248.

satisfactory. Therefore, a half-life at 23° of 112 min has been adopted so that deviations between calculated and observed ratios need not be artificially inflated by simple application of an admittedly crude rate measurement for 2. Accordingly, values of 24.5 kcal/mole for the enthalpy of activation, and 6.00 e.u. for the entropy of activation, for decomposition of 2 have been used in the calculations reported below.

B. Selection of Values for Non-Iteratively-Improved Parameters

We have, for a number of reasons, elected to determine only certain of the parameters appearing in the mechanistic equations via least-squares optimization of the fit to the product-ratio data. The purpose of this section is to explain the values adopted for the remaining, non-iteratively improved parameters.

(1). The parameter $A \equiv \omega/\alpha$ gives the ratio of decomposition events for ring-opened perester 1 which proceed via molecule-induced decomposition to those which involve normal homolytic decomposition but which bypass cage reactions to give a kinetically-free radical pair consisting of a hydrocarbon radical (either ring-opened 3 or ring-closed 4) and a t-butoxy radical. We have taken the value of A to be 0.25 at 100° and have assumed a composite activation energy of -4 kcal/mole. These values are intended to roughly account for the average yield of the lactone 23 of approximately 15% for determinations reported in Table 1 and for the expected lesser importance of molecule-induced decomposition at higher temperatures (p. 236).

Of course, whenever the starting perester is ring-closed 2, A is set to zero.

Preliminary calculations indicated that the fit to the product-ratio data would be improved by choosing A to be smaller than has been done. But it would be improper to allow A to be so chosen because a substantial value is required to account for the formation of the lactone 23, something the product-ratio program knows nothing about.

Incidentally, the values of α employed in all of the calculations are recorded in Table 17, p. 298. These values were chosen with reference to (a) the ratios ω/α, (b) smoothed yields of cage-reaction products which determine the parameter β, and (c) the normalization $\alpha + \beta + \omega = 1$.

(2). The parameter $B \equiv k_5k_d/k_6k_3^{\frac{1}{2}}$ has been assigned a composite preexponential factor of unity and a composite activation energy of 12 kcal/mole in most of the calculations reported below. As noted previously, B controls the competition between hydrogen abstraction by lactonyl radicals (22) from 1,4-cyclohexadiene (k_5) and from cyclohexadienyl radical (k_6). This parameterization, which forces the hydrogen abstraction to occur essentially totally from cyclohexadienyl radical, seemed quite reasonable when we mistakenly had $B \equiv k_5/k_6$,

---

[*] Yields of B quoted in Table 2 apparently represent the combined yields of the cage combination product (ring-closed ether 15), the cage disproportionation product (the methylenecyclopropane 16), and (isomeric) tetrahydronaphthalenes (see pp. 71, 80). Values of β for these reactions were obtained by subtracting calculated yields of tetrahydronaphthalene (see Table 17) from observed yields of B.

but now appears to be indefensible. We shall therefore explore, under heading F, p. 268, the consequences of adopting reasonable values of B.

(3). The parameter $C \equiv k_7 k_d / k_b^{\odot} k_3$ controls the extent of reaction of ring-closed radical **4** with ring-cyclized radical **9**. One can argue, from the manner in which the four radical-radical rate constants are arranged in the definition, that the expected value of C should be unity. For example, if reaction of ring-closed **4** with ring-cyclized **9** (k_7) is slower than reaction of **4** with cyclohexadienyl radical ($k_b^{\odot}$), one might also expect that reaction of **9** with **9** (k_3) would be slower than reaction of **9** with cyclohexadienyl radical (k_d) by about the same amount. If this were rigorously true, we would have C = 1. We have taken C = 0 in Calculation 1, but explore nonzero values in subsequent calculations.

(4). The parameter $D \equiv k_r / k_3^{\frac{1}{2}}$ controls the decyclization of ring-cyclized **9** to ring-opened **3**. We have previously argued that decyclization must be a minor factor under conditions employed in this work (pp. 114, 115). Therefore, we have taken D = 0 for the present, but will later determine how large a value can be accommodated by the data.

As the effect of decyclization on the product ratio R1 should be most pronounced at the lowest initial perester concentrations investigated (p. 114) we have assigned RWT1 = 0 for a number of such runs (see Table 17). This will insure that we do not prejudice the calculated values of R1 at lower perester concentrations, should decyclization be detectable with the present data, by obliging the computer program to distribute any inability to fit the R1 ratios over runs where the mechanistic assumption of no reversibility of the ring cyclization is really inadequate. In this way, systematic errors in the $R1^{calc}$ at low perester concentrations will give a reliable measure of how large D might be.

(5). The parameters γ, δ, and ϵ: The parameter γ describes the probability of getting 10 plus tetrahydronaphthalene, rather than dimer, from the reaction of a pair of ring-cyclized radicals. Similarly, δ and ϵ describe what happens upon reaction of a ring-cyclized radical with a cyclohexadienyl radical (see Chart 7, p. 198). We have previously argued that the average efficiency of conversion of 9 to dihydronaphthalene 10 must be about 40% for reaction in 1,4-cyclohexadiene (pp. 122, 123). As our calculations indicate that reaction of 9 with a cyclohexadienyl radical is a good deal more probable than reaction of a pair of ring-cyclized radicals, this means that we must have $\delta \sim 0.4$. Actually, but equivalently, the values $\frac{1}{2}\gamma = 0.30$ and $\delta = 0.42$ we have routinely employed were chosen to give the predicted yields of ring-opened hydrocarbon 5 approximately correctly. With these values, the predicted yields of 5 may be too high or too low, on the average, but not by more than 3% in any calculation reported. This insures that values of $E = k_a^{⌬}/k_r$ found in the calculations (about 0.14 at 100°) are realistic.

We have assumed that δ and γ are not temperature dependent. As, for example, the ratio of disproportionation to combination decreases from 0.34 to -191° to 0.15 at 85° for ethyl radicals in isooctane (103), some comment on the validity of this assumption is in order. To begin with, even should δ and γ vary smoothly by a factor of two between 0 and 150°, the ability of the mechanistic scheme to correlate the product *ratios* would not be seriously impaired. The reason is that the calculated values of R1 essentially depend on the ratio E/δ, so that an error in the assumed temperature dependence of δ would simply produce a corresponding error in the temperature dependence found for E. At the same time, R2 depends essentially on G/E, so that the temperature dependence of G would also be distorted. On the other hand, calculated yields of the hydrocarbon **5** depend strongly on E but only weakly on δ. Thus, if the latter were appreciably temperature dependent, the calculated yields of **5** should be systematically high at one end of the temperature scale and low at the other. Analysis of the calculated yields of **5** (Table 17, p. 297) reveals that any such systematic error must be small.

(6). The composite activation energies of the parameters F and H have been fixed at 0 and -8 kcal/mole, respectively, for most calculations. The reasoning behind these choices will be considered later.

The parameters subjected to iterative improvement are E, F, G, H, and I. As noted previously, each of these is described by a modified Arrhenius equation (eq. 2.2-23, p. 224) in terms of the value at 100° (optimized for all five) and a composite activation energy (optimized for E, G, and I). Values found for these quantities are recorded in Table 19, p. 303).

C. Tabulation of Quality-of-Fit Quantities and Other Information

A final point before considering in detail the results of the calculations concerns the way in which pertinent information has been recorded. Basically the problem is that the amount of space, time, and money which would be required to record all of the information generated by the computer program for each of the calculations here reported on would be prohibitive. Still, sufficient information must be given to enable the reader to judge the success of various calculations or to explore further points of special interest. The fortunate fact that features which distinguish the various calculations are generally fairly minor ones suggests a compromise procedure in which results are presented at three levels of sophistication:

(1). All calculations are represented in Table 19 (p. 303), where (a) several quantities related to the quality of the fit to the experimental data and (b) the parameter values assumed or found via least-squares optimization are recorded.

(2). For approximately half of the calculations we shall additionally record, for each of the runs, the calculated ratios R1 and/or R2 and the percent relative deviations (RELDEV) between predicted and observed product ratios. This information appears in Table 18 (p. 299).

(3). Finally, Table 17 (p. 296) gives a complete set of information for the calculation which appears to be the most satisfactory regarding the quality of the fit and the soundness of the mechanistic assumptions. This includes experimental information recapitulated for convenience from Tables 1, 2, 4, 5, and 6 in addition to calculated values for a number of quantities of interest besides the ratios R1 and R2.

Tables 17 and 18 have been made vertically compatible so that entries for the same runs (each of which is assigned a run number) can be compared fairly easily. The solid horizontal lines in Tables 17 and 18 serve to compartmentalize the tables into regions corresponding to the earlier data tables; working from the top down, the order of presentation is Table 2, Table 1, Table 6, Table 4, Table 5. Dashed lines between the solid lines in the regions of Tables 2 and 1 separate runs at different temperatures.

We shall now introduce the quality-of-fit quantities tabulated in Table 19. The quantity RUSD, the relative unbiased standard deviation, is defined in eq. 2.4-1,

$$\mathrm{RUSD} = \left[\frac{\sum_{i=1}^{N} \left\{ \left[\frac{R1_i^{\mathrm{calc}} - R1_i^{\mathrm{obs}}}{R1_i^{\mathrm{obs}}} \right]^2 \mathrm{RWT1}_i + \left[\frac{R2_i^{\mathrm{calc}} - R2_i^{\mathrm{obs}}}{R2_i^{\mathrm{obs}}} \right]^2 \mathrm{RWT2}_i \right\}}{\frac{1}{2N} \sum_{i=1}^{N} \{\mathrm{RWT1}_i + \mathrm{RWT2}_i\} \; (2N - 10)} \right]^{\frac{1}{2}} \qquad (2.4\text{-}1)$$

where:

$$\mathrm{RWT1}_i \equiv (R1_i^{\mathrm{obs}})^2 / L1_i \qquad (2.4\text{-}2)$$

and similarly for $\mathrm{RWT2}_i$.

The sum in the numerator of eq. 2.4-1 is simply S (eq. 2.3-1), the sum of the squares of residuals we wish to minimize. This recognition throws light on the meaning of the relative weight quantities

RWT1 and RWT2. Values of these quantities for Calculation 14 are recorded in Table 17. Those for all other calculations were very similar.

The quantity (1/2N) times the sum of the relative weights is simply the average relative weight. The quantity (2N - 10) plays the role of the 'number of observations less one' in the perhaps more familiar relationship for the relative unbiased standard deviation of the mean of a series of measurements on a single quantity. Here, however, we are instructed to divide by the number of degrees of freedom--the number of observations less the number of adjustable parameters (26). The correct value for the latter is uncertain, but 10 will not be too far off. The problem is that there are more than 10 'parameters' which have to be specified for each iteration, but a number of these are obtained other than with reference to the quality of the fit to the product ratio data.

Finally, the expression for RUSD is actually slightly more clever than indicated in eq. 2.4-1 in that provision has been made for omitting certain of the data points for each product ratio from the least-squares fit. Such cases can be recognized in Table 17 by $RWT1_i$ or $RWT2_i = 0$ and are designated for calculations appearing in Table 18 by enclosure of the RELDEV quantities (see below) in parentheses. The result is that certain terms will make no contribution to the sums in eq. 2.4-1 and 2N must be replaced by the actual number of product-ratio observations included in the iterative procedure.

As minimization of RUSD with respect to the parameters differs from the minimization of S only to the (very minor) degree that specific values of the parameters effect the average RWT, RUSD is an appropriate quantity for comparing the success of various calculations. However, the relationship between RUSD and the quality of the fit seems to us less perspicuous than a measure of the average relative deviation between calculated and observed product ratios. Therefore, we shall generally quote[*]

$$\text{AVDEV} = \frac{\sum_{i=1}^{N}\left\{\left|\text{RELDEV R1}_i\right|\text{RWT1}_i + \left|\text{RELDEV R2}_i\right|\text{RWT2}_i\right\}}{\sum_{i=1}^{N}\{\text{RWT1}_i + \text{RWT2}_i\}}, \qquad (2.4\text{-}3)$$

where:

$$\text{RELDEV R1}_i \equiv \left\{\frac{\text{R1}_i^{\text{calc}} - \text{R1}_i^{\text{obs}}}{\text{R1}_i^{\text{obs}}}\right\} \times 100\% \qquad (2.4\text{-}4)$$

and similarly for RELDEV R2_i.

In comparing various calculations, we shall often be interested in the effect of alternative assumptions on how well the ratios R1 and R2 are individually described; or, for the ratios R2, say, whether the

---

[*] There is some question as to whether RWT1 and RWT2 or their square roots should be used as weighting factors in eq. 2.4-3. On first glance, comparison of eqs. 2.4-1 and 2.4-3 supports the latter alternative. However, we believe that the correlation between AVDEV and RUSD will be superior with eq. 2.4-3 defined as is.

average relative deviation reflects principally a lack of success in fitting the data from one or the other of the peresters. That is, a breakdown of AVDEV into various components is potentially of interest. Therefore, we have also recorded in Table 19 the quantities AVDEV R1, AVDEV R2, AVDEV $R1_1$, AVDEV $R1_2$, AVDEV $R2_1$, and AVDEV $R2_2$, where the subscripts to the last four quantities designate the starting perester.

D. Systematic Errors in Calculated or Observed Product Ratios and Suggested Mechanistic Modifications

In assessing the quality of the fit of an assumed relationship to experimental data, two types of considerations are in order. The first is whether the average deviation between calculated and observed quantities is compatible with experimental error. The second is whether such deviations are random, or whether they tend to correlate with environmental factors such as time of observation or details of the experimental procedure.

In the present case, any such correlation should be most apparent in terms of the behavior of the RELDEV quantities (eq. 2.4-4) as a function of reaction temperature or reagent concentrations. Lack of any pattern in the signs and magnitudes of these quantities would suggest that errors of mechanistic oversimplification are less important than experimental errors. Conversely, the presence of sizable systematic errors would point either to inadequate mechanistic assumptions or to systematic errors in the experimental observations.

Calculations based on the simplest interpretation of the mechanistic scheme of Chart 7 do show systematic errors which transcend in magnitude and regularity mere statistical fluctuation. We shall show that allowance for medium effects on the rate 'constants' for certain processes can explain subtleties in the product-ratio data of two kinds which appear to be otherwise inexplicable. One such modification consists in a reciprocal dependence of rate constants for diffusion-controlled processes on the viscosity of the medium, as suggested by theoretical treatments based on hydrodynamic models of the liquid state (e.g., eq. 2.4-7). The other involves the postulation of solvation effects on competitive processes; such effects seem not to have been previously implicated for reactions of nonpolar hydrocarbon radicals.

Deployment of these modifications reduces AVDEV from 6.1% in Calculation 1 to 4.4% in Calculation 15. The figures themselves are not greatly different, but we are inclined to the view that the latter figure represents essentially the accuracy of the data and hence that the improvement is significant.

Consideration of alternatives may appear excessive, but we have wished to put the case as strongly as possible, as a general recognition of such medium effects, and particularly of solvation effects on nonpolar hydrocarbon radicals, would represent a considerable departure from what we feel to be the present view of radical reactions. The present data do not allow the conclusion that medium effects of the two types have been demonstrated experimentally. But this is principally because our experiments have not been designed for that purpose; we have had other concerns. Perhaps the expositions under headings (2) and (3) below will prove sufficiently provocative or suggestive to engender adequate experimental tests.

(1). R1 with Reaction Temperature

The systematic error here is easily detected upon comparison of the fit to the R1 ratios for perester 2 at 70° (runs 9–12) with that for perester 1 at 99° (runs 13–17). We find for Calculation 1 (Table 18) that RELDEV R1[*] averages + 14% for runs 9–12 and - 12% for runs 13–17; the R1 ratios for the two peresters do not mesh smoothly as a function of reaction temperature.

This incompatibility can be at least partially redressed by allowing disproportionation of ring-cyclized 9 with ring-closed 4 to give 10 plus 6. As yields of 6 are derived principally via disproportionation of 4 with cyclohexadienyl radical, and as these yields are more than an order of magnitude larger when 2 is employed as starting perester rather than 1, we must expect that the reaction 4 + 9 will increase yields of 10 to a greater degree at 70° for perester 2 than at 99° for perester 1. As R1 is defined to be % yield 5/% yield 10, the former ratios, which are presently too high, will thus be selectively reduced. Thus, in Calculation 2 (Table 18) we have taken C = 1, which is the expected value according to point (3), page 242. We now find that

---

[*] RELDEV quantities are defined to be (calculated–observed)/observed. Thus, positive RELDEV implies that the calculated result is too high.

RELDEV R1 averages + 13% at 70° and - 11% at 99°. In practice, therefore, reaction of 4 plus 9 is not of much help.

No other mechanistic modifications capable even in principle of repairing the temperature discontinuity come to mind. Neither is it clear why either the 70° or the 99° R1 data should be subject to unusually large experimental error. For the present, the origin of the temperature discontinuity must remain unexplained.

(2). R2 with 1,4-Cyclohexadiene Concentration

Looking again at Calculations 1 and 2, we note that AVDEV for C = 1 (6.82%) is substantially greater than for C = 0 (6.07%). A major reason for the less satisfactory fit is that C = 1 exacerbates already significant systematic deviations which show up in the product ratios R2 from perester 2. We have in runs 1–12 three sets of four experiments featuring a range of 1,4-cyclohexadiene concentrations. Within each of the sets, there is a remarkable tendency to have RELDEV large and positive for the ~ 3 M run and large and negative for the ~ 10 M run, with appropriate gradations in between. The worst case is the set of four runs at 0°, where RELDEV (run 1)–RELDEV (run 4) = 19% in Calculation 1 and 24% in Calculation 2.

This is a sizable systematic error, and one which we must deal with, if we can. Four suggestions may be advanced.

(a). The error might arise from inadequacy of the assumption that formation of products from radicals 3 and 4 is much slower than their interconversion. It can easily be shown that partial trapping of **4** (starting from ring-closed perester **2**) can be described with high accuracy by replacing the expression for $R2^{calc}$ by $R2^{calc} \times (1 + k_a^{\text{⌬}}(ZH)/k_1)$. As the correction term will selectively increase R2 at the higher 1,4-cyclohexadiene concentrations, partial trapping could in principle explain the pattern of the observed deviations. However, using eqs. 1.7-6 (p. 102) and 1.8-12 (p. 138) we can write

$$k_a^{\text{⌬}}/k_1 = 2.3 \times 10^{-2} \exp(1.5/RT) \quad . \qquad (2.4\text{-}5)$$

At 70° this rate-constant ratio has a value of 0.002, so that for ~ 10 M 1,4-cyclohexadiene the multiplicative correction term is 1.02. Thus, the assumption of rapid equilibration of **3** and **4** is valid in the present circumstances.

(b). Our mechanistic scheme assumes that interactions of ring-cyclized radicals in pairs or with cyclohexadienyl radicals may result either in disproportionation or in coupling. In contrast, we have assumed that the reaction of ring-closed radical **4** with cyclohexadienyl radical always yields **6** (plus benzene). Other outcomes are at least possible.

The effect on the R2 ratios of allowing for the alternative disproportionation (to give the methylenecyclopropane **16**) or for coupling is to reduce the systematic error under discussion. That this should be the case can be inferred from the mechanistic equations, but the reasoning is complex and need not concern us here; trial calculations show that incursion of the alternative reactions to the maximum extent allowed by the data is ineffective in redressing the systematic bias. To make headway, we must assume that only one reaction in three of 4 with cyclohexadienyl radical yields 6. As yields of the methylenecyclopropane are substantially independent of the initial perester concentration (see Table 6), this partitioning ratio would imply that the coupling product is formed in approximately twice the yield of 6, or approximately 30% for runs 1–12. This is physically impossible: the deficit in material balances for vpc-detected momomeric products is only about 10% for these runs (p. 123). Moreover, the major portion of this deficit is attributable to dimer formed from ring-cyclized radicals (p. 282).

(c) $R2^{calc}$ goes approximately as the square root of the rate of decomposition of perester (see below, p. 257 , eq. 2.4-11). Thus, a solvent effect which had k_o approximately 60% greater in 1,4-cyclohexadiene than in cyclohexane could repair the systematic nature of the deviations. A solvent effect of this magnitude would probably not be expected, but can not be ruled out in the absence of actual rate measurements. However, such an explanation would be *ad hoc*, and we can rationalize the systematic bias in a perfectly natural way, as in (d).

(d) The rate constant k_D of a diffusion-controlled reaction is often expressed in terms of the so-called Smoluchowski equation,

$$k_D = 4\pi r_{AB} D_{AB} \quad , \tag{2.4-6}$$

where r_{AB} is the sum of the radii of reactants A and B (the collision radius), and $D_{AB} = D_A + D_B$ is the diffusion coefficient for relative motion of A and B. By replacing the diffusion coefficient in eq. 2.4-6 using the Stokes-Einstein relationship for molecular particles (104).

$$D = kT/4\pi\eta r_s \quad ,$$

Debye obtained eq. 2.4-7, where r_s is the hydrodynamic radius of a diffusing particle (which we have taken to be the same for A and B)

$$k_D = 2r_{AB}RT/10^3\eta r_s \qquad (2.4\text{-}7)$$

and η is the viscosity of the medium (105).

Except at very low initial concentrations of perester 1, where a sizable part of the diphenylcyclopropylmethane 6 is formed via abstraction of hydrogen from 1,4-cyclohexadiene, $R2^{calc}$ is roughly proportional to $k_b^{\odot}$, the rate constant for transfer of a hydrogen atom from cyclohexadienyl radical to 4. From eq. 2.4-7, we should therefore expect $R2^{calc}$ to be inversely proportional to the viscosity of the medium if the $k_b^{\odot}$ process is diffusion-controlled, as it may well be.

On the basis of these considerations, the viscosity of 1,4-cyclohexadiene--cyclohexane mixtures was investigated at 20°. As shown in Fig. 21, the viscosity of cyclohexane (0.96(106)) is ~1.6 times that of 1,4-cyclohexadiene (determined to be 0.60). As is usual with binary mixtures, the viscosity of the mixture is quadratic, rather than linear, in the mole (or volume) fractions of the components (107).

The line drawn is for

$$\eta_{\text{mix}} = \eta_{\text{⌬}} + \left(\eta_{\text{⬡}} - \eta_{\text{⌬}}\right) x^2 \quad . \qquad (2.4\text{-}8)$$

where x is the volume fraction of cyclohexane. If we define $\phi \equiv \eta_{\text{⬡}}/\eta_{\text{⌬}}$, we can write

$$\eta_{\text{⬡}}/\eta_{\text{mix}} = \phi / 1 + (\phi - 1)\, x^2 \quad , \qquad (2.4\text{-}9)$$

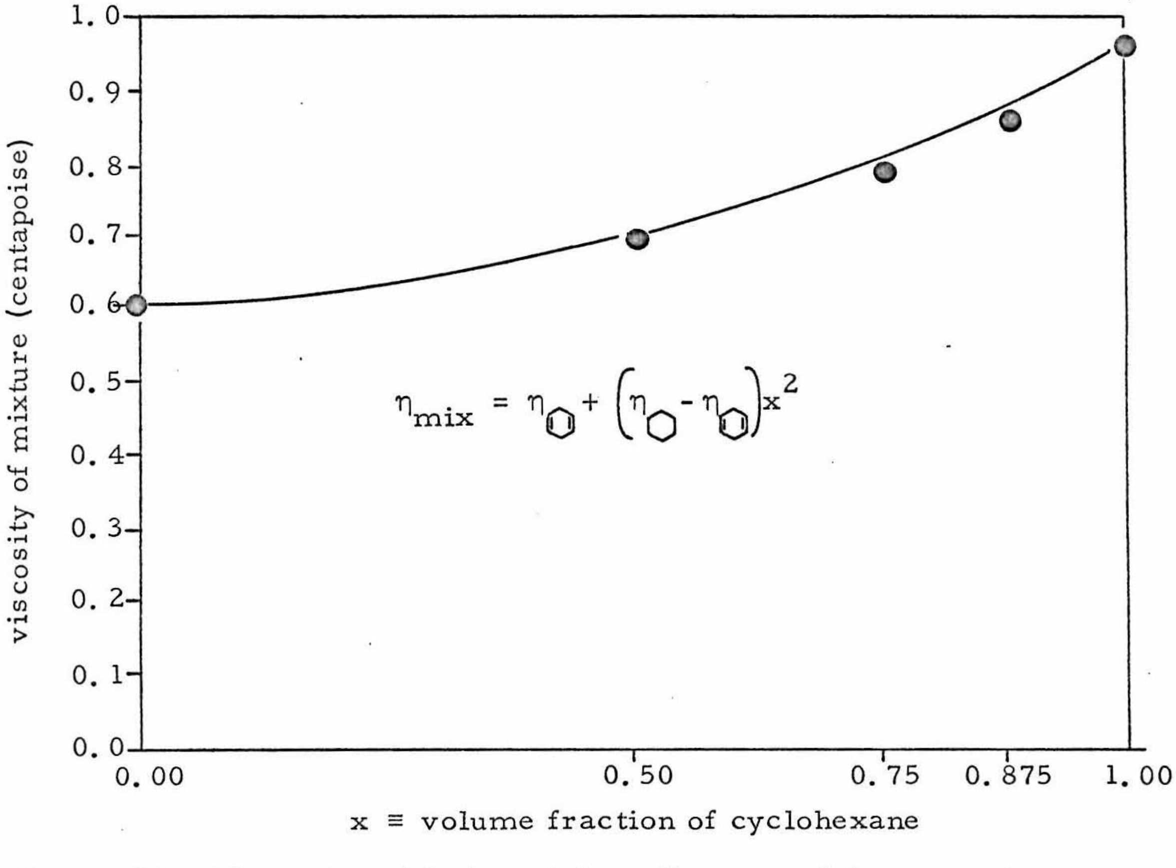


Figure 21. Viscosity of 1,4-cyclohexadiene—cyclohexane mixtures at 20°.

so that using eq. 2.4-7 we have

$$\left(k_b^{\text{⌬}}\right)_{mix} = \left\{\phi/\left(1 + (\phi-1)x^2\right)\right\}\left(k_b^{\text{⌬}}\right)_{\text{⬡}} . \qquad (2.4\text{-}10)$$

Thus, $k_b^{\text{⌬}}$ is predicted to increase with increasing 1,4-cyclohexadiene concentration, so that $R2^{calc}$ can be made to decrease less rapidly with increasing cyclohexadiene concentration than predicted in Calculations 1 and 2. This is the type of correction required to smooth out the systematic deviations found for those calculations.

If we write

$$\frac{d(\underset{\sim}{6})}{d(\underset{\sim}{5})} \cong \frac{k_b^{\text{⌬}}(Z\cdot)(\underset{\sim}{4})}{k_a^{\text{⏣}}(ZH)(\underset{\sim}{3})} = \frac{k_1 k_b^{\text{⌬}}}{k_2 k_a^{\text{⏣}} k_4^{\frac{1}{2}}(ZH)}\left(\alpha k_o(P)/2XF\right)^{\frac{1}{2}} , \qquad (2.4\text{-}11)$$

using the definitions of X and F given previously (pp. 203, 206) we see that formally we must also account for the effect of viscosity on the square root of the rate constant, k_4, for bimolecular reaction of cyclohexadienyl radicals. The effect, within this simple scheme, is to make $R2^{calc}$ dependent on $\left\{\phi/(1 + (\phi-1)x^2)\right\}^{\frac{1}{2}}$. The exact relationship is obtained by replacing G in eqs. 2.1-1—2.1-10 by

$$G = G(x,\phi) = G_{\text{⬡}}\ \phi/\ 1 + (\phi-1)x^2 \quad ^{\frac{1}{2}} , \qquad (2.4\text{-}12)$$

where $G_{\text{⬡}}$ (tabulated in Table 19 as G for calculations where $\phi \neq 1$) is the value of G in cyclohexane solution.

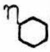
The viscosity data can be described more accurately than by the line shown in Fig. 21 by including a linear term in x in eq. 2.4-8. However, the simple relationship of eq. 2.4-8 has been employed to make explicit our expectation that the shape of the viscosity–

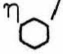
composition relationship will be simply related to the viscosity difference for the pure components. Some such assumption about the shape of the relationship is needed because ϕ may well be temperature dependent. Viscosity data for benzene ($\eta(20^\circ) = 0.65$) between 0 and 80°(108) and for cyclohexane between 15 and 250°(106) were fitted to the Arrhenius equation. The two relationships were then combined to give

η/η $= (0.41 \pm 0.02)\ \exp(0.73 \pm 0.04)/RT)$. (2.4-13)

Benzene, the less viscous at 20°, is predicted to be the more viscous at high temperatures (above 140°).

By rough analogy with this result, we have taken

η/η $\equiv \phi = 1.00\ \exp(0.274/RT)$ (2.4-14)

in Calculation 3. This relationship gives $\phi(20^\circ) = 1.6$ but assumes that the ratio η/η will decrease with increasing temperature, so that the viscosity correction to $R2^{calc}$ will become less important.

Results for the R2 ratios for Calculation 3 are shown in Table 18, with quality-of-fit quantities in Table 19. From the latter, we see that while AVDEV (5.94%) is only about 0.1% better than in Calculation 1, AVDEV $R2_2$ has been reduced by 0.6%. Moreover, on examining RELDEV quantities in Table 18, we find that RELDEV R2 (run 1) - RELDEV R2 (run 4) is 5.6% as compared to 19% in Calculation 1: the systematic error with 1,4-cyclohexadiene concentration has virtually been eliminated from the R2 ratios.

Calculation 4 is the same as Calculation 3, except that we have taken $\phi = 1.6$, independent of temperature. Quality-of-fit quantities in Table 19 show that this assumption gives only a slightly less satisfactory fit to the ratio data.

For all remaining calculations, we have described ϕ via an equation of the form of eq. 2.4-14; i.e., with a preexponential factor of unity and a composite activation energy which gives $\phi(20^\circ)$ as recorded in Table 19.

In Calculation 2 we took $C = 1$ and found the fit to be substantially worse than in Calculation 1 for $C = 0$. With $\phi(20^\circ) = 1.6$, however, setting $C = 1$ in Calculation 5 (Tables 18, 19) improves the quality of the fit. Calculations 6–10 (Table 19) demonstrate that the pairing of $C = 1$, $\phi(20^\circ) = 1.6$ is about the optimum combination.

(3). R1 with 1,4-Cyclohexadiene Concentration

As can be seen for Calculation 14 (Table 17), the $R1^{calc}$ tend to deviate negatively at low cyclohexadiene concentrations and positively at 8–10 M cyclohexadiene; swings of 20–30% in the RELDEV R1 quantities are common. Note that the observed reduced ratios in column 2, p. 297 vary much more sizeably than do the calculated values recorded in column 3. These quantities were defined (eq. 1.8-5, p. 111) to be proportional to k_r/k_a, where the proportionality constant is the fraction of ring-cyclized radicals which are converted to the dihydronaphthalene **10**. Superficially, at least, this makes it appear that the mechanistic scheme predicts the efficiency of conversion of **9** to **10** to be less variable than actually is the case. The current parameterization $\gamma = 0.60$, $\delta = 0.42$ implies conversion efficiencies of 30% for pairwise reaction of ring-cyclized radicals and of 42% for reaction of ring-cyclized radicals with cyclohexadienyl radicals; clearly, little variability in the overall conversion efficiency is possible under this parameterization.

We can maximize the variability by making the outcome for reaction of **9** with **9** as different as possible from that for reaction of **9** with cyclohexadienyl radical. If we choose $\gamma = 0$, we find that $\delta = 0.45$ is required to get the average yield of ring-opened hydrocarbon **5** right. The effect of this parameterization on the R1 ratios can be seen in Table 18 for Calculation 11. We now have AVDEV = 5.03% compared to 5.76% for Calculation 5. However, we find that while the systematic error in RELDEV R1 with cyclohexadiene concentration has been essentially removed from the perester **1** runs (runs 13-26), the situation is not greatly improved for the perester **2** runs (runs 1-12). We conclude that variation of conversion efficiency alone is not capable of fully redressing the systematic nature of the deviations.

A serious objection to the parameterization $\gamma = 0.00$, $\delta = 0.45$ is that a much higher value for γ seemed to be required to account for experimental observations for reaction in triethyltin hydride. To recount the situation, the mechanistic treatment of induced decomposition gave results compatible with rate accelerations and with observed yields of the cage ether **12**, provided that ring-cyclized radicals were allowed to react with triethyltin radicals only infrequently (pp. 170-179). At the same time, consideration of material balances required that **9** be converted to **10** with an efficiency of at least 30% (pp. 133, 134). The implication is, then, that $\gamma \geq 0.6$. For this reason, we reject the parameterization of Calculation 11, even though mathematically it represents a substantial improvement.

Returning again to a consideration of the reduced ratios of Table 17, the other possibility* is that the efficiency of conversion of **9** to **10** is sensibly constant, but that k_r/k_a itself increases with increasing cyclohexadiene concentration. As these processes are not diffusion-controlled, the viscosity effect considered under the previous heading would presumably not be a factor. However, association of radical intermediates with the π-bonds of the olefinic 1,4-cyclohexadiene might measurably affect the rate constants for the two processes. Presumably, the saturated co-solvent cyclohexane would simply act as a space filler.

Medium effects involving solvation of radical intermediates have been generally recognized for approximately the last decade. A review article covering the literature through 1964 has been supplied by Huyser (66). Extensive work has been done on the effects of complexing of chlorine radicals and alkoxy radicals with various solvents, notably olefinic and aromatic materials. In contrast, Huyser is able to report only one well-supported example of a medium effect of the type we are considering here on hydrocarbon radicals, and that example concerns the trichloromethyl radical. This suggests that

---

*Failure to account for significant hydrogen abstraction by **3** from cyclohexane could in principle explain the observed behavior. However, **21** the saturated analog of **3**, abstracts hydrogen from 1,4-cyclohexadiene about 250 times as rapidly as from cyclohexane (see the footnote to p. 335). As the smallest mole ratio of 1,4-cyclohexadiene to cyclohexane is ~1:10, neglect of hydrogen abstraction from the latter is apparently not serious.

'large' solvent effects will be absent unless the possibility exists for polar interactions between the radical intermediate and the solvent.

However, we shall require, to repair the systematic error under discussion, that $k_r/k_a^{⌬}$ vary by only ~ 30% between pure cyclohexane and pure cyclohexadiene; and as solvents may effect the reactivity or relative reactivity of chlorine or alkoxy radicals by up to two orders of magnitude, for presently known cases, it would seem improper to reject out of hand the possibility of solvent effects on nonpolar hydrocarbon radicals of the much smaller magnitude we have in mind.

As is well known, *t*-butoxy radicals may abstract hydrogen from solvent or may undergo β-scission to give acetone plus a methyl radical. This competition, which has been extensively investigated by Walling and Wagner, can perhaps serve as a model for the competition between hydrogen abstraction and ring-cyclization by ring-opened radical **3**. One of Walling and Wagner's experimental observations is that complexing solvents favor decomposition (the scission process) over hydrogen abstraction (42). Not only olefins and aromatic hydrocarbons but also polar materials such as acetic acid and acetonitrile have this effect. This was taken to suggest that part of the effect is due to solvation of a decomposition transition state which involves charge separation as a consequence of the polar nature of the product acetone. However, solvent effects were also observed on the relative rates of abstraction of primary and tertiary hydrogens from 2,3-dimethylbutane, suggesting that the medium must also influence the rates of hydrogen-abstraction reactions. The main element of the interpretation here is that solvation must be at least partially broken to allow the prospective hydrogen donor to properly approach the radical center. If applicable to our situation, this would suggest that complexing of the radical center in 3 with the π-bonds of 1,4-cyclohexadiene should disadvantage hydrogen abstraction from 1,4-cyclohexadiene with respect to the intramolecular ortho-ring cyclization. As a result, k_r/k_a⌬ should increase with increasing 1,4-cyclohexadiene concentration, as required to repair the systematic errors in R1.

To see how great an improvement might result from invoking such a solvent effect, Calculation 12 was carried out where we have replaced $E = k_a$⌬$/k_r$ (independent of solvent composition) by

$$E = E_{⬡}\{1 - 0.0076 * \exp(0.72/RT) * (ZH)\} \qquad (2.4\text{-}15)$$

where $E_{⬡}$ is the value of E in cyclohexane. This relationship causes E to vary linearly with cyclohexadiene concentration by 30% at 0° and 15% at 150° between pure cyclohexane and pure cyclohexadiene. Of course, a linear relationship is not required by any available information, but seems not unreasonable. The lesser effect at 150° is compatible with the demands of the data and with the expectation that association between various species will be broken by higher temperatures.

The quality-of-fit quantities in Table 19 show that a beginning has been made. Specifically, AVDEV R1, at 5.12%, is ~3.5% lower than in Calculation 5 and even 1.4% lower than in Calculation 11. The greatest improvement is shown by the AVDEV $R1_2$ quantities: 10.65%

for Calculation 5; 8.38% for Calculation 11; but only 5.74% for Calculation 12. The reason for this improvement is easily seen in the RELDEV R1 quantities for Calculations 5, 11, and 12 in Table 19; the systematic drift with cyclohexadiene concentration of Calculation 5, only partially repaired in Calculation 11, is hardly detectable in Calculation 12.

However, the AVDEV R2 quantities are so adversely effected that AVDEV itself is higher in Calculation 12 than in either 5 or 11. The reason is not hard to determine; the RELDEV R2 quantities for Calculation 12 (especially for runs 1–12) again vary systematically with the 1,4-cyclohexadiene concentration, but now in the sense opposite to that we sought to correct under the previous subheading.

The reader can verify from eqs. 2.1-4 and 2.4-11 that

$$R2^{\mathrm{calc}} \cong \left[\frac{k_1}{k_a^{\text{⬡}}}\right]\left[\frac{k_b^{\text{⌬}}}{k_2}\right]\frac{(Z\cdot)}{(ZH)} \sim G/E \quad . \qquad (2.4\text{-}16)$$

Eq. 2.4-16 shows that the variation of E given by eq. 2.4-15 is carried directly over onto the R2 ratios although this is not logically required. In line with the reasoning given above, we might expect that solvation of **3** and **4** by cyclohexadiene will favor $k_a^{\text{⬡}}$ over k_1 and $k_b^{\text{⌬}}$ over k_2, but perhaps less strongly in the latter case; a relatively stable dibenzylic radical such as **4** may be less susceptible to interactions with the environment of any type than a primary radical such as **3**. Thus, G/E should vary with the cyclohexadiene concentration, but probably not as strongly as does 1/E.

To see what degree of compensation by G would be required to put the R2 ratio situation right,[*] a series of calculations was begun using

$$G = G(x,\phi)\ \{1 - 0.0038{*}\exp(0.72/RT){*}(ZH)\}\ , \qquad (2.4\text{-}17)$$

where $G(x,\phi)$ is given by eq. 2.4-12. (Comparison to eq. 2.4-16 shows that this corresponds to allowing G to compensate for half the variation built into E.) However, the results were so favorable that only this first calculation, Calculation 13, was carried out. We now find that neither the R1 nor the R2 ratios show significant systematic deviations as a function of 1,4-cyclohexadiene concentration (see Table 18, p. 301). Furthermore, AVDEV (Table 19) has decreased to 4.57%, a figure which is much superior to any previously discussed.

The major remaining problems are the temperature incompatability between 70 and 99° for the R1 ratios (although, with variation of E, this is less severe than previously) and the major discrepancy between calculated and observed R2 ratios for runs 31–35. The latter is discussed under (4) below.

(4), R2 Values from Table 4

A systematic deviation which shows up in all the calculations concerns the R2 ratios from the Table 4 concentration study (runs 31–35). Both the calculated and observed ratios decrease with

---

[*] There are, of course, alternatives. To cite two, we could increase C (compare Calculations 1 and 2) or we could decrease $\phi(20^\circ)$.

decreasing initial perester concentration, but the calculated ratios are consistently, and seriously, too low. In view of the general success of the mechanistic scheme in smoothly correlating widely varying R2 ratios for both peresters, we may perhaps suggest that yields of ring-closed hydrocarbon 6 (which range from 0.3% to 0.1%) are simply in error for runs 31–35. We noted previously (pp. 116 - 118) that commercial 1,4-cyclohexadiene generates upon heating one or more impurities which could be mistaken for 6; perhaps this complication was especially troublesome in these runs.

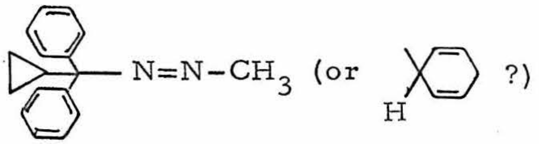
In any case, the R2 ratios for runs 31–35 were assigned zero weight in all the calculations. This has two effects: (a) quality-of-fit quantities are improved; and (b) the possibility is avoided of seriously distorting values of various parameters in a vain attempt to accommodate erroneous experimental data.

E. Prospects for Experimental Verification of Medium Effects on R1 and R2

Although precedent exists only for the viscosity correction to $R2^{calc}$, both this and the solvation correction to E and G are capable of explaining experimentally significant systematic deficiencies in the calculated product ratios. It seems feasible to determine whether these mathematical innovations reflect physical reality.

A test of the importance of solvent effects on the R1 ratios could be made by measuring R1 at ~0° for a series of reactions approximately 1 M in 1,4-cyclohexadiene in which the cosolvent is varied from pure cyclohexane to pure cyclohexene. The latter would presumably complex ring-opened radicals about as well as the unconjugated 1,4-cyclohexadiene, but would not be comparably active as a hydrogen donor. The information necessary to correct for hydrogen abstraction from cyclohexene in the terinary mixtures could be obtained by running 2 in neat cyclohexene. One would of course want to use fairly low initial concentrations of 2 (perhaps 0.01 M) in order to minimize any uncertainty in the 1,4-cyclohexadiene concentrations arising from uncertainty in the amount consumed in the reaction.

The viscosity dependence seems to be on reasonably solid theoretical ground. One might therefore look ahead to experiments which would simultaneously establish unambiguously the reality of the effect and put it to good use. If, for example, the azo compound shown below could be made, decomposition in approximately 1 M 1,4-cyclohexadiene in a range of co-solvents would allow one to simultaneously monitor the influence of the principal solvent (a) at keeping 4 and cyclohexadienyl radical apart and (b) at keeping 4 and methyl radical together (as measured by the effect of solvent on the efficiency of cage recombination). Ring-closed perester 2 would be less satisfactory than the azo compound because of the apparently limited stability of the combination product, the ring-closed *t*-butyl ether 15 (pp. 78, 79). The point would be to quantify and explore the limitations of the anticipated reciprocal influence of viscosity on cage recombination and on rate constants for diffusion-controlled processes.



F. Hydrogen Abstraction by Lactonyl Radicals from 1,4-Cyclohexadiene

Calculations 1–13 have employed the parameterization

$$B \equiv k_5 k_d / k_6 k_3^{\frac{1}{2}} = 1.00 \exp(-12/RT) \qquad (2.4\text{-}18)$$

where k_5 and k_6 are the rate constants for hydrogen abstraction by lactonyl radicals (22) from 1,4-cyclohexadiene and cyclohexadienyl radical, respectively, and k_d and k_3 are the rate constants for the radical-radical reactions 9 + cyclohexadienyl and 9 + 9, respectively. During the period in which nearly all of the calculations were carried out, we erroneously had $B \equiv k_5/k_6$. The parameterization of eq. 2.4-18 seemed reasonable under this incorrect definition, but now appears indefensible (see below). Its effect is to have hydrogen abstraction by 22 occur almost totally from cyclohexadienyl radical. We found, in a series of calculations leading up to Calculation 1, that just this circumstance was required to obtain the best fit to the ratio data.

We seek here to determine the effect on the calculations of 'reasonable' parameterization for B. Fortunately, we have in the hydrogen-abstraction reactions of the dibenzylic ring-closed radical 4 an excellent model for the k_5 and k_6 reactions of the dibenzylic lactonyl radical 22. The reader can confirm from the parameter definitions of eqs. 2.1-4 that

k_bk_d/k_b$k_3^{\frac{1}{2}} = E{*}I/G$.   (2.4-19)

From typical values of E, I, and G listed in Table 19, we can write

$$k_b^{\bigcirc} k_d / k_b^{\circledcirc} k_3^{\frac{1}{2}} \cong 6 \times 10^2 \exp(-10.5/RT) \quad . \qquad (2.4\text{-}20)$$

If the rate-constant ratios for hydrogen abstraction from 1,4-cyclohexadiene and from cyclohexadienyl radical are identical for 4 and for 22, B can be equated to the right-hand side of eq. 2.4-20.

Calculations 5, 11, and 13 were therefore repeated using this parameterization, but with all other non-iterated quantities (C, ϕ, γ, δ, etc.) as before. We found AVDEV to be increased by ~0.8, ~0.8, and ~0.4%, respectively. These figures represent a moderately serious deterioration of the fit to the product-ratio data. However, the structural resemblence of 4 and 22 can hardly suffice to fix B precisely as taken in these calculations; values up to 10 times larger or smaller would not be inconceivable. We therefore tried

$$B = 2 \times 10^2 \exp(-10.5/RT) \qquad (2.4\text{-}21)$$

on Calculations 5 and 13, giving Calculations 14 and 15, respectively. The quality-of-fit quantities tabulated in Table 19 shows that under this parameterization the fit to the product-ratio data can even be slightly improved over taking B to be effectively zero.

The reason is not hard to fathom. The effect of allowing hydrogen abstraction by 22 from 1,4-cyclohexadiene to compete with abstraction from cyclohexadienyl radical is (a) to lower the average 1,4-cyclohexadiene concentration and (b) to increase the steady-state cyclohexadienyl radical concentration. Effect (a) increases the systematic errors in the R1 ratios with cyclohexadiene concentration, though not seriously for the revised parameterization of B. But effect (b) counteracts a temperature incompatibility in the R2 ratios which had been accumulating throughout the series of calculations. This incompatibility had $R2^{calc}$ too high for perester **2** runs 1–12, but too low for the perester **1** runs at 99°. Increasing the cyclohexadienyl radical concentration unilaterally for the perester **1** runs makes it possible to form more ring-closed hydrocarbon with the same values of parameters other than B, and hence to reduce the incompatibility.

For the record, we should note something about the actual competition between hydrogen abstraction from 1,4-cyclohexadiene and from cyclohexadienyl radical by **22**. For Calculation 14 (Calculation 15 is similar) the fractions of abstraction events occurring from 1,4-cyclohexadiene were 0.050, 0.084, 0.141, 0.141, and 0.214 for runs 13–17, respectively. For the series at 150° (runs 21–26), the fractions were about half this large. At 0.001 M perester in neat 1,4-cyclohexadiene (runs 36–39), abstraction was largely from 1,4-cyclohexadiene, owing to diminished steady-state radical concentrations.

G. Relation of Quality-of-Fit to Experimental Error

The question of whether deviations between calculated and observed product ratios of the size we have found are compatible with experimental error is fundamental to a judgement regarding the success of the mechanistic treatment at the present level of sophistication. Unfortunately, a definitive answer to this question can not be given.

One reason is that the size of experimental error is difficult to judge. This would usually be done with reference to the repeatability of the observations, but we have tested such reproducibility in too few cases to draw definitive conclusions. Consideration of the reproducibility of repetitive vpc analyses on a given reaction mixture (most runs were analyzed in triplicate) is not a satisfactory substitute. For the record, however, this reproducibility amounts to ∼ 2.5% for the R1 ratios, ∼ 1% for the R2 ratios from perester **2**, and ∼ 5% from perester **1**.

Several observations suggest that experimental error, arising from uncertainty in reagent concentrations, or from inclusion of variable amounts of adventitious impurities, is larger than considerations of vpc reproducibility alone would indicate. For example, the $R1^{obs}$ from runs 15 and 16, which should be the same, differ by 14%, only about a fifth of which (3%) can be accounted for by the combined scatter in the vpc measurements. Moreover, we have several sets of experiments which lend themselves to examination for consistency. For example, the reduced ratios R, given by % yield **10** x $(ZH)_{av}$/% yield **5**, are defined so as to eliminate the large, but really not very interesting, dependence of the product ratio on the cyclohexadiene concentration. As a result, these quantities vary by less than a factor of two. This would suggest that the observed values should vary smoothly as a function of 1,4-cyclohexadiene concentration, reaction temperature, or initial perester concentration. Examination of appropriate reaction series in Table 17 shows that this is not always the case--that real experimental errors must be present.

A second problem is that we do not know precisely how well the data can be fit. If Calculation 15 were to be subjected to optimization of B, C, ϕ, and the parameters describing the solvation effects on E and G, AVDEV, which is 4.4% for Calculation 15, might drop to 4.0%, or perhaps even less.

We believe that Calculation 15 fits the data satisfactorily with few exceptions. However, the same can not be said for Calculations 5 or 14 or for any calculation not involving the *ad hoc* assumption of solvation effects on E and G. If these effects are real, the fit is satisfactory; otherwise, it is deficient.

If there were precedent for, or independent verification of, solvation effects of the size and type invoked here, we would enthusiastically display Calculation 15 in Table 16 as 'most representative'. Instead, we have chosen Calculation 14 for elaboration of other aspects of the calculations, a number of which are discussed below.

H. Ratio of Rate Constants for Hydrogen Abstraction from 1,4-Cyclohexadiene and *ortho*-Ring-Cyclization by Ring-opened Radical **3**

The rate-constant ratio considered here is $E = k_a^{\text{⬡}}/k_r$. From Calculation 14 we find that

$$k_a^{\text{⬡}}/k_r = 0.050 \exp(0.8/RT) \quad . \qquad (2.4\text{-}22)$$

The reciprocal of eq. 2.4-22 was quoted as eq. 1,8-6, p. 125.

Individual calculations in Table 19 report values which are as much as 0.2 kcal/mole higher and lower than the indicated composite activation energy of -0.8 kcal/mole. In addition, the neglect of any temperature dependence in the conversion efficiency parameters δ and γ could have resulted in overestimation of the true composite activation energy by 0.1–0.2 kcal/mole, if lower temperatures favor radical-radical disportionation over combination as with ethyl radicals (see p. 243); i.e., the true composite activation energy might be -0.9—-1.0 kcal/mole. Moreover, resolution of the temperature incompatibility of the R1 ratios discussed above under heading (1), p. 251, might effect the composite activation energy by 0.5 kcal/mole or more.

Our feeling is that the composite activation energy in eq. 2.4-22 might be incorrect by as much as one kcal/mole.

In contrast, the value of E at 100° (i.e., near the center of the temperature range) seems to be reliably established as 0.145 ± 0.02 M^{-1} $\sec^{-1}$. A major portion of the suggested error limits arises from the average deviation of ~ 10% between observed and calculated yields of ring-opened hydrocarbon 5, as in Calculation 14 of Table 17.

I. The Characteristic Ratio (6:5) for Hydrogen Abstraction by Ring-opened and Ring-closed Radicals from 1,4-Cyclohexadiene

We previously reported that 1,4-cyclohexadiene develops an impurity upon heating whose retention time closely approximates that of ring-closed hydrocarbon 6 on the standard Ucon polar vpc column (pp. 116 – 118). This most unfortunate coincidence places in doubt our contention that the apparent R2 ratios of ~0.004 for 0.001 M ring-opened perester 1 in 1,4-cyclohexadiene (runs 36–39) essentially represent the ratios 6:5 formed via hydrogen abstraction by the (equilibrated) radical precursors from 1,4-cyclohexadiene. However, we found in belatedly measured yields of the solvent-developed impurity reason to believe that the R2 ratios at ~0.25 M 1 (runs 13–26) would not be seriously compromised.

We have therefore carried out Calculations 16 and 17 to determine (a) what sort of values of I, the parameter in question, are required to adequately fit the data in the absence of the disputed runs 36–39, and (b) what is the consequence on the quality of the fit of assuming that no 6 is formed via hydrogen abstraction from 1,4-cyclohexadiene, again leaving out runs 36–39. Instead of I(100°) = 0.0038 as in Calculation 5, we find, for Calculation 16, I(100°) = 0.0046. Although the calculated composite activation energies differ by about 2 kcal/mole, the values for temperatures in the range investigated experimentally agree quite well. In Calculation 17 for I = 0, we find AVDEV $R2_1$ = 14%; comparison to AVDEV $R2_1$ = 5.6% for Calculation 5 shows that this parameterization causes a major deterioration in the fit in the only area in which it could be important.

In Calculation 14, which differs from Calculation 5 only in the adoption of eq. 2.4-21 for B, we find I(100°) = 0.0035, slightly less than that for Calculation 5. The reason for the reduction is that allowance for hydrogen abstraction by lactonyl radicals 22 from 1,4-cyclohexadiene increases the cyclohexadienyl radical concentration and hence the yield of **6** formed via abstraction of hydrogen from cyclohexadienyl radical. Thus, a smaller fraction of the R2 ratios for runs 36–39 is identifiable with hydrogen abstraction by **4** from 1,4-cyclohexadiene. As values of B could be several times larger than those employed in Calculation 14, I(100°) could be smaller yet. We recommend I(100°) = 0.0035 ± 0.0010 as likely to provide for all contingencies.

The composite activation energy for I specifies, for hydrogen abstraction from 1,4-cyclohexadiene, the energy of the transition state leading to **6** with respect to that leading to 5 (see Fig. 11, p. 119). Consideration of the range of values listed in Table 19 and least-squares standard deviations of ~0.5 kcal/mole obtained according to the formalism given in subsection 2 suggests -1.8 ± 1.0 as a reasonable estimate. We then have

$$I = \frac{k_1 k_b^{\text{⌬}}}{k_2 k_a^{\text{⌬}}} = 3 \times 10^{-4} \exp(1.8/RT) \quad . \qquad (2.4\text{-}23)$$

J. Characteristic Ratio (**6**:**5**) for Hydrogen Abstraction from Cyclohexadienyl Radical

The characteristic ratio **6**:**5** for hydrogen abstraction from cyclohexadienyl radicals is of interest for comparison to values already obtained for 1,4-cyclohexadiene (~0.0035 at 100°) and for triethyltin hydride (~0.07 at 100°; see p. 168). From eq. 1.8-12 (p. 138) we know that hydrogen abstraction by **3** is more rapid from triethyltin hydride than from 1,4-cyclohexadiene by a factor of ~50 at 100°. Thus, more use of the active hydrogen donor corresponds to larger 6:5. As cyclohexadienyl radicals should be vastly more reactive than either of these toward the relatively stable dibenzylic ring-closed radical, a much larger characteristic ratio is to be expected. Indeed, the Calculations indicate that the ratio, given by the parameter H, is so large that

$$H = \frac{k_1 k_b^{\odot}}{k_2 k_a^{\odot}} \qquad (2.4\text{-}24)$$

formation of ring-opened hydrocarbon by this pathway is all but undetectable. In Calculation 5 we find H(100°) = 5.6. In Calculation 14 (where the revised parameterization for B, eq. 2.4-21, is employed), we find H(100°) = 20. With solvation corrections to E and $\dot{G}$, (Calculation 13) we have H(100°) = 14. With revised parameterization for B (Calculation 15), the computer was given H(100°) = 50, found that to be too small, increased it to 220, thence to 4800, and finally to 10^{121}.

Even for Calculation 5, which had H(100°) = 5.6, formation of 5 via hydrogen abstraction from cyclohexadienyl radical was not crucial to the success of the fit. This was shown in Calculation 18 where we assumed H(100°) = 10^{10} (i.e., effectively infinite); AVDEV rose by only 0.14% over that for Calculation 5.

The conclusion is that H(100°) is greater than unity, but by an amount which can not be reliably determined with the present data. It is probably safe to recommend H(100°) ≥ 5.

K. Enthalpy Difference of Ring-opened Radical 3 and Ring-closed Radical 4

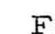
Values of H quoted above were determined for the composite activation energy for H of -8 kcal/mole. As the activation energies of the k_a⌬ and k_b⌬ processes of eq. 2.4-24 may be expected to be both small and similar, the composite activation energy for H may reasonably be equated to the difference in enthalpy of the ring-closed and ring-opened radicals.

From eqs. 2.1-4 we find that

$$\frac{G^{*}k_4^{\frac{1}{2}}}{E^{*}F^{\frac{1}{2}}} = \frac{k_1 k_b^{\text{⌬}}}{k_2 k_a^{\text{⌬}}} \quad . \tag{2.4-25}$$

The composite activation energy of this quantity specifies the difference in energy between the transition state for formation of 6 via abstraction of hydrogen by 4 from cyclohexadienyl radical and the transition state for formation of 5 from 3 plus 1,4-cyclohexadiene. If we employ the numerical results for Calculation 14 (Table 19) and assume a viscosity-related activation energy of 2 kcal/mole for k_4, the rate constant for pairwise reaction of cyclohexadienyl radicals, we find this energy difference to be -13.35 -1.00 - (-0.77) = -11.6 kcal/mole. A survey of other calculations in Table 19 shows that the last figure is remarkably insensitive to the precise assumptions of the least-squares optimization.

If the activation energy for abstraction of hydrogen by ring-opened radical 3 from 1,4-cyclohexadiene is assumed to be 5.8 kcal/mole (see p. 108), and if that for the reaction of $\underset{\frown}{4}$ with cyclohexadienyl radical is taken to be 2 kcal/mole, we have that the enthalpy of ring-closed radical $\underset{\frown}{4}$ is lower than that of $\underset{\frown}{3}$ by 11.6 - 5.8 + 2.0 $\cong$ 8 kcal/mole. These relationships are traced in Fig. 22.

Uncertainty in various assumptions make the enthalpy difference uncertain by perhaps 3 kcal/mole. Firstly, the 5.8 kcal/mole activation energy for the k_a reaction assumes (a) that ring-opened radicals and ethyl radicals are equally reactive toward 1,4-cyclohexadiene; (b) that the activation energy is not effected by transferring the model ethyl radical system from the gas phase into hydrocarbon solution; and (c) that bimolecular reaction of ethyl radicals requires no activation energy (see p. 108). In addition, the viscosity-related activation energies for the k_4 and k_b processes might differ by 1—2 kcal/mole from the values of 2 kcal/mole assumed here. However, a consistent error here would come in only at half strength because k_1/k_2 depends on $k_4^{\frac{1}{2}}/k_b$. Finally, the R2 ratios depend essentially on the product $G^*k_o^{\frac{1}{2}}$, where k_o denotes the rate constant for perester decomposition; an error of 1 kcal/mole in the assumed enthalpy of activation of 24.5 kcal/mole for decomposition of $\underset{\frown}{2}$ would effect k_1/k_2 by 0.5 kcal/mole.

If the classical radicals are really the intermediates, the figure of 8 ± 3 kcal/mole should be compatible with expectations based on bond energies and the like. We shall show in Section Three via a thermochemical cycle, itself subject to sizable uncertainties, that such is evidently the case.

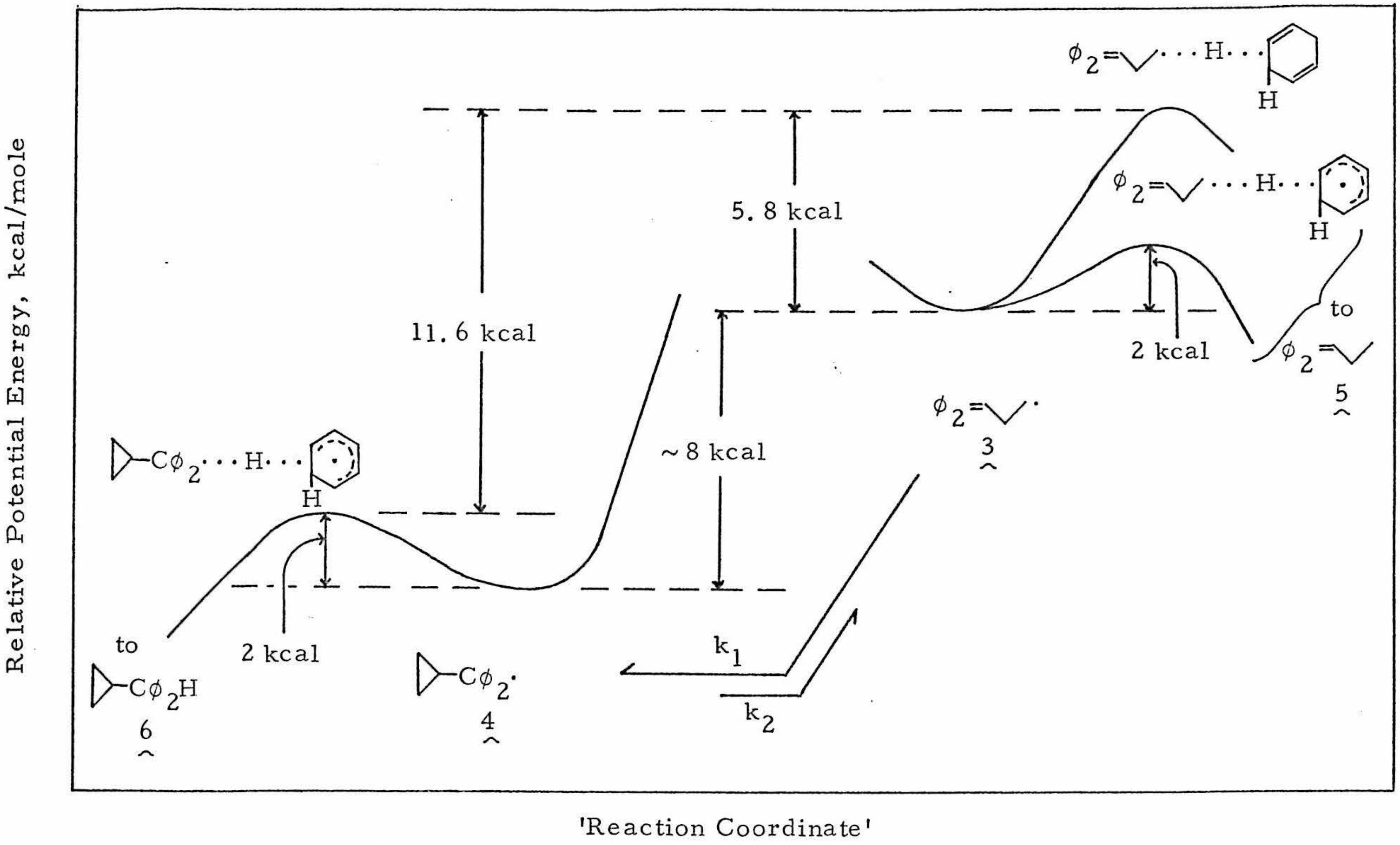


Figure 22. Reaction diagram showing derivation of enthalpy difference (~8 kcal/mole) between ring-opened radical 3 and ring-closed radical 4.

L. Self- and Cross-termination of Ring-cyclized Radicals and Cyclohexadienyl Radicals

The parameter $F = k_3k_4/k_d^2$ measures the competition between self- and cross-termination in a system containing ring-cyclized radicals and cyclohexadienyl radicals. The value of F expected statistically (i.e., if collisions of **9** with **9**, **9** with cyclohexadienyl radical, and of cyclohexadienyl with cyclohexadienyl are equally effective) is 0.25(100). Values found in these calculations range from 0.056 to 0.082. Thus, cross-termination appears to be favored over self-termination by approximately a factor of $(0.25/0.07)^{\frac{1}{2}} \cong 2$. No such bias exists for simple alkyl radicals in the gas phase (109). For electronically dissimilar radicals (i.e., one an electron donor, the other an electron acceptor), cross-termination is favored by factors up to 150(110), but as **9** is a substituted cyclohexadienyl radical, this sort of explanation would not seem to be applicable. Perhaps steric factors are responsible. In any case, the deviation from the statistically expected result is not very large.

In calculations heretofore reported, we have assumed a composite activation energy for F of zero kcal/mole. As the k_3, k_4 and k_d processes may well all be diffusion-controlled, this assumption is not unreasonable. Moreover, from the way in which F is formed from these rate constants, we would expect, even if more than the usual diffusion-controlled activation energies are involved, that the sum of the activation energies for k_3 and k_4 would closely approximate twice that for k_d.

Calculations 19 and 20 explore the consequences of taking the composite activation energy for F to be ± 1 kcal/mole. The quality-of-fit quantities listed in Table 19 show that the assumed value of zero (Calculation 5) is superior to either ± 1, but only marginally so for + 1. Indeed, values other than zero principally affect not the quality of the fit but the values found for the other parameters, though not very strongly except for the composite activation energy for G. Interestingly, the variation for G is just such as to leave the estimated difference in enthalpy of the radicals 3 and 4 unchanged to within 0.1 kcal/mole.

M. Yields of Tetrahydronaphthalene (B)

Columns 2 and 3 of Table 17, p. 298, give calculated and, where available,* observed yields of B (see Chart 4, p. 78) for Calculation 14, where we have used $\gamma = 0.60$, $\delta = 0.42$, and $\epsilon = 0.28$. The value $\gamma = 0.60$ implies that 30% of ring-cyclized radicals which react pairwise come out as tetrahydronaphthalene. Similarly, $\epsilon = 0.28$ means that reaction of 9 with cyclohexadienyl radical involves transfer of a hydrogen atom to 9 some 28% of the time. These values correctly predict yields of B in an average sense.

Comparison of observed and calculated yields in Table 17 shows that the variation with cyclohexadiene concentration is also predicted approximately correctly. Of course, a variety of mechanisms for

---

*See the footnote to p. 241.

destruction of **B** (e.g., Diels-Adler reaction with 1,4-cyclohexadiene, attack by radical intermediates) can be invoked to explain the rather erratic behavior of the observed yields as a function of the 1,4-cyclohexadiene concentration.

N. Formation of Dimers from Ring-cyclized Radicals

If reactions of ring-cyclized radicals with themselves or with cyclohexadienyl radicals do not always result in disproportionation, dimers containing the C_{16} moiety will be formed. Predicted yields for $\gamma = 0.60$, $\delta = 0.42$, and $\epsilon = 0.28$ appear in Table 17, p. 298. The average yield of 'missing C_{16} groups' is 11% for runs employing ring-opened perester **1** and 8% for runs employing **2**. The last of these quantities essentially explains the material balance deficit of approximately 10% for runs employing **2** (pp. 122, 123). However, the average calculated yield for runs employing **1** accounts for only about half the observed material balance deficit of ~ 20%. The remaining deficit of ~ 10%, might be attributable to induced decomposition of **1** by cyclohexadienyl radicals; this would principally affect yields of **5**, **6**, and **10**, but would leave their ratios all but invariant.

O. Formation of Dimers from Cyclohexadienyl Radicals

We consistently observed a product (not biphenyl) at approximately one-fifth the retention time of ring-opened hydrocarbon **5** on the standard Ucon polar column. This product appeared upon decomposition in 1,4-cyclohexadiene of ring-opened perester **1**, ring-closed perester **2**, or saturated perester 8. In no other solvent was similar material observed. Largely on this basis, the material was assumed to result from coupling of cyclohexadienyl radicals. No attempt was made either to determine whether the observed vpc peak might be due to more than a single material (111) or to isolate and characterize the material.

However, peak areas were generally monitored. Yields calculated assuming unexceptional vpc response characteristics for the dimer are displayed in Tables 1, 2, and 3. The yields, it may be seen, increase with increasing 1,4-cyclohexadiene concentration, but not proportionately.

In terms of the present reaction mechanism, we can write

$$\text{mM cyclohexadienyl radical dimer/mM perester taken} =$$

$$\frac{1}{2(\mathrm{P})_o} \int_0^\infty 2\xi k_4 (\mathrm{Z}\cdot)^2 \, dt \quad , \qquad (2.4\text{-}26)$$

where ξ is the fraction of pairwise reactions resulting in formation of the dimer. Using the usual exponential relationship for first-order decomposition between perester concentration and time, as in Appendix B, the definitions of F (eq. 2.1-4) and X (eq. 2.1-8), we can rewrite eq. 2.4-26 in the form

$$\text{mM dimer/mM perester} = \xi\alpha \int_0^1 \frac{F}{2X} \, dz \quad , \qquad (2.4\text{-}27)$$

where α is the fraction of perester decompositions yielding either 3 or 4 and $z \equiv (\mathrm{P})/(\mathrm{P}_o)$ is the variable of integration, as in eqs. 2.1-1—2.1-3.

Yields of dimer calculated from eq. 2.4-27 using the standard three-point Gaussian quadrature (Appendix B) are displayed for Calculation 14 in Table 17, p. 298, alongside the observed quantities. The calculated yields employ values of α taken from a neighboring column of Table 17 together with $\xi = 0.40$.

Comparison of observed and calculated quantities reveals that yields are underestimated for runs employing perester **2**, but overestimated for runs employing **1**. Indeed, if ξ is evaluated for each run so as to produce agreement between the observed and calculated yields, one finds $\xi = 0.38 \pm 0.08$ for all runs, but 0.45 ± 0.05 for runs employing **2** and 0.32 ± 0.04 for runs employing **1**. Thus, the data are not as unmindful of the identity of the starting perester as one might like.

Several considerations may be advanced to account for the roughness of the fit. The lower apparent values of ξ at higher reaction temperatures might indicate that higher temperatures favor disproportionation over combination. Destruction of dimer via radical attack at ~1 M 1,4-cyclohexadiene and via Diels-Alder addition to 1,4-cyclohexadiene at higher cyclohexadiene concentrations could also be important. Moreover, the appearance of the vpc peak of the dimer on the tail of the solvent peak and an observed sensitivity of peak areas to injector temperatures combine to ensure that the quality of the data is low. Radical-induced decomposition via attack of cyclohexadienyl radicals on ring-opened perester **1** would serve to selectively lower yields of the radical dimer at higher cyclohexadiene concentrations.

Finally, the radical dimer might redissociate to cyclohexadienyl radicals (and thus feed over to disproportionation products) on the time scale of the perester decompositions when the starting perester is 1, but not when it is 2. This is not unreasonable because comparable reaction times for ten perester-decomposition half-lives requires a reaction temperature for perester 1 roughly 100° higher than that for perester 2. The comparison of observed and calculated yields of the dimer indicates that some redissociation may have occurred, but can not be rapid on the perester-decomposition time scale.

This is an important point, for we have made no mechanistic provision for the possibility that dimer containing the ring-cyclized moiety might similarly redissociate. Occurrence of the latter would cause the effective values of the conversion efficiency parameters γ and δ to increase abruptly on going from 70° for perester 2 to 99° for perester 1. Assumption of such behavior would unilaterally decrease $R1^{calc}$ at 99—150°. However, the $R1_c^{calc}$ already tend to be too low at 99° but too high at 70°; inclusion of redissociation would increase the temperature incompatibility in the R1 ratios discussed under heading (1), p. 251.

Our conclusion is that the coupling products from cyclohexadienyl and ring-cyclized radicals do not rapidly redissociate on the time scale of the perester decompositions.

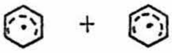
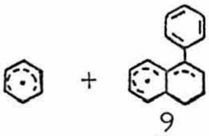
James and Suart report (52) that the fraction of pairwise reactions of cyclohexadienyl radicals in the gas phase at 23—117° which result in coupling rather than disproportionation is 0.69. Our estimate for a similar temperature range in hydrocarbon solution is

$\xi = 0.40$. It is interesting in this connection that the ratio of disproportionation to combination for ethyl radicals at 0° is 0.13 in the gas phase but 0.18 in isooctane solution (103). Our data may confirm the suggestion (103) that solvent cages (or simply the condensed phase) favor disproportionation over combination.

P. Summary of Interactions of Ring-cyclized Radicals and Cyclohexadienyl Radicals

We now have available information concerning the patterns of coupling and disproportionation for 9 with 9, 9 with cyclohexadienyl, and cyclohexadienyl with cyclohexadienyl. We have recorded this information in Table 16 with a view to providing a possible measure of the consistency of the various assumptions and observations.

Table 16. Probabilities of Disproportionation and Combination for Pair-wise Reactions of Two Cyclohexadienyl-type Radicals.

Reactants	Probability of disproportionation	Probability of coupling
	0.6	0.4[a]
 9	0.7[b]	0.3
9 + 9	0.6–0.7[c]	0.3–0.4

[a] Evaluated from observed yields of cyclohexadienyl radical dimer.

[b] Made up of $\delta = 0.42$ (required to fit yields of 5) and $\epsilon = 0.28$ (required to fit yields of tetrahydronaphthalenes B); see Chart 7, p. 198 for definitions of δ and ϵ.

[c] Required to account for yields of dihydronaphthalene 10 for reaction of 1 in triethyltin hydride; see the discussion on pp. 260 – 261.

Cyclohexadienyl radicals and ring-cyclized radicals apparently behave rather similarly. In view of their structural kinship, this is perhaps not surprising. We previously noted that the ratio data in 1,4-cyclohexadiene could be fit better if we assumed that pairwise reaction of ring-cyclized radicals nearly always results in dimerization (Calculation 11, Tables 18, 19). While footnote c above may suffice to reject that parameterization, we can perhaps add here that the structural kinship of cyclohexadienyl radical and 9 would make it difficult to understand why the two cases (rows 1 and 3 in Table 16) should be greatly different.

Q. Extent of Reversibility of the Ring-cyclization Process

Evidence for reversibility of the *ortho*-ring cyclization process (the k_{-r} process of Chart 7, p. 198) should show up most strongly as systematically low predictions for R1 ratios at low initial perester concentrations and high reaction temperatures. Runs 35–38 (initial perester concentrations, 0.001 M; reaction temperatures, 99–125°) best meet these experimental prerequisites. The RELDEV R1 quantities for these runs in Calculation 5 (see Table 18, p. 300) range from -8.5% to -18.6%. Although the calculated ratios are indeed systematically low, it is clear that decyclization can not be very important even under these conditions.

We should perhaps recall here that these runs, and several others at low initial perester concentrations, were not included in the optimization procedure so that comparison of observed ratios to (calculated) ratios in effect extrapolated from measurements at higher perester concentrations could be used to judge the importance of the decyclization process.

A series of calculations were carried out to establish the maximum value for the decyclization parameter $D = k_{-4}/k_3^{\frac{1}{2}}$ compatible with the data. This was done by taking all other parameters as in Calculation 5 while gradually 'turning on' the decyclization and observing the result on the RELDEV R1 quantities for runs 35–38. For these calculations we have assumed a composite activation energy for D of 18 kcal/mole (see below) and have varied the composite preexponential factor. A preexponential factor of 10^6 raised the average RELDEV R1 for the four runs from -12% to zero, while 2×10^6 gave an average RELDEV R1 of +10%. We can therefore take 2×10^6 to be the maximum value allowed for the data.

Using the assumed 18 kcal/mole composite activation energy, this gives $D(100^\circ) \leq 5 \times 10^{-5}$ (liter-sec/mole)$^{-\frac{1}{2}}$. If we further assume $k_3 = 4 \times 10^9 \exp(-2/RT)$ (this gives $k_3 \cong 3 \times 10^8$ sec^{-1} at 100°), we obtain

$$k_{-r} \quad 10^{10} \exp(-19/RT) \quad (M^{-1} \sec^{-1}) \quad . \qquad (2.4\text{-}28)$$

For purposes of comparison, we shall record here the estimate (p. 349) for the *ortho*-ring-cyclization rate constant:

$$k_r = 4 \times 10^{10} \exp(-6.6/RT) \quad (M^{-1} \sec^{-1}) \quad . \qquad (2.4\text{-}29)$$

The ratio k_{-r}/k_r, gives the equilibrium constant for the radicals **3** and **9**. If, then, the entropies of the radicals are not greatly different, the preexponential factor for k_{-r} would appear to be reasonable.

Eqs. 2.4-28 and 2.4-29 state that the ring-cyclized radical 9 lies lower in enthalpy than the ring-opened radical 3 by ~12 kcal/mole. Our prediction that this should be the case was the basis for taking the composite activation energy for D to be 18 kcal/mole. The experimental result we start with is the report by James and Suart that addition of a hydrogen atom to benzene is exothermic by 27 kcal/mole (52). If we can estimate from this the exothermicity for addition of an ethyl radical to benzene, we will have a reasonable model for the *ortho*-ring-cyclization process.

Walling notes that the C–H bond dissociation energy for ethane, the energy required to dissociate molecular hydrogen, and heats of formation of ethane and ethylene can be employed in a thermochemical cycle to calculate a value of 40 kcal/mole for the energy required to dissociate a β-hydrogen atom from the ethyl radical (112). Using an analogous cycle starting from butane instead of ethane, assuming that the dissociation energy of a primary C–H bond in butane is the same as in ethane, and taking heats of formation from standard tables (113), one can calculate $D(Et-CH_2CH_2\cdot) = 22$ kcal/mole. Thus, addition of an ethyl radical to ethylene is less exothermic than addition of a hydrogen atom by ~18 kcal/mole.

A similar comparison indicates that addition of an ethyl radical to butadiene is less exothermic than addition of a hydrogen atom by ~16 kcal/mole.

On this basis, we estimate that addition of an ethyl radical to benzene should be exothermic by 27 - 17 = 10 kcal/mole. This figure is most appropriate for the cyclization of saturated radical 21 to 24, as the latter is an alkyl-substituted cyclohexadienyl radical. Greater exothermicity would be expected for ring-cyclization by 3 because of the more extensive π-system which results. We can estimate from the localization energy considerations of pp. 145–149 that this factor should be 'worth' about 2 kcal/mole, so that ring-cyclization by 3 should be exothermic by ~ 12 kcal/mole.

These considerations neglect any specifically conformational contributions to the relative energies of 3 and 9. However, such factors could well be small.

In contrast, we have previously estimated isomerization of 3 to 4 to be exothermic by 8 ± 3 kcal/mole. In addition, opening of the strained three-membered ring for 4 → 3 may well carry a higher frequency factor than opening of a six-membered ring for 9 → 3. The net result is that the former process is rapidly reversible, but the latter effectively irreversible, under conditions studied.

R. Summary of the Mechanistic Conclusions

The mechanistic scheme of Chart 7, p. 198, gives an average relative deviation of 6.1% between calculated and observed product ratios R1 and R2, where R1 ≡ % yield 5/% yield 10 and R2 ≡ % yield 6/% yield 5. Examination of the success of the basic fit (Calculation 1, Table 18 (p. 299)) on a run-by-run basis reveals the presence of several types of systematic errors--subtleties in the product-ratio data which are not reproduced in the calculated quantities.

Sizable systematic errors of two types could be eliminated, but only upon modification of the mechanistic scheme. The first of these consisted in a strong tendency for calculated values of R2 to deviate positively at low 1,4-cyclohexadiene concentrations and negatively at high concentrations. It was shown that the mechanistic inadequacy could not be attributed to failure of the assumption of rapid reversibility of ring-closed radical **4** with ring-opened radical **3** (heading (a), p. 252). A solvent effect on the rate constants for perester decomposition could in principle be responsible, but was not invoked. It proved possible to eliminate the systematic deviations by taking the rate constants for radical-radical processes, specifically for reaction of ring-closed radical **4** with cyclohexadienyl radical (rate constant $k_b^{\circledcirc}$), to be proportional to the reciprocal of the solvent viscosity, as is suggested by theoretical treatments based on models of the liquid phase (e.g., eq. 2.4-7, p. 255). This subject is discussed under heading (d), p. 254. Viscosities of 1,4-cyclohexadiene--cyclohexane mixtures were measured at 20°; the variation was found to account nicely for the size and nature of the systematic deviations in R2 (Calculation 5, p. 300).

The calculated R1 ratios were found to exhibit negative deviations at low 1,4-cyclohexadiene concentrations and positive deviations at high cyclohexadiene concentrations (heading (3), p. 259). A possible explanation--that inadequate allowance was made for variation of the efficiency with which ring-cyclized radicals **9** are converted to the dihydronaphthalene **10** as a function of reaction conditions--was shown to fail; Calculation 11 (Table 18, p. 300) employed the maximum of variability of conversion efficiency attainable in our mechanistic scheme, but was unable to significantly reduce the scope of the especially severe systematic deviations for runs employing ring-closed perester 2.

It was then necessary to assume that the rate-constant ratio $E = k_a^{\text{⌬}}/k_r$, which controls the partitioning between formation of 5 via hydrogen abstraction and ring-cyclization to 9, is a function of the solvent composition (eq. 2.4-15, p. 263). As with the t-butoxy radical (42), complexing solvents (such as the olefinic 1,4-cyclohexadiene) appear to favor a unimolecular process over bimolecular hydrogen abstraction, perhaps by partial exclusion of the hydrogen donor from the neighborhood of the radical center by association of the latter with solvent. Elimination of the systematic deviations in the R1 ratios required the assumption that E decreases by ~30% at 0° and ~15% at 150° on going from pure cyclohexane as solvent to pure 1,4-cyclohexadiene. It was possible to reduce the average deviation for R1 ratios where the starting perester is 2 from 10-11% to < 6% (Calculations 12, 13, and 15, Table 18) and, with some further modifications, to reduce the overall average deviation from 5.8% (Calculation 5) to 4.4% (Calculation 15).

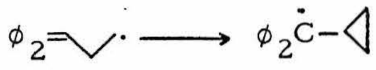
Although solvation effects of even the small magnitude tentatively inferred here seem not to have been previously implicated for reactions of nonpolar hydrocarbon radicals (perhaps simply due to lack of investigation), the resultant improvement in the quality of the fit is sufficiently large to suggest that the assumed effects are real. It appears to be feasible to obtain experimental verification of the assumed medium effects, both regarding the partitioning between hydrogen abstraction and ring-cyclization and the theoretically better justified effect of viscosity on the rates of radical-radical processes (heading E, p. 266).

The rate constant ratio k_a$/k_r$ is found to be 0.145 ± 0.02 at 100° (heading H, p. 272). As we previously had $k_a^{SnH}/k_r \cong 7$ at the same temperature, we conclude that abstraction of hydrogen by ring-opened radicals 3 is more rapid from triethyltin hydride than from 1,4-cyclohexadiene by a factor of ~50 at 100°.

Certain experiments at low initial concentrations of ring-opened perester 1 (0.001 M) seem to give directly the relative amounts of ring-closed hydrocarbon 6 and ring-opened hydrocarbon 5 formed via abstraction of hydrogen from 1,4-cyclohexadiene. However, the experimental validity of these experiments is clouded by the observation that 1,4-cyclohexadiene itself develops one or more impurities which would be mistaken for 6 upon routine vpc analysis. It was shown (a) that the fit to the product ratios at much higher initial perester concentrations (~0.25 M) determines much the same value for the parameter I, the quantity in question (Calculation 16) and (b) that assuming no 6 is formed by hydrogen abstraction from 1,4-cyclohexadiene raises the average deviation for product ratio R2 from 5.6% (Calculation 5) to 14% (Calculation 17) for higher perester concentration runs starting from ring-opened perester 1. We concluded, not entirely without reservations, that hydrogen abstraction from 1,4-cyclohexadiene gives characteristic ratio 6:5 of 0.0035 ± 0.0010 at 100° (heading I, p. 273). The analogous quantity for abstraction from triethyltin hydride is ~0.07, indicating that whereas ring-opened radical 3 abstracts hydrogen from the tin hydride ~50 times more rapidly than from 1,4-cyclohexadiene (see above), ring-closed radical 4 prefers the tin hydride by a factor of ~1000.

In contrast, hydrogen abstraction from the very reactive cyclohexadienyl radical appears to yield 6 and 5 in the ratio of at least 5:1 at 100° (heading J, p. 275).

It was possible to estimate reasonably directly that isomerization of ring-opened radical 3 to ring-closed radical 4 is exothermic by 8 ± 3 kcal/mole (heading K, p. 277).


3 4

$$\Delta H_{isom} = -8 \pm 3 \text{ kcal/mole}$$

Dihydronaphthalene 10 accounts for only about 40% of precursor ring-cyclized radicals 9. The remaining 60% presumably appear as tetrahydronaphthalenes, resulting from addition of a hydrogen atom to 9, or as radical-radical coupling products. Calculated yields of tetrahydronaphthalene correlate reasonably well with observed yields of a substance tentatively assigned that identity (heading M, p. 281). Calculated yields of dimer then account nearly quantitatively for the 10% material balance deficit for observed monomeric products for reactions of ring-closed perester 2, but for only half of the 20% deficit for reactions of ring-opened 1. Radical-induced decomposition of 1 by cyclohexadienyl radicals may play a minor role (heading N, p. 282).

Calculated yields of coupling product from cyclohexadienyl radicals correlate roughly with observed yields. The fraction of pairwise reactions resulting in coupling rather than disproportionation is ~0.4, compared to a report of 0.7 in the gas phase (52). It appears that the radical dimers from coupling of cyclohexadienyl radicals or ring-cyclized radicals (which are substituted cyclohexadienyl radicals) redissociate at best slowly at 100° hrs (heading O, p. 282).

The competition between coupling and disproportionation appears to be similar for pairwise reaction of cyclohexadienyl radicals or of ring-cyclized radicals or for reaction of ring-cyclized radicals with cyclohexadienyl radicals (heading P, p. 286).

The decyclization of ring-cyclized 9 to ring-opened 3 competes at best inefficiently with consumption of 9 in radical-radical reactions even for 0.001 M ring-opened perester at 100–150°. This is shown to be consistent with estimates for the heat of isomerization for cyclization of 3 to 9 and for the rate of the forward process (heading Q, p. 287).

Table 17. Least-Squares Calculation No. 14[a] for Decomposition of Peresters 1 and 2 in Solutions of 1,4-Cyclohexadiene in Cyclohexane.

RUN	Bath Temp. °C	Per-ester Iden-tity	Initial Perester Conc. M	$_{av}$[b] M	R1^{obs}[c]	R1^{calc}[c]	RELDEV[d] R1	RWT1[e]
1	0	2	0.050	2.94	1.57	1.35	-14.0	0.899
2				5.31	2.68	2.49	- 7.3	0.960
3				7.96	3.51	3.77	7.3	0.974
4				10.79	4.49	5.16	14.9	0.981
5	35	2	0.050	2.81	1.35	1.11	-17.5	0.900
6				5.09	2.28	2.04	-10.4	0.961
7				7.63	2.91	3.09	6.2	0.974
8				10.36	4.08	4.23	3.7	0.985
9	70	2	0.050	2.70	0.97	0.96	- 1.0	0.856
10				4.88	1.62	1.75	7.8	0.940
11				7.32	2.48	2.63	6.2	0.968
12				9.93	2.82	3.59	27.4	0.964
13	99	1	0.265	0.90	0.45	0.33	-26.5	0.402
14				1.82	0.75	0.66	-12.6	0.660
15				4.06	1.64	1.44	-12.4	0.904
16				4.06	1.42	1.44	1.1	0.876
17				8.28	2.92	2.89	- 1.0	0.966
18	131	1	0.260	0.91	0.36	0.31	-13.7	0.334
19				1.81	0.66	0.61	- 8.1	0.638
20				3.99	1.33	1.31	- 1.3	0.881
21				8.10	2.58	2.62	1.6	0.964
22	150	1	0.255	0.91	0.33	0.30	- 8.5	0.311
23				1.78	0.58	0.58	0.7	0.592
24				3.92	1.24	1.26	1.3	0.873
25				7.96	2.34	2.51	7.1	0.960
26				7.96	2.33	2.51	7.5	0.960
27	35	2	0.101	2.42	1.14	0.91	-19.9	0.851
28			0.0220	2.51	1.09	1.03	- 5.5	0.862
29			0.0060	2.53	1.21	1.08	-10.9	0.
30			0.0010	2.53	1.11	1.11	0.1	0.
31	110	1	0.270	0.92	0.38	0.33	-13.6	0.332
32			0.030	1.20	0.43	0.42	- 1.9	0.
33			0.030	1.20	0.43	0.42	- 1.9	0.
34			0.0051	1.23	0.44	0.43	- 2.9	0.
35			0.0010	1.23	0.50	0.42	-15.1	0.
36	99	1	0.0010	9.65	4.1	3.34	-18.5	0.
37	110		0.0010	9.45	3.5	3.17	- 9.4	0.
38	125		0.0010	9.34	3.3	3.03	- 8.1	0.
39	144		0.0010	9.20	---	2.87	---	0.

[a] See Table 19 for values of parameters and quality-of-fit quantities.

[b] See Tables 1, 2, 4, 5, and 6 for initial concentrations.

[c] % yield 5/% yield 10.

[d] (calc−obs)/obs x 100%.

[e] Relative weight; see eq. 2.4-2; for explanation of zero values, see pp. 242, 247.

Table 17 (cont.)

RUN	Reduced Ratio[f] R		R2obs[g]	R2calc[g]	RELDEV[d] R2	RWT2[h]	% Yield 5[i]	
	OBSVD	CALC					OBSVD	CALC
1	1.87	2.17	0.715	0.770	7.7	2.00	18.9	19.8
2	1.98	2.14	0.487	0.514	5.6	2.43	26.5	28.2
3	2.27	2.11	0.392	0.396	1.1	2.60	33.7	35.1
4	2.40	2.09	0.335	0.320	- 4.3	2.68	38.5	40.9
5	2.08	2.53	0.769	0.797	3.6	2.05	22.1	19.4
6	2.23	2.49	0.518	0.526	1.5	2.48	31.1	28.3
7	2.62	2.47	0.400	0.402	0.5	2.62	35.5	35.7
8	2.54	2.45	0.325	0.324	- 0.4	2.68	45.0	41.9
9	2.79	2.82	0.763	0.814	6.7	1.72	19.8	18.7
10	3.01	2.80	0.540	0.534	- 1.1	2.22	29.6	27.7
11	2.95	2.78	0.405	0.407	0.4	2.39	35.8	35.3
12	3.52	2.76	0.349	0.327	- 6.2	2.54	37.0	41.8
13	2.01	2.73	0.033	0.033	0.2	0.25	9.0	7.5
14	2.42	2.77	0.020	0.021	3.2	0.38	11.8	13.7
15	2.48	2.83	0.013	0.013	1.9	0.43	20.6	24.6
16	2.86	2.83	0.013	0.013	1.9	0.43	19.7	24.6
17	2.83	2.86	0.010	0.010	- 4.3	0.44	28.6	37.4
18	2.53	2.93	0.052	0.051	- 2.4	0.24	9.5	7.6
19	2.74	2.98	0.028	0.030	7.8	0.36	14.4	13.9
20	3.00	3.04	0.017	0.018	6.3	0.42	22.2	25.2
21	3.14	3.09	0.011	0.012	10.5	0.44	30.4	38.7
22	2.74	3.00	0.051	0.059	16.3	0.20	8.1	7.4
23	3.07	3.05	0.034	0.035	3.0	0.36	13.7	13.4
24	3.16	3.12	0.020	0.021	3.0	0.42	21.7	24.4
25	3.40	3.18	0.013	0.014	4.2	0.44	31.3	37.8
26	3.41	3.18	---	0.014	--	0.	31.5	37.8
27	2.12	2.65	1.17	1.215	3.9	1.73	17.9	16.2
28	2.31	2.44	0.640	0.600	- 6.2	2.13	22.0	19.2
29	2.09	2.34	0.350	0.329	- 6.1	2.19	28.5	20.7
30	2.28	2.28	0.165	0.142	-13.9	2.30	26.9	21.8
31	2.42	2.80	0.044	0.038	-14.3	0.	6.7	7.4
32	2.79	2.84	0.020	0.013	-32.6	0.	9.7	9.3
33	2.79	2.84	0.021	0.013	-35.8	0.	9.5	9.3
34	2.79	2.87	0.012	0.008	-33.7	0.	8.2	9.5
35	2.46	2.90	0.011	0.006	-48.6	0.	9.9	9.5
36	2.35	2.89	0.0040	0.0040	0.3	0.99	--	40.1
37	2.70	2.98	0.0036	0.0038	6.2	0.99	--	40.3
38	2.83	3.08	0.0038	0.0037	- 3.8	1.00	--	41.7
39	--	3.21	0.0037	0.0035	- 5.6	1.00	--	40.6

[f] % yield **10** x (⌬)$_{av}$/% yield **5**. [g] % yield **6**/% yield **5**.

[h] Analogous to RWT1[e]; for explanation of zero values, see pp. 247, 266.

[i] Average deviation between calculated and observed yields ≅ 10%.

Table 17 (cont.)

RUN	% Yield[j] Tetrahydro-naphthalene(s) OBSVD	CALC	% Yield[k] Dimer from 9 CALC	% Yield[l] Cyclohexadienyl-Radical Dimer OBSVD	CALC	Fraction[m] Radical Pairs (≡ α)	Average Value[n] W	X
1	--	6.9	7.6	0.10	0.09	0.67	0.48	0.097
2	--	5.2	5.7	0.13	0.12	0.68	0.37	0.075
3	---	4.2	4.6	0.16	0.15	0.70	0.30	0.064
4	--	3.6	3.9	0.19	0.17	0.72	0.25	0.057
5	--	8.2	9.1	0.12	0.09	0.73	0.52	0.104
6	--	6.4	7.0	0.15	0.12	0.74	0.42	0.080
7	--	5.3	5.8	0.16	0.15	0.76	0.34	0.068
8	--	4.5	4.9	--	0.17	0.78	0.29	0.060
9	--	9.3	10.3	0.12	0.09	0.77	0.56	0.110
10	--	7.4	8.1	0.16	0.12	0.78	0.46	0.085
11	--	6.2	6.7	0.13	0.15	0.80	0.38	0.072
12	--	5.3	5.8	0.15	0.17	0.82	0.32	0.063
13	9.7	11.0	12.4	0.06	0.08	0.65	0.88	0.108
14	7.6	9.9	11.1	0.09	0.11	0.66	0.79	0.078
15	8.2	8.0	8.8	0.12	0.18	0.67	0.63	0.051
16	8.4	8.0	8.8	0.11	0.18	0.67	0.63	0.051
17	5.8	5.9	6.4	0.14	0.26	0.69	0.45	0.036
18	13.6	12.1	13.9	0.08	0.07	0.71	0.89	0.131
19	12.1	11.1	12.5	0.09	0.09	0.72	0.80	0.101
20	10.7	9.0	10.0	0.13	0.14	0.73	0.65	0.069
21	9.5	6.8	7.4	0.17	0.20	0.75	0.48	0.049
22	12.2	12.2	13.9	0.06	0.07	0.71	0.89	0.137
23	15.6	11.2	12.6	0.07	0.09	0.72	0.81	0.107
24	11.5	9.2	10.2	0.10	0.13	0.73	0.66	0.074
25	8.4	7.0	7.6	0.14	0.19	0.75	0.49	0.053
26	10.0	7.0	7.6	--	0.19	0.75	0.49	0.053
27	7.1	8.4	9.4	--	0.08	0.73	0.51	0.117
28	7.1	8.8	9.8	--	0.09	0.73	0.58	0.102
29	6.5	9.1	10.2	--	0.10	0.73	0.62	0.097
30	5.9	9.4	10.5	--	0.11	0.73	0.66	0.092
31	5.5	11.0	12.5	--	0.07	0.65	0.88	0.117
32	13.4	10.6	11.9	--	0.11	0.65	0.85	0.081
33	12.3	10.6	11.9	--	0.11	0.65	0.85	0.081
34	11.9	10.6	11.7	--	0.15	0.65	0.85	0.060
35	13.1	10.5	11.6	--	0.20	0.65	0.85	0.045
36	--	5.5	5.9	--	0.55	0.69	0.42	0.017
37	--	5.8	6.3	--	0.48	0.71	0.43	0.020
38	--	6.2	6.7	--	0.42	0.74	0.44	0.024
39	--	6.5	7.0	--	0.34	0.75	0.46	0.029

[j] See Chart 4, p. 78, for possible structures.

[k] Measures C_{16} fragments in C_{22} and C_{32} coupling products of Chart 7, p. 198.

[l] mM, per mM perester taken; see heading O, p. 282. [m] See p. 247 for estimation procedure.

[n] Values at 11, 50, and 89% averaged with weights of 5/18, 4/9, and 5/18 (94).

Table 18 Selected Data for Least-Squares Calculations 1, 2, 3, 5, 11, 12, 13, 15, 16, and 17.[a]

	Calculation No. 1				Calculation No. 2			
RUN	$R1^{calc}$[b]	RELDEV[c] R1	$R2^{calc}$[d]	RELDEV[c] R2	$R1^{calc}$[b]	RELDEV[c] R1	$R2^{calc}$[d]	RELDEV[c] R2
1	1.38	-12.2	0.792	10.8	1.34	-14.4	0.810	13.2
2	2.45	- 8.5	0.513	5.2	2.48	- 7.5	0.512	5.1
3	3.65	3.9	0.383	- 2.3	3.77	7.2	0.378	- 3.7
4	4.92	9.6	0.307	- 8.4	5.15	14.7	0.300	-10.4
5	1.17	-13.3	0.820	6.6	1.12	-17.1	0.837	8.8
6	2.08	- 8.7	0.528	1.9	2.05	-10.1	0.528	1.9
7	3.09	6.1	0.394	- 1.5	3.10	6.5	0.389	- 2.7
8	4.16	2.1	0.315	- 2.9	4.23	3.7	0.309	- 4.8
9	1.03	6.3	0.839	9.9	1.01	3.7	0.822	7.8
10	1.82	12.4	0.541	0.2	1.80	11.0	0.527	- 2.3
11	2.70	8.7	0.404	- 0.3	2.69	8.5	0.392	- 3.3
12	3.63	28.6	0.324	- 7.2	3.65	29.3	0.313	-10.3
13	0.33	-27.6	0.032	- 3.4	0.33	-26.2	0.034	3.7
14	0.65	-13.9	0.020	- 2.5	0.66	-12.5	0.020	2.2
15	1.41	-14.1	0.012	- 6.0	1.43	-12.6	0.012	- 4.3
16	1.41	- 0.8	0.012	- 6.0	1.43	1.0	0.012	- 4.3
17	2.82	- 3.5	0.009	-12.8	2.88	- 1.5	0.009	-12.7
18	0.31	-14.5	0.051	- 1.0	0.31	-13.2	0.055	5.5
19	0.60	- 8.9	0.030	8.1	0.61	- 8.2	0.032	13.4
20	1.30	- 2.4	0.018	3.9	1.31	- 1.9	0.018	6.0
21	2.58	0.1	0.012	5.3	2.60	0.7	0.012	5.3
22	0.30	- 9.0	0.061	19.0	0.31	- 6.9	0.064	25.7
23	0.58	0.2	0.036	4.7	0.59	1.1	0.037	9.3
24	1.25	0.6	0.020	2.3	1.25	0.9	0.021	4.2
25	2.48	6.0	0.013	1.0	2.49	6.2	0.013	0.8
26	2.48	6.4	0.013	--	2.49	6.6	0.013	--
27	1.01	-11.2	1.248	6.6	0.93	-18.8	1.274	8.9
28	1.05	- 3.9	0.622	- 2.9	1.03	- 5.7	0.639	- 0.2
29	1.05	(-13.1)	0.342	- 2.4	1.07	(-11.7)	0.353	0.8
30	1.05	(- 5.3)	0.149	- 9.8	1.09	(- 1.4)	0.154	- 6.7
31	0.32	-14.8	0.037	(-15.6)	0.33	-13.5	0.040	(- 9.3)
32	0.42	(- 2.7)	0.013	(-37.3)	0.42	(- 1.6)	0.013	(-33.8)
33	0.42	(- 2.7)	0.013	(-40.3)	0.42	(- 1.6)	0.013	(-37.0)
34	0.43	(- 2.8)	0.007	(-39.9)	0.43	(- 1.8)	0.007	(-37.5)
35	0.43	(-14.3)	0.005	(-52.7)	0.43	(-13.5)	0.005	(-51.7)
36	3.26	(-20.4)	0.0042	4.3	3.33	(-18.7)	0.0042	4.3
37	3.12	(-10.9)	0.0039	8.4	3.16	(- 9.7)	0.0039	8.1
38	3.00	(- 9.2)	0.0037	- 3.5	3.02	(- 8.6)	0.0036	- 4.2
39	2.85	--	0.0034	- 7.0	2.85	--	0.0034	- 8.0

[a] See Table 19 for values of parameters and quality-of-fit quantities.

[b] % yield 5/% yield 10.

[c] (calc−obs) /obs x 100%; parentheses indicate points omitted from the least-squares optimization; see footnotes e and h, Table 17.

[d] % yield 6/% yield 5.

Table 18 (cont.)

	Calculation No. 3		Calculation No. 5				Calculation No. 11	
RUN	$R2^{calc}$[d]	RELDEV[c] R2	$R1^{calc}$[b]	RELDEV[c] R1	$R2^{calc}$[d]	RELDEV[c] R2	$R1^{calc}$[b]	RELDEV[c] R1
1	0.738	3.2	1.35	-13.90	0.762	6.63	1.42	- 9.9
2	0.509	4.6	2.48	- 7.40	0.511	4.94	2.52	- 6.0
3	0.400	2.1	3.76	7.07	0.395	0.75	3.75	6.8
4	0.327	- 2.3	5.14	14.50	0.320	- 4.52	5.08	13.1
5	0.776	0.9	1.12	-17.32	0.798	3.71	1.16	-14.4
6	0.530	2.3	2.04	-10.47	0.529	2.11	2.04	-10.5
7	0.413	3.3	3.08	5.90	0.406	1.52	3.02	3.8
8	0.337	3.7	4.21	3.21	0.328	0.83	4.08	- 0.1
9	0.805	5.5	0.98	1.10	0.806	5.63	1.00	3.4
10	0.547	1.3	1.77	8.96	0.536	- 0.77	1.74	7.5
11	0.425	5.0	2.65	6.82	0.411	1.43	2.56	3.2
12	0.346	- 0.7	3.60	27.72	0.332	- 4.86	3.43	21.7
13	0.029	-11.8	0.33	-26.19	0.031	- 5.10	0.38	-16.6
14	0.018	- 7.9	0.66	-12.32	0.019	- 4.08	0.71	- 5.7
15	0.012	- 6.5	1.44	-12.38	0.012	- 6.06	1.45	-11.7
16	0.012	- 6.5	1.44	1.20	0.012	- 6.06	1.45	2.0
17	0.009	-10.1	2.88	- 1.35	0.009	-11.30	2.77	- 5.4
18	0.047	- 8.9	0.31	-13.86	0.051	- 2.35	0.35	- 3.7
19	0.029	2.8	0.60	- 8.48	0.030	7.09	0.65	- 2.2
20	0.018	4.4	1.30	- 1.95	0.018	4.77	1.31	- 1.7
21	0.012	10.7	2.60	0.65	0.012	8.45	2.47	- 4.1
22	0.056	10.1	0.30	- 8.35	0.060	17.25	0.34	2.0
23	0.034	- 0.1	0.58	0.32	0.035	3.73	0.62	6.9
24	0.021	3.1	1.25	0.55	0.021	3.25	1.25	0.6
25	0.014	6.6	2.48	6.03	0.014	4.09	2.36	0.8
26	0.014	--	2.48	6.49	0.014	--	2.36	1.2
27	1.169	- 0.1	0.92	-19.15	1.21	3.37	0.96	-16.1
28	0.581	- 9.2	1.03	- 5.66	0.602	- 5.96	1.08	- 1.1
29	0.319	- 8.8	1.07	-11.47	0.331	- 5.47	1.13	(- 6.6)
30	0.139	-15.9	1.10	- 0.99	0.144	-12.92	1.17	(4.9)
31	0.034	(-22.7)	0.33	-13.62	0.037	(-16.79)	0.37	- 2.8
32	0.012	(-41.3)	0.42	- 1.42	0.012	(-38.14)	0.47	(9.1)
33	0.012	(-44.1)	0.42	- 1.42	0.012	(-41.09)	0.47	(9.1)
34	0.007	(-42.8)	0.43	- 1.57	0.007	(-40.61)	0.48	(8.8)
35	0.005	(-54.4)	0.43	-13.21	0.005	(-53.32)	0.48	(- 4.1)
36	0.0041	3.0	3.34	-18.54	0.0041	2.86	3.18	(-22.5)
37	0.0039	7.8	3.17	- 9.51	0.0039	7.74	3.01	(-14.1)
38	0.0037	- 3.5	3.02	- 8.41	0.0037	- 3.43	2.86	(-13.4)
39	0.0035	- 6.1	2.85	--	0.0035	- 6.07	2.69	--

Table 18 (cont.)

	Calculation No. 12				Calculation No. 13			
					R^f			
RUN	$R1calc^b$	$RELDEV^c$ R1	$R2calc^d$	$RELDEV^c$ R2	OBSVD	CALC	$R2calc^d$	$RELDEV^c$ R2
1	1.55	-1.2	0.691	-3.3	1.87	1.89	0.729	2.0
2	2.64	-1.6	0.491	0.9	1.98	2.00	0.502	3.0
3	3.63	3.4	0.408	4.1	2.27	2.17	0.402	2.5
4	4.43	-1.4	0.361	7.8	2.40	2.41	0.341	1.8
5	1.23	-8.7	0.741	-3.7	2.09	2.28	0.772	0.4
6	2.13	-6.8	0.514	-0.9	2.23	2.39	0.521	0.7
7	2.98	2.4	0.417	4.2	2.62	2.55	0.411	2.7
8	3.73	-8.5	0.360	10.8	2.54	2.75	0.343	5.5
9	1.03	6.0	0.781	2.4	2.79	2.63	0.805	5.5
10	1.78	9.8	0.534	-1.1	3.01	2.74	0.539	-0.3
11	2.52	1.8	0.427	5.4	3.95	2.89	0.420	3.6
12	3.21	13.7	0.363	4.1	3.52	3.08	0.347	-0.5
13	0.37	-18.5	0.029	-12.3	2.02	2.47	0.030	-8.6
14	0.72	-4.7	0.018	-9.9	2.43	2.55	0.019	-7.1
15	1.50	-8.8	0.012	-9.0	2.48	2.72	0.012	-8.0
16	1.50	5.3	0.012	-9.0	2.87	2.72	0.012	-8.0
17	2.73	-6.5	0.009	-9.9	2.84	3.03	0.009	-11.4
18	0.33	-7.7	0.048	-8.1	2.53	2.73	0.049	-4.9
19	0.64	-2.9	0.029	1.8	2.74	2.82	0.029	4.4
20	1.33	0.2	0.017	2.4	3.01	2.99	0.018	3.0
21	2.45	-5.2	0.012	11.6	3.14	3.31	0.012	8.9
22	0.32	-3.3	0.057	11.7	2.75	2.83	0.059	15.2
23	0.61	5.2	0.034	-0.6	3.08	2.92	0.035	1.7
24	1.27	2.1	0.020	1.3	3.17	3.10	0.020	1.8
25	2.33	-0.3	0.014	7.5	3.40	3.41	0.014	4.7
26	2.33	0.1	0.014	--	3.42	3.41	0.014	--
27	1.02	-10.4	1.120	-4.3	2.12	2.37	1.172	0.1
28	1.15	5.4	0.554	-13.5	2.31	2.19	0.580	-9.4
29	1.20	(-0.7)	0.303	-13.4	2.09	2.10	0.318	-9.1
30	1.24	(11.4)	0.131	-20.4	2.28	2.04	0.138	-16.5
31	0.36	-5.4	0.034	(-22.7)	2.43	2.56	0.035	(-19.6)
32	0.46	(7.7)	0.012	(-41.7)	2.79	2.58	0.012	(-39.9)
33	0.46	(7.7)	0.012	(-44.5)	2.79	2.58	0.012	(-42.8)
34	0.47	(7.6)	0.007	(-43.2)	2.79	2.59	0.007	(-41.9)
35	0.47	(-5.1)	0.005	(-54.7)	2.46	2.59	0.005	(-54.0)
36	3.07	(-25.2)	0.0041	2.1	2.35	3.14	0.0041	2.2
37	2.92	(-16.7)	0.0039	7.6	2.70	3.23	0.0039	7.7
38	2.78	(-15.7)	0.0037	-2.9	2.83	3.35	0.0037	-2.9
39	2.62	--	0.0035	-4.7	--	3.51	0.0035	-4.9

[f] % yield **10** x ()$_{av}$/% yield **5**.

Table 18 (cont.)

	Calculation No. 15				Calculation No. 16		Calculation No. 17	
RUN	R1$^{\mathrm{calc}\,b}$	RELDEV^c R1	R2$^{\mathrm{calc}\,d}$	RELDEV^c R2	R2$^{\mathrm{calc}\,d}$	RELDEV^c R2	R2$^{\mathrm{calc}\,d}$	RELDEV^c R2
1	1.56	- 0.5	0.742	3.8	0.756	5.8	0.754	5.5
2	2.68	0.0	0.507	4.1	0.513	5.3	0.503	3.2
3	3.71	5.7	0.404	3.2	0.401	2.2	0.386	- 1.4
4	4.55	1.3	0.342	2.2	0.328	- 2.1	0.311	- 7.1
5	1.24	- 8.5	0.771	0.3	0.786	2.3	0.814	5.8
6	2.15	- 5.8	0.516	- 0.3	0.522	0.8	0.542	4.5
7	3.03	4.0	0.405	1.2	0.402	0.5	0.416	4.0
8	3.80	- 6.8	0.337	3.7	0.325	0.1	0.335	3.2
9	1.02	5.0	0.800	4.8	0.807	5.8	0.789	3.4
10	1.78	9.7	0.529	- 2.1	0.534	- 1.2	0.539	- 0.2
11	2.54	2.2	0.409	1.0	0.408	0.8	0.419	3.4
12	3.23	14.7	0.337	- 3.5	0.330	- 5.5	0.341	- 2.2
13	0.37	-17.8	0.032	- 3.4	0.032	- 3.0	0.031	- 5.0
14	0.72	- 4.1	0.020	- 0.3	0.020	- 0.3	0.018	-12.3
15	1.50	- 8.4	0.013	- 0.6	0.013	0.1	0.010	-26.3
16	1.50	5.8	0.013	- 0.6	0.013	0.1	0.010	-26.3
17	2.74	- 6.0	0.010	- 4.4	0.010	- 3.0	0.006	-42.3
18	0.34	- 6.5	0.049	- 5.3	0.051	- 2.0	0.054	4.4
19	0.65	- 1.8	0.029	4.6	0.030	7.1	0.031	10.9
20	1.34	1.1	0.028	3.9	0.018	4.5	0.017	0.7
21	2.46	- 4.5	0.012	10.5	0.012	8.1	0.010	- 6.1
22	0.32	- 2.2	0.058	13.4	0.060	17.9	0.064	25.2
23	0.62	6.4	0.034	0.3	0.035	3.5	0.037	9.4
24	1.28	3.0	0.020	0.7	0.020	2.2	0.021	3.5
25	2.35	0.4	0.014	4.1	0.013	2.4	0.013	- 3.7
26	2.35	0.8	0.014	--	0.013	--	0.013	--
27	1.01	-11.4	1.174	0.3	1.193	2.0	1.219	4.2
28	1.16	6.6	0.579	- 9.5	0.594	- 7.1	0.618	- 3.5
29	1.23	(1.5)	0.317	- 9.4	0.329	- 5.9	0.340	- 2.8
30	1.28	(14.9)	0.137	-17.0	0.147	-10.9	0.145	-12.1
31	0.36	- 4.4	0.036	(-17.2)	0.037	(-15.9)	0.038	(-13.9)
32	0.47	(8.2)	0.013	(-34.7)	0.013	(-35.7)	0.010	(-48.9)
33	0.47	(8.2)	0.013	(-37.8)	0.013	(-38.8)	0.010	(-51.3)
34	0.47	(7.0)	0.008	(-35.5)	0.008	(-36.3)	0.004	(-65.4)
35	0.47	(- 6.5)	0.006	(-49.8)	0.006	(-48.4)	0.002	(-83.3)
36	3.07	(-25.2)	0.0040	- 0.8	0.0050	(25.8)	0.0003	(-92.1)
37	2.91	(-16.8)	0.0038	6.1	0.0044	(22.0)	0.0004	(-88.8)
38	2.78	(-15.9)	0.0036	- 2.9	0.0038	(1.0)	0.0005	(-86.2)
39	2.61	--	0.0035	- 3.7	0.0033	(-10.3)	0.0007	(-80.6)

Table 19. Quality-of-fit Quantities and Values of Parameters for Least-Squares Calculations 1—20

Quantity[a]	Calculation No.				
	1	2	3	4	5
RUSD[b]	0.0860	0.0945	0.0868	0.0877	0.0846
AVDEV, %[c]	6.07	6.82	5.94	6.04	5.76
AVDEV R1	8.27	8.96	8.33	8.31	8.58
AVDEV $R1_1$	6.59	6.08	6.69	6.69	6.05
AVDEV $R1_2$	9.65	11.30	9.68	9.64	10.65
AVDEV R2	4.91	5.72	4.67	4.85	4.29
AVDEV $R2_1$	5.66	6.46	5.95	6.26	5.66
AVDEV $R2_2$	4.72	5.55	4.35	4.50	3.97
γ[f]	0.60	0.60	0.60	0.60	0.60
δ[f]	0.42	0.42	0.42	0.42	0.42
ϵ[g]	--	--	--	--	--
C	0.00	1.00	0.00	0.00	1.00
$\phi(20°)$[d]	1.00	1.00	1.60	1.60	1.60
E(100°)	0.138	0.142	0.139	0.139	0.142
E(Eact)	- 0.62	- 0.77	- 0.62	- 0.62	- 0.78
F(100°)	0.0751	0.0564	0.0614	0.0624	0.0605
F(Eact)	(0.00)[a]	(0.00)[a]	(0.00)[a]	(0.00)[a]	(0.00)[a]
G(100°)	1.530	1.313	1.247	1.211	1.176
G(Eact)	-13.21	-13.32	-13.07	-13.17	-13.26
H(100°)[e]	18.6	3.9	23.9	33.3	5.6
I(100°)	0.0039	0.0038	0.0038	0.0038	0.0038
I(Eact)	- 2.13	- 2.09	- 2.02	- 2.09	- 1.97

Table 19 (cont.)

Quantity[a]	Calculation No.				
	6	7	8	9	10
RUSD[b]	0.0872	0.0846	0.0866	0.0863	0.0856
AVDEV, %[c]	6.04	5.78	5.78	5.76	5.76
AVDEV R1	8.76	8.43	8.40	8.84	8.63
AVDEV $R1_1$	6.08	6.29	6.01	5.88	5.84
AVDEV $R1_2$	10.94	10.19	10.34	11.27	10.92
AVDEV R2	4.62	4.38	4.42	4.16	4.27
AVDEV $R2_1$	5.83	5.84	5.50	5.82	5.64
AVDEV $R2_2$	4.34	4.03	4.16	3.78	3.95
γ[f]	0.60	0.60	0.60	0.60	0.60
δ[f]	0.42	0.42	0.42	0.42	0.42
ϵ[g]	--	--	--	--	--
C	1.00	0.50	1.00	1.50	1.50
ϕ(20°)[d]	1.30	1.60	2.00	1.60	2.00
E(100°)	0.142	0.140	0.142	0.143	0.143
E(Eact)	- 0.78	- 0.70	- 0.79	- 0.84	- 0.85
F(100°)	0.0592	0.0609	0.0626	0.0596	0.0622
F(Eact)	(0.00)[a]	(0.00)[a]	(0.00)[a]	(0.00)[a]	(0.00)[a]
G(100°)	1.240	1.205	1.116	1.159	1.103
G(Eact)	-13.27	-13.17	-13.25	-13.30	-13.29
H(100°)[e]	4.6	8.6	7.3	3.7	4.3
I(100°)	0.0038	0.0038	0.0038	0.0038	0.0037
I(Eact)	- 2.08	- 2.06	- 1.75	- 2.00	- 1.76

Table 19 (cont.)

Quantity[a]	Calculation No. 11	12	13	14	15
RUSD[b]	0.0722	0.0827	0.0670	0.0858	0.0650
AVDEV, %[c]	5.03	5.89	4.57	5.75	4.37
AVDEV R1	6.47	5.12	5.13	8.69	5.13
AVDEV $R1_1$	4.12	4.35	4.30	6.31	4.30
AVDEV $R1_2$	8.38	5.74	5.79	10.63	5.80
AVDEV R2	4.28	6.29	4.28	4.21	3.99
AVDEV $R2_1$	5.41	5.84	5.54	4.41	3.51
AVDEV $R2_2$	4.01	6.40	3.98	4.16	4.10
γ[f]	0.00	0.60	0.60	0.60	0.60
δ[f]	0.45	0.42	0.42	0.42	0.39
ϵ[g]	0.40	--	--	0.28	--
C	1.00	1.00	1.00	1.00	1.00
$\phi(20°)$[d]	1.60	1.60	1.60	1.60	1.60
E(100°)	0.136	0.154	0.154	0.144	0.154
E(Eact)	- 0.92	- 1.00	- 1.01	- 0.77	- 1.05
F(100°)	0.0643	0.0665	0.0680	0.0657	0.0846
F(Eact)	(0.00)[a]	(0.00)[a]	(0.00)[a]	(0.00)[a]	(0.00)[a]
G(100°)	1.149	1.166	1.243	1.180	1.362
G(Eact)	-13.41	-13.31	-13.42	-13.36	-13.60
H(100°)	6.4	19.9	14.3	11.9	to high to measure
I(100°)	0.0038	0.0038	0.0038	0.0035	0.0035
I(Eact)	- 1.89	- 1.86	- 1.82	- 1.84	- 1.58

Table 19 (cont.)

Quantity[a]	Calculation No.				
	16	17	18	19	20
RUSD[b]	0.0831	0.1032	0.0857	0.0847	0.0859
AVDEV, %[c]	5.32	6.68	5.90	5.79	5.81
AVDEV R1	8.46	9.28	8.52	8.49	8.78
AVDEV $R1_1$	6.02	6.44	6.04	6.23	5.88
AVDEV $R1_2$	10.48	11.63	10.53	10.33	11.15
AVDEV R2	3.53	5.20	4.52	4.38	4.26
AVDEV $R2_1$	3.62	13.97	5.46	5.93	5.69
AVDEV $R2_2$	3.52	4.10	4.29	4.01	3.91
γ[f]	0.60	0.60	0.60	0.60	0.60
δ[f]	0.42	0.42	0.42	0.42	0.42
ϵ[g]	--	--	--	--	--
C	1.00	1.00	1.00	1.00	1.00
$\phi(20^\circ)$	1.60	1.60	1.60	1.60	1.60
E(100°)	0.142	0.138	0.144	0.141	0.143
E(Eact)	- 0.79	- 0.82	- 0.78	- 0.75	- 0.83
F(100°)	0.0642	0.0608	0.0606	0.0631	0.0591
F(Eact)	(0.00)[a]	(0.00)[a]	(0.00)[a]	(1.00)[a]	(-1.00)[a]
G(100°)	1.189	1.329	1.152	1.197	1.175
G(Eact)	-13.18	-13.02	-13.32	-12.78	-13.71
H(100°)[e]	8.5	2.0	(10^{10})	5.5	5.2
I(100°)	0.0046	(0.)[a]	0.0038	0.0038	0.0038
I(Eact)	- 4.10	--	- 1.94	- 1.97	- 2.06

Footnotes for Table 19

[a] Values of parameters are shown between the second and third solid horizontal lines. Those above the dotted line and those below the dotted line but encased in parentheses are assumed values; all others shown were determined in the least-squares optimization. Product ratio and other data for some of these calculations may be found in Tables 17 and 18.

[b] Defined by eq. 2.4-1, p. 246. Values quoted are felt to be good to ± one or two units in the last place.

[c] Eq. 2.4-3, p. 248. In AVDEV RI_J quantities, $R1 \equiv$ % yield **5**/% yield **10**, $R2 \equiv$ % yield **6**/% yield **5**, and J gives the identity of the starting perester (ring-opened perester **1** or ring-closed perester **2**).

[d] Equation of form of eq. 2.4-14 employed, where preexponential factor is unity and composite activation energy is chosen to give $\phi(20^\circ)$ as listed. Exception is Calculation 4, where we have taken $\phi = 1.6$ at all temperatures.

[e] Composite activation energy of -8 kcal/mole assumed for the parameter H; see heading K, p. 277.

[f] Values of these parameters in all cases are such that, with E chosen to optimize the product ratios, the calculated yields of ring-opened hydrocarbon **5** average no more than 3% greater or less than the observed yields. See Chart 7, p. 198 for definitions of γ and δ.

[g] Fit to product ratios R1 and R2 independent of this quantity. Values shown were chosen to give yields of tetrahydronaphthalenes **B** correctly; see Table 17, footnote j. See Chart 7, p. 198, for meaning of ϵ.

APPENDIX B. Kinetic Treatment of Perester Decomposition in the Presence of 1,4-Cyclohexadiene

We derive here kinetic expressions for decomposition of the ring-opened and ring-closed peresters 1 and 2 in the presence of 1,4-cyclohexadiene based on processes depicted in Chart 7, p. 198.

Chart 7 shows that we are concerned with the concentrations of six free-radical intermediates. Starting from perester 1 and invoking the steady-state approximation for each reactive intermediate, we obtain six equations (ZH ≡ 1,4-cyclohexadiene; Z· ≡ cyclohexadienyl radical; P ≡ perester):

$$d(\cdot O\underline{t}Bu)/dt = (\alpha + \omega)k_o(P) - k_{fast}(\cdot O\underline{t}Bu)(ZH) = 0 \qquad (B1)$$

$$d(22)/dt = \omega k_o(P) - k_5(22)(ZH) - k_6(22)(Z\cdot) = 0 \qquad (B2)$$

$$d(3)/dt = \alpha k_o(P) - \left\{k_1 + k_r + k_a^{\text{⌬}}(ZH) + k_a^{\text{⏣}}(Z\cdot)\right\}(3) + k_2(4) + k_{-r}(9) = 0 \qquad (B3)$$

$$d(4)/dt = k_1(3) - \left\{k_2 + k_b^{\text{⌬}}(ZH) + k_b^{\text{⏣}}(Z\cdot) + k_7(9)\right\}(4) = 0 \qquad (B4)$$

$$d(9)/dt = k_r(3) - \left\{k_{-r} + 2k_3(9) + k_d(Z\cdot) + k_7(4)\right\}(9) = 0 \qquad (B5)$$

$$d(Z\cdot)/dt = k_{fast}(\cdot O\underline{t}Bu)(ZH) + \left\{k_5(22) + k_a^{\text{⌬}}(3) + k_b^{\text{⌬}}(4)\right\}(ZH) - \left\{k_6(22) + k_a^{\text{⏣}}(3) + k_b^{\text{⏣}}(4) + k_d(9) + 2k_4(Z\cdot)\right\}(Z\cdot) = 0 \qquad (B6)$$

The concentrations of $\cdot O\underline{t}Bu$ and the lactonyl radical 22 can be eliminated from eq. 6 using eqs. 1 and 2:

$$d(Z\cdot)/dt = \alpha k_o(P)\ \left\{1 + 2A\left[\frac{B(ZH)/(Z\cdot)}{1+B(ZH)/(Z\cdot)}\right]\right\} + \left\{k_a^{\bigcirc}(\underset{\sim}{3}) + k_b^{\bigcirc}(\underset{\sim}{4})\right\}(ZH)$$

$$- \left\{k_a^{\odot}(\underset{\sim}{3}) + k_b^{\odot}(\underset{\sim}{4}) + k_d(\underset{\sim}{9}) + 2k_4(Z\cdot)\right\}(Z\cdot) = 0 \qquad \text{(B7)}$$

We have employed in eq. 7 the definitions of the parameters A and B given in eqs. 2. 1-4.

We now have, in eqs. 3, 4, 5, and 7, four equations in four unknowns. To eliminate one of the unknowns we add eqs. 3 and 4 to get

$$\alpha k_o(P) + k_{-r}(\underset{\sim}{9}) = \left\{k_r + k_a^{\bigcirc}(ZH) + k_a^{\odot}(Z\cdot)\right\}(\underset{\sim}{3})$$

$$+ \left\{k_b^{\bigcirc}(ZH) + k_b^{\odot}(Z\cdot) + k_7(\underset{\sim}{9})\right\}(\underset{\sim}{4}) \quad , \qquad \text{(B8)}$$

and make the assumption that interconversion of $\underset{\sim}{3}$ and $\underset{\sim}{4}$ is much faster than any other processes the two take part in; specifically, we assume $(\underset{\sim}{4}) = k_1(\underset{\sim}{3})/k_2$. Eq. 8 thus becomes after substitution and rearrangement:

$$W \equiv k_r(\underset{\sim}{3})/\alpha k_o(P) =$$

$$\frac{1 + k_{-r}(\underset{\sim}{9})/\{\alpha k_o(P)\}}{1 + E(1 + I)(ZH) + \left(\dfrac{k_b^{\odot}k_r}{k_2k_r}\right)(1 + 1/H)(Z\cdot) + \left(\dfrac{k_1k_7}{k_2k_r}\right)(\underset{\sim}{9})} \qquad \text{(B9)}$$

Eq. 9 is destined to become eq. 2. 1-9.

We can now write the concentrations of $\underset{\sim}{3}$ and $\underset{\sim}{4}$ which appear in eqs. 5 and 7 in terms of the newly defined variable W. Eq. 5 is simply quadratic in $(\underset{\sim}{9})$, and as such we can solve explicitly for $(\underset{\sim}{9})$. The usual form for the roots of the quadratic equation $ax^2 + bx + c = 0$ is

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad .$$

As we have in eq. 5 a, $b > 0$ but $c < 0$, we must take the upper sign. For reasons which once appeared compelling, we have used the equivalent relationship (for the upper sign)

$$x = \frac{-2c}{b + \sqrt{b^2 - 4ac}} \quad .$$

We find (using eq. 13 below for the second step)

$$\underset{\frown}{(9)} = \frac{2\alpha k_o(P)W}{k_d(Z\cdot)\, S(1+T)} = \frac{2W}{S(1+T)}\, (2\alpha k_o(P)X/k_3)^{\frac{1}{2}} \tag{B10}$$

where the shorthand expressions S and T (eqs. 2. 1-5 and 2. 1-6) are given the definitions

$$S \equiv 1 + \left(\frac{k_7 k_1}{k_2 k_r}\right)\left(\frac{\alpha k_o(P)W}{k_d(Z\cdot)}\right) + \frac{k_{-r}}{k_d(Z\cdot)} \quad ; \tag{B11}$$

$$T \equiv \left\{1 + \frac{8\alpha k_o(P)k_3 W}{\left[k_d(Z\cdot)\right]^2 S^2}\right\}^{\frac{1}{2}} \quad . \tag{B12}$$

If we now substitute for $\underset{\frown}{(9)}$ in eqs. 9 and 7, make use of the definition

$$X \equiv \frac{\alpha k_o(P)k_3}{2k_d^{\,2}(Z\cdot)^2} \tag{B13}$$

to replace (Z·), and invoke the definitions of the parameters C, D, F and G given in eqs. 2.1-4, we find that eq. 9 becomes eq. 2.1-9, eq. 7 becomes 2.1-10, and the expressions for S and T become eqs. 2.1-5 and 2.1-6, respectively.

Had we started with ring-closed perester 2 instead of ring-opened perester 1, the initial set of six steady-state equations would have differed in form from those given here only in that the term $\alpha k_o(P)$ would have appeared in eq. 4 instead of eq. 3. As we employed only the sum of eqs. 3 and 4 in this derivation, this distinction is inconsequential, provided that we again assume that 3 and 4 are in rapid equilibrium. Thus, in all of the final equations we can simply take (P) to be the concentration of the perester employed, whether it be 1 or 2, and k_o to be the rate constant for thermal decomposition of that perester. Of course $A = 0$ for perester 2 (p. 204).

We obtain for the product yields eqs. 2.1-1—2.1-3 as follows. We first write

$$d(5)/dt = \left\{k_a^{\text{⬡}}(ZH) + k_a^{\text{⌬}}(Z\cdot)\right\}(3) \quad , \qquad \text{(B14)}$$

so that

final concentration of hydrocarbon 5 =

$$= \alpha \int_0^{\infty} \left\{k_a^{\text{⬡}}(ZH) + k_a^{\text{⌬}}\left(\frac{\alpha k_o(P)k_3}{2k_d{}^2 X}\right)^{\frac{1}{2}}\right\}\left(\frac{k_o(P)W}{k_r}\right) dt$$

$$= \alpha \int_0^{\infty} \left\{E(ZH) + (G/H)\left(\frac{\alpha k_o(P)}{2X}\right)^{\frac{1}{2}}\right\} k_o(P)dt$$

where we have substituted for $(\underset{\sim}{3})$ and for $(Z\cdot)$ using eqs. 9 and 13 and then for other groupings of rate constants using eqs. 2.1-4.

We now pass from an integral over time to an integral over the perester concentration using the relationship

$$-d(P)/dt = k_o(P) \quad ,$$

or

$$dt = -d(P)/k_o(P) \quad .$$

When $t = 0$, $(P) = (P)_o$; when $t = \infty$, $(P) = 0$. Therefore we can write

$$\text{final conc } \underset{\sim}{5} = \alpha \int_0^{(P)_o} \left\{ E(ZH) + (G/H)\left(\frac{\alpha k_o(P)}{2X}\right)^{\frac{1}{2}} \right\} d(P) \quad . \qquad \text{(B15)}$$

We now introduct the integration variable $z \equiv (P)/(P)_o$ into eq. 15. The result is:

$$\text{final conc } \underset{\sim}{5} = \alpha(P)_o \int_0^1 \left\{ E(ZH) + (G/H)\left(\frac{\alpha k_o(P)_o z}{2X}\right)^{\frac{1}{2}} \right\} dz$$

which gives eq. 2.1-1 since % yield $\underset{\sim}{5} = 100(\text{final conc } \underset{\sim}{5})/(P)_o$.

Eqs. 2.1-2 and 2.1-3 are obtained in the same way starting from

$$d(\underset{\sim}{6})/dt = \left\{ k_b^{\text{⌬}}(ZH) + k_b^{\text{⏣}}(Z\cdot) + k_7(\underset{\sim}{9}) \right\} (\underset{\sim}{4}) \qquad \text{(B16)}$$

and

$$d(\underset{\sim}{10})/dt = \left\{ (\tfrac{1}{2}\gamma)\, 2k_3(\underset{\sim}{9}) + \delta k_d(Z\cdot) + k_7(\underset{\sim}{4}) \right\} (\underset{\sim}{9}) \quad . \qquad \text{(B17)}$$

Finally, we need expressions for the precent yield of tetrahydronaphthalenes **B** and for C_{16} groups which become incorporated in dimer via pairwise combination of ring-cyclized radicals or combination of a ring-cyclized radical with a cyclohexadienyl radical. The equations are

$$d(\mathbf{B})/dt = \left\{(\tfrac{1}{2}\gamma)\,2k_3(\mathbf{9}) + \epsilon k_d(Z\cdot)\right\}\,(\mathbf{9})$$

and

$$d(C_{16}\text{ groups in dimer})/dt = \left\{(1-\gamma)\,2k_3(\mathbf{9}) + (1-\delta-\epsilon)k_d(Z\cdot)\right\}\,(\mathbf{9})$$

which give by comparison to eq. 17 easily deduced modifications of eq. 2.1-3.

The range of integration of zero to one in the equations for the product yields permits direct application of the well-known formulas for Gaussian quadrature (94). We note that the integrands of eqs. 2.1-1 and 2.1-3 are insensitive to the value of the integration variable z (i.e., to the instantaneous perester concentration) for values of the arabic-letter parameters which fit the product-ratio data and that the integrand of eq. 2.2-2 for % yield **6** goes only approximately as the square root of z or of (P). This moderate behavior allows us to employ the three-point quadrature formula with insignificant loss of accuracy. This entails evaluating the various integrands for $z = 0.1127\ldots$, $0.500\ldots$, and $0.88729\ldots$ (i.e., for approximately 11, 50, and 89% reaction). These values are then summed using weighting factors of 5/18, 4/9, and 5/18, respectively.

There is but one remaining consideration, that concerning how we take into account the diminution of the 1, 4-cyclohexadiene concentration, incurred in its capacity as hydrogen donor, as the reaction proceeds. The quadrature formalism requires instantaneous cyclohexadiene concentrations at 11, 50 and 89% reaction. The prior consumption of 1, 4-cyclohexadiene at these points can be estimated using the following equations, where subscripts designate values of the integration variable z for which various quantities are to be evaluated:

$$\begin{aligned}
(\mathrm{ZH})_{0.11} - (\mathrm{ZH})_{0.} &\cong 0.11\,(\mathrm{P})_o \Big(d(\mathrm{ZH})/d(\mathrm{P})\Big)_{0.11} \\
(\mathrm{ZH})_{0.50} - (\mathrm{ZH})_{0.11} &\cong \frac{0.39}{2}\,(\mathrm{P})_o \left\{\Big(d(\mathrm{ZH})/d(\mathrm{P})\Big)_{0.50} + \Big(d(\mathrm{ZH})/d(\mathrm{P})\Big)_{0.89}\right\} \\
(\mathrm{ZH})_{0.89} - (\mathrm{ZH})_{0.50} &\cong \frac{0.39}{2}\,(\mathrm{P})_o \left\{\Big(d(\mathrm{ZH})/d(\mathrm{P})\Big)_{0.89} + \Big(d(\mathrm{ZH})/d(\mathrm{P})\Big)_{0.50}\right\}
\end{aligned} \qquad (\mathrm{B18})$$

The instantaneous concentrations of 1, 4-cyclohexadiene are then obtained as the initial concentration less the sum of the first one, two, or three equations for 11, 50 and 89% reaction. The key feature of this approach is that the time-consuming extraction of the roots W and X of eqs. 2. 1-9 and 2. 1-10 need not be carried out for any values of z in addition to those employed in the basic quadrature formulas.

With reference to Chart 7 we can write

$$-\,d(\mathrm{ZH})/dt = \left\{k_{fast}(\cdot\,\mathrm{O}\underline{t}\mathrm{Bu}) + k_5(\mathbf{22}) + k_a^{⌬}(\mathbf{3}) + k_b^{⌬}(\mathbf{4})\right\}\ (\mathrm{ZH})$$

from which we obtain, using eqs. 1, 2, 9, 12, and 2.1-4 in conjunction with $-d(P)/dt = k_o(P)$:

$$d(ZH)/d(P) = 0.8\alpha\left\{1 + \frac{2AB(ZH)\left(\frac{\alpha k_o(P)_o z}{2X}\right)^{\frac{1}{2}}}{1+B(ZH)\left(\frac{\alpha k_o(P)_o z}{2X}\right)^{\frac{1}{2}}} + E(ZH)(1+I)W\right\} \qquad (B19)$$

The factor of 0.8 in the above is meant to broadly account for regeneration of some of the 1,4-cyclohexadiene molecules which become cyclohexadienyl radicals upon reaction of the latter with themselves or other radicals. For example, conversion of a ring-cyclized radical to dihydronaphthalene $\underset{\sim}{10}$ via reaction with cyclohexadienyl radical also produces either 1,4-cyclohexadiene or 1,3-cyclohexadiene. By analogy to gas phase results (52) we expect that twice as much 1,4-cyclohexadiene will be formed in this way as 1,3-cyclohexadiene.

Eq. 19 and eqs. 2.1-9 and 2.1-10 for the variables W and X show that the problem is technically more complex than we have indicated, because values of (ZH), W, and X at each of the three integration points are interdependent. Thus one might assume values of W and X for use in eq. 19, obtain the instantaneous values of (ZH) via eqs. 18, put these into eqs. 2.1-9 and 2.1-10, solve those equations for W and X, put the new values into eq. 19, and iterate to self-consistency. This is the approach taken, except that the iteration to self-consistency is accomplished not within a single least-squares iteration on the parameters, but over several such cycles. For the first cycle of a series, initial approximations to W and X were obtained from empirically derived relationships. The values so obtained were employed to estimate the instantaneous cyclohexadiene concentrations and then as initial approximations to W and X in the iterative extraction of the values of these variables which satisfy eqs. 2.1-9 and 2.1-10. The resultant values were used as the initial approximations to W and X in the next cycle. Provided that the series of iterations converges, this approach results in the availability of better and better approximations to W and X for use in eqs. 18 and 19. This eventually allows the instantaneous cyclohexadiene concentrations to be calculated correctly. In practice, 'eventually' works out to be three or four cycles.

SECTION THREE: NATURE OF THE RADICAL INTERMEDIATES

1. Approaches to the Definition of Nonclassical Character

Free radicals are characterized by the presence of an unpaired electron. In the methyl radical, the ethyl radical, and by analogy the *n*-dodecyl radical, the odd electron appears to be localized on a particular carbon. In the allyl radical and the triphenylmethyl radical, abundant information indicates that the odd electron is distributed over a number of carbon atoms. Neither of these types of radicals would be considered, by analogy with the use of the term in carbonium-ion chemistry, to be nonclassical.

What we have in mind in speaking of nonclassical character is essentially a species which has more than a single significant radical center but one in which the requisite delocalization arises other than through a π-electron system. Adapting Bartlett's definition from carbonium-ion chemistry, we may say that *a free radical is nonclassical if its ground state has delocalized bonding σ electrons (114)*.

This definition identifies the preeminent characteristic most people seem to intuitively take to distinguish the nonclassical radical from the types considered in the opening paragraph. But it is not an operational definition: it does not tell us how the presence or absence of σ-electron delocalization may be determined. In principle, an operational definition is not needed; one could simply carry out a series of quantum-mechanical calculations as a function of geometry, find the equilibrium configuration, and analyze the resultant wave function for the presence or absence of 'significant' σ-electron delocalization in the half-filled orbital. Although some presently available calculational schemes can be used in such an approach, judgements reached in this way have a sterile flavor because of the necessity for rather extensive approximations and because the results of such calculations are often not reliably translated into experimental predictions.

It is necessary therefore to make use of any of several derivative criteria. These may be broadly classed as structural, energetic, spectroscopic, kinetic, and mechanistic.

Let us imagine that a σ bond connects atoms A and B in a generalized molecule in which a carbon-hydrogen bond exists at center C. Further suppose that the above-mentioned hydrogen atom is dissociated with no change in geometry of the atomic arrangement. It may be, when this hypothetical state is allowed to relax, that molecular deformation will be restricted to angular changes about C, with C continuing to be the radical center. But it may also happen that the odd electron becomes strongly delocalized over centers A and B as well.* If this is so, it must be that three electrons--the odd electron plus the two which originally made up the A–B single bond--are asked to support two or perhaps three potentially strong interactions of bonding character between the centers A, B, and C. A probable result will be a diminished concentration of electrons in the region between centers A and B and

---

*It may of course be that formation of a delocalized structure in an activated process.

a resultant increase in the equilibrium A–B distance with respect to that in the hydrocarbon. Similarly, we expect increased B–C and A–C distances with respect to the isomeric hydrocarbons having B–C and A–C bonds and carbon-hydrogen bonds at A and B. That is, σ-electron delocalization should have structural ramifications which are predictable in kind, if not always in degree.

The model chosen here serves to point out that there will be classical radical alternatives in situations wherein a nonclassical radical might form; the initially formed radical center at C might not have become delocalized, or rearrangement might have resulted in a bond between B and C with an essentially nondelocalized radical center at A or a bond between A and C with the B becoming the radical center. The possibilities are then that the configuration of minimum energy (a) corresponds to a σ-electron delocalized species or (b) has a geometry appropriate for one of the classical radical alternatives. In either case, stability alone need not determine from what species the products arise--the relative reactivities of the various possible species will also be important.

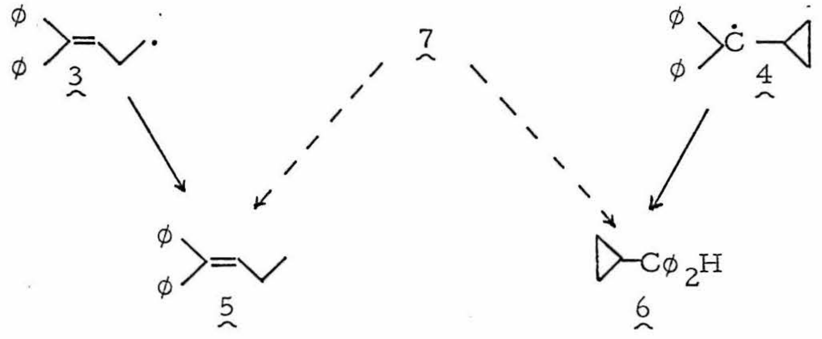
An unstable radical species can not, like a stable hydrocarbon, be subjected to structural analysis by X-ray or electron diffraction or be quantitatively combusted to obtain a heat of formation or a binding energy. To be sure, combination of the C–H bond dissociation energy in the above example with the heats of formation of the dissociated hydrogen atom and the starting hydrocarbon yields the heat of formation of the derived radical. But whether the latter quantity is 'unusual' would probably be judged on the basis of the C–H bond dissociation energy itself; and what would be expected even for formation of a classical radical may be considerably uncertain.

Thus, at least for the present, structural and energetic attributes must serve primarily to help us to picture the nonclassical species conceptually rather than to determine whether a given radical is or is not nonclassical.

Radicals are capable of direct observation via electron-spin reasonance spectroscopy. A principal result is information regarding the distribution of the odd electron. Nonclassical species are expected to show extensive hyperfine interactions with atoms at or near the possible centers of electron delocalization. Rapidly equilibrating classical radicals might show similar results for the time-average spin distribution. If so, it might be possible, as in nuclear magnetic reasonance spectroscopy, to freeze out and study individually one or more of the interconverting species by using low temperatures. Such an approach could in principle allow an unambiguous answer to the question of the nature of the radical intermediates.

In carbonium-ion chemistry, the special stability of nonclassical ions is often manifested by unusually high rates of formation via solvolysis of suitable precursors. However, sole use of kinetic criteria for the absence of nonclassical character can not ultimately be successful, because rates of formation relate not to the energy of the product radicals or ions but to that of transition states for their formation in which there is only partial radical or ionic character. The possibility can not be dismissed that the balance of factors which causes a radical or ion to opt for σ-electron delocalization is a delicate one in which a full free valency or a full charge deficiency may be required to tip the scales in favor of delocalization.

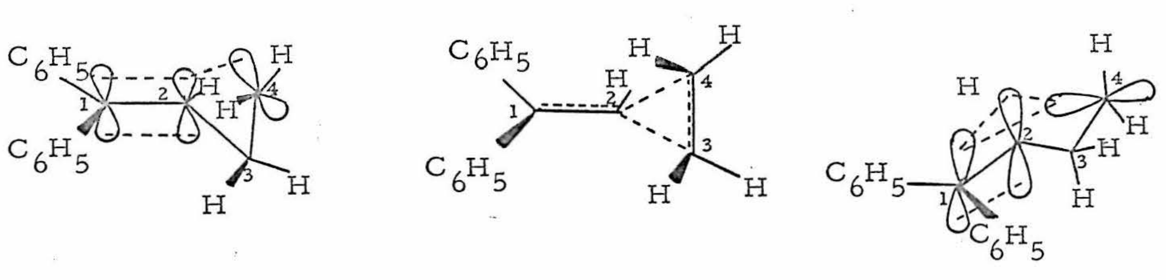
Finally, the nature of the radical intermediates in a given system can be probed mechanistically. A radical which has more than a single center of free valence has the possibility of taking up an atom such as hydrogen at alternative positions to give in general distinguishable products. In this work we have employed product studies as a function of reaction temperature and hydrogen-donor reactivity to obtain data which we feel can be used in part to distinguish between formation of two such products, ring-opened hydrocarbon 5 and ring-closed hydrocarbon 6, from a common intermediate (7) or from a rapidly equilibrating pair of classical, single-product intermediates (3 and 4). We may *imagine* that an appropriate nonclassical radical represents a



structural compromise between the geometries of the classical ring-opened radical 3 and the classical ring-closed radical 4 and that it would be more stable than either, if it is to be the principal product-forming intermediate. But we shall be able to detect its presence only if it gives rise to appreciable amounts of both the isomeric hydrocarbons 5 and 6 on the limited hydrogen-donor diet we have been able to provide (see below).

Possible structures for nonclassical radical 7 are depicted in Chart 8. The homoallylic and bicyclobutonium structures are formally interconvertible by rotation about the C-2—C-3 bond, the difference being that C-4 is appreciably closer to C-2 than to C-1 in the former whereas these distances are comparable in the latter. Semi-empirical Hückel molecular orbital calculations (13a) suggest that strong 1, 4 and 2, 4 interactions are favorable in the analogous carbonium-ion intermediates (but with the phenyl groups replaced by hydrogens), where the orbital system sketched accommodates only two electrons, but that three electrons are better accommodated in the homoallylic-type structure. Moreover, the apparent lack of interconvertibility of cyclobutyl structures with allylcarbinyl and cyclopropylcarbinyl structures in free-radical reactions (15) is in striking contrast to the facile interconversion of structures of all three types in carbonium-ion reactions (14). This suggests that a homoallylic or bisected (see below) structure for 7 is more likely than a bicyclobutonium structure.

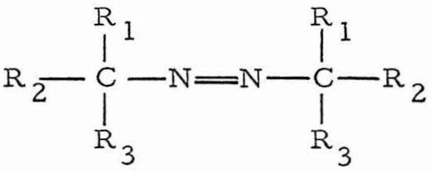
Chart 8. Possible Structures for Nonclassical Radical 7.



Homoallylic Bisected Bicyclobutonium

A strong possibility for a favorable nonclassical structure for the cyclopropylcarbinyl radical has the so-called "bisected" geometry in which carbon atoms 3 and 4 are equivalent. The name comes from the fact that the plane containing C-1 and the three flanking carbon atoms is perpendicular to--bisects--that containing C-2, C-3, and C-4. Bisected geometries have been demonstrated experimentally for cyclopropanecarboxaldehyde (115a), cyclopropyl methyl ketone (115b), phenylcyclopropane (115c) and for cyclopropyl semidione radicals (115d). Perhaps more pertinent is that rather good evidence has been obtained, using methyl groups as a probe for charge delocalization, that transition states in cyclopropylcarbinyl solvolyses have the bisected geometry (116). The key point here is 3,4-dimethyl-substituted compounds solvolyze at virtually the same rate as the 3,3-dimethyl compound, and that each solvolyzes about 10 times as rapidly as the 3-methyl compounds (which in turn solvolyzes about 10 times as rapidly as the unsubstituted compound). If charge delocalization (which must apparently be invoked to account for the unusually high solvolytic rates of cyclopropylcarbinyl derivatives (116)) occurred as in the homoallylic or bicyclobutonium structures either to C-3 or to C-4, but not to both, the 3,4-dimethyl-substituted compounds should solvolyze only about twice as rapidly as the 3-methyl-substituted compounds. By tying back C-3 and C-4 or C-2 and C-3 with methylene bridges of varying lengths (thus introducing varying degrees of ring strain), evidence was also obtained for the lengthening of the 2,3 and 2,4 bonds and the shortening of the 3,4 bond implied by the dotted lines (116).

Moreover, kinetic measurements on rates of decomposition of azo compounds recently reported by Martin et al. (117) bear on the question of the origin of the well-known stabilization of a radical center by cyclopropyl groups (118). Martin studied a series of symmetrical azo compounds in which R_1, R_2, and R_3 were methyl groups and in which one, two, and all three methyl groups on each side were replaced by cyclopropyl groups. The first substitution of cyclopropyl for methyl increased the rate of decomposition (diphenyl ether, 135°) by a factor of 27. With two and three cyclopropyl groups on each side, relative rates were 362 and 2540. And finally, the compound with two cyclopropyl groups and one isopropyl group in each half was found to decompose 286 times as rapidly as the hexamethyl compound.



$$R_2-\overset{\displaystyle R_1}{\underset{\displaystyle R_3}{C}}-N{=}N-\overset{\displaystyle R_1}{\underset{\displaystyle R_3}{C}}-R_2$$

The significant factor is that repeated substitution of cyclopropyl for methyl continues to result in significant rate increases. The rate of decomposition of the tetracyclopropyldiisopropyl compound shows that this can not simply be due to increased steric strain in the azo compound which is relieved in the decomposition transition state. And if the mode of interaction were relief of strain by concerted opening of one cyclopropyl ring (to the allylcarbinyl form), only much smaller rate increases due to statistical factors should have resulted upon successive substitution. Apparently, any number of α-cyclopropyl rings can participate; an attractive possibility would be to have each take up a bisected conformation with respect to the radical center.

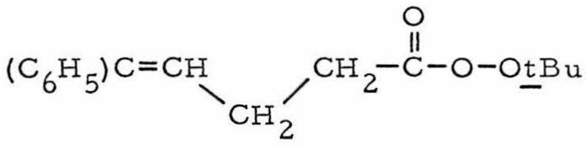
The evidence is that two radical species give rise to 5 and 6 at least at short times after the homolysis of a ring-closed precursor, and that one of these radicals behaves very much as we expect the classical ring-closed radical 4 should behave. It may well be that 4 has a bisected geometry and that investigation by electro-spin resonance spectroscopy or rigorous quantum-mechanical calculation would indicate 'significant' σ-electron delocalization into the cyclopropyl ring, as is implied by the use of dotted lines in representing the bisected form of 7. But it presently appears that the 'classical ring-closed radical' does not give ring-opened products upon hydrogen abstraction from 1,4-cyclohexadiene, triethyltin hydride, or cyclohexadienyl radicals, and by this criteria, at least, there is no evidence demanding it be nonclassical.

In most of what follows, we shall assume the homoallylic form whenever product formation from a nonclassical radical is under consideration. But we must admit the possibility that the 'classical ring-closed radical 4' may be best formulated--from a wave-mechanical viewpoint--as the bisected nonclassical radical 7.

For our purposes here, a radical such as 4 is operationally nonclassical only if it is observed to give multiple products. Different sets of experiments might yield different conclusions in this regard, as might fundamentally different approaches. However, in the absence of spin-resonance experiments or definitive quantum-mechanical calculations, definitional problems seem to be unavoidable. The concept of nonclassical character is therefore necessarily relative and imprecise.

2. Summary of Relevant Experimental Observations

This work was begun in the light of Howden's discovery that thermal decomposition of ring-opened perester **1** in the presence of tri-*n*-butyltin hydride gave ring-opened hydrocarbon **5** and ring-closed hydrocarbon **6** in sensibly constant proportions of 20:1 (21). His experiments covered reaction temperatures from 110 to 150° and initial tin hydride concentrations from 0.056 to 0.56 M (see Table 12, p. 44).



$$(C_6H_5)C{=}CH{-}CH_2{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}O{-}O\underline{t}Bu$$

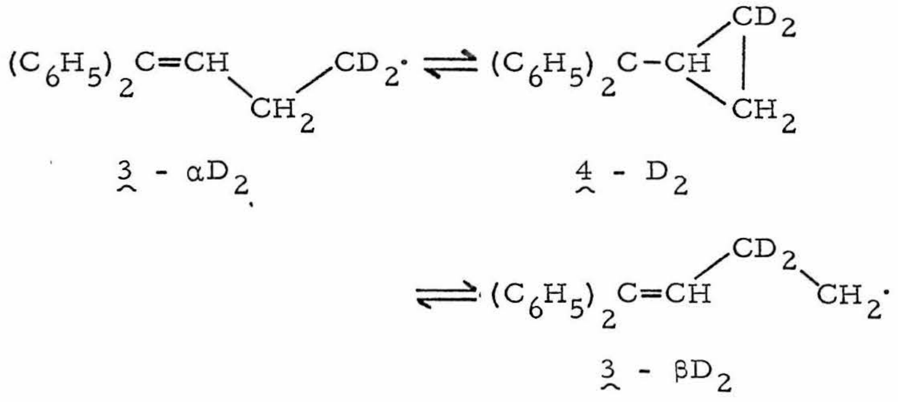
1

The insensitivity of the product ratio to the tin hydride concentration is interpretable in terms of product formation by the classical radicals **3** and **4**, by a nonclassical radical such as **7**, or in terms of any admixture of the two schemes; one has only to postulate rapid equilibration of all radical species which give rise to the isomeric hydrocarbons.

In contrast, the lack of an appreciable temperature effect was taken by Howden to tentatively and indirectly implicate a nonclassical radical, perhaps our **7**, as the product-forming species. This inference was predicated upon his estimation, via a complex thermochemical cycle (119), that isomerization of ring-closed **4** to ring-opened **3** would be endothermic by 24.5 kcal/mole (21, 119). As the difference in activation energy for abstraction of hydrogen by the two radicals from a donor as reactive as tri-*n*-butyltin hydride (120) would not be expected to be of comparable magnitude, product formation from the classical radicals should evidently have been accompanied by a strong dependence of the ratio **6**:**5** on the reaction temperature.

As it happens, the large enthalpy difference estimated by Howden is due to an error of sign in the relationship between the heat of reaction and the enthalpies of the reactants and products (119).* However, at the time this work was begun either Howden's value or a value of 17 kcal/mole derived by us seemed to suggest that the classical radicals might interconvert too slowly to explain the insensitivity of the ratio **6**:**5** to tin hydride concentration.

The possibility of interconversion can easily be tested by examining products from the decomposition of deuterium-labeled **1** for the position of the label. The minimum requirement for the implication of rapidly equilibrating classical radicals **3** and **4** was attained when



3 - αD_2

4 - D_2

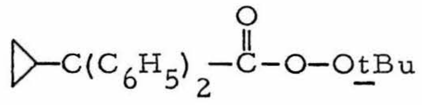
3 - βD_2

---

*One commonly writes equations such as A⟶B + ΔH, where ΔH is the heat of reaction. This erroneously suggests the relationship $\Delta H_f(\text{reactants}) = \Delta H_f(\text{products}) + \Delta H_{rxn}$. The unnatural, but correct, equation has a minus sign.

complete scrambling was found, within experimental error, in appropriate reaction products for decomposition of labeled **1** in cyclohexane and in 1.3 M triethyltin hydride in *n*-octane (pp. 94–96).

Using triethyltin hydride in place of Howden's tri-*n*-butyltin hydride, we were able to confirm the lack of any appreciable effect of the tin hydride concentration on the ratio of **6**:**5** at 125 and 144°. At 10 and 35° using the more reactive ring-closed perester **2**, however, an



2

experimentally significant dependence of the product ratio on the tin hydride concentration was found (see Fig. 8, p. 100). This observation immediately requires that any proper mechanistic scheme advance at least two product-forming intermediates, but leaves open the question of their nature.

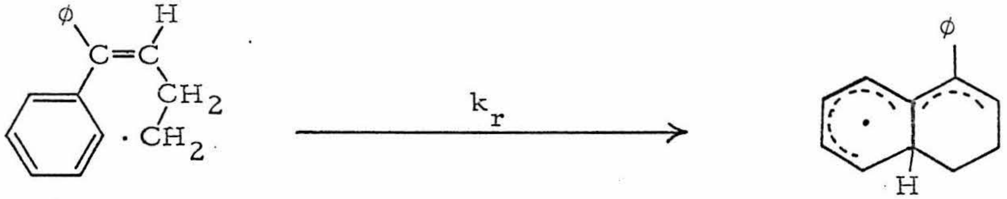
Evidence of another sort may be cited to similar effect. The cage-reaction products which result from decomposition of the isomeric peresters apparently have the ring-opened structure when the perester is ring-opened but the ring-closed structure when the perester is ring-closed (subsection 5 to Section One).

From Howden's vantage point, product formation solely from a nonclassical radical such as **7** not only promised to explain the lack of a hydrogen-donor concentration effect and the small temperature effect on **6**:**5**, but also had a certain elegance of simplicity to recommend it. Given the existence of at least two product-forming free-radical intermediates, a proper respect for such considerations would now appear to favor an interpretation based on the classical radicals.

Such is indeed our conclusion, subject to the definitional problems discussed in the previous subsection. We shall proceed in this subsection to consider additional experimental support for this conclusion and to show via an energy-level scheme that our results in this regard are nicely explicable on the assumption that we are dealing with two intermediates, one of which gives ring-opened product and the other of which gives ring-closed product. Strictly speaking, the trapping results and the cage-product results do not however rule out the possibility that initially formed classical radicals isomerize to a nonclassical species and that ratios of **6**:**5** formed under conditions which permit prior equilibration of the radical intermediates represent essentially the partitioning of such a species to ring-closed and ring-opened product. We have therefore advanced what we feel to be good, if somewhat complex, arguments which are intended to show that such an interpretation is fraught with serious difficulties. Some readers may feel that such arguments are unnecessary--that the self-consistency and reasonableness of the classical-radical interpretation is itself sufficient to establish that interpretation. That self-consistency is further explored in subsection 4, where the energy-level scheme constructed here is extended to one offering absolute rate-constant estimates, the purpose in part being to show that experimentally inferred values of various composite parameters (rate-constant ratios, etc.) do not conceal unreasonable implications. And finally, in subsection 5 we employ a thermodynamic cycle to show that an inferred difference in enthalpy of ring-opened radical 3 and ring-closed radical 4 (see below) is reasonable.

On the presumption that the radical intermediates are ring-closed 3 and ring-opened 4, it is possible to deduce from the intercepts of plots of 6:5 against the tin hydride concentration at 10 and 35° and from values of this ratio observed at 110 and 125° that the transition state for formation of 6 from 4 lies 2.9 ± 0.3 kcal/mole below that for formation of 5 from 3 (see Fig. 9, p. 103). Thus, the small temperature effect which eluded Howden is easily discerned here with our wider temperature range. In addition, the difference in the slopes of the plots of 6:5 against the tin hydride concentration at 10 and 35° was found to imply that the transition state for interconversion of 3 and 4 lies 4.6 ± 0.7 kcal/mole above that for formation of 6 from 4 and 1.7 ± 0.8 kcal/mole above that for formation of 5 from 3. These relationships, originally traced on the reaction diagram, Fig. 10, p. 105, are preserved here in the final diagram, Fig. 23, p. 333.

It was also possible to obtain Arrhenius relationships for the rate-constant ratio which describes, in the present interpretation, the partitioning of ring-opened radicals between <u>ortho</u>-ring cyclization (k_r) and hydrogen abstraction from 1,4-cyclohexadiene and from triethyltin hydride ($k_a^{⌬}$ and k_a^{SnH}) (eq. 2.4-22, p. 272, and eq. 1.8-11, p. 138).



3

9

Elimination of the k_r reference process gave (eq. 1.8-12, p. 138):

$$k_a^{\text{SnH}}/k_a^{\text{⌬}} = 0.7\ \exp(+3.2/RT) \quad . \qquad (3.2\text{-}1)$$

The estimated uncertainties in the activation energies for the precursor eqs. 1.8-11 and 2.4-22 give an estimated standard error of $(0.7^2 + 1.0^2)^{\frac{1}{2}}$ = 1.2 kcal/mole in the activation of eq. 3.2-1.

Construction of a semiquantitative scheme such as Fig. 23 depicting absolute, rather than simply relative, activation energies requires the measurement or the estimation of an absolute activation energy for one reaction of each of the two radicals. Not being equipped to measure absolute rate constants, we must employ the second alternative. Accordingly, we have assumed that the activation energy for hydrogen abstraction by ring-opened radical **3** from 1,4-cyclohexadiene in hydrocarbon solution (the $k_a^{\text{⌬}}$ process) is equal to the literature value of 5.8 kcal/mole for hydrogen abstraction by the ethyl radical from the same donor, but in the gas phase (45).* As can be traced in Fig. 22, this assumption makes it possible to estimate activation energies of 2.6 kcal/mole for hydrogen abstraction by **3** from triethyltin hydride and of 4.3 kcal/mole for isomerization of ring-opened **3** to ring-closed **4**.**

---

*See the discussion on p. 349 regarding the interpretation of the literature value.

**At this point it becomes difficult to continue to give reliable estimates for the uncertainty in relative energy-level placements. The estimated 2.6 kcal/mole for the activation energy of the k_a^{SnH} process may seem a bit low to some, but it is uncertain by 1.2 kcal/mole due to the standard error in $k_a^{\text{SnH}}/k_a^{\text{⌬}}$ as well as by an undetermined amount due to any error in the assumed 5.8 kcal/mole activation energy for the $k_a^{\text{⌬}}$ process. Similarly, the radical-interconversion barrier could well be in error by as much as 2 kcal/mole.

No wonder the classical radicals are so hard to trap relative to their rate of interconversion.

The remaining energy-level placements were made on the basis of the mechanistic treatment of Section Two. From the temperature dependence of the ratio 6:5 for hydrogen abstraction from 1,4-cyclohexadiene (-1.8 ± 1.0 kcal/mole; heading I, p. 273), we can place the transition state for formation of 6 by this route at 4.0 kcal/mole in Fig. 23. We should caution, however, that an experimental complication prevents this from being an unambiguous result (heading I, p. 273).

The dominant routes to 5 and 6 for perester decomposition in 1,4-cyclohexadiene under most conditions employed have 3 reacting with cyclohexadiene but 4, with cyclohexadienyl radical. It was possible to infer the relative energies of the respective transition states to within one kcal/mole (heading K, p. 277). The inference places the transition state for 4 plus cyclohexadienyl radical at 5.8 - 11.6 = -5.8 kcal/mole (Fig. 22, p. 279).

If we also assume a viscosity-related 'activation energy' for disproportionation of 4 with cyclohexadienyl radical of 2 kcal/mole arising from the lesser impedence to diffusion at higher reaction temperatures (hence lower solution viscosities), we can estimate the isomerization of ring-opened 3 to ring-closed 4 to be exothermic by ~8 kcal/mole. The uncertainty in the above assumption and that in the assumed activation energy for the $k_a^{⌬}$ process combine to make the heat of isomerization uncertain by perhaps 3 kcal/mole (heading K, p. 277), but do not effect the conclusion that 4 is considerably the more stable (as regards enthalpy).

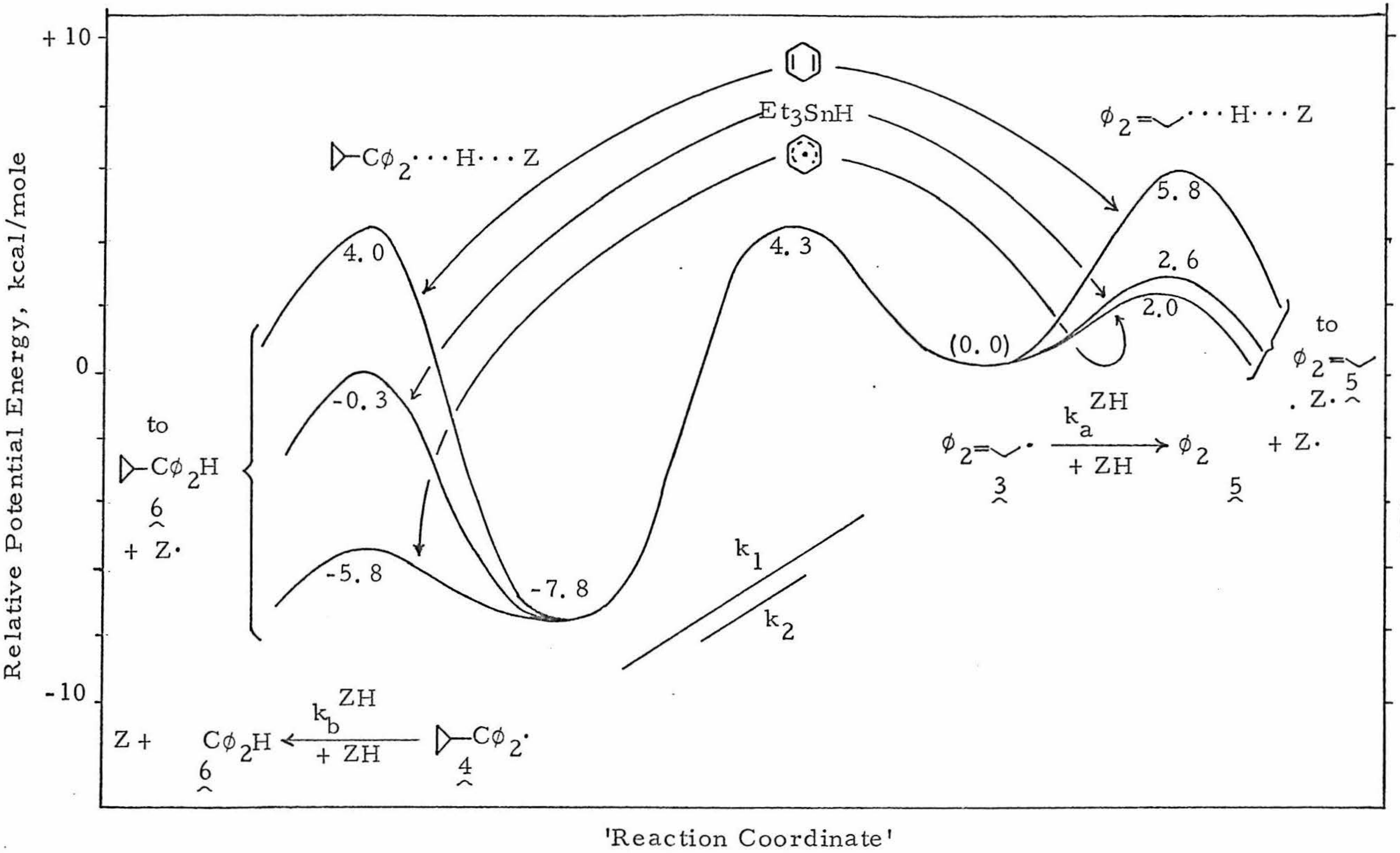


Figure 23. Semi-quantitative reaction diagram for ring-opened radical 3 and ring-closed radical 4 in the presence of 1, 4-cyclohexadiene, triethyltin hydride, and cyclohexadienyl radical. Numbers shown are energy-level placements in kcal/mole relative to assumed energy zero for 3. See Figs. 10, 11, 13, and 22 for construction of the scheme.

To complete the picture, we again assume a 2 kcal/mole viscosity-related activation energy for disproportionation of ring-opened radical 3 with the cyclohexadienyl radical. The difference of about 8 kcal/mole in the transition-state energies for reaction of 3 and 4 with cyclohexadienyl radical should result in a large temperature dependence for the characteristic ratio of 6:5 formed in this way.* However, the ratio itself is sufficiently large (probably greater than 5 at 100°) that the relevant data do not yield more than a minimum value (heading J, p. 275). By way of comparison, the characteristic ratio at 100° for hydrogen abstraction from triethyltin hydride is calculated from eq. 1.7-5 to be 0.078, whereas that for hydrogen abstraction from 1,4-cyclohexadiene is estimated to be 0.0035 ± 0.001 (heading I, p. 273).

Ratios of such quantities yield the relative effect of substitution of one hydrogen donor for a second on the rate constants for hydrogen abstraction by 3 and 4. We can, however, isolate the effect of a hydrogen-donor change on rate constants for the former (the k_a processes) by combining rate-constant ratios for hydrogen abstraction to *ortho*-ring cyclization. Such a procedure gave us eq. 3.2-1, from which we find that at 100° ring-opened radicals abstract hydrogen from triethyltin hydride approximately 50 times more rapidly than from 1,4-cyclohexadiene for equal hydrogen-donor concentrations. On the

---

*The characteristic ratio of 6:5 for abstraction of hydrogen from ZH is given by $k_1k_b^{ZH}/k_2k_a^{ZH}$. See Fig. 23 for definitions of the individual rate constants.

same basis, abstraction from indene is approximately a factor of 5 slower than from 1,4-cyclohexadiene (p. 125).[*]

We can now infer from the characteristic-ratio comparison that ring-closed radicals abstract hydrogen more rapidly from triethyltin hydride than from 1,4-cyclohexadiene by a factor of 0.078 × 50/0.0035 ≅ 1000 at 100°. The relative rate of hydrogen abstraction by 4 from the cyclohexadienyl radical can be fitted into this scheme via an indirect comparison. Thus, the assumption that ring-opened radicals abstract

---

[*] Literature reports (45,54) recapitulated here as eq. 1.8-9, p. 127, show hydrogen abstraction by ethyl radicals in the gas phase at 100° to be more rapid from 1,4-cyclohexadiene than from cyclohexane by a factor of 260. An analogous comparison for hydrogen abstraction by saturated primary radical 21 in solution gives, perhaps fortuitously, a nearly identical value of 250 at 100° when corrected from 152° by a factor of 2.0 using the activation energy quoted in eq. 1.8-9 for ethyl radical reactivities.[**] Thus we have the following scale of relative reactivities toward hydrogen abstraction by primary radicals: cyclohexane, 0.004; indene, 0.2; 1,4-cyclohexadiene, 1.00; triethyltin hydride, 50. We are prompted to offer this reactivity series by the apparent lack of such comparisons for abstraction by hydrocarbon radicals from hydrogen donors greatly more reactive than cyclohexane.

[**] Assuming an efficiency of conversion of the saturated ring-cyclized radical 24 to 1-phenyltetralin 25 of 40% (see p. 141 and heading P, p. 286, for justification), entries in the rightmost column of data Table 3 for rows 2–5 give a rate constant ratio of 0.54 for the partitioning of saturated radicals 21 between cyclization to 24 and abstraction of hydrogen from 1,4-cyclohexadiene to give saturated hydrocarbon 20. The analogous ratio where the hydrogen donor is cyclohexane may be estimated as 67 using results in row 1 of Table 3. To get this estimate we assume that the 73% of products not accounted for by 20 plus the cage products 18 and 19 (p. 82) represent saturated radicals 21 which underwent ring-cyclization to 24 and rearrangement via spiro closure to 27 in the proportion of 1.5:1 (see p. 143). Thus, total conversion of 24 to 25 would have given a yield of 25 of 73 × 1.5/2.5 = 44% as compared to the observed yield of 19.6%. Combining the former with the 5.1% observed yield of 20 and the estimated concentration of cyclohexane at 152° of 7.8 M (see footnote c to Table 3) as in eq. 1.8-5, p. 111, then gives a partitioning ratio of 44 × 7.8/5.1 = 67. The factor of 250 is then obtained as 67 × 2.0/0.54.

hydrogen with equal facility from triethyltin hydride and from the cyclohexadienyl radical implies that ring-closed radicals prefer the latter over 1,4-cyclohexadiene by a factor of $1000 \times 5/0.078 = 65000$. This is of course a minimum value; the actual figure is probably close to 10^9.* Thus the reactivity sequence for hydrogen abstraction by 4 is roughly: 1,4-cyclohexadiene, 1.00; triethyltin hydride, 10^3, cyclohexadienyl radical, $\geq 10^6$.

The pattern is clear: the more reactive the hydrogen donor, the larger the characteristic ratio of 6:5. This result is easily rationalized, assuming the classical radicals to be the product-forming species, as a radical-chemistry example of the usual reciprocal relationship between stability and reactivity. A hydrogen donor in effect constitutes a radical counter. A relatively unreactive hydrogen donor such as 1,4-cyclohexadiene is so predisposed to react with ring-opened radicals that it produces more of the product from 3 than from 4. Cyclohexadienyl radicals, on the other hand, are sufficiently undiscriminating that they do favor the product from the most prevalent radical. Still, they fail to demonstrate the large magnitude of the equilibrium constant which--we shall argue in subsection 4--favors 4 over 3 by factors of roughly 9×10^2 at 100° and of 4×10^4 at 0°.

---

*This, at least, is the value given by the absolute rate-constant scheme of subsection 4.

3. Attempted Reinterpretation in Terms of a Nonclassical Radical

The utterly different natures of the cage-reaction products from ring-opened perester 1 and ring-closed perester 2 and the dependence of the ratio 6:5 on the concentration of triethyltin hydride at 10 and 35° confirm the existence of at least two kinds of product-forming radical intermediates. The cage-reaction products also show that one radical intermediate gives largely or wholly ring-opened product and that a second gives largely or wholly ring-closed product. These would presumably be ring-opened 3 and ring-closed 4. However, it is still possible that at sufficiently long times a third species (e.g., nonclassical homoallylic radical 7) assumes control of product formation and that the characteristic ratios 6:5 represent the partitioning of such a species between ring-closed and ring-opened product. Let us suppose that this is the case and see what conclusions can be reached.

We have noted in subsection 2 that hydrogen abstraction from cyclohexadienyl radical gives 6:5 in the ratio of at least 5:1 at 100°. Let us assume, for the sake of argument, that a donor which reflects precisely the distribution of free valence at the dibenzylic and the terminal primary carbons of 7 gives 6:5 in a ratio of 10:1; i.e., that the ratio of preexponential factors for formation of 6 and formation of 5 is 10:1. If this same preexponential-factor ratio is assumed for the real hydrogen donors (cyclohexadienyl radical, triethyltin hydride, and 1,4-cyclohexadiene), the reaction diagram scheme for formation of 5 and 6 would resemble that of Fig. 24.

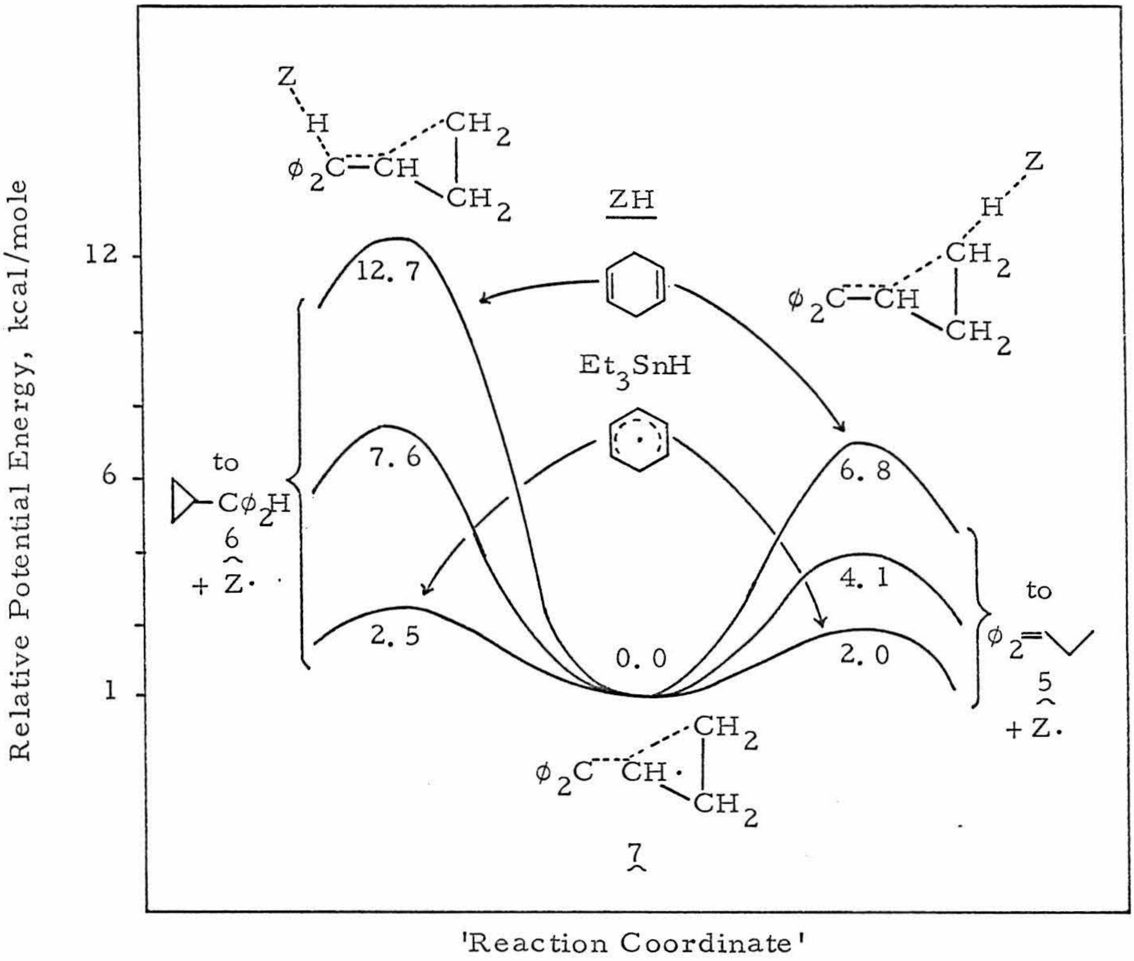


Figure 24. An energy-level diagram for product formation by non-classical homoallylic radical 7 constructed to fit observed ratios of 6:5 at 100°.

In placing the energy levels in Fig. 24 we have employed the observed characteristic ratios at 100°, an assumed activation energy of 2.0 kcal/mole for formation of 5 from 7 plus cyclohexadienyl radical, and the relative rate ratios of 1:1000:$\sim 10^6$ inferred in subsection 2 for hydrogen abstraction to give 6 from 1,4-cyclohexadiene, triethyltin hydride, and cyclohexadienyl radical. The last point, it should be noted, is valid whether the radical giving 6 is the classical radical 4 or is 7.[*]

Note that the dependence of the abstraction barriers on each side on the reactivity of the hydrogen donor is very similar to the behavior seen in Fig. 23. This of itself is most reasonable. However, the characteristic ratio 6:5 is now predicted to universally increase with increasing temperature. This is grossly incorrect. For abstraction from triethyltin hydride, the observed characteristic ratios are 0.29 at 10°, 0.16 at 35°, 0.07 at 110°, and 0.06 at 125° (Fig. 9, p. 103). The scheme also gives a greatly different temperature dependence than was inferred with but slight reservation for hydrogen abstraction from 1,4-cyclohexadiene (heading I, p. 273). Moreover, it directly contradicts the conclusion reached in Section Two (heading K, p. 277) that the transition state for formation of 6 via hydrogen abstraction from cyclohexadienyl radicals lies ~12 kcal/mole below that for formation of 5 from 1,4-cyclohexadiene.[**]

Thus we have in Fig. 24 a scheme which would be reasonable *a priori*, but which fails to account for the actual product-ratio observations. The obvious next approach is to construct an energy-level scheme which does account for the observations and to ask whether the properties it requires of nonclassical radical 7 are reasonable ones.

---

[*] Moreover, the *relative* placement of the hydrogen abstraction transition states for *a given* donor does not require the assumption of any such reactivity series.

[**] We shall show shortly that the revised definitions of the arabic-letter parameters of eqs. 2.1-4 are just such that the composite quantity on the left-hand side of eq. 2.4-25, p. 277, again specifies the enthalpy difference of these two transition states.

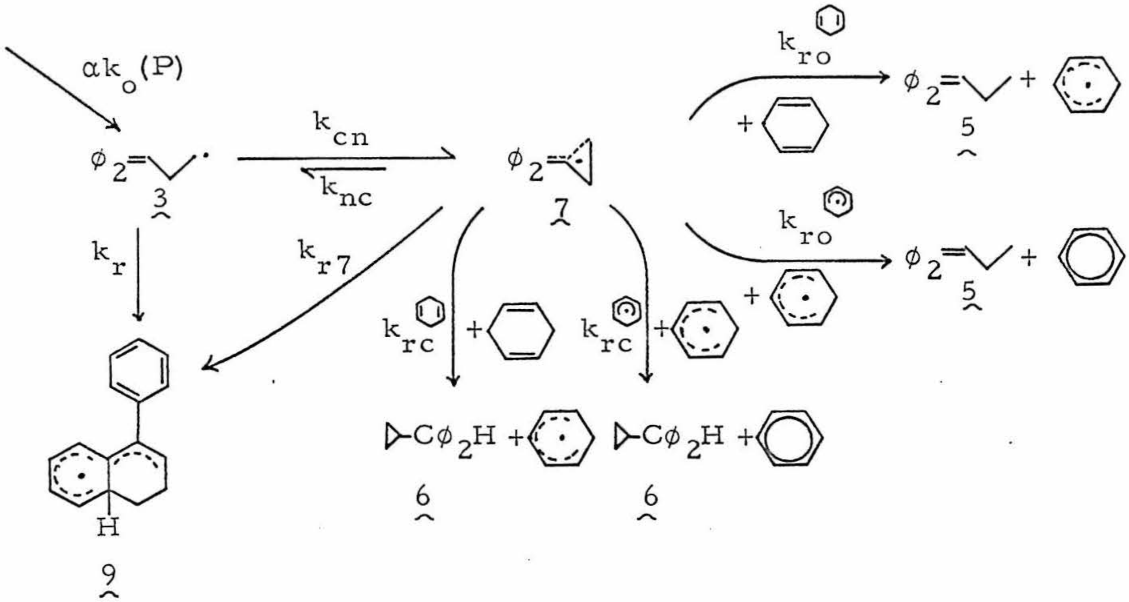
Our first task is to determine what the mechanistic scheme of Section Two requires of a nonclassical radical, if that species alone is to account for formation of ring-opened hydrocarbon 5 and ring-closed hydrocarbon 6 in the observed amounts. This simply amounts to working out the new interpretations of the arabic-letter parameters of eqs. 2.1-4; we already have deduced their values (Table 19, pp. 303 - 307). The new reaction steps we shall consider are shown in Chart 9; these replace analogous steps based on classical radicals which occupy essentially the lower-left quadrant in Chart 7, p. 198. We consider two possibilities: SCHEME A in which *ortho*-ring-cyclization to the radical 9 is again attributed to ring-opened radical 3; and SCHEME B in which the nonclassical radical 7, perhaps in the bicyclobutonium configuration of Chart 8 (p. 322), is assumed to give 9 directly. The new definitions of the affected parameters are given in Chart 9; the others are again as in eqs. 2.1-4, p. 203, except for C, which would change in an obvious way if we were to substitute reaction of 7 with 9 for that of the minor reaction of 4 with 9 of Chart 7. We shall leave it to the interested reader to confirm the redefinitions.*

---

*This may be done for SCHEME A by updating eq. B3 of Appendix B and replacing eq. B4 for d(4)/dt by the appropriate equation for d(7)/dt. Adding these equations together gives the equation which replaces eq. B8. The assumption of rapid interconversion of 3 and 7 then allows eq. B9 to be updated. Comparison of the original and revised eqs. B9 to eq. 2.1-9, p. 206, yields the new definitions for E, G, H, and I. The procedure for SCHEME B is similar except that the concentration of 3 drops out upon addition of the revised eqs. B3 and B4. The result is directly the revised eq. B9 and comparison again yields the new parameter definitions.

A bit more work may, however, be required for the reader to convince himself that deployment of the new parameter definitions leaves the final forms of all other mechanistic equations invarient.

Chart 9. Some relationships for product formation by a nonclassical radical.



SCHEME A: $k_{r7} = 0$

$$E = \frac{k_{cn}k_{ro}^{\text{⬡}}}{k_{nc}k_{r}} \qquad G = \frac{k_{cn}k_{rc}^{\odot}k_{3}^{\frac{1}{2}}}{k_{nc}k_{r}k_{d}}$$

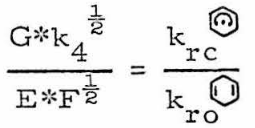
$$H = k_{rc}^{\odot}/k_{ro}^{\odot} \qquad I = k_{rc}^{\text{⬡}}k_{ro}^{\text{⬡}}$$

SCHEME B: $k_{r} = 0$

$$E = k_{ro}^{\text{⬡}}/k_{r7} \qquad G = \frac{k_{rc}^{\odot}k_{3}^{\frac{1}{2}}}{k_{r7}k_{d}}$$

H, I: as in SCHEME A

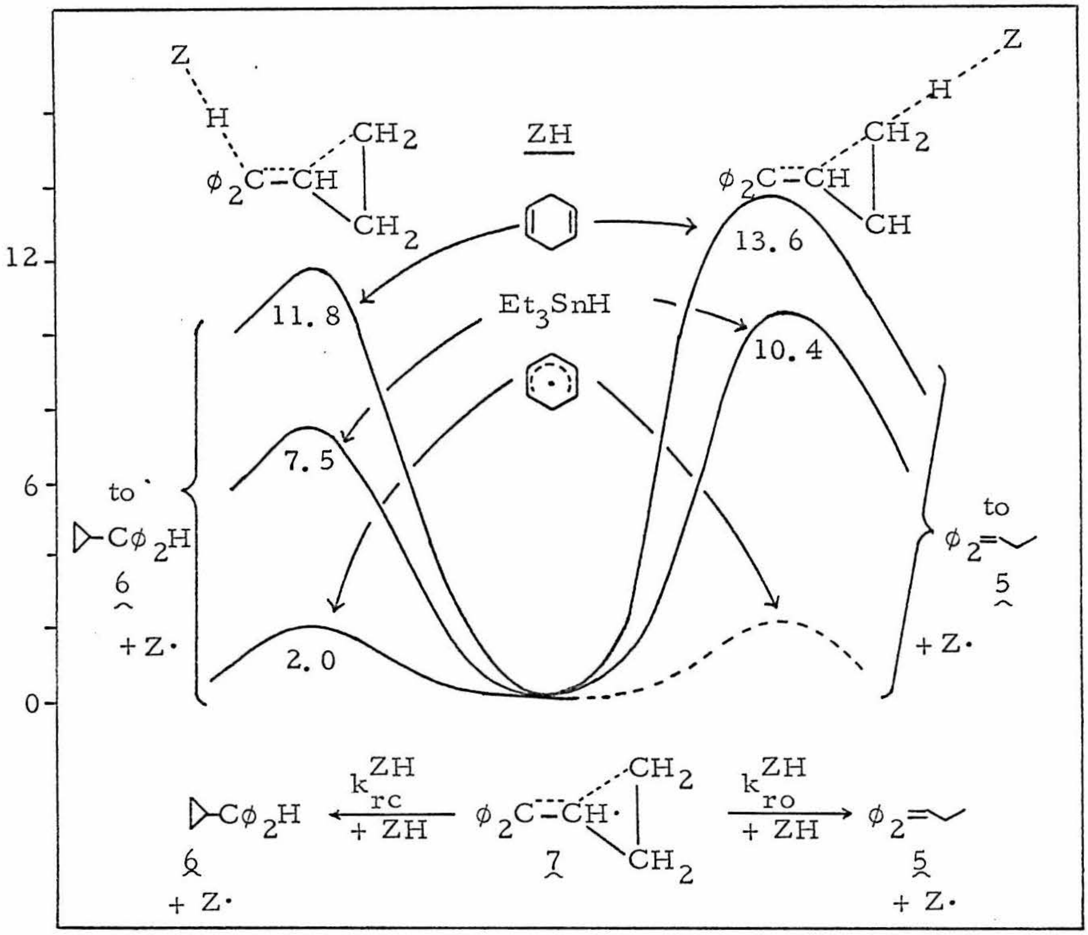
Note that the activation energy of the parameter I, evaluated as -1.8 ± 1 kcal/mole, is again the energy of the transition state for formation of **6** via abstraction from 1,4-cyclohexadiene less that for formation of **5** from the same donor. And the composite quantity



$$\frac{G^*k_4^{\frac{1}{2}}}{E^*F^{\frac{1}{2}}} = \frac{k_{rc}}{k_{ro}} \quad \text{(for SCHEME A or B)}$$

on the left-hand side of eq. 2.4-25, p. 277, again relates the transition-state energies for formation of **6** via hydrogen abstraction from cyclohexadienyl radical and formation of **5** via abstraction from 1,4-cyclohexadiene. All of this is to say what experienced observers will have already recognized: relationships between transition-state energies for formation of products which were placed with cause in Fig. 23 are unaffected by any reformulation having to do with the nature of the radical intermediates which give rise to the hydrocarbon products, so long as rapid equilibration of all such species is again presumed. Thus, we can compile Fig. 25 simply by deleting central hump in Fig. 23 and stitching the two sides together. The only exception is the transition state for formation of ring-opened material via hydrogen abstraction from cyclohexadienyl radical; that placement was not originally made with cause, but rather in the expectation that the activation energy would be minimal. The same assumption now gives a radically different level placement.

Thus we now have a scheme which accounts for the observed temperature dependencies of the characteristic ratios for hydrogen



'Reaction Coordinate'

Figure 25. An energy-level diagram for product formation by nonclassical homoallylic radical 7 constructed to fit the observed dependence of ratios of 6:5 on the reaction temperature.

abstraction from 1,4-cyclohexadiene and triethyltin hydride. We now ask whether the scheme is reasonable in other respects. A first point concerns the location of the lower barrier on the right in Fig. 25. Let us first assume that reaction of 7 with cyclohexadienyl radical to give ring-opened material requires a minimal activation energy, as shown in the figure. We must then conclude from the fact that the same donor gives principally ring-closed material (H > 5 at 100°)[*] that the preexponential factor for k_{rc}  exceeds that for k_{ro} , perhaps by a factor of 10 or so. However, by combining the relative transition-state energies for triethyltin hydride and for 1,4-cyclohexadiene with the characteristic ratios observed at 100° (0.078 and 0.0035, respectively) we can infer the analogous ratios of preexponential factors to be 4×10^{-4} and 1.5×10^{-3}, respectively. As the configurations around the methylene groups in the cyclohexadienyl radical and in 1,4-cyclohexadiene must be virtually indistinguishable, we must apparently attribute the difference of approximately 10^4 in the inferred preexponential factor ratios for these donors to the different natures of the abstraction processes (one being a radical-radical disproportionation), if we are to judge the scheme to be reasonable. The writer does not find so large a difference to be believable.

Moreover, the inferred ratio of preexponential factors for abstruction from 1,4-cyclohexadiene seems itself suspect. As we can show that the classical radical **4** should be energetically more stable than the ring-opened classical radical **3** (see subsection 5), we should expect any hybrid species to more closely resemble the former regarding the distribution of the free valence. We therefore expect in the

---

[*] In deriving this value for H(100°) we have assumed the composite activation energy of -8 kcal/mole reflected in Fig. 22. This parameterization gives H(70°) = 2.5 H(100°) and H(0°) = 52 H(100°). Because significant yields of **6**, the radical-radical product from **4**, are formed only at 0° to 70° for decomposition of ring-opened perester **2** (compare yields of **6** in Tables 1 and 2), these would seem to be the experiments which determine the minimum acceptable value of H. If H had been required to be independent of temperature, we would expect to have found a value substantially larger than quoted here; thus, the argument given here would be reinforced.

23

absence of steric factors that the ratio of preexponential factors should favor the formation of ring-closed material. Thus, the steric factor favoring formation of ring-opened material must be considerably larger than $1/(4 \times 10^{-4}) = 2500$. This does not seem to be a readily acceptable inference.

Suppose we attempt at least partially to circumvent these difficulties by placing the barrier for formation of ring-opened material via hydrogen abstraction from cyclohexadienyl radical just below that for abstraction from triethyltin hydride. Then we arrive at the amazing conclusion that increasing the activity of the hydrogen donor benefits less the process of higher activation energy. Furthermore, regardless of where we place this barrier, it seems incongruous that the substitution of triethyltin hydride for 1,4-cyclohexadiene should favor formation of ring-closed material, by the observed factor of 20 (at 100°) or any other, if formation of the ring-opened material requires the greater activation energy for abstraction from 1,4-cyclohexadiene.

Another pair of points concerns the *ortho*-ring cyclization process. The tip of the activation barrier for that process would appear at 13.6 + 0.8 = 14.4 kcal/mole above our energy zero, since the composite activation energy for E is -0.8 kcal/mole (heading H, p. 272). If we assume that the nonclassical radical undergoes the cyclization, we infer an activation energy of ~14 kcal/mole. As we previously showed that *ortho*-ring cyclization by **3** should be more exothermic than isomerization of **3** to the classical radical **4** (heading Q, p. 287), it is apparent that ring-cyclization by **7** can not be greatly endothermic and would probably be exothermic or thermoneutral. This circumstance is hard to reconcile with an activation barrier of 14 kcal/mole.

We might then prefer SCHEME A, where the classical ring-opened radical is retained to account for the ring cyclization. But if 3 can undergo ring cyclization, presumably it can also abstract hydrogen to give ring-opened hydrocarbon 5. We have already investigated this question with reference to the partitioning between the two kinds of processes for the saturated radical 21 (heading B, p. 138). We found that formation of saturated hydrocarbon 20 occurs in 1 M 1,4-cyclohexadiene at a rate relative to ring cyclization to 24 which is a factor of 16 higher than the analogous rate-ratio for formation of ring-opened hydrocarbon 5 and ring-cyclization to 9 (pp. 140, 150). We concluded that a difference of this magnitude could simply be ascribed to a decrease in the rate constant for ring cyclization by 21 compared to that for cyclization by 3 owing (a) to a smaller activation barrier for cyclization by 3 arising from the greater delocalization of the odd electron in 9 (pp. 145–150) and (b) to the requirement for the freezing out of rotation around two carbon-carbon single bonds in attaining the transition state for cyclization by the saturated radical 21 as compared to that of but one rotation for cyclization by 3 (p. 150).

On the other hand, if most of the ring-opened hydrocarbon 5 resulted from hydrogen abstraction by a nonclassical radical incapable of undergoing the ring-cyclization, the relative rate of formation of 5 to cyclization to 9 would appear anomalously high--the factor of 16 quoted above would appear anomalously low--with respect to expectations based solely on classical radicals. There is no reason to believe that the observed factor of 16 carries such an implication. As we must therefore judge that the observed yields of hydrocarbon 5 are well in line with what should result from hydrogen abstraction by classical ring-opened radical 3 in competition with its ring cyclization to 9, it seems incorrect to attribute ring cyclization, but not hydrogen abstraction, to 3.

The comparison of partitioning ratios for the saturated and unsaturated systems can not, of course, take into account the possibility that isomerization by 3 to a species such as 7 might proceed so rapidly and so completely in that direction that no products are formed from 3. Since some species must cyclize, this must again be SCHEME B, already found to be unattractive in part by virtue of its attribution of a 14 kcal/mole energy barrier for an essentially thermoneutral isomerization of 7 to 9.

Our conclusion is that a nonclassical radical such as 7 can not reasonably be the major precursor of the ring-opened and ring-closed hydrocarbons. Our route to this conclusion has admittedly involved elements of conjecture and speculation. In the final analysis, we can hardly advise Nature that she must restrict the behavior of a nonclassical radical species within the narrow limits of the expectations expressed in this subsection. However, if our conclusion is incorrect, if a radical such as 7 predominates once the species most faithful to the patterns of bonding in the starting peresters have retired, then such a species must behave very remarkably indeed.

4. Absolute Rate Constant Estimates

In subsection 2 we considered an approximate energy-level scheme for interconversion of and hydrogen abstraction by the classical radicals 3 and 4. That scheme can be extended with but little more work to one affording absolute rate-constant estimates.

There are several reasons for the presentation of such a scheme. One is that only in this way can we show that the values found for composite parameters such as E, G, H, and I do not conceal unreasonable implications. We suggested in subsection 3 that interpretation of such quantities in terms of product formation principally from a nonclassical radical results in several apparent inconsistencies. It seems only fair to put the classical-radical interpretation to a similarly demanding test. Moreover, we shall be able to estimate the equilibrium constant for the ring-opened and ring-closed radicals 3 and 4 instead of having to settle for the heat of interconversion alone. We shall also now be able to suggest time scales for the successive mechanistic levels (cage processes, radical equilibration, ring-cyclization) which were employed as an organizational basis in Section One.

A. The Estimation Procedure

We shall first give the rate-constant estimates and shall then note how they were obtained:

k_a $= 2 \times 10^{9}\ \exp(-5.8/RT)\ M^{-1}\ sec^{-1}$ (3.4-1)

$k_1 = 1 \times 10^{11}\ \exp(-4.3/RT)\ sec^{-1}$ (3.4-2)

$k_r = 4 \times 10^{10}\ \exp(-6.6/RT)\ M^{-1}\ sec^{-1}$ (3.4-3)

$k_a^{SnH} = 1.4 \times 10^{9}\ \exp(-2.6/RT)\ M^{-1}\ sec^{-1}$ (3.4-4)

k_b $= 3 \times 10^{10}\ \exp(-2.0/RT)\ M^{-1}\ sec^{-1}$ (3.4-5)

$k_2 = 4 \times 10^{12}\ \exp(-12.1/RT)\ sec^{-1}$ (3.4-6)

$k_b^{SnH} = 1 \times 10^{8}\ \exp(-7.5/RT)\ M^{-1}\ sec^{-1}$ (3.4-7)

k_b $= 2 \times 10^{7}\ \exp(-11.8/RT)\ M^{-1}\ sec^{-1}$ (3.4-8)

k_a $= 2 \times 10^{11}\ \exp(-2.0/RT)\ M^{-1}\ sec^{-1}$ (3.4-9)

Our point of departure is eq. 1.8-8 (p. 127), the ratio of the rate constant for hydrogen abstraction in the gas phase by ethyl radicals from 1,4-cyclohexadiene divided by the squre root of the rate constant for pairwise reaction (combination plus disproportionation) of ethyl radicals (45). The latter rate constant is reported by Shepp and Kutschke (46) to have an average value of $2 \times 10^{10}\ M^{-1}\ sec^{-1}$ in the temperature range 50–100° with an apparent activation energy of 2 ± 1 kcal/mole. In view of the reports that combinations of methyl radicals (47), of isopropyl radicals (48), and of t-butyl radicals (49) require no activation energy, we shall take pairwise reaction of ethyl radicals to have a rate constant of $2 \times 10^{10}\ M^{-1}\ sec^{-1}$, independent of temperature. This gives, in conjunction with eq. 1.8-8,

$$k = 2.5 \times 10^{8}\ \exp(-5.8/RT) \qquad (3.4\text{-}10)$$

for hydrogen abstraction from 1,4-cyclohexadiene by ethyl radicals.

The problem now is to relate this vapor-phase rate constant to that for the same process in hydrocarbon solution. The phase change per se will probably not much affect the activation energy, but many lines of reasoning suggest that preexponential factors for nonpolar processes may be expected to increase on going to the liquid phase by factors of perhaps 4 to 50 (121). This theoretical expectation has only recently become directly testable; Sauer and Ward have reported that addition of a hydrogen atom to benzene at 25° occurs with a rate constant of 3.7×10^7 in the gas phase, but 1.1×10^9 in water (111). This rate increase for the condensed phase process of a factor of 30 is close to the factor of 26 they report for addition of a hydrogen atom to toluene (111).

In writing eq. 3.4-1 for $k_a^{\hexagon}$, we have adopted a rate increase of a factor of eight over eq. 3.4-10. This factor is meant to include a rate increase for going to the condensed phase plus a smaller rate decrease for substituting the relatively ungainly ring-opened radical **3** for the compact, easily accessible ethyl radical as the hydrogen abstractor. Obviously, great precision is not attainable here, but we feel that eq. 3.4-1 should at least be of the correct order of magnitude.

We now readily obtain estimates for k_1 using eq. 2.4-5 (p. 253), for k_r using eq. 2.4-22 (p. 272), and for k_a^{SnH} using eq. 3.2-1.

To estimate k_2 and the k_b processes, we first recall eq. 2.4-25:

$$\frac{G^*k_4^{\frac{1}{2}}}{E^*F^{\frac{1}{2}}} = \frac{k_1 k_b^{\odot}}{k_2 k_a^{\hexagon}} \qquad (3.4\text{-}11)$$

Values of E, F, and G are available from Table 19, and k_4, the rate constant for pairwise reaction of cyclohexadienyl radicals, has been reported by Sauer and Ward (111) to be 1.8×10^9 M^{-1} sec^{-1} in aqueous solution at 25°. They also report a rate constant of $2-5 \times 10^{10}$ for the same process in the gas phase, a factor of 10 or more higher than in solution. In contrast, addition of a hydrogen atom to benzene or to toluene in the gas phase proceeded about a factor of 30 more slowly than in solution. Thus, pairwise reaction of cyclohexadienyl radicals is a diffusion-controlled process. As such, k_4 may obey Debye's eq. 2.4-7, p. 255, which anticipates a reciprocal relationship between a rate constant and the solution viscosity. Pertinent viscosity values are 1.00 centapoise at 20° for water and 0.96 centapoise for cyclohexane (106). If we assume a viscosity-related activation energy of 2 kcal/mole for k_4 (96) and employ values for E, F, and G obtained in 'most-representative' calculation number 14 (p. 305), we find that the left-hand side of eq. 3.4-11 has a value of 2.0×10^6 at 100° and a composite activation energy of -11.6 kcal/mole. Thus, we have that

$$\frac{k_1 k_b^{\odot}}{k_2 k_a^{\bigcirc}} = 0.3 \exp(11.6/RT) \quad . \qquad (3.4\text{-}12)$$

Combining eqs. 3.4-12 and 2.4-5 (p. 253), we obtain

$$k_b^{\odot}/k_2 = 7 \times 10^{-3} \exp(10.1/RT)\ M^{-1} \quad . \qquad (3.4\text{-}13)$$

We already have in eq. 1.7-4 (p. 101) the analogous equation for k_b^{SnH}/k_2, and by combining eqs. 2.4-23 (p. 275) and 2.4-5 we obtain the analogous equation for $k_b^{⌬}/k_2$:

$$k_b^{SnH}/k_2 = 2.4 \times 10^{-5} \exp(4.5/RT)\ M^{-1} \qquad (3.4\text{-}14)$$

$$k_b^{⌬}/k_2 = 6 \times 10^{-6} \exp(0.3/RT)\ M^{-1} \qquad (3.4\text{-}15)$$

Thus we see that estimation of k_2 or of any one of the k_b suffices to determine the other three. We have chosen to estimate $k_b^{\odot}$, the rate constant for transfer of a hydrogen atom from cyclohexadienyl radical to ring-closed radical 4, in the expectation that it should not be greatly different from k_4, the rate constant for pairwise reaction of cyclohexadienyl radicals discussed above. In writing eq. 3.4-5, we have put $k_b^{\odot} = \frac{1}{2} k_4$, but physically this relationship corresponds to taking $k_b^{\odot}$ to be only a fourth as large as k_4; that is, if 4 could be distinguished from the cyclohexadienyl radical only by some chemically and kinetically insignificant factor (such as a remote isotopic label), we would have $k_b^{\odot} = 2\, k_4$ according to the convention employed in this thesis. The factor of 4 is intended to account for the presumptively more stringent orientation for reaction of 4 with cyclohexadienyl radical arising from the steric congestion about the radical center in 4.

Finally, we have chosen $k_a^{\odot}$ as in eq. 3.4-9 on the assumption that reaction of ring-opened radical 3 with cyclohexadienyl radical should be subject to decidedly less severe orientational requirements than reaction of ring-closed 4 with cyclohexadienyl radical.

We shall now comment briefly on the reasonableness of the rate-constant estimates.

We find for the relative concentrations of ring-closed 4 and ring-opened 3 at equilibrium:

$$\begin{aligned} K &= k_1/k_2 = 2.5 \times 10^{-2} \exp(7.8/RT) \qquad (3.4\text{-}16) \\ &= 4 \times 10^{4} \quad \text{at } 0^\circ \\ &= 9 \times 10^{2} \quad \text{at } 100^\circ \\ &= 1 \qquad\quad \text{at } \sim 800^\circ \end{aligned}$$

Apparently, ring-closed radical 4 has both a lower enthalpy, by about 8 kcal/mole, and a lower entropy, by about 7 e.u., than ring-opened radical 3. We shall argue in the following subsection that the estimated enthalpy difference is reasonable. The quantitative reasonableness of the entropy difference is not so easily judged, but we feel that a lower entropy for the ring-closed form is indicated by the orientational requirements for electron delocalization into the phenyl rings in 4 (probably partially offset by the near coplanarity required for conjugation of the phenyl rings with the double bond in 3) and by the presence of a cyclopropyl ring in 4 but a double bond in 3 (e.g., the entropy of formation of propane is 7 e.u. higher than that of cyclopropane). In any case, the enthalpy difference dominates at temperatures employed in this work.

Next we note that the scheme gives steric factors of ~ 14 for triethyltin hydride and ~ 100 for 1,4-cyclohexadiene favoring hydrogen abstraction by ring-opened 3 over that by ring-closed 4. Although we know of no pertinent literature data, we find these steric factors to be intuitively reasonable. The difference between triethyltin hydride and 1,4-cyclohexadiene is within previously quoted estimates of experimental error; e.g., assuming that eqs. 3.4-14 and 3.4-15 are correct near the center of the range of temperatures investigated experimentally (i.e., at ~80°), a difference of 5.3 kcal/mole in the composite activation energies, instead of the quoted 4.2 kcal/mole, would have resulted in identical steric-factor estimates.

Finally, we can construct the parameter H using the rate-constant estimates:

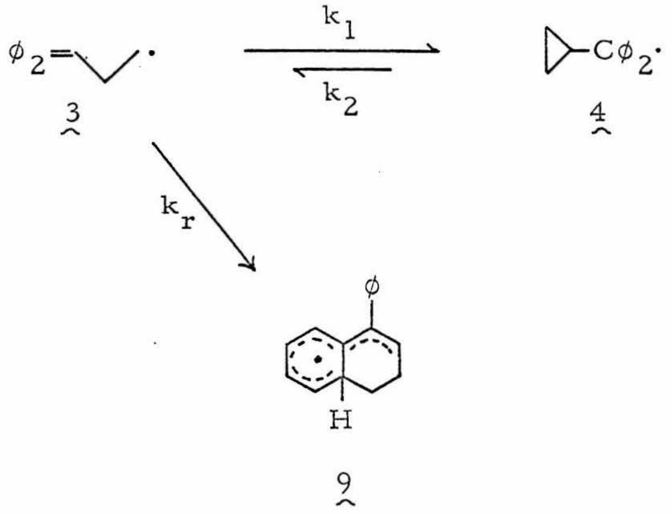
$$H = \frac{k_1 k_b^{\odot}}{k_2 k_a^{\odot}} = 4 \times 10^{-3} \exp(7.8/RT) \quad . \qquad (3.4\text{-}17)$$

Eq. 3.4-17 gives H(100°) = 100, which value is compatible with the roughly estimated lower limit of 5 obtained in Section Two (heading J, p. 275).

B. Characteristic Times for Cage Reaction, Radical Equilibration, and Ring-Cyclization

The mechanistic development in Section One was based on the concept of distinct time scales, or characteristic times, for the principal mechanistic levels which unfold sequentially before each C_{16} hydrocarbon radical between formation in a perester fragmentation and conversion to product. The shortest time period, we have said, is that during which the cage reaction products may be formed before diffusion separates the initial radical pair. If the hydrocarbon radical (at this stage ring-opened 3, if the perester is ring-opened, or ring-closed 4, if the perester is ring-closed) survives this stage, equilibration of the ring-opened and ring-closed forms of the radical, perhaps in competition with product formation via abstraction of hydrogen from a suitable donor becomes the principal order of business. In those cases where equilibration between 3 and 4 is attained before conversion to product occurs, the emphasis now shifts to competition between hydrogen abstraction and ring-cyclization to 9. Finally, if the latter occurs, conversion to nonradical products must usually await the appearance of a second radical species.

We shall give here semiquantitative estimates for the time scales of the first three levels. To do this we shall treat kinetically the abbreviated scheme of reactions shown below, where we shall take the radical species born in an hypothetical perester decomposition to be ring-opened 3 and will ask at subsequent times for the probabilities that the radical is 3, 4, or 9.



The kinetic scheme depicted above leads to a pair of simultaneous first-order linear differential equations whose solution by the method discussed by Benson (122) is reasonably straightforward. The general solution is rather complex but can be considerably simplified in our case since we have definite values of k_1, k_2, and k_r to substitute in. Eqs. 3.4-18 retain the minimum degree of complexity consistent with condition that the sum of the probabilities that the radical exists as **3**, as **4**, or as **9** is identically unity at all times. The next higher level of approximation replaces k_1 in the two exponential terms by the sum $k_1 + k_2 + k_r$.

$$
\begin{aligned}
(\mathbf{3}) &= \left(\frac{k_1+k_r}{k_1+k_2+k_r}\right)\exp(-k_1 t) + \left(\frac{k_2}{k_1+k_2+k_r}\right)\exp\left(-\frac{k_r k_2}{k_1}\,t\right) \\
(\mathbf{4}) &= -\left(\frac{k_1}{k_1+k_2+k_r}\right)\exp(-k_1 t) + \left(\frac{k_1}{k_1+k_2+k_r}\right)\exp\left(-\frac{k_r k_2}{k_1}\,t\right) \qquad (3.4\text{-}18) \\
(\mathbf{9}) &= -\left(\frac{k_r}{k_1+k_2+k_r}\right)\exp(-k_1 t) - \left(\frac{k_1+k_2}{k_1+k_2+k_r}\right)\exp\left(-\frac{k_r k_2}{k_1}\,t\right) + 1
\end{aligned}
$$

The reader can readily confirm that we start out with $(\mathbf{3}) = 1$ and that at long times we have $(\mathbf{9}) = 1$. Predictions for intermediate times are displayed in Table 20 for reaction temperatures of 100, 0, -100, and -150°.

We see from the table that at 100° equilibration of **3** and **4** is underway by 10^{-9} sec and is nearly complete by 10^{-8} sec. The same points are reached at 0° at times which are about a factor of ten longer. We noted in subsection 5C to Section One that yields of analogous cage products are virtually identical for decomposition of ring-opened perester **1** and for that of saturated perester **8** at ~150°. As the hydrocarbon radical from the latter does not have available a reaction step comparable to the rearrangement of **3** to **4**, this broadly implies (assuming that our estimate of k_1 is realistic) that at 100° essentially

Table 20. Relative Probabilities at Several Reaction Temperatures that a Radical Species which is Ring-opened at Time Zero will be Ring-opened (3), Ring-closed (4), or Ring-cyclized (9) at Subsequent Times, as Calculated from Eqs. 3.4-18.

		Time From Formation of 3, sec						
Temp., °C	Radical Species	10^{-9}	10^{-8}	10^{-6}	10^{-4}	10^{-1}	10^{6}	10^{13}
100	3	0.739	0.049	0.001	6×10^{-4}	---	---	---
	4	0.256	0.934	0.976	0.545	---	---	---
	9	0.005	0.017	0.023	0.455	1.000	1.000	1.000
0	3	0.964	0.696	2×10^{-5}	2×10^{-5}	1×10^{-5}	---	---
	4	0.035	0.302	0.994	0.944	0.615	---	---
	9	2×10^{-4}	0.002	0.006	0.006	0.385	1.000	1.000
-100	3	1.000	0.996	0.688	6×10^{-9}	6×10^{-9}	2×10^{-9}	---
	4	4×10^{-4}	0.004	0.312	0.999	0.999	0.344	---
	9	10^{-7}	10^{-6}	10^{-4}	5×10^{-4}	5×10^{-4}	0.656	1.000
-150	3	1.000	1.000	0.998	0.791	6×10^{-13}	6×10^{-13}	3×10^{-13}
	4	2×10^{-6}	2×10^{-5}	0.002	0.209	1.000	1.000	0.640
	9	---	---	7×10^{-8}	7×10^{-6}	3×10^{-5}	3×10^{-5}	0.360

all of the cage product is formed in each case within 10^{-9} sec after the perester fragmentation. Interestingly, Noyes has estimated that the rates of diffusive separation of one-contiguous particles will usually allow about 10^{-9} sec for cage reaction to be effected in ordinary solvents (such as cyclohexane, benzene, etc.) (24).

One interesting feature of the kinetic scheme is that the time required for equilibration of **3** and **4** is independent of whether the radical species is initially ring-opened or ring-closed.* This may at first seem paradoxical, since the rate of conversion of **3** to **4** is much larger than that of **4** to **3**, but the compensating factor is that a much smaller degree of conversion to the alternative form is required if the radical is initially ring-closed **4**.

Following the attainment of equilibrium between **3** and **4**, the radical continues to be most probably ring-closed until about 10^{-4} sec at 100° and 10^{-1} sec at 0°, whence ring cyclization through the small equilibrium concentration of **3** becomes important. At -100 and -150°, the corresponding times are predicted to be about 10 days and 300,000 years. This suggests that it should be possible to directly observe the 'classical ring-closed radical' by esr spectroscopy at low temperatures and perhaps even to conveniently measure the rate of conversion to **9** (which is essentially determined by k_2k_r/k_1). In contrast, the much more rapid equilibration of **3** and **4** would be difficult to monitor with

---

*Specifically, one finds that equal times are required to form any given fraction of the equilibrium concentration of the second radical species whether the first is **3** or **4**.

currently available esr equipment even if a temperature of -150° could be employed.

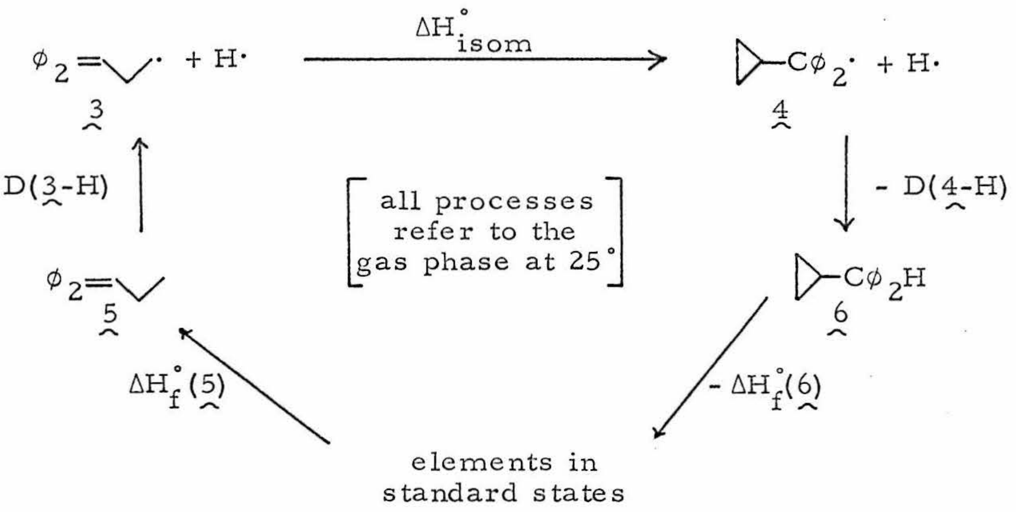
Note that a small probability of being in the ring-cyclized form accumulates on the time scale of the equilibration between 3 and 4; this results from direct competition between ring-cyclization to 9 and rearrangement to 4 while the probability of being in the ring-opened form is still high. Any 'extra' amount of ring-opened hydrocarbon which might be formed in competition with the two processes would similarly be 'early' product. Such material is not accounted for under the mechanistic assumptions of Section Two. As indicated by the probability figures at 0 and 100°, the extent of this early ring-cyclization increases at higher temperatures. However, the conversion to 9 during the radical equilibration is predicted to be only 2.6% at 150°, the highest temperature employed, so the partial failure of the equilibrium assumption is not serious. In any case, there would be no direct effect on the ratio of ring-opened hydrocarbon 5 to dihydronaphthalene 10 treated in Section Two, since the same partitioning factor, $k_a(\mathrm{ZH})/k_r$, would apply at all times. The failure of the assumption would mainly effect the ratio of ring-closed hydrocarbon 6 to ring-opened hydrocarbon 5, as more 5 but less 6 would be formed than we would have predicted. Using eqs. 3.4-1 and 3.4-2 we find that this product ratio would be overestimated by a maximum of about 3% for reaction in neat 1,4-cyclohexadiene at 150°. This is a small factor compared to the experimental uncertaintity in the ratio of 6 to 5 of perhaps 10% under such conditions.

In summary, then, at 100° the cage process are largely completed within 10^{-9} sec of the fragmentation of a molecule of ring-opened perester 1, equilibration of the ring-opened and ring-closed radicals is nearly completed by 10^{-8} sec, and the major portion of ring cyclization and hydrogen abstraction occurs in the neighborhood of 10^{-4} sec. At 0°, comparable figures for the attainment of equilibrium between 3 and 4 and for ring-cyclization are 10^{-7} and 10^{-1} sec.

5. Estimation of Relative Enthalpies of Phenyl- and Methyl-substituted Allylcarbinyl and Cyclopropylcarbinyl Radicals

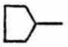
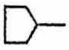
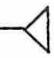
The principal purpose of this subsection is to show that the experimentally inferred difference of -8 ± 3 kcal/mole in the enthalpies of ring-closed radical 4 and ring-opened radical 3 (heading K, p. 277; subsection 2, Section Three) is not inconsistent with chemical and thermodynamic experience. In addition, we shall briefly investigate the manner in which methyl and phenyl substitution may be expected to influence the relative stabilities of so-called ring-opened allylcarbinyl- and ring-closed cyclopropylcarbinyl free radicals.

The thermodynamic cycle diagrammed below shows that the difference in enthalpy of the radicals 3 and 4 may be obtained as the difference of the dissociation energies of the relevant carbon-hydrogen bonds in 5 and 6 less the difference in the enthalpies of the isomeric hydrocarbons. Our approach will be first to estimate the heats of formation of the hydrocarbons. These quantities will then be combined with the estimate $\Delta H^{o}_{isom} = -8 \pm 3$ kcal/mole to infer a value for the difference in the C–H bond dissociation energies. Finally, we shall consider whether that difference is reasonable.



We can estimate $\Delta H^\circ_f(5)$ by correcting the observed ΔH°_f of 58 kcal/mole for 1,1-diphenylethylene (Table 21) for the effect of substitution of an ethyl group for a vinylic hydrogen. Such an approach is sound, although it will probably seem questionable to readers who have not had the occasion to observe the impressive regularities which heats of formation display as a function of molecular structure, particularly for homologous series. We have indicated in Table 21 two comparisons of the type required here. The first shows that the heat of formation of ethylene decreases by 12.2 kcal/mole upon substitution of ethyl for hydrogen to give 1-butene. The second comparison, perhaps more appropriate as a model for relating 1,1-diphenylethylene and 1,1-diphenyl-1-butene, concerns 2-methylpropene ('1,1-dimethylethylene') and 2-methyl-2-pentene: the heat of formation of the latter is 11.6 kcal/mole less than that of the former. Many similar comparisons

Table 21. Literature Values for Heats of Formation (kcal/mole) of Some Hydrocarbons in the Gas Phase at 25°

Compounds	ΔH_f^o	$\delta\Delta H_f^o$	Ref
$CH_2=CH_2$	12.50	12.2	123
$CH_2=CH_2CH_2CH_3$	0.28		123
$(CH_3)_2C=CH_2$	- 3.34	11.6	123
$(CH_3)_2C=CH_2CH_2CH_3$	-14.96		123
$(C_6H_5)_2C=CH_2$	58[a]		128
CH_4	-17.89	55	123
$C_6H_5CH_3$	11.95	52	123
$(C_6H_5)_2CH_2$	37[b]	53[d]	130
$(C_6H_5)_3CH$	64[c]		133
$(C_6H_5)_4C$	90[d]		134
 $-CH_2CH_3$	1.7[e]		124
 CH_3	-25.50	4.87	123
 CH_2CH_3	-30.37		123
$(CH_3)_2CHCH_3$	-32.15	4.77	123
$(CH_3)_2CHCH_2CH_3$	-36.92	5.57	123
$(CH_3)_2CHCH(CH_3)_2$	-42.49		123
cyclopropane	12.73		123
$(C_6H_5)CH_2CH_3$	7.12		123
$CH_3CH_2CH_3$	-24.82	26.5	123
CH_3CH_2- 	1.7		124
$(C_6H_5)CH=CH_2$	35.22		123

Footnotes for Table 21

[a] From $\Delta H_c^{298}(1)$ = 7393.0 ± 0.6 abs kjoules/mole = 1767.0 ± 0.2 kcal/mole (128a). Translation to ΔH_f^o = 40.4 kcal/mole made using standard heats of formation: ΔH_f^o $CO_2(g)$ = 94.052 kcal/mole; ΔH_f^o $H_2O(1)$ = 68.317 kcal/mole (129). Correction to gas phase made using ΔH_v = 17.5 kcal/mole at 25° (128b).

[b] Based on $\Delta H_f^{298}(1)$ = 21.2 kcal/mole (130a). Correction to gas phase accomplished in two steps using ΔH_{fusion} = 4.2 kcal/mole (130b) and $\Delta H_{sublimation}$ = 19.7 kcal/mole (130c). These values give ΔH_{vap} = 15.5 kcal/mole; a direct determination giving 12.7 kcal/mole is available (131), but was not used as it seems too small in comparison to values of 17.5 kcal/mole for 1,1-diphenylethylene (128b) and 17 for 1,1-diphenylethane (132).

[c] This result is based on two determinations of $\Delta H_c(s)$ (2372.2 and 2374.2 kcal/mole) quoted by Cottrell (133). The average gives $\Delta H_f^{298}(s)$ = 39.7 kcal/mole using heats of formation of combusion products quoted in footnote a. Corrected to gas phase using $\Delta H_{sublimation}$ = 23.9 kcal/mole (130c).

[d] Value very approximate; based on an average $\Delta H_c^{298}(s)$ of 3097 kcal/mole from two sources which differed by 11 kcal/mole (134a, 134b). Corrected to a heat of formation using heats of formation of combustion products as in footnote a. The value quoted was then obtained using a heat of sublimation of 28 kcal/mole estimated with reference to values of 19.7 kcal/mole for diphenylmethane and 23.9 kcal/mole for triphenylmethane (130c).

[f] See text.

which may be made from standard compilations of heats of formation (113, 123) such as may be found in the "Handbook of Chemistry and Physics" (113) yield closely similar 'correction factors'.

Thus we obtain $\Delta H_f^o(\underset{\sim}{5})$ as 58 - 12 = 46 kcal/mole. This estimate is probably reliable to ± 2 kcal/mole.

We shall next make use of the orderly variation of ΔH_f^o for successive substitution on methane of phenyl for hydrogen to obtain $\Delta H_f^o(\underset{\sim}{6})$ from ΔH_f^o for methylcyclopropane. It may be seen from Table 21 that disubstitution on methane itself increases ΔH_f^o by 55 kcal/mole, whereas disubstitution on toluene leads to an increase of 52 kcal/mole and disubstitution on diphenylmethane increases ΔH_f by ~53 kcal/mole.*

Unfortunately, no one seems to have anticipated our need for the heat of formation of methylcyclopropane. However, ethylcyclopropane has been studied by Fierens and Nasielski (124). Their heat of combustion at 25°, 808.8 kcal/mole, implies a heat of formation of liquid ethylcyclopropane of -3.1 kcal/mole. The latent heat of vaporization needed to correct this quantity to the gas phase seems to be unavailable, but that of pentane, 4.9 kcal/mole at 25° (125), should be close enough since these C_5 hydrocarbons differ in boiling point at 760 mmhg by only 0.3° (126, 127). This gives ΔH_f^o = 1.7 kcal/mole for ethylcyclopropane.

We can estimate ΔH_f for methylcyclopropane from that for ethylcyclopropane with reference to model processes wherein the role of

---

*This last comparison is considerably less reliable than the others; see footnote d to Table 21.

the cyclopropyl group is taken by the isopropyl and cyclopentyl groups (see Table 21). For the latter we find ΔH_f^o (methylcyclopentane) = ΔH_f^o (ethylcyclopentane) + 4.87 kcal/mole. The analogous comparison for isopropyl gives a correction quantity of + 4.77 kcal/mole. Therefore we estimate $\Delta H_f^o = 6.5$ kcal/mole for methylcyclopropane.

Finally, we estimate $\Delta H_f(6) = 60 \pm 3$ kcal/mole by adding +53 kcal/mole to ΔH_f^o for methylcyclopropane for substitution of two phenyl groups.

Thus we have that 6 is less stable than 5 by ~ 14 kcal/mole. Together with the observed $\Delta H_f^o(4) - \Delta H_f^o(3) = -8 \pm 3$ kcal/mole in cyclohexane--1,4-cyclohexadiene mixtures, this would require D(3-H) - D(4-H) = 22 kcal/mole with an uncertainty of perhaps ± 6 kcal/mole, assuming that transfer of the equilibrium between 3 and 4 to the gas phase does not greatly effect the difference in enthalpy of the two radicals.[*] We have consistently assumed interaction of the radical center in 3 with the double bond to be negligible and now take D(3-H) to be ~98 kcal/mole, this being the observed value for D(C_2H_5-H) (95).

Thus, our estimate for the difference in enthalpy of the ring-closed and ring-opened radicals implies D(4-H) = 76 ± 7 kcal/mole.

Although quantitative data on dibenzylic C–H bond dissociation energies are lacking,[**] we believe this estimate would be reasonable

---

[*] The effect of the transfer would probably be to make the enthalpy difference smaller than in the gas phase by preferential solvation of the less stable ring-opened radical. This might well lower the mean D(4-H) given below by one or two kcal/mole.

[**] D($(C_6H_5)_2$CH–H) = 72 kcal/mole has often been quoted (51, 135). However, no mention of this determination is made in recently

even if the cumulative uncertainty were only ± 3 kcal/mole. In support of this assertion we can cite $D(C_6H_5CH_2\text{-}H)$ = 85 kcal/mole with confidence (95 , 135) and can make a reasonable case for $D((C_6H_5)_3C\text{-}H$ = 75 kcal/mole (51 ,135). The latter value may be obtained as $\frac{1}{2}(11 + 35 + 104)$ from a thermochemical cycle employing the heat of hydrogenation of dissolved hexaphenylethane in ethyl acetate (- 35 kcal/mole (138)) and the heat of dissociation of hexaphenylethane in solution (11 ± 1 kcal/mole, insensitive to solvent (139)) in conjunction with the heat of dissociation of molecular hydrogen in the gas phase. As $D(CH_3\text{-}H)$ is 104 kcal/mole (95), we see that the first substitution of phenyl for hydrogen lowers D(R-H) by 19 kcal/mole. Substitution of a second phenyl group may be expected to effect a smaller decrease (a) because of inhibition of resonance through rotation of the phenyl rings in diphenylmethyl to noncoplanar conformations as the result of repulsive interactions of <u>ortho</u>-hydrogens (140) and (b) by virtue of the commonly observed phenomenon of saturation upon successive substitution.* Thus, $D()C_6H_5)_2CH\text{-}H)$ = 75 kcal/mole would seem to be a reasonable guess, and D(4-H) should not be greatly different; the extra stabilization which would probably be expected for substitution of cyclopropyl for hydrogen in the presence of two phenyl groups in a hypothetical

---

advanced bond dissociation energy compilations (95 ,136 , 137). Apparently those closest to the field have judged the determination to be invalid, along with a number of others which concern benzylic C-H and C-C bonds.

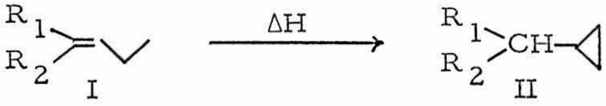
*For example, successive substitution of methyl for hydrogen gives the series $D(CH_3\text{-}H)$ - 104, $D(C_2H_5\text{-}H)$ = 98. 0, $D((CH_3)_2CH\text{-}H)$ = 94. 5, $D((CH_3)_3C\text{-}H)$ = 91 (95).

strain-free system could well be of lesser magnitude than the destabilization of the real system due to an increase in the out-of-plane rotation of the phenyl rings. A similar compensation phenomenon may account for $D((C_6H_5)_3C\text{-}H) \cong 75$ kcal/mole.

We have recorded our estimates of the heats of interconversion of differently substituted allylcarbinyl-cyclopropylcarbinyl free radicals in Table 22. Much of the requisite information on the heats of formation of the isomeric hydrocarbons has been considered in passing above. We require here three additional estimations. The heat of formation of isopropylcyclopropane can be obtained as $1.7 - 5.6 = -3.9$ kcal/mole by correcting that for ethylcyclopropane for substitution of methyl for hydrogen. Table 21 shows that this substitution requires a correction factor of 5.6 kcal/mole where the role of the constant cyclopropyl group is taken by isopropyl. To estimate ΔH_f^o for benzylcyclopropane, we start with $\Delta H_f^o = 7.1$ kcal/mole for ethylbenzene. The hypothetical process here will be to substitute cyclopropyl for methyl. The result is an increase in the heat of formation of 26.5 kcal/mole where the constant group is ethyl rather than our tolyl. We estimate thereby ΔH_f^o(benzylcyclopropane) = 34 kcal/mole. Finally, we estimate ΔH_f^o(<u>trans</u>-1-phenyl-1-butene) as 23 kcal/mole by applying the same 12 kcal/mole correction to ΔH_f^o(styrene) as was done earlier to get $\Delta H_f^o(\underset{\frown}{5})$ from that for 1,1-diphenylethylene.

As shown in the upper region of Table 22, these estimations predict a smooth enhancement of the heat of interconversion of the isomeric hydrocarbons with successive substitution of phenyl or methyl for hydrogen. The trend is undoubtedly due mainly to stabilization of

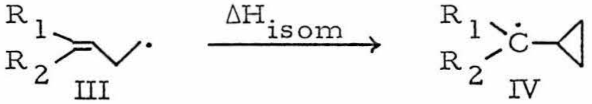
Table 22. Estimated Enthalpies of Interconversion of Some Isomeric Allylcarbinyl and Cyclopropylcarbinyl Hydrocarbons and Free Radicals.



R_1	R_2	$\Delta H_f^o(II)^c$	$\Delta H_f^o(I)^c$	$\Delta H \equiv$ $\Delta H_f^o(II) - \Delta H_f^o(I)$
H	H	6.5^a	0.28^b	6
CH_3	H	1.7^b	-7.59^b	9
CH_3	CH_3	-3.9^a	-14.96^b	11
C_6H_5	H	34^a	23^a	11
C_6H_5	C_6H_5	60^a	46^a	14

[a] Estimated; see text. [b] From Table 21.

[c] kcal/mole; for the gas phase at 25°.



R_1	R_2	$\Delta H_{isom}^{d,e}$	$D(IV\text{-}H)^{e,f}$	$D(III\text{-}H)^{e,f}$
H	H	+ 3	95	98
CH_3	H	+ 3	92	98
CH_3	CH_3	+ 2	89	98
C_6H_5	H	- 5	82	98
C_6H_5	C_6H_5	-8 ± 3^g	76^h	98

[d] Obtained as $\Delta H_f^o(II) - \Delta H_f^o(I) + D(IV\text{-}H) - D(III\text{-}H)$.

[e] kcal/mole; for the gas phase at 25°. [f] Estimated; see text.

[g] Observed value in hydrocarbon solution; see text.

[h] Adopted to fit observed value for ΔH_{isom}; see footnote g.

the double bond in the allylcarbinyl isomer.

Estimates of the C–H bond dissociation energies in the isomeric hydrocarbons, when combined with the relative enthalpies of the hydrocarbons, give the predicted heats of isomerization of the allylcarbinyl-type radical to the cyclopropylcarbinyl form. We have assigned D(C–H) = 98 kcal/mole for all the ring-opened hydrocarbons with reference to D(ethyl-H) = 98.0 (95). The assignments for the cyclopropylcarbinyl structures are intended to broadly reflect the greater kinetic reactivity of methyl hydrogen in methylcyclopropane as compared with a 'typical' primary hydrogen of isopentane. Observed enhancement factors (on a per-hydrogen basis) are about 3 for competitive hydrogen abstraction by t-butoxy radicals at 68° and 5.5 at 0° (118a), about 16 for competitive abstraction by atomic chlorine at 0° (118a) and 6.1 for hydrogen abstraction by the polystyryl radical 79°, determined by comparison of chain-transfer constants (118b). Unfortunately, these data can not be simply translated into differences in bond-dissociation energies. However, some lowering upon substitution of cyclopropyl for methyl on ethane is evidently indicated, and we have employed D(cyclopropylcarbinyl-H) = 95 kcal/mole. We have similarly estimated D(methylcyclopropylcarbinyl-H) = 92 kcal/mole with reference to D(isopropyl-H) = 94.5 kcal/mole, and D(dimethylcyclopropylcarbinyl-H) = 89 kcal/mole with reference to D(t-butyl-H) = 91 kcal/mole (95). It seems reasonable that the extra stabilization for α-cyclopropyl over α-methyl will be diminished by successive substitution of methyl groups for hydrogen at the prospective radical center. Finally, we have assigned D(phenylcyclopropylcarbinyl-H) = 82 kcal/mole with reference to D(benzyl-H) = 85 (95).

The calculated enthalpies of isomerization of the isomeric radicals shown in Table 22 atfirst surprised us; we had expected that substitution of methyl and then phenyl groups onto the parent four-carbon system would smoothly lower the enthalpy of interconversion to the strongly negative figure of -8 kcal/mole observed for the diphenyl-substituted system. It appears that this is not the case--that substitution of methyl nearly equally stabilizes the ring-opened hydrocarbon (hence the ring-opened radical) and the ring-closed radical. Substitution of phenyl for hydrogen is required for the latter factor to become dominant.

We noted in the OVERVIEW that interest came to be focused on the diphenyl-substituted system because the analogous unsubstituted and dimethyl-substituted systems gave, with but one exception, only traces of the ring-closed hydrocarbon as product (pp. 9-10). The motivation for employing methyl and phenyl substituents was to effect closer competition in product formation in order to make the system experimentally tractable. Indeed, Howden found that the diphenyl-substituted system gave ring-closed hydrocarbon 6 and ring-opened hydrocarbon 5 in the proportions of about 20:1 upon decomposition of ring-opened perester 1 in the presence of the powerful hydrogen donor, tri-*n*-butyltin hydride (Table 12).

Estimated enthalpies quoted in Table 22 clearly show that the price of effecting close competition in the formation of products is the creation of an enormous difference in reactivity of the isomeric radicals 3 and 4, as reflected in the strengths of the carbon-hydrogen bonds they may form, offset by a large difference in the stability of the radicals. The natural result, as we have seen in subsection 2, is that hydrogen donors of differing reactivity respect to greater or lesser degrees the intrinsic difference in reactivity of the radicals and so give rise to widely varying ratios of ring-opened and ring-closed products.

The large difference in stability of the isomeric radicals **3** and **4** almost certainly has the additional effect of overriding any driving force for radical stabilization via σ-electron delocalization which may have existed in the parent four-carbon system, where both the allylcarbinyl radical and the cyclopropyl-radical are essentially primary radicals. The apparent failure to observe a nonclassical radical in the system investigated here does not now seem very surprising.

It therefore remains for future researchers to demonstrate the existence of nonclassical free-radical intermediates or to present data which *would* support a general presumption against σ-electron delocalization.

EXPERIMENTAL SECTION

Melting points and boiling points are uncorrected. The melting points were taken on a Büchi apparatus.

Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Infrared spectra were determined using either a Beckman infrared spectrophotometer, Model IR-7, or a Perkin-Elmer Infracord, Model 237.

Nuclear magnetic resonance spectra were routinely recorded with Varian Associates A-60 or A-60A spectrometers. In special cases, a Varian Associates A-56/60A spectrophotometer equipped with a Varian C-1024 Time Averaging Computer was employed.

Gas chromatographic analyses were carried out on a Perkin-Elmer Model 800 gas chromatograph fitted with a flame-ionization detector and a Perkin-Elmer Model 194 printing integrator. The column routinely employed was 6-12 ft of aluminum tubing (1/8 in o. d.) packed with 10% Ucon polar 50 HB 5100 on 80-100 mesh HMDS treated Chromasorb W. Also employed were columns of silicone oil (SE-30) and Apiezon L on the same stationary phase.

1. Solvents (Hydrogen Donors)

Cyclohexane, benzene, and methanol were Matheson Coleman & Bell Chemicals, Spectroscopic Grade, used as received.

Cumene was purified by the method of Vogel (141) before use.

Indene was distilled at atmospheric pressure from sodium and then again under reduced pressure at ~35° through a Vigreaux column. Material from a center fraction was sealed under nitrogen and stored at 0° until use.

***n*-Octane** [Phillips Petroleum Company Pure Grade (99 Mol% Minimum)] was stirred over concentrated sulfuric acid until fresh portions of the acid were only weakly colorized. The hydrocarbon was then washed twice with 10% sodium carbonate solution, dried over magnesium sulfate, and finally distilled from sodium, bp 124.0 - 124.5° at atmospheric pressure.

1,4-Cyclohexadiene was obtained from Columbia Organic Chemicals Co., Inc. and from Aldrich Chemical Co., Inc. The Columbia material was used in experiments reported in Tables 1 and 3. Analysis by vpc on Ucon polar indicated a purity of 99.9%, with impurities of benzene(?), 0.1%, and 1,3-cyclohexadiene(?), 0.02%. Experiments reported in Tables 2, 4, 5, and 6 employed Aldrich preparations, subsequently observed to contain 0.01 -- 0.1% 1,3-cyclohexadiene and to develop an impurity upon heating at approximately the retention time of one of the reaction products from the perester decompositions (142). No purification was undertaken with the exception of distillation at atmospheric pressure through a small Vigreaux column immediately before use.

Triethyltin hydride was prepared from triethyltin bromide (Orgmet, Inc.) by reduction with lithium aluminum hydride. In a typical preparation, 58 g (0.202 mole) triethyltin bromide in 250 ml diethyl ether (Mallinckrodt Anhydrous Ether, Analytical Reagent) was added slowly to 7.7 g (0.20 mole) lithium aluminum hydride in 300 ml diethyl ether. No exothermicity was noted. The reaction mixture was stirred for 4 hr at reflux, after which 28 ml of a 4.45% aqueous sodium hydroxide solution was cautiously added after the reaction flask had been swept with nitrogen. The reaction mixture was then filtered with suction and distilled through a Vigreaux column until the pot temperature reached 65° to remove most of the diethyl ether. The residual material was fractionated through the same column at about 25 mm. A center fraction distilled at 52-53°; 26.5 g (63%). The identity of the product was conclusively established by comparison of an infrared spectrum with that reported in the literature (143).

The triethyltin hydride was either used immediately or was degassed and sealed into specially prepared two-chambered glass vessels at $\sim 10^{-3}$ mm (three freeze-pump-thaw cycles using liquid nitrogen). It was generally possible to transfer the triethyltin hydride from the one chamber to the other immediately before use in the perester decompositions by cooling the recepticle in liquid nitrogen while warming the side with the tin hydride in tepid water. This could usually be done some days, weeks, or occasionally months after the original sealing, but sufficient hydrogen pressure built up in some tubes that the tin hydride would not distill. The main decomposition product appears to be hexaethylditin; in one case, such material was treated with bromine in diethyl ether and the resultant triethyltin bromide was reconverted to triethyltin hydride as above.

Diethyl ether and tetrahydrofuran were refluxed over sodium -- benzophenone (144) for several days and were distilled from the same pot immediately before use.

Tetraethyltin was used as obtained from Orgmet, Inc.

2. Starting Materials and Reaction Products

(γ,γ-Diphenylallyl)acetic Acid. - (γ,γ-Diphenylallyl)carbinyl bromide [43 g, 0.15 mole, prepared by treatment of diphenylcyclopropylcarbinol (Aldrich Chemical Co., Inc.) with phosphorus tribromide as described by Howden (145)] in 400 ml anhydrous ether was added with stirring to 4.0 g (0.165 mole) magnesium shavings in a nitrogen atmosphere over the course of 1 hr. After an additional hour at reflux, the reaction mixture was cooled in a Dry Ice-acetone bath and ca. 20 g finely powdered Dry Ice (about a two-fold excess) were added. After a few minutes at -80°, the bath was removed and the reaction mixture allowed to warm up. At -60° a second portion of 20 g Dry Ice was added. When the reaction mixture had reached -10°, it was poured into 400 ml ice-cold half conc. hydrochloric acid in a separatory funnel. The funnel was shaken and the aqueous layer separated and shaken with 200 ml ether. The combined ether solutions were extracted with two 150-ml quantities of a solution of 20 g (0.5 mole) sodium hydroxide in 300 ml water. The aqueous extracts were acidified with concentrated hydrochloric acid, upon which the white acid crystallized. The solid was collected by filtration, washed liberally with water, and air-dried. The product was crystallized from hexane and gave a first crop, 27.1 g, mp 82.8 -83.5°, and a second crop, 3.0 g, mp 81-82° (total 80%); lit. (146) mp 83-83.5°.

t-Butyl (γ,γ-Diphenyallyl)peracetate. - An initial sample, used for runs displayed in Table 1 and for many of those in Table 8, was material left by Howden. Later samples were prepared by a modification of Howden's procedure (147). In one such preparation, 5 g (20 mmoles) of γ,γ-diphenylallylacetic acid was refluxed for 3 hr with 1.77 ml freshly distilled thionyl chloride in 50 ml spec. grade benzene. The solvent and excess thionyl chloride was then removed on the rotatory evaporator at a bath temperature of 35-40°, after which 50 ml fresh benzene was added to the residue and stripped as before. The crude acid chloride in 50 ml pentane was then added over the course of 0.5 hr to 4 ml t-butyl hydroxide (usually Lucidol t-butyl hydroperoxide - 90, ca. 40 mmoles, 100% excess) and 1.74 ml pyridine (22 mmoles) in 200 ml pentane cooled in an ice-salt bath and stirred magnetically. After an additional 2 hr at about 0°, the pentane solution (from which pyridine hydrochloride had precipitated) was washed with water, with two 150-ml portions of 10% sulfuric acid, and finally with two 150-ml portions of 10% aqueous sodium bicarbonate. The organic layer was then dried over magnesium sulfate and passed through a column of 5 g Florisil, followed by 60 ml pentane. The eluent was then evaporated, affording 5.25 g of slightly yellow oil which solidified on addition of a crystal of authentic perester. The crude perester was crystallized from pentane to give a first crop of 4.0 g, mp 40.5-42°; lit. (147) mp 42-42.5°. A second crop, 0.5 g, had mp 41-42.5°; total, 4.5 g (72%).

t-Butyl 5,5-diphenylperpentanoate was material prepared by Howden (148), crystallized from pentane to mp 50-50.5° before use.

Diphenylcyclopropylacetic acid initially kindly supplied by Dr. Adelbert Maercker, was subsequently prepared by carbonation of diphenylcyclopropylcarbinylpotassium as described by Maercker and Roberts (69).

Diphenylcyclopropylacetyl Chloride. - A solution of 8.7 g diphenylcyclopropylacetic acid (3.44 mmoles) in 11 ml thionyl chloride (15 mmoles) and 10 ml benzene was refluxed for a 3 hr period after which the benzene and excess thionyl chloride were removed on the rotatory evaporator (bath temp. ca. 40°). Benzene (ca. 25 ml) was added and similarly stripped, then ca. 25 ml diethyl ether was added and stripped. The residual yellow oil, which solidified on scratching, gave 6.73 g of light yellow crystals upon sublimation. This material was resublimed; 4.9 g of colorless crystals, mp 66-68° (52%).

Crystallization from n-hexane followed by 'sublimation' at 65-70° (0.3 mm)(the material was liquid for most of the procedure) afforded an analytical sample, mp 68-69°.

Anal. Calcd. for $C_{17}H_{15}ClO$: C, 75.41; H, 5.58; Cl, 13.10. Found: C, 75.05; H, 5.73, Cl, 12.93.

The nmr spectrum of a sample in carbon tetrachloride was as expected and appeared to be unchanged after heating at 88° for 13 hr. Integration following the period of heating indicated, with respect to 10 aromatic protons, 0.9 (tertiary cyclopropyl) protons (multiplet, 2.1-2.6δ), 2.0 (secondary cyclopropyl) protons (multiplet, 0.5-1.1δ), and 1.9 (secondary cyclopropyl) protons (multiplet, 0.0-0.5δ). Separation of the secondary cyclopropyl protons into two groups of resonances was also observed for the precursor acid and for the derived *t*-butyl perester (see below). No trace of vinylic protons (which would indicate ring-opened products) could be found. The carbonyl band of a sample in carbon tetrachloride was found at 1785 cm^{-1}.

Sodium *t*-butyl peroxide was prepared essentially as described by Lorand and Bartlett (27) by treatment of sodium hydride (Metal Hydrides, Inc., 55% suspension in mineral oil, 15.9 g, 0.36 mole) with *t*-butyl (Lucidol, passed through a column of molecular sieves and distilled under reduced pressure, 27.6 g, *ca.* 15% excess) in diethyl ether (1.5 l., freshly distilled from lithium aluminum hydride). The crude product, collected by suction filtration and washed with fresh ether, weighed 36.5 g when dry (114% based on the assay of 55% for the sodium hydride suspension claimed by the manufacturer). Titration with standard hydrochloric acid indicated a neutralization equivalent of 111 (theoretical, 112), compared to 131 for the preparation described by Lorand and Bartlett. The product was ground in a morter and partitioned into several vials which were then sealed with wax and maintained at 0° until use in the conversion of diphenylchclopropylacetyl chloride to *t*-butyl diphenylcyclopropylperacetate.

Declining success of perester preparations with the age of the sodium *t*-butyl peroxide suggests that the material not be used if more than a few months old when stored in the powdered state [Lorand and Bartlett suggest that the material is stable for longer periods if stored in cake form; they also suggest that only freshly prepared material be ground (27)].

t-Butyl Diphenylcyclopropylperacetate. - To 1.07 g (3.95 mmoles) diphenylcyclopropylacetyl chloride in 75 ml pentane at -10° was added 0.87 g (100% excess) powdered sodium t-butyl peroxide. The reaction mixture was maintained between -10 and 0° for two hr with magnetic stirring. A sample withdrawn after 1.5 hr displayed a band in the infrared at 1765 cm^{-1} in place of the carbonyl absorbance of the acid chloride at 1785 cm^{-1}, indicating that the reaction had gone to completion. The pentane solution was filtered with suction through Celite in fine sintered-glass funnel, followed by 50 ml ice-cold pentane. The solution was concentrated at 0° to about 3 ml on a rotatory evaporator and pipetted into a small vessel with a nitrogen-inlet arm. The flask was washed with 5 ml pentane and the resulting solution was added to that in the small vessel, upon which some white crystals formed. The small vessel was flushed with nitrogen and cooled in several stages to -20°, whence crystallization seemed to be complete. The pentane solution was then withdrawn under positive nitrogen pressure with a syringe. Fresh pentane was added and the crystals were dissolved by warming on a steam bath for a minimal period; 15 ml pentane were required to effect solution. On cooling to -20° and scratching, the crystals reformed. After 0.5 hr at -30° the pentane solution was again removed under positive nitrogen pressure. The solution which adhered to the crystals was largely removed by maintaining the crystals in vacuo for 1 hr at -10 to 0°. The yield was 0.53 g (38%).

A nmr spectrum was obtained at a probe temperature of about -10° on a portion of the above material (perester batch (1), p. 389) in carbon tetrachloride. Integration (2 sweeps each way) indicated, with respect to 10 aromatic protons, 3.8 secondary cyclopropyl protons in broad resonances much like those for the acid chloride and 9.2 methyl(t-butyl) protons. There was also a singlet at about 2.1δ corresponding to 0.8 protons; this may arise from water introduced during the prior manipulation of the perester at about 0° in the preparation of the reaction tubes for perester batch (1), as described below (p. 389). No trace of olefinic resonances could be seen.

A sample from another preparation melted with effervescence at about 65° when rapidly heated (perhaps 20 to 30° per min).

Analysis of active oxygen in t-butyl diphenylcyclopropylperactate was undertaken to obtain further evidence that the above preparation does yield the perester and to show that the sensibly constant yield of diphenylcyclopropylmethane of 15% for runs collected in Table 2 is not simply attributable to contamination of the perester by the hydrocarbon. The analytical method employed in the determination of active oxygen is that reported by Silbert and Swern (149).

Two samples of freshly prepared perester were analyzed. The first consisted of 76.4 mg perester plus 11.1 mg diphenylcyclopropylmethane in 25 ml glacial acetic acid containing a trace of ferric chloride. To this was added 2 ml of a nearly saturated sodium iodide solution. The mixture was swirled and allowed to stand in the dark for 15 min in a stoppered flask. Titration of the liberated iodine required 9.90 ml of 0.462 N sodium thiosulfate (standardized against primary standard potassium iodate). Starch solution was added to intensify the end point when the original iodine color had begun to fade. A pair of blank titrations required 0.09 and 0.13 ml of the thiosulfate solution. Using the equation given by Silbert and Swern (149), the above quantities correspond to an active oxygen content for the perester sample of 4.73%. That calculated for $C_{21}H_{24}O_3$ is 4.93%. Therefore, the purity of the perester is 96%.

A second perester sample (77.6 mg) required 9.73 - 0.11 = 9.62 ml of the thiosulfate solution, implying an active oxygen content of 4.58% and a purity of 93%. The average, 94.5%, is quite satisfactory.

To each of the titrated samples was added *ca.* 100 ml quantities of pentane and of water. Each of the two-phase systems was shaken and the aqueous phase drained off. Extraction of the organic layer with 5% sodium bicarbonate solution allowed the isolation of nonacidic materials. The pentane was evaporated and known quantities of diphenylmethane were added to the two samples. Analysis by vpc showed that the first sample contained 11.1 mg diphenylcyclopropylmethane, the precise amount originally taken, but that the second contained only 0.7 mg of diphenylcyclopropylmethane, or of some material of closely similar retention time. Therefore, little diphenylcyclopropylmethane could have been present in the initial perester samples. Portions of the same perester preparation were subjected to degassed thermal decomposition at 70° in cyclohexane and 1,4-cyclohexadiene. Product compositions inferred by vpc analysis agreed favorably with those reported for analogous runs in Tables 1 and 9.

4,4-Diphenyl-3-buten-1-ol-1,1-d_2 was prepared by the method of Howden (150). From 35 g of γ,γ-diphenylvinylacetic acid (151) was obtained 22.9 g (70%) of the labeled alcohol.

4,4-Diphenyl-1-1,d_2-butene-1-yl p-toluenesulfonate was prepared from the above alcohol by a modification of the Tipson procedure for ethyl tosylate (152). The following procedure was found to be satisfactory when using unlabeled materials. To a stirred solution of 22.6 g deuterium-labeled alcohol (10 mmoles) in 50 ml pyridine (dried over and then distilled from barium oxide; stored over sodium hydroxide pellets until use) cooled in an ice-salt bath was added over ca. 10 min a solution of 21.0 g tosyl chloride (11 mmoles, freshly crystallized from ligroin) in 38 ml pyridine. The reaction mixture was maintained in the ice-salt bath for an additional 10 min, after which 250 ml of ice-cold 5 N sulfuric acid was added over ca. 5 min. The crude off-white tosylate oiled out and then solidified on scratching; it was collected by suction filtration, washed liberally with water, and air-dried. Crystallization at 0° of the crude material (35 g) from ca. 400 ml of ether-pentane (about 2:1 by volume) afforded a first crop, 19.7 g, mp 83.5-84.5°; lit. (153) mp 84.5-85.5° for (γ,γ-diphenylallyl)-carbinyl p-toluenesulfonate. Concentration of the mother liquor produced a second crop which was recrystallized from ether-pentane; 1.7 g, mp 83-84°. Total, 21.4 g (57%). A nmr spectrum showed that there had been no rearrangement of the deuterium label.

Deuterium-labeled (γ,γ-diphenylallyl)acetonitrile. - The following procedure was found to be satisfactory when using unlabeled materials. The above deuterium-labeled tosylate (21.4 g, 56 mmoles) and 30 g sodium cyanide (0.6 moles) were placed in a 1-l., three-necked, round-bottomed flask fitted with a glass-paddle stirrer and a reflux condenser with a drying tube. Absolute methanol (450 ml) was added and the reaction mixture was warmed to and maintained at reflux for 12 hr. Most of the sodium cyanide dissolved. The reaction mixture was then distilled with stirring under reduced pressure to remove most of the methanol. Water (400 ml) and diethyl ether (400 ml) were then added. The resultant two-phase system was stirred for 20 min and then poured into a separatory funnel. The red-brown aqueous phase was drained off and the etheral layer was washed with 300 ml water, dried (magnesium sulfate), and evaporated. The brown residue (11.5 g) was crystallized from pentane-ether-acetone and then from 60-70° ligroin to give a first crop of 7.2 g, mp 66-67°. A second crop weighed 1.5 g. The total was 8.7 g (65%).

The nitrile was not investigated by nmr, but the acid which resulted from the following preparation was found by nmr to contain 1.4_2 g-atoms of deuterium per molecule. Presumably the deuterium was washed out in the preparation of the nitrile by reversible attack of cyanide anion at the label position to give the α-cyano carbanion.

Deuterium-labeled (γ,γ-Diphenylallyl)acetic Acid. - The following procedure was found to be satisfactory when using unlabeled materials. The above nitrile (8.7 g) was treated with 65 ml of a 1:1:1 mixture by volume of sulfuric acid, glacial acetic acid, and water at reflux for 1.5 hr. When the reaction mixture had cooled to room temperature, it was poured onto *ca.* 600 ml of a mixture of ice and water. The brownish material which solidified was filtered off and taken up in ether. The etheral solution extracted with quantities of 1 N sodium hydroxide until the aqueous layer remained basic. The combined aqueous extracts were then acidified with hydrochloric acid. The product was removed by filtration, washed liberally with water, air-dried, and then crystallized from ligroin; 7.6 g (81%).

A carbon tetrachloride solution of sample recrystallized from hexane was investigated by nmr to determine the extent of deuteration. Ideally, one would also want to confirm the position of the label, but it was not possible to do this by nmr because the spectrum of the unlabeled acid gives only a somewhat broadened doublet (splitting ca. 3.5 Hz) at 2.3 δ for the four methylene protons; and in the α,α-d_2 compound one would expect a doublet spit by ~7 Hz due to interaction with the vinylic proton of the two remaining methylene protons. It was, however, possible to infer from the deuterium distribution in a reaction product from decomposition of the derived t-butyl perester that the deuterium is in the α-position with respect to the carboxyl group (p. 396); i.e., no detectable scrambling of the α- and β-carbons (such as would be expected if formation of the tosylate or its conversion to the nitrile had involved carbonium-ion intermediates) had occurred in the preparation of the acid.

The deuterium content was found to be $1.4_2 \pm 0.09$ g-atoms per molecule by nmr analysis. To obtain this number, the methylene and olefinic absorbance regions were carefully integrated using 5 sweeps upfield and a similar number downfield. A portion of these were carried out on the labeled sample and then a tube containing the unlabeled acid in a closely similar concentration was substituted in the probe for 2 or 3 sweeps. A further number of sweeps was then carried out on the labeled sample, then on the unlabeled sample, and so on until

10 integral traces had been accumulated for each sample. With respect to one vinyl proton in each case, we found 2.55 ± 0.09 methylene protons for the labeled sample and 3.96 ± 0.08 methylene protons for the unlabeled sample. As the latter value should be 4.00, we adjusted the former upward slightly to 2.58 ± 0.09, from which the deuterium content was obtained by difference. Use of the aromatic absorbance as the standard gave an identical mean value. Thus, the extent of deuteration is 71%.

Deuterium-labeled *t*-butyl (γ,γ-diphenylallyl)peracetate was prepared from the above acid in essentially the manner described for the unlabeled material (p. 376). From 3.3 g of the labeled acid we obtained 1.9 g of the perester, mp 41-42° (46%). This material was used in the label-equilibration studies reported below (p. 394 - 399).

Diphenylcyclopropylmethane, 1-phenyl-3,4-dihydronaphthalene, 1-phenyl-1,2,3,4-tetrahydronaphthalene and 1-phenylnaphthalene were samples prepared by Dr. Adelbert Maercker (69).

1,1-Diphenyl-1-butene was prepared by hydrolysis of the Grignard reagent of (γ,γ-diphenylallyl)carbinyl bromide as described by Howden (146).

_t_-Butyl (γ,γ-diphenylallyl)carbinyl ether was prepared by treatment of the Grignard reagent of (γ,γ-diphenylallyl)carbinyl bromide with *t*-butyl perbenzoate (Ram Chemicals, Inc.) according to the general procedure of Lawesson and Yang for conversion of halides to *t*-butyl ethers (154). From 2.0 g of the bromide was obtained 0.6 g of product by distillation (0.2 mm) of the crude material in a small but thermally inefficient distillation apparatus at a bath temperature of

170-180°. The nmr spectrum of a carbon tetrachloride solution was as expected. Bulb-to-bulb distillation at 0.2 mm and a bath temp of 115-120° afforded an analytical sample which was 98% pure by vpc analysis on Ucon polar (three impurities in about equal amounts, one to somewhat longer retention time).

Anal. Calcd. for $C_{20}H_{24}O$: C, 85.67; H, 8.63. Found: C, 85.42; H, 8.66.

Diphenylmethylenecyclopropane was prepared by treatment of 3-bromopropyltriphenylphosphonium bromide (from treatment of 1,3-dibromopropane with triphenylphosphine) with 2 equivalents of phenyllithium in the presence of excess benzophenone (155). A preparation of this material in 80% yield was shortly thereafter reported by Sisido and Utimoto who employed the same route but used sodium hydride plus a catalytic amount of ethanol as base. Our material was heavily contaminated with biphenyl (presumably formed in our preparation of phenyllithium from bromobenzene), and inefficient purification via chromatography on alumina followed by sublimation *in vacuo* afforded a 20-mg sample which was pure to vpc (Ucon polar) and had mp 66-67° [lit. (156) mp 64.5-65.5°] (0.5%). The compositions and weights of the discarded chromatography fractions indicated an overall yield of 20%. A mass spectrum obtained at low ionizing voltage displayed a parent peak at m/e 206, as required. The nmr spectrum of a sample in carbon tetrachloride was as reported by Sisido and Utimoti (156) and integrated correctly.

1,4-Diphenylbutane was prepared by hydrogenation of 1,4-diphenyl-1,3-butadiene (Aldrich) using standard procedures (157).

The crude yellow oil which was isolated solidified on scratching. The product was crystallized from pentane and had mp 53-55°; lit. (158) mp 51-52°. The nmr spectrum of a sample in carbon tetrachloride solution was as expected. No olefinic protons could be found.

Triethyltin (γ,γ-Diphenylallyl)acetate. - (γ,γ-Diphenylallyl)-acetic acid (1.0 g, 4.0 mmoles) was placed in a thick-walled glass tube, 1 ml triethyltin hydride (6.1 mmoles) and ca. 5 ml n-octane were added, and the tube was sealed. On warming to effect solution of the carboxylic acid, it appeared that the reaction had begun and that the tin ester had started to crystallize from solution. The tube was heated at 135° for one hour and opened after it had cooled to room temperature. The tin ester was collected by filtration in a sintered glass funnel, through which a few ml of tetrahydrofuran was then passed, upon which the ester, but apparently not tin oxides which had also been formed, dissolved. The clear tetrahydrofuran solution was evaporated and the white residue was taken up in and crystallized from n-hexane; 615 mg (34%), mp 121.5-123°. The relatively low yield probably represents inefficient isolation.

The nmr spectrum of a carbon tetrachloride solution indicated, with respect to 10 aromatic protons, 4.0 methylene protons in a doublet (as in the acid) at 2.4 δ, 14.5 ethyl protons in a broadened singlet at 1.2 δ, and the expected vinylic resonance at 6.0 δ (not accurately integrable because of its low intensity). An infrared spectrum in carbon tetrachloride displayed a carbonyl band at 1651 cm^{-1}.

Crystallization from n-hexane afforded an analytical sample of mp 123-124°.

Anal. Calcd. for $C_{23}H_{30}SnO_2$: C, 60.42; H, 6.61, Sn, 25.96. Found: C, 60.47; H, 6.79; Sn, 25.81.

3. Procedures

Degassed Thermal Decompositions of Peresters. - Product studies reported in Tables 1 through 11 were carried out on small quantities of perester, usually 15-30 mg. Generally, a quantity of perester was weighed into a reaction tube fashioned from 8-mm heavy-walled glass tubing and a measured volume (0.5-2 ml) of the solvent or of a solution of two solvents combined in known weights was added. In some cases, particularly for series of runs investigating variable or low perester concentrations (Tables 4, 5, 6) and for runs in Table 11, stock solutions of perester (in n-octane or benzene for runs in Table 11) were made up and aliquots were transferred by syringe to reaction tubes or were diluted to prepare solutions of low perester concentration.

Runs with t-butyl (γ,γ-diphenylallyl)peracetate or t-butyl 5,5-diphenylperpentanoate employed samples freshly recrystallized from pentane to mp 42-43° and mp 50-50.5°, respectively. t-Butyl diphenylcyclopropylperacetate was always freshly prepared material. It was necessary to maintain the latter perester in a stoppered flask at 0° while not actually manipulating the material. On the one occasion on which the perester was handled at room temperature, after about 5 to 10 minutes at room temperature the perester sample instantaneously liquified and decomposed sufficiently rapidly to blow most of the material out of the container. A qualitative examination by vpc of the droplets left on the walls of the container indicated that the usual hydrocarbon products were not formed. It is quite possible that this behavior is not characteristic of the pure perester, for there was always the possibility of contamination by the precursor acid chloride.

One likely result of repeatedly opening a cold flask is concensation of moisture on the contents. The effect on the product composition observed upon thermal decomposition is not known, but it is possible that traces of water and of diphenylcyclopropylacetyl chloride in some samples may have produced hydrochloric acid in sufficient amounts to catalyse the decomposition of the expected cage combination product, diphenylcyclopropylcarbinyl *t*-butyl ether (**15**). We commented previously on the apparent absence of this material in certain runs (p. 78, 79). The following groups of runs were made on common perester preparations: (1) - the runs of Table 2 and those in diethyl ether and cyclohexane at 0.05 M perester in Table 9; (2) - the benzene run at 0.2 M perester and the tetraethyltin run of Table 9, and the runs at 35° in Table 11; (3) - the indene runs in Table 7 and the 'large-scale' decomposition described below wherein diphenylcyclopropylcarbinol was isolated (p. 391); (4) - the runs of Table 6; (5) - the runs at 10° in Table 11. The few other runs reported in the data tables were carried out on separate perester sample.

Reported hydrogen-donor concentrations in all cases and initial perester concentrations for runs in Tables 1, 2, 4, 5, and 6 assume no volume change on mixing and a thermal expansion of 12% per 100°C temperature rise over the room temperature preparation for perester solutions. It was found that 1,4-cyclohexadiene undergoes a volume expansion of 15% when heated in a sealed tube from ca. 25 to 152°; this amounts to 12% per 100°, assuming that the expansion is linear in the temperature (159). Literature values per 100° temperature rise, again assuming linearity, are 12.1% for benzene, 12.0% for cyclohexane, and 11.5% for n-octane (160).

Reaction tubes were degassed using three freeze-pump-thaw cycles and sealed under vacuum. Two procedures were used. In the first, the degassing was carried out at 0.1 to 0.5 mm using a Dry Ice-acetone mixture as coolant. These runs include those of Tables 1, 2, and 3, rows 1 and 2 of Table 7, all but the bottom row of Table 8, and the runs in cyclohexane and diethyl ether in Table 9. In all other cases, degassing was effected at 10^{-4} to 10^{-3} mm using liquid nitrogen.

The sealed reaction tubes were generally immersed in a bath containing an organic solvent of appropriate boiling point at reflux. A constant temperature bath was employed for runs at 10° in Table 11, and an ice-water bath, for runs at 0° in Tables 2 and 9. The following reaction times are typical: for t-butyl diphenylcyclopropylperacetate -- 10 days at 0°, 5 days at 10°, two days at 35°, 12 hr at 70°; for t-butyl (γ,γ-diphenylallyl)peracetate -- 100 hr at 99°, 10 hr at 131°, 2 hr at 152°; for t-butyl 5,5-diphenylperpentanoate -- 140 hr at 100°, 2 hr at 152°.

The general procedure for vpc analysis of reaction mixtures has been previously reported (p. 45).

Special care was taken in runs employing triethyltin hydride as hydrogen donor to minimize contact with air of perester solutions containing the hydride or the hydride itself. Freshly prepared tin hydride was used in the run at 1.89 M hydride in Table 10. In all other cases, hydride which had been stored in vacuo in one chamber of a two-chambered apparatus was freshly distilled to the free chamber, as previously noted (p. 374), immediately before use. For runs reported in Table 11 and at 0.01 M hydride in Table 10, the reactions were thermselves carried out in two-chamber vessels, the tin hydride being placed in one chamber, and distilled to that containing the perester after degassing had been effected. In the other cases, the tin hydride was the last of the ingredients to be placed in the reaction tube and the tube was immediately cooled in Dry Ice-acetone and degassed. In the sets of runs in Table 10 at variable hydride concentrations, the reaction mixtures at the higher hydride concentrations had become quite noticeably cloudy before degassing had been effected. At the end of the reaction period, the major portion of the solvent was distilled to the second chamber by cooling in liquid nitrogen. In the other cases, the freshly opened reaction mixtures were distilled through a short Vigreaux column under aspirator pressure using a bath temperature of 60 to 65° until the volume (initially about 25 ml) had been reduced to 0.5 to 1 ml. A quantity of n-octane (ca. 25 ml) was now added and the distillation of the solvent was repeated. The concentrated reaction mixtures, essentially hydride-free, were then analyzed by vpc using standard procedures.

Isolation of diphenylcyclopropylcarbinol as a secondary reaction product provided evidence for the formation of t-butyl diphenylcyclopropylcarbinyl ether as a primary reaction product in the decomposition of *t*-butyl diphenylcyclopropylperacetate. A sample of this perester (1.6 g from batch (3), p. 389) was subjected to degassed thermal decomposition at 70° in 1.7 M 1,4-cyclohexadiene in cyclohexane. The perester concentration at 70° was initially about 0.086 M. An aliquot of the resulting reaction mixture was analyzed using a weighed amount of diphenylmethane as internal standard. We found (one trace) the following yields for the usual reaction products: 1,1-diphenyl-1-butene, 14%; diphenylcyclopropylmethane, 18%, **B**, 28%, 1-phenyl-3,4-tetrahydronaphthalene, 10%. **B**, it will be recalled, is thought to consist of three reaction products: the above-mentioned *t*-butyl ether; diphenylmethylenecyclopropane, and (isomeric) 1-phenyltetrahydronaphthalenes (p. 71-80). The yield of 28% compares favorably with yields of about 30% for thermal decompositions at 2.7 and 4.9 M 1,4-cyclohexadiene in cyclohexane (Table 2).

The oily residue obtained upon evaporation of the solvent was chromatographed on a column of 75 g Florisil (60-100 mesh) prepared in pentane. Forty 10-ml fractions and ten 20-ml fractions were taken using pentane as eluent, followed by groups of five 20-ml fractions using 2, 5, 10, 20, and 50% diethyl ether in pentane (v/v). Finally, five 20-ml fractions (fractions 76-80) using ether were taken followed by groups of five fractions using 5, 15, 30, and 75% methanol in ether. Visual inspection and analysis of several fractions by vpc (Ucon polar) showed that the hydrocarbon products were concentrated between fractions 20 and 36. Vpc traces of fractions 24, 25, 26, 28, 30, 32, and 34 revealed that some separation of components had occurred, diphenylbutene being concentrated in the early fractions and diphenylcyclopropylmethane, in the later ones. On the other hand, the product **B** and 1-phenyl-3, 4-dihydronaphthalene were rather evenly distributed throughout the series. The ratio of these was also rather constant; 1.2 ± 0.2 for the middle fractions. From this we can state that of the original 28% of **B**, only 10 × 1.2 ≅ 12% is eluted with the hydrocarbon products. Either the rest is appreciably more polar material or is destroyed on the column.

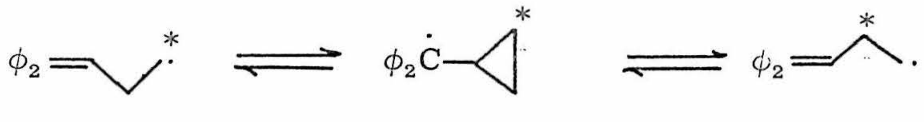
Evidence that the latter alternative is correct was provided by the contents of subsequent fractions. Fractions 70 to 80 (50 and 100% ether) contained appreciable amounts of material. The nmr spectrum of fraction 75 in carbon tetrachloride solution was most revealing. Clearly visible were the highly distinctive resonances of diphenylcyclopropylcarbinol -- a high field doublet due to secondary cyclopropyl protons, split by 6.9 Hz compared to 6.7 for a carbon tetrachloride solution of the authentic material (Aldrich); the singlet hydroxyl resonance at about 1.8 δ; the downfield half of the perturbed quartet due to the tertiary cyclopropyl proton (broad resonances between 0.7 and 2.4 δ obscured the upfield half); and the highly complex aromatic resonances. The vpc trace of the carbon tetrachloride solution of fraction 75 showed a single peak at a retention time of 4.55 min; that of the authentic material in carbon tetrachloride was found to also be 4.55 min.

Fractions 72-79 were combined with a known weight of 1-phenylnaphthalene (retention time about 3.5 min) and analyzed by vpc. The relative peak areas when corrected for the relative sensitivities of the two materials, determined concomitantly for the authentic materials, showed that the combined fractions contained 122 mg of the carbinol, or 11% based on the weight of perester taken.

A lesser amount of material was also concentrated around fraction 66. The nmr spectrum of that fraction in carbon tetrachloride displayed absorbances of the correct shapes and resonance positions for the several types of protons of the ring-opened ether, *t*-butyl (γ,γ-diphenylallyl)carbinyl ether. There was no detectable amount of the analogous ring-opened alcohol in fraction 66. The yield of the ring-opened ether was perhaps 3%, but it is not known whether this material is a primary reaction product or whether it is formed, like the ring-closed carbinol, from the ring-closed ether, either during the thermal decomposition or on the chromatographic column.

Our interpretation of the above observations and the results of other 'large-scale' decompositions (p. 72, 76) is that diphenylcyclopropylcarbinyl *t*-butyl ether is one of the components of **B**.

Thermal decomposition of deuterium-labeled *t*-butyl (γ,γ-diphenylallyl)peracetate was undertaken in cyclohexane and in the presence of triethyltin hydride to determine whether the two methylene groups in a radical intermediate such as ring-opened **3** could be interconverted via a symmetrical species such as ring-closed **4**. In each



3-α labeled labeled **4** 3-β labeled

case, the experimental procedure was first shown to allow the numbers of relevant hydrogen atoms in the main reaction product to be correctly inferred for decomposition of the unlabeled perester.

Unlabeled Perester in Cyclohexane: One gram of t-butyl (γ,γ-diphenylallyl)peracetate in 55 ml cyclohexane was degassed to 0.2 mm using two freeze-pump-thaw cycles and sealed into a reaction tube (150 ml capacity). The reaction tube was immersed in a bath of refluxing n-octane (bp 125°) for 12 hr. The reaction tube was opened at room temperature, the solvent was distilled, and the residue was chromatographed on Florisil (75 g, 60-100 mesh). Fifty 10-ml fractions were taken using pentane as eluent. Fractions 14-25 were combined and twice distilled bulb to bulb at ca. 0.2 mm (bath temperature ca. 95°). An nmr spectrum of the final distillate was obtained in carbon tetrachloride solution in an A-60 micro cell. The resolution was quite decent. Careful integration gave intensities of 30.9±0.8 for the protons at the 4-position (2.35-2.85 δ) and 35.5±1 for those at the 3-position (1.80-2.35 δ) of 1-phenyl-3,4-tetrahydronaphthalene. When corrected for the methylene protons in 1,1-diphenylbutene, the latter figure becomes 33±1.5, so that the proton populations at the two positions are the same within experimental error.

Deuterium-Labeled Perester in Cyclohexane: One gram of t-butyl (γ,γ-diphenylallyl)peracetate specifically labeled with 1.4_2 g-atoms deuterium in the α-position (p. 385) was subjected to the above treatment. The chromatographic fractions 14-25 were again combined and twice distilled. The composition of the distillate as inferred by vpc was 86% '1-phenyl-3,4-dihydronaphthalene', 3% 'diphenylbutene', 6% '1-phenylnaphthalene', and 5% $\underset{\frown}{B}$ [probably labeled tetrahydronaphthalenes (p. 77 , 78)]. Integrated intensities in appropriate resonance regions were corrected for contributions from 'diphenylbutene' and '1-phenylnaphthalene', but not for the 'tetrahydronaphthalenes', whose spectra are not known. Proton populations were calculated assuming 9 aromatic protons in the 'dihydronaphthalene'. The resultant inferences regarding the distribution of deuterium have been given in Fig. 7a, p. 95 .

The present procedure differed from that for the unlabeled perester in that the column chromatography was continued in order to isolate the labeled ring-opened ether 12. Subsequent to the fifty 10-ml fractions, we obtained four 50-ml fractions and then, using 5% diethyl ether in pentane as eluent, six 50-ml fractions. The second of the final six fractions contained most of the product which after distillation in a microapparatus was found by vpc to be 98.5% ring-opened ether. Analysis by nmr gave the following proton populations based on 10 aromatic protons: vinylic, 1.01 ± 0.04, allylic, 1.90 ± 0.04; α to the oxygen function, 0.56 ± 0.04; methyl (in the t-butyl group), 9.23 ± 0.25. This result demonstrates that the perester was originally deuterated in the α-position with respect to the carbonyl function.

Unlabeled Perester in the Presence of Triethyltin Hydride: Details will be given only for the closely similar procedure employed with the labeled perester. The major hydrocarbon reaction product for decomposition in ca. 1 M triethyltin hydride is 1,1-diphenyl-1-butene (Table 10). The ratio of methyl to methylene protons in the recovered diphenylbutene was found by nmr to be 1.55:1.00, in good agreement with the actual 1.5:1.

Labeled Perester in the Presence of Triethyltin Hydride: The reaction was carried out in an apparatus which had two chambers connected by an open tube and connectable by a second route via a break-seal. The deuterium-labeled perester (943 mg) in 10 ml n-octane was placed in one of the chambers. Triethyltin hydride, presently stored in one chamber of a similar two-chambered apparatus, was distilled into the fresh chamber by cooling it in liquid nitrogen while warming the other. n-Octane (5 ml) and 5.4 g of the freshly distilled triethyltin hydride were placed in the second chamber of the reaction vessel. The two halves were jointly degassed to 0.2 mm using three freeze-pump-thaw cycles and the apparatus was sealed off. By this time, the side containing the tin hydride had become cloudy, presumably due to the well-known air oxidation of organotin hydrides (41). Cooling the side containing the perester while warming the other slightly effected the distillation of tin hydride and n-octane into the perester side. A swirling motion was necessary to contain bumping. The tube connecting the two chambers was now sealed off in a gas-oxygen flame. The apparatus was then immersed in a bath of refluxing n-octane for a period of 13 hr.

When the vessel was at room temperature, the reaction-mixture side was opened and 0.5 ml of reaction mixture was transferred to a vial containing a known quantity of 1-phenylnaphthalene. A product analysis was subsequently undertaken by vpc; the results appear in row 11 of Table 10. The reaction vessel was cooled in Dry Ice-acetone, pumped down to 0.2 mm, and again sealed off. The two chambers were now rejoined by breaking the break-seal. The solvent was transferred to the other side by cooling it in liquid nitrogen (boiling point - vapor pressure tables indicate that the C_{16} hydrocarbons of interest should boil at 80 -- 100° at 0.2 mm). A white solid remained. It was twice extracted with 25 ml quantities of boiling pentane. The pentane extracts were filtered and concentrated to a volume of ca. 5 ml, upon which some white solid came out of solution. The whole was poured onto a column of 75 g Florisil prepared in pentane. Thirty 10-ml fractions were taken with pentane as eluent. Those containing the bulk of the hydrocarbon reaction products were combined and distilled bulb to bulb as in the work up of the runs reported above for decomposition in cyclohexane. A nmr spectrum of the distillate in carbon tetrachloride was obtained in an A-60 micro tube. No absorbances other than those expected for the labeled 1,1-diphenyl-1-butene were readily apparent. A careful integration was carried out using five upfield and five downfield sweeps. Integrals for appropriate regions were averaged and corrected for 1.2% of labeled 1-phenyl-3,4-dihydronaphthalene shown to be present by vpc analysis. Proton populations calculated assuming 10 aromatic protons were used directly to compile Fig. 7b, p. 95 .

Interestingly, in both this and the run using unlabeled perester, only traces of diphenylcyclopropylmethane could be found in the fractions from the column chromatography, although the vpc product study on this run (Table 10, row 11) indicated diphenylbutene and diphenylcyclopropylmethane in a ratio of ~11:1. Analysis of the nmr sample indicated only 0.3% of the latter, or a ratio of ~300:1. However, Howden had previously shown diphenylcyclopropylmethane to be a legitimate reaction product for decomposition of the (unlabeled) perester in tri-n-butyltin hydride (by obtaining by preparative gas-phase chromatography a fraction enriched in this material whose nmr spectrum displayed absorbances characteristic of diphenylcyclopropylmethane), so apparently the material is destroyed under the chromatographic conditions.

Air-Induced Decomposition of t-Butyl (γ,γ-Diphenylallyl)-peracetate in the Presence of Triethyltin Hydride. - A n-octane solution 0.08 M in perester and 1 M in triethyltin hydride was made up to determine the feasibility of investigating the kinetics of perester decompositions in triethyltin hydride by monitoring the carbonyl absorbance of the perester at ~1780 cm^{-1} in the presence of the strong, broad Sn-H streaching band of triethyltin hydride at 1813 cm^{-1}. An infrared spectrum obtained on the Perkin-Elmer Infracord Model 237 approximately 10 min after the preparation of the above solution displayed a barely distinct carbonyl absorbance on one slope of the large tin hydride band. The spectrum was measured again 3 hr later under supposedly superior resolution on the Beckman IR-7, but now the carbonyl band was merely a shoulder on the tin hydride band. At 6 hr after preparation of the solution, the spectrum was again obtained on the Infracord; no trace of the carbonyl band could now be discerned. We now, however, noted that a band had appeared at approximately 1650 cm^{-1}, the position previously observed for the carbonyl band in triethyltin (γ,γ-diphenylallyl)peracetate. Rough absorbance measurements indicated a yield of tin ester of about 90% for the 6-hr spectrum.

The reaction mixture was subsequently cooled in an ice bath, upon which white tufts appeared. These were collected by filtration and crystallized from n-hexane to afford triethyltin (γ,γ-diphenylallyl)peracetate (mp 121-123°, melting point on admixture with authentic material undepressed) in 40% yield. The white solid gave infrared and nmr spectra which were in agreement with those of the authentic material.

Subsequent measurements on the rates of the air-induced process were made incidentally to the kinetic determinations of the degassed thermal decompositions discussed below on portions of prepared solutions not required for those determinations. The cosolvent in each case was n-octane. Concentrations differ slightly from those quoted in the legends to Figs. 15 - 18 and in Table 15, since in the latter cases an approximate correction for thermal expansion has been employed.

The reaction mixture for Fig. 18 (0.02 M in perester and 0.72 M in triethyltin hybride) developed the tin ester in 63% yield upon exposure to the air for 4 hrs (as indicated by absorbance measurements at 1651 cm^{-1}). In contrast, one of the degassed samples opened after 3 hr at room temperature gave an apparent yield of tin ester of 5%; but at this point we experienced difficulties in the reproducibility of the base line, so there may actually have been no formation of tin ester.

The reaction mixture of Fig. 17 (1.85×10^{-3} M in perester, 0.44 M in tin hydride) developed the tin ester in yields of 75%, 93%, and 90% after 12, 18, and 36 hr of exposure to the atmosphere at room temperature.

The reaction mixture of Fig. 16 (1.90×10^{-3} M in perester, 0.048 M in tin hydride) indicated yields of 6, 9, and 90% when portions were analyzed after 14, 20, and 74 hr at room temperature.

The reaction mixture of Fig. 15 (2.2×10^{-3} M in perester, 0.0107 M in tin hydride) was maintained in a stoppered flask, after preparation in air, for 5 days. At that time a yield of tin ester of 21% was indicated. After one more day with the flask stoppered, the yield was 30%. The stopper was then left off for one day, after which the yield of tin ester was found to be 92%, and then for a second day, when the yield was 91%.

Several difficulties, such as evaporation of the n-octane and decomposition of the tin hydride (as indicated by deposition of a white solid) over prolonged periods and nonstandard conditions for equilibration of oxygen between the air and the organic solution, make the above observations only semiquantitative. However, it appears that the process is air-induced, that reaction between the air and the tin hydride at least in part generates free radicals, and there is an inhibition period, perhaps representing the consumption of inhibitors or the build up of intermediates involved in the air oxidation. The yields of tin ester may generally be in the range of 85-95%. We argued in subsection 9 (p. 187 , 188) that this indicated that attack of triethyltin hydride on the perester —O—O— bond to give the tin ester was a lower activation energy process that for the alternative attack (see Chart 6, p. 162) to give the tin ether.

Kinetics of Induced Decomposition of t-Butyl (γ,γ-Diphenylallyl)-peracetate in Triethyltin Hydride: The frequency of the infrared transmission minimum for the carbonyl group of triethyltin (γ,γ-diphenylallyl)acetate was determined to be 1651 cm^{-1} by monitoring the transmittance of an 0.01 M solution of the tin ester in n-octane at intervals of 0.5 cm^{-1} over the frequency range 1645-1655 cm^{-1} using the 90-100% transmittance range on a Beckman IR-7. A series of four solutions (0.002, 0.004, 0.006, and 0.010 M) prepared by dilution obeyed Beer's Law when the reference solution was n-octane and when it was 0.2 M triethyltin hydride in n-octane. The average deviation of the absorbance from a visual straight line was 2% in the former case and 6% in the latter. The absorbance readings were obtained, as in the kinetic run for 0.67 M tin hydride and 0.02 M perester discussed below, with reference to an initially set absorbance zero for reference solution in both cells. However, concern was latter encountered with regard to (a) the stability of the instrument over long periods and (b) the reproducibility of the base line as judged by simply removing and then immediately reinserting a cell in the holder. Therefore, in the three kinetic runs at 0.002 M perester, absorbance readings were obtained by recording the 'absorbance' for reference against reference (no attempt being made to adjust the instrument to read identically zero absorbance), of solution against reference, and finally of reference against reference again. The absorbance of the solution was obtained as that the intermediate measurement less the average of the two reference -- reference measurements. A Beer's Law plot for solutions which were 0.0002, 0.0004, 0.0006, 0.0008, and 0.0010 M in tin ester, obtained concomitantly with the kinetic measurements for 0.002 M perester in 0.0097 M tin hydride in n-octane, gave an average deviation of 8% from a visual straight line. We feel that this value represents essentially the reproducibility of the instrument in our difficult observational situation: 1 mm path length, 90-100% transmittance range, slit = 1.5 mm, gain = 3% for the runs at 0.002 M initial perester concentration. Deviations of about this magnitude from optimum first-order lines may be seen in Figs. 15 - 18, pp. 157, 158. For the three runs at 0.044, 0.41, and 0.67 M tin hydride, the absorbance of either 0.01 or 0.001 M tin ester in n-octane was used to relate the limiting absorbancies (A_∞ in eq. 1.9-3) to concentrations, and hence yields, of tin ester arising via induced decomposition of the perester. Yields calculated in this way are shown in Figs. 15 - 18.

Reaction tubes for the kinetic runs were fashioned from lengths of 8 mm pyrex tubing which had been soaked in cleaning solution for one day or more, flushed thoroughly with tap water, scrubbed with Labtone, rinsed well with distilled water and then with acetone, and finally dried at 135° for several hours. For the run displayed in Fig. 17, 14.6 mg of t-butyl (γ,γ-diphenylallyl)peracetate (mp 42.5-43.5°) was weighed into a flask. Into a second flask was weighed 20.92 g of n-octane. Triethyltin hydride stored in a two-chamber evacuated apparatus was freshly distilled as noted under the preparation of the tin hydride. The collection chamber was broken off and 2.947 g triethyltin hydride was weighed into a third flask. The n-octane was now poured onto the tin hydride and the solution was poured between the two flasks a few times to effect mixing. A portion found to weigh 18.53 g was poured onto the perester. The remaining solution was saved to serve as reference solution in the infrared analyses. The flask containing the perester was swirled to dissolve the perester and 1 ml aliquots were transferred by syringe to each of ten reaction tubes which had been constricted at the top for easy sealing. The tubes were quickly attached to a vacuum system by lengths of Tygon tubing, cooled in liquid nitrogen, and degassed to 3×10^{-4} mm using three freeze-pump-thaw cycles. They were then maintained at -80° in Dry Ice-acetone until used (within 48 hr).

Initial concentrations [obtained from the weights recorded above using a specific gravity for triethyltin hydride of 1.25 (our measurement) and for n-octane of 0.704 (91) and assuming no volume change on mixing] were 0.442 M for triethyltin hydride and 1.85×10^{-3} M for the perester. Assuming a standard volume expansion of 12% per 100° temperature rise (p. 390), the concentrations at 110°, the temperature of the thermal decompositions, are 0.41 M and 1.70×10^{-3} M.

The kinetic runs employed a bath of refluxing toluene in a 5-ℓ. flask with a 6 in. diameter opening. The ten reaction tubes were secured by copper wires and lowered en masse into the bath. After a 15, 20, or 30 sec warm-up period, the timer was started and (with the exception of the run of Fig. 15) a first tube was simultaneously pulled and quenched in Dry Ice-acetone. Subsequent tubes were similarly quenched and held at -80° until infrared analysis was undertaken at 1651 cm^{-1}. The procedure for the infrared analysis was given above. At the appropriate time, a tube was warmed to room temperature, shaken to ensure that no separation of components had occurred, and broken at a file mark. The 1-ml quantities of reaction solution usually allowed duplicate analyses for runs of Figs. 15, 16, and 17. The initial concentrations of tin hydride and of perester at 110° (assuming the 12% volume expansion per 100° temperature rise) and the absorbance readings follow [given as reaction time in min, absorbance, absorbance]:

Fig. 15, 0.0097 M, 2.0×10^{-3} M: 10, 0.0062, 0.0059; 25, 0.0094, 0.0101; 40, 0.0128, 0.0130; 60, 0.0187, 0.0208; 80, 0.0245, 0.0264; 130, 0.0326, 0.0364; 180, 0.0362, 0.0364; 310, 0.0373, 0.0385; 550, 0.0370, 0.0376.

Fig. 16, 0.0444 M, 1.75×10^{-3} M: 0, 0.0016, 0.0021; 6, 0.0035, 0.0043; 12, 0.0060, 0.0073; 20, 0.0079, 0.0084; 30, 0.0114, 0.0120; 45, 0.0168, 0.0195; 60, 0.0197, 0.0204; 90, 0.0245, 0.0270; 150, 0.0286, 0.0303; 240, 0.0319, 0.0316.

Fig. 17, 0.41 M, 1.70×10^{-3} M: 0, 0.0230, 0.0217; 2.0, 0.0582, 0.0670; 4.0, 0.0115, 0.0136; 6.0, 0.0129, 0.0173; 9.0, 0.0181, 0.0196; 12, 0.0211, 0.0217; 18, 0.0196, 0.0200; 25, 0.0238, 0.0241; 45, 0.0258; 75, 0.0251, 0.0287.

Fig. 18, 0.67 M, 0.018 M: 0, 0.0023; 3.0, 0.0112; 6.1, 0.0176; 8.0, 0.0217; 12.0, 0.0282; 20, 0.0323; 32, 0.0322; 112, 0.0313.

The absorbance readings listed for Fig. 15 are uniformly lower than those directly measured by 0.0015; the reference solution in that case was n-octane, rather that 0.1 M triethyltin hydride in n-octane, and the tin hydride does absorb slightly at 1651 cm^{-1}.

The absorbance-time data was fitted in each case to eq. 1.9-3, p. 159,

$$A(t) = A_\infty - (A_\infty - A_0) \exp(-k_T t)$$

using the generalized least-squares formalism of Section Two, subsection 2. A_∞, A_0, and k_T were treated as adjustable parameters. The following results were obtained: Fig. 15 -- $A_\infty = 0.0387 \pm 0.0008$, $A_0 = -0.0006 \pm 0.0012$, k_T (min^{-1}) = 0.0130 ± 0.0010, RUSD (relative unbiased standard deviation, given by the square root of the sum of the squares of the deviations between observed and calculated absorbance readings divided by the number of absorbance readings fitted less one) = 0.0015; Fig. 16 -- $A_\infty = 0.03314 \pm 0.0008$, $A_0 = 0.0012 \pm 0.0053$, k_T(min^{-1}) = 0.0150 ± 0.0011, RUSD = 0.0011; Fig. 17 -- $A_\infty = 0.0254 \pm 0.0009$, $A_0 = 0.0023 \pm 0.0012$, k_T(min^{-1}) = 0.128 ± 0.017, RUSD = 0.0018; Fig. 18 -- $A_\infty = 0.0327 \pm 0.0009$, $A_0 = 0.0011 \pm 0.0017$, k_T(min^{-1}) = 0.138 ± 0.015, RUSD = 0.0013 .

In forming the weighing factors L after the fashion of eq. 2.2-14, p. 214, we have assumed a standard error of 0.3 min in each of the quoted reaction times; this quantity principally represents the uncertainty in the effective warm-up periods. In addition, we have equated the standard error in the absorbance readings to the value of RUSD from the previous iteration.

The curved lines in Figs. 15 - 18 were drawn up using the least-squares estimates given above. To prevent overcrowding, duplicate infrared analyses were averaged for plotting. The reader will note that A_0 is usually slightly positive. The apparently finite initial absorbance appears to be due to the perester itself; an 0.02 M solution in *n*-octane gave an absorbance of 0.01 in the 1 mm cells at 1651 cm^{-1}.

Translation of the A_∞ into yields of the tin ester suffers from uncertainties in the A_∞, in the preparation of and absorbance measurements on standard solutions, and in the determination of the initial quantity of perester taken, always approximately 15 mg. The yields quoted in Figs. 15 - 18 are probably good to not better 10-15% (relative).

According to the mechanistic scheme of subsection 9 to Section One, the concentration of triethyltin hydride consumed in the induced decompositions should be 1-2 times the initial perester concentration. This was checked in the case of the run displayed in Fig. 15, where the ratio of initial concentrations of triethyltin hydride (0.0107 M, at room temperature) and perester (2.2×10^{-3} M at room temperature) was smallest. We found the tin hydride concentration in the tube opened at 550 min to be 0.0088 M, or 1.9×10^{-3} M less than the initial concentration. This gives at least partial assurance against the general incursion of additional mechanistic steps which might result in wholesale decomposition of the triethyltin hydride.

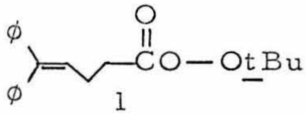
Kinetics of Thermal Decomposition of t-Butyl Diphenylcyclopropylperacetate in Cumene. - A solution of *ca.* 0.1 M perester in cumene was allowed to stand exposed to the air at 73° F (23°C) in a thermostated room. Disappearance of the perester was monitored by recording the infrated spectra of aliquots between 1850 and 1700 cm^{-1} on the Perkin-Elmer Infracord Model 237. This was done at an arbitrary time zero (about 5 min after preparation of the solution), 20, 40, and 270 min later, and after 18 hr. The absorbance readings at the carbonyl maximum of the perester were measured with respect to a valley at 1790 cm^{-1} which appeared between the carbonyl band and a small peak at 1800 cm^{-1} (which itself appeared to be constant throughout the run). The absorbance readings were, in order of increasing time, 0.475, 0.440, 0.377, 0.084, and 0.024. The latter value was taken to be the infinity absorbance, A_∞, in the equation shown below. The data were fitted to the equation

$$A(t) - A_\infty = (A_0 - A_\infty) \exp(-k_0 t)$$

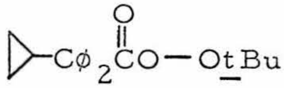
according to the least-squares formalism described in Section Two, subsection 2, where A_0 and k_0 were treated as adjustable parameters. The results have been discussed (pp. 236-240).

Viscosities of several liquids and binary mixtures were determined at 20° using a modified Ostwald viscometer (cleaned in cleaning solution) in conjunction with a constant temperature bath. Flow times for 10-ml quantities of cyclohexane (η = 0.960 cp) and benzene (η = 0.648 cp) were employed to determine the cell constants (161). In general, ten measurements of the flow time were made on each solution. Times were reproducable to three or four parts per thousand. The viscosity of freshly distilled 1,4-cyclohexadiene was found to be 0.595 cp. For mixtures of 1,4-cyclohexadiene and cyclohexane in the proportions (v/v) of 1:7, 1:3, and 1:1, viscosities of 0.845, 0.778, and 0.679 cp, respectively, were found. Freshly distilled indene of the same grade as that used in the perester decompositions (p. 372) gave a flow time corresponding to a viscosity of 1.76 cp. Viscosities of 0.28 and 0.50 cp were found for diethyl ether and tetrahydrofuran. The literature value for the former is 0.233 at 20° (162); the poor agreement suggests that inferred viscosities which lie outside the range of viscosities of the standard materials (benzene and cyclohexane) may deviate systematically from the true viscosities. The viscosity of tetraethyltin was found to be 0.63 cp.

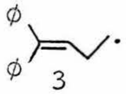
STRUCTURES AND NUMBERS OF COMPOUNDS



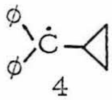
1



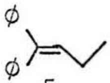
2



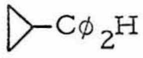
3



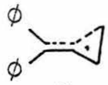
4



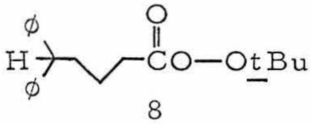
5



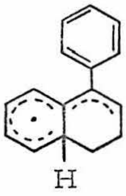
6



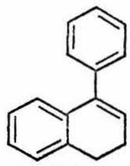
7



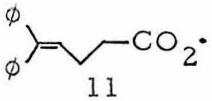
8



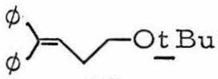
9



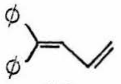
10



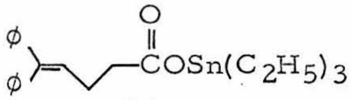
11



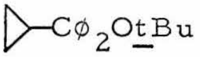
12



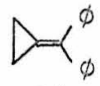
13



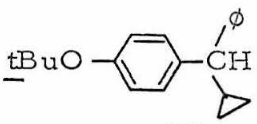
14



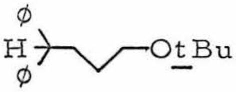
15



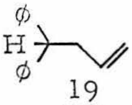
16



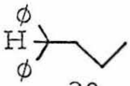
17



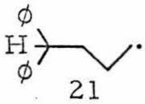
18



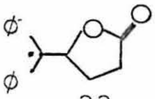
19



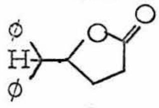
20



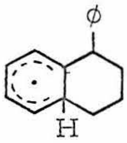
21



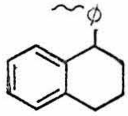
22



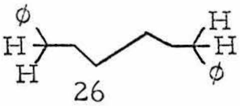
23



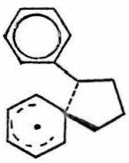
24



25



26



27

28

REFERENCES

1. L. K. Montgomery and J. W. Matt, *J. Am. Chem. Soc.*, **89**, 923 (1967).

2. A. J. Rosen, Ph.D. Thesis, California Institute of Technology, Pasadena, Calif., 1964.

3. D. I. Schuster, Ph.D. Thesis, California Institute of Technology, Pasadena, Calif., 1961.

4. W. A. Pryor, "Free Radicals," McGraw Hill Book Company, New York, N.Y., 1966.

5. C. Walling in "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, New York, N.Y., 1963.

6. R. Freidlina in "Advances in Free Radical Chemistry," Vol. 1, G. H. Williams, Ed., Academic Press, Inc., London, 1965.

7. C. Rüchardt, *Fortschr. chem. Forsch.*, Vol. 6, 251 (1966).

8. P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N.Y., 1965.

9. (a) P. I. Abell and L. H. Piette, *J. Am. Chem. Soc.*, **84**, 916 (1962); (b) P. S. Skell, D. L. Tuleen, and P. D. Readio, *J. Am. Chem. Soc.*, **85**, 2850 (1963).

10. (a) P. D. Bartlett and R. Pincock, *J. Am. Chem. Soc.*, **84**, 2445 (1962); (b) P. D. Bartlett and J. M. McBride, *J. Am. Chem. Soc.*, **87**, 1727 (1965).

11. M. Martin and D. DeJongh, *J. Am. Chem. Soc.*, **84**, 3526 (1962).

12. (a) S. Cristol, G. Brindell, and J. Reeder, *J. Am. Chem. Soc.*, **80**, 635 (1958); (b) D. Trecker and J. Henry, *J. Am. Chem. Soc.*, **85**, 3204 (1963).

13. (a) M. E. H, Howden and J. D. Roberts, *Tetrahedron*, **19**, Suppl. 2, 403 (1963); (b) M. Simonetta and S. Winstein, *J. Am. Chem. Soc.*, **76**, 18 (1954).

14. (a) E. F. Cox, M. C. Caserio, M. S. Silver, and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 2719 (1961); (b) M. C. Caserio, W. H. Graham, and J. D. Roberts, *Tetrahedron*, **11**, 171 (1960), and references therein.

15. (a) J. W. Wilt, L. L. Maravetz, and J. F. Zawadski, *J. Org. Chem.*, **31**, 3018 (1966); (b) L. K. Montgomery and J. W. Matt, *J. Am. Chem. Soc.*, **89**, 6556 (1967).

16. (a) Reference 2, pp. 57-59; (b) C. Walling and P. S. Fredricks, *J. Am. Chem. Soc.*, **84**, 3326 (1962).

17. (a) Reference 2, pp. 41, 62; (b) Reference 3, pp. 49ff; (c) L. K. Montgomery and J. W. Matt, *J. Am. Chem. Soc.*, **89**, 6556 (1967).

18. (a) J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 2509 (1951); (b) E. Renk, P. R. Shafer, W. H. Graham, R. H. Mazur, and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 1987 (1961).

19. (a) Reference 2, pp. 62, 63; (b) Reference 3, p. 51.

20. J. D. Roberts, California Institute of Technology, personal communication, 1967.

21. M. E. H. Howden, Ph. D. Thesis, California Institute of Technology, Pasadena, Calif., 1962.

22. M. Trachtman and J. G. Miller, *J. Am. Chem. Soc.*, **84**, 4828 (1962).

23. Reference 21, pp. 69, 70.

24. R. M. Noyes, *J. Am. Chem. Soc.*, **77**, 2042 (1955).

25. M. Szwarc and J. H. Binks in "Theoretical Organic Chemistry (The Kekulé Symposium)," Special Publication No. 12, The Chemical Society, Butterworths Scientific Publications, London (1959); for detailed references see also reference 59a, p. 400, footnote 26.

26. (a) W. E. Deming, "Statistical Adjustment of Data," John Wiley and Sons, Inc., New York, N. Y., 1943; (b) W. E. Wentworth, *J. Chem. Ed.*, **42**, 96, 162 (1965).

27. J. P. Lorand and P. D. Bartlett, *J. Am. Chem. Soc.*, **88**, 3294 (1966).

28. S. Winstein, C. R. Lindegren, H. Marshall, and L. Ingraham, *J. Am. Chem. Soc.*, **75**, 147 (1953).

29. (a) T. W. Koenig and J. C. Martin, *J. Org. Chem.*, **29**, 1520 (1964); (b) W. G. Bentrude and J. C. Martin, *J. Am. Chem. Soc.*, **84**, 1561 (1962).

30. P. D. Bartlett and R. Hiatt, *J. Am. Chem. Soc.*, **80**, 1398 (1958).

31. R. Hiatt, Ph.D. Thesis, Harvard University, Cambridge, Mass., 1956.

32. P. D. Bartlett and L. B. Gortler, *J. Am. Chem. Soc.*, **85**, 1864 (1963).

33. P. D. Bartlett and D. M. Simmons, *J. Am. Chem. Soc.*, **82**, 1753 (1960).

34. C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., London, 1957, p. 50.

35. R. K. Lyons, *J. Am. Chem. Soc.*, **86**, 1907 (1964).

36. E. Rabinowitch and W. C. Wood, *Trans. Faraday Soc.*, **32**, 1381 (1936); **33**, 1225 (1937).

37. (a) R. M. Noyes in "Progress in Reaction Kinetics," Vol. 1, G. Porter, Ed., Permagon Press, New York, N. Y., 1961; (b) L. Monchick, J. L. Magee, and A. H. Samuel, *J. Chem. Phys.*, **26**, 935 (1957); (c) J. C. Roy, J. R. Nash, R. R. Williams, Jr., and W. H. Hamill, *J. Am. Chem. Soc.*, **78**, 519 (1956).

38. W. Braun, L. Rajbenbach, and F. R. Eirich, *J. Phys. Chem.*, **66**, 1591 (1962).

39. C. G. Swain, W. H. Stockmayer, and J. T. Clarke, *J. Am. Chem. Soc.*, **72**, 5426 (1950).

40. S. Chandrasekar, *Rev. Mod. Phys.*, **15**, 1 (1943).

41. H. G. Kuivila in "Advan. in Organometal. Chem.," Vol. 1, F. G. A. Stone and R. West, Ed., Academic Press, New York, N. Y., 1964.

42. C. Walling and P. J. Wagner, *J. Am. Chem. Soc.*, **86**, 3368 (1964).

43. C. Walling and A. Padwa, *J. Am. Chem. Soc.*, **85**, 1593 (1963).

44. (a) G. M. Burnett and H. W. Melville, Nature, **156**, 661 (1945); (b) M. S. Matheson, E. E. Auer, E. B. Bevilacqua, and E. J. Hart, *J. Am. Chem. Soc.*, **71**, 497 (1949).

45. A. C. Brown and D. G. James, unpublished results, cited in: D. G. James and R. D. Suart, *J. Am. Chem. Soc.*, **86**, 5424 (1964).

46. A. Shepp and K. O. Kutschke, *J. Chem. Phys.*, **26**, 1020 (1957).

47. A. Shepp, *J. Chem. Phys.*, **24**, 939 (1956).

48. E. L. Metcalfe and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 4620 (1962).

49. E. L. Metcalfe, *J. Chem. Soc.*, 3560 (1963).

50. Reference 59a, p. 103.

51. M. Szwarc, *Disc. Faraday Soc.*, **10**, 337 (1951).

52. D. G. James and R. D. Suart, *Chem. Commun.*, 484 (1966).

53. (a) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **34**, 11 (1938); (b) A. F. Trotman-Dickenson, *Chem. Ind. (London)*, 379 (1965); (c) J. A. Kerr, *Chem. Reviews*, **66**, 465 (1966) and references therein.

54. P. J. Boddy and E. W. Steacie, *Can. J. Chem.*, **39**, 13 (1961).

55. S. Seltzer, *J. Am. Chem. Soc.*, **83**, 2625 (1961); (b) S. Seltzer, *J. Am. Chem. Soc.*, **85**, 14 (1963); (c) S. Seltzer and F. T. Dunne, *J. Am. Chem. Soc.*, **87**, 2628 (1965); (d) T. W. Koenig and W. D. Brewer, *Tetrahedron Letters*, 2773 (1965); (e) A. A. Zavitsas and S. Seltzer, *J. Am. Chem. Soc.*, **86**, 3836 (1964).

56. A. F. Trotman-Dickenson, "Gas Kinetics," Butterworths Scientific Publications, London, 1955, pp. 199-202.

57. R. F. Bridger and G. A. Russell, *J. Am. Chem. Soc.*, **85**, 3754 (1963).

58. (a) S. Winstein, R. Heck, S. Lapporte, and R. Baird, *Experentia*, **12**, 138 (1956); (b) S. Lapporte, Ph.D. Thesis, University of California, Los Angeles, Calif., 1955.

59. (a) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961; (b) J. D. Roberts, "Notes on Molecular Orbital Calculations," W. A. Benjamin, Inc., New York, N. Y., 1962.

60. Reference 59a, p. 55.

61. Reference 59a, p. 335.

62. C. A. Coulson, *J. Chem. Soc.*, 1435 (1955).

63. (a) Reference 25, p. 266; (b) Reference 59a, p. 402.

64. (a) C. A. Coulson, *Proc. Roy. Soc.*, **A169**, 413 (1939); (b) Reference 59a, pp. 167, 168.

65. J. S. Roberts and H. A. Skinner, *Trans. Faraday Soc.*, **45**, 339 (1949).

66. E. S. Huyser in "Advances in Free Radical Chemistry," Vol. 1, G. H. Williams, Ed., Academic Press, Inc., London, 1965.

67. A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1961, p. 22.

68. S. W. Benson, *J. Chem. Ed.*, **42**, 502 (1965).

69. A. Maercker and J. D. Roberts, *J. Am. Chem. Soc.*, **88**, 1742 (1966).

70. G. Houghton, *J. Chem. Phys.*, **40**, 1628 (1964).

71. N. C. Baird and M. J. S. Dewar, *J. Am. Chem. Soc.*, **89**, 3966 (1967).

72. (a) S. Seltzer and E. J. Hamilton, Jr., *J. Am. Chem. Soc.*, **88**, 3775; (b) T. Koenig and R. Wolf, *J. Am. Chem. Soc.*, **89**, 2948 (1967); (c) T. W. Koenig and W. D. Brewer, *Tetrahedron Letters*, 2773 (1965).

73. Reference 59a, p. 55.

74. D. Barnard, K. R. Hargrave, and G. M. C. Higgins, *J. Chem. Soc.*, 2845 (1956).

75. P. D. Bartlett and T. Funahashi, *J. Am. Chem. Soc.*, **84**, 2596 (1962).

76. (a) P. J. Lingane and J. H. Christe, *J. Electroanal. Chem.*, **10**, 284 (1967); (b) P. J. Lingane, Ph.D., Thesis, California Institute of Technology, Pasadena, Calif., 1967, pp. 73, 89; (c) Reference 26a, p. 156.

77. W. P. Neumann and K. Rübsamen, *Chem. Ber.*, **100**, 1621 (1967).

78. W. P. Neumann, E. Petersen, and R. Sommer, *Angewandte* (Int. Ed. in English), **4**, 599 (1965).

79. Reference 34, pp. 85-96.

80. A. K. Sawyer, personal communication to H. G. Kuivala, quoted in reference 41.

81. H. G. Kuivila, State University of New York at Albany, personal communication, 1967.

82. C. Walling and V. P. Kurkov, *J. Am. Chem. Soc.*, **89**, 4895 (1967).

83. S. Weiner, personal communication, California Institute of Technology, 1967.

84. A. Rajbenbach and M. Szwarc, *Proc. Chem. Soc.*, 347 (1958).

85. F. Carrock and M.Szwarc, *J. Am. Chem. Soc.*, **81**, 4138 (1959).

86. Reference 4, p. 169.

87. Unpublished results of the author.

88. L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, p. 179.

89. Reference 4, p. 167.

90. N. L. Allinger, M. A. Miller, F. A. VanCatledge, and J. A. Hirsch, *J. Am. Chem. Soc.*, **89**, 4345 (1967).

91. "Handbook of Chemistry and Physics," 48th ed, The Chemical Rubber Co., Cleveland, Ohio, 1967, pp. F-39, C-438.

92. Reference 91, p. C-681.

93. W. P. Neumann, K. Rübsamen, and R. Sommer, *Chem. Ber.*, **100**, 1063 (1967).

94. H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry," D. Van Nostrand Company, Inc., Princeton, N. J., 1956, pp. 479–481.

95. J. A. Kerr, *Chem. Reviews*, **66**, 465 (1966).

96. S. W. Benson, "The Foundations of Chemical Kinetics," McGraw Hill Book Company, New York, N. Y., 1960, pp. 499, 502.

97. T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworths, Scientific Publications, London, 1954, p. 276.

98. I. B. Rabinovich, V. I. Telnoi, P. N. Nikolaev, and G. A. Razuvaev, *Dokl. Akad. Nauk., USSR*, **138**, 852 (1961).

99. A. L. Yergey and F. W. Lampe, *J. Am. Chem. Soc.*, **87**, 4204 (1965).

100. (a) Reference 4, pp. 14, 15; (b) Reference 34, p. 146.

101. J. T. Golden, "FORTRAN IV; Programming and Computing," Prentice-Hall, Inc., Englewood Clifts, N. J., 1965, pp. 175-180.

102. "USER'S PRELIMINARY REFERENCE MANUAL for the experimental FORmula MAnipulation Compiler (FORMAC)," International Business Machines Corporation, 1964.

103. P. S. Dixon, A. P. Stefani, and M. Szwarc, *J. Am. Chem. Soc.*, **85**, 2551 (1963).

104. A. M. North, "The Collision Theory of Chemical Reactions in Liquids," Methuen and Co., Ltd., 1964, p. 108.

105. P. Debye, *Trans. Electrochem. Soc.*, **82**, 265 (1942).

106. (a) Reference 91, p. F-36; (b) International Critical Tables, 1st ed, Vol. 7, McGraw Hill Book Company, New York, N. Y., 1930, p. 217; (c) Reference 123, pp. 235, 236.

107. E. McLaughlin, *Quart, Rev.*, **14**, 236 (1960).

108. (a) "International Critical Tables," 1st ed. Vol. 5, McGraw Hill Book Company, New York, N. Y., 1929, p. 14; (b) Kh. M. Khalilov, *J. Phys. Chem., USSR*, **36**, 1341 (1962).

109. Reference 4, p. 316.

110. Reference 34, p. 146.

111. M. C. Sauer, Jr., and B. Ward, *J. Phys. Chem.*, **71**, 3971 (1967).

112. Reference 34, p. 52.

113. Reference 91, p. D-51.

114. Preface to reference 8.

115. (a) L. S. Bartell, B. L. Carrall, and J. P. Guillory, *Tetrahedron Letters*, 705 (1964); (b) L. S. Bartell and J. P. Guillory, *J. Chem. Phys.*, **43**, 647, 654 (1965); (c) G. L. Closs and H. B. Klinger, *J. Am. Chem. Soc.*, **87**, 3265 (1964); (d) G. A. Russell and H. Malkus, *J. Am. Chem. Soc.*, **89**, 160 (1967).

116. P. von R. Schleyer and G. W. Van Dine, *J. Am. Chem. Soc.*, **88**, 2321 (1966).

117. J. C. Martin, J. E. Schultz, and J. W. Timberlake, *Tetrahedron Letters*, 4629 (1967).

118. (a) C. Walling and P. S. Fredricks, *J. Am. Chem. Soc.*, **84**, 3326 (1962); (b) Reference 2, p. 54.

119. M. E. H. Howden, Research Notebook No. 1251, California Institute of Technology, Pasadena, Calif., pp. 139, 140.

120. H. G. Kuivila and E. J. Walsh, Jr., *J. Am. Chem. Soc.*, **88**, 571 (1966).

121. (a) Reference 96, pp. 504, 509; (b) Reference 104, pp. 102, 103; (c) F. R. Mayo, *J. Am. Chem. Soc.*, **89**, 2654 (1967); (d) K. J. Laidler, "Chemical Kinetics," 2nd ed, McGraw Hill Book Company, New York, N. Y., 1965, p. 201.

122. Reference 96, pp. 39-42.

123. F. D. Rossini *et al.*, "Selected Values of Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Institute Research Project 44, Carnegie Press, Pittsburgh, Pa., 1953, pp. 464-483.

124. P. J. C. Fierens and J. Nasielski, *Bull. Soc. Chim. Belg.*, **71**, 187 (1962).

125. Reference 91, p. D-188.

126. R. V. Volkenburgh, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *J. Am. Chem. Soc.*, **71**, 172 (1949).

127. Reference 91, p. C-449.

128. (a) J. Coops and G. J. Hoijtink, *Chem. Abs.*, **44**, 5828 (1950); (b) W. S. Holmes and E. Tyrrall, *Chem. and Ind.*, 662 (1956).

129. Reference 97, p. 123

130. (a) G. S. Parks and J. R. Mosley, *J. Am. Chem. Soc.*, **72**, 1850 (1950); (b) "Handbook of Physics and Chemistry," 39th ed, The Chemical Rubber Co., Cleveland, Ohio, 1957, p. 2136; (c) A. Aihara, *Bull. Soc. Chem. Japan*, **32**, 1242 (1959).

131. K. L. Wolf and H. Weghofer, *Z. physikal. Chem.*, **39B**, 194 (1938).

132. K. L. Wolf and H. Weghofer, *Z. physikal. Chem.*, **39B**, 194 (1938).

133. Reference 97, p. 127.

134. (a) J. Coops, D. Mulder, J. W. Dienski, and J. Smittenberg, *Rec. trav. chim.*, **66**, 153 (1947); (b) Reference 91, p. D-188.

135. M. Szwarc, *Chem. Rev.*, **47**, 75 (1950).

136. S. W. Benson, *J. Chem. Ed.*, **42**, 502 (1965).

137. Reference 91, p. F-156.

138. H. E. Bent and G. R. Cuthbertson, *J. Am. Chem. Soc.*, **58**, 170 (1936).

139. K. Ziegler and L. Ewald, Liebigs *Ann.*, **473**, 163 (1933).

140. F. J. Adrian, *J. Chem. Phys.*, **28**, 608 (1958).

141. A. I. Vogel, *J. Chem. Soc.*, 607 (1948).

142. This thesis, p. 117.

143. H. Kriegsmann and K. Ulbricht, *Z. Anorg. Chem.*, **328**, 90 (1964).

144. This procedure was suggested by Dr. A. Maercker.

145. Reference 21, p. 124.

146. M. E. H. Howden, A. Maercker, J. Burdon, and J. D. Roberts, *J. Am. Chem. Soc.*, **88**, 1732 (1966).

147. Reference 21, p. 209.

148. Reference 21, p. 210.

149. L. S. Silbert and D. Swern, *Anal. Chem.*, **30**, 385 (1958).

150. Reference 21, p. 185.

151. Reference 21, p. 184.

152. R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

153. Reference 21, p. 120.

154. S. Lawesson and N. C. Yang, *J. Am. Chem. Soc.*, **81**, 4230 (1959).

155. We are indebted to Mr. S. Murayama for suggesting this synthetic approach based on the preparation of diphenylmethylenecyclobutane reported by K. V. Scherer, Jr., and R. S. Lunt, III, *J. Org. Chem.*, **30**, 3215 (1965).

156. K. Sisido and K. Utimoto, *Tetrahedron Letters*, 3267 (1966).

157. We thank Dr. David Evans for performing the hydrogenation.

158. J. S. Salkind and F. B. Fundyler, Ber., **69**, 128 (1936).

159. R. R. Dreisbach, "Pressure-Volume-Temperature Relationships of Organic Compounds," Handbook Publishers, Inc. Sandusky, Ohio, 1952, p. 283.

160. "Selected Values of the Properties of Hydrocarbons," Circular of the National Bureau of Standards C411, U. S. Government Printing Office, Washington, D. C., 1947, pp. 64, 67, 69.

161. F. Daniels, J. H. Mathews, J. W. Williams, P. Bender, and R. A. Alberty, "Experimental Physical Chemistry," McGraw Hill Book Company, New York, N. Y., 1956, pp. 379, 380.

162. Reference 91, p. F-37.

PROPOSITION NO. 1

Abstract

A reinvestigation is proposed of the important work of Waits and Hammond on the experimental separation of primary and secondary recombination in cage processes. Systems are suggested which may be more amenable to a definitive result than we believe is that employed by Waits and Hammond.

Discussion

Whenever pairs of radical fragments are produced in solution via thermal or photochemical dissociation reactions, the possibility exists that cage reaction may occur--that the particals may for example (re)-combine instead of diffusing apart. Two types or stages of cage reaction are distinguished theoretically: (a) Primary recombination, in which the particles react without ever attaining a separation of more than a molecular diameter in excess of the sum of the molecular radii; and (b) Secondary recombination, in which reaction occurs following a period of essentially free diffusion (1).

Workers in the field have shown a lively interest in the question of whether cage recombination can occur with substantial probability if particles become separated by one or more layers of solvent molecules, as is pictured for secondary recombination, or whether one simply has collapse of the initial solvent cage after perhaps 10^{-11} or 10^{-12} sec to give either the cage product or separated radicals. Braun, Rajbenbach, and Eirich have argued that the former is correct for formation of ethane in the thermolysis of acetyl peroxide (2). The decomposition of acetyl peroxide appears to occur by scission of the –O–O– bond to give a pair of acetoxy radicals which may combine or decarboxylate in competition with diffusive separation (3). After both acetoxy radicals have decarboxylated, the derived methyl radicals may combine to form ethane. By studying the effect of viscosity for reaction in a series of hydrocarbons on the cage yields of ethane and methyl acetate (which may be formed while only one of the acetoxy radicals has decarboxylated), Braun et al. were able to infer a rate constant of about 2×10^9 $\sec^{-1}$ for decarboxylation of acetoxy radicals at 65° (2). They also inferred an average initial separation of methyl radicals of about 50 A in *n*-octane, where the yield of cage ethane is about 6%. Most of the cage ethane is undoubtedly formed in decomposition events in which the methyl radicals are initially separated by considerably less than this average distance, but the implication is clear that diffusive recombination is possible. Unfortunately, the necessity for rather extensive approximations in their treatment makes this result of unknown validity.

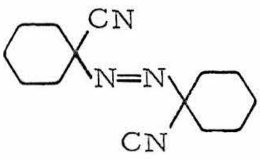
Noyes has studied quantum yields for production of free iodine atoms from photodecomposition of molecular iodine in solution (4). The quantum yields are always less than unity, and the deviation from unity is ascribed to cage recombination of iodine atoms. By treating the solvent as a viscous continuum, Noyes was able to estimate the mean interatomic distance attained by atoms separating with excess kinetic energy before essentially free diffusion becomes possible. For 4047 A light in hexane solution, this distance is calculated to be about 4 A over and above the sum of the radii for two iodine atoms, and 17% of decomposition events are observed to result in cage recombination. For light of longer wavelengths and decomposition in a considerably more viscous solvent, the calculated separations are only a few tenths of an angstrom, but the process at 4047 A in hexane would seem to involve secondary rather than primary recombination.

Waits and Hammond have concluded that coupling of caged α-cyanocyclohexyl radicals in chlorobenzene solution occurs by primary rather than secondary recombination (5). They compared the effect of added radical scavengers (bromine, iodine, 1,1-diphenyl-2-picryl-hydraxyl (DPPH)) on the efficiency of the cage combination with the predictions of a theoretical model due to Noyes (6) which assumes random diffusion of the radical pair during the time in which cage reaction may take place (i.e., that the cage process involves secondary recombination). If ϕ is the probability that the molecular pair, which otherwise would have recombined, instead reacts with scavenger, then Noyes' theory predicts that

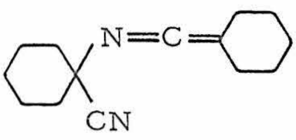
$$\phi \cong 2a(2\pi k_s(S))^{\frac{1}{2}}$$

where a is a constant, (S) is the concentration of added scavenger, and k_s is its rate constant for reaction with the caged radical species. Thus, a plot of the efficiency of formation of cage product in the presence of scavenger, $1 - \phi$, against the square root of the scavenger concentration should yield a straight line with an intercept of unity.

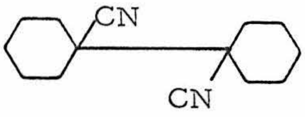
Waits and Hammond tested this expectation for thermal decomposition of N-(1-cyanocyclohexyl)-pentamethyleneketenimine (RR') in the presence of DPPH (Fig. 1) and of 1, 1'-azocyanocyclohexane (RN_2R) in the presence of bromine and iodine (Fig. 2). In Fig. 2 only the



RN_2R



RR'



RR

bromine scavenging results are shown, but we should note that those for iodine define an almost indistinguishable line. In each case, the intercept of the straight line is about 1. 1 rather than 1. 0. In contrast, plots of 1 - ϕ against the first power of the scavenger concentrations did give good straight lines with intercepts of unity.

Another point of interest is that extensive interference with cage recombination is not observed at scavenger concentrations of ca 10^{-2} M as predicted by Noyes (1), but only at much higher concentrations where, Waits and Hammond argue, interference with primary recombination seems unavoidable. They suggested (a) that their case either involves primary recombination or that primary and secondary recombination are not experimentally separable and (b) that a scavenger can compete with the cage process only if it happens to constitute one of the solvent molecules making up the cage wall. A treatment suggesting that this circumstance should lead to the observed linear scavenging relationship was presented.

If correct, this conclusion is of great significance regarding the nature of diffusive processes in solution. However, we feel that several important experimental and interpretational ambiguities prevent

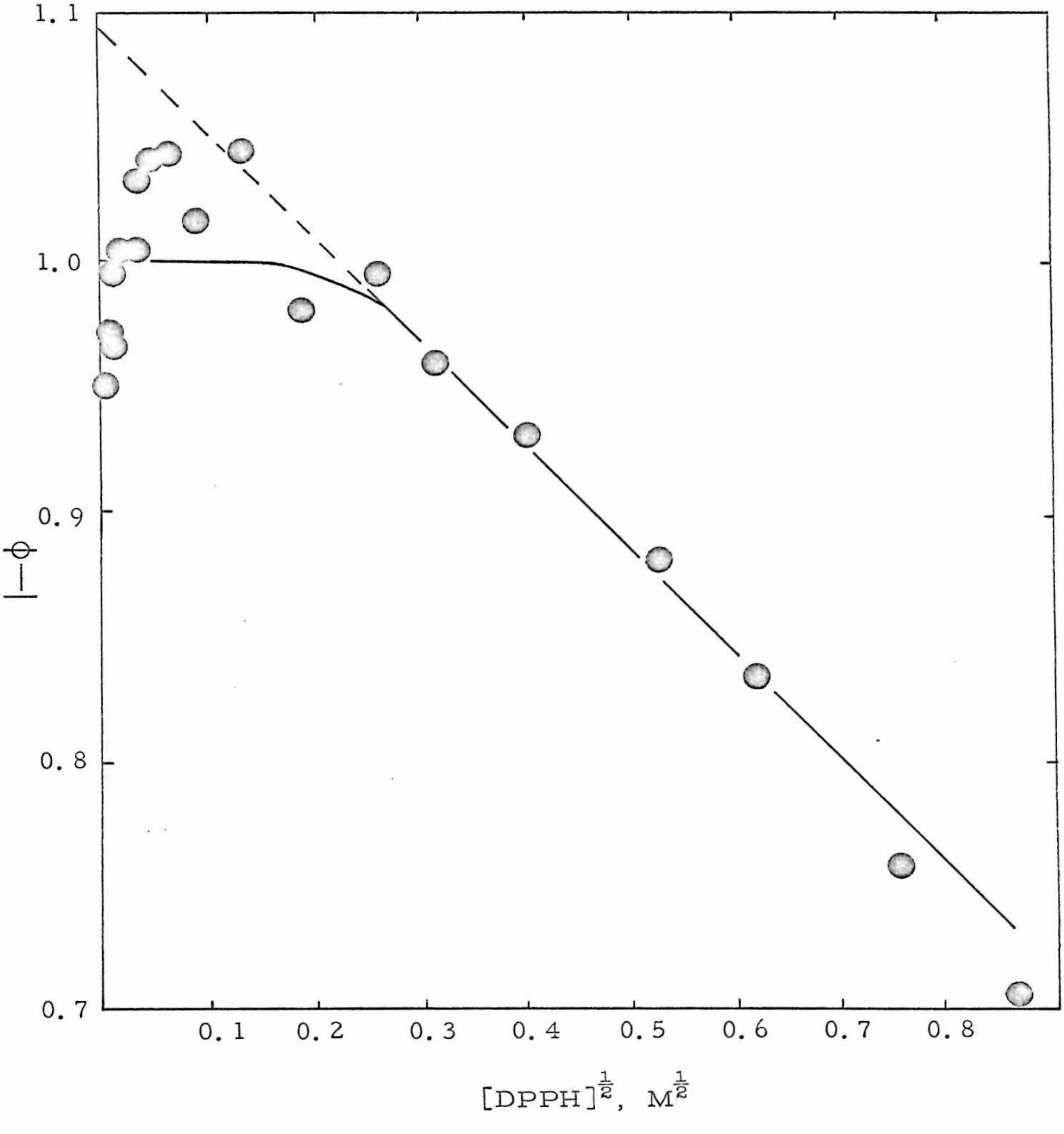


Figure 1. Dependence of relative cage efficiency on the square root of the DPPH concentration for RR' decomposition by Waits and Hammond (5).

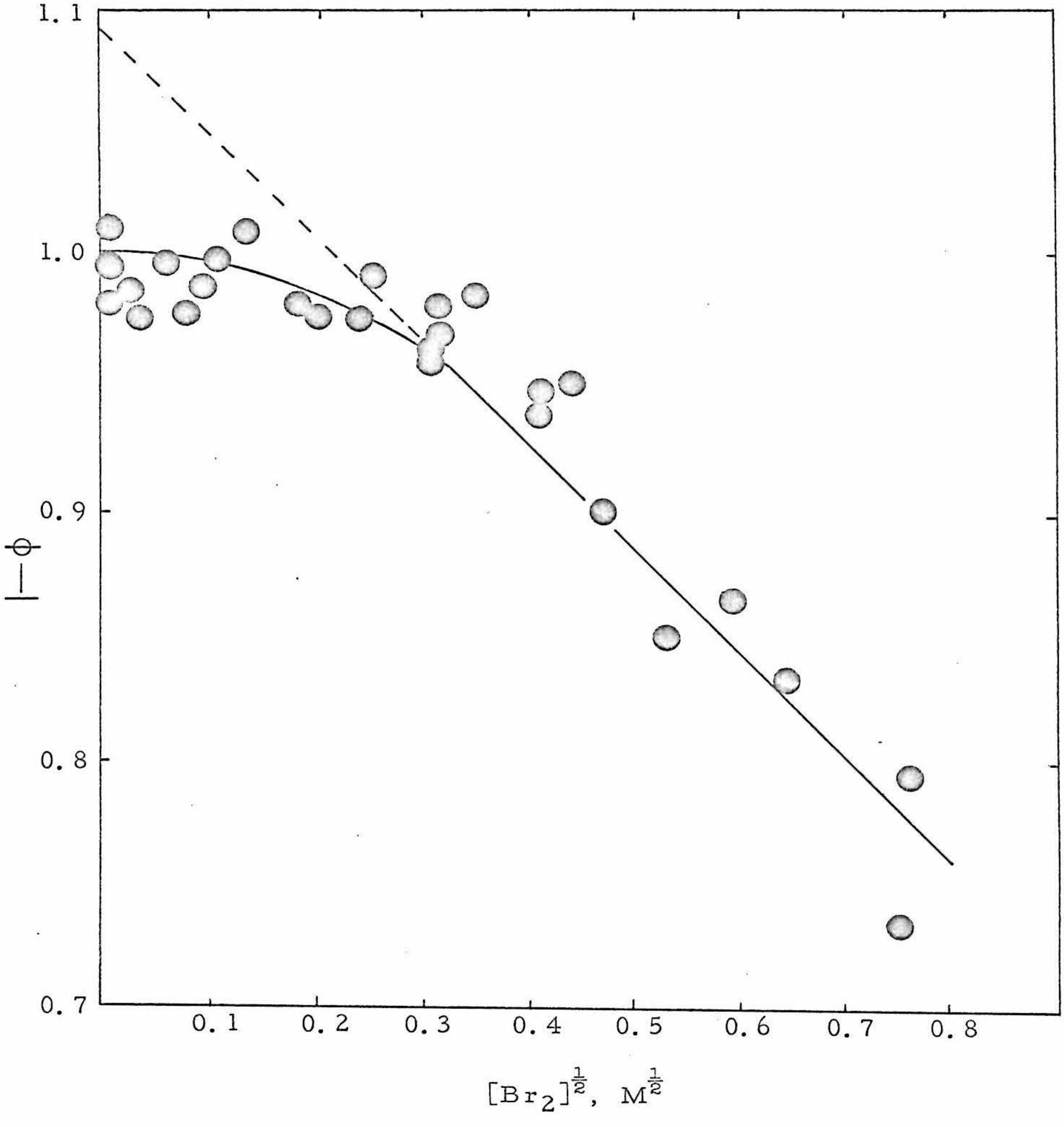


Figure 2. Dependence of relative cage efficiency on the square root of the bromine concentration for RN_2R decomposition by Waits and Hammond (5).

ready acceptance of this conclusion. The nature of one such ambiguity can be seen in Fig. 1. The abscissa in that figure is essentially linear in the yield of the cage product, 1, 1-dicyanobicyclohexyl (RR); the value $1 - \phi = 1.0$ corresponds to a 27% yield of RR. Thus one can see that the yield of RR increases with decreasing (DPPH) and reaches a maximum of about 29% for $(\mathrm{DPPH})^{\frac{1}{2}} = 0.05$ (5). As the DPPH concentration is further reduced, however, the yield of RR decreases with striking regularity to a value of about 24% (5). A natural explanation for situations of this type would be that as the concentration of the radical scavenger is continually decreased a point is reached at which once-formed RR begins to be attacked by radicals produced in subsequent decomposition events. But the initial concentration of the radical source, RR' in this case, was only about 1.7×10^{-5} M, and it is difficult to accept the suggestion that some radical intermediate will attack RR in preference to the chlorobenzene solvent when the concentration of the latter is about 10^{6} greater than that of the former.

In any case, the yield of RR does vary appreciably at low scavenger concentrations. Waits based his interpretation of the data on the assumption that a 27% yield of RR signifies the absence of cage scavenging. If one instead adopts a value of 29%, the effect is to relabel the abscissa in such a way that the dotted extension of the solid line in Fig. 1 comes very close to $1 - \phi = 1.0$. If correct, this would obviate Waits' conclusion that the square root relationship predicted by Noyes assuming a secondary recombination mechanism fails.

No such obvious reinterpretation can be suggested for the bromine (or iodine) scavenging results (Fig. 2). However, in both this and the above case, the necessity of using scavenger concentrations on the order of 1 M introduces the possibility that medium effects may substantially influence the yields of RR which would be formed in the absence of scavenging of the caged radicals. The following comparison is relevant in this regard. Schuler (7) has reported that the rate constant for reaction of methyl radicals with iodine is a factor of 16 greater than that for reaction of methyl radicals with the stable free radical galvinoxyl (8). However, Bartlett and Funahashi have found that galvinoxyl reacts with cyanoisopropyl radicals ten times as rapidly as does iodine (8). If we assume that cyanoisopropyl radicals do not react with galvinoxyl more rapidly than do methyl radicals, we conclude that methyl radicals react with iodine at least 160 times as rapidly as do cyanoisopropyl radicals.

Cyanocyclohexyl radicals and cyanoisopropyl radicals should be of closely similar reactivity. If Schuler's and Bartlett's work are correct, this would suggest first of all that reaction of cyanocyclohexyl with iodine (and also with bromine and DPPH) may not be sufficiently rapid to support the inference of Waits and Hammond that reaction of a caged cyanocyclohexyl radical with an adjacent iodine molecule will occur with high probability. Secondly, the implication is that scavenging of methyl radicals from azomethane decomposition (photolytic if this is possible in the presence of iodine or bromine) may be possible with scavenger concentrations of 0.01 to 0.1 M. If so, any worries about medium effects could be dispensed with.

It is therefore suggested that the essentials of the work of Waits and Hammond be repeated using azomethane or an azo compound yielding radicals of reactivity comparable to methyl radicals (such as cyclopropyl or vinyl radicals). In addition, use of optically active azo compounds yielding substituted cyclopropyl (9) or vinyl (10) radicals would permit simultaneous investigation of the residual optical activity in the cage coupling product formed in the presence of varying amounts of scavenger. Such a study could in principle yield additional information regarding the behavior with time of the probability per unit time that the caged radicals recombine. Noyes' relationship (6) assumes an initial rapid buildup of this probability (which may be thought of as a time-dependent rate constant for cage reaction), followed by a decay with $t^{-3/2}$ as the radical pair is increasingly separated by diffusion. It might be possible to partially test this time behavior, provided that the results do not strongly confirm the conclusion of Waits and Hammond that secondary recombination is unimportant.

References

1. R. M. Noyes, *J. Am. Chem. Soc.*, **77**, 2042 (1955).

2. W. Braun, L. Rajbenbach, and F. R. Eirich, *J. Phys. Chem.*, **66**, 1591 (1962).

3. (a) M. Szwarc and L. Herk, *J. Chem. Phys.*, **29**, 438 (1958); (b) L. Herk, M. Feld, and M. Szwarc, *J. Am. Chem. Soc.*, **83**, 2998 (1961); (c) J. W. Taylor and J. C. Martin, *J. Am. Chem. Soc.*, **89**, 6904 (1967).

4. L. F. Meadows and R. M. Noyes, *J. Am. Chem. Soc.*, **82**, 1872 (1960).

5. (a) H. P. Waits and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 1911 (1964).

6. R. M. Noyes in "Progress in Reaction Kinetics," Vol. 1, G. Porter, Ed., Permagon Press, New York, N. Y. 1961, and references therein.

7. R. H. Schuler, *J. Phys. Chem.*, **68**, 3873 (1964).

8. P. D. Bartlett and T. Funahashi, *J. Am. Chem. Soc.*, **84**, 2596 (1962).

9. H. M. Walborsky and Chen-Jong Chen, *J. Am. Chem. Soc.*, **89**, 5499 (1967).

10. L. A. Singer and N. P. Kong, *J. Am. Chem. Soc.*, **89**, 5251 (1967).

PROPOSITION NO. 2

Abstract

From the standpoint of computation time, the problem of orbital exponent optimization in even minimum-basis-set SCF Hartree-Fock calculations is a vexing one. We suggest that it may be possible to employ derivative aspects of a calculation using trial exponents, such as a Mulliken population analysis, in the exponent optimization. A reasonably good correlation of net charge on hydrogen with optimized hydrogen exponent is cited for a series of eight hydrides in partial support of the proposal.

Discussion

With the advent of flexible and reasonably rapid programs for the calculation of multicenter molecular integrals, it has become possible to carry out SCF calculations within the SCF Hartree-Fock LCAO framework on a variety of polyatomic molecules. Because of present limitations in the molecular integral calculations and the generally rapid increase in computation time with increased complexity of the molecular system, such calculations have mainly employed minimum basis sets when Slater-type orbitals have been used. With the minimum basis set restriction, it seems especially necessary to make each orbital as suitable as possible by optimization of all orbital exponents.

There are several possible approaches to the problem of exponent optimization. One would be to employ the formalism of eqs. 2.2-3 to 2.2-6 of this thesis (pp. 209, 210), where the function S would be interpretated as the molecular energy. Ransil has employed such an approach for a series of monohydrides (those in Fig. 1) (1), where the necessary derivatives with respect to the orbital exponent parameters were evaluated numerically. He was guardedly optimistic about the general feasibility of his approach. However, it can be shown that $2n^2 + 1$* calculations are required for each successive trial optimization (see p. 211), three to five of which were required in Ransil's work. Thus, the number of calculations required to effect the optimization rises discouragingly steeply with increasing complexity of the molecular system. In addition, it is doubtful that the accuracy required for numerical stability could be attained for complex systems where one must contend with round off error and errors due to the approximate evaluation (perhaps to one part in 10^5 or 10^6) of large numbers of molecular integrals.

A similar approach has been advanced for Gaussian-type orbitals in which formulas for analytic evaluation of the necessary derivatives are given (2). We are unaware of whether the scheme is feasible for Gaussian orbitals or whether it can be extended to Slater-type orbitals.

Exponent optimizations for polyatomic systems have employed what may be called the brute-force method. This consists in cyclically optimizing the exponents by calculating the energy for a trial value and for incremented and decremented exponent values and determining the energy minimum by a parabolic fit (3, 4, 5, 6). For BH_3 where there are four independent exponents, optimization required some 45 separate

---

*The value of n is given by the number of independent exponents.

calculations having a computation time of 5 minutes each (3). Clearly such circumstances place rather severe limitations on any hopes for rigorously optimizing exponents for the more complicated systems which have been treated by calculations of the type under consideration (7), at least for the present generation of computers.

We suggest that it may be possible to employ results from a current computation which are only indirectly related to the molecular energy to optimize the exponents or at least to enable cyclic optimization to be begun with better approximations to the exponents than would otherwise be possible. Specifically, we suggest that an approach of the general type which underlies the Slater rules (8), in which the concept of mutual shielding of the electrons is employed, may be feasible. We would however seek to evaluate the effect of shielding in each case for the wave function obtained using trial exponents, perhaps employing elements of a Mulliken population analysis (9).

Slater rules suggest effective nuclear charges of 3.25 for the 2s and 2p orbitals of neutral carbon, 3.60 for C^+, and 2.90 for C^- (8). We believe that a correlation of orbital exponent with charges on atoms in molecules may be generally useful. In Fig. 1 such a correlation is investigated for hydrogen atoms in hydrides where the net charge on hydrogen is 1 – the gross atomic electron population (9). The monohydrides were calculated by Ransil (1), except for H_2 (10). The BH_3 calculation is due to Palke and Lipscomb (3), CH_4 is due to Pitzer (4), and H_2O, to Pitzer and Aung (5). The correlation is especially good for the monohydrides, CH_3 and H_2O deviating somewhat from a line which could be drawn through the other points. Still, we feel that results are encouraging. Extension to atoms contributing several orbitals to the minimum basis set would be more difficult; perhaps the major and most sensitive changes from exponents given by Slater rules would however be found for the valence-shell electrons. Effects on the orbital exponents due to the presence of neighboring atoms might conceivably be expressable in terms of overlap populations (9).

It is uncertain just where such an investigation would lead, but the potential value is, we feel, sufficiently great to warrent the attempt.

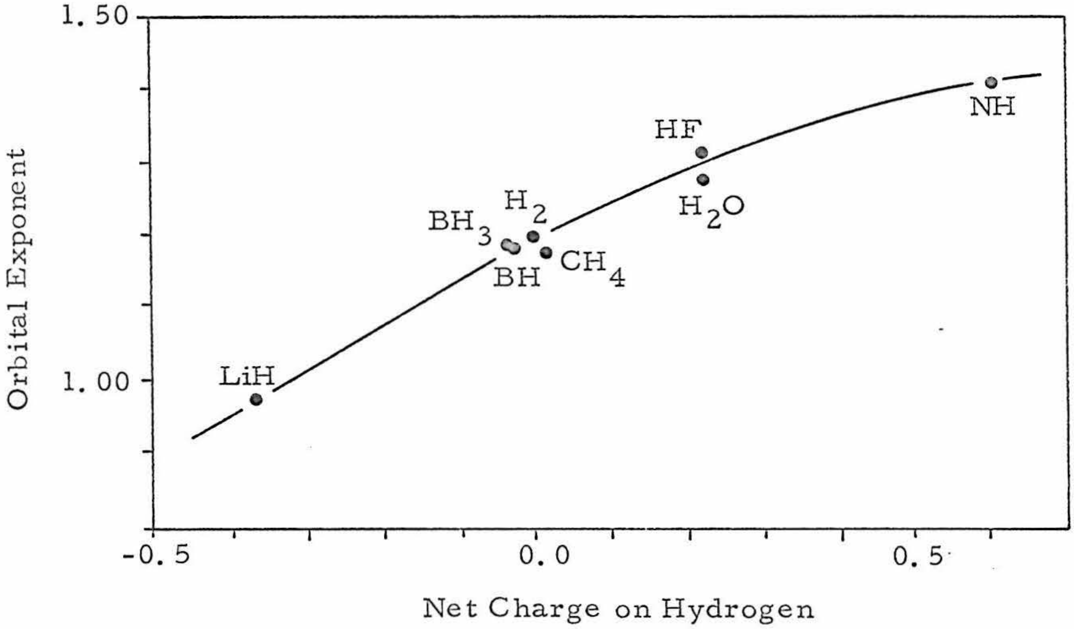


Figure 1. Correlation of exponent for 1s Slater-type orbital on hydrogen with calculated net charge on hydrogen in minimum-basis-set fully optimized SCF LCAO MO calculations.

References

1. B. J. Ransil, Rev. Mod. Phys., 32, 245 (1960).
2. T. K. Lim and M. A. Whitehead, J. Chem. Phys., **45**, 4400 (1967).
3. W. E. Palke and W. N. Lipscomb, J. Chem. Phys., **45**, 3948 (1967).
4. R. M. Pitzer, J. Chem. Phys., **46**, 4871 (1967).
5. S. Aung, California Institute of Technology, personal communication, 1968.
6. M. P. Barnett in "Methods in Computational Physics," Vol. 2, B. Alder, S. Fernbach, and M. Rotenberg, Eds., Academic Press, New York, N. Y., 1963.
7. W. E. Palke and W. N. Lipscomb, J. Am. Chem. Soc., **88**, 2384 (1966).
8. C. A. Coulson, "Valence," Oxford University Press, Oxford, 1961, pp. 40-42.
9. R. S. Mulliken, J. Chem. Phys., **23**, 1833, 1841 (1955).
10. R. G. Parr, "Quantum Theory of Molecular Electronic Structure," W. A. Benjamin, Inc., New York, N. Y. 1963, p. 14.

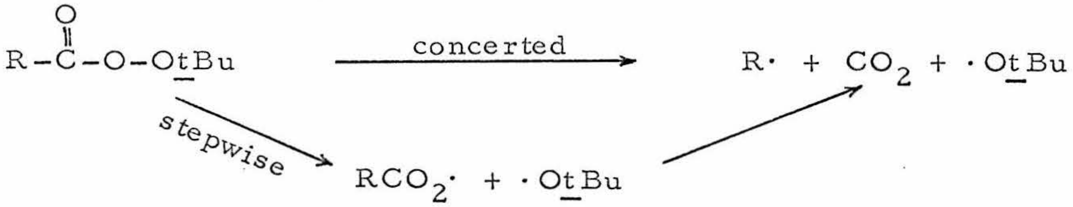
PROPOSITION NO. 3

Abstract

The decomposition of t-butyl peresters, RCO_2Ot-Bu, proceeds by a concerted two-bond scission when the derived radical R· is as or more stable than a secondary alkyl radical, but apparently by simple scission of the –O–O– bond when R is methyl. It is suggested that peresters decompose by a superposition of the two kinds of processes when R is primary alkyl and that this can be demonstrated via a kinetic deuterium isotope effect.

Discussion

Extensive kinetic investigations of the rates of thermal decomposition of t-butyl peresters, RCO_2Ot-Bu, have now been reported. Half-lives at 100° for decomposition in chlorobenzene (and literature references) are given in Table 13, p. 51 of this thesis. The variation of a factor of nearly 10^5 in the half-lives between the fastest and the slowest signifies a major dependence, under certain conditions at least, of reaction rate on the stability of the derived radical R·. This indicates that the more reactive peresters decompose primarily by the concerted pathway in which R· is largely formed in the decomposition transition state.

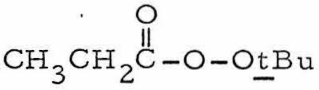


However, it may still be that the less reactive peresters decompose by the stepwise mechanism with initial scission of only the –O–O– bond. This possibility was briefly explored earlier in this thesis (Section One, subsection 3). We suggested there that the regular decrease in D(C–H) for successive substitution of methyl groups for hydrogen atoms in methane (1) should lead to a geometric progression of decomposition rates for a series of peresters where R is methyl, ethyl, isopropyl, and _t_-butyl, if the decomposition is concerted in all of these cases. Actual relative rates at 110° relative to methyl = 1.00 are: long chain primary aliphatic, 1.6 to 1.8; isopropyl, 17; _t_-butyl, 200. If we take the decomposition rate of the perester with R = ethyl to be the same as the mean of those with R = long chain primary aliphatic, we see that the second substitution of methyl for hydrogen on methane increases the rate of decomposition by a factor of ten and the third substitution effects an additional increase of a factor of twelve. The first substitution, on the other hand, increases the decomposition rate by less than a factor of two.

Trachtmann and Miller, the researchers who investigated the long chain primary aliphatic peresters, took this modest rate increase to indicate that the decomposition is stepwise both in their cases and for R = methyl (2). But this interpretation need not be correct. It might be that concerted decomposition is much slower than stepwise decomposition for R = methyl, but that the rate of the former is greatly increased for R = ethyl or primary aliphatic, whereas the rate constant for simple –O–O– bond scission is scarcely effected. The result could be a modest increase in the sum of the rates of the two processes.

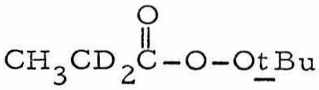
An entirely reasonable rate sequence can be constructed if it is assumed that approximately 0.98 units of each of the relative rates quoted above arises via –O–O- scission and that the rest (0.02 for methyl, 0.7 for ethyl or primary, 16 for isopropyl, and 199 for *t*-butyl) represents the contribution of the concerted process. Thus, approximate relative rates for concerted decomposition would be: methyl, 1.00; ethyl, 0.7/0.02 = 35; isopropyl, 800 = 35 x 23; *t*-butyl, 10,000 = 800 x 12.

We suggest that the perester with R = methyl decomposes essentially by simple scission of the –O–O– bond and that peresters where R is as or more stable than a secondary alkyl radical decompose mainly by the concerted breaking of two bonds, but that the two processes are of approximately equal importance for R = ethyl or primary aliphatic. We further suggest that this interpretation can be tested by measuring and comparing the decomposition rates for I and II.



$CH_3CH_2\overset{\overset{O}{\|}}{C}-O-O\underline{t}Bu$

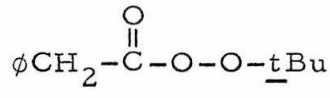
I



$CH_3CD_2\overset{\overset{O}{\|}}{C}-O-O\underline{t}Bu$

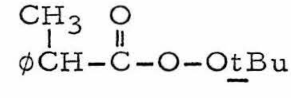
II

A number of secondary kinetic isotope effects have been measured for systems in which a tetrahedrally hydridized carbon is converted to a free-radical center. This is the type of transformation which takes place for decomposition of I or II if the concerted pathway is followed. Rate constant ratios (k_H/k_D) for such processes fall into the range 1.13 to 1.17 per α-deuterium (3). Especially pertinent are the values k_H/k_D = 1.17 per α-deuterium in labeled III and 1.14 per α-deuterium in labeled IV, both peresters which from their reactivity (Table 13, p. 51) surely decompose by the concerted pathway (3a). On the other hand,



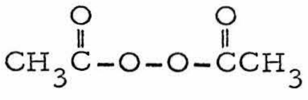
$\phi CH_2-\overset{O}{\overset{\|}{C}}-O-O-\underline{t}Bu$

III



$\phi\overset{CH_3}{\overset{|}{C}}H-\overset{O}{\overset{\|}{C}}-O-O\underline{t}Bu$

IV



$CH_3\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}CH_3$

V

massively labeled acetyl peroxide (V, 85% d_6), reliably established to undergo simple –O–O– scission (4), decomposed at a rate which was within one or two percent of that of unlabeled acetyl peroxide (3a). Thus, deuterium substitution has negligible effect on the rate of formation of acyloxy radicals.

If I undergoes about 40% concerted and 60% stepwise decomposition, as we anticipate, the secondary isotope effect should be about $1.15 \times 0.4 + 1.00 \times 0.6 = 1.06$ per deuterium, and k_I/k_{II} should be about $1.06^2 = 1.12$. If not significant amount of concerted decomposition occurs for I, k_I/k_{II} should be about 1.00.

A difference in decomposition rate of 12% could be detected by measuring k_I and k_{II} by standard techniques (such as by infrared), but it may be more satisfactory to use a competitive technique. Thus one would subject a solution containing known amounts of I and II to partial decomposition, isolate the unchanged perester, and analyze the isolated material for deuterium content, perhaps by nmr spectroscopy. If I and II are initially present in equal concentrations and k_I/k_{II} is 1.12, after three decomposition half-lives for I, 12.5% of I and 15.6% of II would be unchanged. Thus the ratio of II:I would be 1.25, or 25% greater than initially. Similarly, after five half-lives the ratio of II:I would be 1.46. The molecular weights of I and II are sufficiently low that isolation via distillation and other procedures should be possible at temperatures at which the peresters are thermally stable.

References

1. (a) C. Walling, "Free Radicals in Solution," Wiley, New York, 1957, p. 50; (b) J. A. Kerr, *Chem. Reviews*, **66**, 465 (1966).

2. M. Trachtmann and J. G. Miller, *J. Am. Chem. Soc.*, **84**, 4828 (1962).

3. (a) T. W. Koenig and W. D. Brewer, *Tetrahedron Letters*, 2773 (1965); (b) S. Seltzer, *J. Am. Chem. Soc.*, **83**, 2625 (1961); (c) S. Seltzer, *J. Am. Chem. Soc.*, **85**, 14 (1963); (d) S. Seltzer and F. T. Dunne, *J. Am. Chem. Soc.*, **87**, 2628 (1965).

4. (a) M. Szwarc and L. Herk, *J. Chem. Phys.*, **29**, 438 (1958); (b) L. Herk, M. Feld, and M. Szwarc, *J. Am. Chem. Soc.*, **83**, 2998 (1961); (c) W. Braun, L. Rajbenbach, and F. R. Eirich, *J. Phys. Chem.*, **66**, 1591 (1962); (d) J. W. Taylor and J. C. Martin, *J. Am. Chem. Soc.*, **89**, 6904 (1967).

PROPOSITION NO. 4

Abstract

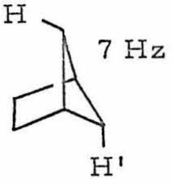
Two mechanisms have been proposed to account for the observation of long-range proton spin-spin coupling across four bonds in saturated cyclic systems. A third is suggested, and experiments are proposed to lend support to this one for couplings across five saturated bonds which will be sought in the experiments.

Discussion

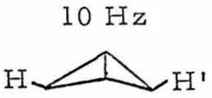
There have now been a number of reports of measurable proton spin-spin couplings across four saturated bonds. In rigid but unstrained systems such as I, coupling constants, $^4J_{HH'}$, of magnitude 1.0 to 2.2 Hz have been observed between equatorial protons (1). In a number of highly strained substituted bicyclo(2.1.1)hexanes (II), four bond couplings of 6 to 8 Hz have been reported (2). And in the even more highly strained bicyclobutane (III) and bicyclo(1.1.1)pentane (IV), four bond couplings of 10 to 18 Hz have been observed (3). In one case (V), a coupling formally through five saturated bonds has been found (4).

Two suggested explanations of the origin of the four-bond couplings have appeared in the literature. Using a semiempirical valence-bond treatment, Barfield (5) has predicted that the four-bond case should show an angular dependence reminiscent of that found by Karplus (6) for vicinal coupling constants. The magnitude of the

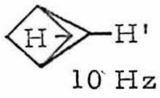
I



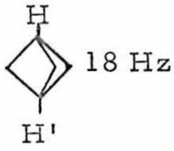
II



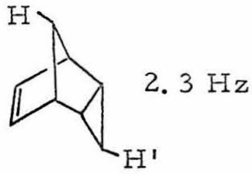
III



IV

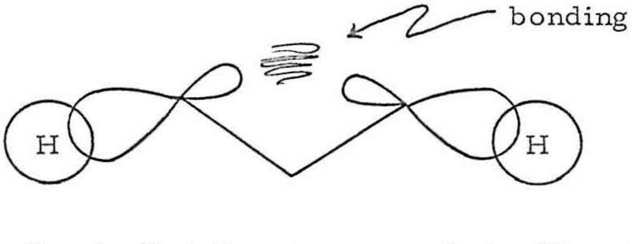


IV



V

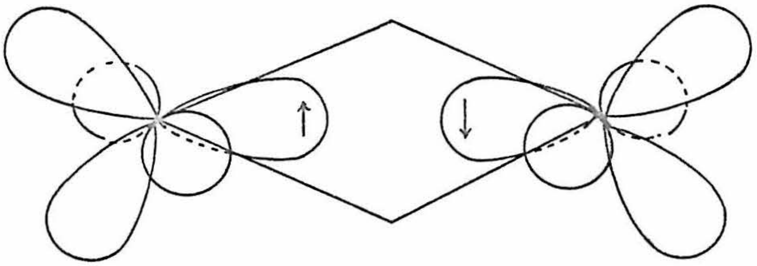
coupling is predicted to range from about -0.4 to +1.2 cps. This is of the same order of magnitude as the couplings which have been reported in systems like I, but is smaller--possibly significantly so--than those observed for II–IV. Meinwald and Lewis (2a) earlier had suggested that $^4J_{HH'}$ couplings might occur through overlap between the small lobes of the orbitals directed 180° away from the directions of the 1,3 carbon to proton bonds, and thus pointing toward each other.



Our suggestion is that the presence of significant ring strain is the factor which makes possible large long range couplings such as depicted above. We picture the role of ring strain as being to increase the importance of non-perfect-pairing structures, some of which have, for example, a bond between the carbon atoms to which the remote hydrogen atoms of interest are bound.

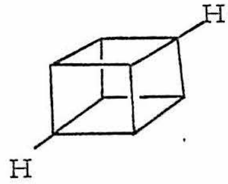
The bonding in cyclopropane has been discussed by a number of authors (7). Walsh suggested a model in which each carbon is sp^2-p hybridized with a trigonal hybrid from each carbon directed toward the center of the ring (7a). For our purposes, this is the most convenient picture. The important concept, stressed in the Coulson-Moffitt 'banana'bond' model as well (7b), is that significant deviations from perfect pairing are to be expected in strained saturated cyclic systems.

Cyclobutane is another example of such a situation. Here, a Walsh-type of model would provide a rationalization for a direct transfer of spin information between 1, 3 carbon atoms (although this has not yet been observed):

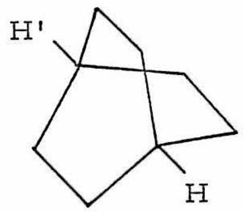


It is not suggested that such a model is a fully adequate description of the bonding in cyclobutane, but only that the angle strain provides a driving force (which must be sought quantum mechanically) for the introduction of <u>some</u> character of this type. However it is described, the basic effect in the transfer of spin information is presumed to arise from deviations from perfect pairing.

It is proposed that there will be a measurable five-bond coupling in cubane (VI) arising through some direct bonding between apex carbon atoms which permits more efficient transfer of spin information than is possible through the intervening carbon-carbon bonds. The overall effect would presumably work through an intra-atomic Hund coupling between electron spins similar to that discussed by Koide and Duval (8). It is further proposed that the formal five-bond coupling in VI be compared with that in bicyclo-(2. 2. 2)-octane (VII).



VI



VII

The five-bond couplings would be sought in each case in the ^{13}C satellites of material deuterated at all positions but the two of interest. In the case of cubane, the synthesis would follow that of Eaton and Cole (9), starting with fully deuterated 2-cyclopentenone. The apex protons would be introduced during the two perester decompositions required. Bicyclo-(2. 2. 2)-octane fully deuterated in the methylene positions would be synthesized from the di-t-butyl perester of d_{12}-bicyclo-(2. 2. 2)-octane-1, 4-dicarboxylic acid. The deuterated dicarboxylic acid would be prepared by the method of Roberts, Moreland, and Frazer (10) from ethylene dibromide-d_4 and diethyl 3, 3, 4, 4-d_4-succinate.

The apex inter-atomic distance in VI has been determined by x-ray crystallography to be 2. 69 A (11). That in VII should be

$1.54 + 2(1.54)\sin(19.5^\circ) = 2.57$ A. As there should be no appreciable angle strain in VII, the bonding should be essentially sp^3. In VI, however, the C-H bonds are expected to have more than 25% s-character. The amount could be estimated from the ^{13}C-H coupling constant determined in the experiments. At the same internuclear distance, the result of the difference in hybridization will be to make overlap between the backside lobes more favorable in bicyclooctane. This prediction is simply a manifestation of the well-known fact that increasing admixture of s with p character increases the directionality of the resulting hybrid (12).

Thus, both by virtue of the hybridization and the internuclear distance factors, $^5J_{HH'}$ coupling should be favored in the case of bicyclooctane, if the suggestion of Meinwald and Lewis is correct. If, as is expected, cubane has a measurable five-bond coupling and bicyclooctane does not, the mechanism proposed here would be supported at the expense of that of Meinwald and Lewis. Through-bond coupling such as that proposed by Barfield (5) might be expected to be unimportant. In his study, as well as in that by Karplus (6), the calculations emphasize the necessity for coplanarity of the involved bonds. In the cubane case, two 90° angles are involved. Moreover, the maximum predicted coupling for the four-bond case (5) is about an order of magnitude lower than that predicted in similar fashion for the three-bond case (6), and one might reasonably expect an additional falloff for coupling through five bonds.

References

1. (a) Y. Osawa and M. Neeman, *J. Am. Chem. Soc.*, **85**, 2856 (1963); (b) A. Rassat, C. Jefford, J. Lehn, and B. Waegell, *Tetrahedron Letters*, 233 (1964).

2. (a) J. Meinwald and A. Lewis, *J. Am. Chem. Soc.*, **83**, 2769 (1961); (b) K. Wiberg, B. Lowery, and B. Nist, *J. Am. Chem. Soc.*, **84**, 1594 (1962).

3. K. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Connor, P. Schertler, and J. Lavanisch, *Tetrahedron*, **21**, 2749 (1965).

4. K. Tori and M. Ohtsuru, *Chem. Commun.*, 886 (1966).

5. M. Barfield, *J. Chem. Phys.*, **41**, 3825 (1964).

6. M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

7. (a) A. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949); (b) C. Coulson and W. Moffitt, *Phil. Mag.*, **40**, 1 (1949); (c) G. Handler and J. Anderson, *Tetrahedron*, **2**, 345 (1958).

8. S. Koide and E. Duval, *J. Chem. Phys.*, **41**, 315 (1964).

9. (a) P. Eaton and T. Cole, Jr., *J. Am. Chem. Soc.*, **86**, 962 (1964); (b) P. Eaton and T. Cole, Jr., *J. Am. Chem. Soc.*, **86**, 3157 (1964).

10. J. D. Roberts, W. Moreland, and W. Frazer, *J. Am. Chem. Soc.*, **75**, 637 (1953).

11. E. B. Fleischer, *J. Am. Chem. Soc.*, **86**, 3889 (1964).

12. K. Wiberg, "Physical Organic Chemistry," Wiley, New York, 1957, p. 31.

PROPOSITION NO. 5

Abstract

Much is now known about the dependence of the activation energy for hydrogen-atom abstraction reactions on the heat of the abstraction reaction. Experiments are proposed to determine the dependence of the activation energy on the C–H bond dissociation energy for symmetrical thermoneutral processes.

Discussion

In the field of free-radical chemistry, successful and useful correlations of structure and reactivity have been found in the area of abstraction reactions. For a generalized reaction

$$R\cdot + H - X \longrightarrow R - H + X\cdot \qquad + \Delta H \quad , \tag{1}$$

the Evans and Polanyi relationship (1) states that the activation energy, E_{act}, is given by

$$E_{act} = A - B|\Delta H| \tag{2}$$

for exothermic reactions ($\Delta H \leq 0$) and

$$E_{act} = A + (1 - B)|\Delta H| \tag{3}$$

for endothermic reactions, where A and B are constants characteristic of a particular reaction series. The case of $R\cdot$ = methyl has been carefully investigated and it is found that the activation energies for exothermic reactions are closely fit by eq. 4 (lb).

$$\begin{aligned} E_{Me} &= 14.5 - 0.49|\Delta H| \\ &= 0.49[D(C-H) - 74.3] \end{aligned} \tag{4}$$

The second line follows from the first because $\Delta H = D(C-H) - D(CH_3-H)$. Trotman-Dickenson considers eq. 4 to be of sufficient predictive value to allow the deduction of C–H bond dissociation energies for the cycloalkanes (C_3 to C_7) from measured activation energies for hydrogen abstraction by methyl radicals (lb).

Although eq. 4 applies strictly only for hydrogen abstraction by methyl radicals, the regular decrease in the activation energy envisioned by eq. 4 as the C–H bond dissociation energy of the donor is decreased may be expected for abstraction by other hydrocarbon radicals as well. Useful generalization to other reaction series would thus be possible if but one additional factor were known. The missing link is the dependence of the parameter A of eqs. 2 and 3 on the nature of the radical R· of eq. 1. Equivalently, what is presently unknown is the dependence of the activation energy on the C–H bond dissociation energy for symmetrical thermoneutral abstraction reactions. This quantity is 14.5 kcal/mole for abstraction from methane by methyl radicals (lb). We propose that the activation energies be measured for the analogous processes involving t-butyl and cyclohexadienyl radicals:

$$(CH_3)_3C\cdot + (CH_3)_3C^{*}-H \longrightarrow (CH_3)_3C-H + (CH_3)_3C\cdot^{*}$$

A recent scheme advanced by Johnston and Paar predicts a slight lowering of E_{act} for such processes as D(C–H) is decreased (2), perhaps to 13 kcal/mole for t-butyl [D(t-butyl-H) = 91 kcal/mole (1c)] and to 11 kcal/mole for cyclohexadienyl [D(cyclohexadienyl-H) = 70 kcal/mole (3)]. Determination of the actual values would allow a test to be made of the predictive value of Johnston and Paar's scheme and would enable future schemes to be calibrated more broadly and representatively.

Experimentally, the determinations would involve photolytic decomposition of azo compounds, L–N=N–L, where L is labeled t-butyl or labeled cyclohexadienyl, in the gas phase in the presence of the appropriate hydrocarbon, UH, where U is unlabeled t-butyl or cyclohexadienyl. Appropriate reaction products would be collected and analyzed for label content relative to that in the starting azo compound. The idea is that the label content would be diminished to the extent that the exchange reactions depicted above compete with bimolecular consumption of radicals. If rate constants for the latter processes are denoted by k_1 (neglecting isotope effects) and the rate constant for the hydrogen-abstraction process is denoted by k_2, one can show that consideration of loss of label in the reaction products determines the ratio $k_2/k_1^{\frac{1}{2}}$. Bimolecular reaction of t-butyl radicals is known to require no activation energy (4) and bimolecular reaction of cyclohexadienyl radicals occurs at a rate which is within a factor of ten of the rate calculated by collision theory (5), suggesting a minimal or nonexistant activation energy here as well. Thus experiments at several temperatures would yield k_2, as desired.

The labeled azo compounds would be prepared by oxidative coupling of appropriately labeled amines with iodine pentafluoride, as described by Stevens for preparation of 2, 2'-azoisobutane (6). Use of completely deuterated 2, 2'-azoisobutane would allow convenient determination by nmr or mass spectroscopy of the deuterium and hydronium content of the coupling product, hexamethylethane. However, the ratio of disproportionation to coupling is 4. 6:1 for _t_-butyl radicals (7), and existence of a primary isotope effect for disproportionation of d_9-_t_-butyl radicals could change this ratio appreciably. Thus, yields of d_{18}-, d_9-, and d_0-hexamethylethane would not directly represent the relative amounts of pairwise reaction of the various combinations of labeled and unlabeled _t_-butyl radicals. It may therefore be preferable to employ a single deuterium label in each _t_-butyl group. One could partially reduce methylene bromide with tri-_n_-butyltin deuteride (8), add the Grignard reagent of the resulting d_1-methyl bromide to acetone, and convert the monolabeled _t_-butyl alcohol to the amine using the Ritter procedure (9), as employed by Barber and Lunt for conversion of 1-methylcyclohexanol to the amine (10). The relative amounts of di-, mono-, and unlabeled hexamethylethane could be inferred by mass spectroscopy.

Monolabeled cyclohexadienyl amine could be prepared starting from 2-bromotoluene. Hydrolysis of the Grignard reagent of this compound with deuterium oxide and oxidation of the resulting toluene would afford ring-labeled benzoic acid. Birch reduction of the acid would afford the labeled 1, 4-dihydrobenzoic acid (11), and amination followed by Hofmann degradation would yield the desired cyclohexadienylamine.

Following the reaction of the azo compound, the mixture of isomeric dimers (5), expected to be formed in about 70% yield (3), would be collected by preparative gas chromatography and analyzed by mass spectroscopy. If reaction temperatures as high as 100° should prove to be necessary to effect the desired competition between hydrogen abstraction and dimerization, reaction times would have to be held to less than 100 hours to prevent redissociation of once-formed dimer (12).

References

1. (a) M. G. Evans and M. Polanyi, *Trans. Faraday. Soc.*, **34**, 11 (1938); (b) A. F. Trotman-Dickenson, *Chem. Ind. (London)*, 379 (1965); (c) J. A. Kerr, *Chem. Reviews*, **66**, 465 (1966) and references therein.
2. H. S. Johnston and C. Parr, *J. Am. Chem. Soc.*, **85**, 2544 (1963).
3. D. G. James and R. D. Suart, *Chem. Commun.*, 484 (1966).
4. E. Metcalfe, *J. Chem. Soc.*, 3560 (1963).
5. M. C. Sauer, Jr. and B. Ward, *J. Phys. Chem.*, **71**, 3971 (1967).
6. T. E. Stevens, *J. Org. Chem.*, **26**, 2531 (1961).
7. W. A. Pryor, "Free Radicals," McGraw-Hill Book Company, New York, 1966, p. 317.
8. H. G. Kuivila in "Advan. in Organometal. Chem.," Vol. 1, F. G. A. Stone and R. West, Ed., Academic Press, New York, 1964.
9. J. J. Ritter and J. Kalish, *J. Am. Chem. Soc.*, **70**, 4048 (1948).
10. H. J. Barber and E. Lunt, *J. Chem. Soc.*, 1187 (1960).
11. M. E. Kuehne and B. F. Lambert, *J. Am. Chem. Soc.*, **81**, 4278 (1959).
12. This thesis, pp. 284, 285.