STUDIES OF CYCLOPROPYLCARBINYL-ALLYLCARBINYL FREE RADICALS

Thesis by

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DEDICATION

To my parents, who created the atmosphere which made it possible for me to accomplish this work;

To Stephanie, for her patience during and her assistance in the execution of this work, but especially for her love;

To Elizabeth Jeane, in the hope that this work may perhaps someday help to inspire in her the desire to seek after truth and to explore the world around her.

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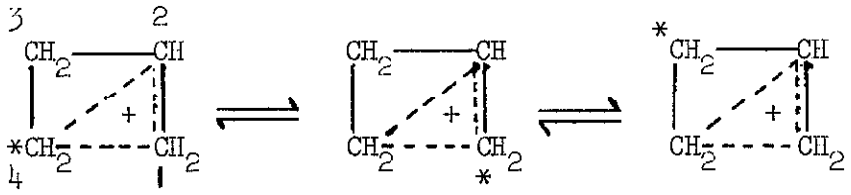
ABSTRACT

The di-t-butyl peroxide-initiated decarbonylations of cyclopropylacetaldehyde and dimethylcyclopropylacetaldehyde in the presence of benzyl mercaptan have been carried out and the chain-transfer constants of neopentane, n-butane, 2,3-dimethylbutane, methylcyclopropane, and isopropylcyclopropane with styrene at 79.1° have been determined in an attempt to ascertain the nature and number of the intermediates involved in interconversions of certain cyclopropylcarbinyl and allylcarbinyl derivatives in free-radical reactions. These interconversions are shown to be reversible. It is concluded that the nonclassical homoallyl radical and the classical allylcarbinyl radical are the intermediates involved in the free-radical interconversion of the cyclopropylcarbinyl and allylcarbinyl skeletons. No evidence is found for the existence of a nonclassical dimethylhomoallyl radical; the classical dimethylcyclopropylcarbinyl and (γ,γ-dimethylallyl)-carbinyl radicals are probably the only intermediates involved in the free-radical interconversion of the dimethylcyclopropylcarbinyl and (γ,γ-dimethylallyl)-carbinyl skeletons.

TABLE OF CONTENTS

INTRODUCTION

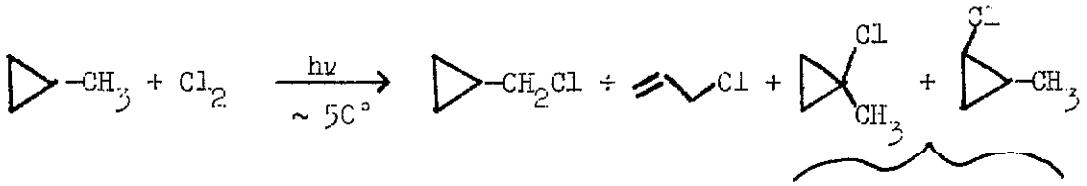
In recent years the interconversion of cyclopropylcarbinyl, allylcarbinyl, and cyclobutyl derivatives in carbonium ion reactions has been studied extensively; and equilibrating, unsymmetrical, non-classical "bicyclobutonium" ions (I a-c) have been proposed as intermediates to account for the kinetic data and product distributions observed (1). It was a logical progression to investigate the free-radical reactions of related compounds to determine whether or not similar rearrangements might take place and whether or not similar corresponding free-radical intermediates might have to be invoked.



Ia Ib Ic

Previous and Concurrent Studies Involving Unsubstituted Cyclopropylcarbinyl-Allylcarbinyl Radicals

Historically, Roberts and Mazur initiated work on the cyclopropylcarbinyl free radical by a study of the vapor-phase photochlorination of methylcyclopropane (at approximately 50°). The monochlorinated products, as analyzed by infrared spectroscopy, were a mixture containing 34% of cyclopropylcarbinyl chloride, 35% of allylcarbinyl chloride, 21% of a mixture tentatively identified as 1- and 2-chloro-1-methylcyclopropane, and 10% of intermediate fractions (equation 1) (2).



34% 35% 21%

monochlorides (relative %'s)

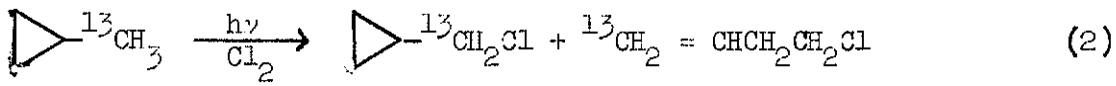
+ polychlorinated material (1)

The same reaction was carried out in the liquid phase at -20° by Brown and Borkowski (3), who identified the major low-boiling product as cyclopropylcarbinyl chloride. It was subsequently shown in these laboratories that their product contained allylcarbinyl chloride as well (4).

The vapor-phase photochlorination of methylcyclopropane was recently investigated in greater detail by Renk, et al. (6,7). The product mixtures were examined by vapor-phase chromatography (v.p.c.) and found to be exceedingly complex, containing up to twenty different components. The major monochlorinated products were isolated by preparative v.p.c. and shown to be cyclopropylcarbinyl chloride and allylcarbinyl chloride. The ratio of these chlorides was dependent upon the extent of completion of the reaction and also the rate of introduction of chlorine. The yield of allylcarbinyl chloride decreased as the reaction was carried further toward completion, presumably on account of addition of chlorine to the double bond. Ratios of cyclopropylcarbinyl chloride to allylcarbinyl chloride thus varied from 16:1 to 1:2. As in the above investigations, no cyclobutyl chloride was detected. Ring-chlorinated monochlorides were identified; but none of the higher-boiling polychlorinated products.

Of great significance, the same study (6) showed that the photochlorination of methyl-^{13}C-cyclopropane proceeded without isotope-

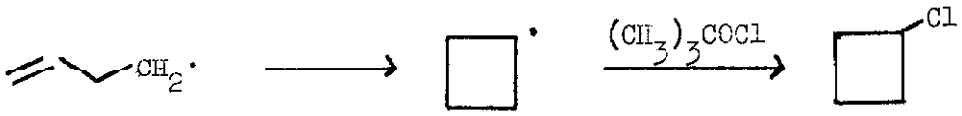
position rearrangement (i.e., without measurable carbon scrambling, as determined within 5% accuracy by nuclear magnetic resonance spectroscopy) to yield cyclopropylcarbinyl-α-^{13}C chloride and allyl-γ-^{13}C-carbinyl chloride (equation 2).



$$\triangle\!-{}^{13}CH_3 \xrightarrow[Cl_2]{h\nu} \triangle\!-{}^{13}CH_2Cl + {}^{13}CH_2{=}CHCH_2CH_2Cl \qquad (2)$$

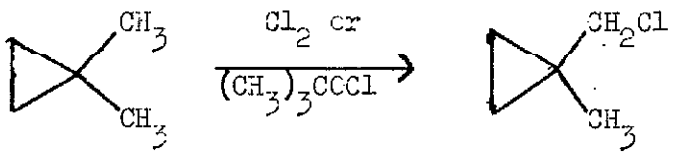
While the present studies were being concluded, Walling and Fredricks (9) reported yet another study of the liquid-phase photochlorination of methylcyclopropane. Their experiments were in general carried out using a large excess of hydrocarbon to chlorine (6:1 volume ratio). Use of larger amounts of the chlorinating agent resulted in altered product distributions; in particular, the amount of polychlorinated materials increased. Their results were anomalous in that there was apparently very little allylcarbinyl chloride formed and also their product compositions apparently reflected polar side reactions possibly involving hydrogen chloride. The product distributions, as determined by v.p.c., were respectively at 0° and 68°: cyclopropylcarbinyl chloride, 56.3% and 55.6%; 2-chlorobutane, 6.1% and 9.8%; 1,3-dichlorobutane, 7.3% and 8.0%; 1,3-dichloro-2-methylpropane, 5.5% and 3.5%; 1,2,4-trichlorobutane, a trace at both temperatures; unidentified C_4H_7Cl, 2.4% and 6.2%; and unidentified higher boiling material, 22.4% and 16.9%. The authors proposed that the 1,3-dichlorobutane and 1,3-dichloro-2-methylpropane resulted from a radical displacement on carbon with opening of the cyclopropane ring. Control experiments indicated that the 2-chlorobutane resulted from electrophilic attack upon the cyclopropane ring of methylcyclopropane by hydrogen chloride.

Walling and Fredricks (9) also studied the reaction of methylcyclopropane with a less reactive chlorinating substrate, t-butyl hypochlorite, using experimental conditions similar to those described above. In these experiments, the product distributions reported respectively at 0° and 68° were: cyclopropylcarbinyl chloride, 42.0% and 27.9%; allylcarbinyl chloride, 4.2% and 19.6%; a component tentatively identified as cyclobutyl chloride from its v.p.c. retention time, 8.9% and 10.2%; unidentified C_4H_7Cl components ("two peaks, probably ring-chlorinated material"), 10.2% and 15.4%; and approximately eight high-boiling unidentified components, 34.7% and 26.9%. It is significant that the yield of allylcarbinyl chloride increases with temperature at the expense of cyclopropylcarbinyl chloride, a point which will be discussed later in this thesis when the mechanism(s) of these reactions are discussed. It should also be noted that the identification of cyclobutyl chloride as a reaction product is somewhat tenuous; even should its presence be verified, it is not clear--or likely--that it arises via a free-radical reaction. The authors suggest that the cyclobutyl product might arise via an irreversible isomerization of the allylcarbinyl free radical to the cyclobutyl radical (equation 3); but that process seems improbable as cyclobutane products have not been detected--although sought for--in any other reactions believed to proceed through cyclopropylcarbinyl or allylcarbinyl free radical intermediates.

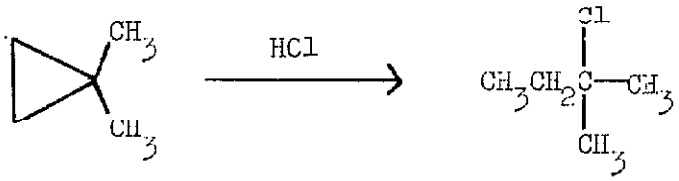


(3)

Walling and Fredricks (9) also studied the reactions of 1,1-dimethylcyclopropane with t butyl hypochlorite and with chlorine. With t-butyl hypochlorite the major product, identified by its n.m.r. and infrared spectra, was the chloromethyl derivative (52.4% at 0°; 67.1% at 68°). In the case of chlorine 1-methyl-1-(chloromethyl)-cyclopropane was again the predominant product (67.3% yield at 0° when products analyzed immediately after reaction); however, here too sufficient hydrogen chloride is produced so that competitive electrophilic ring opening becomes a serious side reaction, as much as 45% 2-methyl-2-chlorobutane being produced in a reaction sample allowed to stand (equations 4 and 5).

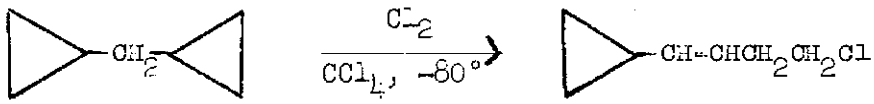


(4)



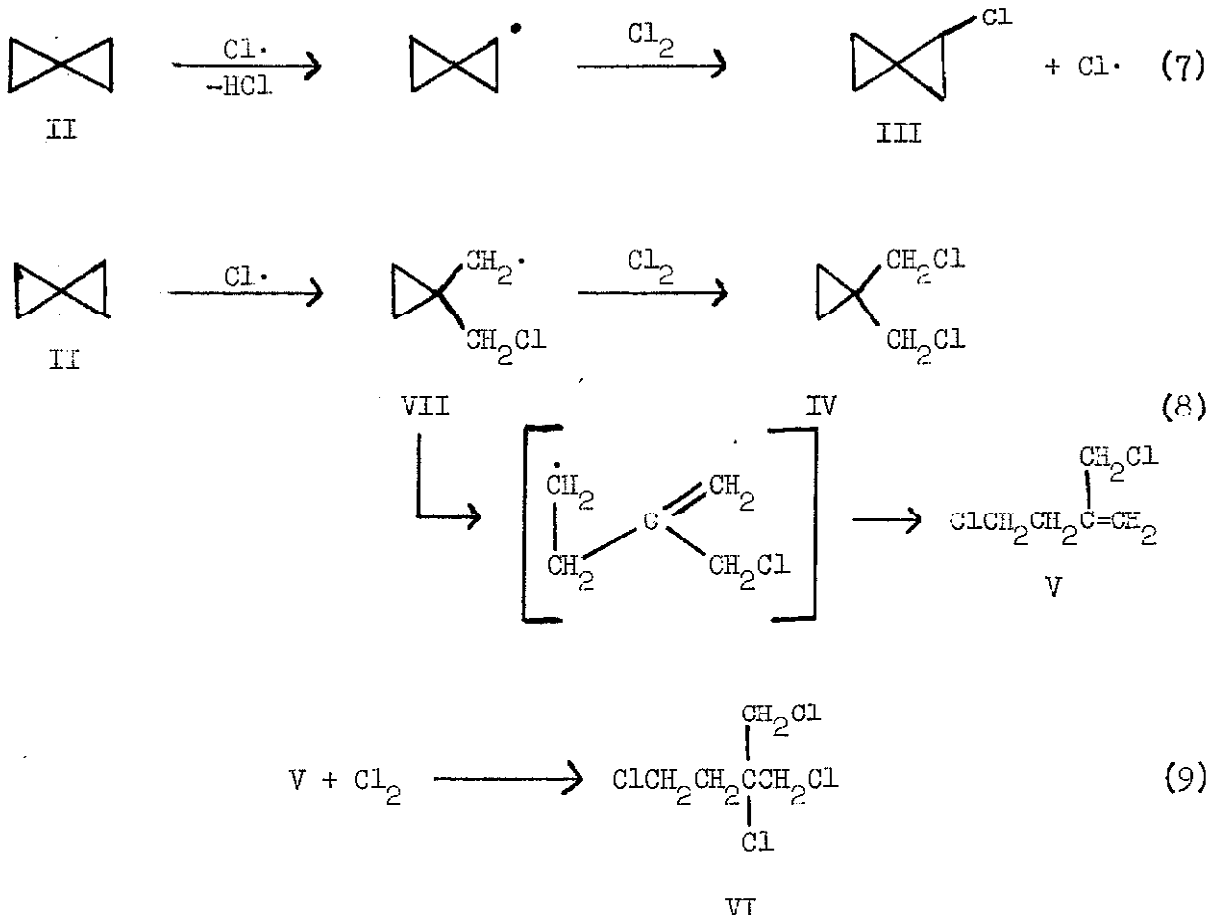
(5)

By contrast, the photochlorination of dicyclopropylmethane in carbon tetrachloride at -80° resulted in the production only of the rearranged allylcarbinyl product, 1-cyclopropyl-4-chloro-1-butene, despite the low temperature at which the reaction was carried out (equation 6) (10).



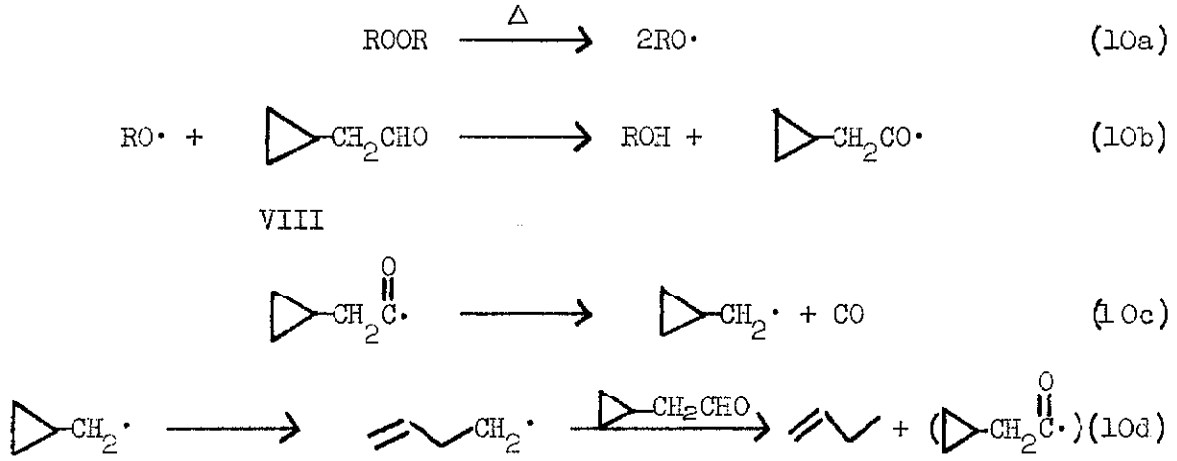
(6)

Another reaction in which cyclopropylcarbinyl-type free radicals are produced is the chlorination of spiropentane (II), recently investigated by Applequist, Fanta, and Henrikson (12). The four major products isolated from the photochlorination, thermal chlorination, and liquid-phase chlorination of II were identified as chlorospiropentane (III), 1,1-di-(chloromethyl)-cyclopropane (IV), 2-(chloromethyl)-4-chloro-1-butene (V), and 1,2,4-trichloro-2-(chloromethyl)-butane (VI), the relative yield of each being dependent upon the exact reaction conditions. Chlorospiropentane arises via the usual chlorination mechanism, as indicated in equation 7. The other products presumably arise via a cyclopropylcarbinyl-type radical (VII) formed by a ring-opening radical displacement on a spiropentane carbon atom by atomic chlorine (cf., the formation of 1,3-dichlorobutane and 1,3-dichloro-2-methylpropane during the chlorination of methylcyclopropane, discussed above), a reaction step which might be considered analogous to addition of a free radical to a double bond. Formally the radical VII can react with chlorine with or without ring opening to yield respectively the allylcarbinyl product V or the cyclopropylcarbinyl product IV (equation 8). Just as allylcarbinyl chloride formed during the chlorination of methylcyclopropane may be consumed by excess chlorine to give 1,2,4-trichlorobutane (see above), so addition of chlorine to the double bond of V yields product VI (equation 9). A small amount of 1-chloro-1-(chloromethyl)-cyclobutane was also found among the reaction products; but this product almost certainly resulted from addition of chlorine to the double bond of the methylenecyclobutane which was known to contaminate the spiropentane.



The cyclopropylcarbinyl free radical has been generated at higher temperatures than those previously discussed via the peroxide-initiated radical decarbonylation of cyclopropylacetaldehyde (VIII). This reaction was studied first by Urry and Hartzler (13) and later in greater detail by Schuster (15). In particular, Schuster investigated the decarbonylation of cyclopropylacetaldehyde at a temperature of 130-140° under a variety of experimental conditions: aldehyde dissolved in diphenyl ether, reaction initiated by di-t-butyl peroxide; aldehyde neat, reaction initiated by di-t-butyl peroxide; aldehyde neat, reaction initiated by benzoyl peroxide; and aldehyde dissolved in diphenyl ether, reaction initiated by benzoyl peroxide. The yields varied depend-

ing upon the exact conditions; but the only monomeric hydrocarbon product isolated in all of the above cases was the rearranged allylcarbinyl product, 1-butene. A highly simplified scheme of the above decarbonylation reaction is given in equations 10a-10d; only the initiation and chain-carrying steps (in the absence of any hydrogen chain transfer substrate more reactive than the aldehyde itself) are shown. One possible mode of formation of the product is via the hypothetical isomerization of the classical cyclopropylcarbinyl free radical (IX) to the classical allylcarbinyl free radical (X) which can react with the original aldehyde to give 1-butene (equation 10d). It will be shown later in this thesis that at this relatively elevated temperature even the presence of so potent a chain-transfer agent as benzyl mercaptan leaves the hydrocarbon product distribution unaltered: within experimental accuracy only 1-butene is isolated although methylcyclopropane was actively sought.



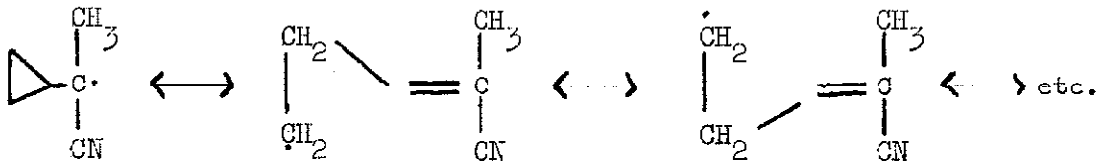
In her investigation of skeletal interconversions in allylcarbinyl, cyclopropylcarbinyl, and cyclobutyl Grignard reagents, Hamilton (16) had occasion to study the reaction of the Grignard reagents derived

from cyclopropylcarbinyl and allylcarbinyl chlorides with cobaltous chloride in ether. Although there is disagreement as to the exact mechanism of this reaction, it is generally agreed that the products are derived from alkyl free radicals generated in the course of the reaction (17,18). From the Grignard reagents derived from a mixture of 95% cyclopropylcarbinyl and 5% cyclobutyl chlorides there was obtained a mixture of low-boiling monomeric hydrocarbons consisting of 68% 1-butene, 18% trans-2-butene, 10% cis-2-butene, 4% cyclobutane and possibly a trace of methylcyclopropane. When the reactant halide was allylcarbinyl chloride contaminated with 0.4% of cyclobutyl chloride, the analogous product mixture contained 50% 1-butene, 29% trans-2-butene, 20% cis-2-butene, and about 0.3% cyclobutane. In both cases the cyclobutane product probably was derived from the reactant cyclobutyl chloride.

Thus far we have reviewed studies concerned only with the product distributions from reactions involving supposedly cyclopropylcarbinyl and/or allylcarbinyl free radicals as intermediates. We turn now to a consideration of investigations wherein the rate of formation of the free-radical intermediate(s) in such systems was also studied.

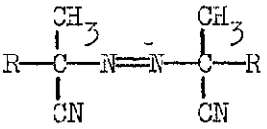
Over a period of years Overberger and his co-workers have studied the decomposition of a series of azo-bis-nitriles derived from the corresponding methyl alkyl ketones (19-21). Their results are summarized in Table 1. It may be seen that the azo-bis-nitrile derived from methyl cyclopropyl ketone decomposes anywhere from 3.3 to 42.8 times faster than the other azo nitriles. This rate enhance-

ment was originally attributed to the formation of a radical stabilized by "carbon-carbon radical hyperconjugation (21)," the first such suggestion for a cyclopropylcarbinyl radical, thusly:



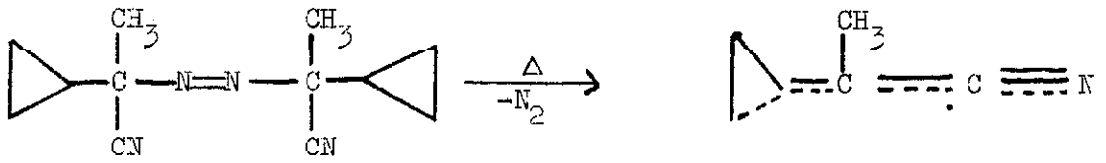
Very recently Overberger, Tobkes and Zweig (22) determined the products resulting from the decomposition of the azo-bis-nitrile derived from methyl cyclopropyl ketone, 2,2'-azobis-2-cyclopropylpropionitrile (IX), both in hexane solution at 40° and at 69° and in the solid state at 25° and at 40°. In solution the major product was an "unidentified brown polymeric material of low molecular weight" which was shown by n.m.r. and infrared spectroscopy to contain cyclopropyl and nitrile groups and to lack other sources of unsaturation. Also isolated were the cyclopropylcarbinyl coupling product X (in 14%-19% yield) and a material tentatively identified as 1-methylcyclopenten-5-one azine XI (6-7% yield). The azine was postulated to have been formed via the rearrangement of the ketenimine form XII of the intermediate radical XIII resulting from the decomposition of IX. These relationships are illustrated in equations 11a and 11b. In the solid state the yield of the dinitrile X increased greatly (63-80%) while the yield of the azine XI became negligible and the yield of polymer dropped. The great increase in coupling product was believed to have resulted from an increase of "cage" recombinations of the intermediate radicals, a process obviously favored in the solid state where diffusion apart

TABLE 1

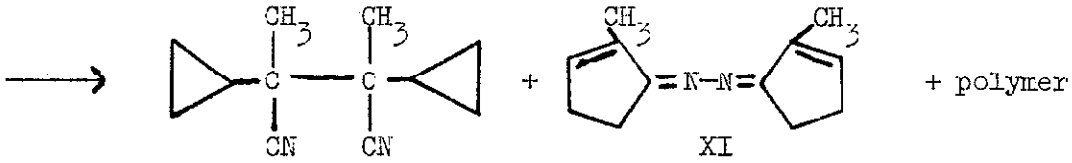
Decomposition of Azo Compounds 

R	Azo nitrile mp, °C	Temp., °C	kx10^4 sec^{-1}	Ea kcal/mole	Ref.
Cyclo-C_3H_5	64-65	80.2	33	28	20
Cyclo-C_3H_5	76-77	80.2	25	26	20
CH_3		80.2	1.60-1.72	34	19
CH_3CH_2		80.2	0.80-0.94	31	19
n-propyl		80.2	1.65-1.74	33	19
iso-propyl		80.2	1.02-1.03	32	19
n-butyl		80.2	1.58		19
iso-butyl	56-57	80.2	10	29	20
iso-butyl	74-76	80.2	7.1	29	20
t-butyl	114-116	80.2	0.77	35	20
t-butyl	116-118	80.2	1.09	30	20
Cyclo-C_4H_7	81.5-82.5	80.5	1.51		21
Cyclo-C_4H_7	38-42	80.5	1.51		21
Cyclo-C_5H_9	96.5-97.6	80.5	1.30		21
Cyclo-C_5H_9	72.2-74.5	80.5	1.31		21
Cyclo-C_6H_{11}	108.6-109.4	80.5	2.27		21

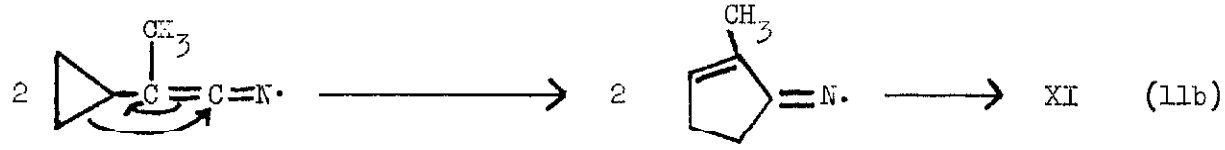
of the initially formed geminate radicals becomes exceedingly difficult and slow.



IX XIII (11a)

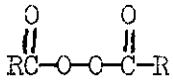


X XI + polymer



XII XI (11b)

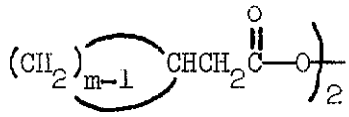
Decomposition of the diacyl peroxides XIV



XIV

can lead to the generation of free radicals R· . It can be shown from data in the literature (23,24,11) that the rate of decomposition of the peroxides XIV depends upon the nature of R; hence, there must be R–C as well as O–O bond stretching in the transition state for the reaction. There is a positive correlation between increasing stability of the radical R· and increasing rate of decomposition of the corresponding peroxide, in the same manner as was observed by Bartlett and Hiatt (25) for the decomposition of a series of t-butyl peresters, $R-\overset{O}{\overset{\|}{C}}-O-O-C(CH_3)_3$.

In particular Hart and Wyman (11) studied the decomposition in carbon tetrachloride of a series of diacyl peroxides XV derived from the corresponding cycloalkylacetic acids. All the peroxides in this series except the one



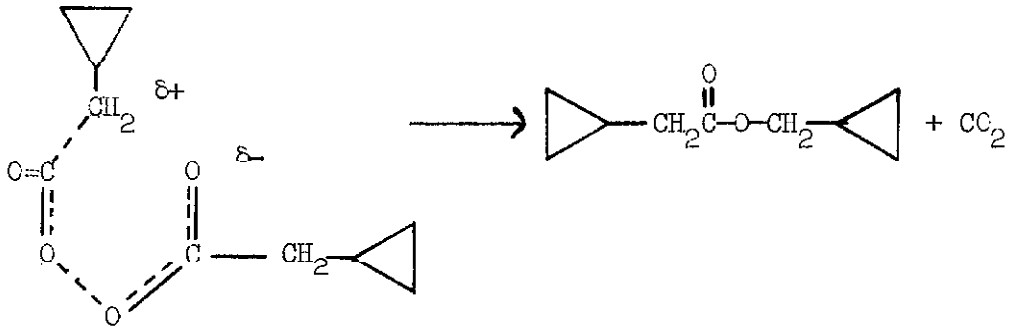
$m = 3,4,5,6$

XV

derived from cyclopropylacetic acid (XV, m=3) decomposed at approximately the same rate and gave similar product distributions, the predominant components being 65-75% alkyl chloride and 15-30% ester, as illustrated in equation 12. Moreover, the rates of decomposition were approximately the same as those for acetyl, propionyl, and n-butyryl peroxides (23) which also yield primary alkyl radicals upon decomposition. Cyclopropaneacetyl peroxide (XV, m=3) decomposed faster than the others, but the rate data at that time were erratic and not reproducible, the rate enhancement varying from a factor of 10 to one of 600 depending upon the particular sample. Also the product distribution from this peroxide was atypical, the only major product isolated (aside from carbon dioxide) being the ester cyclopropylcarbinyl cyclopropylacetate; no alkyl chloride product was detected, although sought for. Hart and Wyman were not sure whether to attribute this rate and product data to the formation of a resonance-stabilized cyclopropylcarbinyl free radical, to an acid-catalyzed decomposition, or to a reaction mechanism involving the formation of the ester product directly from a cyclic transition state having

appreciable carbonium ion character. This last postulate is illustrated in equation 13.

$$RC(=O)-O-O-C(=O)R \xrightarrow[\Delta]{CCl_4} CO_2 + RCl + RCO_2R + RCO_2H \qquad (12)$$



(13)

In an attempt to solve this conundrum, Hart and Cipriani (26) very recently reexamined the decomposition of carefully purified cyclopropanecacetyl peroxide in carbon tetrachloride over the temperature range 44-56.7°. This time reproducible first-order kinetics were obtained. Although its rate of decomposition was generally not as rapid as observed by Hart and Wyman (11), still the peroxide was found to decompose approximately 55 times faster than cyclohexaneacetyl peroxide (XV, m=6). The enthalpy of activation for cyclopropaneacetyl peroxide was determined as 24.3 kcal/mole, about 1.5-2.0 kcal/mole less than the corresponding enthalpy of activation for cyclohexaneacetyl peroxide; the entropy of activation was 3.1 cal/degree mole. The decomposition of the peroxide was found to be fairly sensitive to acid catalysis, particularly by strong acids or unconverted acid chloride (from the synthesis of the peroxide). Certainly some free radicals were produced by the decomposition of cyclopropaneacetyl peroxide, as

it initiated the polymerization of styrene at 60°, albeit less efficiently than benzoyl peroxide. The situation with respect to the product distribution remained the same; i.e., ambiguous. Again the major product (56% yield) was found to be the ester cyclopropylcarbinyl cyclopropylacetate; again very little, if any, of the normal alkyl chloride product was detected. Moreover a goodly percentage of the alkyl moiety (32-40%) could not be accounted for; the authors proposed that it may have gone to polymer. Since the rates reported are those for disappearance of peroxide, it still cannot be said with certainty in view of the product distribution whether the rate enhancement here observed is due to the formation of a stabilized cyclopropylcarbinyl radical or possibly to the predominance of a fast polar decomposition. In conjunction with evidence to be presented later in this thesis, however, it would seem that at least part of the rate enhancement results from a radical process.

In addition to their product studies described above, Walling and Fredricks (9) also carried out competitive chlorination experiments on successive pairs of paraffinic hydrocarbons from which it is possible to calculate the relative rates of abstraction of specific hydrogen atoms in those substrates by t-butoxy and chlorine radicals to yield the appropriate alkyl radicals. These results are summarized in Tables 2 and 3. From these tables it may be seen that a methylcyclopropane methyl hydrogen atom is abstracted about 3 times faster than a "typical" primary neopentane hydrogen atom by a t-butoxy radical at 68°, about 5.5 times faster by a t-butoxy radical at 0°, and about 16.5 times faster by a chlorine radical at 0°. Since these

TABLE 2

Relative Reactivities of Paraffins toward

t-Butoxy Radicals Per Hydrogen Atom[a,b]

Paraffin	Conditions	Relative Reactivity: Cyclohexane H as standard	Relative Reactivity: Neopentane H as standard
Cyclohexane	68°, CCl_4	1.00	7.7
	0°, CCl_4	1.00	17.8
Cyclopentane	68°, CCl_4	1.04	8.0
	0°, CCl_4	0.89	15.9
Cyclobutane	40°, $CFCl_3$	.71	-
	0°, $CFCl_3$	.51	9.1
Cyclopropane	68°, $CFCl_3$	.027	0.21
	0°, $CFCl_3$	.010	0.18
Neopentane	68°, $CFCl_3$	.13	1.00
	0°, $CFCl_3$	.056	1.00
n-Butane	0°, $CFCl_3$	.27	4.8
Methyl-cyclopropane	68°, $CFCl_3$	.27-.49[c]	2.1-3.7
	0°, $CFCl_3$	.21-.39	3.8-6.8
1,1-Dimethyl-cyclopropane	68°, $CFCl_3$	.36-.54[c]	2.8-4.1
	0°, $CFCl_3$	.18-.35	3.3-6.3

(a) Data taken from Reference 9.

(b) On this scale a primary allylic C-H bond would have a relative reactivity of 1.6-2.6 at 68° and 0.67-1.12 at 0° (27) relative to a cyclohexane C-H bond as standard, or 12-20 relative to a neopentane C-H bond as standard.

(c) Relative reactivity per methyl hydrogen.

TABLE 3

Relative Reactivities of Paraffins toward

Chlorine Radicals Per Hydrogen Atom[a]

Paraffin	Conditions	Relative Reactivity
Cyclohexane	0°, CCl_4	1.00
Cyclopentane	0°, CCl_4	1.35
Cyclobutane	0°, CCl_4	1.19
Methylcyclopropane	0°, $CFCl_3$	1.41[b]
Neopentane	0°	0.085[c]

(a) Data taken from Reference 9.

(b) Relative reactivity per methyl hydrogen.

(c) Relative reactivity calculated assuming same relative reactivity of neopentane to cyclopentane for chlorine radicals as found for t-butoxy radicals in Table 2.

relative rates were followed by monitoring the disappearance of the competitive substrates, the known presence of the rapid, polar, electrophilic cyclopropane-ring-opening reactions referred to above must cast some uncertainty upon the accuracy of the calculated rate enhancements for the production of cyclopropylcarbinyl radicals relative to neopentyl radicals. Nonetheless, it is likely that at least some portion of the rate acceleration so calculated is valid.

It will be valuable to conclude this section with a brief discussion of the product distributions realized from reactions in which cyclobutyl free radicals are generated as intermediates at temperatures up to 250°. Cyclobutane upon vapor-phase chlorination (2), liquid-phase chlorination at 0° (9), or chlorination with t-butyl hypochlorite at 0° (9) yields only cyclobutyl chloride. The products derived from the photolysis of methyl cyclobutyl ketone from 60-250° either have the cyclobutane skeleton preserved or result from fragmentation of the cyclobutane ring; but none have either the cyclopropylcarbinyl or allylcarbinyl skeleton (28). The Hunsdiecker reaction of silver cyclobutanecarboxylate with bromine yielded entirely cyclobutyl bromide (29). Decarbonylation of cyclobutanecarboxaldehyde at 130-140° afforded cyclobutane exclusively (15).

To summarize the results of this section: cyclopropylcarbinyl free radicals give rise to cyclopropylcarbinyl and/or allylcarbinyl products; products with the cyclobutyl skeleton are not found. In general the yield of product with an allylcarbinyl skeleton relative to that with a cyclopropylcarbinyl skeleton from a given cyclopropylcarbinyl radical appears to increase with increasing temperature and

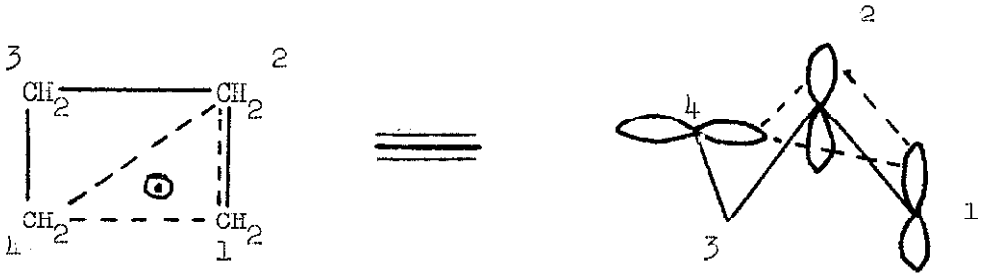
to decrease with increasing reactivity of substrate. Cyclobutyl radicals give rise to cyclobutyl products and not cyclopropylcarbinyl or allylcarbinyl products. In some instances cyclopropylcarbinyl radicals are generated with apparent rate enhancement.

Possible Mechanisms for the Interconversion of Cyclopropylcarbinyl and Allylcarbinyl Derivatives in Free Radical Reactions

The purpose of this section is to lay the groundwork for the interpretation of the experimental results already discussed as well as those to be presented later in this thesis, also to provide insight as to this author's reasons for approaching the problem in the particular way he did.

From the results presented in the previous section, it is clear that in order to explain the interconversion of the cyclopropylcarbinyl and allylcarbinyl skeletons in free-radical reactions there must be an intermediate or intermediates capable of yielding both types of products.

At the outset, in view of the failure of cyclopropylcarbinyl and allylcarbinyl systems to yield cyclobutyl products and the failure of cyclobutyl systems to yield cyclopropylcarbinyl or allylcarbinyl products in free radical reactions, a result in stark contrast to the facile interconversion of all three skeletons in reactions involving carbonium ion intermediates (1,30), it seemed reasonable to eliminate from consideration as an intermediate a non-classical "bicyclobutyl" free radical XVI.



XVI

However, simple Hückel Molecular Orbital (HMO) calculations indicated there might be reason to search for a resonance-stabilized non-classical, "homoallylic" free radical (XVIIa) as an intermediate in such reactions (31-33). The homoallyl radical has as indicated

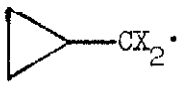
XVII

a) x=H
b) x=CH_3
c) x=C_6H_5

a 1,2 and 2,4 interaction but differs from the bicyclobutyl radical XVI in that it lacks a significant 1,4 interaction. In particular, in the most up-to-date calculations, balancing delocalization and strain energies but ignoring non-bonded and interelectronic repulsions, Howden (33) predicted for a favorable configuration of XVIIa (R_{12} = 1.34 Å; $R_{23} = R_{34}$ = 1.54 Å; R_{24} = 2.25 Å) a net stabilization of approximately 4.0 kcal/mole relative to the allylcarbinyl radical XIXa. Further Howden's calculations indicated, in agreement with the observed data discussed above, that a bicyclobutyl species would not be important in the free-radical reactions of cyclopropylcarbinyl and allyl-

carbinyl derivatives. The homoallyl radical could lead to either cyclopropylcarbinyl or allylcarbinyl products and will be discussed in more detail in a later section of this thesis.

A priori the most likely candidates as intermediates in these reactions are the classical cyclopropylcarbinyl and allylcarbinyl free radicals (XVIII and XIX respectively) themselves. For purposes of nomenclature in this thesis only, when X = H we refer to XVIIIa, XIXa, or XVIIa as the "unsubstituted" cyclopropylcarbinyl, allylcarbinyl, or homoallyl free radical respectively; when X = R (R = anything) we refer to a "substituted" species.



$CX_2 = CHCH_2CH_2\cdot$

XVIII

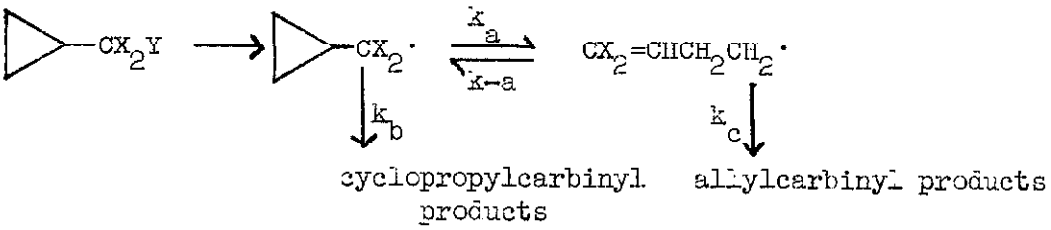
a) x=H
b) $x=CH_3$
c) $x=C_6H_5$

XIX

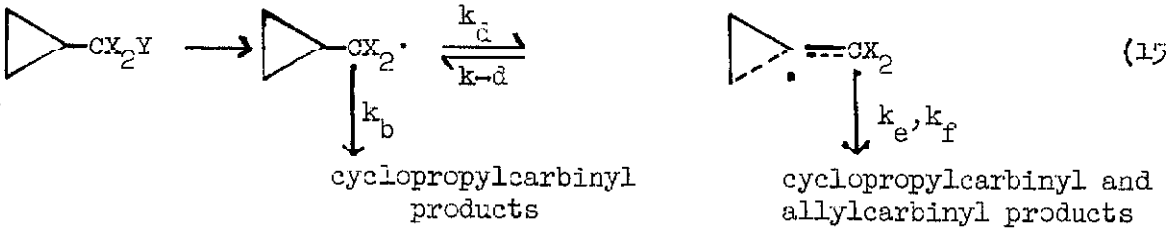
a) x=H
b) $x=CH_3$
c) $x=C_6H_5$

The most likely mechanisms for the interconversion of cyclopropylcarbinyl and allylcarbinyl derivatives in free-radical reactions are given in schemes 14-18. The intermediates given in the schemes are those described above. Nevertheless, any delocalized intermediate would be essentially kinetically indistinguishable from the homoallyl radical. Scheme 17 is indistinguishable from one in which the cyclopropylcarbinyl derivative reacts in the rate-determining step to yield directly a classical allylcarbinyl free radical capable of reacting with the substrate to give both cyclopropylcarbinyl and allylcarbinyl products; but the latter postulate

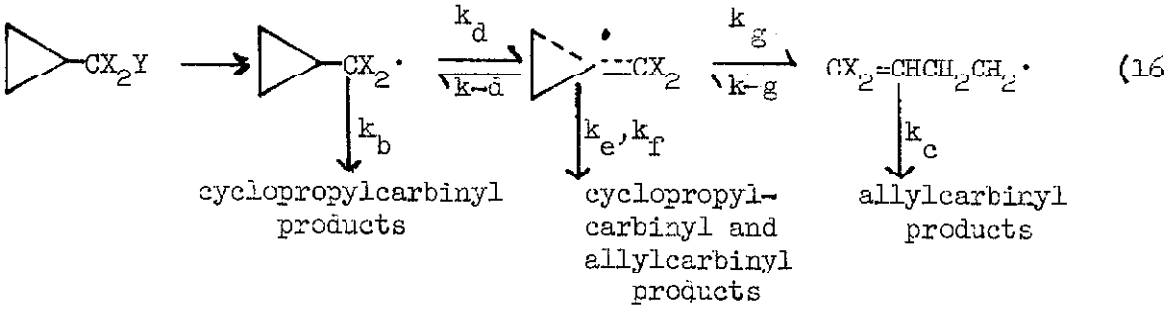
seems unreasonable, especially in view of the large amounts of cyclopropylcarbinyl products occasionally encountered in such reactions. Scheme 16 is included for completeness only, as it could not be distinguished experimentally from schemes 14 or 15 if one or the other of them represented reality.



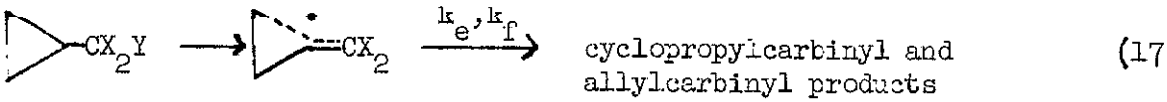
(14)



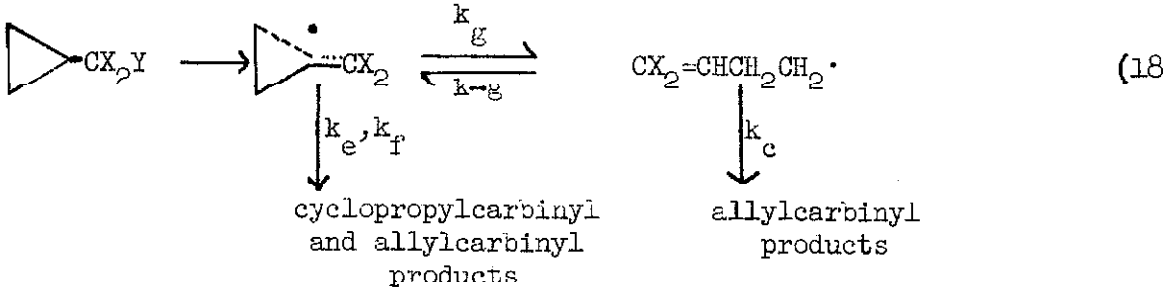
(15)



(16)



(17)



(18)

The question of the extent of reversibility of any of the schemes under discussion is one which can only be satisfied experimentally; evidence bearing on this point is discussed in a later section of this thesis (pp. 61-63).

Partial evidence helping to distinguish between these possibilities, bearing particularly upon the number of intermediates involved in these interconversions, could be obtained by a study of the product distributions realized upon the unequivocal generation of the initial "cyclopropylcarbinyl" radical in the presence of a hydrogen-atom chain-transfer reagent sufficiently reactive that all products could be assumed to have resulted from reaction of this reagent with the intermediate or intermediates of interest. In justification of this assertion, consider the following kinetic arguments, which are based upon analogous arguments first used by Seubold (34) in his study of the rearrangement of the neophyl radical generated by the peroxide-initiated decarbonylation of β-phenylisovaleraldehyde and by Cristol and co-workers (35) in their study of the addition of p-thiocresol to norbornadiene: (Any reader who so desires may at this point, without any loss of continuity, skip over these kinetic derivations to the conclusions which follow on p. 29 , referring back to the derivations when necessary).

We consider the following general initiation scheme 19 for the generation of a radical $R_1\cdot$ by the peroxide-initiated decarbonylation of the aldehyde R_1CHO in the presence of a reactive chain transfer agent ZH; it will soon be readily evident, however, that the conclusions to be drawn from this kinetic argument are independent of the means of generation of $R_1\cdot$.

$$(In)_2 \xrightarrow{k_i} 2In\cdot \qquad (19)$$

$$In\cdot + ZH \xrightarrow{k_n} InH + Z\cdot$$

$$Z\cdot + R_1CHO \xrightarrow{k_1} ZH + R_1CO\cdot$$

$$R_1CO\cdot \xrightarrow{k_m} R_1\cdot + CC$$

Case 1: We consider first a kinetic scheme 20 analogous to scheme 14. All products are assumed to be formed by hydrogen abstraction from ZH. The radical $R_1\cdot$ has available two modes of reaction: it may isomerize or abstract hydrogen; and vice versa for the radical $R_2\cdot$.

Thus

$$R_1\cdot + ZH \xrightarrow{k_1} R_1H + Z\cdot \qquad (20)$$

$$R_1\cdot \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} R_2\cdot$$

$$R_2\cdot + ZH \xrightarrow{k_3} R_2H + Z\cdot$$

From elementary kinetics we have for the rate of formation of the products,

$$\frac{d(R_2H)}{dt} = k_3(R_2\cdot)\ (ZH) \qquad (21)$$

and

$$\frac{d(R_1H)}{dt} = k_1(R_1\cdot)\ (ZH) \qquad (22)$$

Now for small percentage conversions to product, we have for the ratio of products

$$\frac{(R_2H)}{(R_1H)} \simeq \frac{d(R_2H)}{d(R_1H)} \qquad (23)$$

Making the steady-state approximation for the radical $R_2\cdot$:

$$\frac{d(R_2\cdot)}{dt} = k_2(R_1\cdot) - k_{-2}(R_2\cdot) - k_3(R_2\cdot)(ZH) \cong 0 \qquad (24)$$

or

$$(R_2\cdot) = \frac{k_2(R_1\cdot)}{k_3(ZH) + k_{-2}} \qquad (25)$$

From (21), (22), (23), and (25), we have

$$\frac{(R_2E)}{(R_1E)} \cong \frac{k_3k_2(R_1\cdot)(ZH)}{[k_3(ZH) + k_{-2}]k_1(R_1\cdot)(ZH)} \qquad (26)$$

$$= \frac{k_3k_2}{k_1[k_3(ZH) + k_{-2}]}$$

We can now deal with two limiting situations.

Case 1a: Let us assume that the radical species $R_1\cdot$ and $R_2\cdot$ are not rapidly reversible; i.e., we deal with an irreversible isomerization; i.e., $k_3(ZH) \gg k_{-2}$.

Then from (26),

$$\frac{(R_2H)}{(R_1H)} \cong \frac{k_2}{k_1(ZH)} .$$

The product ratio in this instance should be inversely proportional to the concentration of reagent ZH; i.e., the product of the ratio of products and the concentration of reagent ZH should remain constant as the concentration of ZH is varied.

Case 1b: Here we assume that the radical species $R_1\cdot$ and $R_2\cdot$ are rapidly equilibrating; i.e.,

$$k_{-2} \gg k_3(ZH) .$$

Then

$$\frac{(R_2H)}{(R_1H)} \cong \frac{k_2 k_2}{k_1 k_{-2}} = \text{constant.}$$

For rapidly equilibrating isomers $R_1\cdot$ and $R_2\cdot$ as intermediates the ratio of products should be constant, independent of the (initial) concentration of ZH.

Case 2: We now consider a kinetic scheme 27 analogous to scheme 15. Again all products are assumed to arise via hydrogen abstraction from ZH. The initially formed classical radical $R_1\cdot$ can either react to form product R_1H or isomerize irreversibly to a delocalized radical N· capable of yielding both products R_1H and R_2H.

$$R_1CO\cdot \xrightarrow{k_m} R_1\cdot + CO \qquad (27)$$

$$R_1\cdot + ZH \xrightarrow{k_1} R_1H + Z\cdot$$

$$R_1\cdot \xrightarrow{k_4} N\cdot$$

$$N\cdot + ZH \xrightarrow{k_5} R_1H + Z\cdot$$

$$N\cdot + ZH \xrightarrow{k_6} R_2H + Z\cdot$$

The rates of formation of the products R_1H and R_2H are given by

$$\frac{d(R_2H)}{dt} = k_6(N\cdot)(ZH) \qquad (28)$$

and

$$\frac{d(R_1H)}{dt} = k_1(R_1\cdot)(ZH) + k_5(N\cdot)(ZH) \qquad (29)$$

For small percentage conversions to products we have again

$$\frac{(R_2H)}{(R_1H)} \cong \frac{d(R_2H)}{d(R_1H)} \cdot \tag{30}$$

Thus

$$\frac{(R_2H)}{(R_1H)} \cong \frac{k_6(N\cdot)}{k_1(R_1\cdot) + k_5(N\cdot)} \tag{31}$$

Making the steady-state approximation for N·:

$$\frac{d(N\cdot)}{dt} \cong 0 = k_4(R_1\cdot) - k_5(N\cdot)(ZH) - k_6(N\cdot)(ZH) \tag{32}$$

or

$$(N\cdot) = \frac{k_4(R_1\cdot)}{(k_5 + k_6)(ZH)} \cdot \tag{33}$$

Putting (33) into (31), we have after cancellation

$$\frac{(R_2H)}{(R_1H)} \cong \frac{k_6k_4}{k_5k_4 + k_1(k_5 + k_6)(ZH)} \cdot \tag{34}$$

In this instance then it is predicted that the ratio of products $(R_2H)/(R_1H)$ should decrease in accordance with equation 34 as the initial concentration of ZH is increased.

Case 3: Now we consider a kinetic scheme 35 analogous to scheme 17, one in which a delocalized, nonclassical radical is the sole intermediate leading to products.

$$\begin{aligned} R_1CO &\xrightarrow{k_n} N\cdot + CO \\ N\cdot + ZH &\xrightarrow{k_5} R_1H + Z\cdot \\ N\cdot + ZH &\xrightarrow{k_6} R_2H + Z\cdot \end{aligned} \tag{35}$$

The expressions for the rates of formation of products R_1H and R_2H are easily derived as

$$\frac{d(R_2H)}{dt} = k_6(N\cdot)(ZH) \tag{36}$$

and

$$\frac{d(R_1H)}{dt} = k_5(N\cdot)(ZH); \tag{37}$$

whence,

$$\frac{d(R_2H)}{k_6} = \frac{d(R_1H)}{k_5} . \tag{38}$$

Integration of both sides of Equation 38 yields

$$\frac{(R_2H)}{k_6} = \frac{(R_1H)}{k_5} \text{ or } \frac{(R_2H)}{(R_1H)} = \frac{k_6}{k_5} = \text{constant} . \tag{39}$$

For the case of both products being derived from only one intermediate, the ratio of products is predicted to be independent of the concentration of ZH. This conclusion rests on firmer grounds than any of the others as fewer approximations went into its derivation.

Case 4: Finally we treat a kinetic situation 40 analogous to scheme 18. Here the initially formed nonclassical radical may react with ZH to yield either product R_1H or R_2H and may isomerize to $R_2\cdot$ which can yield only R_2H as product. As usual all products are assumed to arise via hydrogen abstraction from ZH.

$$R_n CO\cdot \xrightarrow{k_n} N\cdot + CO \tag{40}$$

$$N\cdot + ZH \xrightarrow{k_5} R_1H + Z\cdot$$

$$N\cdot + ZH \xrightarrow{k_6} R_2H + Z\cdot$$

$$N\cdot \xrightarrow{k_7} R_2\cdot$$

$$R_2\cdot + ZH \xrightarrow{k_3} R_2H + Z\cdot$$

With assumptions like those in Cases 1 and 2 above it can be shown that

$$\frac{(R_2H)}{(R_1H)} \cong \frac{k_6(N\cdot) + k_3(R_2\cdot)}{k_5(N\cdot)} . \tag{41}$$

Making the steady-state approximation for $R_2\cdot$:

$$\frac{d(R_2\cdot)}{dt} = k_7(N\cdot) - k_3(R_2\cdot)(ZH) \cong 0 \tag{42}$$

$$\therefore$$

$$(R_2\cdot) = \frac{k_7(N\cdot)}{k_3(ZH)} . \tag{43}$$

Whence, from (41) and (43),

$$\frac{(R_2H)}{(R_1H)} \cong \frac{k_6}{k_5} + \frac{k_7}{k_5(ZH)} . \tag{44}$$

The relative proportion of R_2H should decrease somewhat as the original concentration of ZH is increased.

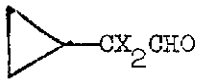
The important conclusions which can be drawn from the above discussion are the following: As the concentration of the reactive chain-transfer agent is increased, the ratio of the products $(R_2H)/(R_1H)$ is

predicted to remain constant in only two instances, in the case where the products are formed from only one (presumably nonclassical) intermediate and in the case of rapidly equilibrating (presumably classical) intermediates. In all other instances, when more than one intermediate are involved regardless of their electronic nature, the ratio of products is predicted to change in the direction of less R_2H as the initial concentration of the reagent ZH is increased. Thus an appropriate product study should enable one to distinguish between Cases 1b and 3 (schemes 14b and 17) on the one hand and Cases 1a, 2, and 4 (schemes 14a, 15, and 18) on the other.

Further evidence of a different nature which could also be brought to bear on distinguishing among schemes 14-18 would be an appropriate kinetic study telling on the rate of formation of the initial intermediate. Presumably the initially-formed resonance-stabilized radical intermediate of schemes 17 and 18 would be produced at a faster measurable rate than the classical strained radical intermediate of schemes 14-16 as determined by comparison of the rates of formation of intermediates with appropriate model compounds in an appropriate reaction.

In fact it was hoped that a combination of these two types of approaches, an appropriate rate study and an appropriate product study, would enable us to determine both the nature and the number of intermediates involved in the free-radical interconversion of cyclopropylcarbinyl and allylcarbinyl derivatives in the two systems of immediate interest to us: the unsubstituted cyclopropylcarbinyl system (XVIIIa and XIXa) and the dimethylcyclopropylcarbinyl system (XVIIIb and XIXb).

It was decided that an appropriate product study would be the investigation of the hydrocarbon product distributions resulting from the t-butyl-peroxide-initiated decarbonylations of cyclopropylacetaldehyde (XXa) and dimethylcyclopropylacetaldehyde (XXb) in the presence of varying concentrations of benzyl mercaptan as a chain-transfer agent.



XX

a) x=H
b) $x=CH_3$

These systems were chosen for study because the advantages of unequivocally generating free radicals of known structure by decarbonylation had been recently demonstrated in these laboratories (36), because the starting aldehydes were relatively readily accessible, and because the catalytic potency of benzyl mercaptan as a chain-transfer agent in the decarbonylation of aldehydes had been demonstrated (37).

For the rate study it was necessary to choose a system in which the desired radicals would be generated unequivocally in a measurable rate-determining step without interference from side reactions, such as the polar decompositions sometimes encountered in the reactions of peroxides (11,26) and peresters (25,38,39). The decomposition of appropriate azo compounds (40) seemed a reasonable candidate for such a system, but the starting materials are only difficultly accessible. Instead it was decided to achieve our ends by determining the chain-transfer constants relative to polymerizing styrene (41) of methylcyclopropane, isopropylcyclopropane, and appropriate model hydrocarbon compounds. Despite its

simplicity and the ready availability of starting materials, this technique as a means of measuring the relative reactivities of hydrocarbons toward the polystyryl radical has not been applied since the classic study of Gregg and Mayo (42), possibly because the original investigations were industrially oriented and the low chain-transfer constants of hydrocarbons in general rendered their use as polymerization regulators inefficient and expensive. The theory of chain transfer of a growing polymer with solvent has been discussed elsewhere (41) and will not be elaborated in this thesis. Suffice it to say that the chain-transfer constant relative to polymerizing styrene for a given hydrocarbon solvent represents the ratio of the rate constant for hydrogen abstraction from solvent by the growing polymer radical to the rate constant for addition of the polymer radical to monomer; i.e., by definition

$$C = \frac{k_{tr}}{k_p} \qquad (45)$$

Thus at a given temperature the relative rates of free-radical hydrogen abstraction from the pertinent hydrocarbons will be given by the ratio of their chain-transfer constants.

The results of the decarbonylation and chain-transfer studies are presented, discussed, and interpreted later in this thesis.

Previous Studies of Substituted Cyclopropylcarbinyl-Allylcarbinyl Radicals

To date there have been few investigations of reactions possibly involving substituted cyclopropylcarbinyl and/or allylcarbinyl free radicals.

The first study to deal with a substituted cyclopropylcarbinyl free radical is one which has already been described in an earlier section (pp. 9-12), the investigation by Overberger and co-workers of the decomposition of the azo-bis-nitrile derived from methyl cyclopropyl ketone (20-22).

Schuster (15) examined the di-t-butyl peroxide-initiated decarbonylation of dimethylcyclopropylacetaldehyde (XXb) at a temperature of 130-140°. When XXb was decarbonylated neat or in diphenyl ether solution, there was found only one monomeric hydrocarbon product, 2-methyl-2-pentene, the rearranged allylcarbinyl product. When, however, the decarbonylation was carried out in the presence of an approximately equimolar amount of benzyl mercaptan, the hydrocarbon product was found to consist of both 2-methyl-2-pentene and isopropylcyclopropane in a ratio of 41:9. These results will be discussed later in this thesis in conjunction with the present studies of the decarbonylation of this aldehyde.

Howden (43) has examined a variety of reactions in which diphenylcyclopropylcarbinyl (XVIIIc) and/or (γ,γ-diphenylallyl)-carbinyl free radicals (XIXc) might be expected to be intermediates. As would be expected, only products with cyclopropylcarbinyl or allylcarbinyl skeletons but none

with a cyclobutyl skeleton were isolated. In particular, it will be most instructive to consider the following results obtained by Howden.

The thermal decomposition in chlorobenzene of the perester t-butyl (γ,γ-diphenylallyl)-peracetate, $(C_6H_5)_2C{=}CHCH_2CH_2CO_2OC(CH_3)_3$, was studied at 110° in the presence of varying amounts of the extremely active hydrogen donor tributyltin hydride, and the distribution of monomeric hydrocarbon products was determined in each case. As the initial concentration of the hydride was varied from 0.056 M to 0.56 M, initial perester concentration being maintained constant, the ratio of the rearranged cyclopropylcarbinyl product diphenylcyclopropylmethane to the unrearranged allylcarbinyl product 1,1-diphenyl-1-butene remained essentially invariant at 5:95 (actually a slight increase from 4.5:95.5 to 6:94 was observed). This is a kinetic situation analogous to that which was analyzed in the last section (equations 20-44, pp. 24-29), the possible radical intermediates under consideration being the allylcarbinyl radical XIXc ($R_1\cdot$), the cyclopropylcarbinyl radical XVIIIc ($R_2\cdot$), and the nonclassical diphenylhomoallyl radical XVIIc ($N\cdot$). From our analysis we see that the constant ratio of products thus obtained can be explained as resulting from a rapid equilibrium of two (possibly classical) radicals (Case 1b) or from a single (presumably nonclassical) radical reacting to give both products (Case 3).

Next the rate of decomposition of t-butyl (γ,γ-diphenylallyl)-peracetate in chlorobenzene at 109.7° ($k_1 = 7.7\times10^{-5}$ sec^{-1}) was found to be only 1.4 times greater than the rate of decomposition of its saturated analog, t-butyl 5,5-diphenylperpentanoate ($k_1 = 5.5\times10^{-5}$ sec^{-1}), which decomposed at approximately the same rate as t-butyl peracetate

(k_1 = 5.3x10^{-5} sec^{-1}). In view of the large rate accelerations observed by Bartlett and Hiatt (25) for concerted perester decompositions, this lack of rate enhancement precluded the formation of the resonance-stabilized diphenylhomoallyl radical (XVIIc) in the initial step; instead the classical (γ,γ-diphenylallyl)-carbinyl radical (XIXc) must have been the radical initially generated.

Finally the effect of temperature variation on the ratio of products obtained from the decomposition of t-butyl (γ,γ-diphenylallyl)-peracetate in the presence of tributyltin hydride was studied; all other reaction variables being maintained constant, a change in the temperature of decomposition from 110° to 150° produced only a negligible, if any, change in the product ratio of diphenylcyclopropylmethane to 1,1-diphenyl-1-butene.

To explain this last result (44), let us consider the two schemes 46 and 47 still consistent with all the other results presented above. In these schemes "A·" denotes the radical XIXc; "C·" denotes the radical XVIIIc, "N·" denotes the radical XVIIc; "A" denotes the allylcarbinyl product; "C" denotes the cyclopropylcarbinyl product; "K" denotes the equilibrium constant for the isomerization of XIXc to XVIIIc; the small "k's" denote the specific rate constants for the processes indicated. The argument to be presented can, of course, be generalized to other similar situations.

$$(C_6H_5)_2C - CHCH_2CH_2\overset{O}{\overset{\|}{C}}-O-t\text{Bu} \longrightarrow A\cdot$$

$$A \xleftarrow[Bu_3SnH]{k_A} A\cdot \underset{k_r}{\overset{k_r}{\rightleftharpoons}} C\cdot \xrightarrow[Bu_3SnH]{k_C} C \qquad (46)$$

$$A\cdot \xrightarrow{k_x} N\cdot \xrightarrow[Bu_3SnH]{k'_A} A \qquad (47)$$

$$N\cdot \xrightarrow[Bu_3SnH]{k'_C} C$$

Scheme 46 represents the rapid equilibrium of two radicals, each of which can react with the reactive hydrogen donor to yield the corresponding product (presumably essentially irreversibly). For this situation we may write

$$\frac{\text{rate of formation of C}}{\text{rate of formation of A}} = \frac{\frac{dC}{dt}}{\frac{dA}{dt}} = \frac{k_C(C\cdot)(Bu_3SnH)}{k_A(A\cdot)(Bu_3SnH)} = \frac{k_C(C\cdot)}{k_A(A\cdot)}$$

$$= \frac{k_C}{k_A} K = \frac{dC}{dA} \cong \text{ratio of products } \frac{C}{A}; \qquad (48)$$

$$\underline{\text{i.e.}}, \quad \frac{k_C}{k_A} K = \text{ratio of products.} \qquad (49)$$

Now Howden (45) has estimated the enthalpy of isomerization for the rearrangement of the (γ,γ-diphenylallyl)-carbinyl radical to the diphenylcyclopropylcarbinyl radical as -24.5 kcal/mole. For so substantial an enthalpy difference it follows that there will be a large change in the equilibrium constant K as the temperature is raised from 110° to 150° (approximately, log K = 13.9 at 110°; log K = 12.6 at 150°). The energies of activation for free-radical hydrogen abstraction reactions are generally small, usually in the range 5-10 kcal/mole (46); the energy of activation for abstraction of hydrogen from tributyltin hydride might be even smaller.

At any rate the difference in activation energy for abstraction of hydrogen from tributyltin hydride by the (γ,γ-diphenylallyl)-carbinyl radical or the diphenylcyclopropylcarbinyl radical should be quite small, not more than two or three kcal/mole. Thus there should not be much change in the ratio of rate constants k_C/k_A over the temperature range 110°-150°. Therefore, from the latter conclusion and equation 49, one should expect a measurable (possibly large) change in the ratio of products C/A as the temperature is increased from 110° to 150°. This is contrary to the observed results; hence, scheme 46, the rapid equilibrium of classical radicals, does not satisfactorily explain the lack of a temperature effect upon the ratio of products.

In the other alternative, scheme 47, the initially-formed allylcarbinyl radical isomerizes to the nonclassical diphenylhomoallyl radical from which both cyclopropylcarbinyl and allylcarbinyl products are formed. In this case we may write

$$\frac{\frac{dC}{dt}}{\frac{dA}{dt}} = \frac{k'_C(N\cdot)(Bu_3SnH)}{k'_A(N\cdot)(Bu_3SnH)} = \frac{k'_C}{k'_A} \simeq \text{ratio of products } \frac{C}{A} \quad . \tag{50}$$

The ratio of rate constants approximates the ratio of products. As above, the difference in activation energy for abstraction of hydrogen from tributyltin hydride by either reactive site of the homoallyl radical is expected to be quite small. Hence the ratio of rate constants k'_C/k'_A should change only slightly over the 40°-temperature range from 110°-150°. The ratio of products according to this scheme is thus predicted to remain essentially constant from 110° to 150°, as was observed. We conclude that Howden's observations on the diphenylcyclopropylcarbinyl sys-

tem are consistent with the intervention of a delocalized nonclassical diphenylhomoallyl radical as the agent for the interconversion of the allylcarbinyl and cyclopropylcarbinyl skeletons.

RESULTS, DISCUSSION, AND CONCLUSIONS

Decarbonylation Results and Discussion

General: In the experiments to be described below, the aldehydes of interest were mixed together with varying amounts of benzyl mercaptan; the reaction vessel was heated to the desired temperature; t-butyl peroxide was added to initiate the reaction (and later as needed); and the decarbonylation was allowed to proceed until gas evolution became interminably slow. Gaseous products non-condensable at -77° were collected over mercury and examined by infra-red spectroscopy; the low-boiling liquid products, including the monomeric hydrocarbon products of special interest, distilled out of the reaction flask into a Dry Ice-cooled trap and were examined by v.p.c.; the residue in the reaction flask was also examined by v.p.c. Details are given in the Experimental Section.

In general the gaseous products were found to consist of carbon monoxide (from decarbonylation of the aldehyde), methane (from reaction of the methyl radicals resulting from fragmentation of the t-butoxy radicals produced by decomposition of the initiator), an unidentified gas (probably olefinic) absorbing near 890 cm^{-1} (47), and occasionally carbon dioxide (origin uncertain).

In addition to monomeric hydrocarbons the low-boiling liquid fraction generally contained acetone (from fragmentation of t-butoxy radicals), t-butyl alcohol (resulting from hydrogen abstraction by t-butoxy radicals), recovered di-t-butyl peroxide, and, on occasion, unidentified components.

The residue in the reaction flask would consist of recovered starting materials, high-boiling unidentified liquid components, and a white solid, possibly dibenzyl disulfide.

These results are those which would be normally expected for the di-t-butyl peroxide-initiated decarbonylation of an aldehyde, a reaction which has recently been discussed in great detail by Schuster (48), whose discussion will not be repeated here. In the presence of benzyl mercaptan, a potent hydrogen donor, it has been suggested (49, 37,48) that the chain-propagation steps for decarbonylation of an aldehyde are as indicated by equations 51-53.

$$R'S\cdot + RCHO \longrightarrow R'SH + RCO\cdot \qquad (51)$$

$$RCO\cdot \longrightarrow R\cdot + CO \qquad (52)$$

$$R\cdot + R'SH \longrightarrow RH + R'S\cdot \ . \qquad (53)$$

The major products arise via abstraction of hydrogen from benzyl mercaptan. The extent of decarbonylation probably depends upon the relative rate of step 52 compared to the reverse of step 51. Loss of carbon monoxide from an acyl radical can be a slow process (50).

In the results presented below we shall dwell only upon the identity of the monomeric hydrocarbon products, resulting from step 53.

Heptanal.--The decarbonylation of heptanal was carried out to serve as a model for the decarbonylations of dimethylcyclopropylacetaldehyde and cyclopropylacetaldehyde. The decarbonylation of heptanal at 122-138° in the presence of benzyl mercaptan led to the formation of small amounts of n-hexane (2-3% yield), in accord with the results of

Barrett and Waters (37). This small yield of hydrocarbon is probably due to a slow decarbonylation step 52, as discussed above, the resulting n-hexyl radical being a high-energy primary radical.

Cyclopropylacetaldehyde.--It was hoped that the decarbonylation of cyclopropylacetaldehyde in the presence of benzyl mercaptan would lead to the formation of both 1-butene and methylcyclopropane, whose relative concentrations could be determined as a function of initial mercaptan concentration for reasons discussed in the second section of the Introduction, above. However, the di-t-butyl peroxide-initiated decarbonylation of cyclopropylacetaldehyde at 109-124° in the presence of a large excess of benzyl mercaptan apparently yielded only 1-butene and no methylcyclopropane, although as much as 1% of the amount of 1-butene might conceivably have gone undetected. From results to be presented below, there is now reason to believe that a more diligent search might have revealed the presence of a trace of methylcyclopropane among the reaction products. Even the presence of a trace of methylcyclopropane, however, would not have rendered feasible the use of this system for a product study of the type desired. The elucidation of the nature of the unsubstituted cyclopropylcarbinyl-allylcarbinyl radical intermediates had to await the gathering of the kinetic data presented in the next section.

The isolation of 1-butene as the only monomeric hydrocarbon product from this reaction was in accord with the similar result by Schuster (15) for the decarbonylation of the neat aldehyde at higher temperatures and with the trend noted earlier that the extent of

allylcarbinyl product upon production of a "cyclopropylcarbinyl" radical increases with increasing temperature. This result in itself is compatible with the formation of the product from either classical or nonclassical radicals.

Allylcarbinyl compounds are known to be thermodynamically more stable than the corresponding cyclopropylcarbinyl compounds (2). Furthermore the enthalpy of isomerization of a hypothetical cyclopropylcarbinyl free radical XVIIIa to the allylcarbinyl radical XIXa has been estimated by Schuster (51) as -7.9 kcal./mole and by Howden (45) as -16.5 kcal./mole. The driving force for the formation of 1-butene via such an isomerization at 110° is readily apparent.

The formation of allylcarbinyl products from a nonclassical homoallyl radical XVIIa should also be favored over the formation of cyclopropylcarbinyl products. For the favored configuration of XVIIa noted earlier (33) one can calculate the LCAO molecular orbital wave functions

$$\psi_1 = 0.62787\ \chi_1 + 0.70699\ \chi_2 + 0.32549\ \chi_4 ,$$

$$\psi_2 = 0.46023\ \chi_1 - 0.88780\ \chi_4 ,$$

and $$\psi_3 = 0.62787\ \chi_1 - 0.70699\ \chi_2 + 0.32549\ \chi_4$$

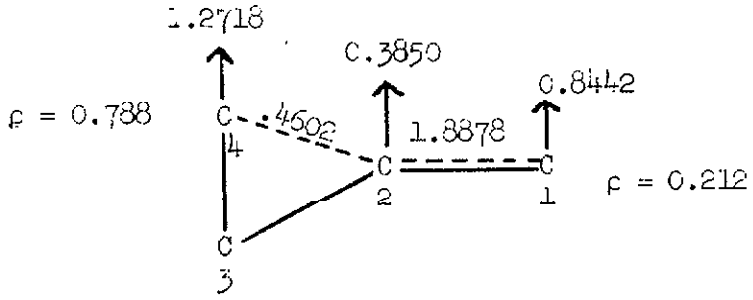
(where the "χ's" stand for atomic orbitals centered on carbon atoms 1, 2, and 4 of XVIIa) which correspond to the energy levels

$$E_1 = \alpha + 1.126\ \beta ,$$

$$E_2 = \alpha$$

and $$E_3 = \alpha - 1.126\ \beta$$

and from which one can calculate the bond orders, Coulson free-valence indices, and spin densities as indicated in diagram XXI (52).



XXI (R_{12} = 1.34 Å; $R_{23} = R_{34}$ = 1.54 Å; R_{24} = 2.25Å)

It is evident that the spin density is largely located on C_4 (79%), to which extent the homoallyl radical should resemble the allylcarbinyl radical. Comparison of the free-valence indices likewise indicates that the free-radical reactivity of the nonclassical species is largely located on C_4, favoring the formation of allylcarbinyl products in a free-radical reaction.

Dimethylcyclopropylacetaldehyde.--The di-t-butyl peroxide-initiated decarbonylation of dimethylcyclopropylacetaldehyde at 125° has been carried out in the presence of various initial concentrations of benzyl mercaptan. The results, such as they are, are summarized in Table 4.

At the outset it must be admitted that these results do not represent the acme of desired accuracy. The aldehyde used in these experiments was only 90+ %-pure. It turned out that acetone (from the decomposition of t-butyl peroxide) and isopropylcyclopropane were unresolvable on the v.p.c. column (diisodecyl phthalate packing) used

TABLE 4

Hydrocarbon Product Distributions from the Decarbonylation of Dimethylcyclopropylacetaldehyde

Run No.	Wt., g.[a] RCHO	Wt., g.[b] DTBP	Molar ratio[c] R'SH/RCHO	Rel. %,[d] 2-methyl-2-pentene	Rel. %,[e] acetone-isopropyl-cyclopropane
2	0.531	1.43	0.360	94.6	5.4
5	0.408	2.21	1.005	62.8[f] 54.4[g]	37.1[f] 45.6[g]
1	0.632	1.19	1.04	—[h]	—[h]
6[i]	0.89	—	1.07	82	18
4	0.225	1.22	8.16	—[k]	—[k]
3	0.467	1.80	8.16	71	29

(a) Corrected for purity of starting aldehyde.

(b) Di-t-butyl peroxide, initiator.

(c) Moles mercaptan/moles aldehyde. This molar ratio is approximately equal to the concentration ratio for the same compounds. Assuming no change of volume upon mixing, the original mercaptan concentration changes from approximately 1.9 M to approximately 7.4 M as the molar ratio changes from 0.360 to 8.16.

(d, e) Relative areas under the v.p.c. peaks assigned to 2-methyl-2-pentene and acetone-isopropylcyclopropane, respectively.

(f) First half of experiment.

(g) Second half of experiment.

(h) Not known which v.p.c. peak to assign to isopropylcyclopropane.

(i) See Reference 15.

(k) Not enough hydrocarbon products trapped to analyze by v.p.c.

to analyze the low-boiling liquid fraction. Further, as experience in analyzing the liquid fraction increased, the number of unidentified components likewise increased; and it is possible that one or more of these unidentified components might be other monomeric hydrocarbon products. Also, it would appear from Run 5 that acetone was not formed uniformly in a given experiment, more being produced toward the end of a run than at the beginning. Finally, on account of the small quantities of starting aldehyde utilized in each run, the percentage conversions to products were larger (from the necessity to produce measurable quantities of products) than would be theoretically desirable (cf. kinetic Cases 1-4, pp. 24-29).

Nevertheless, despite these difficulties, if it be assumed that the trend of acetone formation is similar from one run to the next, one can note a definite trend from Run 2 to Run 0 to Run 3 for an increase in the amount of isopropylcyclopropane relative to 2-methyl-2-pentene as the molar ratio of benzyl mercaptan to dimethylcyclopropylacetaldehyde is increased. In fact, considering only Runs 2 and 3 and recalling the kinetic law predicted for the case of an irreversible isomerization of one classical radical to another (Case 1a, p.24), we note that the product of the concentration of mercaptan with the ratio of products (2-methyl-2-pentene: isopropylcyclopropane) in Run 2 is 1.9 x 94.6/5.4 = 33.3 and in Run 3 is 7.4 x 71/29 = 18.1. The deviation from the rate law predicted for Case 1a in our case is less than that observed by Seubold (34) when he concluded that the rearrangement observed upon production of the neophyl radical (β,β-dimethylphenethyl

radical) could best be explained by an irreversible isomerization of the neophyl radical to the α,α-dimethylphenethyl radical.

Thus it seems fair to state that the results of the above product study of the dimethylcyclopropylcarbinyl system are most consonant with the interpretation that an irreversible isomerization of the classical dimethylcyclopropylcarbinyl radical to the classical (γ.γ-dimethyallyl)-carbinyl radical is responsible for the observed hydrocarbon product distributions. At any rate the evidence thus far presented definitely must be said to favor the intervention of more than one radical intermediate leading to products in this system (schemes 14a, 15, or 18). The only reservation, as noted above, concerns the absolute accuracy of these results; but it will be noted in the next section that further kinetic data on the dimethylcyclopropylcarbinyl system leads to the same conclusion concerning the nature of the radical intermediates.

Chain-Transfer Results and Discussion

The results pertinent to the determination of the chain-transfer constants relative to polymerizing styrene at 79.1° of neopentane, n-butane, methylcyclopropane, 2,3-dimethylbutane, and isopropylcyclopropane are summarized in Tables 5-10. Exact details as to the calculations of the quantities listed in these tables may be found in the Experimental Section. Here it need only be mentioned that it has been shown (41,42) that the chain-transfer constant of a hydrocarbon solvent with styrene may be calculated from a knowledge of the degree of polymerization of styrene for a given sample according to Equation 54:

$$\frac{1}{\overline{P}} = \frac{1}{\overline{P}_o} + C\,\frac{[S]}{[M]} \qquad (54)$$

where $\overline{P}$ represents the degree of polymerization of styrene for a given sample; $\overline{P}_o$ represents the degree of polymerization of styrene in the absence of any external transfer agent; C represents the chain-transfer constant of a given transfer agent; and [S] and [M] represent respectively the concentrations of hydrocarbon solvent (the transfer agent) and styrene monomer.

The transfer constants themselves are summarized in Table 11 along with the transfer constants of n-heptane and t-butylbenzene at 79.1°, as calculated from the data of Gregg and Mayo (42).

For a hydrocarbon solvent, the bulk chain-transfer constant (measured) is the sum of chain-transfer constants for each individual hydrogen atom in the molecule (41); hence, it is possible to calculate from the transfer data in Table 11 transfer constants and thus relative reactivities for individual hydrogen atoms of interest. These results are presented in Table 12.

It will be noted from Tables 6-11 that the mean deviations of the transfer constants determined are on the average approximately 20 to 25% of the value of the respective transfer constants. Twenty-five per cent represents a fair estimate as to the accuracy of the absolute value of the chain-transfer constants determined in this work. This accuracy is comparable to that for many of the values determined by Gregg and Mayo (42); in particular, all their relatively low transfer constants. The relative reactivities of Table 12 are

TABLE 5

Degree of Polymerization of Styrene at 79.1°

Sample No.	$[\eta]^a$	$\overline{M}_n{}^b$	$\overline{P}_o{}^c$	$\frac{1}{\overline{P}_o} \times 10^5$	% Polymerization
161-4	2.12	468000	4500	22.24	10.9
161-5	2.16	478000	4600	21.75	11.5
161-6	2.28	517000	4970	20.12	9.0
161-7	2.11	466000	4480	22.33	9.5
161-8	2.01	433000	4170	24.00	20.4
190-1	2.27	513000	4930	20.28	9.8
190-2	2.43	564000	5420	18.45	13.6
190-3	2.14	473000	4550	21.97	9.6
224-4	2.06	451000	4340	23.06	9.6
240-6	2.15	477000	4590	21.81	9.6
Ave.	2.17	484000	4650	21.60	—

(a) Intrinsic viscosity of a dilute solution of polystyrene sample in benzene. See Experimental Section.

(b) Number average molecular weight of polystyrene sample. See Experimental Section.

(c) Average degree of polymerization of polystyrene sample. See Experimental Section.

TABLE 6

Chain-Transfer Constant of Neopentane with Styrene at 79.1°

Sample No.	$\frac{[NP]}{[Styrene]}$ [a]	% Polymerization	$[\eta]$ [b]	$\bar{M}_n$ [c]	$\bar{P}$ [d]	$\frac{1}{\bar{P}} \times 10^5$	$C \times 10^5$
277-1	0.358	12.1	2.10	462000	4450	22.49	2.48
277-2	1.11	9.8	2.02	438000	4220	23.72	1.91
277-3	3.08	5.2	1.62	329000	3160	31.61	3.25
Ave.							2.5 ± 0.5 [e]

(a) Ratio of concentrations of neopentane to styrene corrected for amount of neopentane in vapor phase.

(b) Intrinsic viscosity. See Experimental Section.

(c) Number average molecular weight. See Experimental Section.

(d) Average degree of polymerization. See Experimental Section.

(e) Average chain-transfer constant and mean deviation.

TABLE 7

Chain-Transfer Constant of n-Butane with Styrene at 79.1°

Sample No.	$\frac{[\text{Butane}]}{[\text{Styrene}]}$ [a]	$[\eta]$ [b]	$\bar{M}_n$ [b]	$\bar{P}$ [b]	$\frac{1}{\bar{P}} \times 10^5$	$C \times 10^5$	% Polymerization
224-2	3.05	0.62	86000	826	121.08	32.6	0.98
190-7	1.58	1.34	249000	2400	41.70	12.7	1.46
190-8	1.86	1.30	238000	2290	43.65	11.9	1.56
190-6	1.56	1.38	250000	2410	41.58	12.8	2.94
190-5	0.92	1.84	385000	3700	27.01	5.92	5.57
190-4	0.40	1.98	425000	4090	24.46	7.19	5.75
224-1	1.30	1.84	384000	3700	27.05	4.19	7.32
224-3	0.73	1.99	429000	4130	24.23	3.61	9.65
190-10	4.36	1.67	336000	3230	30.95	2.14	14.3
Best guess [c]							3.3 ± 0.8 [c]

(a) Ratio of concentrations corrected for amount of n-butane in vapor phase.

(b) See Footnotes to Table 6.

(c) Average chain-transfer constant and mean deviation for Samples 224-1, 224-3, and 190-10.

TABLE 8

Chain-Transfer Constant of Methylcyclopropane with Styrene at 79.1°

Sample No.	$\frac{[MCP]}{[Styrene]}^{a}$	% Polmer-ization	$[\eta]^{b}$	$\bar{M}_n{}^{b}$	$\bar{P}^{b}$	$\frac{1}{\bar{P}} \times 10^5$	$C \times 10^5$
240-1	0.48	12.5	2.08	454000	4370	22.89	2.71
240-2	0.91	11.8	1.86	392000	3770	26.55	5.45
240-3	2.02	10.1	1.82	379000	3650	27.41	2.88
240-4	3.25	8.5	1.60	317000	3050	32.82	3.45
240-5	2.80	10.2	1.56	306000	2940	33.98	4.41
Ave.							3.8 ± 0.9^{b}

(a) Ratio of concentrations of methylcyclopropane to styrene corrected for amount of methylcyclopropane in vapor phase.

(b) See Footnotes to Table 6.

TABLE 9

Chain-Transfer Constant of 2,3-Dimethylbutane with Styrene at 79.1°

Sample No.	$\frac{[DMB]}{[Styrene]}$[a]	% Polmerization	$[\eta]$[b]	$\bar{M}_n$[b]	$\bar{P}$[b]	$\frac{1}{\bar{P}} \times 10^5$	$C \times 10^5$
308-2	0.72	20.9	2.00	432000	4150	24.08	3.46
308-3	1.56	16.1	1.88	396000	3810	26.26	2.99
308-5	0.38	24.4	1.99	429000	4120	24.24	7.00
Ave.							4.5 ± 1.7[b]

(a) Ratio of concentrations of 2,3-dimethylbutane to styrene corrected for amount of 2,3-dimethylbutane in vapor phase.

(b) See Footnotes to Table 6.

TABLE 10

Chain-Transfer Constant of Isopropylcyclopropane with Styrene at 79.1°

Sample No.	$\frac{[ICP]}{[Styrene]}$[a]	% Polmerization	$[\eta]$[b]	$\bar{M}_n$[b]	$\bar{P}$[b]	$\frac{1}{\bar{P}} \times 10^5$	$C \times 10^5$
332-1	0.38	24.7	2.13	471000	4530	22.07	1.22
332-2	0.76	24.5	2.12	468000	4500	22.24	0.84
Ave.							1.0 ± 0.2[b]

(a) Ratio of concentrations of isopropylcyclopropane to styrene corrected for amount of isopropylcyclopropane in vapor phase.

(b) See Footnotes to Table 6.

TABLE 11

Chain-Transfer Constants of Some Hydrocarbons with Styrene at 79.1°

Hydrocarbon	Transfer Constant $C \times 10^5$
Neopentane	2.5 ± 0.5
n-Butane	3.3 ± 0.8
Methylcyclopropane	3.8 ± 0.9
2,3-Dimethylbutane	4.5 ± 1.7
Isopropylcyclopropane	1.0 ± 0.2
n-Heptane	$6.3 \pm ?$ [a]
t-Butylbenzene	1.8 ± 0.8 [a]

(a) Calculated from the data of Gregg and Mayo (42).

TABLE 12

Relative Reactivities of Selected Hydrocarbon Hydrogen Atoms toward the Polystyryl Radical at 79.1°

Hydrocarbon	Hydrogen Atom	Transfer Constant per Hydrogen Atom $C \times 10^5$	Relative Reactivity
Neopentane	primary	0.208	1.00
n-Butane	secondary	0.512[a]	2.46
Methylcyclopropane	methyl	1.27[b]	6.10
2,3-Dimethylbutane	tertiary	1.00[c]	4.80
Isopropylcyclopropane	tertiary	negligible[d]	negligible[d]

(a) Calculated assuming relative reactivity of a n-butane primary hydrogen atom is same as that of a neopentane hydrogen atom.

(b) Calculated assuming negligible transfer constant for cyclopropane ring hydrogens.

(c) Calculated assuming relative reactivity of a 2,3-dimethylbutane primary hydrogen atom is same as that of a neopentane hydrogen atom.

(d) Calculated assuming same transfer constant for methyl hydrogens as for a neopentane hydrogen.

undoubtedly more accurate than the transfer constants from which they are derived, inasmuch as ratios of quantities are usually more reliable than the values of the quantities themselves.

As independent checks upon the validity of the results determined in this work, the following should be noted. From Table 11, the chain-transfer constant of neopentane at 79.1° (2.5×10^{-5}) is precisely 4/3 that of the constant estimated from the results of Gregg and Mayo (42) for t-butylbenzene at the same temperature (1.8×10^{-5}). This is the result that would be predicted, as Seubold (34) has shown that the neophyl radical is generated without anchimeric assistance and neopentane contains 12 reactive protons to 9 for t-butylbenzene. Secondly, the data of Table 12 can be used to calculate the bulk chain-transfer constants for other normal hydrocarbons with styrene at 79.1°. In particular, the chain-transfer constant for n-heptane at 79.1° should be equal to six times the transfer constant for a neopentane hydrogen atom plus ten times the transfer constant for a n-butane secondary hydrogen atom; i.e., $6 \times 0.208 \times 10^{-5} + 10 \times 0.512 \times 10^{-5} = 1.2 \times 10^{-5} + 5.1 \times 10^{-5} = 6.3 \times 10^{-5}$. Comparison with Table 11 reveals that 6.3×10^{-5} is exactly the value of the transfer constant of n-heptane at 79.1°, as determined from the data of Gregg and Mayo (42). This exact correspondence is undoubtedly fortuitous, but nevertheless encouraging. Thirdly the relative reactivity of a methylcyclopropane methyl hydrogen in comparison with a neopentane hydrogen is of the same order of magnitude as the same quantity determined for methylcyclopropane and neopentane hydrogen atoms toward the t-butoxy and chlorine radicals by Walling and Fredricks (9) and reported above in Tables 2 and 3, pp. 16 and 17 . Finally, from

Table 12, the relative reactivities of typical primary, secondary, and tertiary carbon-hydrogen bonds toward the polystyryl radical in solution at 79.1° as determined in this study (1.00:2:46:4.80) are quite similar to the liquid-phase relative reactivities of primary, secondary, and tertiary carbon-hydrogen bonds towards the chlorine radical at 80° (1.0:2.4:3.6), as interpolated from Walling's Table 8.3 (53) which was derived from the results of Hass, McBee, and Weber (54). The polystyryl radical appears to be slightly more selective than the chlorine radical, as would be expected.

We consider further now some of the specific results from Tables 6-12.

n-Butane.--The results for n-butane listed in the last two columns of Table 7 constitute a definite and unexpected quasi exponential correlation between per cent polymerization and apparent chain-transfer constant; the greater the former, the lower the latter. This phenomenon is contrary to theory; the chain-transfer constant for a given solvent should be independent of the extent of conversion of styrene monomer to polymer. Fortunately this behavior was observed only in this one case, the relationship between per cent polymerization and chain-transfer constant for all the other hydrocarbons examined in this study showing neither an inverse nor a direct correlation to any extent, as may be seen by inspection of Tables 6, 8, 9, and 10. The most logical explanation for the quasi-exponential relationship found in the case of n-butane is that the n-butane may have contained some trace impurities which were far more active as transfer agents but which were quickly consumed in the course of the polymerization. This would account for the low molecular

weights and consequent high apparent chain-transfer constants observed for very low percentage conversions to polymer as well as for the nature of the dependence. According to this reasoning the apparent chain-transfer constants determined at higher percentage conversions should be more reliable. It is for this reason that only the last three values for the transfer constant listed in Table 7 have been used to determine the average chain-transfer constant for n-butane at 79.1°. And as was pointed out above, the value so determined (3.3×10^{-5}) seems eminently reasonable, correlating very well with other independent data.

Methylcyclopropane.—It is our intent here to show that the transfer constant determined for methylcyclopropane (3.8×10^{-5} at 79.1°; cf., Table 8) in this study is a fair measure of the rate of abstraction of hydrogen atoms from the methyl group of methylcyclopropane relative to the rate of polymer growth.

If the growing polystyryl radical were to react with methylcyclopropane by a ring-opening radical displacement on a ring carbon atom, the result would be the formation of an alkyl radical more reactive than the polystyryl radical itself. Such a radical would in all probability continue the chain of polymer growth by adding to a new styrene monomer unit to produce another polystyryl radical and would thus have no effect whatever on the determination of the transfer constant. The same would be true for a radical formed by addition of the polystyryl radical to the double bond of possible olefinic impurities in the methylcyclopropane. (The methylcyclopropane used in these experiments was shown by v.p.c. to be better than 99% pure, the

most likely contaminant being 1-butene.) Thus we need consider only processes which by atom transfer could terminate a kinetic chain of polymer growth.

The only such process left to eliminate as a possible serious source of error is chain-transfer by the ring protons of methylcyclopropane. But it has been shown in many studies that hydrogen atoms may be atstracted from a cyclopropane ring or that a cyclopropyl free radical may be generated only with great difficulty (11, 15, 46, 55-57). In particular the results of Trotman-Dickenson and Steacie (46) show that methyl radicals will abstract hydrogen from cyclopropane only one-tenth as readily as from n-butane. Hence all the ring protons in methylcyclopropane together, from the results of Table 11, would be expected to contribute to the bulk chain-transfer constant of methylcyclopropane to the extent of no more than 0.3×10^{-5}. Such a contribution is effectively negligible for our considerations; for it is far less than the expectancy for reasonable experimental error in the value of the transfer constant and would not affect the qualitative and barely affect the quantitative results of Table 12. Hence for all practical considerations in this thesis we can ignore chain transfer by the ring protons of a cyclopropane ring, both in this instance and in the case of isopropylcyclopropane.

Thus it seems reasonable that only the methyl hydrogens of methylcyclopropane contribute to its chain-transfer constant; and this conclusion leads to the relative reactivity value of 6.10 for a methylcyclopropane hydrogen relative to a neopentane hydrogen (toward the polystyryl radical), as indicated in Table 12. A methylcyclopropane hydrogen is seen to be more than twice as reactive as a secondary hydrogen and

more reactive even than a tertiary hydrogen toward the polystyryl radical. This result, coupled with the relative reactivity results of Walling and Fredricks (9) and the results of Hart and Cipriani (26) on the decomposition of cyclopropaneacetyl peroxide discussed in the Introduction, can leave but little doubt that radical abstraction of a methyl hydrogen from methylcyclopropane is anchimerically assisted. Indeed the greater chain-transfer constant for methylcyclopropane than for isopropylcyclopropane should lead to the same conclusion. Since the initially formed cyclopropylcarbinyl free radical is generated with rate enhancement, it would seem most probable that this intermediate should be represented as the nonclassical homoallyl radical XVIIa.

Isopropylcyclopropane.—To be fair, it must be admitted that as yet there is not sufficient data on the chain-transfer constant of isopropylcyclopropane. Nevertheless, in contrast to the conclusion just reached about the nature of the unsubstituted cyclopropylcarbinyl radical initially generated, there is no evidence in Tables 11 or 12 to justify a similar conclusion for the dimethylcyclopropylcarbinyl radical. If there is no anchimeric assistance involved in abstraction of the tertiary hydrogen from isopropylcyclopropane by the polystyryl radical and if chain transfer by the ring protons of isopropylcyclopropane is negligible, then a priori one would expect that the chain-transfer constant of 2,3-dimethylbutane should be just twice that of isopropylcyclopropane. To within our experimental accuracy this is precisely what is observed. In fact it would appear that the chain-transfer constant for isopropylcyclopropane is slightly less than would be expected. This might be attributed to an inductive electron-attracting effect of the cyclopropyl

ring inhibiting radical attack on the alkyl hydrogens, the electron-releasing properties of the corresponding isopropyl group on 2,3-dimethylbutane should act in the opposite direction. Such an effect would be expected to be rather small for a radical reaction, particularly a reaction involving the "donor" polystyryl radical. With respect to the tertiary hydrogen, one might expect from steric considerations that the bulky polystyryl radical might have difficulty approaching it; this might be a partial explanation for the enhanced reactivity of methylcyclopropane relative to isopropylcyclopropane, but the tertiary hydrogens of 2,3-dimethylbutane should be just as difficultly accessible to the polystyryl radical as the isopropylcyclopropane tertiary hydrogen. One could argue that on account of these steric considerations it would be unreasonable to expect to be able to detect anchimeric assistance in the abstraction of one proton out of seven. But nevertheless the fact remains that our chain-transfer study has produced no evidence whatsoever for rate enhancement in the free-radical abstraction of the tertiary proton of isopropylcyclopropane by the polystyryl radical.

Thus all evidence points to the fact that the initial free-radical intermediate generated in the dimethylcyclopropylcarbinyl system is the classical dimethylcyclopropylcarbinyl radical XVIIIb.

Such a result is not necessarily incompatible with the initial formation of the delocalized homoallyl radical in the unsubstituted cyclopropylcarbinyl system. In that system the homoallyl radical is formed in preference to a strained primary cyclopropylcarbinyl or an unstrained primary allylcarbinyl radical. In the dimethylcyclopropylcarbinyl system the effect of the two methyl substituents apparently is

either to stabilize the adjacent (tertiary) radical center to the extent that electron delocalization offers no energetic advantage to offset the partial loss of this stabilization or to localize the spin density of the "delocalized" dimethylhomoallyl radical XVIIb on the α-carbon to such an extent that XVIIb becomes experimentally indistinguishable from a classical dimethylcyclopropylcarbinyl radical XVIIIb. A similar sensitivity of the nature of cyclopropylcarbinyl-type intermediates to substituent effects in carbonium ion reactions has been noted elsewhere (58).

Reductions with Tributyltin Hydride

To round out the picture concerning the mechanisms for the interconversion of cyclopropylcarbinyl and allylcarbinyl derivatives in free-radical reactions of the cyclopropylcarbinyl and dimethylcyclopropylcarbinyl systems, exploratory work was carried out with an eye to determining explicitly whether or not products with a cyclopropylcarbinyl skeleton could be isolated from a free-radical reaction in which the original substrate possessed the allylcarbinyl skeleton. Such a study would reveal whether or not any allowance for a reversible step should be made in connection with our working hypothetical mechanistic schemes 14-18.

Kuivila and his co-workers (59) claim to have shown that reductions of alkyl halides by tributyltin hydride proceed via a free-radical mechanism, presumably involving alkyl free radicals as part of a chain reaction. Tributyltin hydride also happens to be one of the most powerful hydrogen atom donors known (60). Thus it was felt that reduction of

allylcarbinyl bromide and of (γ,γ-dimethylallyl)-carbinyl bromide with tributyltin hydride should result in the generation of the allylcarbinyl and (γ,γ-dimethylallyl)-carbinyl radicals respectively and that if the free-radical pathway from the respective cyclopropylcarbinyl to the allylcarbinyl skeletons were at all reversible, then cyclopropylcarbinyl products should be trapped out. These reactions were in fact carried out. The important results are presented below; exact details may be found in the Experimental Section.

Allylcarbinyl Bromide.--The reduction of allylcarbinyl bromide with tributyltin hydride at room temperature led to the formation of 1-butene and a trace of methylcyclopropane, identified by v.p.c. analysis. It was not possible in this instance to estimate the relative percentages of these two products. This result indicates that for the unsubstituted cyclopropylcarbinyl system the free-radical interconversion of the cyclopropylcarbinyl and allylcarbinyl skeletons is a reversible process.

(γ,γ-Dimethylallyl)-carbinyl Bromide.--The reduction of (γ,γ-dimethylallyl)-carbinyl bromide with tributyltin hydride at room temperature led to the formation of 2-methyl-2-pentene and a trace amount of isopropylcyclopropane (v.p.c. analysis). In duplicate experiments the relative percentage of 2-methyl-2-pentene was found to be in the range 94.4-99.1% and that of isopropylcyclopropane was crudely estimated to be about 0.22-0.03%. The ratio of 2-methyl-2-pentene to isopropylcyclopropane then is very roughly in the range 430-3300. If the classical (γ,γ-dimethylallyl)- carbinyl and dimethylcyclopropylcarbinyl radicals are the

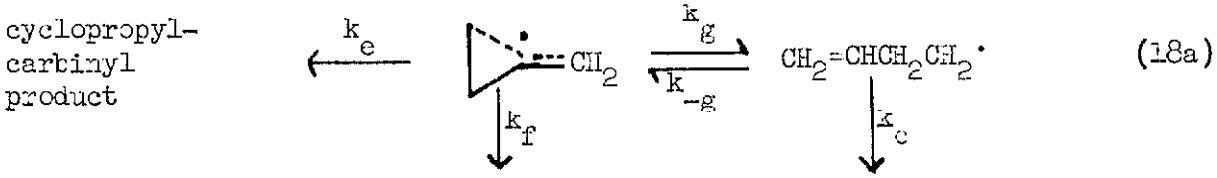
intermediates involved in the reaction and if their rate constants for hydrogen abstraction from the very reactive tributyltin hydride are approximately the same (cf., equation 49), then an upper limit of about 3.6-4.5 kcal./mole can be placed on the thermodynamic stabilization of the former radical (XIXb) over the latter (XVIIIb)--an upper limit because it seems doubtful that under the reaction conditions the two radicals are truly equilibrated and because it seems likely that under conditions of true equilibration the relative percentage of the radical XVIIIb should be greater than the amount of isopropylcyclopropane realized from this reaction. This calculated stabilization is in agreement with the estimates of Schuster (51) and Howden (45) for the enthalpy of isomerization for XVIIIb to XIXb, -5 kcal./mole and +3 kcal./mole respectively. At any rate the presence of isopropylcyclopropane among the reaction products indicates that for the dimethylcyclopropylcarbinyl system also the free-radical interconversion of the cyclopropylcarbinyl and allylcarbinyl skeletons is a reversible process. Trace amounts of 2-methylpentane and 2-methyl-1-pentene were also identified among the reaction products.

Conclusions

Unsubstituted Cyclopropylcarbinyl System.--We are now in a position to evaluate all the evidence relative to the interconversion of unsubstituted cyclopropylcarbinyl and allylcarbinyl skeletons in free-radical reactions and to suggest a mechanism which best correlates all the available data, results from this thesis as well as results of

others. As has been discussed above, kinetic data from this study, Walling and Fredricks (9), and Hart and Cipriani (26) demands the initial formation of a delocalized radical intermediate, presumably the homoallyl radical XVIIa. Thus for this system we must decide whether scheme 17 or scheme 18 (cf., p. 22) best accommodates the product distribution data. The general trend to an increase in the amount of allylcarbinyl products relative to the amount of cyclopropylcarbinyl products with an increase in temperature has been noted in the Introduction. Unfortunately this trend is gleaned from results of various different types of reactions; no detailed study of the effect upon product distribution of changes in temperature for a single reaction has yet been carried out for this system. (Walling and Fredricks (9) did report the product distributions at two temperatures, 0° and 68°, for the chlorination of methylcyclopropane with t-butyl hypochlorite. See the Introduction.) Nevertheless the trend seems real. There would appear to be a fairly severe change in the ratio of allylcarbinyl to cyclopropylcarbinyl products with temperature. Now, as was indicated in our discussion of Howden's results on the diphenylcyclopropylcarbinyl system (pp. 34-38), if all the cyclopropylcarbinyl and allylcarbinyl products are formed from a single non-classical radical (scheme 17), a drastic change in the ratio of products with temperature should not be expected (cf., equation 50 and discussion immediately following). But there is a fairly drastic change in the ratio of products with temperature. These results can best be accommodated by the intermediacy of two radical intermediates. Hence, we propose the isomerization of the initially-generated homoallyl radical to another less stable radical intermediate which is capable of reacting

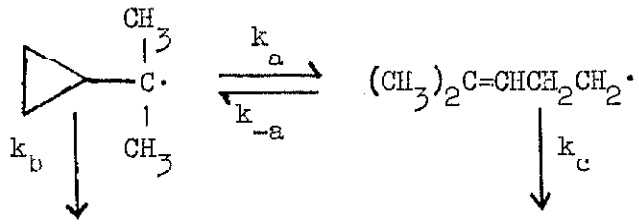
with substrate to yield allylcarbinyl products with a greater specific rate constant than that for the similar reaction with the homoallyl radical, namely the classical allylcarbinyl free radical. Finally, we have just seen that the entire process should be reversible. Thus scheme 18 best accounts for the interconversion of unsubstituted cyclopropylcarbinyl and allylcarbinyl derivatives in free-radical reactions, as is illustrated below in scheme 18a.



(18a)

$$k_c \gg k_f > k_e$$

Dimethylcyclopropylcarbinyl System.—As has been discussed at great length above, there is at present no evidence to require the intervention of a nonclassical dimethylhomoallyl free radical as an intermediate in the interconversions of dimethylcyclopropylcarbinyl and (γ,γ-dimethylallyl)-carbinyl derivatives in free-radical reactions. All the available evidence can be accommodated by mechanism 14b (cf., scheme 14) shown below wherein products are formed from two classical radicals which are expected to equilibrate only quite slowly starting from either direction.



(14b)

dimethylcyclopropylcarbinyl product

(γ,γ-dimethylallyl)-carbinyl product

$$k_a \gg k_{-a}$$

EXPERIMENTAL

All boiling points and bath temperatures are uncorrected. Vapor-phase chromatograms, unless otherwise stated, were obtained using a Perkin-Elmer Model 154-C Vapor Fractometer. Infrared spectra were taken using a Beckman IR-7 spectrometer. Nuclear magnetic resonance spectra were taken using a Varian Associates A-60 high resolution spectrometer.

Heptanal.—Reagent heptanal (Matheson Coleman and Bell) was used in the decarbonylation experiments recorded below without further purification. It was shown by v.p.c. analysis to be chromatographically pure.

Cyclopropylacetaldehyde.—Cyclopropylacetaldehyde used in the decarbonylation experiments recorded below was prepared in these laboratories by D. I. Schuster (61). It was shown to be better than 95%-pure by infrared and v.p.c. analyses.

Cyclopropylcarbinol.—Cyclopropylcarbinol was prepared by the lithium aluminum hydride reduction of cyclopropanecarboxylic acid (Columbia Organic Chemicals, Inc.) according to standard procedures (62,63) as modified by Schuster (64). The yield of pure, colorless cyclopropylcarbinol, b.p. 119-124° (745.4 mm.), $n^{25}D$ 1.4304, from 200.7 g. of the acid was 128.6 g. (76.5%).

Cyclopropylcarbinyl Bromide and Isomers.—The reaction of cyclopropylcarbinol with phosphorus tribromide at 0°, after the

procedure of Roberts and Mazur (2), led to the formation of cyclopropylcarbinyl bromide, allylcarbinyl bromide, and cyclobutyl bromide. In a typical experiment there was obtained from 128.6 g. of cyclopropylcarbinol 206.8 g. (85.8% yield) of a mixture of bromides, b.p. 104–108° (747 mm.), $n^{25}D$ 1.4721. The nature and purity of the products were confirmed by infrared and v.p.c. analyses. The relative percentages of the isomers, determined by weighing the area under their v.p.c. peaks, were: cyclopropylcarbinyl bromide, 52.3%; cyclobutyl bromide, 23.2%; and allylcarbinyl bromide, 24.6%.

Cyclopropylacetonitrile and Isomers.—The reaction of a mixture of cyclopropylcarbinyl bromide, allylcarbinyl bromide, and cyclobutyl bromide with sodium cyanide, following the procedure of Schuster (65), led to the formation of cyclopropylacetonitrile, allylacetonitrile, and a trace of cyclobutanecarbonitrile. In a typical experiment, there was obtained from 67.35 g. of the isomeric bromides and 37 g. of sodium cyanide 25.1 g. (61.9% yield) of a stiflingly pungent mixture of nitriles, b.p. 138–145° (745 mm.), $n^{22}D$ 1.4218. The nature and purity of the major products were confirmed by infrared and v.p.c. analyses. The relative percentages of the isomers, determined by weighing the area under their v.p.c. peaks, were: cyclopropylacetonitrile, 73.1%; allylacetonitrile, 26.9%; cyclobutanecarbonitrile, trace. The identity of the trace nitrile was inferred from the fact that its v.p.c. retention time was identical to that of the product resulting from the reaction of cyclobutanecarboxamide with phosphorus oxychloride in pyridine at 0°, a reaction known (66) to produce the corresponding nitrile from an amide. The product of the phosphorus oxychloride reaction was identified as cyclobutane-

carbonitrile from the method of synthesis and its infrared spectrum: peak at 2250 cm^{-1} characteristic of a nitrile function and peaks at 1440, 997, and 925 cm^{-1} which might be attributed to the cyclobutyl ring (47).

Cyclopropylacetonitrile.—Following the procedure developed by Schuster (67), the mixture of cyclopropylacetonitrile and allylacetonitrile described directly above was allowed to react with a neutral, saturated aqueous solution of potassium permanganate, leading to the complete consumption of the olefinic nitrile and to an average 75% recovery of essentially pure cyclopropylacetonitrile, b.p. 148° (747 mm.), $n_D^{24.5}$ 1.4227. V.p.c. analysis showed that the recovered cyclopropylacetonitrile was still contaminated with a trace of cyclobutanecarbonitrile.

Dimethylcyclopropylacetonitrile.—Dimethylcyclopropylacetonitrile was prepared by the methylation of cyclopropylacetonitrile with methyl bromide and sodamide in liquid ammonia, according to the procedure of Newman, Fukunaga, and Miwa (68) as modified particularly for this reaction by Schuster (69). In a typical experiment, there was obtained from 11.66 g. of cyclopropylacetonitrile, 7.12 g. (45.5% yield) of dimethylcyclopropylacetonitrile, b.p. 145-148° (744 mm.). The identity and purity of the product was established by infrared and v.p.c. analyses.

Dimethylcyclopropylacetaldehyde was prepared by the inverse addition of a standard solution of lithium aluminum hydride in ether (70)

to a solution of dimethylcyclopropylacetonitrile in ether, according to the procedure developed by Schuster (71). In a typical experiment, there was obtained from 7.12 g. of dimethylcyclopropylacetonitrile, 3.18 g. (43.5% yield) of dimethylcyclopropylacetaldehyde. The identity of the product was established by comparison of its infrared spectrum with that of an authentic sample of the aldehyde. Schuster recommended purification of the aldehyde by redistillation under nitrogen; but the dimethylcyclopropylacetaldehyde so purified and used in the decarbonylation experiments described below was shown by v.p.c. analysis to be 90%-pure, there being eight unidentified peaks in the chromatogram in addition to that of the aldehyde. Most recently it has been the experience of this author that dimethylcyclopropylacetaldehyde can be absolutely purified by preparative vapor-phase chromatography on a Carbowax column.

Decarbonylation Apparatus and Procedure.—The apparatus in which the decarbonylation experiments were carried out was as follows: The reaction vessel was an 8-ml. glass bulb equipped with a thermowell, a small glass-enclosed magnetic stirring bar, and a 3-ml. standard-taper dropping funnel. The bulb was also connected in series to an air-cooled cold finger, a stopcock, a Dry Ice-cooled trap (2 Dry Ice-cooled traps in the case of cyclopropylacetaldehyde), a three-way stopcock, and a 250-ml. inverted graduated cylindrical separatory funnel filled with mercury and connected through Tygon tubing to a 300-ml. leveling bulb. The three-way stopcock was also connected to an outlet for a gas infrared cell, an outlet to a vacuum pump, and a nitrogen inlet connected to the nitrogen source via a mercury bypass.

The general procedure for decarbonylation of an aldehyde in the presence of benzyl mercaptan was as follows: The aldehyde and mercaptan were placed in the reaction vessel and then degassed by three cycles of freezing, evacuating, and thawing. After the last cycle, the system was filled with nitrogen at atmospheric pressure and so maintained for the duration of the reaction. An oil bath was then raised into position and electrically heated to the desired reaction temperature, the temperature of the bath being maintained constant by a Fenwal Series 560 Control Thermoregulator. The temperature in the reaction flask was read from a thermometer inserted in the thermowell. Both the oil bath and reactants were simultaneously magnetically stirred. When the desired temperature was reached (a matter of a couple of minutes only), di-t-butyl peroxide was added to the reaction flask from the dropping funnel under nitrogen pressure to initiate the decarbonylation. As the reaction proceeded, more peroxide was added as needed. The gas evolved was collected in the separatory funnel over mercury, its volume being measured at atmospheric pressure by balancing the levels of mercury in the separatory funnel and leveling bulb. The lower-boiling reaction products distilled out of the reaction vessel and were condensed in the Dry Ice-cooled trap. The reaction was continued until gas evolution ceased or became interminably slow. The gaseous products were transferred to an evacuated 10-cm. gas cell, in which they were analyzed by infrared spectroscopy. The Dry Ice-trapped liquid fraction and the residue in the reaction flask were analyzed by v.p.c., using either diisodecyl phthalate packing (heptanal and dimethylcyclopropylacetaldehyde experiments) or tetraisobutylene packing (cyclopropylacetaldehyde experiment).

Decarbonylation of Heptanal.—Two runs were made of the di-t-butyl peroxide-initiated decarbonylation of heptanal in the presence of benzyl mercaptan. In a typical run, 0.5 g. (0.00438 mole) of heptanal, 1.5 ml. (0.0128 mole) of benzyl mercaptan, and approximately 0.73 g. (0.005 mole) of di-t-butyl peroxide were allowed to react according to the general decarbonylation procedure described above. The temperature in the reaction flask ranged from 123-138° throughout the duration of the reaction (9.3 hours). There was trapped 0.20 g. of liquid which was shown by v.p.c. analysis to consist of di-t-butyl peroxide (54.6 relative %), t-butyl alcohol (34.6%), acetone (8.6%), and n-hexane (3.8%). The yield of n-hexane was thus 0.0076 g. (2.01%). The evolved gas collected (68 ml.) was shown by infrared analysis to consist of mostly methane, some carbon monoxide, and an unidentified component (peak at 890 cm^{-1}). The reaction residue was shown by v.p.c. analysis to consist of recovered starting materials, t-butyl alcohol, and several unidentified components, possibly coupling products. There was also a white solid found in the reaction flask, possibly benzyl disulfide.

Decarbonylation of Cyclopropylacetaldehyde.—The general decarbonylation procedure was used for the decarbonylation of this aldehyde except that two Dry Ice-cooled traps were used in series and all the initiator was originally present in the reaction vessel and was degassed along with the aldehyde and mercaptan. Cyclopropylacetaldehyde (0.87 g.; 0.0103 mole) was decarbonylated in the presence of 6 ml. (6.35 g., 0.0512 mole) of benzyl mercaptan, initiated by 1.91 g. (0.0131 mole) of di-t-butyl peroxide. The temperature in the flask ranged from 109°

to 124° over the 47-hour reaction period. (Three minutes were required for the system to approach thermal equilibrium after being heated from 42° to 120°.) The gas collected (90 ml.; 34.9% yield) was shown by infrared analysis to consist of methane, carbon monoxide, air, and an unidentified component absorbing at 890 cm^{-1}. The residue in the reaction flask was not investigated. The liquid condensed in the first Dry Ice trap was shown by v.p.c. analysis to consist of acetone, t-butyl alcohol, di-t-butyl peroxide, and 1-butene. There was apparently no methylcyclopropane, although as much as 1% of the amount of 1-butene might conceivably have gone undetected.

Decarbonylation of Dimethylcyclopropylacetaldehyde.--Five runs were made of the di-t-butyl peroxide-initiated decarbonylation of dimethylcyclopropylacetaldehyde in the presence of benzyl mercaptan according to the general decarbonylation procedure described above. Specific experimental details are summarized in Table 13 (cf., Table 4, p. 44). In general, the temperature in the reaction flask was near 125°. Typically the evolved gas was shown by infrared spectroscopy to consist of predominantly carbon monoxide, some methane, a small amount of an unidentified component absorbing near 890 cm^{-1}, and occasionally a trace amount of carbon dioxide (cf., Table 13). The liquid collected in the Dry Ice trap was shown by v.p.c. analysis to consist of recovered di-t-butyl peroxide, t-butyl alcohol, acetone, 2-methyl-2-pentene, isopropylcyclopropane, and several unidentified components, including possible aldehyde contaminants. (The aldehyde used in these experiments was shown by v.p.c. analysis to be 90% pure.) Acetone and isopropylcyclopropane were unresolvable on the diisodecyl phthalate column used to analyze this liquid fraction. The relative

TABLE 13

Decarbonylation of Dimethylcyclopropylacetaldehyde

	Run 1	Run 2	Run 3	Run 4	Run 5
Wt. RCHO[a,b], g.	0.612	0.531	0.467	0.225	0.408
Moles RCHO[a]	0.00546	0.00475	0.00416	0.00201	0.00365
Vol. R'SH[c], ml.	1	0.2	4	1.92	0.43
Moles R'SH[c]	0.00851	0.00171	0.0340	0.0165	0.00367
Wt. DTBP[d], g.	1.19	1.43	1.80	1.22	2.21
Moles DTBP[d]	0.00815	0.00977	0.0123	0.00836	0.0151
Rn. Time, hr.	9.75	4.8	4.5	3.25	32
Rn. Temp., °C.	120-130	111-123	126	126-128	110-124
Vol. Gas, ml.	60	75	72	54	107
Gaseous Products	CO CH_4 890[e] CO_2 ?	CO CH_4	CO CH_4 890[e] CO_2	CO CH_4 890[e] CO_2	CO CH_4 890[e] CO_2
Wt. Liquid Trapped, g.	0.08	0.11	0.13	f	g

(a) Dimethylcyclopropylacetaldehyde.

(b) Weight corrected for purity of aldehyde.

(c) Benzyl mercaptan.

(d) Di-t-butyl peroxide.

(e) Compound having an IR absorbtion near 890 cm^{-1}.

(f) Not enough liquid trapped to analyze by v.p.c.

(g) Not determined.

percentages of 2-methyl-2-pentene and combined acetone-isopropylcyclopropane were determined from the relative areas under their respective v.p.c. peaks and are presented in Table 4, p. 44. The residue in the reaction vessel consisted of a solid, possibly benzyl disulfide, and a liquid phase shown by v.p.c. analysis to consist of di-t-butyl peroxide, benzyl mercaptan, dimethylcyclopropylacetaldehyde, and unidentified components (perhaps coupling products) but no t-butyl alcohol or monomeric hydrocarbons.

Neopentane.—Phillips 66 Research Grade 2,2-dimethylpropane (neopentane) was used in the chain-transfer experiments described below without further purification.

n-Butane.—In most cases Matheson Coleman and Bell Instrumental Grade n-butane was used in the chain-transfer experiments described below without further purification. In the case of samples 224-1,2, and 3 (cf., Tables 7 and 16), the n-butane was refluxed over sodium for 2 hours (to remove possible peroxidic impurities) prior to use.

2,3-Dimethylbutane.—Phillips 66 Research Grade 2,3-dimethylbutane, used in the chain-transfer experiments described below, was distilled through a 60-cm. glass-helix-packed column in order to free it from trace amounts of commercial Du Pont No. 6 inhibitor prior to use: b.p. 57.2° (745 mm.).

Methylcyclopropane.—Methylcyclopropane was prepared by the reduction of 1,3-dibromobutane with zinc dust in ethanol (72). In a typical

experiment, the yield of methylcyclopropane from 121.44 g. of 1,3-dibromobutane and 146.51 g. of zinc dust was at least 27.66 g. (87.4%). The methylcyclopropane used in the chain-transfer experiments described below was purified by being refluxed over aqueous potassium permanganate for 2 hours and then over sodium for another 2 hours; it was then degassed and transferred under vacuum by bulb-to-bulb distillation to a special air-tight glass cylinder with Teflon screw-valve, in which it was stored prior to use. Methylcyclopropane so treated was shown by v.p.c. analysis (electronic integration) to be 99.3% pure, the likely impurity being 1-butene.

Cyclopropanecarbonyl Chloride.—Cyclopropanecarbonyl chloride was prepared in accordance with standard procedures for the preparation of acid chlorides (73). A typical preparation is described. In a 100-ml., three-necked flask equipped with a stopper, small dropping funnel, and a reflux condenser fitted with a calcium chloride drying tube, was placed 61 g. (0.512 mole; 36.9 ml.) of thionyl chloride. The flask was heated gently on the steam bath (in the hood) as 22.16 g. (0.256 mole; 20.2 ml.) of cyclopropanecarboxylic acid (Columbia Organic Chemicals, Inc.) was added from the dropping funnel during the course of 30 minutes. When all the acid had been added, the flask was heated for another hour. Then the dropping funnel was replaced by another stopper and the reflux condenser by a 30-cm. column packed with glass helices; and the reaction mixture was fractionally distilled. In addition to excess thionyl chloride, there was collected 22.5 g. (84.0% yield) of pure colorless cyclopropanecarbonyl chloride, b.p. 113-118° (742 mm.), $n^{25}D$ 1.4510 (lit., b.p. 114-119° (63)). The structure of

the product was confirmed by its infrared spectrum with characteristic peaks at 1045 and 1070 cm^{-1} (cyclopropyl), 695 cm^{-1} (carbon-chlorine bond), and 1785 cm^{-1} (acid chloride carbonyl) (47). The purity of the product was ascertained by v.p.c. analysis.

Dimethylcyclopropylcarbinol.--This alcohol has previously been prepared in these laboratories by the reaction of ethylcyclopropanecarboxylate and methylmagnesium chloride in ether (74) and by the reaction of methylmagnesium iodide with methyl cyclopropyl ketone (75). In this study it was prepared by the reaction of methylmagnesium iodide with cyclopropanecarbonyl chloride at 0°. A typical preparation follows.

In an oven-dried, 500-ml., round-bottomed, three-necked flask, equipped with a dropping funnel, mechanical stirrer, and reflux condenser, was placed 10.97 g. (0.45 mole) of magnesium turnings, covered with 50 ml. of anhydrous ether. From the dropping funnel was added a solution of 28 ml. (63.9 g.; 0.45 mole) of methyl iodide in 85 ml. of ether dropwise, with stirring, at a rate sufficient to maintain good reflux. The addition required 2 hours. The dark solution was refluxed for 3 hours until most of the magnesium had been consumed. The reaction mixture was then cooled to below 0° in an ice-salt bath. There was added over a 3-hour period from the dropping funnel a solution of 22.0 g. (0.210 mole) of cyclopropanecarbonyl chloride in 30 ml. of ether dropwise, with stirring, at such a rate as to maintain the temperature below 5°. (In a similar experiment conducted at the temperature of refluxing ether, no dimethylcyclopropylcarbinol could be isolated.) Stirring was continued overnight as the reaction mixture warmed gradually to room temper-

ature. The solution was then poured into a large separatory funnel in which had previously been placed about 90 g. of ice and 120 ml. of cold, saturated aqueous ammonium chloride solution. The funnel was shaken until the magnesium alcohol complex had dissolved as much as possible. The layers were separated. The aqueous layer was further extracted with two 25-ml. portions of ether. The ether extracts were combined and dried over anhydrous potassium carbonate. The dried ethereal solution was filtered through a plug of glass wool into a 200-ml. round-bottomed flask, from which the ether was distilled off through a narrow 30-cm. Vigreux column. The residue was transferred to a 50-ml. round-bottomed flask and distilled through the same column. There was collected 12.67 g. of crude product, b.p. 117-123° (744 mm.), $n^{25}D$ 1.4330 (lit. (74,76,77), b.p. 120-121° (743.5 mm.), $n^{25}D$ 1.4307; b.p. 123.7° (760 mm.), $n^{20}D$ 1.4335; b.p. 121-123°, $n^{25}D$ 1.4338), which was shown by v.p.c. analysis and by comparison of its infrared spectrum with an infrared spectrum of authentic dimethylcyclopropylcarbinol (78) to consist of at least 10.34 g. (49.2% yield) of dimethylcyclopropylcarbinol.

Isopropenylcyclopropane.—Isopropenylcyclopropane was prepared by the sulfuric acid-induced dehydration of dimethylcyclopropylcarbinol, following the procedure of Van Volkenburgh and co-workers (79) as applied by Slabey and Wise (76) and Schuster (80). In a typical experiment there was obtained from 10.24 g. of dimethylcyclopropylcarbinol and 2 drops of concentrated sulfuric acid 5.49 g. (65.2% yield) of pure isopropenylcyclopropane.

Isopropylcyclopropane.—Isopropylcyclopropane was prepared by the hydroboration-protonation of isopropenylcyclopropane according to the general procedure of Brown and Murray (81).

To a magnetically stirred solution of 47.68 g. (0.581 mole) of isopropenylcyclopropane and 6.01 g. (0.159 mole) of sodium borohydride in 158 ml. of diglyme under nitrogen at 0°, there was added 27.1 ml. (0.222 mole) of boron trifluoride etherate in 79.1 ml. of diglyme over a period of 2.25 hours. The reaction mixture was stirred for another 30 minutes. Then 63.6 g. (0.859 mole) of propionic acid was added to the reaction flask; the contents were stirred at room temperature for 5 hours. Finally the reaction mixture was heated (by an oil bath) so that ether and the low-boiling hydrocarbon reaction products could distil out of the flask. This crude product mixture was shown by v.p.c. and IR analyses to consist of ether, 2-methylpentane, isopropylcyclopropane, 2-methyl-1-pentene, and 2-methyl-2-pentene. (Individual components were separated and collected by preparative v.p.c. and their infrared or n.m.r. spectra were examined and compared with spectra of authentic samples.) The approximate relative percentages of the hydrocarbon products were: 2-methylpentane, 10.0%; isopropylcyclopropane, 77.8%; 2-methyl-1-pentene, 6.7%; and 2-methyl-2-pentene, 5.6%. The crude product mixture was washed twice with dilute aqueous sodium bicarbonate solution and then three times with water. The layers were separated and the organic layer was dried over Drierite overnight. Careful fractional distillation through an efficient 100-cm. metal-helix-packed column permitted separation of isopropylcyclopropane from ether and the companion hydrocarbons. Overall there was collected 36.0 g. (73.5% yield) of hydro-

carbons. The cut of isopropylcyclopropane used in the chain-transfer experiments described below had b.p. 58.5-58.8° (745 mm.) (lit. (82), b.p. 58.37° (760 mm.)); it was shown by v.p.c. analysis to be 98.6% pure, the most likely impurities being 2-methylpentane and 2-methyl-1-pentene. The n.m.r. spectrum of isopropylcyclopropane was relatively easy to interpret; all the resonances occurred at high field. There was the expected (but unsymmetrical) doublet for the methyl protons, and at even higher field 2 partially resolved multiplets characteristic of cyclopropane ring protons. No resonance for the tertiary proton could be detected.

Preparation of Polystyrene Samples and Determination of Chain-Transfer Constants.--The general procedure is modeled after the procedure of Gregg and Mayo (83).

Before preparing each new batch of polystyrene samples, commercial styrene monomer was purified by washing 200 ml. of monomer four times with 50-ml. portions of 5% aqueous sodium hydroxide solution (to extract inhibitor), then rinsing four times with 50-ml. portions of distilled water, the last wash being neutral to litmus. The styrene was dried over calcium chloride in the refrigerator and distilled under nitrogen before use, b.p. 35° (10.5 mm.).

The procedure for the preparation of polystyrene samples in the absence of any external transfer agents follows. The monomer was weighed into clean, heavy-walled glass tubes, which were then attached to the vacuum line and cooled in liquid nitrogen. Then the tubes were evacuated and dry nitrogen was admitted a total of three times. Next the system

was degassed three times by cycles of thawing, refreezing, and re-evacuating the tubes. Finally the tubes were sealed under approximately 1 mm. of pressure. Samples were stored in Dry Ice before and immediately following immersion in a thermostatted oil bath maintained at 79.1 ± 0.2°. The duration of immersion was varied for various samples.

The procedure for the preparation of polystyrene samples in the presence of neopentane, n-butane, or methylcyclopropane was the same as that just described above except that the very volatile hydrocarbons were attached to the vacuum line in a special air-tight glass cylinder with a Teflon screw-valve and were transferred to the sample tubes by bulb to bulb distillation at 1 mm. prior to the degassing of the combined styrene-hydrocarbon samples. The weight of the hydrocarbon used in these samples was determined from the gain in weight of the sample tube plus styrene after the transfer of the hydrocarbon and the sealing of the sample tube.

The procedure for the preparation of polystyrene samples in the presence of 2,3-dimethylbutane or isopropylcyclopropane was the same as that for the preparation of polystyrene samples in the absence of any hydrocarbon transfer agent except that in these cases the hydrocarbon was also weighed into the sample tube before it was attached to the vacuum line.

In all cases, the average degree of polymerization for each polystyrene sample was determined as follows. Each sample tube was chilled in Dry Ice-acetone or liquid nitrogen as was appropriate and was opened by cracking with a hot glass rod. The polystyrene solution was transferred to a 500-ml Erlenmeyer flask containing 250 ml. of magnetically stirred methanol so as to precipitate the polymer; this

solution was let stand for 24 hours. The precipitate was then collected on a Buchner funnel, dissolved in 25 ml. of benzene, and let stand for another 24 hours. The polymer was then further purified by two more cycles of precipitation in 200 ml. of methanol followed by solution in benzene. Finally the polymer was reprecipitated, collected on a tared sintered-glass crucible, dried under vacuum at 100° for over 8 hours, and weighed. From the weight of the polymer and the original weight of styrene monomer the percentage polymerization was determined. Determination of the intrinsic viscosity $[\eta]$, of a dilute solution of the polystyrene in benzene according to the procedure described in Daniels, et al. (84) then permitted estimation of the average number molecular weight, $\overline{M}_n$, of the polymer and hence the average degree of polymerization, $\overline{P}$, of the polystyrene sample according to equations 55 and 56 (85):

$$\overline{M}_n = 167000\ [\eta]^{1.37}\ ; \qquad (55)$$

$$\overline{M}_n = 104\overline{P}\ . \qquad (56)$$

For samples with transfer agents the chain-transfer constant for the hydrocarbon with styrene could then be determined from equation 54, p. 47.

The experimental results relative to the determination of the chain-transfer constants of neopentane, n-butane, methylcyclopropane, 2,3-dimethylbutane, and isopropylcyclopropane with styrene at 79.1° have already been presented in Tables 5-10, pp. 48-52. Further experimental details for the same samples are given in Tables 14-19 below.

A word of explanation is necessary about the calculation of the ratio of concentrations of hydrocarbon to styrene in Tables 6-10. These

ratios were determined from the original amounts of reactants in the sample tubes as given in Tables 15-19, a first-order correction being applied for the amount of hydrocarbon in the vapor phase. It was assumed in all cases for purposes of this calculation that the sample tube capacity was 23 ml. (a good approximation) and that only the hydrocarbon solvent was present in the vapor phase to an appreciable extent (a good approximation). From the known densities of styrene and hydrocarbon solvent, and assuming no change of volume upon mixing, it was possible to calculate the volume of sample tube unoccupied by the liquid phase. The amount of hydrocarbon in the vapor phase then could be calculated by assuming the hydrocarbon to be an ideal gas at a pressure determined by a Raoult's Law correction to the normal vapor pressure of hydrocarbon at 79.1°. This amount would then be subtracted from the original amount of hydrocarbon present; and the corrected ratio of concentrations of hydrocarbon to styrene could then be calculated from the corrected amount of hydrocarbon in the liquid phase and the original amount of styrene present.

Tributyltin Hydride (60).--In a one-liter, three-necked, round-bottomed flask equipped with a mechanical stirrer, pressure-equalizing addition funnel, and a nitrogen bubbler was placed 2.5 g. (0.0660) mole of lithium aluminum hydride dissolved in 200 ml. of ether. Nitrogen was passed through the stirred solution at all times. To this solution was added slowly (over an hour or so) 51.45 g. (0.158 mole) of tributyltin chloride dissolved in 95 ml. of ether. The resulting solution was allowed to stir for another hour at room temperature. The excess lithium aluminum hydride was then destroyed by slow addition of water. The ether layer

TABLE 14

Preparation of Polystyrene Samples at 79.1° in Absence of Transfer Agents[a]

Sample No.	Original weight styrene, g.	Total time in bath, hrs.	% Polymerization
161-4	8.4	24	10.9
161-5	3.7	24	11.3
161-6	8.6	18	9.0
161-7	8.8	18	9.5
161-8	8.5	44	20.4
190-1	6.00	21	9.8
190-2	4.96	21	13.6
190-3	5.28	21	9.6
224-4	5.04	24	9.6
240-6	4.74	22	9.6

(a) Cf. Table 5.

TABLE 15

Preparation of Polystyrene Samples at 79.1° in Presence of Neopentane[a]

Sample No.	Original weight styrene, g.	Original weight neopentane, g.	Total time in bath, hrs.	% Polymerization
277-1	4.77	1.27	49.3	12.1
277-2	4.56	3.63	120.0	9.8
277-3	4.00	8.62	218.0	5.2

(a) Cf. Table 6.

TABLE 16

Preparation of Polystyrene Samples at 79.1° in Presence of n-Butane[a]

Sample No.	Original weight styrene, g.	Original weight n-butane, g.	Total time in bath, hrs.	% Polymerization
224-2	4.21	7.24	89.0	0.98
190-7	4.80	4.35	21.0	1.46
190-8	4.58	4.87	21.0	1.56
190-6	5.07	4.52	43.0	2.94
190-5	5.10	2.73	21.0	5.57
190-4	5.12	1.23	21.0	5.75
224-1	4.85	3.65	61.8	7.32
224-3	4.69	2.03	48.0	9.65
190-10	1.89	4.80	96.8	14.3

(a) Cf. Table 7.

TABLE 17

Preparation of Polystyrene Samples at 79.1° in Presence of Methylcyclopropane[a]

Sample No.	Original weight styrene, g.	Original weight MCP,[b] g.	Total time in bath, hrs.	% Polymerization
240-1	4.62	1.30	48.0	12.5
240-2	4.46	2.33	63.25	11.8
240-3	4.95	5.54	99.25	10.1
240-4	4.28	7.61	138.0	8.5
240-5	3.44	5.36	138.0	10.2

(a) Cf. Table 8.

(b) Methylcyclopropane.

TABLE 18

Preparation of Polystyrene Samples at 79.1° in Presence of 2,3-Dimethylbutane[a]

Sample No.	Original weight styrene, g.	Original weight DMB,[b] g.	Total time in bath, hrs.	% Polymerization
308-2	4.95	2.98	121.0	20.9
308-3	4.17	5.44	169.5	16.1
308-5	5.99	1.89	95.5	24.4

(a) Cf. Table 9.

(b) 2,3-Dimethylbutane.

TABLE 19

Preparation of Polystyrene Samples at 79.1° in Presence of Isopropylcyclopropane

Sample No.	Original weight styrene, g.	Original weight ICP,[b] g.	Total time in bath, hrs.	% Polymerization
332-1	5.74	1.81	91.7	24.7
332-2	4.80	3.00	129.7	24.5

(a) Cf. Table 10.

(b) Isopropylcyclopropane.

was separated, washed twice with 50-ml. portions of water, dried over magnesium sulfate, and let stand under nitrogen overnight. The magnesium sulfate was filtered off; the ether was stripped off under reduced pressure and heating. Finally the residue was fractionally distilled under vacuum. The yield of colorless, odoriferous tributyltin hydride, b.p. 89.5-90° (1.5-2.0 mm.), was 30.65 g. (66.6%).

(γ,γ-Dimethylallyl)-carbinyl bromide was prepared by the procedure of Caserio (75). A typical preparation is described.

In a 500-ml., three-necked, round-bottomed flask, equipped with a thermometer, a dropping funnel, and a magnetic stirring bar, was placed 153.6 g. (0.90 mole) of 48% hydrobromic acid. This aqueous solution was cooled to 3° by ice-water cooling. Then there was added dropwise 18.17 g. (0.181 mole) of dimethylcyclopropylcarbinol over 13 minutes. The mixture was stirred for another 7 minutes as the temperature in the flask rose to 8°. The reaction mixture was placed in a separatory funnel, and the upper organic layer was separated. This was washed with 40 ml. of water; and then the now lower organic layer was removed and dried over anhydrous calcium chloride. The crude product was distilled through a short Vigreux column in vacuo. The yield of (γ,γ-dimethylallyl)-carbinyl bromide, b.p. 81-83° (79 mm.), identified by comparison of its infrared spectrum with that of Caserio for an authentic sample of the bromide, was 19.0 g. (64.4%). The product was shown to be pure by v.p.c. and n.m.r. analyses.

Allylcarbinyl Bromide.—The allylcarbinyl bromide used in the experiment with tributyltin hydride described below was prepared in these laboratories by M. S. Silver and was shown to be pure by v.p.c. and n.m.r. analyses.

Tributyltin Hydride and (γ,γ-Dimethylallyl)-carbinyl Bromide.—Duplicate experiments were carried out, the procedure being based on a procedure for a similar reaction by Howden (86) and on the sketchy procedures outlined by Kuivila and co-workers (59).

In a small two-necked flask equipped with a nitrogen inlet and an adapter leading to a Dry Ice-acetone-cooled trap were placed 4.00 g. (0.0137 mole) of tributyltin hydride and 2.08 g. (0.0128 mole) of (γ,γ-dimethylallyl)-carbinyl bromide. The reaction mixture was agitated by nitrogen bubbling for 95 minutes, then heated so that low-boiling products could distil into the cold trap. The distillate was analyzed by v.p.c. (diisodecyl phthalate packing) and shown to consist of at least 8 components. Comparison of retention times (and analysis of per cent composition by the width-at-half-height technique) showed these components to be (in order of increasing retention time): 2-methylpentane, 3.63 relative %; isopropylcyclopropane, c. 0.22%; 2-methyl-1-pentene, 0.33%; 2-methyl-2-pentene, 94.4%; four unidentified components, total of 1.39%. It is likely that at least two of the unidentified components may be organotin compounds. The yield of identified hydrocarbons was 93.5%. The yield of 2-methyl-2-pentene was 0.97 g. (89.0%).

In the duplicate run, the product distribution was shown by v.p.c. analysis to be: 2-methylpentane, 0.44%; isopropylcyclopropane,

0.03-0.07%; 2-methyl-1-pentene, 0.28%; 2-methyl-2-pentene, 99.10%; four unidentified components, total of 0.25%. The yield of hydrocarbons was 0.54 g. (52%).

Tributyltin Hydride and Allylcarbinyl Bromide.--The reaction of 3.80 g. (0.0130 mole) of tributyltin hydride and 2.40 g. (0.0178 mole) of allylcarbinyl bromide was carried out exactly as described above for the reaction of tributyltin hydride with (γ,γ-dimethylallyl)-carbinyl bromide. The hydrocarbon products were shown by v.p.c. analysis (tetraisobutylene packing) to consist of predominantly 1-butene, a trace of methylcyclopropane, and possibly some cis- or trans-2-butene.

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PROPOSITIONS

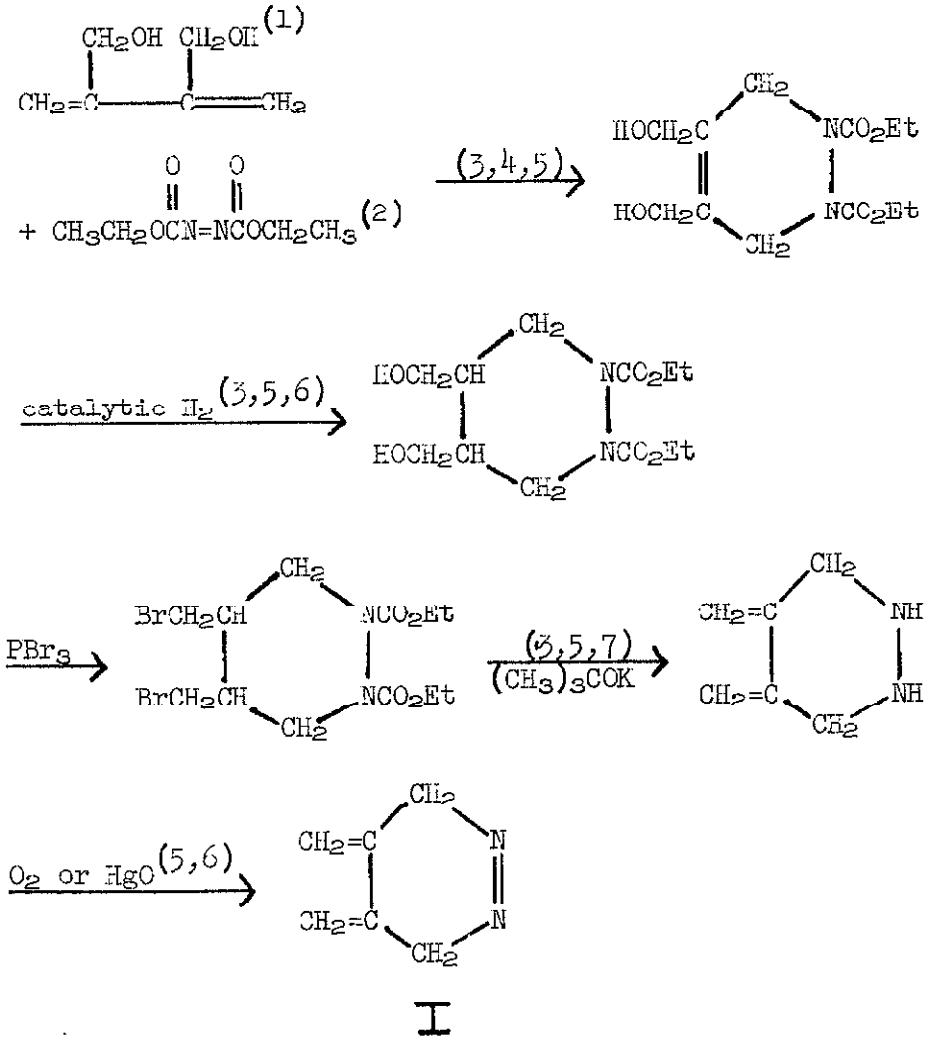
PROPOSITION NO. 1

Abstract

A synthesis is proposed for the cyclic azo compound, 4,5-dimethylene-3,4,5,6-tetrahydropyridazine (I).

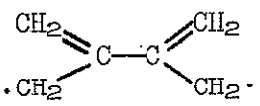
Discussion

A proposed synthesis for the cyclic azo compound I is outlined below. References are given to the syntheses of the starting materials and to procedures for the individual steps:



I

The azo compound would be of interest as precursor to the as-yet-not-synthesized biradical diallylene (II), a prototype biradical (cf., for example, Schlenk's hydrocarbon (8)), which is predicted by molecular orbital theory to have a triplet ground state (9,10). The biradical could form such interesting organic compounds as III (1,2-dimethylenecyclobutane (11,12)) and IV (13). Further, it would be of interest to investigate the scavenging of the biradical. And a study of the decomposition of I or of 1 labeled in either or both of the methylene positions could shed light on the mechanism of the decomposition of cis-azo compounds; in particular, labeled I could be utilized to investigate the possibility, suggested by Hammond and co-workers (14), that there may be a non-radical decomposition path for azo compounds involving the transition state V. If a non-radical decomposition path such as that suggested were involved, all of the label should be retained in the methylene groups of product III.



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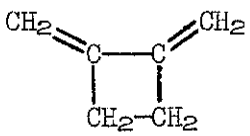

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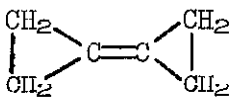

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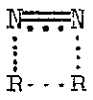


V

PROPOSITION NO. 2

Abstract

A competition reaction is proposed wherein it is suggested that a large primary deuterium kinetic isotope effect will be measured for an intermolecular hydride ion transfer from carbon to carbon.

Discussion

The magnitude of the primary deuterium kinetic isotope effect has been much used in recent years as a criterion of mechanism (15-17). Whereas ratios k_H/k_D as large as the theoretical maximum have been measured for proton or hydrogen atom transfers from carbon to some other atom in the rate-determining step (16,17), there appears thus far to be no well-documented example of a large isotope effect for a similar rate-determining hydride transfer, measured ratios k_H/k_D ranging only up to three (17-23). (The example cited by Wiberg (17) of a large isotope effect for a hydride transfer—the oxidation of alcohols by diazonium ions (24)—is now conceded by the original investigator to be a transfer of radical character (25). Very recently Lachowicz and Critter (26) have reported an isotope effect k_H/k_D of 6.8 $\pm$ 0.5 for the silver metal-catalyzed Cannizzaro reaction of benzaldehyde and benzaldehyde-α-C_1 with sodium hydroxide in 50% aqueous ethanol; the authors proposed a mechanism involving hydride transfer on the catalyst surface but admitted that a free-radical mechanism for this reaction has not been ruled out.) Since theory makes no distinction as to the nature of the hydrogen species being transferred with respect to the magnitude of the isotope effect (15-17), there would appear to be no reason why a carefully chosen ex-

ample of a hydride transfer reaction should not show an isotope effect of magnitude comparable to favorable examples of proton or hydrogen atom transfers.

Bartlett and Tate (27) and, to some extent, Swain and co-workers (23) have argued that the relatively strongly bonded nature of the activated complex to be expected for a hydride transfer might be responsible for the small isotope effects thus far realized in such cases. But the second-order-approximation theory of the magnitude of deuterium isotope effects, reviewed by Westheimer (15), suggests that the above rationalization may only be correct insofar as the bonding in the activated complex is not "fully symmetrical."

$$\underset{\underline{k}_1 \quad \underline{k}_2}{A\cdots H\cdots B}$$

I

If I represents the activated complex for a hydrogen transfer reaction $AH + B \longrightarrow A + HB$, then "fully symmetrical bonding" implies that the hydrogen species is equally bonded to both A and B; i.e., that the force constants $\underline{k}_1$ and $\underline{k}_2$ for the A-H and B-H stretching motions, respectively, are equal. If the force constants $\underline{k}_1$ and $\underline{k}_2$ are equal and are the same for both hydrogen and deuterium, as is generally assumed, then to this order of approximation the zero-point energy for the two isotopic activated complexes will be the same. Hence, with these assumptions the difference in activation energy for the two isotopic reactions will reflect almost completely the difference in zero-point energies of the ground state A-H and A-D stretching vibra-

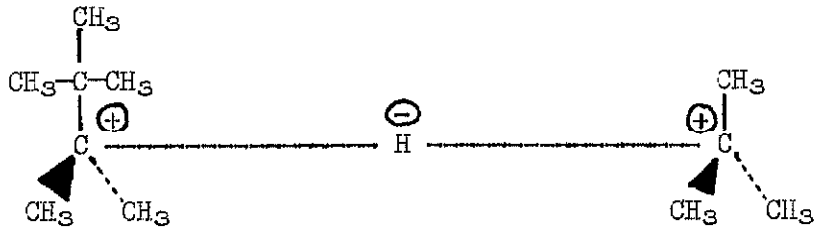
tions; and this difference-in-zero-point-energies contribution to the isotope effect k_H/k_D will be a maximum.

By a "fully symmetrical hydride transfer" is meant a hydride transfer (reaction) with a "fully symmetrical" activated complex in the sense defined above.

Now a survey of those hydride transfer reactions for which isotope effects have been measured reveals no example where a fully symmetrical hydride transfer is likely (17-23). A consideration of the various types of reactions involving hydride transfers (28,29) suggests that a likely case for a symmetrical hydride transfer from carbon is one from a hydrocarbon to a carbonium ion (28,30-35).

Hence, it is proposed that the primary deuterium isotope effect be measured for the abstraction of hydride ion from 2,2,3-trimethylbutane (triptane) by t-butylcarbonium ion; and it is suggested that the magnitude of the isotope effect so measured should approach the theoretical maximum under favorable experimental conditions.

This conclusion is based on the assumption that there will be a linear, almost symmetrical transition state for the hydride transfer; to wit:



II

The steric requirements of the two tertiary carbonium ions are such as to make it difficult to visualize any other transition state geometry of lower energy.

The isotope effect should be measured in a reaction in which t-butylcarbonium ion competes for the tertiary "hydride" atoms of triptane and triptane-2-d (2,3,3-trimethylbutane-2-d). (The triptane-2-d could be conveniently synthesized by the hydroboration of triptene, 2,3,3-trimethyl-1-butene (36) with perdeuterodiborane, followed by protonolysis with propionic acid (37).) In a properly devised reaction system, the magnitude of the isotope effect could be calculated from the relative amounts of deuterated and undeuterated isobutane formed as products, analysis of these hydrocarbons to be effected by nuclear magnetic resonance spectroscopy or, preferably, by mass spectrometry.

Such a system might be the reaction in sulfuric acid as solvent of t-butylcarbonium ion, derived from t-butyl alcohol or isobutene, with the isotopically isomeric triptanes (38-42, 31-33). In related sulfuric acid systems it has been established that hydride transfer is rate-determining and that equilibrium is not instantaneously established; indeed, by a judicious choice of reaction conditions one can ensure that the product distribution resulting from hydride transfer is kinetically controlled (31-33,35,43). A possibly alternative system is the reaction with the triptanes in liquid sulfur dioxide of t-butylcarbonium ion derived either from the decomposition of the t-butyl oxocarbonium hexafluoroantimonate complex (from pivalyl fluoride and antimony pentafluoride), $(CH_3)_3CCO^+SbF_6^-$, or from the direct reaction of t-butyl fluoride and antimony pentafluoride (44).

PROPOSITION NO. 3

Abstract

Possible experiments are proposed to demonstrate more conclusively—if true—the free-radical nature of the intermediates involved in the reductions of alkyl halides by organotin hydrides.

Discussion

Recently Kuivila, Menapace, and Warner (45) have asserted that reductions of alkyl halides by organotin hydrides such as tri-n-butyltin hydride or triphenyltin hydride (45-50) proceed via a free-radical mechanism, probably "a chain mechanism in which an organotin radical abstracts a halogen atom from the halide in one step, and the resulting alkyl radical abstracts a hydrogen atom from the organotin hydride in the other step." Seyferth and co-workers (50) have found Kuivila's evidence "convincing." It would be fairer, however, and more objective to say that Kuivila's evidence is consistent with a free-radical mechanism but not conclusive.

Aside from the inherent interest in arriving at the truth with respect to the mechanism of such reactions, establishing beyond doubt the true nature of the alkyl intermediates involved in these reductions is of interest inasmuch as some of the conclusions reached concerning the mechanisms for the interconversion of the cyclopropylcarbinyl and allylcarbinyl skeletons and the dimethylcyclopropylcarbinyl and (γ,γ-dimethylallyl)-carbinyl skeletons in free-radical reactions were based on the assumption that in the reduction of allylcarbinyl bromide and of (γ,γ-dimethylallyl)-carbinyl bromide with tri-n-butyltin

hydride alkyl free-radical intermediates were indeed involved (51).

The general stoichiometry of such reductions is indicated in equation 1. The propagating steps for a generalized chain mechanism for such reactions (nature of intermediates not indicated) are presented in equations 2 and 3.

$$(4-n)RX + R'_nSnH_{4-n} \longrightarrow (4-n)RH + R'_nSnX_{4-n} \quad (1)$$

$$\text{Step 1:} \quad R'Sn + RX \longrightarrow R'SnX + R \quad (2)$$

$$\text{Step 2:} \quad R + R'SnH \longrightarrow RH + R'Sn \quad (3)$$

The fact that reduction of optically active α-phenylethyl chloride with triphenyltin deuteride yields racemic α-deuterio-phenylethane under conditions which do not cause the racemization of the halide (45) eliminates a possible S_N2 mechanism and is evidence that the reaction probably involves either alkyl free-radical or carbonium ion intermediates. However, Kuivila's observation that the relative rates for reduction of the halides in his investigation (45) paralleled more closely the relative rates of abstraction of halogen atoms from alkyl halides by methyl radicals than S_N1 solvolysis reactivities—in particular, cyclopropylcarbinyl chloride underwent no reduction at all whereas α- and γ-methylallyl chloride were readily reduced at room temperature by triphenyltin hydride, relative reactivities opposite to that for the solvolyses of the same cyclopropylcarbinyl and allyl halides in aqueous ethanol (52)—is not necessarily consistent only "with a mechanism in which the rate of formation of an alkyl free radical is the prime factor in determining reactivity of a halide"; it is also consistent with the less plausible

but still possible alternative interpretation that the rate-determining step of the reduction involves the abstraction of hydrogen from the organotin hydride by the alkyl intermediate, whether free radical or carbonium ion; i.e., step 2 might be slower than step 1. If such were the case, the reactivities of the various alkyl intermediates might be expected to be in inverse order to their relative stabilities; i.e., the more stable alkyl intermediates would be slower to abstract hydrogen from the hydride than the less stable intermediates. This would be true regardless of whether such alkyl intermediates were free radicals or carbonium ions. And if the intermediates were carbonium ions, then the relative reactivities of the halides would tend to be in inverse order to the stabilities of the carbonium ions produced upon solvolysis; i.e., in the order observed. To express the conclusion which has just been reached in another way, while it is true that the order of halide reactivities toward organotin hydrides observed is not consistent with an S_N1-type of ionization as the rate-determining step, such an observation does not necessarily rule out the possibility that alkyl carbonium ions may be involved as intermediates in these reductions. In fact it is possible that, depending upon exactly which tin hydride and alkyl halide are used as reactants and the exact reaction conditions, there may be both free-radical and carbonium ion mechanistic pathways available. One might even imagine a four-center mechanism with considerable carbonium ion or free-radical character. For example, the azo-bis-isobutyronitrile-catalyzed reductions of benzyl chloride, chlorocyclohexane, and bromobenzene undoubtedly involved alkyl free radicals as intermediates (45).

The reduction of alkyl halides by each organotin hydride should be examined in greater detail to determine whether a free-radical or carbonium ion-type mechanism is operative. In particular, in order to determine in each case whether or not "free" alkyl free radicals are involved as reaction intermediates, the following experiments are proposed as diagnostic aids.

An attempt should be made to trap out the possible free radical intermediates. One method of doing this would be to carry out the reduction of the halide with the organotin hydride in the presence of a monomer such as vinyl acetate, acrylonitrile, or methyl methacrylate to determine whether or not free radicals might be detected by initiating polymerization (53). It is known, for example, that tri-n-butyltin hydride will by itself merely add across the double bond of acrylonitrile or methyl acrylate rather than initiate polymerization (46), will not attack the nitrile or ester function while adding across the double bond (46), and will react preferentially with a carbon-bromine bond in the presence of an (unactivated) olefinic linkage (50); hence, initiation of polymerization would very likely indicate the presence of alkyl free-radical intermediates. Other radical trapping agents such as diphenylpicrylhydrazyl (54) or the very reactive galvinoxyl (55) might be used similarly if appropriate control experiments indicated that they were not being consumed in some undesired side reaction with one or the other of the reagents.

Another possible way of determining more conclusively the nature of the alkyl intermediates involved in these reactions would be to utilize the fact that the "cyclopropylcarbinyl" carbonium ion and free radical give radically different types of product distributions (56). Thus if

the reduction of cyclopropylcarbinyl bromide with an appropriate organotin hydride involved a carbonium ion intermediate under kinetically controlled reaction conditions, one might expect the hydrocarbon products to consist largely of cyclobutane and methylcyclopropane with some 1-butene (52,57). On the other hand, if a free-radical intermediate were involved in the reduction, the hydrocarbon products would be expected to consist largely of 1-butene, and no cyclobutane should be observed (58).

PROPOSITION NO. 4

Abstract

It is proposed that the possible role of polar directive effects in radical displacement reactions be investigated for donor-type free radicals as they have been investigated for acceptor-type free radicals. A model experiment is discussed.

Discussion

The possible importance of polar factors in reactions involving free-radical intermediates has been stressed by several authors (59-62). Aside from polymerization processes, however, such phenomena have been investigated mainly in the case of radical displacement reactions of highly electrophilic ("acceptor") radicals, notably chlorine (63-68). In particular, polar effects have been held to be responsible for the Hammett-type correlations observed for abstraction of hydrogen atoms from substituted toluenes and cumenes by such acceptor radicals as the chlorine radical, the bromine radical, peroxy radicals, the t-butoxy radical, and the trichloromethyl radical (59,61,62). Polar effects have also been held to be largely responsible for product distributions in chlorination reactions involving alkyl chlorides (64-66), acid chlorides (65-67), esters (65-67), acids (63,65-67), and nitriles (67), although at least one author has stated that the directive effects evident in these chlorination reactions were due to hyperconjugation in the resulting alkyl radicals rather than to a polar effect (69). For example, a typical product distribution of monochlorides from the liquid-phase photochlorination of butyric acid (67) is shown below (numbers in

parentheses represent percent of monochloride products derived from attack of a chlorine radical at that position):

$$\underset{(31\%)}{CH_3}\text{—}\underset{(64\%)}{CH_2}\text{—}\underset{(5\%)}{CH_2}\text{—}COOH \quad .$$

This product distribution is quite different from what one would expect purely on the basis of the bond dissociation energies of the various carbon-hydrogen bonds.

In general, the following factors have been shown to be of importance in determining the position of attack within a molecule (and hence the product distribution) in radical displacement reactions: the bond dissociation energy of the bond being broken; the bond strength of the bond being formed; the stability of the resulting radical (includes hyperconjugation effects); the amount of bond breaking in the transition state; and polar effects both in the molecule being attacked and in the attacking species. The term "polar effects" implies appropriate polar contributions to the transition state of the reaction. Steric effects appear to be of importance only when very large radical intermediates are involved (61).

As indicated above, the less electrophilic "donor" radicals have been thus far virtually neglected in studies of this kind. The literature contains some scattered references to investigations of reactions involving the methyl radical where polar effects might be important (70-73) and a couple of references to exploratory work on the phenyl radical (62,74); otherwise, nothing.

The ratio of relative reactivities of cyclohexane and toluene toward the chlorine radical has been estimated as 11.4 by Russell and Brown (68); Edwards and Mayo (70) have found the corresponding ratio toward the methyl radical to be 6.4. Something other than a polar effect would appear to be responsible for these results, probably the amount of bond breaking in the transition state. By contrast, Price and Morita (71) have found the ratio of the rate constants for abstraction of hydrogen from the α and β positions of isobutyryl chloride by methyl radical to be 12.4; the corresponding ratio for the chlorine radical (63) is 1.5. Polar effects might be responsible for the difference in the magnitude of the ratios in this latter example.

It is clear that an assessment of the importance of polar directive effects in radical displacement reactions of donor radicals would be of value in estimating the overall importance of polar effects in reactions of free radicals in general. To this end it is proposed that a systematic investigation of polar effects in radical displacement reactions of donor radicals be undertaken after the methods of the investigations of similar effects in reactions involving acceptor radicals.

In particular, a good experiment with which to start would be a study of the relative rates of hydrogen abstraction from the α, β, and γ positions of butyric acid by a series of donor radicals including the methyl radical, the ethyl radical, the isopropyl radical, the t-butyl radical, and the phenyl radical. These rates could be measured by successively deuterating the α, β, and γ positions in butyric acid

and determining the corresponding amounts (by mass spectrometry) of RD and RH formed for small percentage conversions upon attack by R·, following the method of Price and Morita (71). Similarly the rates could be obtained by successively tritiating the available positions and measuring the specific activity of the "RH" formed along with that of recovered starting acid. The radicals could be generated by conventional methods. The butyric acid radicals formed would presumably eventually dimerize or telomerize (72,73). Kinetic isotope effects would be automatically taken into account (and estimated) by the above procedure, or by a combination of the above procedures. The product distributions with each donor radical could be determined; comparison of the product distributions along the series of donor radicals would hopefully provide a qualitative measure of the importance of polar directive effects in this instance. Similar experiments could, of course, be carried out for other compounds with other functional groups.

The only factors aside from polar effects in the respective attacking radicals which could vary from a set of experiments with one donor radical to a set with the next would be the bond strength of the bond being formed and the amount of bond breaking in the transition state. If the polar effect predominated in these experiments, presumably there would be relatively more attack on the $\underline{\alpha}$ position of butyric acid as one moved along the series from phenyl to methyl to $\underline{t}$-butyl radical; if the other energetic factors were of prime importance, presumably the relative order of attack on the $\underline{\alpha}$ position might be reversed and instead there might be relatively more attack on the $\underline{\beta}$ position along the series phenyl, methyl, ethyl, isopropyl, and $\underline{t}$-butyl radical.

PROPOSITION NO. 5

Abstract

It is proposed that the temperature dependence of the product distributions resulting from the generation of the cyclopropylcarbinyl and dimethylcyclopropylcarbinyl free radicals in the presence of an active hydrogen donor be studied: in the former instance to verify that two radical intermediates must be invoked to account for the product distributions observed; in the latter instance to search for evidence of a nonclassical dimethylhomoallyl radical intermediate.

Discussion

The theory and significance of a study of the temperature dependence of the product distributions resulting from the generation of a cyclopropylcarbinyl-type free radical in the presence of the active hydrogen donor tributyltin hydride has been discussed at length in this thesis, pp. 35-38, in connection with a discussion of the evidence for the existence of a nonclassical diphenylhomoallyl radical (75). Briefly, it was shown that for two isomeric radicals differing significantly in free energy the product distribution resulting from hydrogen abstraction could be expected to change significantly with a reasonably small change in reaction temperature; the same result, of course, would be predicted for two radicals differing to a lesser extent in free energy provided only that the product distribution be examined over a sufficiently large temperature range. For two isomeric radicals differing in free energy by 4.6 kcal./mole, a temperature change of 100 degrees would produce approximately a ten-fold change in their equilibrium constant. If products

were to be formed from only one (nonclassical) radical intermediate, the product distribution would not be expected to depend critically upon the reaction temperature.

Thus it is proposed that the temperature dependence of the hydrocarbon product distributions resulting from the generation of the "cyclopropylcarbinyl" and dimethylcyclopropylcarbinyl free radicals in the presence of tributyltin hydride be examined critically over the experimentally feasible portion of the temperature range 0-180°. The radicals could be generated by decarbonylation of the appropriate aldehydes or by decomposition of the appropriate t-butyl peresters with appropriate initiators.

Evidence has been presented in this thesis (76) for the initial generation from the cyclopropylcarbinyl skeleton of a delocalized homoallyl radical (XVIIa, p.20). Further it was tentatively concluded (77) from the general trend of an increase in the amount of allylcarbinyl products at higher temperatures in a variety of reactions that both the homoallyl and the classical allylcarbinyl free radicals had to be invoked to account for the interconversion of the cyclopropylcarbinyl and allylcarbinyl skeletons in free-radical reactions. The temperature study of this system proposed above should serve as a check on the validity of this tentative mechanistic conclusion. (The homoallyl and allylcarbinyl free radicals may differ by 4 kcal./mole or more in their energy content (75).)

It was also tentatively concluded in this thesis that the interconversion of the dimethylcyclopropylcarbinyl and (γ,γ-dimethylallyl)-carbinyl skeletons in free-radical reactions from evidence to date can best be explained by the reversible isomerization of the classical

dimethylcyclopropylcarbinyl and (γ,γ-dimethylallyl)-carbinyl free radicals (78). It can be argued, however, that this evidence may not be accurate enough or may be insufficient. It is puzzling that there should be evidence for a nonclassical homoallyl radical (XVIIa, p. 20) and for a diphenylhomoallyl radical (XVIIc, p. 20) but not for the corresponding dimethylhomoallyl radical (XVIIb, p. 20). The temperature study of this system proposed above then should serve to confirm the tentative mechanistic conclusions reached in this thesis or to turn up evidence consistent with the existence of a nonclassical dimethylhomoallyl radical.

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