THE SYNTHESES AND THERMAL DECOMPOSITIONS OF SIX-MEMBERED CYCLIC DIACYL PEROXIDES

Thesis by

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

California Institute of Technology
Pasadena, California
1979

(Submitted May 22, 1978)

to my parents

Acknowledgement

My most sincere thanks go to my research director and dear friend, Professor Peter Dervan, who has been a constant source of encouragement and optimism. I shall always be grateful for the times we had to talk science and philosophy.

I'd like to give a special thanks to all the people who've made Caltech a more tolerable place including Steve Nesbitt, Amy Abe, Tom O'Neill, Dave Baillargeon, Mike and Jean Ingle, and a very warm thanks to Dave (Flip) Erwin.

Thank you Freddy for being my swim coach.

In order of their appearance, I'd like to thank those people who initially encouraged me and contributed some things very valuable to my life: Professors Phyllis Dunbar, Robert Boikess, Nina Roscher, Donald (DJ) Shombert, Gregory Herzog, Wilma Olson, Joan Valentine, and Stanley Mandeles. Along with them I'd like to thank my very special friend Susan Groh, who taught me how to have a good time in spite of it all.

Thanks go to Mrs Debbie Chester who is ultimately responsible for the final and certainly most attractive form of this thesis. She gets a special thanks for tolerating me and my handwriting.

The National Institutes of Health, Earle C. Anthony Fellowships, and Caltech are greatly appreciated for their generous financial support.

ABSTRACT

meso- and dl-2,3-Dimethylsuccinyl peroxides (5) and (6), cis- and trans-1,2-hexahydrophthaloyl peroxides (7) and (8), and bicyclo[3.1.0]hexanediacyl peroxide (9) have been synthesized. Products of their thermal decomposition in dichloromethane and THF suggest they decompose by a stepwise mechanism via the intermediacy of a carboxy diradical. The decomposition of erythro- and threo-2,3-dimethylpropiolactone was stereospecific and requires that the pathway and/or intermediate in this decomposition be different from that of the decomposition of peroxides (5) and (6). Thermal decomposition of (5)-(8) in methanol afforded saturated and unsaturated methyl ethers. Mechanisms involving the intermediacy of a radical cation are discussed.

Direct and sensitized irradiation of (5)-(8) were performed. The peroxides were quite photolabile. Benzophenone, anthracene, and tetracene were effective sensitizers. An electron transfer rather than an energy transfer mechanism for the effectiveness of anthracene and tetracene is proposed.

Induced decomposition of the cyclic diacyl peroxides by triphenylphosphine and dimethylsulfide to stereospecifically lead to the corresponding cyclic anhydrides was observed.

Copper (I) rapidly induced the decomposition of peroxides (5)-(8) to afford the corresponding olefins in low to moderate yields.

Induced decomposition of peroxides (5)-(8) by aromatic hydrocarbons was observed. Emission of light was observed from the reaction of dl-(6) and rubrene. The observations are consistent with chemically initiated electron transfer luminescence (CIEEL).

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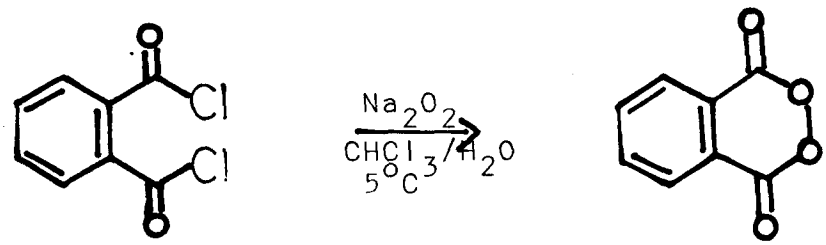
A. SYNTHESES AND CHARACTERIZATION OF CYCLIC DIACYL PEROXIDES

1. Synthesis of Five- and Six-Membered Cyclic Diacyl Peroxides.

The syntheses of cyclic diacyl peroxides, unlike their acyclic counterparts, have appeared infrequently in the literature. One of the first cyclic diacyl peroxides to be prepared was phthaloyl peroxide (1).[1,2]



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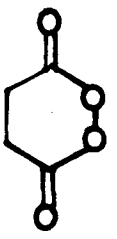
In 1955 Russell reported a procedure wherein a dilute solution (0.3M) of phthaloyl chloride in chloroform was added to a dilute solution (0.3M) of aqueous, buffered sodium peroxide. Monomeric phthaloyl peroxide as determined by freezing point depression in benzene was obtained. Previous attempts to synthesize it had resulted in insoluble polymeric peroxide.[3-5] Succinyl peroxide (2) was reported in 1951 but no spectral data or decomposition chemistry was given.[6] Phenylmaleoyl peroxide (3) was recently synthesized and decomposed.[7] Adam introduced a new class of five-membered ring cyclic peroxides (4).[8] These latter



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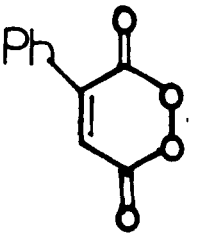

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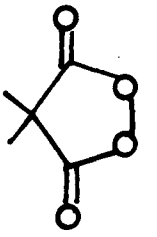
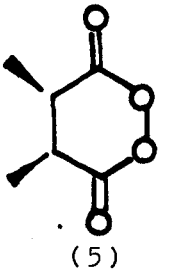


(4)

two procedures required the use of 90% hydrogen peroxide in methanesulfonic acid. A second synthesis to compounds (4) substituted sodium peroxide for hydrogen peroxide.[9]

To our knowledge then, there are only two, perhaps three, six-membered cyclic diacyl peroxides in the literature. The mechanism of the decomposition of cyclic diacyl peroxides is still not well understood. We will describe in this thesis the syntheses and study of five new six-membered ring cyclic diacyl peroxides. These succinyl peroxides provide access to stereochemical and kinetic tests of peroxide fragmentation pathways as well as information on the scope and limitations on the use of cyclic peroxides in synthesis.



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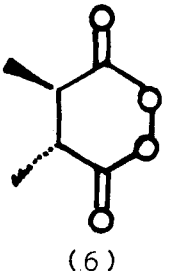

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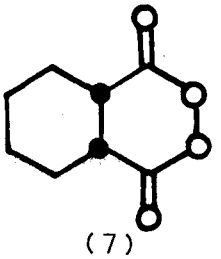

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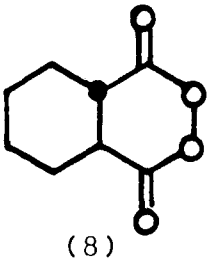

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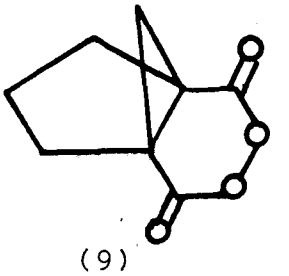

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2. Characterization of Cyclic Diacyl Peroxides.

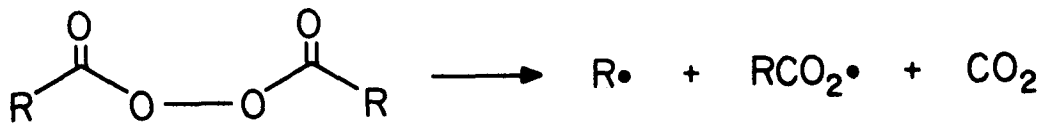
Because of the weak and reactive oxygen-oxygen bond,[10] cyclic diacyl peroxides generally cannot be isolated by vapor phase chromatography and are usually not sufficiently volatile to be distilled or sublimed. The carbonyl stretching frequencies in their infrared spectra are one useful distinguishing feature of these species.[10] Iodometric titration is the most frequently reported chemical method for determination of "active oxygen" content.[10,58] Phthaloyl peroxide (1) in earlier reported syntheses was later shown to be polymeric, insoluble peroxide. Thus, it is necessary to establish the cyclic and monomeric nature of these peroxides. Phthaloyl peroxide (1) and phenylmaleoyl peroxide (3) were shown to be monomeric by cryoscropic molecular weight determination.[1,7] The malonyl peroxides (4) were shown to be monomeric by vapor phase osmometry.[8]

B. THERMAL DECOMPOSITION OF CYCLIC DIACYL PEROXIDES

Acyclic diacyl peroxides are well known in the chemical literature. They have been a convenient source of alkyl and aryl radicals and have been employed as radical chain initiators in polymerization reactions.

Their usefulness derives in part from their mode of decomposition. Homolytic cleavage of the oxygen-oxygen

bond is quite facile (typical Ea ∿ 30 kcal·mole^{-1}).[10] Whether this process is concerted with concurrent cleavage of the carbon-carbon bond or stepwise is a subject of controversy.[10] For acetyl peroxide (R=CH_3), attempts to



trap the acetoxy radical as well as a variety of labelling studies have led to further controversy. If the acetoxy radical does exist, its rate of decarboxylation is very fast having been measured as 1.6 x 10^9 sec^{-1} at 60°C (Ea = 6.6 kcal/mole and A = 3.5 x 10^{13} sec^{-1}).[11] Other carboxy radicals have been trapped (R=Ph).[10]

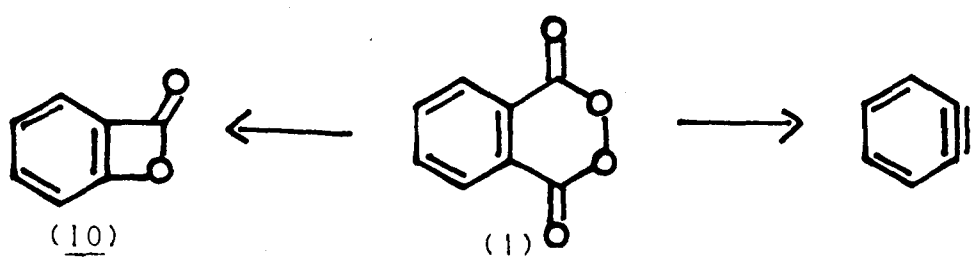
Induced decomposition by peroxide-generated radicals usually leads to higher than first order kinetics.[10,12] However, induced decomposition is apparently more important when R equals an aryl or functionalized (unsaturated or halogenated) acyl group. Induced decomposition can also be minimized at low concentrations where chain termination steps begin to compete with propagation steps.

Thus acetyl peroxide shows first order kinetics when initial concentrations are less than 0.1M.[10,13,14]

An extensive list of substituted acyclic, aroyl, and acyl peroxides, discussions on modes of decomposition and references are included in Reference 10.

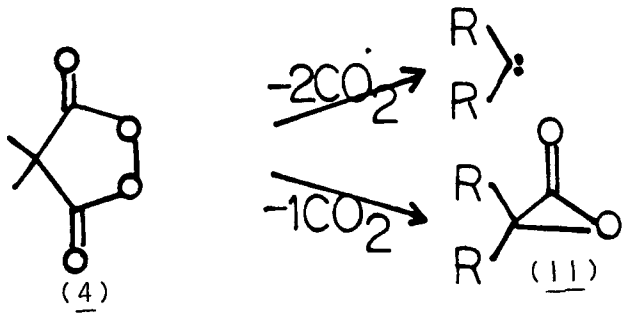
A less well-studied field is that of cyclic diacyl peroxides.[15] In acyclic diacyl peroxides after initial oxygen-oxygen (and carbon-carbon?) bond cleavage, the two reacting centers can diffuse away (in competition with cage reactions) to decarboxylate, hydrogen abstract, and so forth. By incorporating the diacyl peroxy linkage in a ring, intramolecular reaction pathways for decomposition are introduced.

Phthaloyl peroxide, (1) was the first reported and confirmed monomeric cyclic diacyl peroxide.[1,2] Its potential as a precursor to benzyne was demonstrated by both thermal and photochemical decompositions.[16-18] Low temperature irradiation of (1) yielded evidence for the β-lactone (10).[19,20]



(10) (1)

Cyclic malonyl peroxides, (4), have more recently become of interest. Not only did loss of two moles of CO_2 afford carbene, but loss of one mole produced the theoretically interesting α-lactone, (11).[8,21,22]



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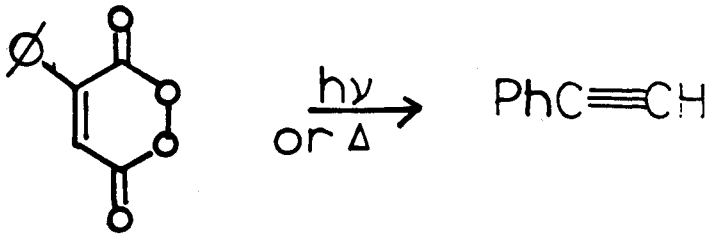
One report of a cyclic diacyl peroxide, phenylmaleoyl peroxide, (3), gave between 13% and 82% phenylacetylene upon thermal or photochemical decomposition.[7]



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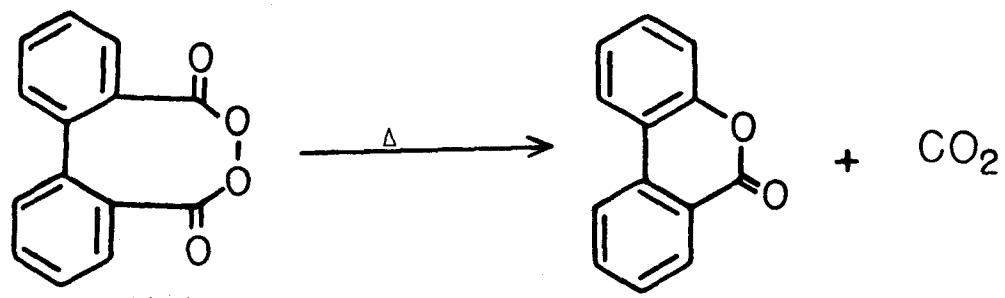
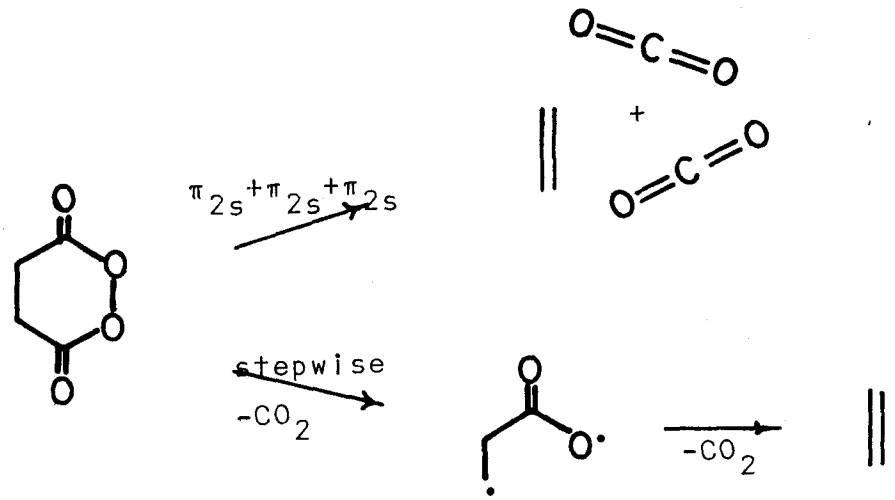
Diphenoyl peroxide, (12), has been prepared[23,24] and decomposed[25] to benzocoumarin.



(12)

This is essentially the extent to which cyclic diacyl peroxides have been investigated. Although they have been shown to be highly reactive and to provide routes to theoretically interesting molecules their general synthetic utility has not been explored.

Perhaps more importantly, the mechanism of these decompositions has not been elucidated. The diacyl peroxide linkage in a six-membered ring could very well provide access to a concerted $[\pi_{2s} + \pi_{2s} + \pi_{2s}]$ cycloreversion as well as stepwise decomposition pathways.

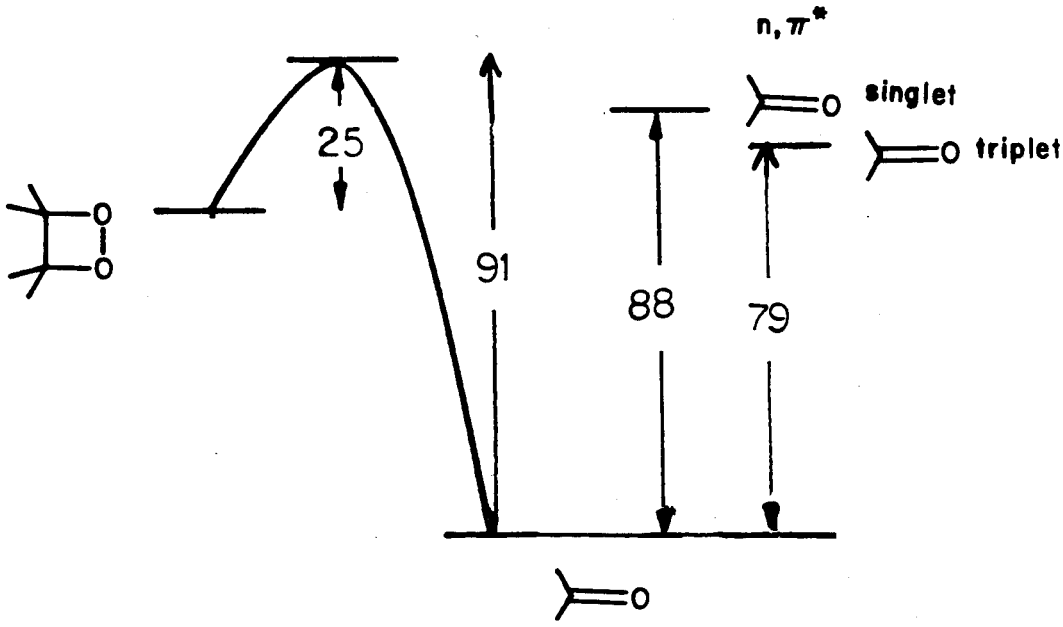


Whether concerted or stepwise, an additional mechanistic question lies in the possibility of generating electronically excited states of products. Peroxides such as dioxetanes, (13), and α-peroxylactones, (14), have led to excited state carbonyl products upon thermal decomposition.[26] Scheme 1 depicts an energy diagram[27,28] for tetramethyldioxetane which is typical for many of these systems. Note should be taken of the large exothermicity of this reaction. The energy can and does show up as light upon internal conversion of the molecule to ground state.

Scheme 2 is a similar diagram for dl-2,3-dimethylsuccinyl peroxide, (6). [27] Cyclic diacyl peroxides provide similar energetic potential to populate at least the π,π^* triplet state of the product olefin. Scheme 2 also points out that the ground state triplet may be significantly lower than the spectroscopic triplet due to considerable twisting about the carbon-carbon axis.[31]

In 1977 Schuster reported the observation of light from the decomposition of 3,6-diphenyl-3,5-cyclohexadiene-1,2-trans-dicarboxylic acid chloride, (15) in the presence of hydrogen peroxide.[32] From the products, the cyclic diacyl peroxide (16) was proposed as an intermediate. Schuster also proposed that a symmetry forbidden [$\pi_{2s} + \pi_{2a} + \pi_{2s}$] cycloreversion would lead directly to the excited state of p-terphenyl. Although the emission of light and the mode of decomposition may be the result

Scheme I



Thermochemical Values for Scheme 1

Tetramethyldioxetane[27]

4C - $(C)(H)_3$	4(-10.08)
2C - $(C)_3(O)$	2(- 6.60)
2O - (O)(C)	2(- 4.5)
+ cyclobutane corr	+26.0

ΔH_f = -36.5 kcal/mole

E_a for unimolecular decomposition[29] = 25 kcal/mole

Acetone[27]

ΔH_f = -51.7 kcal/mole

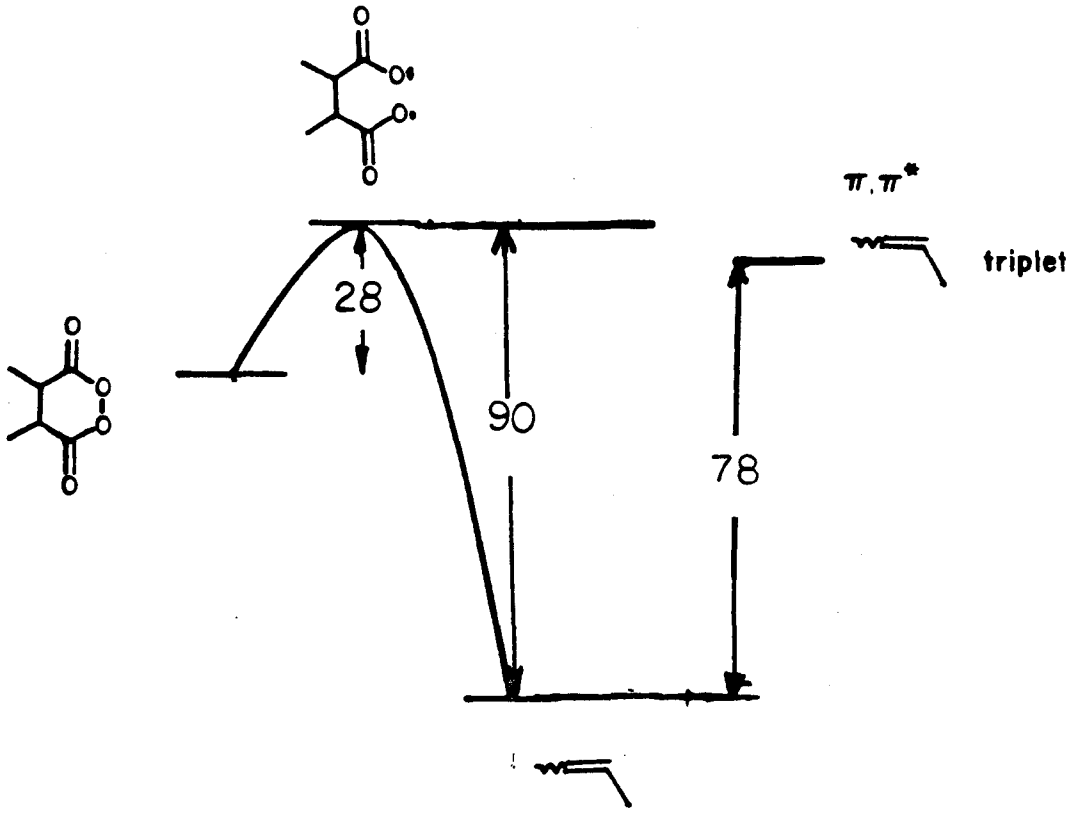
Singlet Acetone[30]

E_S = 88 kcal/mole

Triplet Acetone[30]

E_T = 79-82 kcal/mole

Scheme 2



Thermochemical Values for Scheme 2

ΔH_f 2,3-Dimethylsuccinyl Peroxide, (6).[27]

2C - $(C)(H)_3$	2(- 10.08)
2C - $(C)_2(CO)(H)$	2(- 1.8)
2CO - $(C)(O)$	2(- 33.4)
2O - $(CO)(O)$	2(- 19.0)

ΔH_f = -128.6 kcal/mole

E_a for unimolecular decomposition[16] = $\sim$ 2 .0 kcal/mole

ΔH_f trans-2-butene[27]

2C - $(C_d)(H)_3$	2(- 10.08)
$2C_d$ - $(C)(H)$	2(8.59)

ΔH_f = - 2.98 kcal/mole

ΔH_f cis-2-butene[27]

ΔH_f trans-2-butene + 1 kcal = -1.98 kcal/mole

ΔH_f CO_2[27]

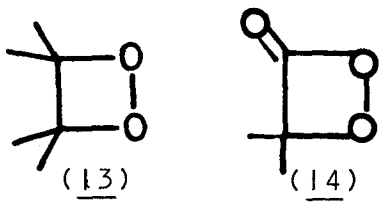
ΔH_f = -94.05 kcal/mole

Singlet 2-Butene[30]

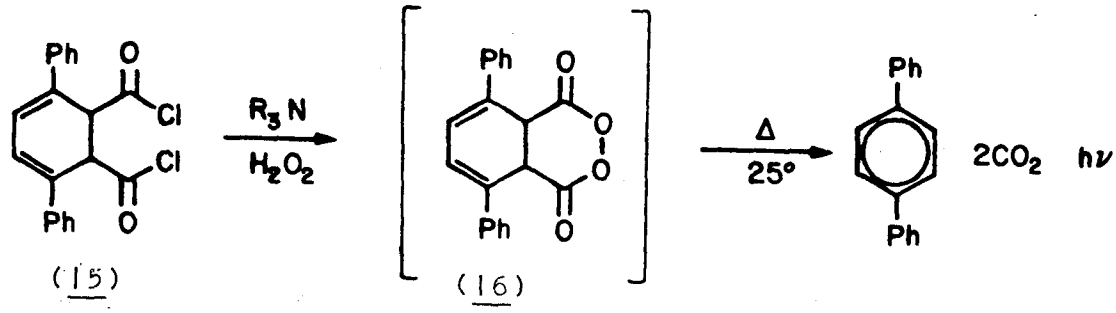
E_S = 138 kcal/mole

Triplet 2-Butene[30]

E_T = 78.2 kcal/mole



(13) (14)



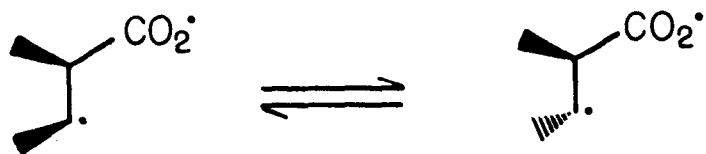
(15) (16)

of other phenomena as discussed later in Section E of this thesis, this pathway has not been ruled out.

In the Results and Discussion section we will examine the mechanism of these six-membered cyclic diacyl peroxide decompositions. meso- and dl-2,3-Dimethylsuccinyl peroxides, (5) and (6) were chosen as candidates for this study.

The stereochemistries of the products should provide insight about the mechanism of decomposition. A concerted $[\pi_{2s} + \pi_{2s} + \pi_{2s}]$ cycloreversion would give solely cis-2-butene from meso-(5) and trans-2-butene from dl-(6). Triplet photosensitization experiments of 2-butene have shown the branching ratio to be 1:1 cis:trans.[33-35] Thus, should a triplet state of 2-butene be achieved upon thermal decomposition of (5) or (6), an equimolar mixture of cis- and trans-2-butenes would be expected. If an intermediate(s)

such as a carboxy diradical(s), (17), was produced which did not subsequently lead to excited states, products



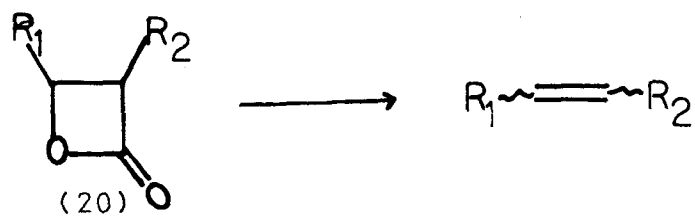
(17a) (17b)

reflecting the relative rates of rotation, cleavage and closure for this intermediate(s) might be obtained. In the event of the formation of (17), closure to β-lactones, (18) and (19), as well as cleavage to 2-butene is possible.

(18) (19)

Similarities in product stereochemistry may reflect common pathways and common intermediates. Triplet-2-butene and/or the carboxy radical(s), (17), may fit this latter proposal. It should be further noted that a concerted pathway is not necessarily a requirement for the generation of electronically excited states. The stepwise pathway could likewise provide access to such species.

In a formal sense, the thermal decomposition of β-lactones might also afford carboxy-diradicals on decomposition, and hence would provide insight on the behavior of such species for comparison with the succinyl peroxide decomposition. The course of the thermal decomposition of β-lactones has only recently been established.[36-39] Sultanbawa prepared several isomeric β-lactones (20) which he found (by nmr and vpc) to thermally



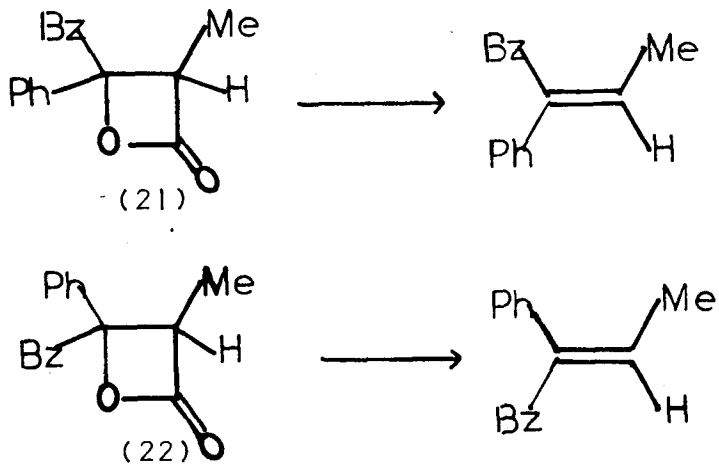
(20)

$R_1 = R_2 = (CH_2)_3Me$

$R_1 = CH_2CH_2CMe{:}CH_2$ $R_2 = CH_2CH_2C{:}CCH_2OCH_2Ph$

decompose stereospecifically (> 95%).[37,38] By assigning configuration of starting material by chromatographic elution time, he concluded that the decomposition occurred with cis-elimination of CO_2.

Adam confirmed this report by the decomposition of the cis- and trans-isomers (21) and (22). Although he did not report the isomeric purity of the starting material, stereospecific syntheses and nmr analysis established the



(21)

(22)

configuration of the β-lactones. The products clearly established that cis-elimination of CO_2 had occurred.[39]

Sultanbawa proposed a concerted and a carboxy diradical pathway for the mechanism of this decomposition.[38] Although he clearly disfavored the latter due to the stereospecificity of the reaction, neither mechanism was experimentally eliminated.

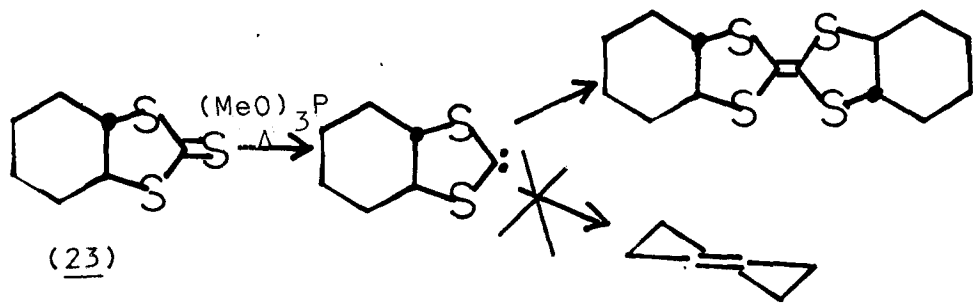
By the synthesis of erythro- and threo-2,3-dimethylpropiolactone, (18) and (19), we will be able to explore their thermal decomposition and their potential as precursors to the carboxy diradical - (17).

Trans-Cyclohexene

trans-Cyclohexene is an elusive strained alkene. Models suggest that the six-membered ring can just barely accommodate sufficient twist to allow bonding overlap between the olefin p orbitals.

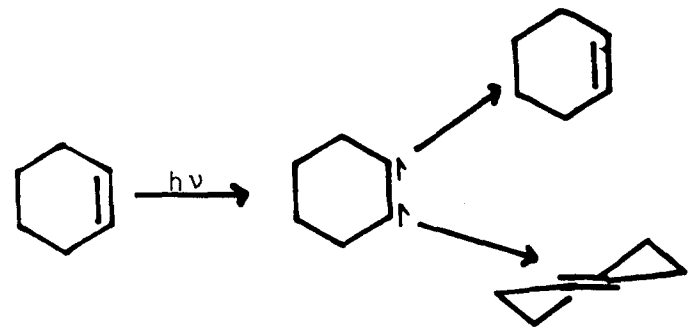
A single report has appeared which describes the unsuccessful thermal attempt to produce trans-cyclohexene

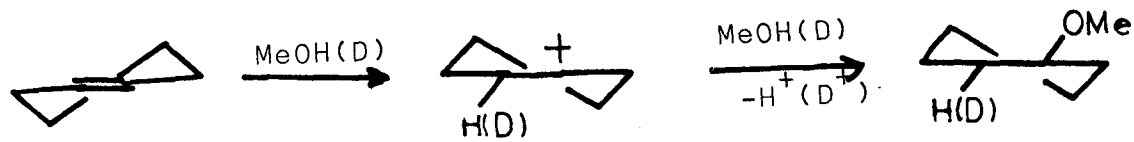
from the thiocarbonate, (23).[40]



(23)

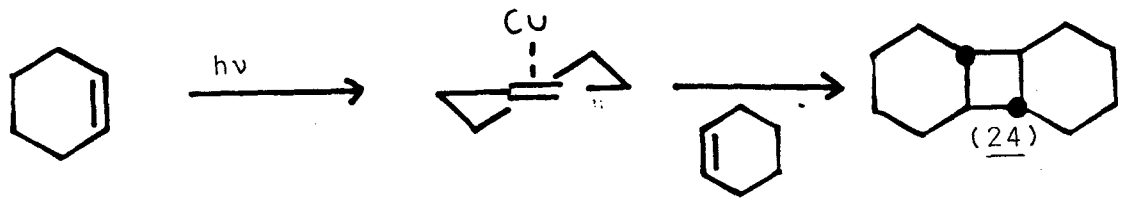
trans-Cyclohexene has been reported in several papers as arising upon photolysis of cis-cyclohexene.[41-48] Presumably, upon sensitization, cyclohexene is raised to its triplet state where it can then isomerize back to ground state cis- or trans-olefin. In protic alcoholic media, trans-cyclohexene undergoes protonation followed by nucleophilic trapping of the resulting carbonium ion.[41-48]



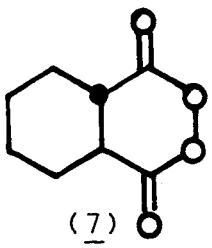


The methyl ether products are distinctive to six- and seven-membered ring olefins whose trans-intermediates are basic enough to undergo protonation. In methanol-O-d deuterium incorporation is observed. Smaller and larger rings as well as acyclic olefins have photochemistry distinctive from this. Recently, spectral observation of trans-1-phenylcyclohexene has been reported.[49] The trans-alkene was generated by photolysis (300-430 nm) of the cis-alkene and had a lifetime of ∿ 9 μsec. This intermediate disappeared in acidic, alcoholic media consistent with Kropp's and Marshall's reports.

Photolysis of cis-cyclohexene in the presence of a copper(I) triflate sensitizer yielded trans-anti-trans-tricyclo[6.4.0.$0^{2,7}$] dodecane, (24), as the major dimer product.[50] Kochi reasoned that trans-cyclohexene could be stabilized by the presence of copper long enough to undergo a thermally allowed [$\pi_{2a} + \pi_{2s}$] cycloaddition to yield this distinctive dimer.



We have prepared two new peroxides, (7) and (8), with the consideration of the possibility of generating trans-cyclohexene.



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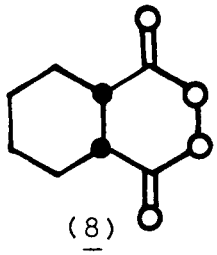
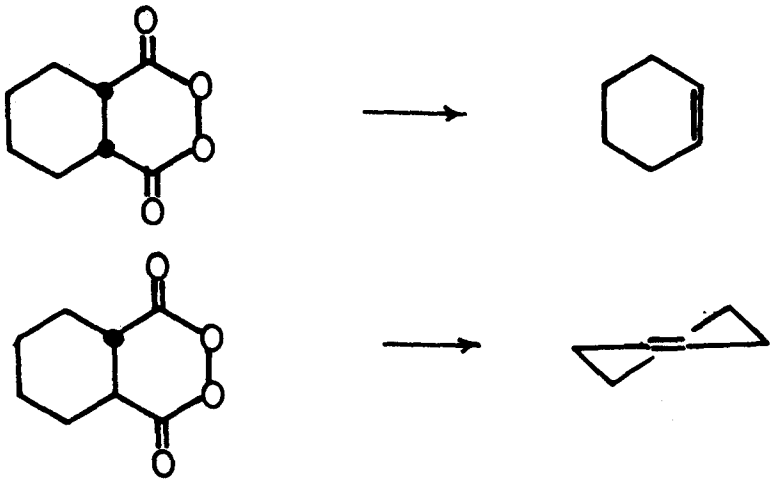


(8)

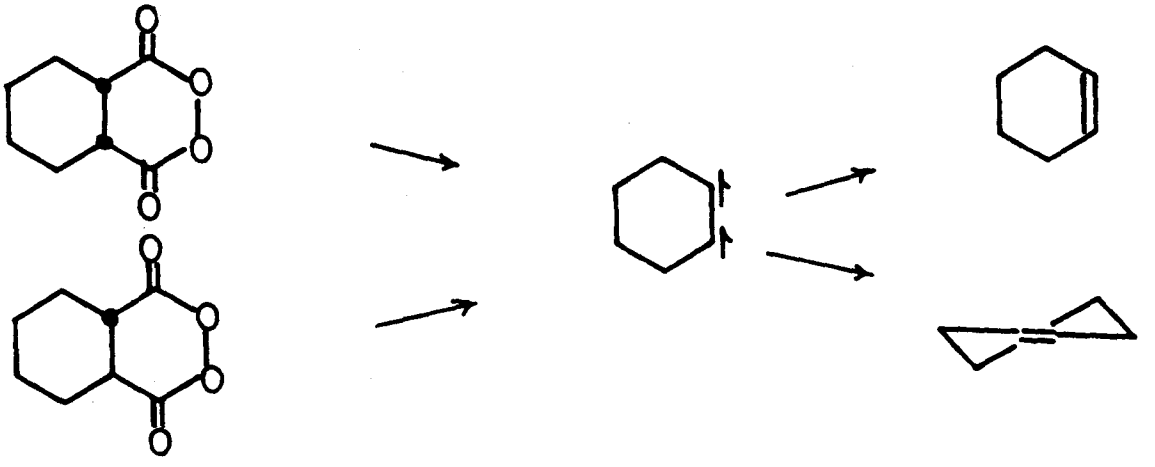
These peroxides should provide additional information concerning the mechanism of the decomposition of cyclic diacyl peroxides. Concerted $[\pi_{2s} + \pi_{2s} + \pi_{2s}]$ cyclo-reversion should afford trans-cyclohexene from (8) but not (7) Alternatively, other concerted processes might yield trans-cyclohexene from (7). In any event, only one isomer should give trans-cyclohexene if the same concerted process is operating in both. However, if we are capable of populating the triplet state of the olefin upon thermal decomposition, then trans-cyclohexene might be expected from (7) and (8). Finally, if a stepwise process is operating which does not lead to triplet, it is unknown whether any trans-cyclohexene will be produced from (7) or (8). Scheme 3 summarizes this discussion. In every case where cis-cyclohexene is produced, no trapping products are expected. In every case where trans-cyclohexene is impli-

Scheme 3

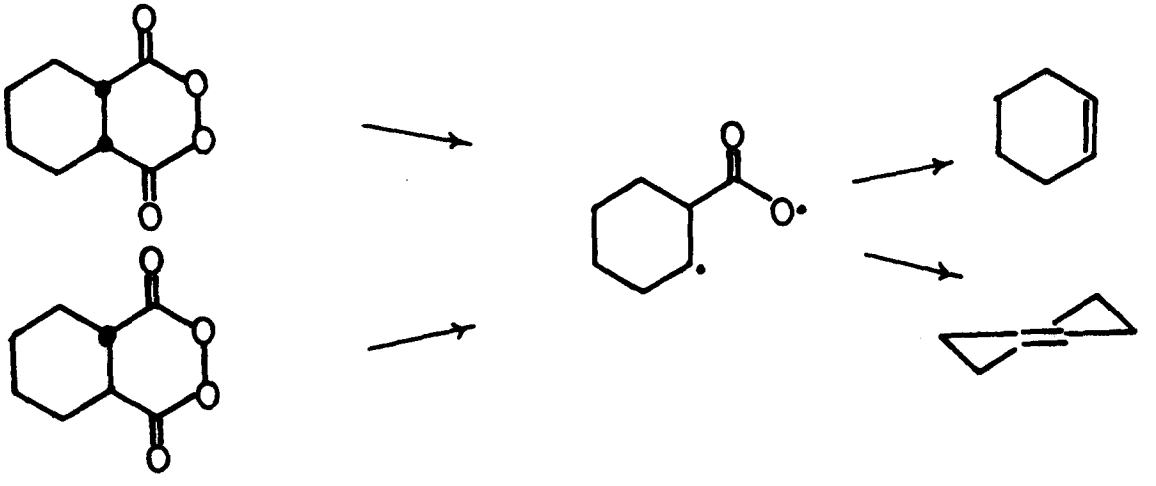
Concerted



Stepwise or Concerted Leading to Triplet



Stepwise



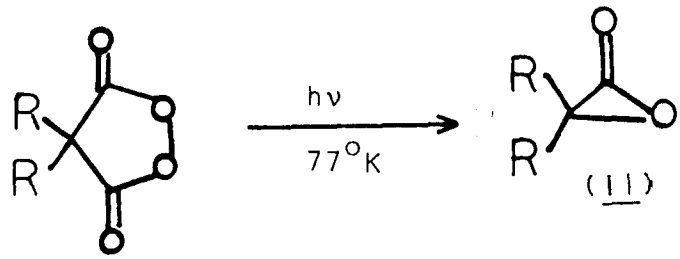
cated, trapping products are expected.

C. PHOTOCHEMICAL DECOMPOSITION

Direct irradiation of diacyl peroxides has been found to be one of the most useful means of generating radicals in solution. Kochi reported a number of acyclic diacyl peroxides as well as peresters which upon photolysis in an esr cavity afforded specific radical centers at a variety of temperatures.[51,52] The observed photolability is presumably due to the homolysis of the weak oxygen-oxygen bond with a quantum efficiency near unity.[52]

Cyclic peroxides undergo photochemical decomposition with equal ease. Here, however, the products are not free radicals but often unstable species which like the former can be conveniently generated by low temperature irradiation.

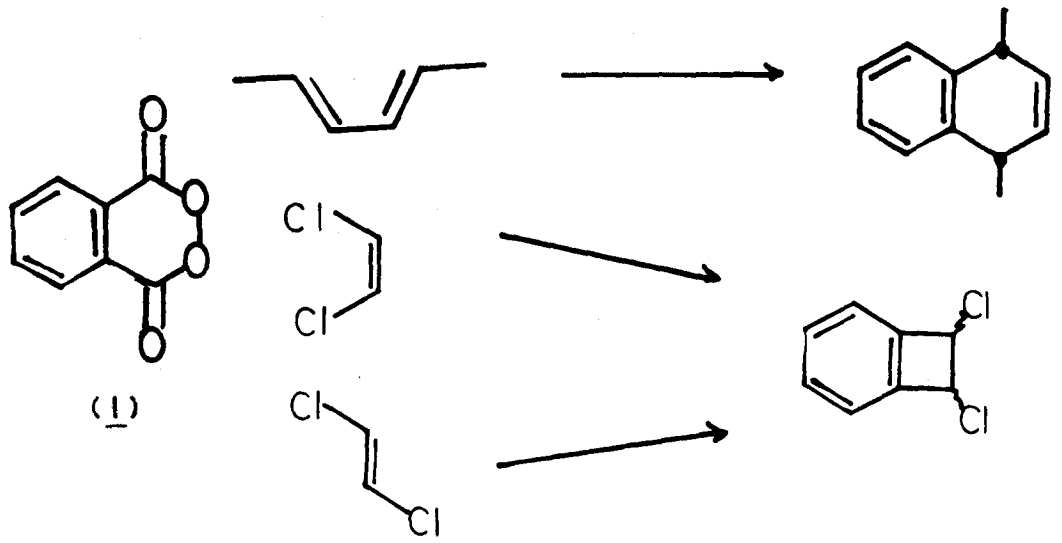
Cyclic malonyl peroxides, (4), prepared by Adam, upon thermolysis or room temperature irradiation in hydrocarbon



(4) (11)

solvents yielded only polymer.[8] However, upon irradiation at much lower temperatures (77°K) Adam and Chapman found infrared evidence for the elusive α-lactone (11).[21]

Jones and DeCamp generated benzyne at room temperature by photolysis through Pyrex of phthaloyl peroxide (1) in the presence of a variety of substituted olefins.[18] The yield of benzyne products was higher than by other thermal routes. They also concluded that only singlet ground states



(1)

of benzyne were involved due to the stereospecificity of its 4+2 adduct with 2,4-hexadiene. Phthaloyl peroxide was also irradiated in an Argon matrix at 8K with long

wavelength (> 340 nm) light. Chapman provided IR evidence for the formation of the unsaturated β-lactone, (10).[20]

Martin and King reported the direct as well as sensitized irradiation of phenylmaleoyl peroxide (3).[7] They reported 80% decomposition to give a 63% yield of phenylacetylene after a 5 hour direct irradiation through Pyrex at room temperature.

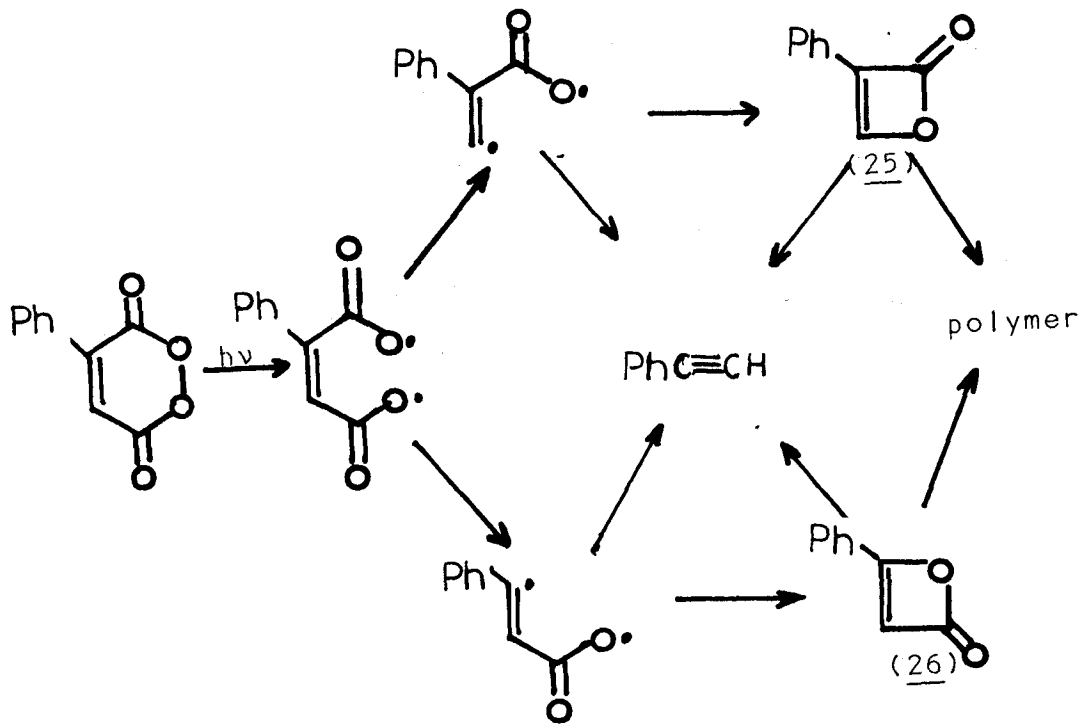
Sensitized decompositions of diacyl peroxides have appeared in several reports. Luner and Szwarc reported the decomposition of acetyl peroxide in benzene or isooctane in the presence of anthracene or napthacene.[53] Products arising from methyl radicals and CO_2 were produced.

In a careful mechanistic study, Walling investigated the decomposition of benzoyl peroxide in the presence of a variety of sensitizers.[54] Important is the fact that sensitizers with carbonyl groups and triplet energies below 59 kcal did not sensitize the decomposition but anthracene whose triplet energy is 42 kcal, did. Walling suggested that since no low-lying triplet state is available, a "non-Frank-Condon" process must be operating. This was demonstrated by his observed quenching rate of $\sim 10^6$. This is roughly three orders of magnitude slower than what is usually observed for diffusion controlled energy transfer.[55]

The report by Martin and King of the sensitized irradiations of phenylmaleoyl peroxide, (3),[7] leaves several puzzling questions. Direct irradiation through Pyrex of 0.02M solution of the peroxide in CCl_4 showed 80% decomposition in 5 hours. In the presence of benzophenone and benzil, the percent decomposition was slightly higher. Walling suggested, at least for the acyclic peroxides, benzil does not sensitize their decomposition. Although the necessary control was done to show the phenylmaleoyl peroxide did not decompose in the dark with or without sensitizer, the extent of decomposition without sensitizer was considerable during direct irradiation. Whether or not benzophenone or benzil sensitized this decomposition is not clear.

In almost all the photodecompositions reported for cyclic diacyl peroxides, the excited states and/or precursor(s) to observed products are not addressed. Homolysis of the oxygen-oxygen bond is often assumed. One could equally well imagine the concerted elimination of one mole of CO_2 to give observed lactone products or two moles of CO_2 to give benzyne (from phthaloyl peroxide), carbenes (from cyclic malonyl peroxides), or phenylacetylene (from phenylmaleoyl peroxide). Jones addressed the problem of the electronic and spin state of benzyne but did not suggest whether it arose from a concerted or stepwise decomposition of excited singlet, triplet or hot

ground state phthaloyl peroxide.[18] Martin and King suggested a stepwise mechanism leading to two carboxy diradicals which presumably operated in the thermal, sensitized, and direct irradiation decompositions.[7] These carboxy diradicals were proposed as precursors to the proposed β-lactones (25) and (26).[7]



In our present study we will examine the conditions and extent of decomposition under both direct and sensitized irradiations for all four peroxides (5)-(8). We have available for this study the stereochemistry of the cis- and trans-2-butenes as well as the analytical conditions for the analysis of the relatively stable and iso-

lated erythro- and threo-2,3-dimethylpropiolactones (18) and (19) (see Results and Discussion). We expect, for example, that if the carboxy diradical triplet is the immediate precursor to 2-butene and that it decarboxylates before internal conversion to ground state singlet, 2-butene should be "born" as a triplet and give cis and trans products (50-50) reflecting the branching ratio of triplet-2-butene.[33-35]

As in the thermal decompositions considered earlier, the β-lactone and 2-butene stereochemistries from two different stereochemical precursors (5) and (6) should provide evidence for or against common intermediates.

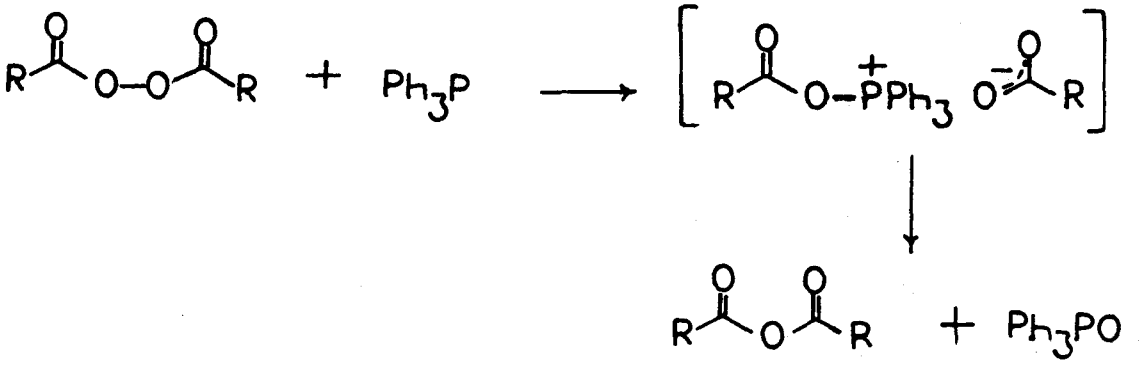
D. INDUCED DECOMPOSITION BY NUCLEOPHILES, ELECTROPHILES AND REDOX METALS

Not only is the oxygen-oxygen bond of peroxides quite thermally and photochemically labile, but a variety of nucleophilic and electrophilic reactions have been found to take place at this center.[10] In addition, as discussed more fully in Section E, reduction of the peroxidic linkage can be affected by fairly mild oxidizing agents.

1. Nucleophiles.

Amines, phosphines, arsines, sulfides, olefins, enanimes, phenols, and anions have all been found to induce decomposition of diacyl peroxides.[10] Of particular note are phosphines. The reaction of diacyl peroxides

with compounds R_3P (R = alkyl, aryl) yields anhydrides and phosphine oxides, often quantitatively. The mechanism includes initial nucleophilic attack of the phosphorous on the oxygen-oxygen linkage. Labelling experiments suggest the intermediacy of an ion pair.[56,57]



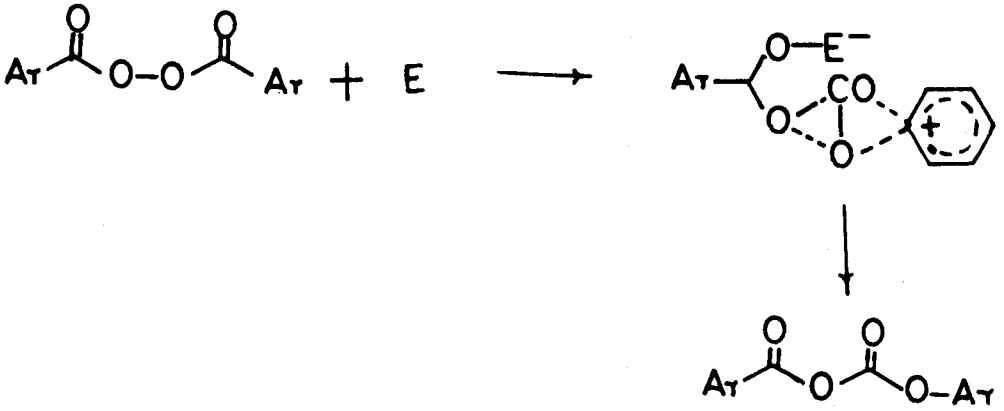
Thus, it is expected that reaction of cyclic peroxides will lead to the corresponding cyclic anhydrides. Since the carbon-carbonyl bond is not broken the reaction should proceed stereospecifically and allow convenient determination of the stereochemistry of the peroxide by analysis of the anhydride.

Halide ions induce decomposition of peroxides.[10] The reaction of iodine has become a useful quantitative measurement for "active oxygen" content.[58]

2. Electrophiles.

Lewis acids of boron, aluminum, and antimony can induce "carboxy inversion." Examples of this type of chemistry come from aryl diacyl peroxides.[10] Free metals, salts, and alkyls of mercury, tin, and lead also induce

decomposition.[10]



In both the nucleophilic and electrophilic reactions, product mixtures are often complex and mechanisms of decomposition are not straightforward.

3. Transition Metals.

Metals of variable valence capable of readily donating as well as accepting electrons can induce decomposition of diacyl peroxides by electron transfer. Iron, cobalt, manganese, and copper have been utilized to accelerate decomposition of diacyl peroxides at room or lower temperatures.[10] Most well studied is the copper (I)-copper (II) system. Kochi has shown that copper (I) can induce decomposition of diacyl peroxides by electron transfer.[59-63] The resulting carboxy radical species rapidly decarboxylates to carbon dioxide and an alkyl radical. The alkyl radical can then be oxidized by copper (II). Products arising from elimination or substitution of the oxidized alkyl radical are found. The reaction kinetics suggest greater complexity, however, and Kochi has proposed an alkyl copper intermediate

preceding the oxidation step.[59]

It would be nearly impossible to examine every known electrophilic or nucleophilic reaction for peroxides (5)-(9) in this thesis. However, it is likely that the cyclic structure could afford new reaction pathways unavailable in the acyclic analogs.

E. AROMATIC HYDROCARBON INDUCED DECOMPOSITION-CHEMILUMINESCENCE

Two predominant schemes have arisen to explain most chemiluminescent reactions. In the first, a high energy reactant molecule undergoes an exergonic reaction sufficient to generate an electronically excited state of the product molecule. Examples of this type of decomposition are 1,2-dioxetanes, Dewar benzene, and α-peroxylactones.[26] The second process is known as electron transfer chemiluminescence (ecl). It is known for many organic systems where both a radical cation and radical anion can be electrochemically generated and allowed to diffuse together and "annihilate" with subsequent light emission.[68]

Recently, a third type of chemiluminescence was discovered in Schuster's labs which is related to ecl.[25] Upon decomposing diphenoyl peroxide (1), he observed no emission of light. However, upon adding various, common energy acceptors such as diphenylanthracene or perylene,

he observed light emission. In fact, the intensity (rate of emission) was a function of the aromatic hydrocarbon energy acceptor. He was able to show that the peroxide decomposed with an observed first order rate constant which was a function of hydrocarbon concentration, $k_{obsvd} = k_1 + k_2$[aromatic hydrocarbon]. k_1 is the rate constant for the unimolecular decomposition of the peroxide. Experimental conditions could easily be set such that k_1 (the thermal decomposition of the peroxide) was insignificant and $k_{obsvd} = k_2$[aromatic hydrocarbon]. The hydrocarbon was a catalyst whose effectiveness (increased rate) was a function of its oxidation potential. The relationship between the oxidation potential and the observed k_2 with diphenoyl peroxide, (12), can be seen in Table 1. This suggested the electron transfer mechanism shown in Scheme 4 called Chemically Initiated Electron Exchange Luminescence (CIEEL). Here, an aromatic hydrocarbon (ArH) is a powerful enough reductant to transfer an electron to the peroxidic bond. Then, in the cage, the peroxide molecule can decompose to some radical anion species (PDP-peroxide decomposition product) which can donate its electron back to the radical cation. This latter step is analogous to ecl and the expected fluorescence is observed. In general, peroxidic bonds are

easily reduced[89] (irreversibly) and thus it seems an intriguing possibility that aromatic hydrocarbons might decompose peroxides (5) through (8) with the emission of light.

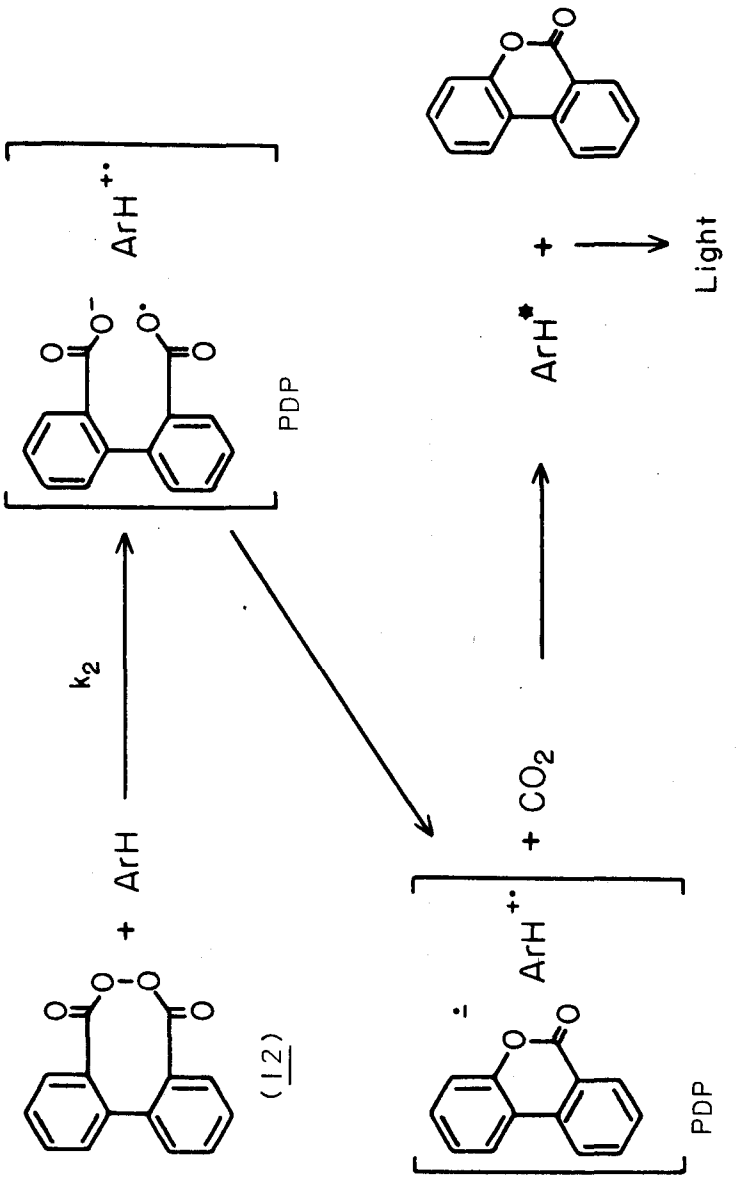
Table 1. Oxidation Potentials of Aromatic Hydrocarbons† and Their Reaction Rate with Diphenoyl Peroxide (12)[25]

Aromatic Hydrocarbon	E_{ox}	k_2 with (12)
Rubrene	0.82	14.7
Tetracene	0.95	4.52
Perylene	1.06	1.45
DPA	1.22	0.103
Coronene	1.23	0.100
Anthracene	1.35	0.056
Pyrene	1.36	0.034

†E_{ox} measured against standard calomel electrode (SCE), Reference 91.

Scheme 4

Chemically Initiated Electron Exchange Mechanism for Chemiluminescence of Diphenoyl Peroxide.



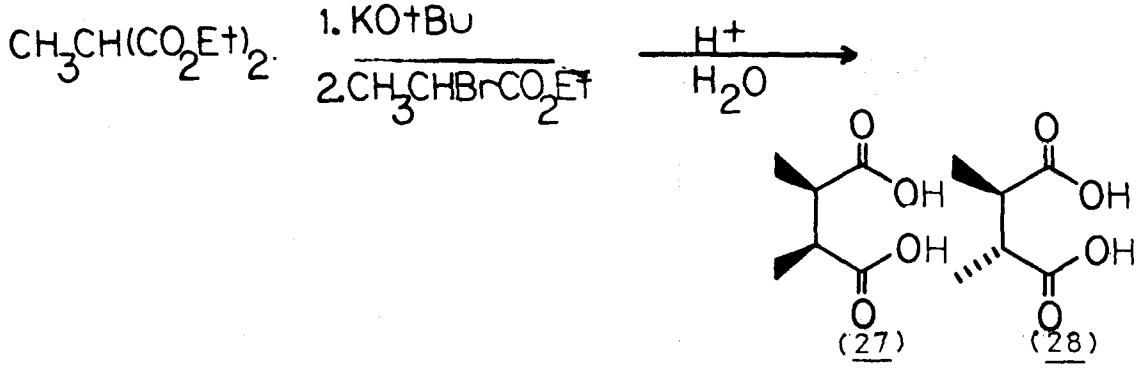
II. RESULTS AND DISCUSSION

In this section we will describe the syntheses of six-membered cyclic diacyl peroxides. We will examine the thermal, photochemical and induced decomposition of these species. The composition and stereochemistry of the products will allow some conclusions on the mechanism of these fragmentation reactions.

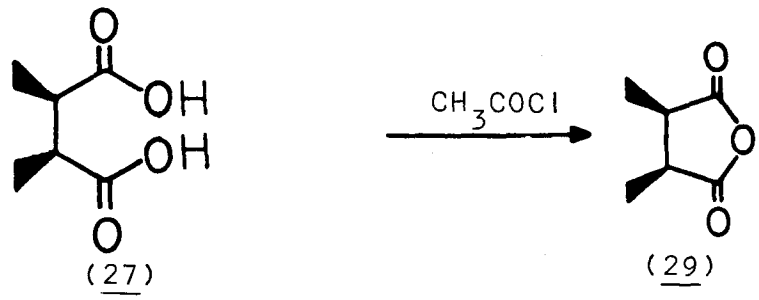
A. SYNTHESIS AND CHARACTERIZATION OF SIX-MEMBERED CYCLIC DIACYL PEROXIDES

1. Preparation of meso- and dl-2,3-Dimethylsuccinic Acids, (27) and (28), Anhydrides, (29) and (30), and Methyl Esters, (31) and (32).

A mixture of meso - and dl-2,3-dimethylsuccinic acids, (27), and (28), was synthesized by a reported two step route from diethyl methylmalonate and α-bromopro-



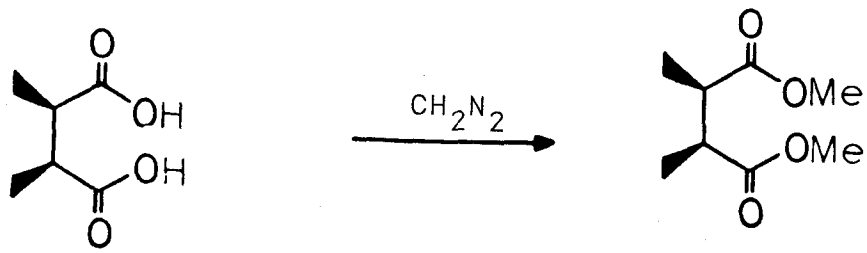
pionate.[70] Recrystallizations from concentrated HCl yielded the diacid enriched in the meso-isomer (> 99%). The dimethylsuccinic acids, (27) and (28), could be converted to their corresponding anhydrides, (29) and (30), respectively, by treatment with acetyl chloride.[70]



(27) (29)

Conversion of the water soluble dl-(28) enriched fraction to anhydride and recrystallization from carbon tetrachloride yielded > 97% isomerically pure dl-2,3-dimethylsuccinic anhydride, (30). Both isomers could be separated by vapor phase chromatography (vpc).

Melting point data (meso-(27): m.p. 210°C, lit. m.p. 209°C; dl-(28): m.p. 128°C, lit. m.p. 120-125°C)[70] allowed initial sterochemical assignment of the acids. Treatment of either diacid with an ethereal solution of diazomethane afforded the corresponding dimethyl esters (31) and (32). The isomeric purity of each was analyzed by vpc.

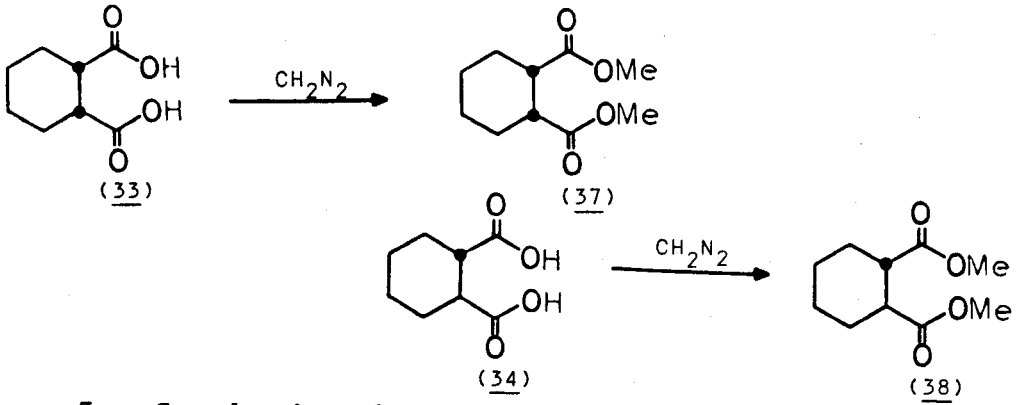


(27) (31)

2. Synthesis of cis- and trans-Dimethyl-1,2-Hexahydrophthalates, (37) and (38).

cis- and trans-1,2-Hexahydrophthalic acids, (33) and (34), and anhydrides, (35) and (36), were commercially available.

Treatment of (33) and (34) with an ethereal solution of diazomethane afforded the corresponding dimethyl-1,2-hexahydrophthalates, (37) and (38), respectively.



3. Synthesis of meso- and dl-2,3-Dimethylsuccinyl Peroxides, (5) and (6).

meso-2,3-Dimethylsuccinyl peroxide, (5), was prepared by treatment of meso-2,3-dimethylsuccinic acid, (27), with phosphorous pentachloride to provide the intermediate diacid chloride, (39), which was then added in dichloromethane to an aqueous, buffered solution of sodium peroxide. Similarly, dl-2,3-dimethylsuccinyl peroxide, (6), was prepared by successive treatment of dl-2,3-dimethylsuccinic anhydride, (30), with phosphorous pentachloride and an aqueous, buffered solution of sodium peroxide. The peroxides were obtained as white powders

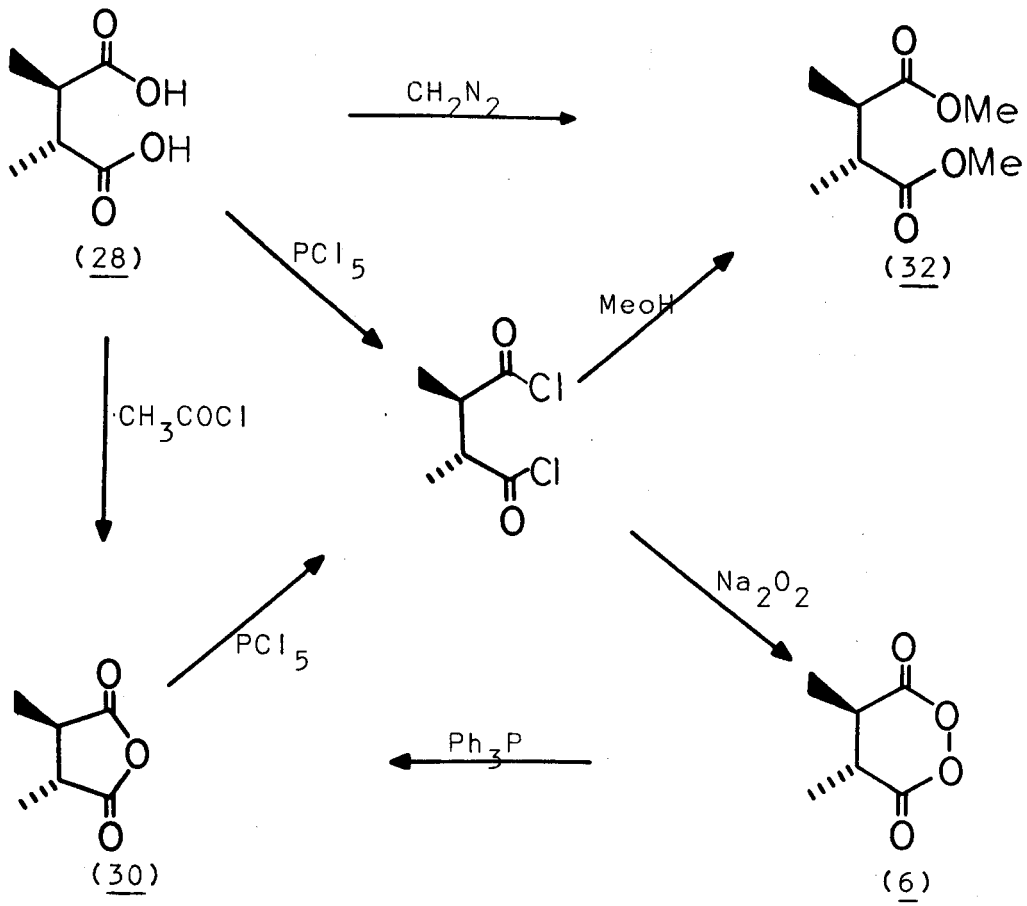
after precipitation from dichloromethane-hexane. Scheme 5 shows the interconversion of products, starting materials and intermediate diacid chlorides. meso- and dl-Dimethyl-2,3-dimethylsuccinates, (31) and (32) as well as meso- and dl-2,3-dimethylsuccinic anhydrides, (29) and (30), could be conveniently separated by vpc. Thus, the isomeric purity of these systems could be easily monitored. Both meso- and dl-peroxides, (5) and (6), were prepared in > 95% and often > 98% isomeric purity.

Both peroxides were white powders. Both were soluble in methylene chloride, chloroform, acetonitrile, and slightly soluble in tetrahydrofuran. The dl-peroxide, (6), was soluble in benzene. Both peroxides detonated when heated and often detonated upon attempted drying.

The peroxides were particularly difficult to get out of solution and were often prepared in situ as stock solutions in dichloromethane.

Detailed discussion of their spectral, chemical and physical characterization appears in Part 6 of this Section (IIA.6).

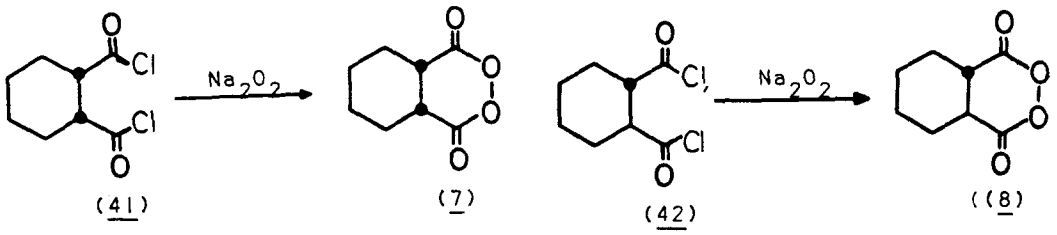
Scheme 5


OH
OH
O
O
(28)
CH_2N_2
OMe
OMe
O
O
(32)
PCl_5
MeoH
CH_3COCl
Cl
Cl
O
O
Na_2O_2
PCl_5
Ph_3P
O
O
O
O
(30)
O
O
O
(6)

4. Synthesis of cis- and trans-1,2-Hexahydrophthaloyl Peroxides, (7) and (8).

cis- and trans-Hexahydrophthaloyl peroxides, (7) and (8) were prepared by treatment of their corresponding commerically available dicarboxylic acids, (33) and (34), or anhydrides, (35) and (36), with phosphorous pentachloride followed by treatment of the intermediate diacid chlorides, (41) and (42) with an aqueous buffered solution of sodium peroxide.

The isomeric purity of the samples was > 95% as determined by quality of starting material and the dimethyl hexahydrophthalates, (37) and (38), resulting from the reaction of methanol with the intermediate diacid chlorides. The reactions depicted in Scheme 5 for the meso- and dl-



(41) (7) (42) ((8)

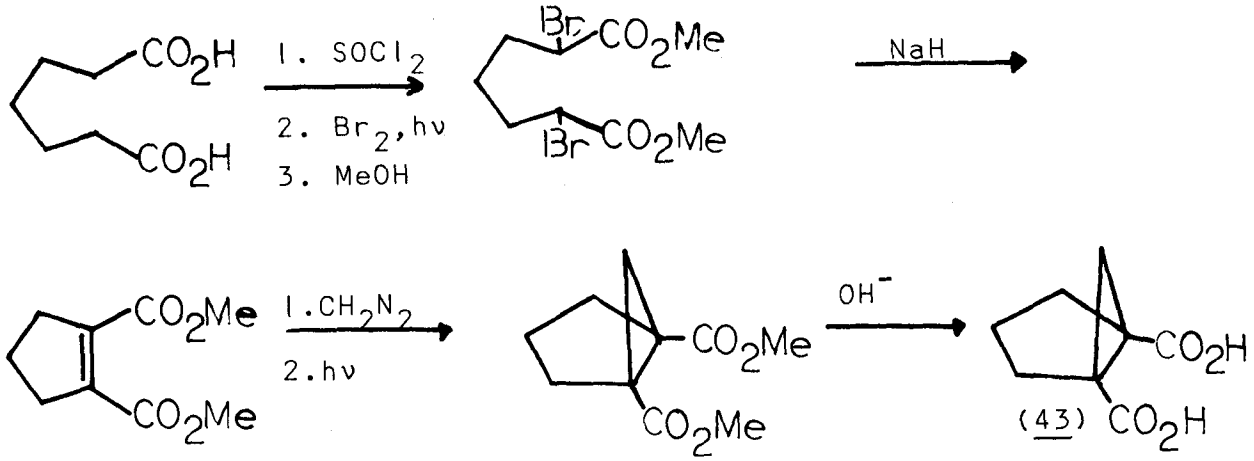
peroxides, (5) and (6), apply equally well here. However, vpc conditions could not be found to sufficiently separate the cis- and trans-hexahydrophthalic anhydrides, (35) and (36), precluding the reaction of triphenylphosphine with the peroxides as a final check of isomeric purity.

Both (7) and (8) were white crystalline compounds which decomposed rapidly and often explosively when heated to 60-70°C. Both were soluble in chloroform, dichloromethane, benzene, tetrahydrofuran and acetonitrile.

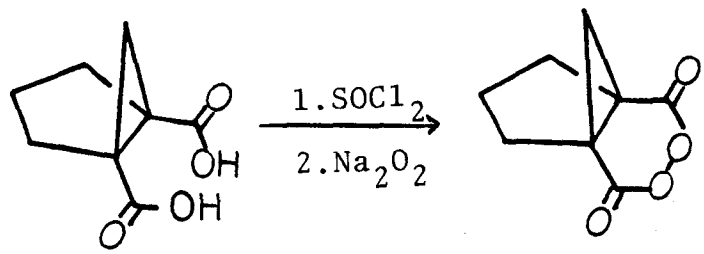
These compounds could be prepared in reasonable yields and were stored as solids in a dessicator until use at -20°C.

5. Synthesis of Bicyclo[3.1.0]hexane-1,2-diacyl Peroxide, (9).

Bicyclo[3.1.0]hexane-1,2-dicarboxylic acid, (43), was prepared by a four step route from pimelic acid as described elsewhere.[71] The diacid, (43), was treated



with thionyl chloride followed by an aqueous buffered solution of sodium peroxide to yield peroxide (9).



(43) (9)

The peroxide was a white crystalline powder which detonated upon heating to ∿ 120°C or with mild friction. It was soluble in chloroform, dichloromethane, and benzene.

6. Characterization.

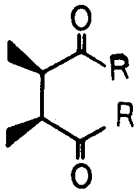
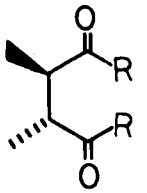
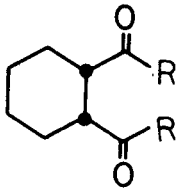
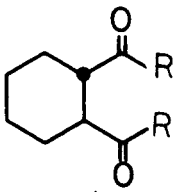
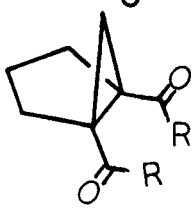
a. Spectral

The nmr spectra of peroxides (5)-(9) are consistent with their structures.

The ultraviolet spectra are unexceptional. Tailing, low extinction absorption begins above 300 nm ($\varepsilon \sim 1$-10) and continues until cut off by solvent (at 250 nm $\varepsilon \sim 10^2$, Table 25, Experimental Section).

Two strong carbonyl stretches (see Table 2) are characteristic of these peroxides and distinguish them from their corresponding anhydrides and acid chlorides. These peaks are quite useful quantitatively. Extinction coefficients in a 0.1 mm path length cell were determined for peroxides meso-(5) and trans-(8). Not correcting

Table 2. Infrared Spectra of Diacyl Compounds[†]

	Anhydride (RR=0)	Diacid Chloride (R=Cl)	Dimethyl-esters (R=OCH_3)	Peroxide (RR=00)
	1840cm^{-1} 1780	1790	1730	1810 1778
	1860 1790	1790	1730	1811 1782
	1860(ether) 1795	1790(neat)	----	1803 1775
	1862 1790	1787	----	1800 1775
	1858 1790	1782	----	1795 1775

[†]Spectra were recorded in CH_2Cl_2 or $CHCl_3$ unless otherwise indicated.

for path length, $A = \varepsilon c$ (A-absorption, ε-extinction coefficient, c-concentration). For meso-(5), $\varepsilon_{1810cm^{-1}} = 2.5$ and $\varepsilon_{1778cm^{-1}} = 3.8$. For trans-(8), $\varepsilon_{1800cm^{-1}} = 2.5$ and $\varepsilon_{1775cm^{-1}} = 3.7$ (Table 25, Experimental Section).

b. Chemical

Iodometric titration by the method of Swern was attempted.[58] Table 34 in the Experimental Section lists the results. The procedure used specifically called for isopropanol as solvent. However, none of the listed peroxides were soluble in that solvent. Benzoyl peroxide, however, was soluble with large excesses of isopropanol after initial solution in methylene chloride. In a 50-50 mixture of isopropanol and methylene chloride, titration gave a quantitative report of active oxygen in commercial benzoyl peroxide. However, removal of isopropanol gave unusually low results. Peroxides (5)-(8) were soluble in methylene chloride but addition of isopropanol to the 50-50 level caused cloudiness and partial precipitation of the peroxide. Most titrations gave 70-80% "active oxygen" content. However, in some cases even identically prepared samples significantly differed.

Although one conclusion to be reached is that these peroxides may not be pure peroxide, several facts must first be considered. Procedure plays a large role in precision and accuracy.[58] Isopropanol is the necessary sol-

vent (as shown by the benzoyl peroxide sample) yet causes the dissolution of peroxides (5)-(8).

Adam has reported that the infrared carbonyl absorption can be used as accurately as iodometric titration for determination of the concentration of diacyl peroxides.[72] No other carbonyl absorption appears in the spectrum and all likely contaminants (diacids, anhydrides, acid chlorides) can be distinguished from the peroxide. The polymeric material which appears after decomposition of the peroxide, is not present in a freshly prepared sample.

A particularly worrisome contaminant is n-hexane. This was the solvent used to cause dissolution of the peroxides leading to their isolation. Even after drying on a vacuum line, some hexane remained on the sample as evidenced in vpc traces and nmr spectra. For example an nmr spectrum of a typical sample (cis-)showed 12 mole % n-hexane. This would then, indeed, be one source of error in this titration.

c. Molecular Weight Determination

Two sets of freezing point depressions in benzene were performed to determine the molecular weight of the peroxides. Tables 3a and 3b summarize the results and include other compounds for comparison. The results showed peroxide cis-(7) and trans-(8) to be monomeric.

Table 3a. Cryoscopic Determination of Molecular Weight-1

Sample	mg solute/g benzene	Molecular Weight (exptl.)	(calc.)
dl-anhydride-(30)	3.20/0.457	219 ± 103	128
dl-anhydride-(30)	15.6 /0.446	127 ± 20	128
cis-peroxide-(7)	7.60/0.448	195 ± 26	170
cis-peroxide-(7)	11.9 /0.448	165 ± 11	170
trans-peroxide-(8)	21.9 /0.478	207 ± 19	170

Table 3b. Cryoscopic Determination of Molecular Weight-2

Sample	mg solute/g benzene	Molecular Weight (exptl.)	(calc.)
dl-anhydride-(30)	19.2 /2.30	121 ± 8	128
cis-peroxide-(7)	19.4 /0.947	214	170
trans-peroxide-(8)	16.7 /1.02	214 ± 68	170
Benzoyl peroxide	18.8 /2.30	209 ± 6	240

Table 4. Vapor Pressure Osmometry-Molecular Weight Determination

Peroxide	mg solute/ ml solvent	Solvent	Molecular Weight (exptl.)	(calc.)
cis-peroxide-(7)	19.50	CH_2Cl_2	1463	170
trans-peroxide-(8)	14.36	CH_2Cl_2	2309	170
cis-peroxide-(7)	23-33 mgs	C_6H_6	1356 ± 219	170
trans-peroxide-(8)	22.42	C_6H_6	766	170

meso-(5) was not soluble in benzene and large enough quantities of dl-(6) were not available to determine molecular weights cryoscopically.

Vapor pressure osmometry was also performed on peroxides cis-(7) and trans-(8). Table 4 summarizes the results. A more complete listing of molecular weights determined by this method appears in Table 33 in the Experimental Section.

The third entry in Table 4 is the average of four samples. Standard deviation is larger than the expected molecular weight. All other entries are single results.

The results in Table 4 are quite surprising. Other compounds including peroxides (benzoyl peroxide and diphenoyl peroxide) gave consistent and accurate results. The extremely high molecular weights of peroxides (7) and (8) stand in contrast to the freezing point data.

In fact, the peroxide samples used for the determinations listed in Tables 3b and 4 were identical.

Tables 3a and 3b list cryoscopic molecular weight determinations performed six months apart on different samples of peroxides and with different electronic equipment. (Freezing point curves of determinations in Table 3a were plotted electronically on an x-y recorder interfaced with a millivolt meter. The results were calibrated against ferrocene. Freezing point curve of results in Table 3b were obtained from a digital millivolt meter and plotted by hand. Results were calibrated against dl-anhydride-(30).)

We do not know what the nature of the difficulty with the vapor pressure osmometer is, but irreproducible readings and drifting suggest these results are not reliable.

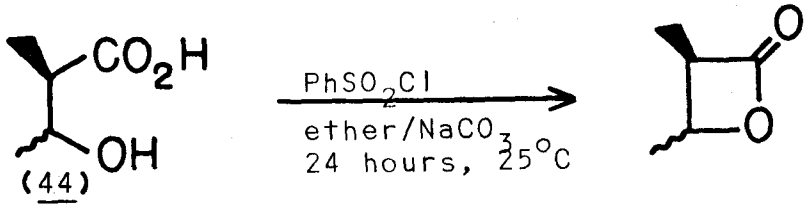
We prepared our peroxides according to a procedure specifically designed to yield monomeric phthaloyl peroxide.[1] Although we cannot exclude the possibility that some samples may have higher molecular weight material present (and thus explaining the slightly high readings in Table 3b) we have cryoscopic molecular weight evidence that they are predominantly monomeric. Discussion concerning the decomposition of these peroxides in this thesis will assume that they are monomeric.

Although the molecular weights of peroxides meso-(5) and dl-(6) were not determined, their similar synthetic origin, similar spectra (infrared), and similar decomposition behavior lead us to assume they are likewise monomeric.

B. THERMAL DECOMPOSITION OF DL- AND MESO-2,3-DIMETHYL SUCCINYL PEROXIDES (5) AND (6) AND CIS- AND TRANS-1,2-HEXAHYDROPHTHALOYL PEROXIDES (7) AND (8).

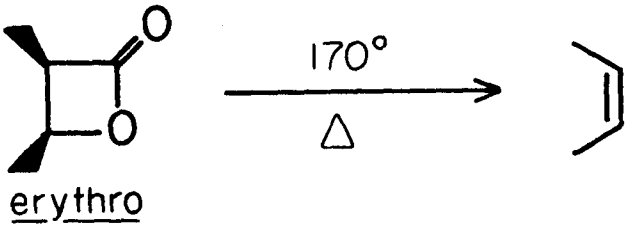
1. Synthesis of erythro- and threo-2,3-Dimethylpropiolactones, (18) and (19).

erythro- and threo-2,3-Dimethylpropiolactones, (18) and (19), were synthesized as a mixture by treatment of erythro- and threo-3-hydroxy-2-methylbutanoic acids, (44), with benzenesulfonyl chloride in ether at room tem-

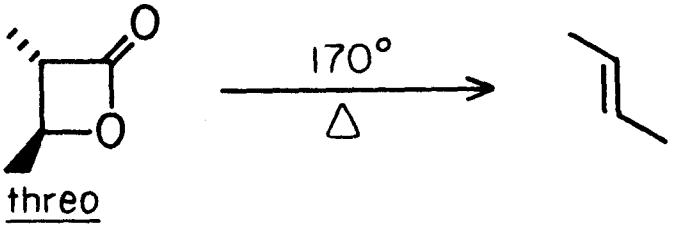


perature for 24 hours.[73] The yields of this reaction were typically poor (∿ 5%). Methanesulfonyl chloride and toluenesulfonyl chloride worked no better. Even careful distillation could not separate these lactones from unreacted sulfonyl chloride. They were isolated as pure

liquids by preparative gas chromatography. A strong carbonyl stretching frequency in the infrared at 1820 cm^{-1} is consistent with the β-lactone functionality.[78] The nmr spectra are consistent with structures (18) and (19). Stereochemical assignment was made after they were collected isomerically pure (≥ 98%) as shown by analytical vpc. β-Lactones have been shown to decompose stereospecifically with cis-elimination, to give olefin products.[33-36] The isomers were collected as they eluted from the gas chromatograph into n-octane and pyrolyzed 229 minutes at 171°C. The first eluting peak afforded 99.7% pure trans-2-butene and was assigned the threo configuration. The second eluting peak afforded 98.7% pure cis-2-butene and was assigned the erythro configuration.



erythro



threo

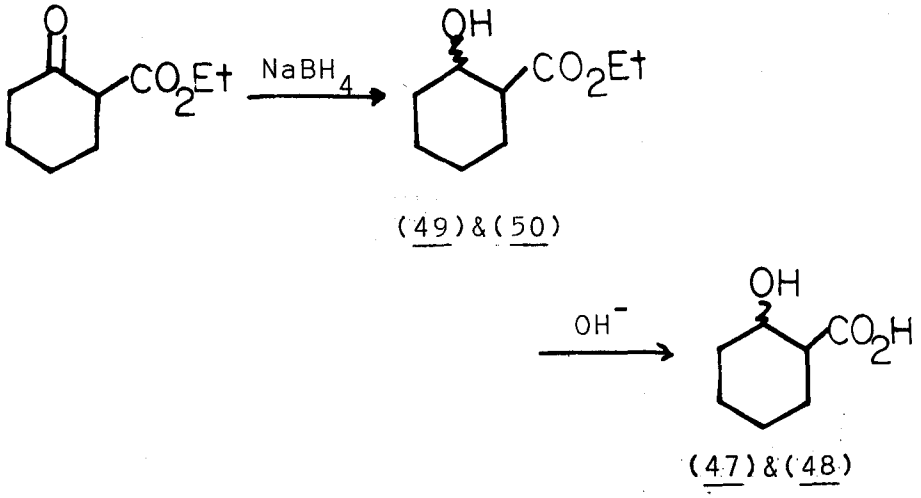
The β-lactones were extraordinarily sensitive to vpc conditions and showed significant tailing on vpc columns (10% UCON or 10% PMPE, 90-150°C). In fact, as concentrations were lowered and more sensitive attenuations for vpc analysis were required, the β-lactone peaks tailed more and repetitive electronic integrations often showed large error.

In the presence of trace quantities of glacial acetic acid at room temperature, no significant decomposition took place in 15 hours. However, in the presence of trace quantities of concentrated HCl, rapid decomposition took place in 5 minutes.

2. Synthesis of cis- and trans-1,2-Hexahydrophthalolactones, (45) and (46).

cis- and trans-2-Hydroxycyclohexanecarboxylic acids, (47) and (48), were prepared by the carbonylation of cyclohexanone[74] followed by reduction to and hydrolysis of cis- and trans-ethyl-2-hydroxycyclohexanecarboxylates, (49) and (50).[75]

The stereochemistries of acids (47) and (48) were determined in two ways.



Treatment of (47) and (48) (as a mixture) with diazomethane afforded the dimethyl esters, (51) and (52) which could be preparatively collected pure by vpc and whose nmr spectra were compared with literature values[76] shown in Table 5.

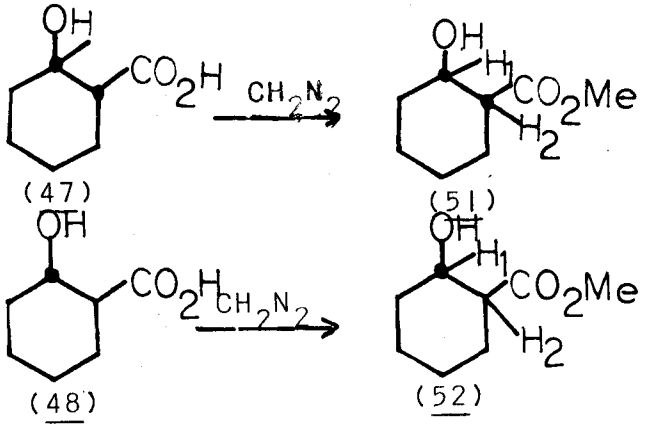
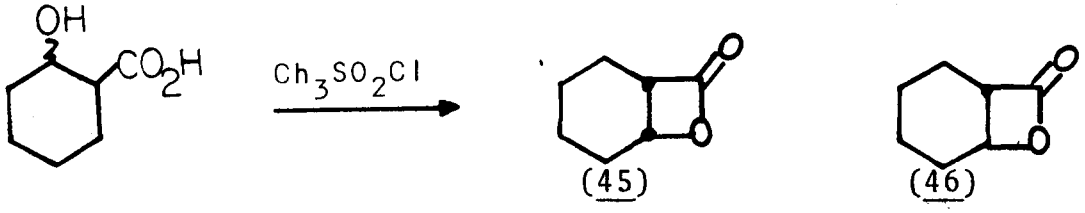


Table 5. Reported and Found nmr Spectra for (51) and (52).

	cis-(51)		trans-(52)	
	H_1	H_2	H_1	H_2
Found	δ4.18	δ2.40	δ3.70	δ2.30
Reported[76]	δ4.15	δ2.50	δ3.75	δ2.28

Hydrolysis of diethyl esters (49) and (50) with sodium hydroxide did not change the isomeric composition of products (47) and (48). However, it was reported that hydrolysis with potassium hydroxide yields the thermodynamically more stable trans isomer.[77] Refluxing hydrolysis of a mixture of (49) (73%) and (50) (27%) with KOH yielded a sample which when treated with diazomethane afforded nearly pure (> 94%) (48) as determined by vpc.

Treatment of (47), (48), or a mixture of the two with methanesulfonyl chloride in ether afforded a product mixture whose infrared spectrum showed an intense absorption at 1820 cm^{-1} indicative of the β-lactone function.[78]



(45) (46)

In addition, however, was a stronger, broader peak at 1725 cm^{-1}. Neither distillation nor attempted preparative gas chromatography successfully yielded pure β-lactone.

3. Thermal Decomposition of meso- and dl-2,3-Dimethylsuccinyl Peroxides, (5) and (6), in Dichloromethane and Tetrahydrofuran.

Solutions of (5) or (6) in CH_2Cl_2 or THF (0.001-0.006M) were heated to 92°C for four minutes. The reaction was complete as determined by examination of the peroxide carbonyl region (1800-1775 cm^{-1}) in the infrared. Table 6 shows the ratios of trans- to cis-2-butenes. Yields of 2-butenes were typically between 40-60% as determined by analytical vpc. These solutions were also subjected to gas phase pyrolyses at 278°C and 357°C in a vacuum flow oven. Results appear in Table 6.

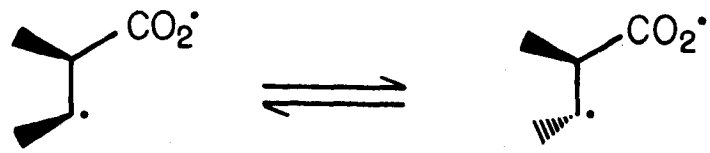
The remarkable similarity of trans- to cis-2-butene ratios under a variety of conditions from both (5) and (6) suggests a common intermediate or set of intermediates. Although these peroxides possess sufficient energy to populate the triplet state of 2-butene upon decomposition, the ratios in Table 6 do not reflect the branching ratios observed in the photosensitized isomerization of 2-butene.[33-35] Although formation of electronically excited triplet 2-butene cannot be ruled out, these ratios

Table 6. Pyrolysis of meso-(5) and dl-(6) in CH_2Cl_2 and THF.[†]

Peroxide	Temperature		
meso-(5)	92°C	69.37 ±1.89	30.63 ±1.89
meso-(5)	278°C	68.32 ±2.28	31.68 ±2.28
meso-(5)	359°C	62.65 ±2.76	37.35 ±2.76
dl-(6)	92°C	68.85 ±1.87	31.15 ±1.87
dl-(6)	278°C	60.97 ±1.37	39.03 ±1.37
dl-(6)	357°C	62.18 ±3.14	37.82 ±3.14

[†]Overall yields 40-60%. Yields and ratios determined by analytical vpc (13% DBT, 25°C) using 2-methylbutane as an internal standard.

do reflect the thermodynamic ratios of 2-butene as shown in Table 7.[79] A reasonable intermediate is the carboxy diradical (17). We cannot distinguish between a single



(17a) (17b)

intermediate or an equilibrated set of intermediates such as (17a) and (17b).

Table 7. Thermodynamic Ratios of 2-Butenes.[†]

Temperature (C)		
25°	76%	24%
27°	76%	24%
127°	68%	32%
227°	64%	36%
327°	62%	38%
427°	61%	39%
527°	60%	40%
627°	59%	41%
727°	59%	41%

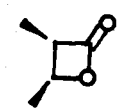
[†]Calculated from data provided in Reference 79.

This mechanism suggests that the carboxy diradical can further decarboxylate to produce 2-butenes, or close to give β lactones (18) and (19). Table 8 shows the yields and ratios of the β-lactones along with the 2-butenes resulting from the solution pyrolyses (92°C) of (5) and (6). (It is worthwhile to point out that the decompositions were run at higher concentrations (∿ 20 x 0.001M) so that the β-lactones could be detected. The lower concentrations are preferred to minimize induced decomposition.) Typical overall yields were 50-70% as determined by analytical vpc. The trans- to cis-2-butene ratios are similar to those reported in Table 6. A mechanism consistent with these data is shown in Scheme 6. Neither the cis- and trans-2-butenes nor the erythro- and threo-β-lactones (18) and (19) isomerized under the reaction conditions. In addition, the β-lactones did not thermally decompose under the reaction conditions.

It is interesting to note that this carboxy diradical has been suggested as a possible intermediate in β-lactone thermal[38] and photochemical[80-83] decompositions. Although in the thermal decomposition it was ruled out[38] as unlikely due to the high stereospecificity of the reaction, it could not be experimentally eliminated. As discussed earlier, thermal decomposition of β-lactones

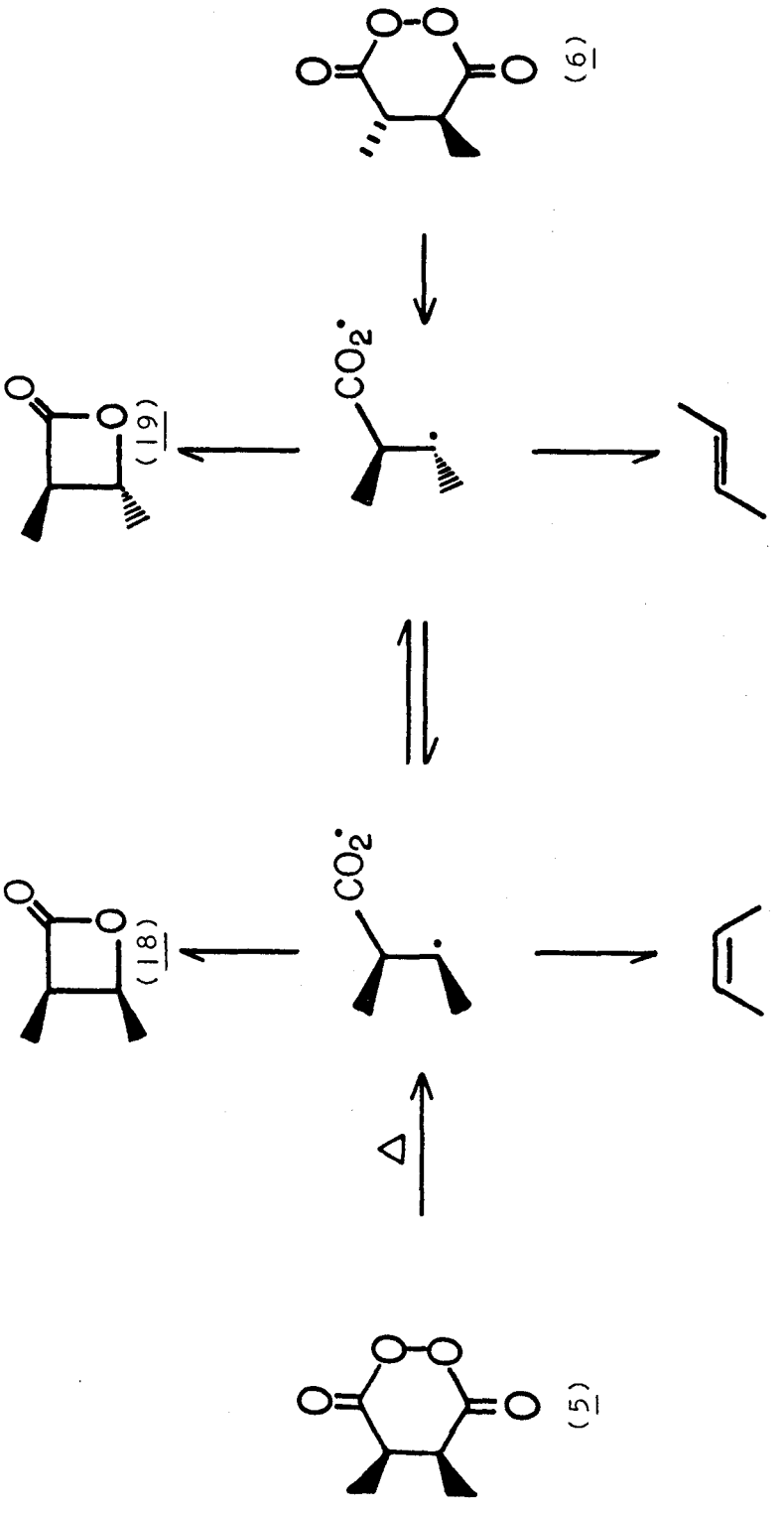
erythro-(18) and threo-(19), afforded pure cis- and trans-2-butenes respectively. Our results demand that the intermediates in the peroxide and β-lactone decompositions cannot be identical.

Table 8. Ratios of cis- and trans-2-Butenesand erythro and threo-2,3-Dimethylpropiolactones from Thermal Decomposition of Peroxides (5) and (6) in CH_2Cl_2 at 92°C.†

				
meso-(5)	61.0 ±2.25	28.2 ±0.78	7.56 ±1.32	3.29 ±0.96
dl-(6)	60.1 ±2.21	27.7 ±1.62	9.95 ±1.45	2.22 ±0.64

†Overall yields 50-70%. Yields determined by analytical vpc (2 butene: 13% DBT, 25°C; β-lactone: 10% PMPE, 90°C) against 2-methylbutane and dodecane as internal standard.

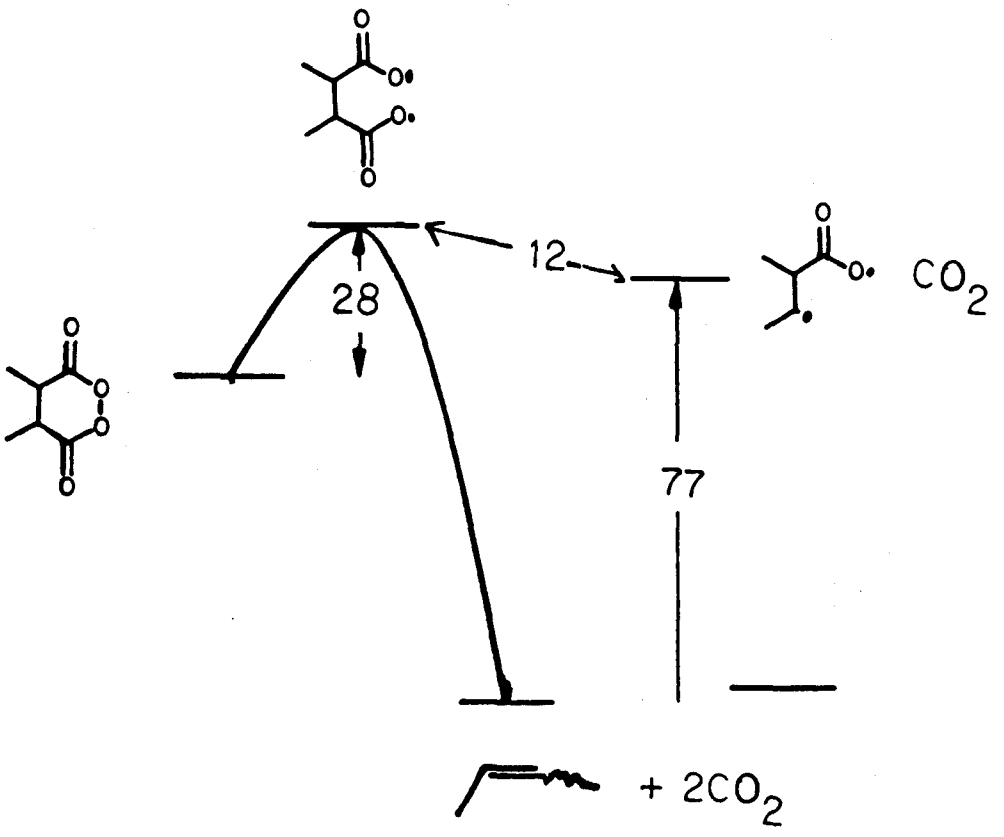
Scheme 6



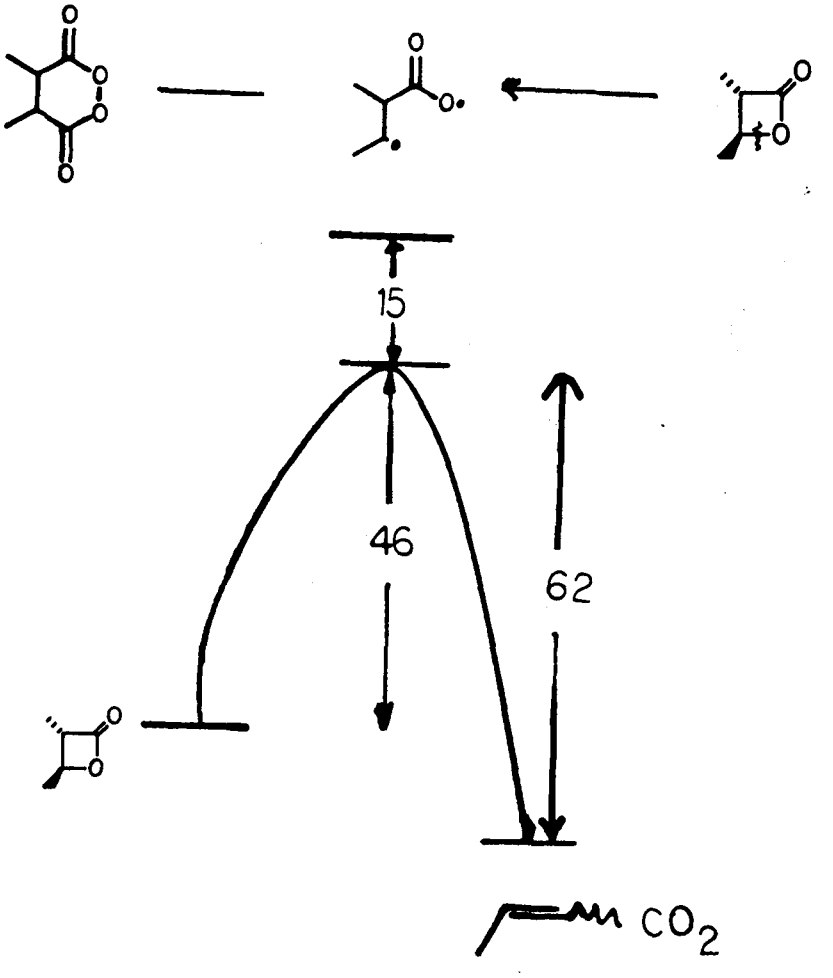
Thermochemical estimates[27] and kinetics[10] of the cyclic diacyl peroxide (6) decomposition suggest that the ΔH_f (heat of formation) of the carboxy diradical (17) should be $\sim$ -19 kcal/mole. This is consistent with estimates calculated independently (-18.86 and -18.2 kcal/mole). See Scheme 7 and accompanying calculations. Similar calculations estimate that the β-lactone should decompose (via carbon-oxygen bond cleavage) with an E_a (activation energy) of 60.9 kcal/mole. This would yield a carboxy diradical of similar energy (-18.86 kcal/mole) to that estimated for the carboxy diradical in the diacyl peroxide decomposition. However, β-propiolactone decomposes with an E_a = 45.9 kcal/mole.[84]

Several mechanistic hypotheses can be advanced to explain these observations. The first is that the peroxide decompositions proceed through a carboxy diradical (17) which has the properties k(rotation) >> k(cleavage) > k(closure) and the β-lactones decompose via a stereospecific concerted process of lower energy which does not involve the intermediacy of (17). Alternatively, both decompositions involve the intermediacy of a carboxy diradical (17) but the carboxy diradical from the β-lactone is lower in energy (by about 15 kcal/mole; calculated E_a minus observed E_a). See Scheme 8 and accompanying calculations. Preliminary GVB-CI calculations on the formyl radical ($HCO_2\cdot$) have shown that two

Scheme 7



Scheme 8



Estimation[27] of Thermochemical Values in Schemes 7 and 8

Note: Abbreviations used in Schemes 7 and 8 and calculations

ΔH_f - heat of formation

ΔH_r - heat of reaction

E_a - activation energy

E(X-Y) - bond dissociation energy of bond X-Y

ΔH_f threo-2,3-Dimethylpropiolactone, (18)

2C	- $(C)(H)_3$	- 20.16
1C	- $(C)_2(H)(CO)$	- 1.8
1C	- $(C)_2(H)(CO)$	- 7.00
1CO	- (C)(O)	- 33.4
1O	- (CO)(C)	- 41.3
Ring Correction		+ 23.9
		-79.76 kcal/mole

ΔH_f trans-2,3-Dimethylsuccinyl Peroxide, (6)

2C	- (C)(H)	- 20.16
2C	- $(C)_2(H)(CO)$	- 3.6
2CO	- (C)(O)	- 66.8
1O	- (CO)(O)	- 38.0
		-128.56 kcal/mole

ΔH_f $CH_3CH_2CH(CH_3)CO_2H$

2C	- $(C)(H)_3$	- 20.16
1C	- $(C)_2(H)_2$	- 4.95
1C	- $(C)_2(H)(CO)$	- 1.8
1CO	- $(C)(O)$	- 33.4
1O	- $(CO)(H)$	- 60.3
		-120.61 kcal/mole

ΔH_f $CH_3CH_2CH(CH_3)(CO_2\cdot)$

2C	- $(C)(H)_3$	- 20.16
1C	- $(C)_2(H)_2$	- 4.95
1C	- $(C)_2(H)(CO_2\cdot)$	- 39.0
		- 64.11 kcal/mole

ΔH_f $CH_3CH_2CH(CH_3)OCOH$

2C	- $(C)(H)_3$	- 20.16
1C	- $(C)_2(H)_2$	- 4.95
1C	- $(C)_2(H)(O)$	- 1.8
1O	- $(C)(CO)$	- 41.3
1C	- $(O)(H)$	- 29.5
		- 97.71 kcal/mole

Bond energies (dissociation energies) calculated as the difference between ΔH_f of molecule with bond in question and ΔH_f of radical intermediates formed by breaking that bond.

$E(CO_2\text{-}C)$; $CH_3CO_2\text{-}CH_3$

$$E = \Delta H_f(CH_3\cdot) + \Delta H_f(CH_3CO_2\cdot) - \Delta H_f(CH_3CO_2CH_3)$$
$$= (34.3) + (-47.5) - (-98.0) = 84.8 \text{ kcal/mole}$$

$E(C\text{-}CO_2)$; $CH_3\text{-}CO_2H$

$$E = \Delta H_f(CH_3\cdot) + \Delta H_f(\cdot CO_2H) - \Delta H_f(CH_3CO_2H)$$
$$= (34.3) + (-50) - (-103.8) = 88.1 \text{ kcal/mole}$$

$E(C\text{-}H)$; $CH_3CH_2CH(CH_3)\text{-}H$

$$E = \Delta H_f(H\cdot) + \Delta H_f(CH_3CH_2C\cdot(CH_3)) - \Delta H_f(CH_3CH_2CH_2CH_3)$$
$$= (52.1) + (13.7) - (-32.2) = 98.0 \text{ kcal/mole}$$

$E(CO_2\text{-}H)$; $CH_3CH_2CH(CH_3)CO_2\text{-}H$

$$E = \Delta H_f(H\cdot) + \Delta H_f(CH_3CH_2CH(CH_3)CO_2\cdot) -$$
$$- \Delta H_f(CH_3CH_2CH(CH_3)CO_2H)$$
$$= (52.1) + (-64.11) - (-120.61) = 108.6 \text{ kcal/mole}$$

$E(OC\text{-}H)$; $H\text{-}CO_2H$

$$E = \Delta H_f(H\cdot) + \Delta H_f(\cdot CO_2H) - \Delta H_f(HCO_2H)$$
$$= (52.1) + (-50) - (-90.5) = 92.5 \text{ kcal/mole}$$

ΔH_f Carboxy Diradical (17)

1) threo-2,3-Dimethylpropiolactone (18) → (17)

$\Delta H_f(17) = \Delta H_f(18) + E_a$ (or E_a')

E_a' (calculated) = $E(CO_2\text{-}C)$ - ring strain energy

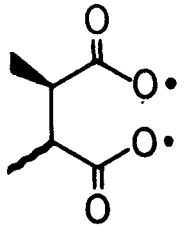
= 84.8 - 23.9 = 60.9 kcal/mole

E_a (experimental) = 45.9 kcal/mole[84]

$\Delta H_f'(17) = (-79.76) + (60.9) = -18.9$ kcal/mole or

$\Delta H_f(17) = (-79.76) + (45.9) = -33.9$ kcal/mole

2) <u>trans</u>-2,3-Dimethylsuccinyl peroxide (<u>6</u>) →
Dicarboxy Diradical (<u>53</u>) → (<u>17</u>) + CO_2



(<u>53</u>)

$\Delta H_f(\underline{17}) = \Delta H_f(\underline{53}) + \Delta H_r(\underline{53} \rightarrow \underline{17}) - \Delta H_f(CO_2)$

$\Delta H_f(\underline{53}) = \Delta H_f(\underline{6}) + E_a$

E_a estimated from preliminary kinetics (see Section 5) and typical values for the Arrhenius Parameter ($\sim 1 \times 10^{15}$) in diacyl peroxide decompositions.[10]

For (<u>d1</u>)-(<u>6</u>) at 48.5°C, $k = 1.89 \times 10^{-4}$ sec^{-1}.

Using $k = Ae^{-E_a/RT}$, E_a = 27.7 kcal/mole.

$\Delta H_f(\underline{53})$ = (-128.56) + (27.7) = -100.9 kcal/mole

$\Delta H_r(\underline{53} \rightarrow \underline{17})$ assumed $\approx \Delta H_r(CH_3CO_2\cdot \rightarrow CH_3\cdot + CO_2)$

$= \Delta H_f(CH_3\cdot) + \Delta H_f(CO_2) - \Delta H_f(CH_3CO_2\cdot)$

= (34.3) + (-94.05) - (-47.05) = -12.25 kcal/mole

$\Delta H_f(\underline{17})$ = (-100.9) + (-12.25) - (-94.05)

$\approx$ -19.06 $\approx$ -19 kcal/mole

3) $CH_3CH_2CH(CH_3)CO_2H \rightarrow (\underline{17}) + H_2$

$\Delta H_f(\underline{17}) = \Delta H_f(CH_3CH_2CH(CH_3)CO_2H) + E(CO_2\text{-}H) +$

$E(C\text{-}H) - E(H\text{-}H)$

$= (-120.61) + (108.6) + (98.0) - (104.2) =$

-18.2 kcal/mole

$\underline{\Delta H_f \text{ Diradical (54)}}$

1) threo-2,3-Dimethylpropiolactone ($\underline{18}$)$\rightarrow$($\underline{54}$)

$\Delta H_f(\underline{54}) = \Delta H_f(\underline{18}) + E_a''$

$E_a'' = E(C\text{-}CO_2)$ - ring strain energy

$= (88.1) - (23.9) = 64.2$ kcal/mole

$\Delta H_f(\underline{54}) = (-79.76) + (64.2) = -15.6$ kcal/mole

2) $CH_3CH_2CH(CH_3)OCOH \rightarrow (\underline{54}) + H_2$

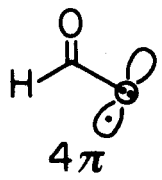
$\Delta H_f(\underline{54}) = \Delta H_f(CH_3CH_2CH(CH_3)OCOH) + E(C\text{-}H)$

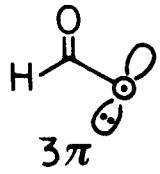
$+ E(OC\text{-}H) - E(H\text{-}H)$

$= (-97.71) + (98.0) + (92.5) - (104.2) =$

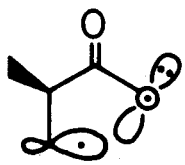
$= -11.41$ kcal/mole

electronic states, 3π and 4π, are separated by about 8 kcal/mole with the 4π being lowest.[85]

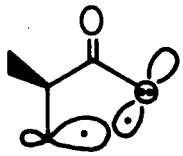




We can arbitrarily assign similar electronic states to the carboxy-diradical (17) yielding (17)-3π and (17)-4π.



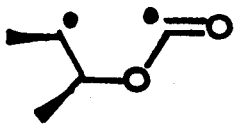
17-3π



17-4π

We would expect the 4π configuration to cleave or close quite rapidly since the lone electron is in the plane of the forming bonds whereas the lone electron in the 3π configuration is orthogonal to the incipient bonds. Thus, carboxy-diradical (17)-4π might be expected to have the properties k(cleavage), k(closure) >> k(rotation) and (17)-3π - k(cleavage), k(closure) << k(rotation). Our stereochemical results would suggest then that (17)-3π can rise from the peroxide decompositions and that the (17)-4π can arise from the β-lactone. The lower energy

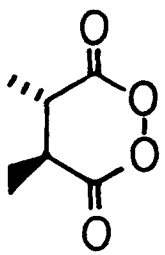
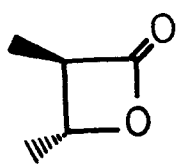
of (17)-4π would be consistent with the observed lower than predicted activation energy of β-lactones. Schemes 7 and 8 along with accompanying calculations substantiate this discussion. A third, diradical, non-concerted pathway for the decomposition of β-lactone lies in the possibility of generating intermediate (54). Thermochemical estimates suggest that this intermediate lies 64.2 kcal/mole above the β-lactone and thus is a less likely intermediate (see calculations of Schemes 7 and 9). Table 9 summarizes the experimental observations and proposed mechanisms.



(54)

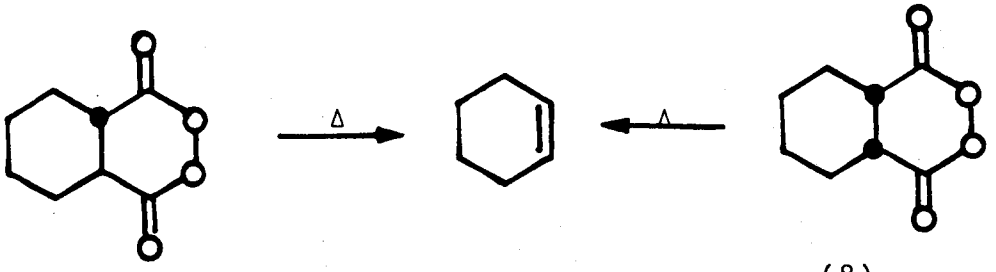
In summary, the stereochemical and kinetic data have shown that the cyclic diacyl peroxides (5) and (6) and β-lactones (18) and (19) decompose by different pathways (stepwise or concerted) and/or via intermediates of different properties (3π and 4π carboxy diradicals). Distinguishing between these mechanisms remains to be accomplished.

Table 9. Experimental Observations; Mechanistic Hypotheses

	Kinetic (ΔH_f of intermediate or transition state)	Stereo-chemistry	Mechanism 1	Mechanism 2	Mechanism 3
	-19 kcal/mole	random	Carboxy diradical (17)-3π	Carboxy diradical (17)	Carboxy diradical (17)
	-34 kcal/mole	stereospecific	Carboxy diradical (17)-4π	Concerted	Diradical (54)

4. Thermal Decomposition of cis- and trans-Hexahydrophthaloyl Peroxides (7) and (8), in Dichloromethane.

cis- and trans-Hexahydrophthaloyl peroxides, (7) and (8), were decomposed at 100°C in CH_2Cl_2 to afford 27% and 32% cyclohexene, respectively as determined by vpc. Infrared analysis (at ∿ 1775 cm^{-1}) indicated the reaction was complete. However, considerable unidentified carbonyl



(7) (8)

containing material remained (not starting material).

The low yields of cyclohexene and the infrared analysis may reflect the production of polymer which is often reported in these decompositions.[10,22,25] Cyclohexene was the only volatile product. Under these conditions, no trans-cyclohexene could be detected. Subsequent sections will describe several trapping experiments.

5. Kinetics.

Rate datawere obtained for peroxides (5)-(8) at 46.9°Cand 48.5°C. Table 10 summarizes the results. The appearance of 2-butene was measured by vpc against internal standard, 2-methylbutane (Runs 1-7). The dis-

appearance of peroxides was measured by following the disappearance of the peroxide carbonyl absorption at $\sim$ 1775 cm^{-1} in the infrared (Runs 8-11). Evaluation of rate constants by the method of least squares shows very few satisfactory lines could be obtained. Figures 3 and 4 in the Experimental Section graphically display the data.

Measuring the appearance of 2-butenes does not satisfactorily measure the rate. Other products such as β-lactones and polymer are likewise being produced. In fact in several runs, 2-butene appears to reach a maximum and then begins to disappear (Figure 3 run 7). Other processes including the reaction of 2-butene with peroxide or radical intermediates (induced decomposition) may successfully compete with the first order decomposition and not lead to 2-butene products.

The disappearance of the carbonyl stretching frequency (1775 cm^{-1}) is a legitimate means of following the decomposition. However, higher concentrations (0.1M) were required which is generally undesirable in peroxide chemistry where first order processes are desired.[10] Other carbonyl containing material (products) arise in this region of the infrared making the analysis difficult at > 50% decomposition.

Table 10. Kinetics of the Thermal Decomposition of Peroxides (5)-(8)

Run[a]	Peroxide	T°C	Solvent	Molarity	Rate Constant ($sec^{-1} \times 10^4$)	r^{2b}	Method
1	meso-(5)	46.9	THF	0.006	8.87	0.87	c
2	meso-(5)	46.9	THF	0.001	4.61 (2.71)	0.99[d] (0.65)	c
3	meso-(5)	46.9	THF	0.001	3.38 (2.57)	0.98[d] (0.93)	c
4	meso-(5)	46.9	THF	0.001	2.17	0.94	c
5	dl-(6)	46.9	THF	0.006	2.84	0.90	c
6	dl-(6)	46.9	THF	0.006	1.74	0.64	c
7	dl-(6)	46.9	CH_2Cl_2	0.006	0.97	0.13	c
8	meso-(5)	48.5	CH_2Cl_2	0.1	4.68	0.93	e
9	dl-(6)	48.5	CH_2Cl_2	0.1	1.89	0.98[d]	e
10	cis-(7)	48.5	CH_2Cl_2	0.1	3.60	0.90	e
11	trans-(8)	48.5	CH_2Cl_2	0.1	3.76	0.96	e

[a]Run Corresponds to data listed in Tables 39a and 39b, Experimental Section

[b]r^2 - Least squares fit

[c]Followed appearance of 2-butene with respect to an internal standard by vpc.

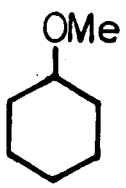
[d]Where more than one value is reported, the numbers in parentheses were evaluated based on all the points in a run. The first listed value corresponds to the best line.

[e]Followed disappearance of infrared carbonyl stretching frequency ($\sim$ 1775 cm^{-1}).

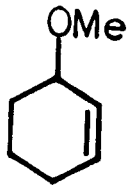
In general, the rate constants range from 1-9 x 10^{-4} sec^{-1} similar to rate constants observed or calculated for other diacyl peroxides.[10] Using a typical value for A (Arrhenius parameter) ~ 1 x 10^{15},[10] and k(dl-(6)) = 1.89 x 10^{-4} sec^{-1}, E_a = 27.7 kcal/mole.

6. Synthesis of Methoxycyclohexane, (55) and 3-Methoxycyclohexene, (56).

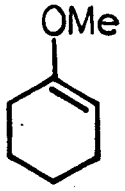
Commercially available alcohols, cyclohexanol and 2-cyclohexen-1-ol, were converted to their sodium salts upon treatment with sodium hydride. Further treatment with iodomethane yielded methoxycyclohexane (55), and 3-methoxycyclohexene, (56), respectively. 2-Methoxycyclohexene, (57), was commercially available. Nmr, ir, and mass spectral analysis were consistent with their structures.



(55)



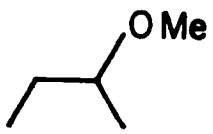
(56)



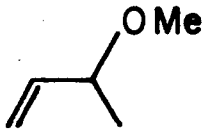
(57)

7. Synthesis of 2-Methoxybutane, (58), 2-Methoxy-3-Butene, (59), Z- and E-2-Methoxy-2-Butene, (60) (61), and 2-Methoxy-1-Butene, (62).

Commercially available alcohols, 2-butanol and 3-butene-1-ol, were converted to their sodium salts by reaction with sodium hydride. Treatment of these salts with iodomethane yielded 2-methoxybutane, (58), and 2-methoxy-3-butene, (59), respectively.

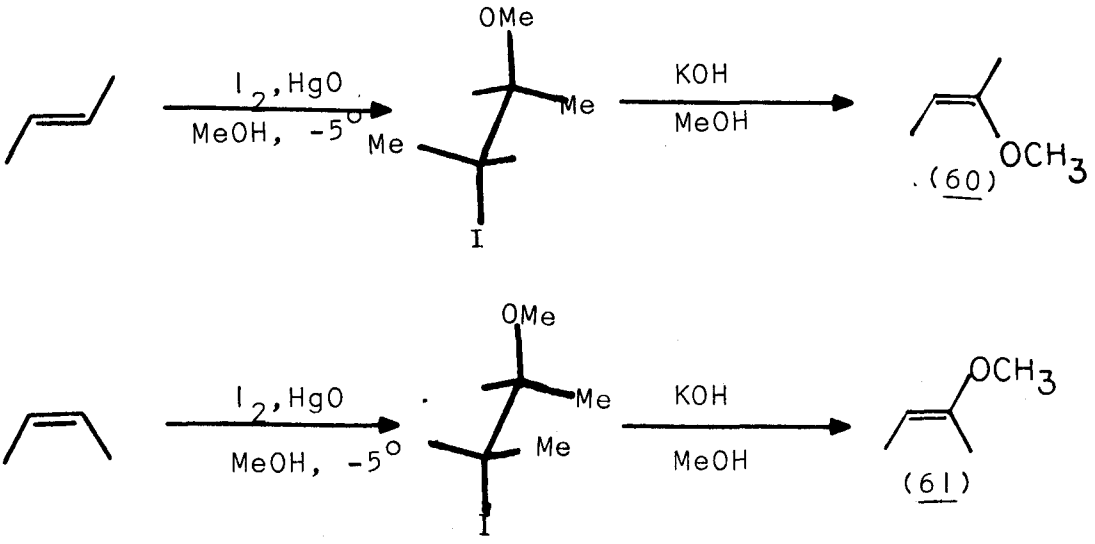


(58)

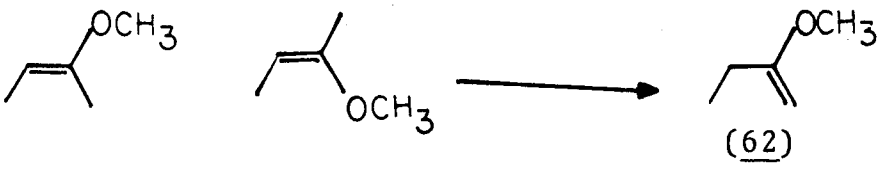


(59)

Z- and E-2-methoxy-2-butene, (60) and (61) were prepared by treatment of trans- and cis-2-butene (respectively) with iodine and mercuric oxide in cold methanol (-50°C), followed by treatment of the isolated iodomethoxy compound with potassium hydroxide in hot methanol.[86] Stereospecific addition and elimination steps and comparison of literature nmr and ir spectra[87] confirmed their structures and configurational assignment.



Fortuitiously, 2-methoxy-1-butene, (62), appeared as an isomerization product when preparative collection of either (60) or (61) was attempted. These ethers were



apparently quite sensitive to vpc column conditions (3/8" 10' 10% UCON on Chrom P, 70°C). In spite of significant silylation (to remove active and acidic sites - several 100 μl shots of $[(CH_3)_3Si]_2NH$ were put on the vpc column) this isomerization took place. The structure of (62) was confirmed by comparison of ir and nmr spectra with those reported.[87] Reexamination of (60) and (61) by ir and nmr confirmed their purity. There was no (62) in the original samples.

8. Analysis of Deuterium Incorporation

Cyclohexylmethylether-d_1, (55)-d_1, was prepared from the corresponding alcohol (obtained from D. Santilli) by the procedure described for (55).

Table 11 lists the fragmenting masses of cyclohexylmethylether (55) and (55)-d_1.

As expected the fragmentation patterns are complex and become roughly equivalent below the base peak ion 71. Fortunately, the abundance of the molecular ion is fairly high. Since the M+1 peak is only ∿ 10% of the molecular ion, we used this peak to estimate the extent of deuterium incorporation. Two samples of a mixture of (55) and (55)-d_1 were prepared. As Table 12 shows, without any corrections, the relative abundance of peaks 114 and 115 closely approximates (within several percent) the actual composition of the cyclohexylmethyl ethers. Because the

Table 11. Mass Spectra of (55) and (55)-d_1

Mass	Relative Abundance	
	(55)	(55)-d_1
116	0	2
115	1	22
114	19	1
113	6	0
87	0	1
86	1	8
85	10	6
84	3	3
83	3	17
82	14	3
81	2	0
80	0	1
79	1	0
73	0	3
72	6	39
71	100	100
68	0	5
67	6	3
59	1	8
58	16	11

Mass	Relative Abundance (55)	(55)-d_1
57	1	9
56	1	6
55	8	7
54	4	3
53	3	2

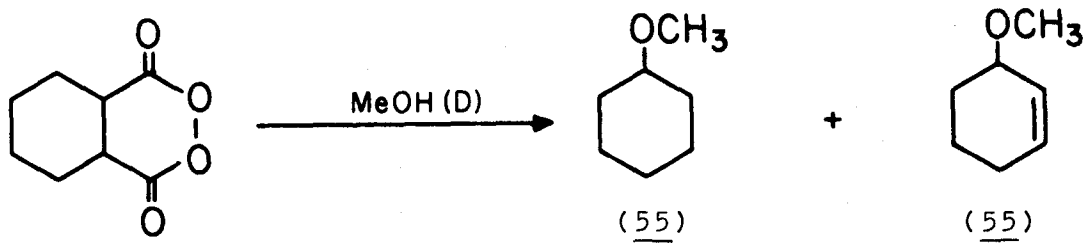
Table 12. Mass Spectra of Prepared Mixtures of (55) and (55)-d_1

	Mole % (55) /(55)-d_1	Relative Abundance % I15/114
Sample 1	73.0/27.0	70.5/29.5
Sample 2	31.8/68.2	30.9/69.1

M+1 peak is ∿ 10% in relative abundance to the M peak, we will not be able to detect deuterium incorporation until the M+1 peak contributes > 10-15%. Thus, in succeeding discussions of deuterium experiments, significant deuterium incorporationwill be assumed when the M+1 peak contributes > 15%.

9. Thermal Decomposition of meso- and dl-2,3-Dimethylsuccinyl Peroxides, (5) and (6), and cis- and trans-1,2-Hexahydrophthaloyl Peroxides, (7) and (8), in Methanol.

When cis- and trans-1,2-hexahydrophthaloyl peroxides, (7) and (8) were heated in dry methanol to 95°C for four minutes, the cyclohexylmethyl ether, (55), was observed in about 0.5% yield as determined by analytical vpc.

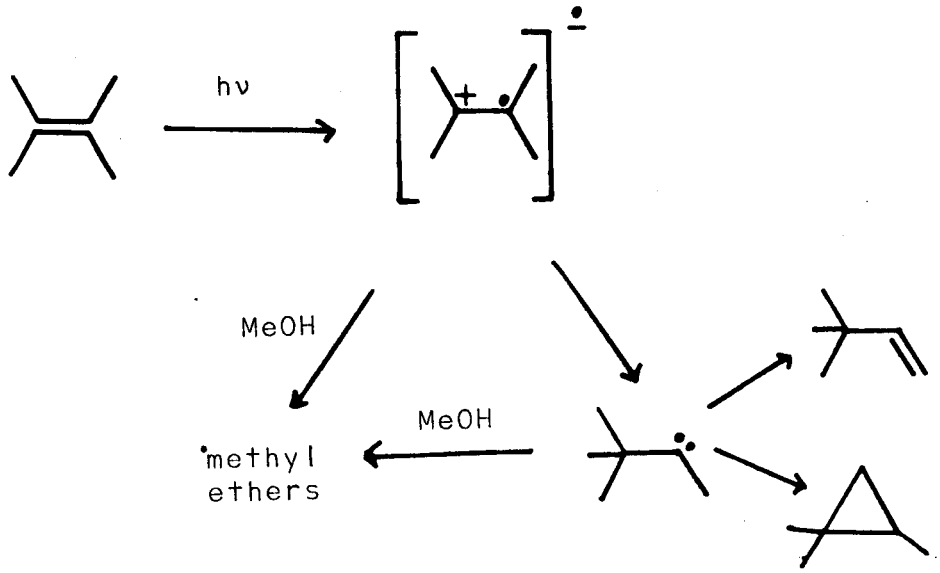


(55) (55)

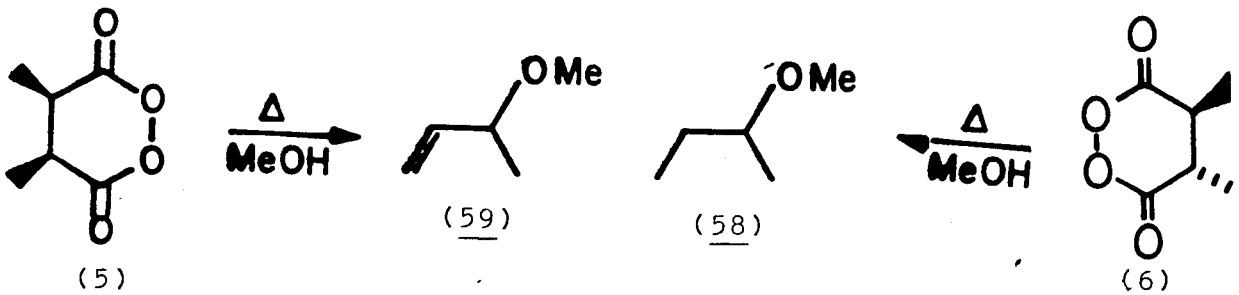
Based upon Kropp's observations,[48] we did not expect a high yield. He observed that unsubstituted cyclohexene underwent very inefficient photoprotonation. However, addition of small amounts of mineral acid significantly increased the

yield. Addition of 1% sulfuric acid to our methanol decomposition samples did not alter the yields of (55). In addition, careful examination of the volatile products by vpc revealed that 3-methoxycyclohexene, (56), was also a product in the decomposition of (7) and (8). These assignments were confirmed by gas chromatography interfaced mass spectrometry (GC-MS). Decomposition in methanol-O-d revealed no significant incorporation of deuterium (see preceding discussion) as would be expected in (55) if the "protonation" of trans-cyclohexene was occurring. This latter result along with the appearance of (56) is reminiscent of Kropp's more recent work on the direct irradiation of olefins.[88-92] Tetra- and trisubstituted olefins were found to afford saturated and unsaturated methyl ether products upon direct photolysis in methanol. In non-protic media, these olefins formed rearranged products suggesting a carbene intermediate. Kropp has attributed this behavior as resulting from promotion of an electron to a Rydberg excited state which closely resembles a radical cation in reactivity.[88-89]. See Scheme 9.

Scheme 9



meso- and dl-2,3-Dimethylsuccinyl peroxides, (5) and (6) yielded between 2-4% methyl ethers (58) and (59) upon thermal decomposition in methanol. GC-MS and coinjection with authentic samples confirmed these assignments. Unfortunately, E- and Z-2-methoxy-2-butene, (60) and (61), and 2-methoxy-1-butene, (62), could not be seen in nor separated from solvent.

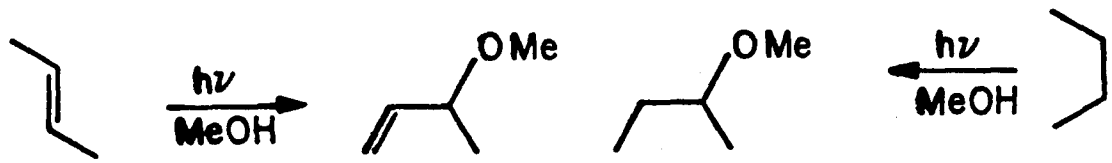


(5) (59) (58) (6)

Dimethoxymethane was identified by GC-MS and coinjection with an authentic sample. It appeared in nearly all the peroxide decompositions in methanol. However, the amount varied. By vpc, the yield was sometimes similar to the methyl ethers, sometimes 10-20 times greater.

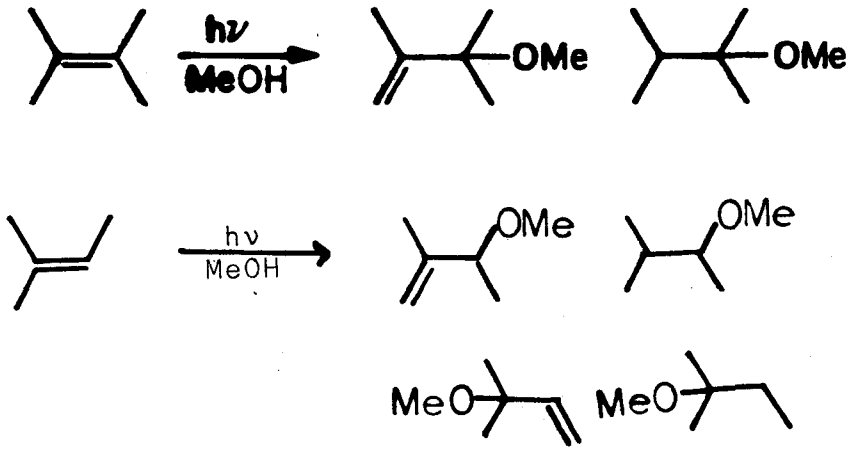
The appearance of (58) and (59) likewise suggests radical-cation-like chemistry.

We've independently irradiated saturated solutions of cis- and trans-2-butene in methanol. After 241 minutes at 10-30°C through quartz optics, trans-2-butene yielded 0.002% (58) and 0.002% (59) while seeing a net conversion of 0.5% trans- to cis-2-butene. Similarly, cis-2-butene afforded 0.006% (58) and 0.004% (57) accompanied by a net conversion of 6.5% cis- to trans-2-butene. This contrasts to the 67% yield of methyl ethers from a 4 hour irradiation of tetramethylethylene and the 14.5% yield of methyl ethers



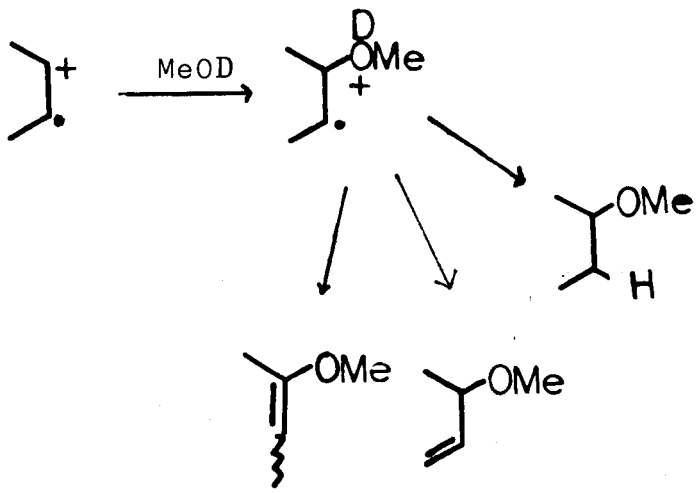
(59) (58)

from 2-methyl-2-butene after 72 hours irradiation in methanol. This is in remarkable agreement to Kropp's prediction of reactivity based upon substitution.



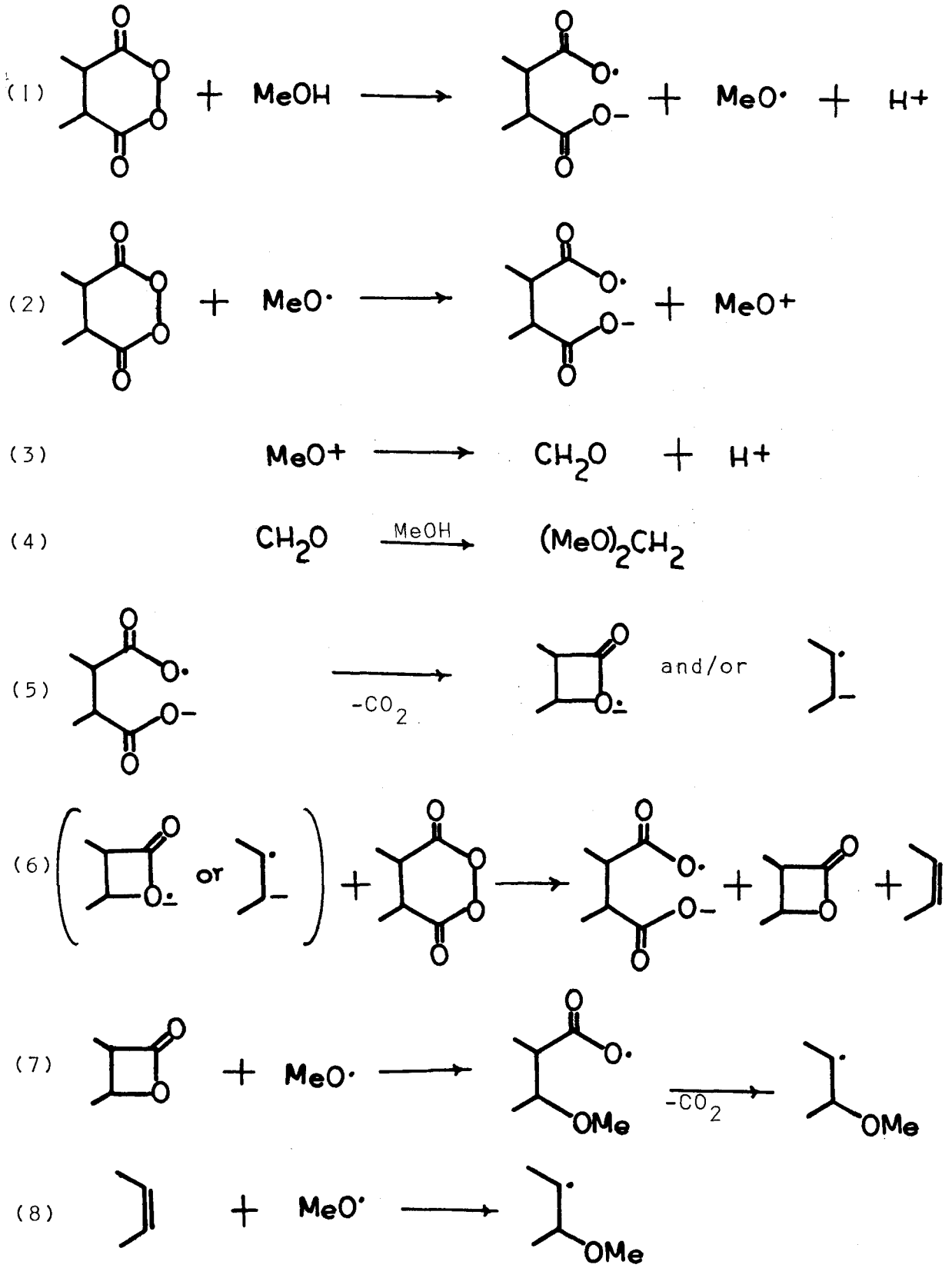
Decomposition of meso-(5) and dl-(6) at 97°C in methanol-O-d afforded (58) and (59). GC-MS analysis gave no evidence of deuterium incorporation in any instances. This suggests that the protonation process was not operating. Scheme 10 shows the expected fate of a radical cation of 2-butene. In no instance would deuterium incorporation be expected.

Scheme 10



We have shown by thermochemical estimates (see Scheme 2) that there is enough energy available upon decomposition of (5) and (6) to populate at least the triplet state of 2-butene. We have no reason to rule out electronically excited states, but two obvious ground state routes cannot be overlooked. The appearance of dimethoxymethane, a formaldehyde equivalent, suggests that methanol has been oxidized. Scheme 11 shows a possible pathway to the radical anion of peroxides (5) and (6) with concurrent oxidation of methanol. In Section E of this thesis where induced chemistry producing the radical anion of peroxides (5) and (6) is suspected, significant amounts of olefin are afforded. β-Lactones and olefins are products in the

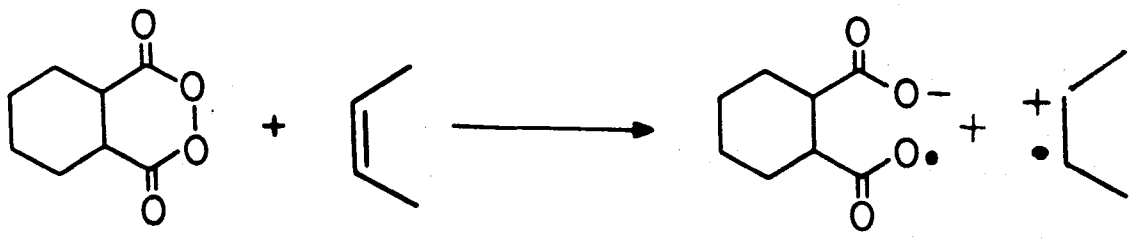
Scheme II


(1)
MeOH
MeO·
H+
(2)
MeO·
MeO+
(3)
MeO+
CH2O
H+
(4)
CH2O
MeOH
(MeO)2CH2
(5)
-CO2
and/or
(6)
or
(7)
MeO·
OMe
-CO2
OMe
(8)
MeO·
OMe

thermal decomposition of (5) and (6). Reactions (7) and (8) of Scheme 11 suggest alternative pathways to the observed methyl ethers (58) and (59) through the same radical intermediate which arises from methanol capture of the radical cation (Scheme 10).

Scheme 12 presents a less than reasonable mechanism for the production of radical cation. The oxidation po-

Scheme 12



tential of cis- and trans-2-butene (E_{ox} = 2.26 ev vs. Ag - 0.01M $AgClO_4$, E_{ox} ~ 1.62 ev vs SCE)[93] is much higher than those aromatic compounds which slowly decompose diacyl peroxides (see Section E). Nevertheless, we have considered this possibility as well.

We have decomposed cis- and trans-(7) and (8) in the presence of large excesses of cis-2-butene in methanol.

No methyl ethers corresponding to the trapping of 2-butene were observed. If methoxy radical ($CH_3O\cdot$) is formed, in general, under peroxide decomposition conditions, the methyl ethers do not arise by its attack on 2-butene.

An alternative explanation for these results would suggest that cyclohexene more efficiently induces decomposition (E_{ox} = 2.05 ev vs Ag - 0.01M $AgClO_4$; 1.41 ev vs SCE)[93] thus leading solely to its radical cation or that cyclohexene more effectively competes for methoxy radical.

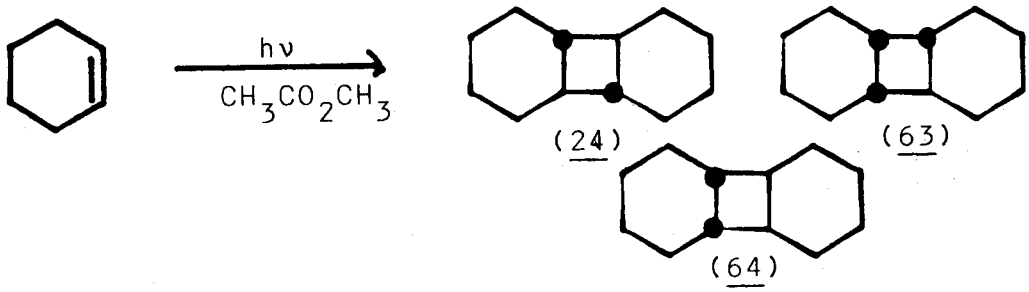
The thermal decomposition of (5) in the presence of a large excess of cyclohexene in methanol produced methyl ethers (58) and (59) but did not yield any cyclohexyl methyl ethers. This rules out the above proposition.

Freshly prepared samples of erythro- and threo-2,3-dimethylpropiolactones in methanol were heated in the presence of decomposing (7) and (8). Although it was difficult to determine if the lactone had decomposed (without peroxide under similar conditions it did not), there were no detectable traces of the butylmethyl ethers (58) or (59).

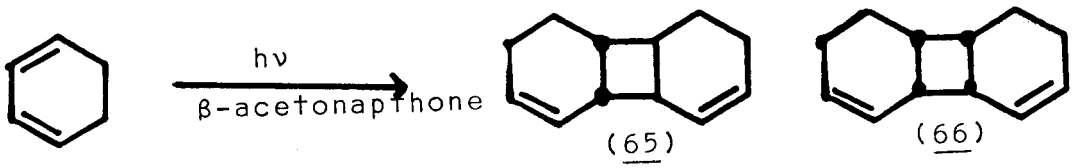
From the chemistry, it appears we are directly forming a radical cation, possibly through some excited state intermediate. The photochemistry of 2-butenes yielding similar products is suggestive of the same or closely related processes.

10. Preparation of Cyclohexene Dimers.

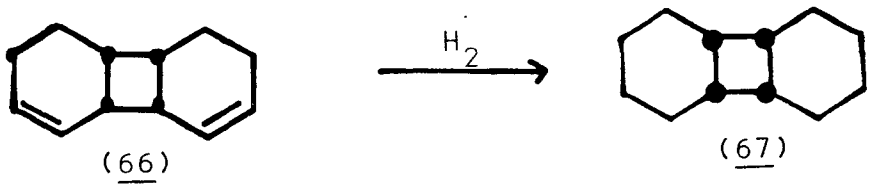
Cyclohexene was irradiated in the presence of methyl acetate to yield three dimers, trans-anti-trans-tricyclo[6.4.0.$0^{2,7}$]dodecane, (24), cis-trans-tricyclo-[6.4.0.$0^{2,7}$]dodecane, (63) and cis-anti-cis-tricylco-[6.4.0.$0^{2,7}$]dodecane, (64).[50] Their structures were confirmed by nmr, cmr and mass spectral analysis and agree with those reported.[50]



Cyclohexadiene was irradiated in the presence of β-acetonapthone to yield unsaturated dimers cis-anti-cis-tricyclo[6.4.0.$0^{2,7}$]dodeca-3,11-diene, (65) and cis-syn-cis-tricyclo[6.4.0.$0^{2,7}$]dodeca-3,11-diene, (66).[94]



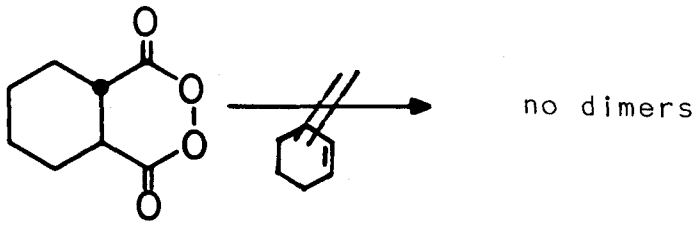
Dimer (66) was hydrogenated to yield cis-syn-cis-tricyclo-[6.4.0.$0_2^{2,7}$]dodecane, (67). The structure was confirmed by nmr and cmr and agreed with those reported.[50]



(66) (67)

11. Thermal Decomposition of trans-1,2-Hexahydrophthaloyl Peroxide, (8), in Cyclohexene.

trans-Hexahydrophthaloyl peroxide, (8), was decomposed in neat cyclohexene. Coinjection with authentic samples on two analytical vpc columns (25% Carbowax and 10% SF-96) as well as GC-MS on m/e peak 164 showed no detectable trace of dimers formed.

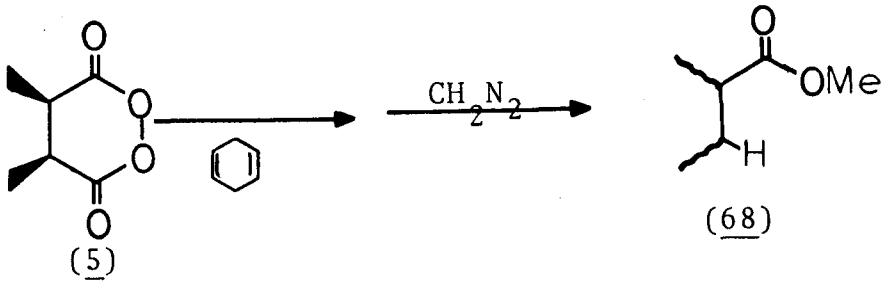


12. Thermal Decomposition of meso-2,3-Dimethylsuccinyl Peroxide, (5), in the Presence of Piperylene.

A solution of cis-piperylene and meso-2,3-dimethylsuccinyl peroxide, (5), was heated to 92°C in THF. VPC analysis showed no isomerization or disappearance of cis-piperylene.

13. Thermal Decomposition of meso-2,3-Dimethylsuccinyl Peroxide, (5), and trans-1,2-Hexahydrophthaloyl Peroxide, (8), in the Presence of 1,4-Cyclohexadiene.

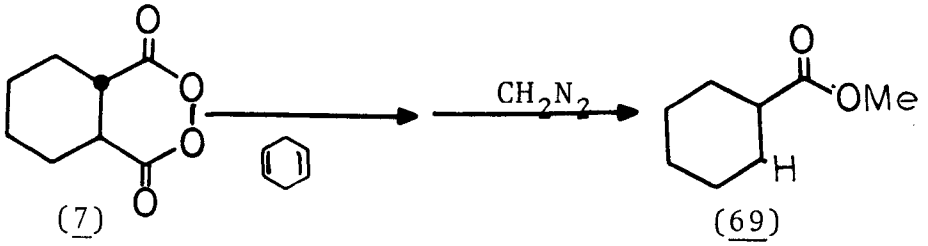
meso-2,3-Dimethylsuccinyl peroxide, (5), was thermally decomposed in the presence of 1,4-cyclohexadiene. Treatment of this pyrosylate with diazomethane yielded a trace of a product tentatively identified as methyl 2-methylbutyrate (68) by coinjection with an authentic sample. Likewise, trans-hexahydrophthaloyl peroxide, (8),



(5) (68)

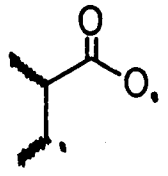
was decomposed in the presence of 1,4-cyclohexadiene and after treatment with diazomethane, yielded a trace of a

product tentatively identified as methyl cyclohexane-carboxylate (69) by coinjection with an authentic sample.

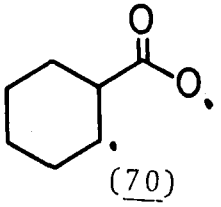


(7) (69)

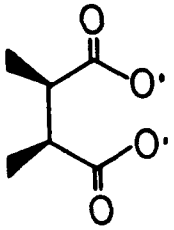
Although it would be exciting to consider that these products arose via hydrogen abstraction from the intermediate carboxy diradicals, (17) and (70), it is just as likely that they arose from the dicarboxy diradicals, (53) and (71).



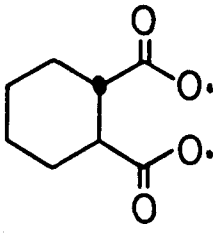
(17)



(70)



(53)



(71)

In both sequences, identical intermediates are generated making the task of distinguishing between them by this method unlikely.

14. Summary

erythro- and threo-2,3-Dimethylpropiolactones, (18) and (19), have been prepared and isolated. Evidence suggests that cis- and trans-1,2-hexahydrophthalolactones, (45) and (46) have been prepared. They have not been isolated.

Thermal decomposition of meso- and dl-2,3-dimethylsuccinyl peroxide, (5) and (6), afforded trans- and cis-2-butenes and erythro- and threo-2,3-dimethylpropiolactones, (18) and (19). The fact that the ratio of trans- to cis-2-butenes and threo- to erythro-β-lactones was the same from (5) and (6) implies a common intermediate. Carboxy diradical(s), (17), was proposed as the likely intermediate(s) which has the property $k_{closure} < k_{cleavage} << k_{rotation}$. β-lactones (18) and (19) were shown to thermally decompose stereospecifically, consistent with other reports.[36-39] It is clear that β-lactones and cyclic diacyl peroxides decompose by different pathways or via different intermediates, and several mechanisms were proposed.

Decomposition of (5)-(8) in methanol leads to saturated and unsaturated methyl ethers. A radical cation of the product olefins has been invoked as the

likely intermediate. Products arise exclusively from decomposing peroxide, not from secondary chemistry on olefin or lactone products.

There has been no evidence for the intermediacy of trans-cyclohexene in the thermal decomposition of (7) and (8).

Decomposition of (5) and (8) in 1,4-cyclohexadiene has provided permissive evidence for the intermediacy of a dicarboxy diradical (53) and (71) or a carboxy diradical (17) and (70), respectively.

C. PHOTOCHEMICAL DECOMPOSITION OF DL- AND MESO-2,3-DIMETHYLSUCCINYL PEROXIDES, (5) AND (6), AND CIS- AND TRANS-1,2-HEXAHYDROPHTHALOYL PEROXIDES, (7) AND (8).

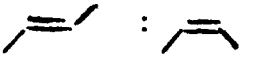
1. Direct Irradiation of dl- and meso-2,3-Dimethylsuccinyl Peroxides (5) and (6), and cis- and trans-1,2-Hexahydrophthaloyl Peroxides (7) and (8).

All four peroxides (5)-(8) were quite photolabile. Although the peroxides absorb only slightly above 300 nm (see Table 25) they decomposed rapidly without sensitizers above this wavelength. Because of the availability and ability to analyze erythro- and threo-dimethyl-β-propiolactones, peroxides meso-(5) and dl-(6) are considered first. Because of the thermal lability of

the peroxides, the production of "thermal" butene and lactone products in the injector port of the gas chromatograph, and the fact that the β-lactones were difficult to distill quantitatively, at room temperature, 10^{-5} mm, it was desirable to determine at what point the peroxides had completely photodecomposed. This was determined in three ways. The first and simplest was examination by infrared. After 20-30 minutes of irradiation through Pyrex at 0°C, no peroxide could be seen but other carbonyl containing products obscured the region and left this assessment less than absolute. The second method is shown in Table 13. The yield and ratio of 2-butene products was analyzed from both distilled and undistilled samples with respect to time. Their convergence was taken as an indication that all the peroxide was consumed at 20-30 minutes. Finally, from the distilled samples, the pot residue was taken up in solvent and analyzed by vpc for "thermal" butene and lactone products. None were found after 20 minutes. Thus it was concluded that the decomposition was complete at this time and products could be conveniently analyzed without distillation.

Tables 14a and 14b show the results of several irradiations of 0.06-0.1M peroxides (5) and (6) in dichloromethane through Pyrex at 0°C for 20-30 minutes. (Each entry line in the Table represents an individual run.

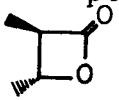
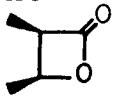
Table 13. Yields and Ratios of 2-Butenes from Photolysis of Peroxides, meso-(5) and dl-(6)

Sample[†]	Irradiation Time Minutes		% Yield
meso-u	5	67 : 33	46
meso-u	10	70 : 30	44
meso-u	20	72 : 28	44
meso-u	30	72 : 28	45
meso-d	0	77 : 23	3
meso-d	5	79 : 21	27
meso-d	10	78 : 22	36
meso-d	20	70 : 30	46
meso-d	30	71 : 29	44
dl-u	0	71 : 29	31
dl-u	5	59 : 41	35
dl-u	10	57 : 43	34
dl-u	15	56 : 44	34
dl-u	30	56 : 44	34
dl-d	0	67 : 33	4
dl-d	5	63 : 37	21
dl-d	10	56 : 44	29
dl-d	15	56 : 44	36
dl-d	30	56 : 44	33

[†]meso-u-meso undistilled meso-d distilled

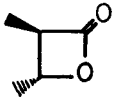
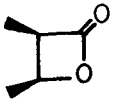
dl-u-dl undistilled dl-d distilled

Table 14a. Direct Irradiation of meso-(5) and dl-(6) at 0°C in CH_2Cl_2.[†]

Sample	Irradiation time (mins)	Relative per cent 		Yield	Relative per cent 		Yield
meso-(5)	20	71.6	28.4	44.2	81.3	18.7	1.5
meso-(5)	30	71.5	28.5	44.8	83.3	16.8	1.5
meso-(5)	20	71.0	29.0	43.0	----	----	---
meso-(5)	30	71.6	28.4	42.6	85.1	14.9	1.3
meso-(5), Na_2CO_3	20	70.3	29.7	46.5	----	----	---
meso-(5), Na_2CO_3	30	70.8	29.2	43.7	84.4	15.6	1.5
dl-(6)	30	56.5	43.6	34.1	76.9	23.1	1.4
dl-(6), Na_2CO_3	30	61.2	38.8	28.3	----	----	---
dl-(6)	20	53.7	46.3	38.8	----	----	---
dl-(6)	30	57.7	42.3	33.7	91.8	8.10	4.2
dl-(6), Na_2CO_3	20	58.3	41.7	34.1	----	----	---
dl-(6), Na_2CO_3	30	59.0	41.0	34.2	93.9	6.08	4.1

[†]Yields and ratios of 2-butenes determined by analytical vpc (13% DBT, 25°C against 2-methyl butane) yields and ratios of β-lactones (18) and (19) determined by vpc (10% PMPE, 90°C, against dodecane).

Table 14b. Direct Irradiation of Peroxides, meso-(5) and dl-(6) at 0°C in CH_2Cl_2. (Normalized 2-Butene and β-lactone Values).†

Sample	Irradiation time (mins)				
meso-(5)	20	69.1	27.6	2.67	0.613
meso-(5)	30	69.1	27.6	2.70	0.544
meso-(5)	30	69.5	27.6	2.53	0.442
meso-(5), Na_2CO_3	30	68.3	28.3	2.81	0.518
dl-(6)	30	54.1	42.0	3.04	0.910
dl-(6)	30	51.2	37.7	10.2	0.897
dl-(6), Na_2CO_3	30	52.7	36.6	10.0	0.650

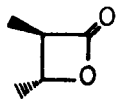
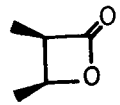
†Values normalized from data in Table 14a.

Several were repeated). Table 15 summarizes the data in Table 14b. Solid sodium carbonate was added to several samples as it was in the thermal decompositions. There does not seem to be a significant difference with or without it. The results for peroxide meso-(5) are consistent from sample to sample in both 2-butene and β-lactone yields and ratios. However, in the dl-(6) sample, the lactone ratios and yields changed considerably from run to run. Controls showed that under the irradiation conditions, the lactones did not decompose or isomerize.

Table 16 shows the results of direct irradiation for 30 minutes of all four peroxides (5)-(8) using selected filters. Those filters which cut off significant portions of light and thus light intensity (see Footnote A Table 16) not only have lower yields of olefin in the same time period but have different ratios of products (in the dl- and meso-dimethylsuccinyl peroxide series).

A trend is apparent in the ratio of 2-butenes from the meso- and dl-peroxides. That this ratio change upon going from 100°C to 0°C is not unexpected. However in contrast to the thermal decompositions, the ratios of 2-butene products are not the same for both peroxides. Most significantly, the cis-2-butene is approaching nearly 50% from the dl-isomer as the filter becomes more selective in wavelength and the intensity is lowered.

Table 15. Direct Irradiation of Peroxides meso-(5) and dl-(6) at 0°C in CH_2Cl_2.[a]

Sample				
meso-(5)[b]	69.0 ± 0.50	27.8 ± 0.35	2.68 ± 0.12	0.529 ± 0.071
dl-(6)[c]	52.7 ± 1.45	38.7 ± 2.85	7.75 ± 4.08	0.819 ± 0.146

[a]Value derived from Table 14b, error in standard deviation.

[b]Absolute yields between 43-48%.

[c]Absolute yields between 30-40%.

Table 16. Direct Irradiation of (5)-(8) Through Selected Filters

Peroxide	Filter[a]	Olefin Yield[b]	(Ratio
meso-(5)	Pyrex	43%	(71/29)
meso-(5)	Corning 5970+$CuSO_4$[c]	20%	(67/33)
meso-(5)	Corning 7380+$CuSO_4$	18%	(64/36)
dl-(6)	Pyrex	34%	(56/44)
dl-(6)	Corning 5970+$CuSO_4$	21%	(52/48)
dl-(6)	Corning 7380+$CuSO_4$	21%	(52/49)
cis-(7)	Pyrex	40%	
cis-(7)	Corning 5970+$CuSO_4$	15%	
cis-(7)	Corning 7380+$CuSO_4$	6%	
trans-(8)	Pyrex	---	
trans-(8)	Corning 5970+$CuSO_4$	13%	
trans-(8)	Corning 7380+$CuSO_4$	5%	

[a]Transmission characteristics of filters are as follows: Pyrex: 270 nm (0%), 280 nm (5%), 290 nm (15%), 300 nm (30%), 310 nm (50%), 320 nm (70%), 330 nm (80%), 340 nm (85%), > 350 nm (90%); 5 cm 10% $CuSO_4$ solution: 300 nm (0%), 320 nm (7%), 340 nm (48%), 360 nm (67%), 380 nm (73%), 400 nm (77%), 420 nm (79%), 440 nm (80%), 460 nm (81%), 480 nm (79%), 500 nm (75%), 520 nm (64%), 540 nm (47%), 560 nm (27%), 580 nm (10%), 600 nm (2%); Corning Filter #5970: 300 nm (10%), 310 nm (27%), 330 nm (47%), 340 nm (62%), 350 nm (71%), 360 nm (75%), 370 nm (76%), 380 nm (75%), 390 nm (71%), 400 nm (53%), 410 nm (28%), 420 nm (1%). Corning Filter #7380: 300 nm (1%), 310 nm (1%), 320 nm (1%), 330 nm (1%), 340 nm (1%), 350 nm (1%),

Footnotes for Table 16 continued

360 nm (42%), 370 nm (64%), 380 nm (73%), 390 nm (78%), 400 nm (80%), 410 nm (82%), > 420 nm (∿85-87%); Corning Filter #5970 and 5 cm 10% $CuSO_4$ solution: 300 nm (0%), 310 nm (0%), 320 nm (1%), 330 nm (6%), 340 nm (12%), 350 nm (16%), 360 nm (19%), 370 nm (20%), 380 nm (19%), 390 nm (16%), 400 nm (8%), 410 nm (2%).

[b] All samples were distilled and products analyzed by vpc (13% DBT, 25°C for 2-butene, 90°C for cyclohexene).

[c] 5 cm 10% $CuSO_4$ solution.

It's not unreasonable to propose that the peroxides, after promotion to their first excited singlet state can deactivate by a variety of processes such as intersystem crossing or internal conversion and that the dissection of these processes is peroxide dependent. The subsequent appearance of products (and their stereochemistry) is process dependent. Because of our observation of the β-lactones in the pyrolysis of (5) and (6) and other reports of α-lactone[21] and β-lactone[20] production during the photolysis of other peroxides, it's not surprising to find the β-lactones in our photolysis mixtures. This provides evidence for the intermediacy of the carboxy radical, (17), in the photochemical as well as the thermal decomposition. It is unfortunate, however, that the reproducibility of the β-lactone ratios and yields could not be more carefully controlled. Along with the observation of 2-butene ratios, the lack of similar sets of products implies "different" or "non-equilibrating" intermediates.

The mechanism whereby triplet carboxy diradical decarboxylates before internal conversion to give 2-butene triplet is certainly not the sole pathway for 2-butene production and can be ruled out as such. This does not rule it out, however, from operating in part.

2. Sensitized Irradiation of dl- and meso-2,3-Dimethylsuccinyl Peroxides (5) and (6) and cis- and trans-1,2-Hexahydrophthaloyl Peroxides (7) and (8).

Because of Walling's[54] and others[53] observations that peroxide decomposition could be sensitized (presumably through the triplet) and in pursuit of the nature of the species giving photoproducts in the direct irradiations, we attempted several sensitization experiments. A Corning 5970 filter and 5 cm aqueous 10% $CuSO_4$ solution were chosen to give maximum access to wavelengths (see Footnote A, Table 16) where sensitizers would absorb but the peroxides would not decompose. Even under these conditions, significant decomposition occurred in 15 minutes. Irradiation times were cut to four or five minutes in an attempt to minimize the peroxide decomposition. It was originally intended to run these irradiations at 10:1 peroxide to sensitizer concentrations. However, at 1:1 ratios, enhanced sensitization (see Table 17) was observed for peroxide cis-(7). Thus 1:1 ratios at 0.02-0.03M were used. Table 18 gives the yield of olefins as followed by analytical vpc as well as decomposition of peroxide as followed by infrared. All these samples were distilled prior to vpc analysis

Table 17. Yield of Cyclohexene from Sensitized Decomposition of Peroxide cis-(7)[†]

Sensitizer:	None	Naphthalene	Anthracene	Acetophenone	Benzophenone	Benzil	Tetracene
0.02M	3%	3%	49%	7%	43%	4%	41%
0.003M	5%	5%	23%	7%	21%	6%	16%
0.003M	--	5%	21%	6%	12%	7%	---

[†]Yield of cyclohexene determined by analytical vpc (DBT, 60°C) against n-heptane as an internal standard.

Table 18. Sensitized Irradiations of Peroxides (5) through (8)

Sensitizer	% Olefin Production/% Peroxide Decomposition							
	meso-(5)[a]		dl-(6)[a]		cis-(7)[b]		trans-(8)[b]	
None	3	0	3	3	3	2	3	2
Naphthalene	3	--	3	--	3	--	3	--
Anthracene	31	77	13(24)[b]	> 79	49	> 81	62	> 72
Anthracene + O_2	--	34	---	40	--	38	--	22
Acetophenone	4	5	3	5	7	6	8	10
Benzophenone	8	32	9(12)[b]	> 51	43	> 77	53	> 91
Benzil	4	6	3	10	4	4	4	0
Acetone	3	--	3	--	6	--	3	--
Tetracene	13	76	13(20)[b]	--	41	--	54	68
Tetracene[c]	5	--	4	--	4	--	3	--

[a] 4 minute irradiation 0°C except where noted in parentheses

[b] 5 minute irradiation at 0°C.

[c] Control sample, no irradiation

and because they were not run to completion, examination for β-lactones was not considered. It is immediately obvious from Table 18 that anthracene, benzophenone and tetracene were effective sensitizers, though to varying degrees, for all four peroxides. A note of caution concerning the assessment of these numbers in more than a qualitative way is sounded. As noted in the Experimental Section, effort was taken to provide equal illumination to all samples, to reproducibly add sensitizer to samples, and to irradiate for the same time periods. It should be noted that some dl-dimethylsuccinyl peroxide (6) samples were irradiated an extra one minute (values in parentheses in Table 18) with significant change in yields of olefin. The results from a ten-fold change in concentration of sensitizer can be seen in Table 17 for cis-(7) as well as reproducibility of observations.

Considering the characteristics of the filter which have a 20% maximum transmittance at 370 nm, it is likely that naphthalene, acetophenone, and acetone simply did not absorb very much or any irradiation. However, examination of Table 19 indicates that anthracene and benzophenone as well as benzil should absorb in this region. Similar to Walling's observations,[54] benzil did not have sufficient energy (E_T = 53.4 kcal) to sensitize the decomposition. Both anthracene and tetracene were effective even though their triplet energies

Table 19. Absorption Characteristics of Selected Sensitizers[30]

	E_S(kcal)	(nm)	E_T(kcal)	ε_{313}	ε_{366}
Naphthalene	92	311	60.9	$\sim 10^2$	~ 0
Anthracene	76.3	375	42.0	$\sim 10^3$	$\sim 10^4$
Acetophenone	78.7	363	73.7	~ 10	~ 5
Benzophenone	75.4	379	68.6	~ 10	$\sim 10^2$
Benzil	59.0	485	53.4	$\sim 10^2$	$\sim 10^2$
Acetone	88	325	79-82	~ 3	~ 0
Tetracene	60.7	471	29.3	--	--

were below that of benzil. Walling observed that peroxides have no low-lying triplet states and his kinetic analysis suggested that energy transfer to quencher from triplet sensitizer was slower ($k = 3.2 \times 10^6$ 1/m·s) than expected for a Franck-Condon process ($k = 10^9$ 1/m·s) but faster than known chemical reactions (hydrogen abstraction) of the benzophenone triplet (10^2-10^5).[54] It has been reported that some aromatic hydrocarbons (benzene or toluene) sensitize the decomposition of peroxides via their first excited singlet.[95] Addition of oxygen to the anthracene sample quenched, at least in part, the decomposition.

Based on Schuster's[25] and our observations of induced decomposition by aromatic hydrocarbons (see Results and Discussion in Section E of this thesis) it's not unreasonable to suspect an electron transfer rather than an energy transfer is responsible for the decompositions. Briefly, Schuster elegantly showed that aromatic hydrocarbons can induce the decomposition of diacyl peroxides by electron transfer and that the rate of this decomposition is a function of oxidation potential of the hydrocarbon. Though tetracene is reasonably effective, anthracene is barely competitive with thermal decomposition.

In the present experiments, as shown in Table 18, tetracene samples which were prepared and handled similarly to the photolysis samples (0°C but kept in the dark) showed little decomposition. Yet in light, anthracene and tetracene effected rapid decomposition at 0°C. It is not unreasonable to propose that the oxidation potential of these aromatic hydrocarbons should be significantly lower in their excited states. For example, the new oxidation potential may be related to the difference between the ground state oxidation potential and the excited state(s) of the sensitizer. This might make both anthracene and tetracene better "inducers" than the fastest reported thermally, rubrene.[25]

In the present system, it might prove quite difficult to provide evidence for this mechanism chemically. One desirable way would be to obtain sensitizers with sufficient triplet energies to permit rapid energy transfer ($k \gtrsim 10^9$) but such high oxidation potentials that induced decomposition would be much slower (k = f(oxidation potential) = 10^{-2}-10^2 l/m·s when E_{ox} = 0.9-1.2 ev).[25] For comparison, sensitizers with triplet energies insufficient to affect energy transfer ($k \rightarrow 0$) but reasonably low oxidation potentials such that induced decomposition becomes competitive or predominant might be considered. From the meso-(5) and dl-(6) peroxides, it might be hoped that "pure triplet energy" transfer gives a set of 2-butene ratios distinctive from "pure electron" transfer. Examination of the ratios of cis- and trans-2-butene products in Table 20 shows, however, that this analysis is inconclusive. Controls showed that both cis- and trans-2-butenes were stable and did not isomerize in the presence of anthracene or tetracene under photolysis conditions, but isomerized (up to 15% crossover to the other isomer in 5 minutes) and were consumed during sensitized irradiation with benzophenone. In addition, in all our photolyses, some direct decomposition was undoubtedly occurring. To dissect out that component would be quite difficult.

Table 20. Sensitized and Induced Decomposition of meso- and dl-2,3-Dimethylsuccinyl Peroxides in CH_2Cl_2. Ratio of trans- to cis-2-butene.[†]

	Anthracene, 0° hν-5 min	Tetracene, 0° hν-5 min	Benzophenone, 0° hν-5 min	Rubrene, 20° dark-24 h
meso-(5)	72:28(31%)	72:28(13%)	76:24(8%)	69:31(55%)
dl-(6)	67:33(24%)	69:31(20%)	65:33(12%)	73:22(38%)

[†]Ratio and yields of 2-butenes measured against 2-methylbutane by vpc (DBT, 25°C).

A more sophisticated physical experiment suggests itself based upon the fact that aromatic hydrocarbon induced decomposition results in the formation of singlet aromatic hydrocarbon.[25] Thus, although these systems undoubtedly fluoresce when irradiated as well as undergo intersystem crossing (and other deactivation mechanisms) one might expect enhanced fluorescence as a function of peroxide concentration.

D. INDUCED DECOMPOSITION OF DL- AND MESO-2,3-DIMETHYLSUCCINYL PEROXIDES, (5) AND (6), AND CIS- AND TRANS-1,2-HEXAHYDROPHTHALOYL PEROXIDES, (7) AND (8).

1. Reaction of Triphenylphosphine with Peroxides, (5) through (8). Reaction of Dimethylsulfide with Peroxides (5), (7), and (8).

When peroxides, (5)-(8) were mixed with a several-fold excess of triphenylphosphine in dichloromethane, infrared analysis showed complete disappearance of peroxide and appearance of carbonyl absorptions characteristic of the corresponding anhydride after 20-30 minutes.

dl-(6) which was prepared from 98% isomerically pure dl-2,3-dimethylsuccinyl chloride yielded 30% of > 99% isomerically pure dl-2,3-dimethylsuccinic anhydride (30) upon reaction with triphenylphosphine as determined by

analytical vpc. Similarly, meso-(5) which was prepared from > 99% isomerically pure meso-2,3-dimethylsuccinyl chloride yielded 71% of > 97% pure meso-2,3-dimethylsuccinic anhydride (29).

A mixture of meso-(5) (66%) and dl-(6) (34%) afforded a mixture of anhydrides meso-(29) (60%) and dl-(30) (40%) in 41% yield as determined by vpc. Although stereospecific, this reaction did not provide quantitative yields of anhydride as expected. A likely competing reaction which was originally not anticipated is the reduction of peroxide by triphenylphosphine analogous to the aromatic hydrocarbon induced chemistry discussed in Section E. The oxidation potential of triphenylphosphine has been determined to be 0.83 ev vs. Ag, 0.1M $AgNO_3$ (1.17 ev vs. SCE).[97] Based on Schuster's observations, this should readily reduce diphenoyl peroxide with an estimated second order rate constant of $\sim 6 \times 10^{-2}$ $1/mole^{-1}$ sec^{-1} (extrapolated from Schuster's graphs and data).[25] We have shown in Section E that peroxides (5)-(8) react more slowly with aromatic hydrocarbon than diphenoyl peroxide. Second order rate constants for the decomposition of benzoyl peroxide by nucleophiles have been determined and with trimethylphosphite, $k_2 = 1.4 \times 10^{-3}$ $1/mole^{-1}$ sec^{-1}.[10] Thus we might expect these two processes to become competitive. We have also shown that olefin is a predominant product in the aromatic hydrocarbon induced

decomposition of peroxides (5)-(8). (Section E). Table 21 shows the yield of olefin as determined by vpc from peroxides (5), (7) and (8) in the presence of triphenylphosphine and dimethylsulfide (E_{ox} = 1.41 ev vs Ag, 0.1M $AgNO_3$, 1.7 ev vs SCE).[93] Examination of the infrared spectra showed appearance of typical anhydride carbonyl absorptions. From meso-(5) with excess triphenylphosphine, 65.3% meso-2,3-dimethylsuccinic anhydride (99.5% isomerically meso) was obtained as determined by vpc. Similarly, with excess dimethylsulfide, 28.1% meso-anhydride (97.2% isomerically meso) was obtained.

Thus, the reaction of meso-(5) with triphenylphosphine gave a combined quantitative yield of olefin (46.2%) and anhydride (65.3%). The product yield was not similarly quantitative from dimethylsulfide (a second unidentified product with ir absorption at 1710 cm^{-1} was obtained in significant quantity). In all three peroxides examined, no more olefin was observed than was obtained for the control. Thus, if olefin arises solely from electron transfer decomposition in this reaction, triphenylphosphine reduces the peroxide and dimethylsulfide does not, consistent with what would be predicted from their oxidation potentials.

Since both dimethylsulfide and triphenylphosphine afford anhydride by presumably similar mechanisms, these results imply that electron transfer decomposition is

Table 21. Percent Olefin from Induced Decomposition with Triphenylphosphine and Dimethylsulfide[†]

Peroxide	1 hr Control	1 hr Ph_3P	1 hr CH_3SCH_3	3 hr Ph_3P	3 hr CH_3SCH_3
meso-(5)	10%	46.2%	11.6%	---	---
cis-(7)	3.9%	9.2%	3.7%	---	3.8%
trans-(8)	4.2%	12.0%	2.6%	11.9%	4.0%

[†]Samples distilled and yields determined by analytical vpc against n-heptane.

distinct from nucleophilic decomposition.

2. Reaction of Copper (I) with Peroxides (5)-(8).

In the presence of copper (I), all four peroxides, (5)-(8), underwent rapid decomposition with concomitant oxidation of copper (I) to copper (II). The yields of olefin ranged from 10-40% as determined by vpc.

Traces of β-lactones, (18) and (19) were observed in distillates of reaction mixtures of (5) and (6) with cuprous acetate. Due to inefficient distillation, quantities or yields were not determined. Ratios of 2-butenes are similar to those observed in other induced and thermal decompositions (68-70% trans, 32-30% cis). Tables 43-44 in the Experimental Section list the results.

Without isolating the peroxide (a low yield step), the reaction solvent (dichloromethane) was removed at reduced pressure and acetonitrile added. An equimolar mixture (based on starting dicarboxylic acid or anhydride) of cuprous acetate or cuprous bromide was added. After stirring for several hours at 0-10°C, yields of 25-42% cyclohexene based on starting diacid were obtained as determined by vpc. (Table 45 in Experimental Section).

3. Summary

The cyclic diacyl peroxides (5)-(8) rapidly reacted with nucleophiles triphenylphosphine and dimethylsulfide to yield the corresponding cyclic an-

hydrides (39), (30), (35) and (36). Significant quantities of olefins were obtained as well in the triphenylphosphine decomposition. The relatively low oxidation potential of triphenylphosphine suggests induced decomposition by electron transfer may be operating.

Similarly, rapid decomposition of the peroxides (5)-(8) by copper (I) salts was affected yielding 10-40% olefins. From meso-(5) and dl-(6), trans- and cis-2-butenes were obtained in ratios similar to those reported for the thermal decompositions.

E. AROMATIC HYDROCARBON INDUCED DECOMPOSITION OF DL- AND MESO-2,3-DIMETHYLSUCCINYL PEROXIDES (5) AND (6) AND CIS- AND TRANS-1,2-HEXAHYDROPHTHALOYL PEROXIDES (7) AND (8).

The trans- to cis-2-butene ratios resulting from the thermal decomposition of peroxides (5) and (6) did not correspond to the photostationary branching ratios[33-35] expected from electronically excited 2-butenes. However, in the presence of rubrene, the dl-dimethylsuccinyl peroxide (6) emitted faintly visible light in a very dark room. Because of Schuster's observations of light emission from diphenoyl peroxide and his proposed CIEEL mechanism, we explored the possibility that this mode of decomposition was operating in our peroxides (5) through (8).

Table 22 shows a semiquantitative analysis following the disappearance of peroxide with time in the presence of several aromatic hydrocarbons. Several points should be noted. As the peroxide decomposed, other ill-defined carbonyl containing products (possibly polymeric material) appeared in the same region of the infrared obstructing the analysis (See Figures 5-9 Experimental Section). In addition, due to infrared limitations of peroxide concentration (preferably at 0.1-0.2M) and aromatic hydrocarbon solubilities (0.03-0.04M), the samples were quite concentrated and the ratio of aromatic hydrocarbon to peroxide was less than one. This is in contrast to the studies of diphenoyl peroxide which were conducted at 10^{-5}M peroxide with 10 to 100 fold excesses of hydrocarbon. UV studies were considered but the lack of a peroxide maximum above 200 nm and the intense absorption by all of the dyes prevented this. Studies at peroxide concentrations of 0.005M in a long path length cell were also discarded because of complicating absorption by dichloromethane and lack of temperature control. In addition, attempts to reproduce Schuster's work with diphenoyl peroxide at 3×10^{-3}M and rubrene concentrations at $1\text{-}2 \times 10^{-3}$M did not give first order kinetics in the infrared (see Figure 10 Experimental Section).

We also attempted to follow the appearance of product from peroxides (7) and (8) in the presence of rubrene, naphthacene, and diphenylanthracene in dichloromethane at 14°C. Again, the rubrene samples gave immediately higher yields of cyclohexenes as determined by vpc. Especially important to note is the very low maximum yield of cyclohexene (∿ 20%) in contrast to the thermal and photochemical samples. The infrared clearly showed the appearance of other carbonyl containing material (which is neither lactone nor anhydride). Schuster reported between 60-75% benzocourmarin with the remaining material polymer.[25] Interestingly, he did his reactions between two to three orders of magnitude more dilute. It seems reasonable, that at higher peroxide concentration, induced decomposition by the intermediate peroxide radical anion or subsequent decomposition products (PDP$^{\cdot}$) could induce further peroxide decomposition as well as transfer an electron back to the aromatic hydrocarbon. Exactly how the polymeric material arises is not known but high concentrations of peroxide are not desirable for clean kinetics or product determinations.[10]

In spite of the lack of precise quantitative data, it can be seen that all four peroxides do undergo decomposition in the presence of aromatic hydrocarbons. The

Table 22. Percent[a] Peroxide Decomposition in the Presence of Aromatic Hydrocarbons in Dichloromethane at 14±3°C

Peroxide	Aromatic Hydrocarbon	Time: Initial[b]	30 min	120 min	360 min
(6) (0.15M)	Rubrene (0.037M)	57	> 60[c]	---	---
	Perylene (0.046M)	12	57	> 59[c]	---
	DPA (0.025M)	1	29	42	---
(5) (0.12M)	Rubrene (0.045M)	24	59	---[c]	---
	Perylene (0.039M)	0	12	18	23
	DPA (0.030M)	0	8	12	---
(8) (0.07M)	Rubrene (0.047M)	4	27	40	---
	Perylene (0.040M)	4	4	6	---
	DPA (0.031M)	0	4	5	---
(7) (0.10M)	Rubrene (0.044M)	14	38	---[c]	---
	Perylene (0.040M)	9	12	15	20
	DPA (0.035M)	1	7	7	---
	Rubrene (0.046M)	5	7	32	39

Table 22 Footnotes

[a]Error in repeated infrared analyses ($\sim$ 1775 cm^{-1}) of the same sample was often 3-4%.

[b]Initial time was between3-5 minutes.

[c]Because of other carbonyl containing material, the peroxide peak could no longer be seen. See Figures 5-9, Experimental Section.

Table 23. Percent Yield Cyclohexene in Presence of Aromatic Hydrocarbons in Dichloromethane at 14±2°C

Peroxides	Aromatic Hydrocarbon	Time 3hrs	8hrs	32hrs	73hrs
(7) (0.011M)	Rubrene	13%	20%	22%	23%
	Naphthacene	3%	5%	8%	11%
	DPA	2%	3%	6%	9%
(8) (0.010M)	Rubrene	9%	13%	17%	19%
	Naphthacene	1%	3%	6%	8%
	DPA	1%	3%	5%	7%

---

most significant change occurs with rubrene, followed by perylene and diphenylanthracene which is consistent with the CIEEL mechanism and Schuster's observations.

It is also quite clear that the dl-dimethylsuccinyl peroxide (6), decomposed faster in the presence of the aromatic hydrocarbons than did peroxides (5), (7) and (8). This rate difference probably explains why light emission can be visibly detected from the reaction of rubrene with dl-(6) and diphenoyl peroxide (12) but not from the former three. It is likely that light is emitted from (5), (7) and (8) with rubrene (as well as the other dyes) but undoubtedly of very low intensity.

The decomposition of commercially available benzoyl peroxide by rubrene was also examined. The results appear in Figure 9.

Chemically initiated electron exchange appears to be a general phenomenon of cyclic and acyclic diacyl peroxides. Whether or not luminescence can be observed for all these peroxides remains to be determined by more sensitive light detection methods.

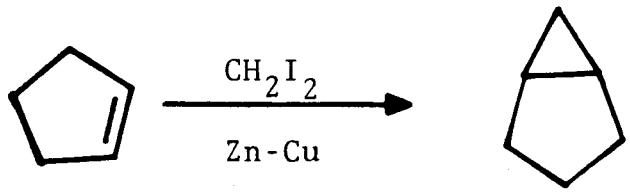
Without quantitative kinetic data, it's hard to speculate on the precise mechanism or requirements of the initial electron transfer. It appears, however, that there is a broad range of rates from peroxide to peroxide. Further exploration toward determining how structure affects the rate is important.

F. THERMAL AND PHOTOCHEMICAL DECOMPOSITION OF BICYCLO[3.1.0]HEXANEDIACYL PEROXIDE (9).

1. Thermal Decomposition of Bicyclo[3.1.0]hexanediacyl Peroxide (9).

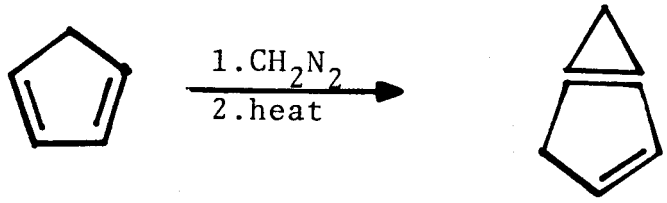
Bicyclo[3.1.0]hexanediacyl peroxide (9) was heated as a neat solid in a vacuum until (an explosive) decomposition took place. The volatile products were distilled into a cold trap containing a hydrocarbon solvent (usually hexane or benzene-d_6). Analytical vpc and GC-MS showed a large number of six-carbon prod-

ucts. Table 48 (in the Experimental Section) lists the products and yields. Identification of cyclohexane, cyclohexene, 1,3- yclohexadiene, and benzene was made by coinjection (vpc) with commercially available authentic samples. Bicyclo[3.1.0]hexane (72) was independently prepared by a modification of the Simmons-Smith procedure.[100] Bicyclo[3.1.0]hex-2-ene (73) was independently pre-



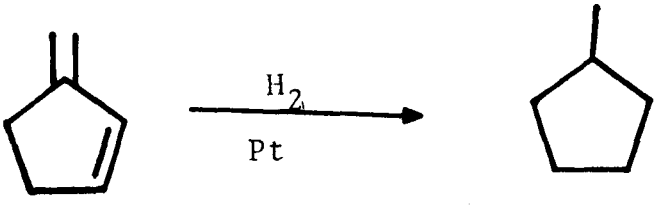
(72)

pared and shown not to be a product in the decomposition of (9).[101]



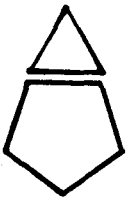
(73)

The major product as determined by vpc was methylene cyclopentene (74) (∿ 11%) which was isolated by preparative vpc and identified by nmr comparison with a literature assignment.[102] In addition, it cleanly hydrogenated over a platinum oxide catalyst and one atmosphere of hydrogen to methylcyclopentane.



(74)

An nmr (at -30°C) of the crude pyrosylate showed peaks corresponding to methylene cyclopentene (74), hexane (a known contaminant of the starting material) and a third compound which was tenatively identified as $\Delta^{1,5}$-bicyclo[3.1.0]hexene (75). The nmr absorptions (in benzene-d_6) can be assigned to (75) as follows; δ2.40 ppm (multiplet, J = 4.0Hz): four allylic protons; δ1.97 ppm (triplet, J = 4.0Hz): two homoallylic protons; and δ0.61 ppm (singlet): two cyclo-



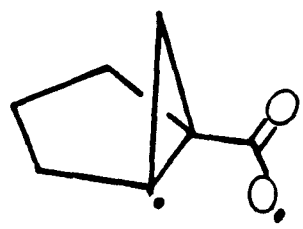
(75)

propene protons. (The chemical shift of the methylene group in cyclopropene is δ0.92 ppm[103] and in methylcyclopropene, δ0.83 ppm.[104] The chemical shifts of the allylic methylene and homoallylic methylene protons in cyclopentene are δ2.28 and 1.90 ppm, respectively.)[103] The latter two absorptions assigned to (75) integrate one to one.

Hydrogenation of the crude pyrosylate over platinum oxide showed complete disappearance of peaks due to cyclohexene and methylene cyclopentene (see Table 49 in Experimental Section) and appearance of cyclohexane. Controls showed that under the hydrogenation conditions 8-20% bicyclo[3.1.0]hexane converted to cyclohexane. Table 49 shows an increase in bicyclo[3.1.0]hexane as well as formation of cyclohexane.

These data provide preliminary permissive evidence for the intermediacy of $\Delta^{1,5}$-bicyclo[3.1.0]hexene (75).

The other products may be rationalized as arising from the rearrangement and/or disproportionation of (75) or an intermediate such as the carboxy diradical



(76).

(76). The lability of some of these compounds (Table 48 in the Experimental Section shows after one day at 0°C, (74) almost completely disappeared) makes quantitative

and qualitative vpc analysis especially difficult.

2. Photolysis of Bicyclo[3.1.0]hexanediacyl Peroxide (9).

Irradiation of peroxide (9) at -78°C and 0°C for a total of one hour through Pyrex under conditions where peroxides (5)-(8) rapidly and significantly decomposed in 10 minutes showed no decomposition by nmr.

III. EXPERIMENTAL

All reactions of diacyl peroxides were carried out in glassware that had been washed with methanol-disodium ethylene diamine tetraacetic acid (EDTA), rinsed with water, and dried. This was to minimize the possibility of induced decomposition by adventitious metal ions.

Elemental analyses were performed by the Caltech analytical facility.

Melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected. All temperatures are reported in degrees Celsius (C).

Proton nuclear magnetic resonance (nmr) spectra were recorded on a Varian A-60A, EM-390 or XL-100 spectrometer. Carbon nuclear magnetic resonance (cmr) spectra were recorded on a Varian XL-100 spectrometer. Chemical shifts are reported as parts per million downfield from tetramethylsilane (TMS) in δ units. Coupling constants are reported in cycles per second (Hz). Magnetic resonance data are reported in the order: chemical shift; multiplicity (for nmr only), s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet; number of protons (for nmr only); assignments.

Infrared spectra were recorded on a Perkin-Elmer 257 Grating or Beckman IR 4210 infrared spectrometer.

Mass spectra were recorded on a DuPont 21-492B spectrometer. Gas chromatography-mass spectra (GC-MS)

were run on a Finnegan 3200 E.I. mass spectrometer interfaced to a Finnegan 9500 gas chromatogrph at the Jet Propulsion Laboratory (JPL) by Ray Haack. GC-MS data in the decomposition of peroxide (9) were obtained on a Hewlett Packard gas chromatograph interfaced to an EAI QUAD 300 mass spectrometer with the assistance of Jon Burke.

Analytical vapor phase chromatography (vpc) was performed on a Hewlett-Packard 5700A or 5720A gas chromatograph with flame ionization detector, equipped with a Hewlett-Packard 3370B digital integrator for quantitative analysis. Nitrogen was used as carrier gas. Preparative vpc was performed on a Varian Associates 920 gas chromatograph equipped with thermal conductivity detector. Helium was used as the carrier gas. Analytical and preparative gas chromatograph columns are listed in Table 24. All 0.125 in columns are stainless steel, all 0.25 inand 0.375 in columns are aluminum unless stated otherwise in the description. The 0.125 in were used in analytical work. The 0.250 in and 0.375 in columns were used in preparative work. Peak assignments were made by coinjection with authentic samples and/or GC-MS analysis. Relative retention times (RRT) are reported.

Table 24. VPC Columns

Column Designation	Description
DBT	10' x 0.125", 10% dibutyl tetrachlorophthalate on 100/120 Chromosorb P A/W
DBT	20' x 0.125", 10% dibutyl tetrachlorophthalate on 100/120 Chromosorb P A/W
Carbowax 20M	10' x 0.125", 10% Carbowax 20M on 100/120 Chromosorb W
PMPE	10' x 0.125", 10% poly-m-phenyl ether (6 ring) on 100/120 Chromosorb W A/W DMCS
SE-30	10' x 0.125", 25% SE-30 on 100/120 Chromosorb P
SF-96	10' x 0.125", 10% SF-96 on 100/120 Chromosorb P A/W
UCON	10' x 0.125", 10% UCON-550X on 100/120 Chromosorb W
UCON-GC-MS	5' x 2 mm (ID), glass 3% UCON-550X on 100/120 Chromosorb W A/W DMCS

Column Designation	Description
Carbowax 20M-GC-MS	5' x 2 mm (ID), glass, 3% Carbowax 20M on 80/100 Chromosorb W
DBT	5 ' x 0.125", glass, 10% dibutyl tetrachlorophthalate on 60/80 Chromosorb P DMCS
SE-30	20' x 0.375", 25% SE-30 on 45/60 Chromosorb P
UCON	10' x 0.375", 20% UCON-550X on 60/80 Chromosorb W
PMPE	10' x 0.375", glass, 10% poly-m-phenylether on Chromosorb W A/W DMCS

Detector response for all hydrocarbons and olefins (2-butenes) was assumed to be linear. Other compounds were weighed and analyzed with respect to a weighed internal standard and appropriate response corrections were made. All yields determined by vpc were measured against an internal standard.

Reagent grade chemicals were used without further purification and were obtained from the Chemical Samples Co., Aldrich Chemical Co., or MCB, Inc.

Dichloromethane was dried over phosphorous pentoxide and distilled. Methanol was dried over magnesium turnings and distilled. Tetrahydrofuran (THF) was dried over the sodium ketyl of benzophenone and distilled.

Saturated ethereal solutions of diazomethane used throughout much of this work for analytical analysis was prepared by dissolving 1g potassium hydroxide in 10 ml water in a 100 ml erlenmeyer flask. After addition of 40 ml of ether and cooling to 0°C, 1g N-nitrosomethylurea was added. After several minutes the ethereal layer turned yellow after which it was added directly to the reactant by careful decantation off the aqueous layer.

meso- and dl-2,3-Dimethylsuccinic Acids, (27) and (28).[70]

To 1200 ml of anhydrous t-butanol distilled from sodium in a 2 l. three necked round bottom flask was added 35.8g (0.916 mol) potassium. After the potassium had dissolved, 164g (0.941 mol) of diethyl methyl malonate was added rapidly followed by the addition of 141g (0.778 mol) of ethyl-α-bromopropionate. The opaque white reaction mixture was allowed to reflux for 2 hr, then allowed to stand at room temperature overnight. t-Butanol was distilled from the reaction mixture and the yellow-white residue extracted into ether. The ethereal extract was washed with water, dried ($MgSO_4$), concentrated and distilled, yielding 198.5g (0.724 mol, 93.1%) of the triester diethyl 2-carboethoxy-1,2-dimethylsuccinate: b.p. 100°C (0.01 mm); ir ($CDCl_3$) 1730 cm^{-1} (C=O); nmr ($CDCl_3$) δ4.4-3.9 (m, 6, $OC\underline{H}_2CH_3$), 3.3 (q, 1, C$\underline{H}$), 1.55 (s, 3, $C\underline{H}_3$) and 1.25 ppm (m, 6, $C\underline{H}_3$). The triester (198.5g, 0.724 mol) was added to 1 l. of 6 N HCl in a 2 l. round bottom flask and allowed to reflux until the organic layer had completely disappeared (12-15 hr). The water-hydrochloric acid was removed by distillation leaving a wet yellow-white solid. Heating was then commenced to a bath tempterature of ∿ 200°C. The solid melted with evolution of CO_2. This decarboxylation took ∿ 3 hr.

After cooling, the brown solid residue was heated and dissolved in refluxing concentrated HCl. After cooling and crystallization, two crops of crystals were obtained. Stereochemical purities were determined by reaction of 5-10 mg of each crop with excess ethereal diazomethane and analyzed by analytical vpc (see below).

First crop, 20.1g (23.6% based on triester), m.p. 197-201°C, 91% meso-(27) and 9% dl-(28). Second crop, 34.1g (40.1% based on triester), m.p. 124-125°C, 22.2% meso-(27) and 77.8% dl-(28). The first crop was recrystallized from 180 ml of 10 N HCl to yield 13.7g (68.2% recovery) of 99.3% meso-(27) and 0.7% dl-(28).

meso-Dimethyl-2,3-dimethylsuccinate, (31).

To 80 mg (0.55 mmol) of meso-(27) was added 20 ml of a saturated ethereal solution of diazomethane. After the yellow color of the diazomethane disappeared, the ether was removed by distillation and the remaining oil was purified by preparative vpc (UCON, 150°C) to afford meso-(31); ir ($CDCl_3$) 1730 cm^{-1} (C=O); nmr ($CDCl_3$) δ3.68 (s, 6, OCH_3), 2.75 (m, 2, CH), and 1.20 ppm (d, 6, CH_3).

dl-Dimethyl-2,3-dimethylsuccinate, (32).

To 80 mg (0.55 mmol) of dl-(28) was added 20 ml of a saturated ethereal solution of diazomethane. After the yellow color of diazomethane disappeared, the ether

was removed and the remaining oil purified by preparative vpc (UCON, 150°C) to afford dl-(32); ir ($CDCl_3$) 1730 cm^{-1} (C=O); nmr ($CDCl_3$) δ3.68 (s, 6, $-OCH_3$), 2.80 (m, 2, CH) and 1.20 ppm (d, 6, CH_3).

Analysis by analytical vpc (UCON, 130°C) gave relative retention times of 1.00 and 1.12 for meso-(31) and dl-(32), respectively.

meso-2,3-Dimethylsuccinic Anhydride, (29).[70]

To 99.3% meso-(27) (1.0g, 0.0068 mol) was added 1.5 ml acetyl chloride. The mixture was allowed to react at 60°C for 3 hr. Acetyl chloride and acetic acid were removed by distillation. The remaining solid was recrystallized from ether yielding 0.49g (0.0038 mol, 56%) meso-(29); m.p. 39-40°C, 99.4% meso-(29) and 0.6% dl-(30) as determined by analytical vpc (PMPE, 180°C); ir (CH_2Cl_2) 1840 and 1780 cm^{-1} (C=O); nmr ($CDCl_3$) δ3.25 (m, 2, CH) and 1.30 ppm (d, 6, CH_3).

dl-2,3-Dimethylsuccinic Anhydride, (30).

To 77.8% dl-(28) (34.1g, 0.234 mol) was added 40 ml acetyl chloride. The mixture was allowed to react at 60°C for 3 hr. After removing the acetyl chloride, acetic acid by distillation, the solid was recrystallized twice from CCl_4 affording 18.8g (0.147 mol, 62.8%) dl-(30); m.p. 86-88°C, 97.5% dl-(30) and 2.5% meso-(29), determined by analytical vpc (PMPE, 180°C); ir (CH_2Cl_2)

1860 and 1790 cm^{-1} (C=O); nmr ($CDCl_3$) δ2.85 (m, 2, CH) and 1.42 ppm (d, 6, CH_3).

Analysis by analytical vpc (PMPE, 180°C) gave relative retention times of 1.30 and 1.00 for meso-(29) and dl-(30), respectively.

meso-2,3-Dimethylsuccinyl Chloride (39).

To 3.0g of meso-2,3-dimethylsuccinic acid (0.021 mol, 99.5% meso) was added 10.0g (0.048 mol) phosphorous pentachloride. The mixture was allowed to react with stirring at 80-90°C for 3 hr. The phosphorous oxychloride was removed by distillation at room temperature under reduced pressure. The remaining diacid chloride and phosphorous pentachloride were added to 25 ml ether from which the phosphorous pentachloride precipitated. After filtration, the ether was distilled and the diacid chloride trap to trap distilled yielding 2.2g (0.012 mol, 59.2%) meso-2,3-dimethylsuccinyl chloride (39); b.p. 40-50°C (0.1 mm); ir (CH_2Cl_2) 1790 cm^{-1} (C=O); nmr ($CDCl_3$) δ3.22 (2, m, CH) and 1.45 (6, d, CH_3).

Several drops of freshly prepared diacid chloride (39) were added to 0.5 ml methanol. The sample was shown by analytical vpc (UCON, 130°C) to be the dimethyl ester with isomeric composition meso-(31) (99.0%) and dl-(32) (1.0%).

dl-2,3-Dimethylsuccinyl Chloride, (40).

As described for the meso-isomer, 2.7g of dl-2,3-dimethylsuccinic anhydride (0.021 mol, 97.2% dl) was added to 10.0g (0.048 mol) phosphorous pentachloride. Workup and distillation yielded 2.9g (0.016 mol, 78.0%) dl-2,3-dimethylsuccinyl chloride, (40); b.p. 40-50°C (0.1 mm); ir (CH_2Cl_2) 1790 cm^{-1} (C=O); nmr ($CDCl_3$) δ3.35 (2, m, CH) and 1.32 (6, d, CH).

Several drops of freshly prepared diacid chloride (40) were added to 0.5 ml methanol. The sample was shown by analytical vpc to be the dimethyl ester with isomeric composition meso-(31) (2.2%) and dl-(32) (97.8%).

meso-2,3-Dimethylsuccinyl Peroxide (5).

The freshly prepared diacid chloride, (39) (2.2g 0.012 mol) was dissolved in 75 ml of dichloromethane and slowly added at 0°C with stirring to a solution containing 3.0g (0.038 mol) sodium peroxide, 3.0g Na_2HPO_4, and 3.0g NaH_2PO_4 in 75 ml water. Stirring was continued for 3 hr and the solution was allowed to warm to room temperature. The dichloromethane layer was separated, dried ($CaCl_2$) and concentrated. Addition of n-hexane yielded a white precipitate which was collected by filtration: 65 mg (0.45 mmol, 3.8% based on (39)); ir (CH_2Cl_2) 1810

and 1778 cm^{-1} (C=O); nmr ($CDCl_3$) δ2.98 (m, 2, C<u>H</u>) and 1.38 (d, 6, C<u>H</u>$_3$).

<u>dl</u>-2,3-Dimethylsuccinyl Peroxide (<u>6</u>).

As described for the preparation of <u>meso-</u>(<u>5</u>), diacid chloride, (<u>40</u>) (2.9g, 0.016 mol) was dissolved in 75 ml of dichloromethane and added at 0°C to an aqueous solution of sodium peroxide. After the dichloromethane layer was dried ($CaCl_2$) and concentrated, addition of n-hexane yielded a white precipitate which was collected by filtration: 40 mg (0.28 mmol, 1.7% based on (<u>40</u>)); ir (CH_2Cl_2) 1811 and 1782 cm^{-1} (C=O); nmr ($CDCl_3$) δ3.05 (m, 2, C<u>H</u>) and 1.35 ppm (d, 6, C<u>H</u>$_3$).

<u>Note</u>: Both peroxides were extremely soluble in most solvents and very hard to get out of solution, thus the low isolated yields. In addition, the peroxides exploded quite easily upon warming or drying. Therefore, it was convenient and safer to handle these as stock solutions, usually in dichloromethane. Neither the spectra nor behavior of these peroxides appeared to be different with or without intermediate isolation. Concentrations were determined by infrared (see below).

cis-1,2-Hexahydrophthaloyl Chloride, (41).

To 4.0g (0.023 mol) of cis-1,2-hexahydrophthalic acid (or 3.6g of cis-1,2-hexahydrophthalic anhydride) was added 12.0g (0.57 mol) phosphorous pentachloride. The mixture was allowed to react with stirring for 3 hr. Phosphorous oxychloride was removed by distillation at room temperature under reduced pressure. Phosphorous pentachloride was sublimed into the distilling head at 80-90°C (pot temp.) under reduced pressure. When all the phosphorous pentachloride had been removed from the reaction pot, the distilling head was replaced. Trap to trap distillation afforded 4.88g (0.0232 mol, 100%) of cis-1,2-hexahydrophthaloyl chloride, (41); b.p. 80-90°C (0.1 mm); ir (CH_2Cl_2) 1790 cm^{-1} (C=O); nmr ($CDCl_3$) δ3.30 (m, 2, C<u>H</u>-), 2.10 (m, 4, C<u>H</u>$_2$-CH) and 1.55 ppm (m, 4, -C<u>H</u>$_2$-).

cis-Dimethyl-1,2-Hexahydrophthalate, (37).

Several drops of freshly prepared (41) were added to 0.5 ml methanol to yield the corresponding dimethyl ester. The isomeric composition was determined by analytical vpc (Carbowax 20M, 160°C) to be cis-(37) (> 99%). The product was isolated by preparative vpc (Carbowax 20M, 180°C); nmr ($CDCl_3$) δ3.65 (s, 6, OCH_3), 2.85 (m, 2, C<u>H</u>-C_3) and 2.10-1.30 ppm (m, 8, -C<u>H</u>$_2$).

trans-1,2-Hexahydrophthaloyl Chloride, (42).

As described for the cis-isomer, to 4.0g (0.023 mol) of trans-1,2-hexahydrophthalic acid (or 3.6g trans-1,2-hexahydrophthalic anhydride) was added 12.0g (0.57 mol) of phosphorous pentachloride. The mixture was allowed to react with stirring at 80°C for 3 hr. After removal of the phosphorous oxychloride and phosphorous pentachloride, distillation afforded 4.12g (0.019 mol, 85.8%) of trans-1,2-hexahydrophthaloyl chloride, (42); b.p. 80-90°C (0.1 mm); ir (CH_2Cl_2) 1787 cm^{-1} (C=O); nmr ($CDCl_3$) δ3.00 (m, 2, -CH-), 2.30 (m, 2), 1.90 (m, 2) and 1.35 ppm (m, 4, CH_2).

trans-Dimethyl-1,2-Hexahydrophthalate, (38).

Several drops of freshly prepared diacid chloride (42) were added to 0.5 ml methanol to yield the dimethyl ester. The isomeric composition was determined by analytical vpc (Carbowax 20M, 160°C) to be cis-(37) (1.5%) and trans-(38) (98.5%). The product was isolated by preparative vpc (Carbowax 20M, 180°C); nmr ($CDCl_3$) δ3.80 (s, 6, OCH_3), 2.63 (m, 2, $CH-C_3$) and 2.20-1.2 ppm (m, 8, $-CH_2-$).

cis-1,2-Hexahydrophthaloyl Peroxide, (7).

As described for the preparation of meso-(5), the freshly prepared diacid chloride cis-(4) (4.88g, 0.0232 mol) was dissolved in dichloromethane and added at 0°C to an aqueous solution of sodium peroxide. After the dichloromethane fraction was dried ($CaCl_2$) and concentrated, addition of n-hexane yielded a white precipitate; 1.1g (0.0065 mol, 28% based on (41); ir (CH_2Cl_2) 1805 and 1780 cm^{-1} (C=O); nmr ($CDCl_3$) δ3.10 (m, 2, CH) and 2.50-1.50 ppm (m, 8, $-CH_2-$).

trans-1,2-Hexahydrophthaloyl peroxide, (8).

As described for the preparation of meso-(5), the freshly prepared diacid chloride trans-(42) (4.12g, 0.019 mol) was dissolved in dichloromethane and added at 0°C to an aqueous solution of sodium peroxide. After the dichloromethane fraction was dried ($CaCl_2$) and concentrated, addition of n-hexane yielded a white precipitate; 0.90 (0.0053 mol, 25% based on (42)); ir (CH_2Cl_2) 1800 and 1775 cm^{-1} (C=O); nmr ($CDCl_3$) δ2.90 (m, 2, CH) and 2.30-1.10 ppm (m, 8, $-CH_2-$).

1,5-Bicyclo[3.1.0]hexanediacyl Chloride.

To 4.0g (0.024 mol) of bicyclo[3.1.0]hexane-1,5-dicarboxylic acid,[71] (43), was added 10 ml of thionyl chloride. After refluxing 2 hr, the excess thionyl

chloride was removed by distillation, and the diacid chloride, (4.6g, 89%) was trap to trap distilled; b.p. 80-90°C (0.1 mm); ir ($CHCl_3$) 1782 cm^{-1} (C=O); nmr ($CDCl_3$) δ2.8-1.6 ppm.

Synthesis of Bicyclo[3.1.0]hexane-1,2-diacyl Peroxide, (9).

Similar to the procedure described for peroxide meso-(5), 4.6g (0.022 mol) of 1,2-bicyclo[3.1.0]hexane-diacyl chloride in 75 ml of chloroform (or dichloromethane) was added at 0°C to 3.0g (0.038 mol) aqueous sodium peroxide. After drying, concentrating, and recrystallization from chloroform-hexane or chloroform-carbon tetrachloride, 1.2g (0.0071 mol, 32%) of a white powder, was obtained: ir ($CDCl_3$) 1795 and 1775 (C=O); nmr ($CDCl_3$) δ2.5-1.75 (m, 6, CH_2) and 1.45 ppm (d, 2, cyclopropyl CH_2); nmr (C_6D_6) δ2.33 (m, 3), 1.77 (m, 2) 1.28 (m, 1) and 0.9 ppm (d, 2).

Infrared Molar Absorptivity of Peroxide Carbonyl Groups.

Stock solutions of peroxides meso-(5) and trans-(8) in dichloromethane were prepared at different concentrations by dilution series. Infrared examination in a 0.1 mm solution cell as shown in Table 25 allowed calculation of extinction coefficients ($A = \varepsilon c$,

A = absorption, ε = extinction coefficient, c = molar concentration). For meso-2,3-dimethylsuccinyl peroxide, (5), $\varepsilon_{1810cm^{-1}} = 2.5$ and $\varepsilon_{1778cm^{-1}} = 3.8$. For trans-1,2-hexahydrophthaloyl peroxide, (8), $\varepsilon_{1800cm^{-1}} = 2.5$ and $\varepsilon_{1775cm^{-1}} = 3.7$

Table 25. Infrared Absorption of Peroxides, (5) and (8) in CH_2Cl_2

	Molarity	0.116	0.101	0.058	0.023	0.029
meso-(5)	$A_{1810cm^{-1}}$	0.311	0.247	0.147	0.074	0.071
	$A_{1778cm^{-1}}$	0.467	0.372	0.214	0.111	0.101
	Molarity	0.153	0.0767	0.0511	0.383	
trans-(8)	$A_{1800cm^{-1}}$	0.389	0.197	0.135	0.099	
	$A_{1775cm^{-1}}$	0.600	0.303	0.198	0.146	

Ultraviolet Spectra of Peroxides, (5) through (8).

Stock solutions of peroxides (5) through (8) in dichloromethane were prepared and concentrations varied in dilution series. Because no maxima were observed before the dichloromethane cutoff, extinction coefficients were determined at a number of wavelengths as indicated in Table 26 in a 1 cm path length cell.

Table 26. Ultraviolet Spectra of Peroxides, (5)-(8), Molar Extinction Coefficients

λ(nm) Peroxides	360	340	320	300	290	280	270	260	250	240
meso-(5)	0.89	1.42	3.32	8.84	15.97	28.26	53.43	104.0	-----	----
dl-(6)	0.42	0.99	2.81	8.11	14.64	27.54	57.68	122.4	228.0	----
cis-(7)	----	----	1.32	9.89	17.50	35.34	64.89	109.4	186.8	----
trans-(8)	----	0.81	2.48	8.20	14.79	26.56	48.59	92.91	169.0	262.20

Molecular Weight Determination

1. Cryoscopic Determination in Benzene-#1

Samples of dl-anhydride-(30), cis-peroxide (7) and trans-peroxide (8) were prepared in ∿ 0.5 ml benzene. Table 27 lists the results and shows the calculations. Temperature was measured by Iron-Constantan thermocouple. Freezing point curves were plotted by a Hewlett-Packard X-Y recorder interfaced to a millivolt meter. Calibration was previously performed by J. Bercaw and D. Erwin on ferrocene.

2. Cryscopic Determination in Benzene-#2

Table 28 lists the freezing point depression readings obtained from samples of anhydride dl-(30), of known molecular weight. Table 29 lists freezing point depression (R in millivolts) and shows the calculations. Data in Tables 28 and 29 were obtained from a digital readout millivolt meter and the freezing point depression curves were plotted by hand. The calibration curve plotted in Figure 1 was obtained from data in Table 28. Least squares analysis of R(millivolt reading) versus M(molality) yielded the relationship: $(0.280-R)/0.250 = M$ ($r^2 = 0.99$).

Table 27. Cryoscopic Determination of Molecular Weight, #1

Sample	Wgt. solute	Wgt. C_6H_6	R[a]	M[b]	Molecular Weight (exptl)	(calc)
dl-(30)	3.2 mg	0.4570g	0.203	0.0526	133	
			0.209	0.0210	333	
			0.206	0.0368	190	
			(average)		219±103[d]	128
dl-(30)	15.6 mg	0.4460g	0.156	0.316	110	
			0.164	0.258	136	
			0.157	0.311	112	
			0.172	0.232	151	
			(average)		127± 20[d]	128
cis-(7)	7.6 mg	0.4483g	0.197	0.0840	202	
			0.199	0.0740	229	
			0.194	0.0100	170	
			0.195	0.0950	178	
			(average)		195± 26	170

Sample	Wgt. solute	Wgt. C_6H_6	R^a	M^b	Molecular Weight (exptl)	(calc)
cis-(7)	11.9 mg	0.4483g	0.181	0.168	158	
			0.184	0.153	173	
			(average)		165± 11	170
trans-(8)	21.9 mg	0.4777g	0.176	0.196	234	
			0.173	0.212	216	
			0.167	0.243	189	
			0.171	0.222	206	
			0.167	0.243	189	
			(average)		207± 19	170

[a]R = Reading in mvolts of freezing point of benzene vs ice-water as determined by an Iron-Constantan thermocouple.

[b]M = Molality calculated from (0.213-R)/0.189 = M from calibration supplied by J. Bercaw and D. Erwin.

[c]mw = molecular weight = mg solute/(g solvent)(M).

[d]standard deviation

Table 28. Calibration for Cryoscopic Molecular Weight Determination with dl-Anhydride (30).

Wgt. (30)	Wgt. C_6H_6	M[a]	R[b]
18.57 mg	0.8662g	0.167	0.235
			0.238
			0.234
		(average)	0.236±0.002[c]
11.76 mg	0.9898g	0.0928	0.248
			0.252
			0.246
		(average)	0.249±0.003
3.46 mg	1.122g	0.0241	0.266
			0.271
			0.276
		(average)	0.271±0.005
26.82 mg	1.167g	0.179	0.234
			0.228
			0.228
		(average)	0.230±0.003

[a]M = molal based on a molecular weight of 128.

[b]R = reading in mvolts of freezing point of benzene vs ice-water as determined by an Iron-Constantan thermocouple.

[c]Standard deviation

Table 29. Cryoscopic Determination of Molecular Weight, #2

Sample	Wgt. solute	Wgt. C_6H_6	R^a	M^b	Molecular Weight (exptl)	(calc)
cis-(7)	19.42 mg	0.9471g	0.256	0.096	214	
			0.256	0.096	214	
			0.256	0.096	214	
			(average)		214	170
trans-(8)	16.69 mg	1.0189	0.266	0.056	292	
			0.255	0.100	164	
			0.258	0.088	186	
			(average)		214± 68	170
Benzoyl peroxide	18.79 mg	1.087	0.259	0.084	206	
			0.259	0.084	206	
			0.260	0.080	216	
			(average)		209± 6	240

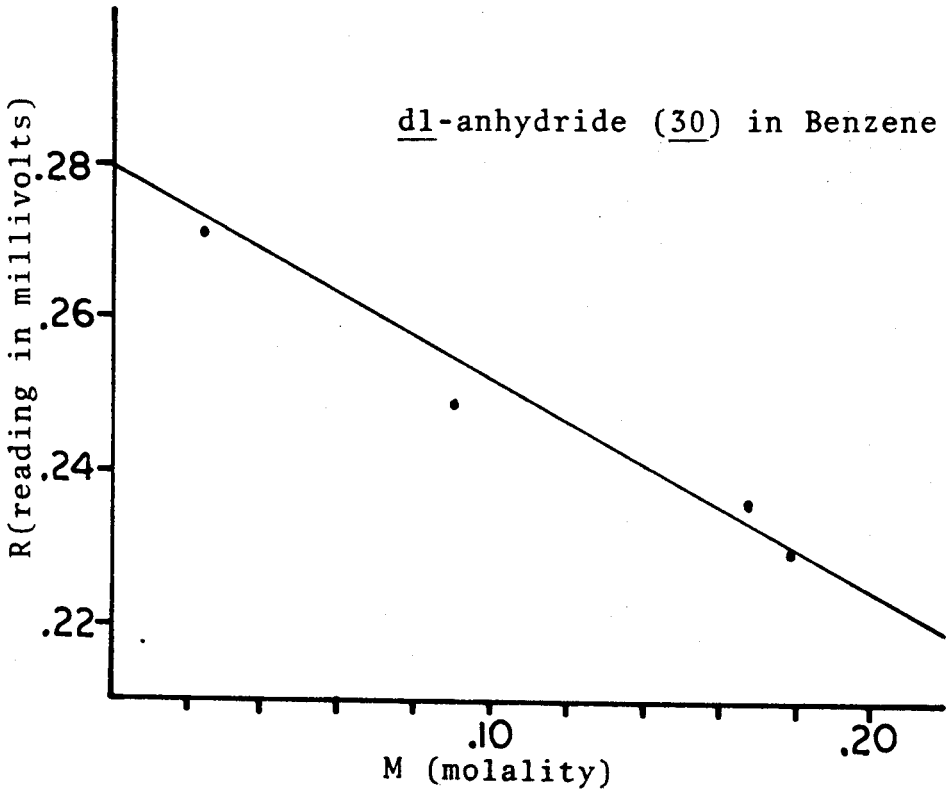
Sample	Wgt. solute	Wgt. C_6H_6	R[a]	M[b]	Molecular Weight (exptl)	(calc)
d1-(30)	19.17 mg	2.301g	0.262	0.072	116	
			0.262	0.072	116	
			0.264	0.064	130	
			(average)		121± 8	128

[a] R = Reading in mvolts of freezing point of benzene vs ice-water as determined by an Iron Constantan thermocouple.

[b] M = Molality calculated from (0.280-R)/0.250 = M from calibration of Table 28. Figure 1 shows line from data. Intercept and slope were determined by the method of least squares (r^2 = 0.99).

[c] molecular weight = mg solute/(g solvent)(M).

Figure 1. Calibration for Cryoscopic Molecular Weight Determination



3. Vapor Pressure Osmometry

Tables 30 and 31 list the calibration readings for known samples of benzil in dichloromethane and benzene, respectively. Although the higher vapor pressure of dichloromethane gave more sensitive readings, drift, high noise, and changing calibration conditions made it less reproducible as Table 30 shows for calibration standards run on three different days. Table 32 compiles the calibration data as fitted to lines by the method of least squares. Figure 2 graphically represents this data. Calculations are described in Table 32. Table 33 lists the results for each sample run.

Iodometric titration.[58]

A standard solution of sodium thiosulfate (0.006-0.008M) was prepared and calibrated against potassium periodate as described in Ayres.[98] Samples of peroxides between 5-20 mg as indicated in Table 34 were dissolved in 10 ml dichloromethane and 10 ml 2-propanol. Solutions of peroxides became cloudy. Glacial acetic acid (1 ml) and 1 ml of a saturated, aqueous potassium iodide solution were added with appearances of a yellow color. Gentle warming followed by sodium thiosulfate titration yielded the results listed in Table 34. Sample run numerals indicate a specific peroxide preparation and

Table 30. Calibration for Molecular Weight Determination-Vapor Pressure Osmometry in Dichloromethane with Benzil

Day	Sample	M[a]	Average R[b]
1	1	0.0110	13.26±0.37
1	2	0.123	75.87±0.06
1	3	0.0476	30.30±0.22
1	4	0.0690	50.67±0.23
1	5	0.0812	43.39±0.06
2	1	0.0470	33.63±0.18
2	2	0.153	16.77±0.23
2	3	0.0641	43.80±0.24
2	4	0.0985	63.10±0.14
2	5	0.0281	24.64±0.19
3	1	0.192	113.1 ±0.10
3	2	0.0385	30.16±0.13
3	3	0.0865	56.57±0.24

[a] molarity

[b] R = readings taken at 2.0, 2.5, 3.0 and 3.5 minutes and averaged. Errors are standard deviations.

Table 31. Calibration for Molecular Weight Determination-Vapor Phase Osmometry in Benzene with Benzil

Sample	M[a]	R[b]
1	0.0385	16.34±0.01
2	0.0695	29.30
3	0.105	44.14±0.10
4	0.0121	5.72±0.12
5	0.0963	40.77

[a]molarity

[b]R= readings taken at 2.0, 2.5, 3.0 and 3.5 minutes and averaged. Errors are standard deviation.

Table 32. Calibration Constants for Vapor Phase Osmometry ($R = a_1C + b$)[a]

Solvent	a_1[b]	b[c]	r^2[d]
CH_2Cl_2 (day 1)	550.6	6.16	0.95
CH_2Cl_2 (day 2)	553.1	8.40	1.00
CH_2Cl_2 (day 3)	539.6	9.59	1.00
C_6H_6	416.32	0.49	1.00

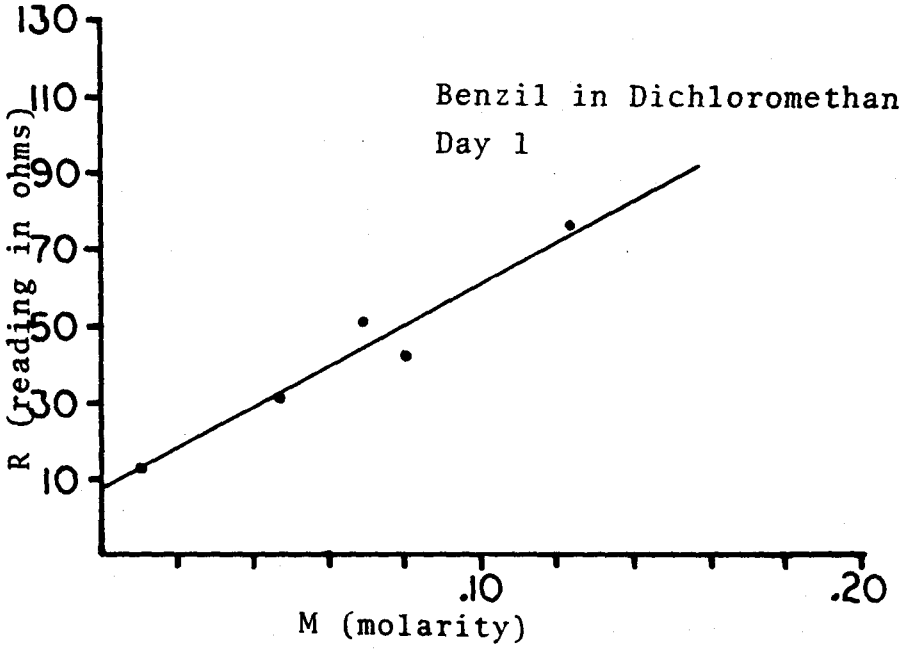
[a]determined by the method of least squares

[b]a_1 = slope plotting R(reading) versus C(concentration, M)

[c]b = intercept

[d]least squares fit

Figure 2. Calibration For Vapor Phase Osmometry



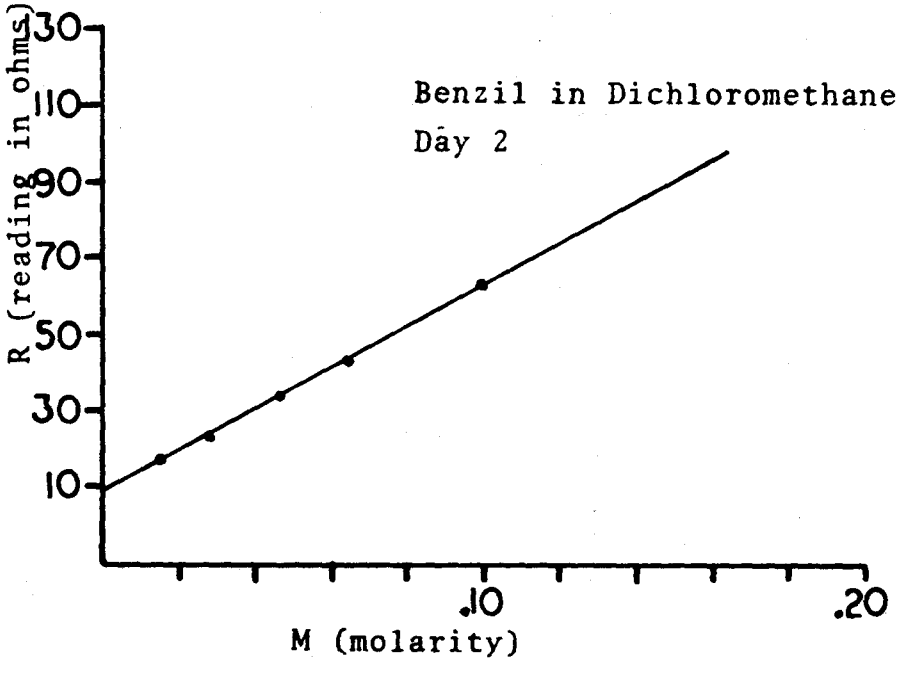
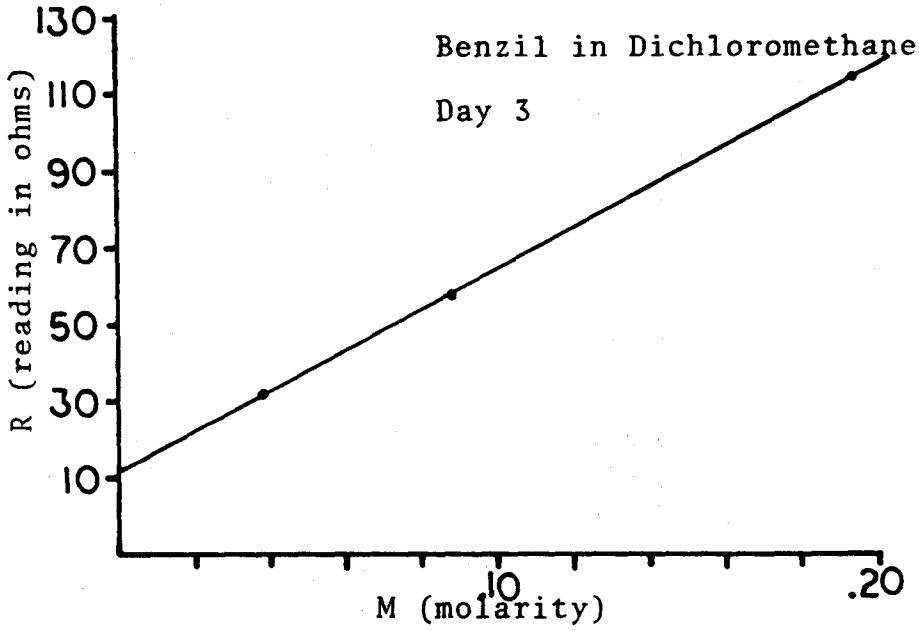


Figure 2.-continued.



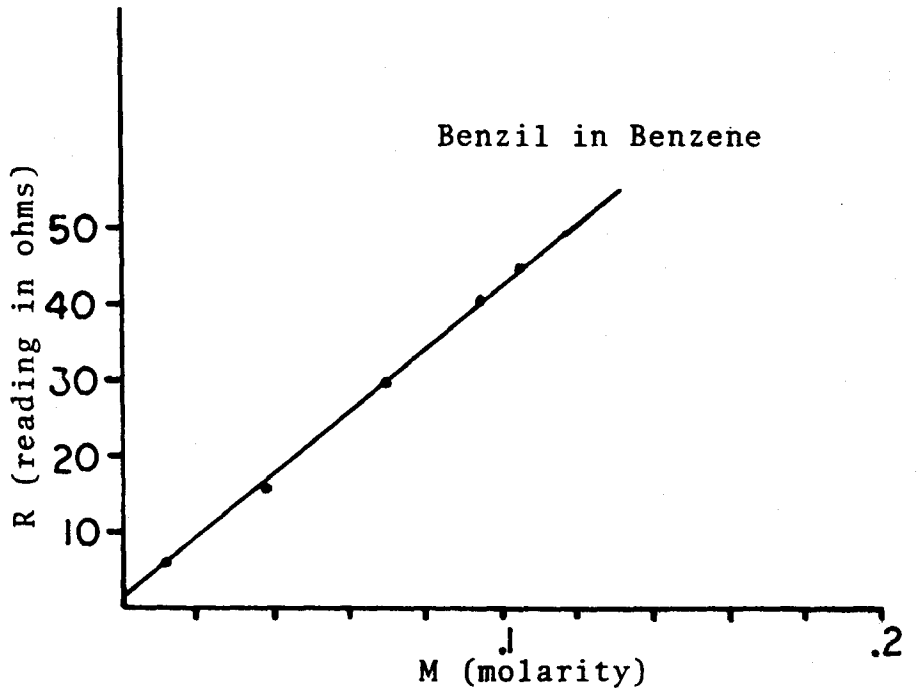


Table 33. Molecular Weight as Determined by Vapor Pressure Osmometry

Sample	Solvent	$\frac{\text{mg solute}}{\text{ml solvent}}$	R[a]	Molecular Weight (exptl)[b]	(calc)
Benzoyl peroxide	CH_2Cl_2	14.89	42.16±0.25	246.7	242
Benzoyl peroxide	CH_2Cl_2	8.75	28.67±0.33	247.5	242
Peroxide-(12)	CH_2Cl_2	8.86	26.78±0.06	278.1	240
Peroxide-(12)	CH_2Cl_2	13.84	37.86±0.10	264.2	240
p-Terphenyl	CH_2Cl_2	8.24	28.06±0.20	231.8	230
p-Terphenyl	CH_2Cl_2	12.28	36.47±0.38	242.0	230
trans-stilbene	CH_2Cl_2	10.95	40.76±0.20	187.1	180
trans-stilbene	CH_2Cl_2	27.72	91.62±0.17	184.2	180
trans-stilbene	CH_2Cl_2	14.10	51.97±0.23	179.9	180
Peroxide cis-(7)	CH_2Cl_2	19.50	15.77±0.46	1463	170
Peroxide trans-(8)	CH_2Cl_2	14.36	11.84±0.46	2309	170
Peroxide cis-(7)	C_6H_6	33.34	12.19±0.12	1186	170

Sample	Solvent	$\frac{\text{mg solute}}{\text{ml solvent}}$	R[a]	Molecular Weight (exptl)[b]	(calc)
Peroxide cis-(7)	C_6H_6	36.83	13.51±0.15	1178	170
Benzoyl peroxide	C_6H_6	13.71+ 3.3 mg n-hexane	22.85±0.66	317.0	181
Peroxide trans-(8)	C_6H_6	22.42	12.68±0.11	766	170
Peroxide cis-(7)	C_6H_6	23.75	14.37±0.16 12.57±0.09	1425 1637	170 170

[a] R = reading-ohms

[b] molecular weight (mw) = $(a_1/R-b)$ mg/ml, a_1 and b are constants calculated for solvent in Table 32.

Table 34. Iodometric Titrations of Peroxides (5)-(8)

Peroxide	Sample Run	mol weighed	mol titrated	Percent active O_2
Benzoyl Peroxide (commercial)	1a	0.0158	0.0160	101
	1b[a]	0.0580	0.263	45.3
	1c[b]	0.142	0.00792	5.6
	1d	0.0570	0.0560	98.2
	1e	0.0232	0.024	103
meso-(5)	2	0.0515	0.0380	73.7
dl-(6)	3	0.205	0.0999	48.7
cis-(7)	4a	0.0870	0.0683	78.5
	4b	0.567	0.0440	77.8
	5a	0.167	0.097	58.1
	5b	0.0714	0.0517	72.4
	6	0.122	0.0817	67.0
trans-(8)	7a	0.0837	0.0622	74.4
	7b	0.0618	0.0490	79.8
	7c	0.0467	0.0370	79.4
	8	0.0743	0.0419	56.4

[a]No 2-propanol added, dichloromethane only.

[b]50-50 two-phase mixture of dichloromethane and water.

lower case letters with the same numeral indicate repetitive titrations of the same sample.

3-Hydroxy-2-methyl Butanoic Acid, (44).

Following the procedure of Adam et al.,[39] 10 ml (0.286 mol) of diisopropylamine in 270 ml of dry THF were added to a dry, three-necked 1 l. flask fitted with a reflux condenser and argon inlet. A hexane solution of n-butyllithium (170.6 ml, 0.273 mol) was slowly syringed into the flask followed by 10.1g (0.137 mol) of propionic acid in 140 ml THF. After stirring for 1 hr, a solution of 6.0g (0.136 mol) of acetaldehyde in 50 ml THF was added. The white suspension was allowed to stir overnight then poured onto ice and extracted once with 250 ml of ether. The aqueous layer was then acidified with 6N hydrochloric acid and continuously extracted with ether for 8 hr. The ethereal solution was concentrated and the yellow oil distilled yielding 8.4g (54%) of (44): b.p. 90-100°C (0.2 mm); ir ($CDCl_3$) 3500-2500 (CO_2H, OH) and 1710 cm^{-1} (C=O); nmr ($CDCl_3$) δ7.70 (s, 2, $CO_2\underline{H}$, $\underline{OH}$), 4.05 (m, 1, $C\underline{H}$-OH), 2.50 (m, 1, $\underline{CH}$-CO_2H), 1.20 (m, 6, $\underline{CH_3}$).

erythro and threo-2,3-dimethylpropiolactones (18) and (19).

The hydroxy acid, (44), (1.0g, 1.0085 mol) was dissolved in 80 ml of dry ether and allowed to stir 24 hr in the presence of 10g sodium carbonate and benzenesul-

fonyl chloride. After filtering, the ether was removed by atmospheric distillation affording a yellow oil which was shown to contain both isomeric β-lactones by analytical vpc (PMPE, 80°C). Relative retention times of erythro-(18) and threo-(19) are 1.36 and 1.00, respectively. These were separated and collected (in small amounts) by preparative vpc (PMPE, 105°C). Yields determined by analytical vpc (PMPE, 90°C) for similar reactions using 0.25g, (44), 2.5g sodium carbonate and 0.66 ml (0.0086 mol) methane sulfonyl chloride, 1 ml (0.0086 mol) benzenesulfonyl chloride or 1.63g (0.0086 mol) of toluene sulfonyl chloride are shown in Table 35. Spectra for each isomer are reported below: erythro-2,3-dimethylpropiolactone (18): ir ($CDCl_3$) 1820 cm^{-1} (C=O); nmr ($CDCl_3$) δ 4.35 (d of q, 1, J = 6.0Hz, 7.5Hz, CH_3 CH-O), 3.20 (d of q, 1, J = 7.5Hz, CH_3CH-COO), 1.60 (d, 3, J = 6.0Hz, CH_3-CHO), and 1.45 (d, 3, J = 7.5Hz, CH_3-CHCO), exact mass (15 ev) m/e calcd. for $C_5H_8O_2$: 100.052; obsd. 100.051. threo-2,3-dimethylpropiolactone (19): ir ($CDCl_3$) 1820 cm^{-1} (C=O); nmr ($CDCl_3$) δ 4.75 (m, 1, CH-OCO), 3.75 (m, 1, CH-CO), 1.40 (d, 3, J = 6.0Hz, CH_3-CHO) and 1.22 (d, 3, J = 7.5Hz, CH_3-CHCO), exact mass (15 ev) m/e calcd. for $C_5H_8O_2$: 100.052; obsd. 100.052.

Table 35. Percent Yield and Ratio of erythro- and threo-2,3-Dimethylpropiolactones (18) and (19) from Synthesis

	Benzenesulfonyl Chloride	Methanesulfonyl Chloride	Toluenesulfonyl Chloride
24h/yield	3%	3%	0.7%
threo/erythro	6	1	6
72h/yield	3%	3%	4%
threo/erytho	8	0.6	1

Note: Quantities of the β-lactones (18) and (19) were in general too small to handle or weigh. Thus, the following experiments were conducted with isomerically pure (> 98%) material obtained by preparative vpc (PMPE-glass, 105°C). n-Octane was stored over solid sodium carbonate.

Decomposition of erythro- and threo-Dimethylpropiolactones in n-Octane.

The first eluant (RRT=1.00) from a 100 μl shot of the mixtures of β-lactones (PMPE-glass, 105°C) was taken up in 100 μl of n-octane, sealed in vacuo in a base washed, 6 mm, O.D. Pyrex tube, and heated to 171°C for 229 min. Analysis by analytical vpc (DBT, 25°C) showed trans-2-butene (99.7%) and cis-2-butene (0.3%) as the only volatile reaction products.

The second eluant (RRT = 1.36) was similarly collected and pyrolyzed, to yield cis-2-butene (98.7%) and trans-2-butene (1.3%) as determined by analytical vpc (DBT, 25°C).

Determination of vpc Response Factors of erythro- and threo-2,3-Dimethylpropiolactones to 2-Butene.

threo-2,3-Dimethylpropiolactone (19) was preparatively collected into 400 μl of C_6D_6 containing unknown amount of naphthalene. The nmr spectrum showed 2.05 mol of β-lactone to 1 mol of naphthalene. Electronic integration on vpc showed a response of 0.567 counts for β-lactone to 1 count naphthalene. Pyrolysis of this nmr sample for 543 min at 171°C provided 0.95 mol of trans-2-

butene to 1 mol naphthalene as determined by nmr. VPC analysis gave upon electronic integration 0.349 counts of trans-2-butene to 1 count of naphthalene. This calculates to a molar response factor of 0.752 counts/mol β-lactone to 1 count/mol 2-butene.

Thermal Decomposition of erythro- and threo-2,3-Dimethylpropiolactones (18) and (19) at 100°C.

Samples of isomerically pure β-lactones (18) and (19) were preparatively collected (PMPE, 105°C) into 100 μl of n-octane with dodecane as internal standard. Analytical vpc analysis (PMPE, 80°C) showed no disappearance of starting material nor appearance of 2-butene after pyrolysis in a sealed 6 mm O.D. base washed tube at 100°C for 4 min.

Reaction of β-lactones (18) and (19) with Acetic Acid.

β-lactones (18) and (19) were preparatively collected (PMPE-glass, 105°C) into separate 200 μl samples of n-octane. Glacial acetic acid (1 μl) was added to each. As determined by analytical vpc (PMPE, 80°C), no detectable decomposition occurred in the first 3 hr. However, after 15 hr, 92% erythro-(18) and 91% threo-(19) remained.

No isomerization of either lactone was detected.

Reaction of β-lactones (18) and (19) with Hydrochloric Acid.

β-lactones (18) and (19) were preparatively collected (PMPE, 105°C) into separate 200 μl samples of n-octane. Concentrated HCl (2 μl) was added to each. Analytical vpc (PMPE, 80°C) showed that after 5 min 70% erythro-(18) remained, after 90 min 35% threo-(19) remained and after 210 min 17% threo-(19) remained. No isomerization of either β-lactone was detected.

cis- and trans-ethyl-2-hydroxycyclohexane carboxylates, (49) and (50).

Ethyl-2-ketocyclohexylcarboxylate was prepared as previously described[74] from cyclohexanone and diethylglyoxlate in 43% overall yield: nmr ($CDCl_3$) δ 4.23 (q, 2, $-OC\underline{H}_2CH_3$), 3.38 (t, 1, $-C\underline{H}-CO_2Et$), 2.21 (m, 2, $-C\underline{H}_2CO-$), 2.21 (m, 2, $C\underline{H}_2-CCHCO$), 1.65 (m, 4, CH_2CH_2) and 1.39 ppm (t, 3, $OCH_2C\underline{H}_3$). The keto ester (17.0g, 0.1 mol) was placed in 250 ml methanol and cooled to 0°C. Sodium borohydride (2.0g, 0.05 mol) was added dropwise with stirring. After the vigorous foaming subsided, the reaction mixture was allowed to warm to room temperature and stirred for 11-12 hr, then acidified with 1N HCl. The methanol and water were removed under reduced pressure affording a yellow oil and white solid which were taken up into ether, washed with saturated aqueous sodium chloride, dried ($MgSO_4$) and concentrated.

Analysis by analytical vpc (Carbowax 200°C) revealed two product peaks in 73-27 ratio, relative retention times 1.00 and 1.32, identified (see below and Results and Discussion) as the cis- and trans-isomers, (49) and (50), respectively. Preparative vpc (Carbowax, 200°C) yielded analytical samples. cis-(49): ir ($CHCl_3$) 3600-3400 (OH) and 1705 cm^{-1} (C=O); nmr ($CDCl_3$) δ 4.18 (q, 2, $-OCH_2CH_3$), 4.10 (m, 1, HC-OH), 3.2 (s, 1, -OH), 2.5 (m, 1, $HC-CO_2Et$), 2.0-10.0 (m, 8, CH_2) and 1.25 ppm (t, 3, OCH_2CH_3); trans-(50): ir ($CHCl_3$) 3600-3350 (OH) and 1710 cm^{-1} (C=O); nmr ($CDCl_3$) δ 4.20 (q, 2, $-OCH_2CH_3$), 3.8 (m, 1, HC-OH), 3.0 (s, 1, -OH), 2.5-1.0 (m, 9, CH_2 and $CH-CO_2Et$), and 1.3 ppm (t, 3, OCH_2CH_3)

cis- and trans-2-hydroxycyclohexane carboxylic acids, (47) and (48). Hydrolysis of Hydroxyesters cis-(49) and trans-(50).

The isomeric mixture of hydroxy esters (49) and (50) (1.5g, 0.009 mol) was dissolved in 10 ml of hot water containing 2.5g sodium hydroxide. After stirring 4 hr, 1g (78%) of diacid (49) and (50) was obtained as an oil which crystallized upon standing; ir ($CHCl_3$) 3500-2600 (-OH, CO_2H) and 1690 cm^{-1} (C=O); nmr ($CDCl_3$) δ 7.0 (s, 2, $-CO_2H$, -OH); 4.23 (m, 1, HC-OH), 2.6 (m, 1, $HC-CO_2H$), and 2.15-1.30 ppm (m, 8, CH_2).

cis- and trans-methyl-2-hydroxycyclohexanecarboxylates, (51) and (52).

The isomeric mixture of hydroxyacids, cis-(47) (73%) and trans-(48) (27%) prepared as described above (1.0g, 0.007 mol) was treated with a saturated ethereal solution of diazomethane to yield a mixture of cis- and trans-methyl-2-hydroxy carboxylates (51) (71%) and (52) (29%). Analytical samples of each isomer were preparatively collected by vpc (Carbowax, 180°C). Relative retention times of cis-(51) and trans-(52) were 1.00 and 1.30, respectively. cis-(51): nmr ($CDCl_3$) δ 4.18 (m, 1, H-COH), 3.7 (s, 3, OCH_3), 3.2 (s, 1, -OH), 2.4 (m, 1, $CH-CO_2CH_3$), 2.0-1.2 (m, 8, CH_2). trans-(52): nmr ($CDCl_3$) δ 3.7 (s, 3, OCH_3), 3.7 (m, 1, HC-OH), 3.05 (s, 1, OH), and 2.5-1.0 ppm (m , 9, CH_2 and $CH-CO_2CH_3$).

trans-2-Hydroxycyclohexanecarboxylic acid, (48). Hydrolysis of cis- and trans-ethyl-2-hydroxycyclohexane carboxylates (49) and (50).[77]

The isomeric mixture of the hydroxydiethyl esters, (49) and (50), (10g, 0.05 mol) was added to 100 ml of a 7.5 N KOH solution and refluxed 24 hr. After concentration and acidification with concentrated HCl, the solution was extracted into ether, dried ($MgSO_4$), and concentrated to an oil. Recrystallization from ethyl acetate-petroleum ether yielded an off white powder (5.4g 62%) (48):

m.p. 105°C (reported[77] 111°C). Treatment of 0.5g (0.003 mol) of this powder with a saturated ethereal solution of diazomethane and examination of the products by analytical vpc (Carbowax, 200°C) yielded the trans-methyl ester (52) containing 6% methyl ester (51).

cis- and trans-1,2-Hexahydrophthalolactones (45) and (46).

trans-2-hydroxycyclohexanecarboxylic acid (0.50g, 0.0035 mol) was dissolved (suspended) in 30 ml dry ether with 5.0g sodium carbonate. After stirring 2 hr at room temperature, 1 ml (1.48g, 0.013 mol) of methanesulfonyl chloride was added and stirring continued 35 hr. Filtration and concentration afforded a yellow oil: ir (neat) 1815 (C=O, β-lactone) and 1730 cm^{-1} (C=O, unidentified). Distillation did not separate the two (or more) substances. Analytical vpc analysis (PMPE, 150°C) showed more than three irregular and tailing peaks. Attempted preparative collection by vpc (PMPE, 150°C; UCON, 150°C) of a portion of the eluting material and distillation (room temperature, 10^{-4} mm) provided unchanged infrared spectra. This procedure gave similar results from cis-(47) (76% cis) or trans-(48) (94% trans).

Thermal Decomposition of Peroxides meso-(5) and dl-(6) in Dichloromethane and Tetrahydrofuran.

Stock solutions of peroxides meso-(5) and dl-(6) were each prepared in dichlormethane and THF at 0.001-

0.006M or 0.1-0.2M as indicated in Tables 36-38. 2-Methylbutane was weighed and added to all stock solutions. Dodecane was weighed and added to those samples subjected to analysis for β-lactones (18) and (19) (dichloromethane samples only, 0.1-0.2M). All pyrolyses were conducted upon measured (100 μl) samples in degassed, sealed (in vacuo) base and EDTA washed 6 mm O.D. Pyrex tubes. Where indicated, 20-30 mg solid sodium carbonate was added to sample prior to pyrolysis.

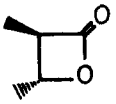
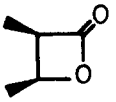
1. Solution Pyrolyses at 92°C.

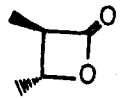
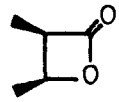
Sample tubes were immersed in a silicon oil bath at 92±3°C for 4 min. The samples were frozen (77°K), opened and distilled at room temperature on a vacuum line. Ratios and yields of 2-butenes were determined by analytical vpc (DBT, 25°C). Relative retention times of trans-2-butene, cis-2-butene, and 2-methylbutane are 1.00, 1.10, and 1.30, respectively. Ratios and yields of β-lactones erythro-(18) and threo-(19) were determined by analytical vpc (PMPE, 90°C). Relative retention times of erythro-(18), threo-(19), and dodecane are 1.00, 1.52, and 1.92, respectively. Table 36 lists each run for ratios and yields of 2-butenes. Table 37 lists each run for ratios of 2-butene and β-lactones (18) and (19).

Table 36. Ratios and Yields of 2-Butene from Thermal Decomposition of meso-(5) and dl-(6) at 92°C.

Sample	Solvent	Molarity			Yield %
meso-(5)	THF	0.006	66.89	33.11	48.6
meso-(5)	THF	0.006	69.39	30.61	53.7
meso-(5)	THF	0.001	72.30	27.70	74.8
meso-(5)	CH_2Cl_2	0.006	67.33	32.67	76.1
meso-(5)	CH_2Cl_2	0.006	68.86	31.14	75.0
meso-(5)	CH_2Cl_2	0.002	70.65	29.35	90.8
meso-(5)	CH_2Cl_2	0.002	70.16	29.84	89.7
dl-(6)	THF	0.005	69.54	30.46	31.2
dl-(6)	THF	0.005	69.54	30.45	27.8
dl-(6)	THF	0.003	70.00	30.00	33.7
dl-(6)	THF	0.003	72.73	27.27	13.6
dl-(6)	THF	0.003	68.64	31.36	34.8
dl-(6)	CH_2Cl_2	0.006	67.23	32.77	46.1
dl-(6)	CH_2Cl_2	0.006	66.61	33.39	38.8
dl-(6)	CH_2Cl_2	0.004	68.06	31.94	40.6
dl-(6)	CH_2Cl_2	0.004	67.31	32.69	21.3

Table 37. Ratios of 2-butenes and β-lactones erythro-(18) and threo-(19). Thermal Decomposition of meso-(5) and dl-(6) in Dichloromethane at 92°C

Sample	Molarity				
meso-(5)	0.15	64.1	27.7	6.29	1.89
meso-(5)	0.15	63.5	27.5	6.90	2.17
meso-(5)	0.15	62.6	27.1	7.57	2.71
meso-(5)†	0.15	59.3	29.2	8.34	3.14
meso-(5)†	0.15	57.6	28.4	9.97	3.98
meso-(5)†	0.15	57.3	28.2	10.2	4.33
meso-(5)	0.17	61.8	28.0	6.43	3.77
meso-(5)	0.17	59.0	29.8	6.99	4.15
meso-(5)	0.17	60.2	27.2	7.50	5.05
meso-(5)†	0.17	62.3	28.4	6.32	3.04
meso-(5)†	0.17	62.2	28.3	6.91	2.60
meso-(5)†	0.17	61.9	28.2	7.31	2.62
dl-(6)	0.20	58.6	28.8	10.6	1.99
dl-(6)	0.20	59.4	29.2	9.48	1.94
dl-(6)	0.20	58.4	28.8	10.5	2.25
dl-(6)	0.17	65.0	25.0	8.79	1.17
dl-(6)	0.17	63.9	25.3	9.10	1.71
dl-(6)†	0.17	59.6	26.3	12.01	2.14
dl-(6)	0.06	60.3	27.6	9.40	2.67

Sample	Molarity				
d1-(6)	0.06	58.3	26.7	11.6	3.42
d1-(6)	0.06	59.1	27.0	11.9	2.00
d1-(6)†	0.06	61.4	30.0	7.04	1.54
d1-(6)†	0.06	59.1	28.9	9.17	2.81
d1-(6)†	0.06	58.6	28.6	9.85	2.94

†Solid sodium carbonate added

Table 38. Gas Flow Pyrolyses of Peroxides meso-(5) and dl-(6) at 278°C and 351°C

Sample	Temp	Solvent	Molarity			Yield %
meso-(5)	278	THF	0.006	66.98	33.02	47.8
meso-(5)	278	THF	0.001	72.57	27.43	47.8
meso-(5)	278	CH_2Cl_2	0.006	65.62	34.38	79.0
meso-(5)	278	CH_2Cl_2	0.002	69.44	30.56	66.0
meso-(5)	278	THF	0.001	68.86	31.14	39.0
meso-(5)	278	THF	0.006	68.02	31.98	37.6
meso-(5)	278	THF	0.006	66.78	33.22	42.9
dl-(6)	278	THF	0.005	60.76	39.24	18.9
dl-(6)	278	THF	0.003	62.93	37.07	27.2
dl-(6)	278	CH_2Cl_2	0.006	59.74	40.26	38.0
dl-(6)	278	CH_2Cl_2	0.004	60.46	39.54	17.9
meso-(5)	359	THF	0.001	65.14	34.86	44.4
meso-(5)	359	CH_2Cl_2	0.006	60.50	39.50	100.
meso-(5)	359	CH_2Cl_2	0.002	65.44	34.56	69.0
meso-(5)	359	THF	0.006	64.99	35.51	47.2
meso-(5)	359	THF	0.006	64.19	35.81	59.6
meso-(5)	359	THF	0.006	59.66	40.34	59.4
meso-(5)	359	THF	0.006	59.14	40.86	61.9
dl-(6)	357	THF	0.005	62.64	37.36	29.3

Sample	Temp	Solvent	Molarity			Yield %
dl-(6)	357	THF	0.003	66.22	33.78	29.4
dl-(6)	357	THF	0.003	63.27	36.73	36.7
dl-(6)	357	CH_2Cl_2	0.006	60.38	39.62	51.4
dl-(6)	357	CH_2Cl_2	0.004	63.54	36.46	40.4
dl-(6)	357	CH_2Cl_2	0.004	57.04	42.96	32.9

2. Thermal Decomposition of meso-(5) and dl-(6) at 278°C and 359°C in Gas Flow Chamber.

Aliquots (8-10 μl) of stock samples meso-(5) and dl-(6) were injected into an evacuated heated oven (200 cm^3) for 5 sec, then collected into a liquid nitrogen cold trap. Table 38 lists the 2-butene ratios from each run.

Thermal Decomposition of Peroxides cis-(7) and trans-(8) in Dichloromethane.

Stock solutions of cis-(7) (0.005M) and trans-(8) (0.004M) were prepared with n-heptane weighed and added as internal standard. Aliquots (100 μl) were prepared in sample tubes as previously described for peroxides (5) and (6), and immersed in a silicon oil bath at 98±3°C. VPC analysis (DBT, 60°C), of the distilled samples showed a 27% yield of cyclohexene from (7) and 32% yield from (8). Relative retention times of n-heptane and cyclohexene are 1.00 and 1.22, respectively.

Infrared spectral analysis of the undistilled samples revealed no sign of starting material but considerable irregular absorption between 1800-1700 cm^{-1}. These absorptions were not present in the starting material.

Kinetics of the Thermal Decomposition of Peroxides (5)-(8).

1. Thermal Decomposition of Peroxides (5) and (6): Appearance of 2-Butenes.

Sample tubes prepared as described above (0.001-0.006M) were immersed in a Formabath at 46.9±0.1°C for indicated time periods. Timing was controlled with an electronic timer (± 0.05 min). Reaction samples were immediately cooled to 77°K, opened and distilled. Yields and ratios determined by analytical vpc (DBT, 25°C) of 2-butene products with respect to the time appear in Table 39a. Each experimental run performed is listed. Corresponding plot of the rate data appear in Figure 3.

2. Thermal Decomposition of Peroxides (5)-(8): Disappearance of Peroxides (5)-(8).

Samples of peroxides (5)-(8) (∿ 0.1M) were immersed in a Formabath at 48.5±1°C and heated for indicated time periods. Disappearance of peroxide was measured by infrared at 1775 cm^{-1} in 0.1 mm matched solution cells. Table 39b lists the results. Corresponding plots of the rate data appear in Figure 4. A summary of the rate constants obtained by the method of least squares appears in Table 10.

Table 39a. Appearance of 2-Butene[†] from Pyrolysis of Peroxides meso-(5) and dl-(6) at 46.9°C.

Run

1 meso-(5) THF 0.006M

Time (sec)	60	120	180	240	300	360	420	480	540	600	1200
% 2-Butene	11	14	35	36	40	42	54	39	48	51	70
Ratio	66	68	67	70	69	71	71	68	69	70	69
trans/cis	34	32	33	30	31	29	29	32	31	30	31

2 meso-(5) THF 0.001M

Time (sec)	0	300	600	1200	1200	1800
% 2-Butene	1	11	26	42	43	32
Ratio	--	75	73	73	73	72
trans/cis	--	25	27	27	27	28

Run

3 meso-(5) THF 0.001M

Time (sec)	0	300	600	1200	1800
% 2-Butene	1	7	21	33	36
Ratio trans/cis	--	76	73	73	72
	--	24	27	27	28

4 meso-(5) THF 0.001M

Time (sec)	300	600	1800
% 2-Butene	6	19	34
Ratio trans/cis	70	73	72
	30	27	28

5 dl-(6) THF 0.006M

Time (sec)	120	240	300	300	480	480	600	720	720	900
% 2-Butene	9	17	15	17	23	18	25	26	25	28
Ratio trans/cis	81	73	72	73	72	73	70	73	73	72
	19	27	28	28	28	27	30	27	27	28

Run

6 d1-(6) THF 0.006M

Time (sec)	0	120	180	240	300	360	420	1200
% 2-Butene	3	14	16	15	22	17	20	26
Ratio trans/cis	67/33	64/36	64/36	66/34	66/34	66/34	66/34	66/34

7 d1-(6) CH_2Cl_2 0.006M

Time (sec)	0	180	180	360	540	540	720	720	900	900	1080	1080	1140
% 2-Butene	2	15	17	25	26	32	26	29	32	24	18	21	15
Ratio trans/cis	68/32	69/31	69/31	69/31	69/31	71/29	69/31	67/33	70/30	70/30	68/32	70/30	74/26

[†]determined by analytical vpc (DBT, 25°C).

Table 39b. Disappearance of Carbonyl Stretching Frequency (at 1775 cm^{-1}) from Pyrolysis of Peroxides (5)-(8) at 48.5°C.

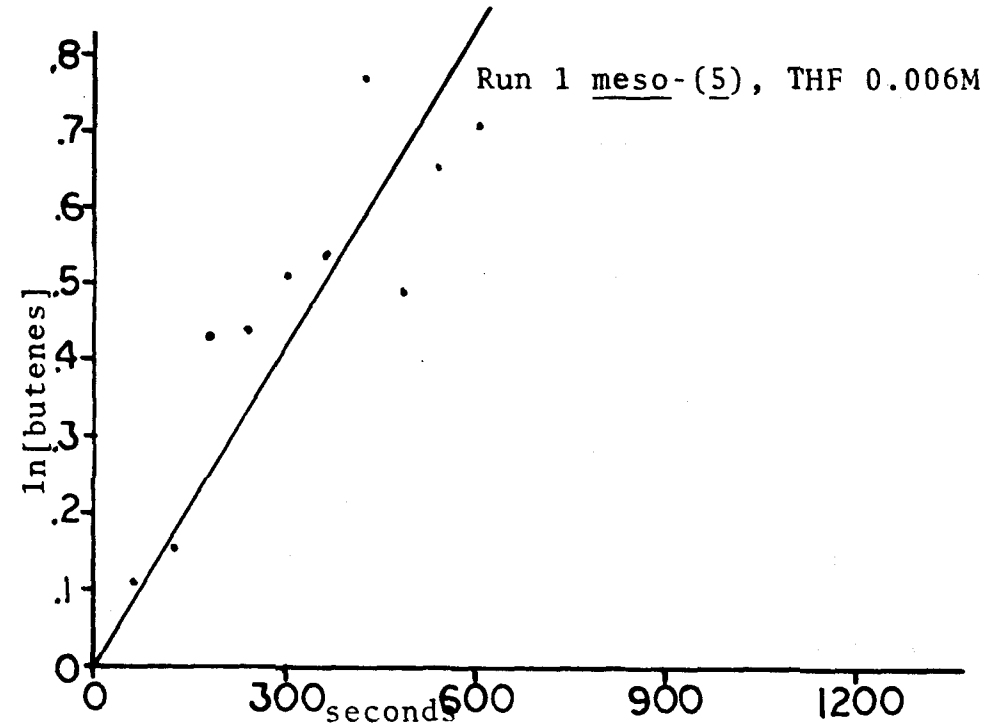
Run									
8	meso-(5) 0.1M CH_2Cl_2								
Time (sec)	0	300	480	600	720	900	1200		
% remaining†	100	88	81	77	64	63	60		
9	dl-(6) 0.1M CH_2Cl_2								
Time (sec)	0	180	300	480	600	840			
% remaining†	100	91	95	91	88	86			
10	cis-(7) 0.1M CH_2Cl_2								
Time (sec)	0	180	300	480	600	720	900	1200	1500
% remaining†	100	98	80	76	76	70	66	64	58

11 trans-(8) 0.1M CH_2Cl_2

Time (sec)	0	180	300	540	600	900	1020	1380	1740
% remaining†	100	88	81	72	75	64	60	56	49

†followed by infrared at ∿ 1775 cm^{-1}

Figure 3. Kinetics: Appearance of 2-Butenes



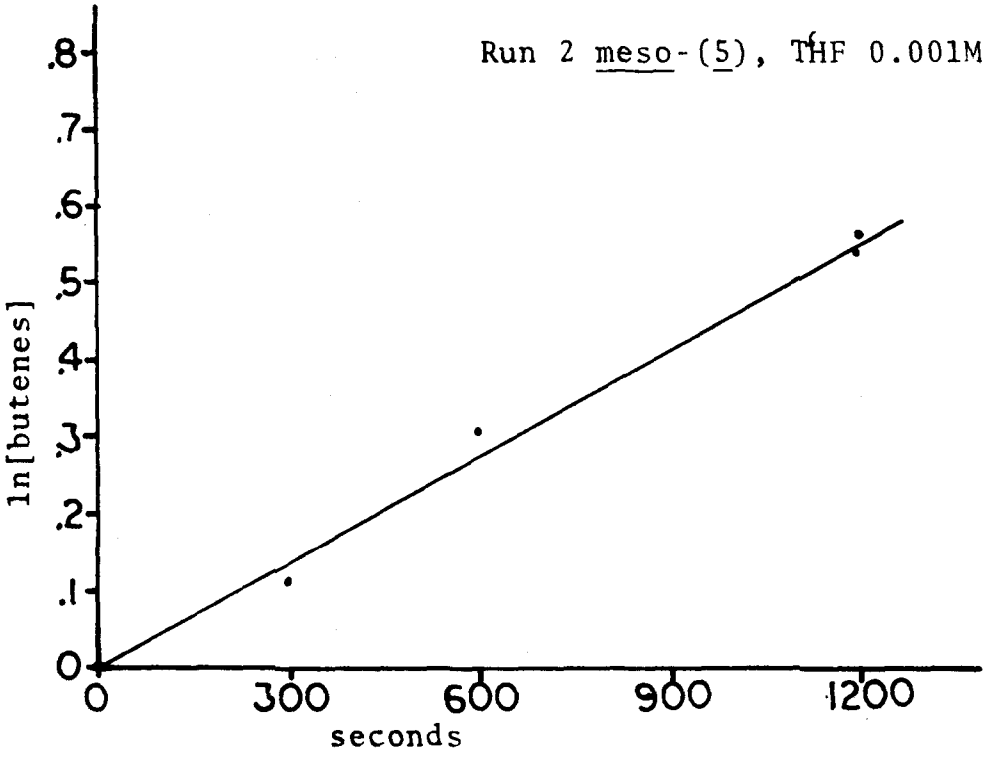
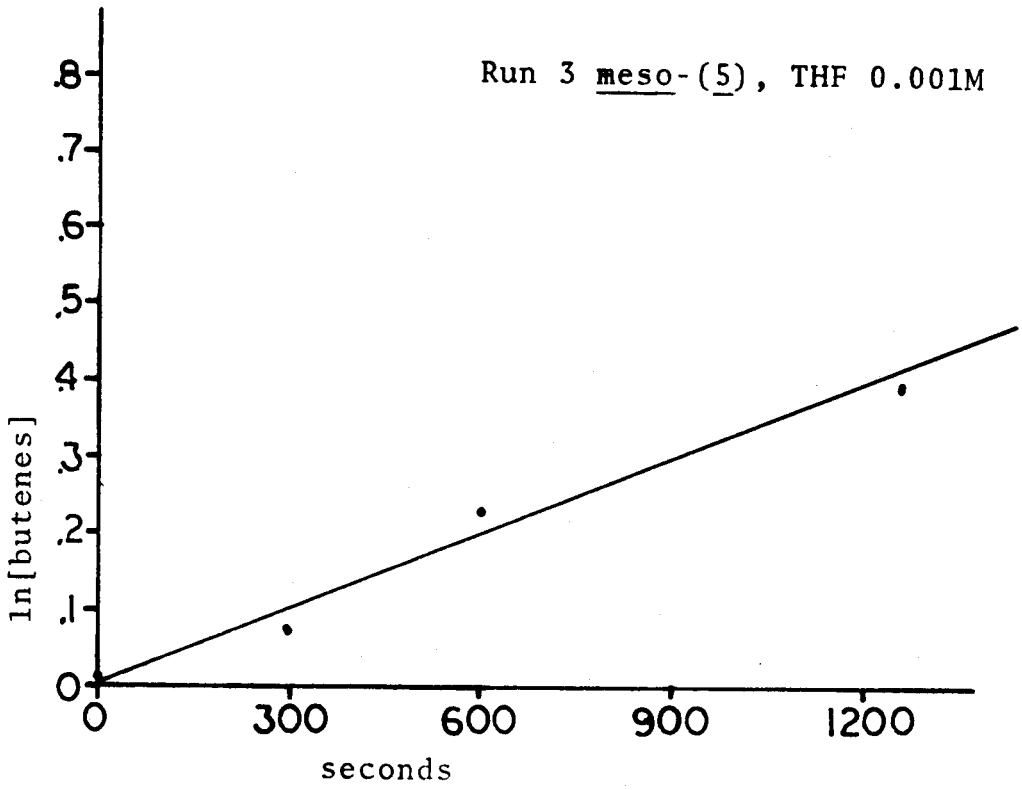


Figure 3.-continued



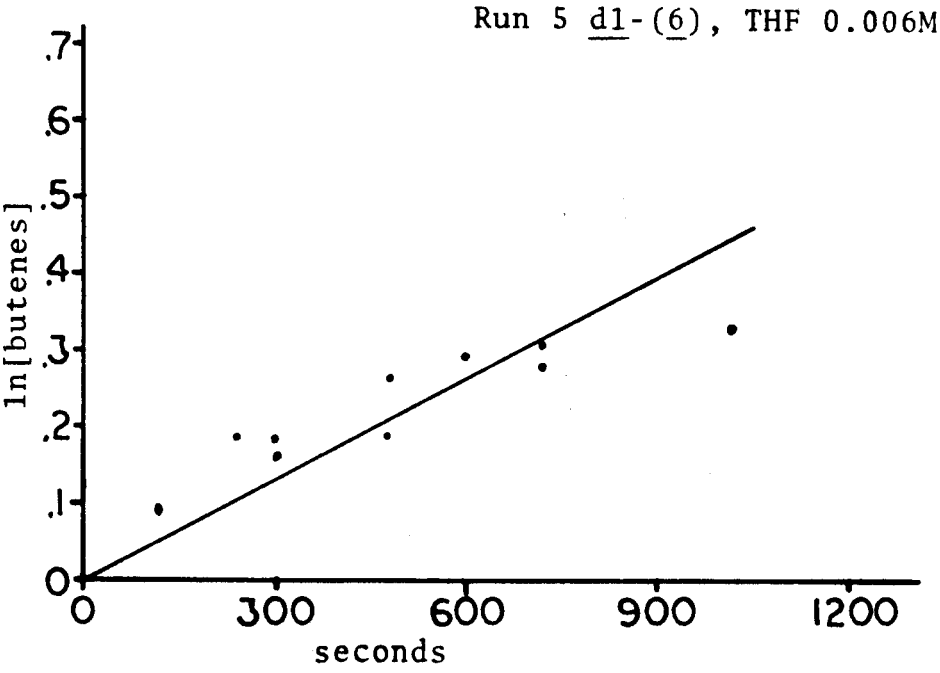
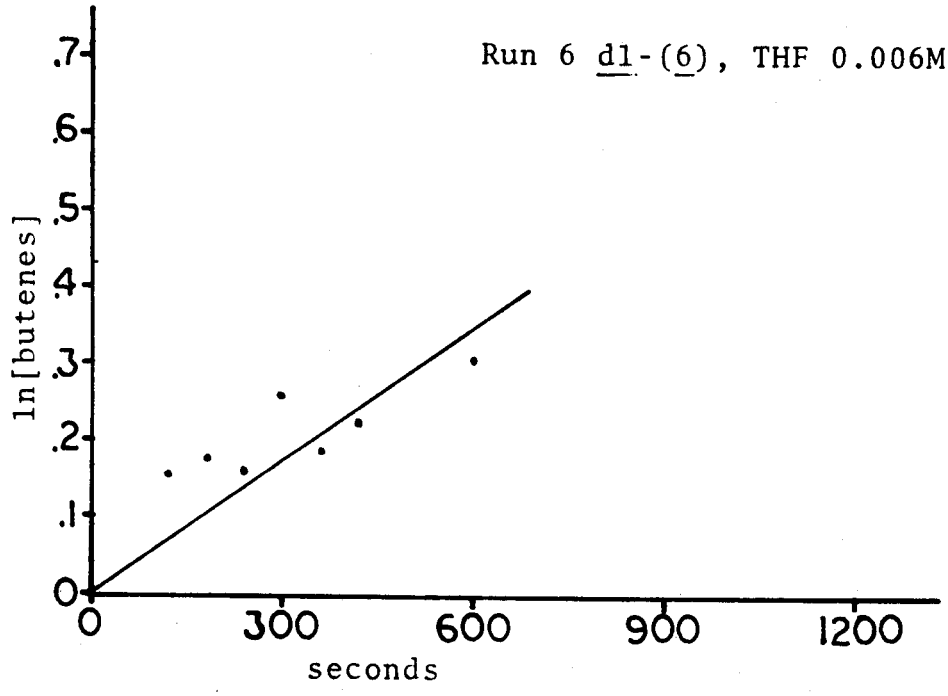


Figure 3.-continued



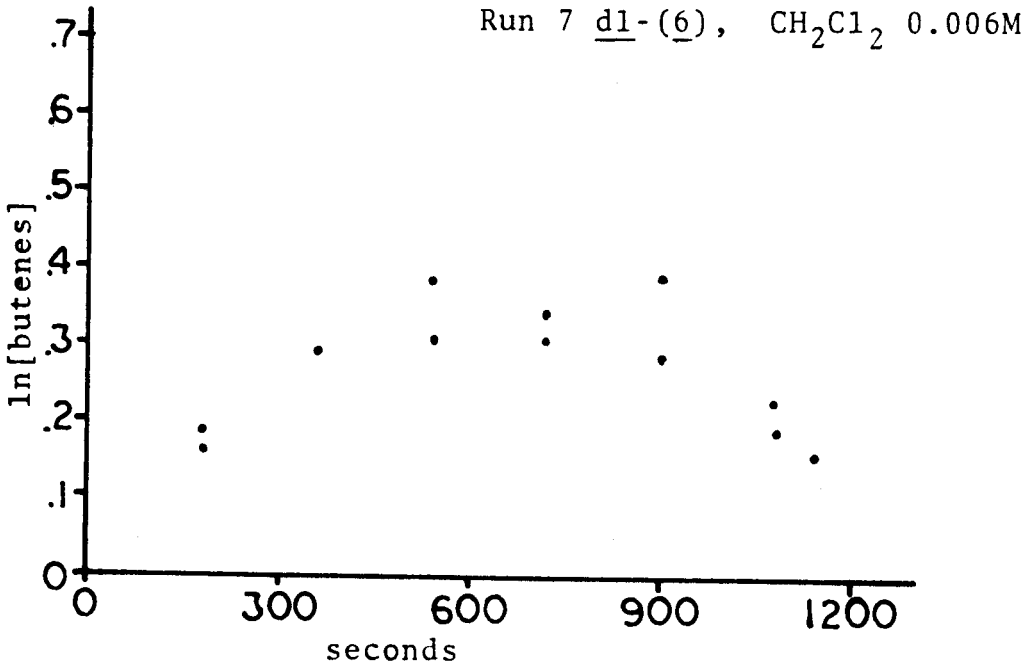


Figure 4. Kinetics: Disappearance of Peroxides

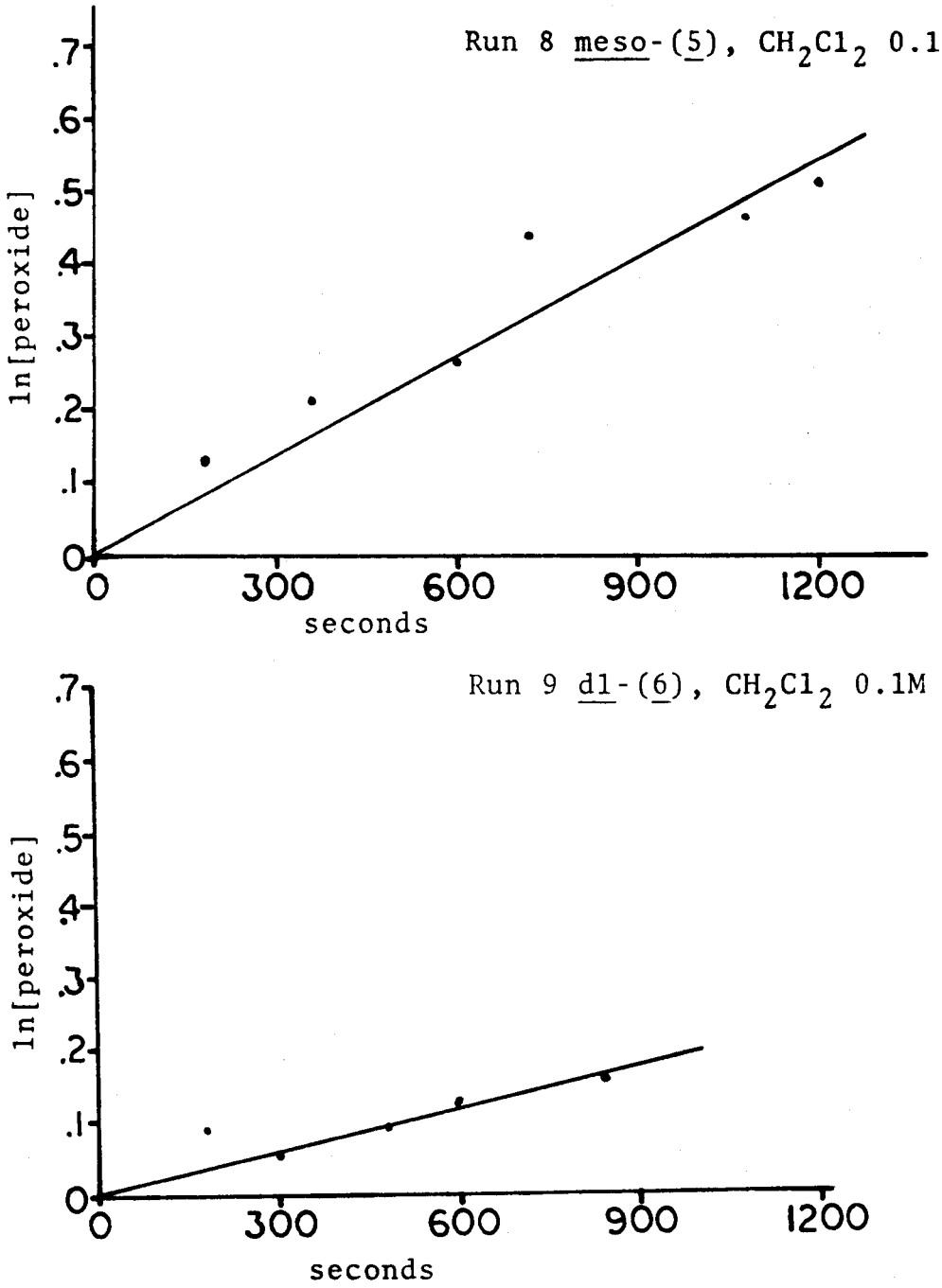
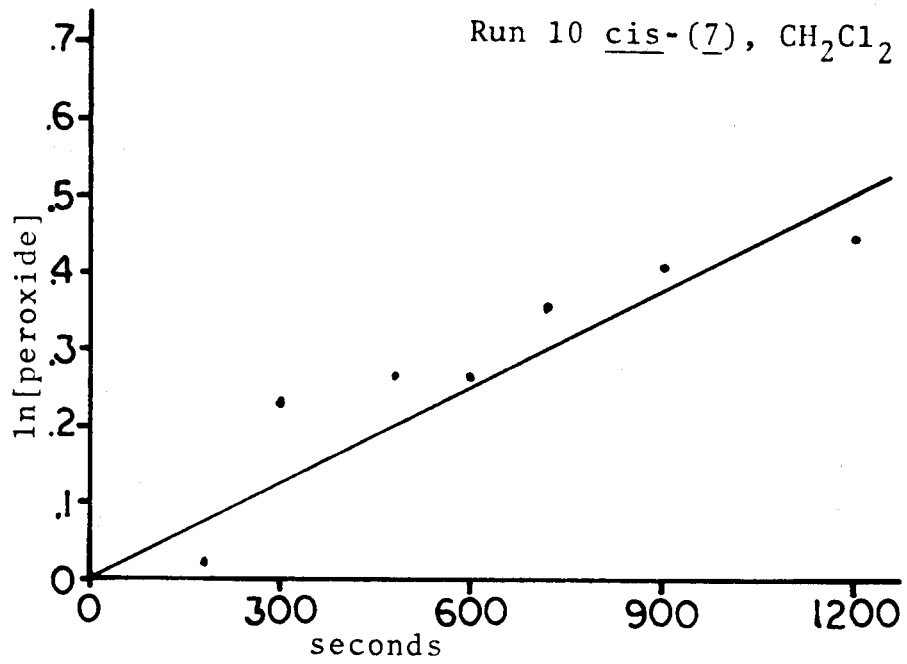
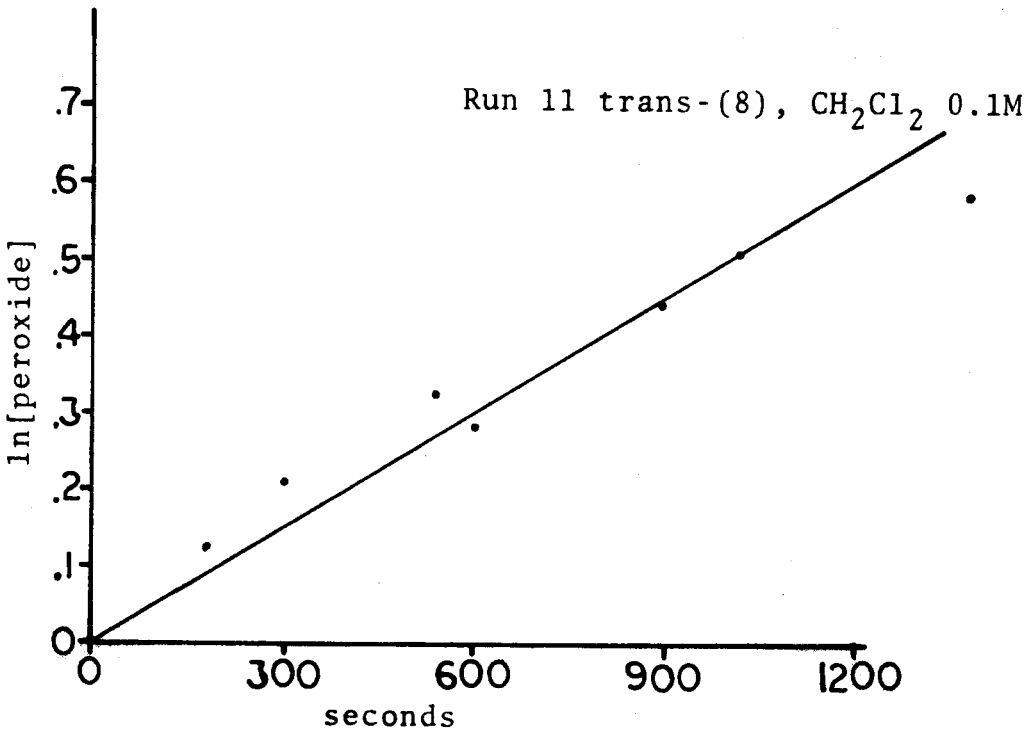


Figure 4.-continued





Methoxycyclohexane, (55).

Into a 250 ml three-necked round bottom flask containing 200 ml of dry THF and 10.0g (0.1 mol) of cyclohexanol cooled to 0°C was added 7.18g (0.15 mol) of sodium hydride as a 50% oil dispersion. After turning gray-white, 56.6g (0.4 mol) of methyl iodide was slowly added at room temperature. When addition was complete, the mixture was refluxed 24 hr, then poured onto ice and extracted with ether. The ether was removed by distillation. The remaining methyl iodide and THF were trap to trap distilled with the product and unreacted starting material. A pure sample was collected by preparative vpc (SE-30, 120°C): ir (neat) 1105 cm^{-1} (C=O); nmr ($CDCl_3$) δ 3.3 (s, 3, -O$\underline{CH_3}$), 3.1 (m, 1, $\underline{CH}$-O), 2.0-1.0 ppm (m, 10H, ring CH_2's) mass spectrum (75 ev) m/e (rel. intensity) 115 (1), 114 (19), 113 (6), 86 (1), 85 (10), 84 (3), 83 (3), 82 (14), 81 (2), 79 (1), 72 (6), 71 (100), 67 (6), 59 (1), 58 (16), 57 (1), 56 (1), 55 (8), 54 (4), 53 (3).

Methoxycyclohexane-d_1, (55)-d_1.

2-Deutero-1-cyclohexanol (from D. Santilli) was treated as described above to give 2-deutero-1-methoxycyclohexane: mass spectrum (75 ev) m/e (rel. intensity) 116 (2), 115 (22), 114 (1), 87 (1), 86 (8), 85 (6), 84 (3), 83 (17), 82 (3), 80 (1), 73 (3), 72 (39), 71 (100),

68 (5), 67 (3), 59 (8), 58 (11), 57 (9), 56 (6), 55 (7), 54 (3), 53 (2).

(55)-d_0 (8.10 mg) and (55)-d_1 (3.00 mg) were mixed and mass spectrum examined: (complete spectrum not listed) (75 ev) m/e (rel. intensity) 115 (42), 114 (100), 113 (2),

(55)-d_0 (4.20 mg) and (55)-d_1 (9.03 mg) were mixed and mass spectrum examined: (75 ev) m/e (rel. intensity) 115 (100), 114 (45), 113 (2).

3-Methoxycyclohexene, (56).

After rinsing 1g (0.02 mol) of a 50% oil dispersion of sodium hydride with benzene and drying with a flow of argon gas, 50 ml of anhydrous THF was added followed by dropwise addition of 2-cyclohexene-1-ol at room temperature. After the mixture turned gray-white and hydrogen evolution ceased, 2.5 ml (0.04 mol) methyl iodide was added and the mixture refluxed for 2 hr. It was then poured onto ice and extracted into ether. The ether was removed by atmospheric distillation. The remaining methyl iodide and THF were distilled along with the product. Pure (56) was isolated by preparative vpc (SE-30, 150°C): ir (neat) 3010 (=C-H), 1645 (C=C) and 1100 cm^{-1} (C-O); nmr ($CDCl_3$) δ 6.8 (m, 2, H-C=C-H), 3.65 (m, 1, CH-O), 3.3 (s, 3, OCH_3), 2.1-1.7 ppm (m, 6, ring CH_2's); mass spectrum (75 ev) m/e (rel. intensity) 113 (4), 112 (76), 111 (41), 97 (40), 85 (6), 84 (100), 83 (8), 81 (41),

80 (29), 79 (63), 78 (8), 77 (22), 71 (9), 69 (32), 67 (9), 58 (9), 53 (10), 54 (16), 53 (20), 52 (8), 51 (11), 50 (6).

2-Methoxycyclohexene (57).

2-Methoxycyclohexene (57) was purchased from Chemical Samples Co., mass spectrum (75 ev): m/e (rel. intensity) 113 (6), 112 (77), 111 (61), 97 (52), 84 (100), 83 (16), 81 (16), 79 (18), 77 (8), 69 (11), 67 (8), 55 (10), 54 (31), 53 (12), 51 (6).

Relative retention times of methoxycyclohexane (55), 3-methyoxycyclohexene (56), and 2-methoxycyclohexene (57) were 1.00, 1.49, and 2.15 (DBT, 90°C), 1.00, 1.09, and 1.32 (SE-30, 90°C), and 1.00, 1.36, and not located (UCON, 80°C) respectively. 2-Methoxycyclohexene (57) tailed very badly on two vpc columns (DBT, SE-30, 90°C).

2-Methoxybutane (58).

To 3.3g (0.069 mol) of sodium hydride in a 50% oil dispersion in 30 ml ether was added 5.0g (0.068 mol) of 2-butanol over 1 hr at room temperature. The light brown mixture was allowed to reflux 1 hr after which 10g of methyl iodide (0.070 mol) was added with an additional 3 hr of reflux. The cooled brown solution was poured onto ice, and the ethereal solution separated and dried ($MgSO_4$). Fractional distillation yielded a mixture of diethyl ether and (58). The sample was purified by preparative

vpc (SE-30, 80°C): ir (neat) 1090 cm^{-1} (C-O-C); nmr ($CDCl_3$) δ 3.3 (s, 3, CH_3O), 3.2 (q, 1, J = 5Hz, $C\underline{H}$ OCH_3), 1.48 (m, 2, $C\underline{H}_2$), 1.1 (d, 3, J = 6Hz, $C\underline{H}_3CH$-O) and 0.90 ppm (t, 3, J = 7Hz, $C\underline{H}_3CH_2$); mass spectrum (75 ev) m/e (rel. intensity) 89 (0.7), 88 (3), 87 (3), 73 (33), 60 (9), 59 (100), 58 (17), 57 (16), 56 (9), 55 (7), 45 (29), 43 (12), 41 (38).

2-Methoxy-3-butene (59).

To 1.3g (0.03 mol) of sodium hydride in a 50% oil dispersion in 40 ml of dry THF was added 2.0g (0.03 mol) of 3-buten-1-ol (Aldrich). After 10 min at room temperature and a color change from gray to brown, 3 ml (0.05 mol) of methyl iodide was added. After refluxing for 2 hr, the cooled solution was poured onto ice and extracted with ether and dried (K_2CO_3). The diethyl ether was partially removed by distillation. The sample was quite volatile and could not be separated from ether, THF or methyl iodide by distillation. A pure sample was isolated by prepartive vpc (SE-30, 70°C): ir (neat) 3060 (=C-H), 1635 (C=C), 1115 and 1095 cm^{-1} (=C-O-C); nmr ($CDCl_3$) δ 5.8 (m, 1, =$C\underline{H}$-C), 5.1 (m, 2, =$C\underline{H}$), 3.7 (m, 1, $C\underline{H}$-OCH_3), 3.25 (s, 3, $OC\underline{H}_3$) and 1.2 ppm (1.2, d, J = 6Hz, $C\underline{H}_3CH$); mass spectrum (75 ev) m/e (rel. intensity) 87 (3), 86 (51), 85 (12), 72 (5), 71 (78), 69 (5), 59 (41), 56 (13), 55 (71), 54 (6), 53 (14), 52 (2), 51 (4), 50 (3), 45 (5) 43 (20), 42 (4), 41 (100).

E-2-methoxy-2-butene (60).[86]

Into a 1000 ml, three-necked round bottom flask fitted with a dry ice condenser containing 400 ml of dry methanol and 43.0g (0.20 mol) of mercuric oxide at -5°C was added ∿ 19 ml of trans-2-butene previously condensed with a dry ice condenser into a 25 ml flask. Small portions of powdered iodine (total 125g, 0.5 mol) were added such that the internal temperature of the flask never rose above 0°C. Additional trans-2-butene was periodically added to compensate for any losses. After complete addition of iodine, the dark orange-red suspension was filtered yielding a dark brown filtrate from which a dark brown oil precipitated upon addition of water. After several washings with saturated $NaHSO_4$ solution, the oil and methanol-water layer became clear white and were easily separated yielding 32.8g (0.153 mol) of erythro-2-methoxy-3-iodobutane: nmr ($CDCl_3$) δ 4.3 (m, 1, $C\underline{H}$-OCH_3), 3.3 (s, 3, $OC\underline{H}_3$), 2.8 (m, d of q, 1, $C\underline{H}$-I), 1.8 (d, 3, $C\underline{H}_3$-CHI), and 1.15 ppm (d, 3, $C\underline{H}_3$-$CHOCH_3$). Without further purification, this sample was added to 11.3g potassium hydroxide dissolved in 30 ml hot methanol. After 1 hr at reflux, the methanolic solution was poured onto 50 ml water, extracted into ether, dried (K_2CO_3) and distilled. The fraction collected at 55-70°C yielded pure (60): ir (neat) 1675 cm^{-1} (C=C); nmr ($CDCl_3$)

δ 4.34 (q, 1, =C-H), 3.42 (s, 3, -OCH_3), 1.72 (s, 3, $\underline{CH_3}$-C(O)=), and 1.55 ppm (d, 3, $\underline{CH_3}$-CH=); mass spectrum (75 ev) m/e (rel. intensity) 87 (5), 86 (100), 85 (30), 71 (53), 59 (9), 56 (27), 55 (62), 54 (8), 53 (11), 43 (71), 42 (5), 41 (56).

Z-2-methoxy-2-butene (61).[86]

Following the same procedure as described for (60), 19 ml of cis-2-butene was allowed to react with 125g iodine and 43.0g mercuric oxide in 400 ml of cold methanol. Workup yielded a clear oil which was threo-2-methoxy-3-iodobutane: nmr ($CDCl_3$) δ 4.25 (m, 1, C$\underline{H}$-OCH_3), 3.37 (s, 3, $OC\underline{H_3}$), 3.18 (m, 1, C$\underline{H}$-I), 1.83 (d, 3H, $\underline{CH_3}$-$CHOCH_3$-) and 1.22 ppm (d, 3H, $\underline{CH_3}$-CHI). After treatment of this oil with potassium hydroxide in methanol and extraction into ether, distillation yielded pure (61) boiling at 50-55°C: ir (neat) 1683 cm^{-1} (C=C); nmr ($CDCl_3$) δ 4.45 (m, 1, =C$\underline{H}$-), 3.53 (s, 3, $OC\underline{H_3}$), 1.78 (m, 3, $\underline{CH_3}$-CHO-) and 1.50 ppm (m, 3, $C\underline{H_3}$-CH=); mass spectrum (75 ev) m/e (rel. intensity) 87 (6), 86 (100), 85 (29), 71 (6), 59 (9), 57 (6), 56 (29), 55 (56), 54 (7), 53 (11), 45 (4), 43 (66), 42 (7), 41 (61).

2-Methoxy-1-butene, (62).

In the preparative vpc collections of (60) and (61) (UCON, 70°C), another isomer was formed which eluted first. This was collected and identified as (62): ir (neat) 1655 cm^{-1} (C=C); nmr ($CDCl_3$) δ 3.81 (s, 3, $=CH_2$), 3.52 (s, 3, OCH_3), 2.04 (q, 2, J = 6Hz, CH_2CH_3) and 1.03 ppm (t, 3, J = 6Hz, CH_3CH_2); mass spectrum (75 ev) m/e (rel. intensity) 87 (5), 86 (76), 85 (29), 72 (2.5), 71 (42), 59 (6.5), 57 (8), 56 (30), 55 (35), 54 (6), 53 (8), 43 (42), 42 (9), 41 (64).

Reexamination of the reaction distillates of (60) and (61) by nmr and ir showed that (62) was not present but arose on the vpc column.

Relative retention times of 2-butenes, dimethoxymethane, 2-methoxy-3-butene, methoxybutane, 2-methoxy-1-butene, Z-2-methoxy-2-butene and E-2-methoxy-2-butene are 1.00, 2.40, 3.02, 3.31, 4.03, 6.38, and 6.38, (UCON, 25°C) respectively. The relative retention time of methanol to 2-butene (UCON, 25°C) is 5.54-6.24 (roughly where maximum of peak occurs). Peaks due to E- and Z-2-methoxy-2-butene in vpc traces could not be seen under tailing peak of methanol.

Thermal Decomposition of Peroxides (5)-(8) in Methanol.

Samples of (5), (6), (7) and (8) (1 mg) were each placed in base and EDTA washed 6 mm O.D. Pyrex tubes with 75-100 μl of methanol or methanol-O-d . The peroxides were not soluble in methanol. The samples were degassed (1 freeze thaw cycle), sealed in vacuo and pyrolyzed 4 min at 97±3°C. Analytical vpc relative retention times (identified below as RRT) and GC-MS permitted identification of methyl ethers (58) and (59) (UCON, 25°C and UCON-GC-MS, 25°C) (55) and (56) (UCON, 80°C and UCON-GC-MS, 80°C).

1. Thermal Decomposition of Peroxide meso-(5) in Methanol

Four peaks eluted before methanol: 1(RRT=1.0)-cis- and trans-2-butene; 2(RRT=2.4)-dimethoxymethane: mass spectrum (75 ev) m/e (rel. intensity) 75 (37), 45 (100), 44 (4), 31 (11); 3(RRT=3.0) 2-methoxy-3-butene (59): mass spectrum (75 ev) m/e (rel. intensity) 86 (17), 85 (6), 72 (6), 71 (100), 59 (37), 56 (14), 55 (60), 54 (9), 53 (17), 51 (6), 50 (6), 43 (54), 42 (9), 41 (100), 40 (6), 39 (37); 4(RRT=3.33)-2-methoxybutane (58): mass spectrum (75 ev) m/e (rel. intensity) 73 (10), 71 (15), 60 (5), 59 (100), 58 (3), 57 (8), 56 (5), 55 (13), 45 (18), 43 (10) 43 (5), 41 (35), 39 (10).

2. Thermal Decomposition of Peroxide meso-(5) in Methanol-O-d

Four peaks eluted before methanol: 1(RRT=1)-cis- and trans-2-butene; 2(RRT=2.4)-dimethoxymethane; mass spectrum (75 ev) m/e (rel. intensity) 75 (37), 47 (4), 45 (100), 44 (4), 31 (11), 29 (37); 3(RRT=3.0)-2-methoxy-3-butene (59): mass spectrum (75 ev) m/e (rel. intensity) 86 (17), 85 (6), 71 (100), 59 (37), 56 (14), 55 (60), 54 (9), 53 (17), 51 (6), 50 (6), 43 (54), 42 (9), 41 (100), 40 (6), 39 (37), 38 (6); 4(RRT=3.33)-2 methoxybutane (58): mass spectrum (75 ev) m/e (rel. intensity) 73 (13), 71 (13), 60 (5), 59 (100), 59 (5), 57 (8), 55 (13), 45 (18), 43 (3), 42 (5), 41 (33), 39 (10).

3. Thermal Decomposition of Peroxide dl-(6) in Methanol

Five peaks eluted before methanol: 1(RRT=1.0)-cis- and trans-2-butene; 2(RRT=2.5)-unidentified; mass spectrum (75 ev) m/e (rel. intensity) 57 (80), 56 (44), 55 (8), 44 (4), 43 (76), 42 (40), 41 (100), 39 (20); 3(RRT=2.9)-2-methoxy-3-butene (59): mass spectrum (75 ev) m/e (rel. intensity) 86 (19), 71 (100), 59 (38), 56 (12), 55 (62), 53 (19), 43 (44), 42 (12), 41 (94), 39 (31); 4(RRT=3.1)-2-methoxybutane (58): mass spectrum (75 ev) m/e (rel. intensity) 71 (100), 59 (100), 55 (67), 45 (33), 41 (100); 5(RRT=3.5)-unidentified; mass spectrum very poor.

4. Thermal Decomposition of Peroxide dl-(6) in Methanol-O-d

Five peaks eluted before methanol: 1(RRT=1)-cis- and trans-2-butene; 2(RRT=2.5)-unidentified; mass spectrum (75 ev) m/e (rel. intensity) 86 (8), 71 (4), 58 (3), 57 (86), 56 (49), 55 (7), 44 (3), 43 (78), 42 (42), 41 (100), 40 (5), 39 (22); 3(RRT=2.9)-2-methoxy-3-butene (59): mass spectrum (75 ev) m/e (rel. intensity) 86 (16), 85 (5), 72 (5), 71 (100), 59 (30), 56 (3), 55 (59), 54 (8), 53 (19), 51 (5), 80 (5), 45 (8), 53 (19), 51 (5), 80 (5), 45 (8), 43 (46), 42 (3), 41 (89), 40 (5), 39 (38), 38 (5); 4(RRT=3.1)-2-methoxy-butane (58): mass spectrum (75 ev) m/e (rel. intensity) 73 (14), 71 (32), 59 (100), 58 (9), 57 (9), 55 (18), 45 (9), 41 (18), 39 (9); 5(RRT=3.5)-unidentified; mass spectrum (75 ev) m/e (rel. intensity) 72 (14), 59 (71), 56 (43), 55 (29), 45 (14), 44 (14), 43 (17), 42 (29), 41 (100), 39 (14).

5. Thermal Decomposition of Peroxide cis-(7) in Methanol

Two peaks eluted after methanol. The first was identified as (55): mass spectrum (75 ev) m/e (rel. intensity) 114 (7), 85 (14), 82 (18), 72 (7), 71 (100), 67 (11), 58 (21), 55 (18), 54 (7), 53 (7), 45 (14), 43 (18), 42 (7), 41 (43), 39 (14).

6. Thermal Decomposition of Peroxide cis-(7) in Methanol-O-d

Several unidentified peaks eluted before methanol(UCON, 25°C). None had retention times corresponding to methyl ethers (58) or (59). One was tentatively identified as dimethoxymethane (RRT=2.4) by co-injection. Two major peaks eluted after methanol (UCON, 80°C): 1(RRT=1)-methoxycyclohexane (55): mass spectrum (75 ev) m/e (rel. intensity) 115 (1), 114 (9), 85 (11), 83 (3), 82 (17), 81 (2), 79 (2), 72 (7), 71 (100), 67 (8), 58 (17), 57 (2), 56 (2), 55 (14), 54 (6), 53 (6), 51 (2), 45 (10), 43 (14), 42 (6), 41 (42), 40 (2), 39 (13); 2(RRT=1.3)-3-methoxycyclohexene (56): mass spectrum (75 ev) m/e (rel. intensity) 113 (2), 112 (31), 111 (31), 98 (3), 97 (52), 85 (6), 84 (90), 83 (12), 82 (7), 81 (36), 79 (46), 78 (4), 77 (18), 70 (3), 69 (48), 68 (6), 67 (18), 66 (5), 65 (4), 57 (4), 56 (7), 55 (21) 54 (18), 53 (28), 52 (7), 51 (15), 50 (6), 45 (15), 44 (2), 43 (61), 42 (7), 41 (100), 40 (10), 39 (63).

7. Thermal Decomposition of Peroxide trans-(8) in Methanol-O-d

Several unidentified peaks eluted before methanol (UCON, 25°C). None had retention times corresponding to methyl ethers (58) or (59). One was tenta-

tively identified as dimethyoxymethane by coinjection with an authentic sample. Two major peaks eluted after methanol (UCON, 80°C): 1(RRT=1.0)-methoxycyclohexene (55): mass spectrum (75 ev) m/e (rel. intensity) 114 (10), 85 (13), 82 (13), 72 (100), 67 (13), 58 (21), 55 (21), 45 (17), 43 (13), 44 (38), 39 (17); 2(RRT=1.4)-3-methoxycyclohexene (56): mass spectrum (75 ev) m/e (rel intensity) 112 (23), 111 (23), 97 (4), 84 (60), 83 (27), 82 (27), 81 (40), 79 (27), 77 (20), 72 (20), 70 (20), 69 (47), 67 (13), 47 (13), 56 (27), 55 (33), 54 (20), 53 (33), 51 (13), 45 (13), 43 (40), 42 (20), 41 (100), 39 (40).

8. Thermal Decomposition of Peroxide meso-(5) in the Presence of Cyclohexene in Methanol.

Peroxide (5) (5.0 mg) was added to 50 µl of methanol containing 33 mg of cyclohexene in a 6 mm O.D. pyrolysis tube, degassed, sealed in vacuo, and heated to 100°C for 4 min. VPC analysis (UCON, 25°C) showed four peaks besides the butenes (RRT=1.0) eluting before methanol: 1(RRT=2.0)-unidentified; 2(RRT=2.5)-dimethoxymethane; 3(RRT=3.1)-2-methoxy-3-butene (59); 4(RRT=3.4)-2-methoxybutane (58). vpc analysis (UCON, 80°C and DBT, 80°C) showed no peaks corresponding to methyl ethers (55) or (56).

9. Thermal Decomposition of Peroxide trans-(8) in the Presence of 2-butene in Methanol.

Peroxide (8) (4 mg) was placed in a 6 mm O.D. pyrolysis tube with 100 µl cis-2-butene saturated (by bubbling cis-2-butene through methanol 1 min) methanol, degassed, sealed in vacuo, and heated to 100°C for 4 min. VPC analysis (UCON, 25°C) showed no peaks corresponding to methyl ethers (58) or (59).

10. Thermal Decomposition of Peroxide cis-(7) in the Presence of β-lactone threo-(19) in Methanol.

A freshly collected sample of isomerically pure (19) in methanol (estimated concentration about two-five times that of observed β-lactone products in peroxide (5) and (6) decompositions by placing similar size shot on same vpc column (PMPE, 90°C) under same conditions) was placed into a 6 mm O.D. pyrolysis tube with 4 mg of (7), degassed, sealed in vacuo, and heated to 100°C for 4 min. VPC analysis (UCON, 25°C) revealed no peaks corresponding to methyl ethers (58) or (59).

11. Thermal Decomposition of Peroxide cis-(7) in the Presence of β-lactone erythro-(18) in Methanol.

A freshly preparatively collected sample of 80% erythro-(18) (20% threo-(19) in methanol and 5 mg of (7) were prepared and pyrolyzed as described for threo-(19) above. Analytical vpc analysis (UCON, 25°C)

was complicated by unidentified peaks. However, no methyl ethers ((58) or (59)) detectable.

12. Thermal Decomposition of (8) in presence of threo-2,3-Dimethylpropiolactone (19) in Methanol.

A sample was prepared and pyrolyzed as above with 4 mg peroxide (8). Vpc analysis (UCON, 25°C) was complicated by unidentified products. No peaks corresponding to methyl ethers (58) or (59) were detectable.

Irradiation of cis-2-Butene in Methanol-O-d

A 100 µl aliquot of a saturated solution of cis-2-butene in methanol-O-d (prepared by bubbling cis-2-butene through 2 ml MeOD for 30 sec) was placed in a 6 mm O.D. quartz tube, degassed sealed in vacuo, and irradiated for 241 min at 0°C with a Hanovia 450 W lamp, quartz optics. Two major peaks besides cis-2-butene (RRT=1.0) eluted before methanol; 1(RRT=3.3)-2-methoxy-3-butene (58): mass spectrum (75 ev) m/e (rel. intensity) 86 (15), 71 (59), 59 (22), 58 (15), 56 (4), 55 (37), 54 (7), 51 (7), 50 (7), 45 (4), 44 (4), 43 (100), 42 (11), 41 (59), 40 (4), 39 (22), 38 (7); 2(RRT=3.6)-2-methoxybutane (59): mass spectrum (75 ev) m/e (rel. intensity) 74 (7), 73 (5), 71 (2), 60 (4), 59 (100), 58 (10), 57 (5), 56 (5), 55 (3), 53 (10), 51 (1), 46 (4), 45 (13), 44 (2), 43 (17), 42 (12), 41 (19), 40 (3), 39 (7), 38 (1).

Before irradiation the composition of the methanol solution as determined by analytical vpc (DBT, 25°C) was 99.6% cis-2-butene, 0.3% trans-2-butene, 0.1% 1-butene, 0% methyl ethers. After 241 min of irradiation, composition of the methanol solution (DBT, 25°C and UCON, 25°C) was 0.9% butane, 3.3% 1-butene, 56.7% trans-2-butene, 37.8% cis-2-butene, 0.2% 2-methoxybutane (58) and 1.0% 2-methoxy-3-butene (59).

Irradiation of trans-2-Butene in Methanol.

A 100 µl aliquot of a saturated solution of trans-2-butene in methanol was degassed, sealed in vacuo and irradiated with a Hanovia 450 W lamp in a quartz tube. After 240 min at 0°C, 2 major peaks besides 2-butene (RRT=1.0) eluted before methanol: 1(RRT=3.0)-2-methoxy-3-butene (59); 2(RRT=3.4)-2-methoxybutane (58). Before irradiation the composition of the methanol solution was 0.85% butane, 0.22% 1-butene, 96.2% trans-2-butene 2.7% cis-2-butene and 0% methyl ethers. After 241 min irradiation the composition was 0.85% butane, 0.30% 1-butene, 95.5% trans-2-butene, 3.3% cis-2-butene, 0.002% 2-methoxy-2-butene (59) and 0.002% 2-methoxybutane (58).

Thermal Decomposition of meso-2,3-Dimethylsuccinyl Peroxide (5) in the Presence of Piperylene.

cis-Piperylene (32 µl, 0.69 mmol) and 9.91 mg meso-

(5) (0.069 mol) were heated in 1 ml THF for 4 min at 95°C. Analytical vpc analysis (DBT, 60°C) before and after saw no isomerization or disappearance of cis-piperylene.

trans-anti-trans-tricyclo[6.4.0.$0^{2,7}$]dodecane (24), cis-trans-tricyclo[6.4.0.$0^{2,7}$]dodecane (63), and cis-anti-cis-tricyclo[6.4.0.$0^{2,7}$]dodecane (64).[50]

Cyclohexene (82g) in 350 ml of benzene with 20g methyl acetate was irradiated for 14 hr at 0°C with a 450 W Hanovia medium pressure lamp through quartz optics. Benzene, unreacted cyclohexene, and methyl acetate were distilled. A second fraction containing the dimers was distilled at 0.1 mm. Six peaks were identified by analytical vpc (Carbowax 20M, 135°C) comparison of reported retention times and cmr spectra.[50] Yields reported are relative. Preparative gas chromatography (Carbowax 20M, 135°C) yielded analytical samples of the dimers: 1(RRT=1.0, reported RRT=1.0)-(24) (15%), nmr ($CDCl_3$) δ 1.9-1.00 ppm (m, 20); cmr ($CDCl_3$) δ 50.21 (CH), 30.97 (CH_2-CH) and 26.52 ppm (CH_2-CH_2); 2(RRT=1.23, reported RRT=1.23)-(63) (36%), nmr ($CDCl_3$) δ 1.9-1.0 ppm (m, 20); cmr ($CDCl_3$) δ 44.11, 41.56, 39.40, 38.80, 30.98, 27.14, 26.69, 26.47, 25.75, 23.71, 22.88 and 22.31 ppm; 3(RRT=1.32, reported RRT=1.35)-(64) (17%), nmr ($CDCl_3$) δ 2.04 (m, 4, -CH) and 1.30 ppm (m, 16, CH_2); cmr ($CDCl_3$) δ 34.15 (CH), 27.04 (CH_2-CH) and

23.05 ppm ($C\underline{H}_2$-CH_2); 4(RRT=1.62, reported RRT=1.60)-unidentified (2%); 5(RRT=2.03, reported RRT=1.78)-3-cyclohexylcyclohexene (13%), unisolated; 6(RRT=2.38, reported RRT=2.17)-3,3'-bicyclohexenyl (17%), unisolated.

cis -syn-cis-tricyclo[6.4.0.$0^{2,7}$]-3,11-dodecadiene (66).

Cyclohexadiene (40.6g) in 300 ml of isopentane with 4.5g β-acetonapthone was irradiated for 24 hr at 0°C with a Hanovia 450 W medium pressure lamp through quartz optics. Distillation of the isopentane followed by vacuum distillation (0.1 mm) of the remaining oil yielded 29g of a clear liquid boiling at 57-60°C. Analytical vpc (Carbowax 20M, 115°C) showed two major peaks 1(RRT=1.0)-cis-anti-cis-tricyclo[6.4.0.$0^{2,7}$]-3,11-dodecadiene (65), unisolated; 2(RRT=1.5)-cis-syn-cis-(66), nmr ($CDCl_3$) δ 5.8 (m, 4, =C-H), 3.0-2.5 (m, 4, C$\underline{H}$) and 2.2-1.5 ppm (m, 8, $C\underline{H}_2$).

cis-syn-cis-tricyclo[6.4.0.0.^{2,7}]dodecane (67). Hydrogenation of Cyclohexadiene Dimer (66).

A sample of cyclohexadiene dimer (66) (containing about 25% dimer (65)) was placed over 1g of Pd/C in 100 ml of ethanol and 1 atmosphere of hydrogen at room temperature. Stirring was continued until hydrogen uptake ceased (∿ 4 hr). Analytical vpc analysis (Carbowax 20M, 115°C) showed two products: 1(RRT=1.0)-cis-anti-

cis-(64) (∿ 25%), identified by coinjection with an authentic sample; 2(RRT=1.6)-cis-syn-cis-(67) (∿ 75%), nmr ($CDCl_3$) δ 2.40 (m, 4, CH) and 1.9-1.3 ppm (m, 16), cmr ($CDCl_3$) δ 34.85 (CH), 23.13 and 22.86 ppm (CH_2).

The relative retention times of cyclohexene and cyclohexene dimers trans-anti-trans-(24), cis-trans-(63), cis-anti-cis-(64), and cis-syn-cis (67) are 1.00, 6.11, 7.45, 8.12, and 12.8 (Carbowax, 115°C) and 1.00, 8.91, 10.4, 10.8, and 12.4 (SF-96, 150°C), respectively.

Thermal Decomposition of Peroxide trans-(8) in Cyclohexene

Peroxide (8) (90 mg) was placed in a 7 mm O.D. tube with 500 μl of cyclohexene, degassed sealed in vacuo, and heated to 100°C for 3.75 min. Analytical vpc analysis (Carbowax 20M, 115°C) revealed one major peak after cyclohexene (RRT=1.0): (RRT=6.3). This peak coinjected with cyclohexene dimer (24). Analytical vpc analysis (SF-96, 150°C) revealed one major peak after cyclohexene (RRT=1.0): (RRT=10.6). This did not coinject with (24) (RRT=8.90). A GC-MS scan (Carbowax-GC-MS, 115°C) on m/e 164 was carried out and no peaks were observed.

Methyl-2-methylbutyrate (68)

To methyl 2-methylbutyric acid (1.0g, 0.01 mol) in 10 ml of dry ether was added 30 ml of an ethereal solution of diazomethane at 0°C. After evolution of nitrogen

ceased, the ether was removed by distillation. Preparative vpc (SE-30, 150°C) of the residue yielded an analytical sample of (68): ir (neat) 1740 cm^{-1} (C=O), nmr ($CDCl_3$) δ 3.63 (s, 3, OCH_3), 2.34 (q, 1, HC-O), 1.55 (m, 2, CH_2), 1.13 (d, 2, CH_3CH-O) and 0.90 ppm (t, 2, CH_3CH_2). An analytical sample of (68) in cyclohexadiene was prepared. Cyclohexene (RRT=1.0), eluted before (68) (RRT=4.1) (UCON, 25°C).

Methyl Cyclohexanecarboxylate (69).

To cyclohexanecarboxylic acid (8.34g, 0.06 mol) in 20 ml ether was added an ethereal solution of diazomethane at 0°C. After nitrogen evolution ceased, the solution was concentrated and distilled yielding 5.84g (69): ir (neat) 1735 cm^{-1} (C=O); nmr ($CDCl_3$) δ 3.68 (s, 3, OCH_3), 2.28 (m, 1, CH-O) and 2.0-1.2 ppm (m, 10, ring CH_2). This was purified by preparative vpc (SE-30, 170°C). Dodecane (RRT=1.0) eluted after (69) (RRT=0.8) (UCON, 120°C).

Thermal Decomposition of Peroxide trans-(8) in Dichloromethane/1,4-Cyclohexadiene.

Peroxide (8) (13.49 mg) was dissolved in 1 ml dichloromethane and dodecane (internal standard) was added. A 200 µl aliquot was added to 6 µl 1,4-cyclohexadiene

and degassed, sealed in vacuo and pyrolyzed for 4 min at 100°C in a 6 mm O.D. Pyrex tube. This sample was analyzed by analytical vpc (UCON, 120°C). After dichloromethane, cyclohexadiene and cyclohexene, only dodecane (RRT=1.0) eluted. The remainder of the sample was added to an equal volume of a saturated ethereal solution of diazomethane. Appearance of a small peak (RRT=0.8) before dodecane coinjected with methylcyclohexane carboxylate (69).

Thermal Decomposition of Peroxide meso-(5) in 1,4-Cyclohexadiene.

Peroxide (5) (8.0 mg) was placed in a 6 mm O.D. Pyrex tube with 100 µl of 1,4-cyclohexadiene, degassed, sealed in vacuo, and heated to 100°C for 4 min. An aliquot was examined by analytical vpc (UCON, 25°C). Besides cyclohexene, benzene (impurities in 1,4-cyclohexadiene) and cyclohexadiene, one peak eluted which did not correspond to methyl 2-methylbutyrate (68). The remaining sample was added to an equal volume of a saturated ethereal solution of diazomethane and analyzed by vpc (UCON, 25°C). A peak (RRT=4.0, eluting after cyclohexene RRT=1.0) coinjected with an authentic sample methyl 2-methylbutyrate (68).

Photolysis of meso- and dl-2,3-Dimethylsuccinyl Peroxides (5) and (6), and cis- and trans-1,2-Hexahydrophthaloyl Peroxides (7) and (8).

1. Direct Photolyses.

All photolysis samples were prepared as 0.06-0.1M stock peroxide solutions. Peroxides stock solutions of (5) and (6) were prepared with a weighed amount of 2-methylbutane and dodecane as internal standards. Peroxide stock solutions of (7) and (8) were prepared with a weighed amount of n-heptane as internal standard. Sodium carbonate (20-30 mg) was added to the sample tubes as a solid when indicated. All samples were prepared in thoroughly nitrogen-degassed, Spectrograde dichloromethane. Measured aliquots of 100 or 200 µl were placed in EDTA washed, 6 mm O.D. Pyrex tubes, degassed one additional time by freeze pump-thawing, and sealed in vacuo. Samples were kept at 77°K in the dark before and after photolysis until analysis. All samples were irradiated at 0°C in a quartz dewar. Effort was made to reproducibly place the samples in position before the lamp. A Hanovia 450 W lamp with quartz cooling jacket was utilized along with indicated filters (Footnote a, Table 16 lists the transmission characteristics of the filters). Samples were irradiated for the indicated time periods which were carefully monitored

(± 0.1 min) with an electronic timer. All samples were vacuum distilled unless otherwise indicated. Olefin and β-lactone products and yields were determined by vpc against internal standards. Percent decomposition of peroxide was followed by infrared at 1775 cm^{-1} in matched 1 mm solution cells. Table 13 lists yields and ratios of 2-butenes from photolysis with respect to time. Table 14a lists the yields and ratios of 2-butene and β-lactones from photolysis under indicated conditions. Each table entry represents a single run. Table 16 (Results and Discussion) lists yield of olefin from photolysis of (5)-(8) through several filters.

2. Sensitized Photolyses.

All samples were prepared and handled as in the direct photolyses. Stock solutions were prepared 0.02-0.03M peroxide. Dodecane was not added to the meso-(5) and dl-(6) peroxide samples and analysis for β-lactones was not performed. Stock solutions of sensitizer were prepared as indicated in Table 40 and added to each sample as indicated. Tetracene was weighed out individually for each sample to give 0.03 or 0.04M in 100 or 200 μl solutions. Acetone (1 μl; .135M) was added neat to each sample.

3. Irradiation of Peroxides in Presence of Anthracene and Oxygen.

Samples were prepared as described for sensi-

tized photolysis. Instead of a freeze-pump thaw cycle, 50 ml of oxygen at 25°C and 760 nm was allowed to diffuse into evacuated manifold and sample held at 77°K. These samples were then sealed and irradiated and analyzed by infrared as described for the others.

Reaction of Peroxides meso-(5) and dl-(6)

Aliquots (100 µl) of stock solutions of meso-(5) and dl-(6) (0.01M) in dichloromethane (containing pentadecane as internal standard) were treated with 10 mg (0.038 mmol, 0.38M) of triphenylphosphine at room temperature. After 1 hr at room temperature 70.5% 2,3-dimethylsuccinic anhydride (meso 97.2%, dl, 2.8%) from (5) and 30.2% 2,3-dimethylsuccinic anhydride (meso-1.0%, dl 99%) from (6) were obtained as determined by analytical vpc (PMPE, 130°C).

A mixture of meso-(5) (2.91 mg, 0.020 mmol, 65.7%) and dl-(6) (1.52 mg, 0.011 mmol, 34.3%) was prepared and allowed to react with 30 mg (0.11 mmol) triphenylphosphine overnight at 25°C in 1 ml ether-THF (50-50) to afford 40.7% of a mixture of meso-2,3-dimethylsuccinic anhydride (59.6%) and dl-2,3-dimethylsuccinic anhydride (40.4%).

Table 40. Stock Solutions of Sensitizers

	Mg/ml CH_2Cl_2	M	$\frac{\mu l \text{ added}}{100 \mu l \text{ stock}}$	Sensitizer Molarity
Naphthalene	41.39	0.323	8	0.02M
Anthracene	23.12	0.130	17	0.02M
Acetophenone	39.18	0.323	8	0.02M
Benzophenone	62.0	0.340	8	0.02M
Benzil	69.67	0.331	8	0.02M
Naphthalene	4.93	0.038	8	0.003M
Anthracene	6.76	0.038	8	0.003M
Acetophenone	5.17	0.043	8	0.003M
Benzaphenone	6.60	0.036	8	0.003M
Benzil	6.51	0.031	8	0.002M

Reaction of Peroxide (9) with Excess Triphenylphosphine.

Freshly prepared (9) (20 mg, 0.12 mmol) was dissolved in 0.5 ml chloroform containing 60 mg (0.23 mmol) triphenylphosphine. After standing at room temperature 20 min, an infrared spectrum revealed complete disappearance of (9) and appearance of product consistent with the corresponding tricyclic anhydride: ir ($CHCl_3$) 1858 and 1790 cm^{-1} (C=O).

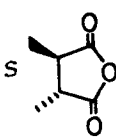
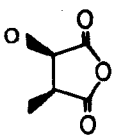
Reaction of Peroxide (5) with Triphenylphosphine and Dimethylsulfide.

A stock solution of (5) (0.0278M) in dichloromethane was prepared containing 2-methylbutane and n-pentadecane as internal standards. Table 41 lists the yields and ratios of 2-butenes determined by analytical vpc (DBT, 25°C) and yields and ratios of anhydrides (PMPE, 130°C) after stirring 300 µl aliquots of each with either 20 mg (0.076 mmol) triphenylphosphine or 9 µl (0.12 mmol) dimethylsulfide for 1 and 3 hr at 28°C. Distillation preceded 2-butene analyses . Undistilled samples were analyzed for anhydrides.

Reaction of Peroxides cis-(7) and trans-(8) with Triphenylphosphine.

Peroxides (7) and (8) (50 mg, 0.029 mmol) were each placed in 500 µl dichloromethane. Triphenylphosphine

Table 41. Products from the Reaction of meso-(5) with Triphenylphosphine and Dimethylsulfide

Sample	Yield Butenes	Ratio 		Yield Anydrides		Ratio 
Control	10.0	70.2	29.8	7.5	---	---
Ph_3P	46.2	68.0	32.0	65.4	0.5	99.5
CH_3SCH_3	11.6	67.6	32.4	28.1	2.8	97.2

(10 mg, 0.038 mmol) was added. After 20-30 min at room temperature, the infrared spectrum of each was examined; cis-(7) + Ph_3P; ir (CH_2Cl_2) 1862 and 1790 cm^{-1} (anhydride C=O). trans-(8) + Ph_3P; ir (CH_2Cl_2) 1865 and 1790 cm^{-1} (anhydride C=O).

Neither cis- nor trans-1,2-hexahydrophthalic anhydride could be separated efficiently by analytical vpc (Carbowax 20M, PMPE, UCON). In addition, neither was very soluble in dichloromethane. Thus the stereochemistry and yields for this reaction were not determined.

Reaction of Peroxides cis-(7) and trans-(8) with Triphenylphosphine and Dimethylsulfide.

Stock solutions of (7) (0.022M) and (8) (0.019M) were prepared in dichloromethane. Heptane was added as internal standard. Table 42 lists the yield of cyclohexene determined by analytical vpc (DBT, 60°C) after stirring 1 ml of each stock solution with either 35 mg (0.133 mmol) triphenylphosphine or 30 µl (0.43 mmol)dimethylsulfide followed by distillation. trans-(8) + Ph_3P; ir (CH_2Cl_2) 1865 and 1790 cm^{-1} (anhydride C=O). trans-(8) + DMS; ir (CH_2Cl_2) 1865 and 1790 cm^{-1} (anhydride C=O) and 1710 cm^{-1} (unidentified-equal in intensity to 1790 cm^{-1} peak).

Table 42. Cyclohexene from Reactions of Peroxides cis-(7) and trans-(8) with Triphenylphosphine and Dimethylsulfide

Peroxide	Conditions	Yield % Cyclohexene	
		1 hr	3 hr
cis-(7)	Control	3.9	---
cis-(7)	Ph_3P	9.2	---
cis-(7)	DMS	3.7	3.8
trans-(8)	Control	4.2	---
trans-(8)	Ph_3P	12.0	11.9
trans-(8)	DMS	2.6	4.0

Cuprous Acetate.[99]

Into 120 ml of glacial acetic acid and 20 ml acetic anhydride which were thoroughly degassed with nitrogen was added 8.0g (0.056 mol) copper oxide. This mixture was refluxed three days until complete disappearance of the red copper oxide and appearance of a white precipitate formed. The dark blue acetic acid solvent was removed by filtration under nitrogen leaving a 4.0g (0.033 mol, 60%) off-white crystalline solid which was thoroughly dried under vacuum. In spite of precautions, some oxidation to copper (II) did occur (as determined by color change toward green-blue). Although samples were only used while off-white or yellow, exact amounts of copper (II) present were not known and differed from sample to

sample and with age.

Reaction of Peroxides meso-(5) and dl-(6) with Cuprous Acetate.

Stock solutions of (5) and (6) in dichloromethane (with 2-methylbutane as internal standard) as indicated in Table 43 were prepared. Aliquots (100 µl) were added to solid cuprous acetate in a sealed 5 ml flask. Immediate color change from yellow to dark green accompanied gas evolution. Stirring was continued at room temperature for 30 min followed by distillation. Yields of 2-butenes were determined by analytical vpc (DBT, 25°C). In separate runs, distillations were performed on a vacuum line (10^{-4} nm, 25°C) for determination of β-lactones (18) and (19). Though yields and ratios were not determined, traces of (18) and (19) were observed by vpc (PMPE, 90°C) in these reactions.

Reaction of Peroxides cis-(7) and trans-(8).

Table 44 lists the concentrations of reactants. Cuprous acetate (and a weighed amount of benzene as internal standard) was dissolved in 300 µl of dry, degassed acetonitrile in a 5 ml flask fitted with a stir bar and septum. The solution was light yellow. The indicated peroxide was dissolved in 200 µl solvent and syringed into the cuprous acetate solution. The solution im-

mediately turned dark blue-green and evolved carbon dioxide. After stirring for 60-90 min at room temperature, the volatile materials were vacuum transferred and analyzed by analytical vpc (DBT, 25°C). Yields of cyclohexene are reported in Table 44.

Conversion of cis- and trans-1,2-Hexahydrophthalic Acids to Cyclohexene.

As described earlier, cis-(7) and trans-(8) were prepared from the corresponding dicarboxylic acids or anhydrides via their diacid chlorides. The diacid chloride (usually 4.0-4.3g) was treated with 3.0g sodium peroxide in water-dichloromethane. The organic layer was separated, dried ($CaCl_2$) and concentrated. This was taken up in dry, degassed acetonitrile containing a weighed amount of n-hexane as internal standard. This solution was slowly added to an equimolar amount (based on starting dicarboxylic acid) of copper (I) (cuprous bromide or cuprous acetate) suspended and partially dissolved in 50 ml acetonitrile. Yields of cyclohexene were determined by analytical vpc (DBT, 25°C) and based upon starting diacid chloride. Table 45 lists the results.

Table 43. Reaction of Peroxides meso-(5) and dl-(6) with Cuprous Acetate

Peroxide	Concentration Peroxide	Concentration CuOAc	Ratio Peroxide/ CuOAc	Yield(%)	Composition	
meso-(5)	0.086M	0.397M	0.217	30.5	69.4	30.5
meso-(5)	0.086M	1.11M	0.007	51.6	70.3	29.5
dl-(6)	0.110M	0.247M	0.445	27.8	70.5	29.5
dl-(6)	0.110M	0.735M	0.150	53.2	70.4	29.6

Table 44. Reaction of Peroxides cis-(7) and trans-(8) with Cuprous Acetate

Peroxide	Concentration Peroxide	Concentration CuOAc	Ratio Peroxide/ Cu	% Yield Olefin
trans-(8)	0.062M	0.35M	0.18	13.6
trans-(8)	0.11	0.302	0.36	12.3
trans-(8)	0.26	0.043	6.0	19.3
trans-(8)	0.15	0.12	1.3	32.9
trans-(8)	0.26	0.20	1.3	38.2
trans-(8)	0.14	0.74	0.19	18.2
trans-(8)	0.12	0.13	0.92	42.7
trans-(8)	0.11	0.35	0.31	34.9
trans-(8)	0.23	0.22	1.1	35.1
trans-(8)	0.081	0.12	0.68	29.0
trans-(8)	0.058	0.092	0.63	23.7
cis-(7)	0.17	0.23	0.75	37.2
cis-(7)	0.15	0.70	2.2	39.4
cis-(7)	0.12	0.19	0.63	39.8
cis-(7)	0.12	0.12	1.0	34.2

Table 45. Percent Yield Cyclohexene from Reaction of Unisolated Peroxides cis-(7) and trans-(8) with Copper (I)

Peroxide	Cu^I	Time of Reaction 1 hr	2 hr	3 hr
cis-(7)	CuBr	--	38	--
cis-(7)	CuBr	--	42	--
cis-(7)	CuOAc	--	36	--
cis-(7)	CuBr	--	35	--
cis-(7)	CuOAc	--	30	--
trans-(8)	CuBr	30	--	42
trans-(8)	CuOAc	--	42	35
trans-(8)	CuBr	25	--	26
trans-(8)	CuOAc	25	--	26

Reaction of Peroxides (5)-(8) with Aromatic Hydrocarbons

Stock peroxide solutions of 0.1-0.15M were prepared in degassed, spectrograde dichloromethane. Samples of aromatic hydrocarbons were prepared to be 0.03-0.04M when added to 0.5 ml of peroxide stock solution. These were allowed to stand in the dark in sealed vials at room temperature (22°C) for the indicated time periods. Controls were run in all cases and showed less than 3-4% decomposition over 5 hr. Reaction was followed by dis-

appearance of the carbonyl absorption in the infrared at 1775 cm^{-1} (Table 22 and Figures 5-9). Reaction of (7) and (8) with aromatic hydrocarbons was also followed by appearance of cyclohexene (Table 22).

Diphenoyl Peroxide (12)[23,24]

As previously described,[23,24] 4.2g (0.02 mol) of phenanthrene quinone (Aldrich) was treated with 2.4g (0.02 mol) of trimethylphosphite at room temperature in 100 ml of degassed dichloromethane for 1 hr, followed by ozone at -78°C (∿ 30 min). The ozonized material was filtered while cold and the filtrate concentrated to a yellow-orange powder under reduced pressure at room temperature. Cold methanol was added and the precipitate collected and recrystallized three times from methanol-dichloromethane yielding 0.31g (7%) peroxide (12): ir (CH_2Cl_2) 1764 with shoulder 1770 cm^{-1} (C=O).

Reaction of Diphenoyl Peroxide (12) with Rubrene.

A stock solution of diphenoyl peroxide (12) (6.12 x 10^{-2} M) in dichloromethene was mixed with an equal volume (5 ml) of a rubrene solution (dichloromethane) in a 6 mm path length infrared cell. Transmission was followed with respect to time at 1780 cm^{-1}. Table 46 lists three runs with respect to time indicating initial per-

Figure 5. Reaction of meso-(5) with Aromatic Hydrocarbons

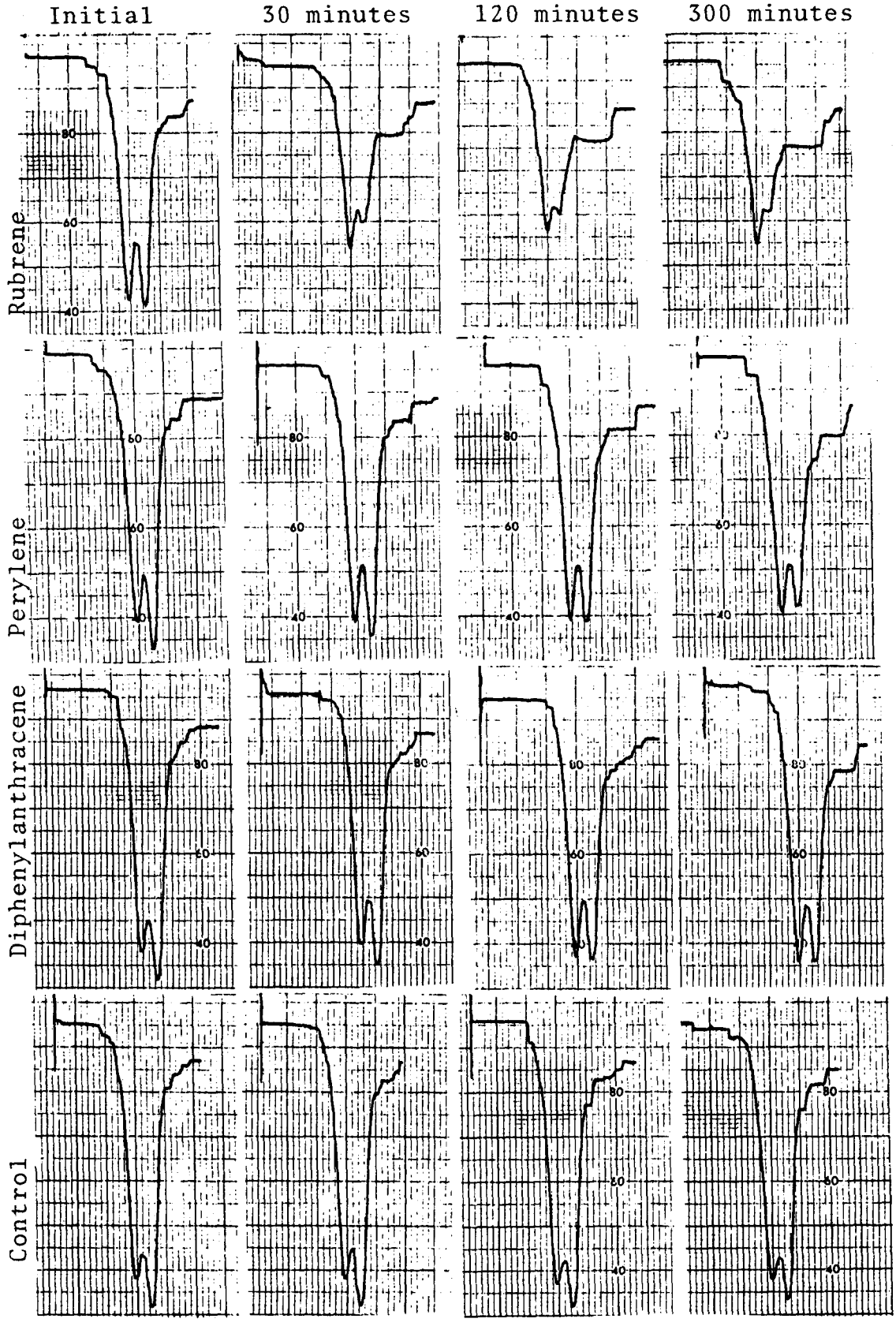


Figure 6. Reaction of d1-(6) with Aromatic Hydrocarbons

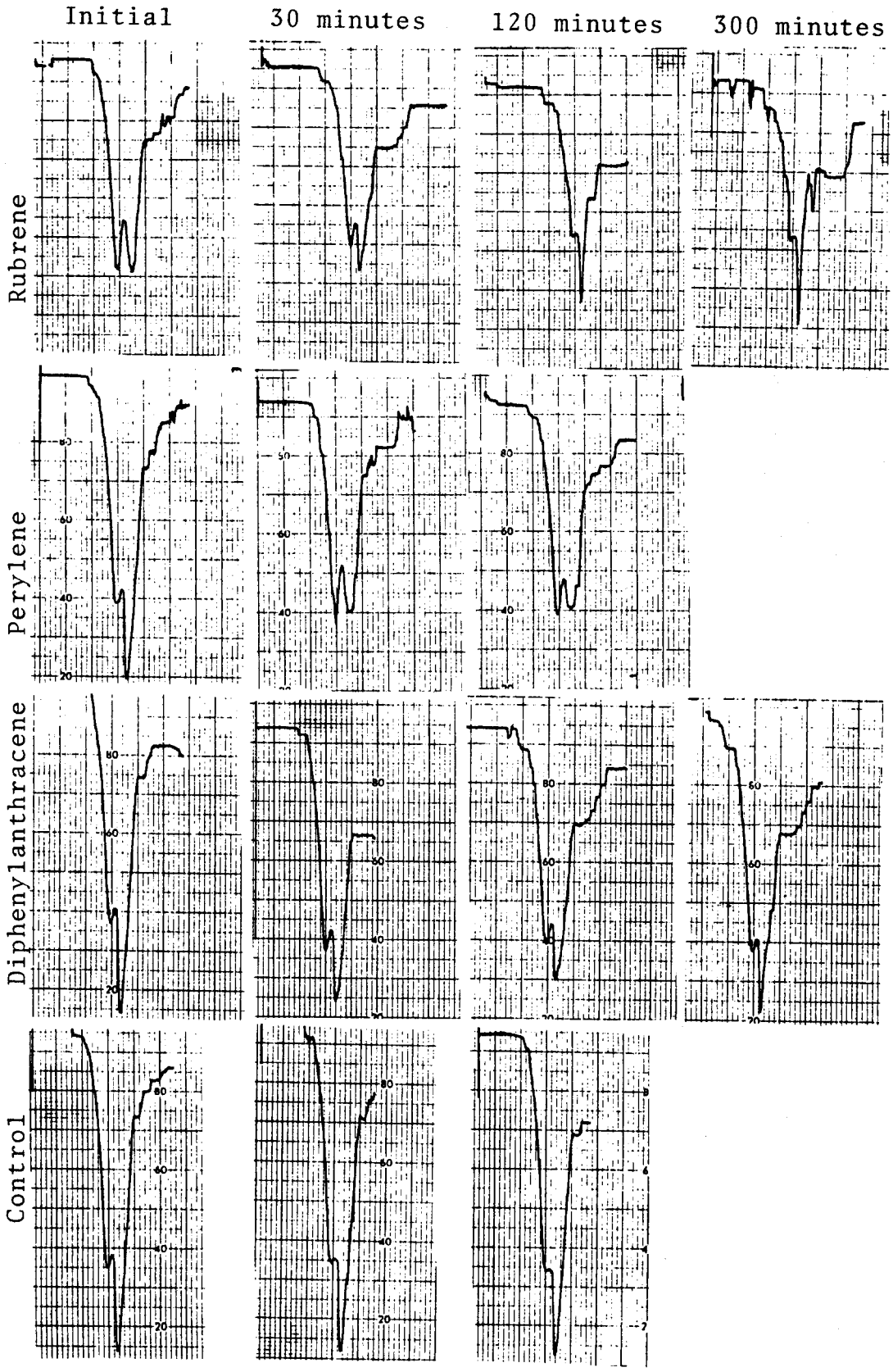


Figure 7. Reaction of cis-(7) with Aromatic Hydrocarbons

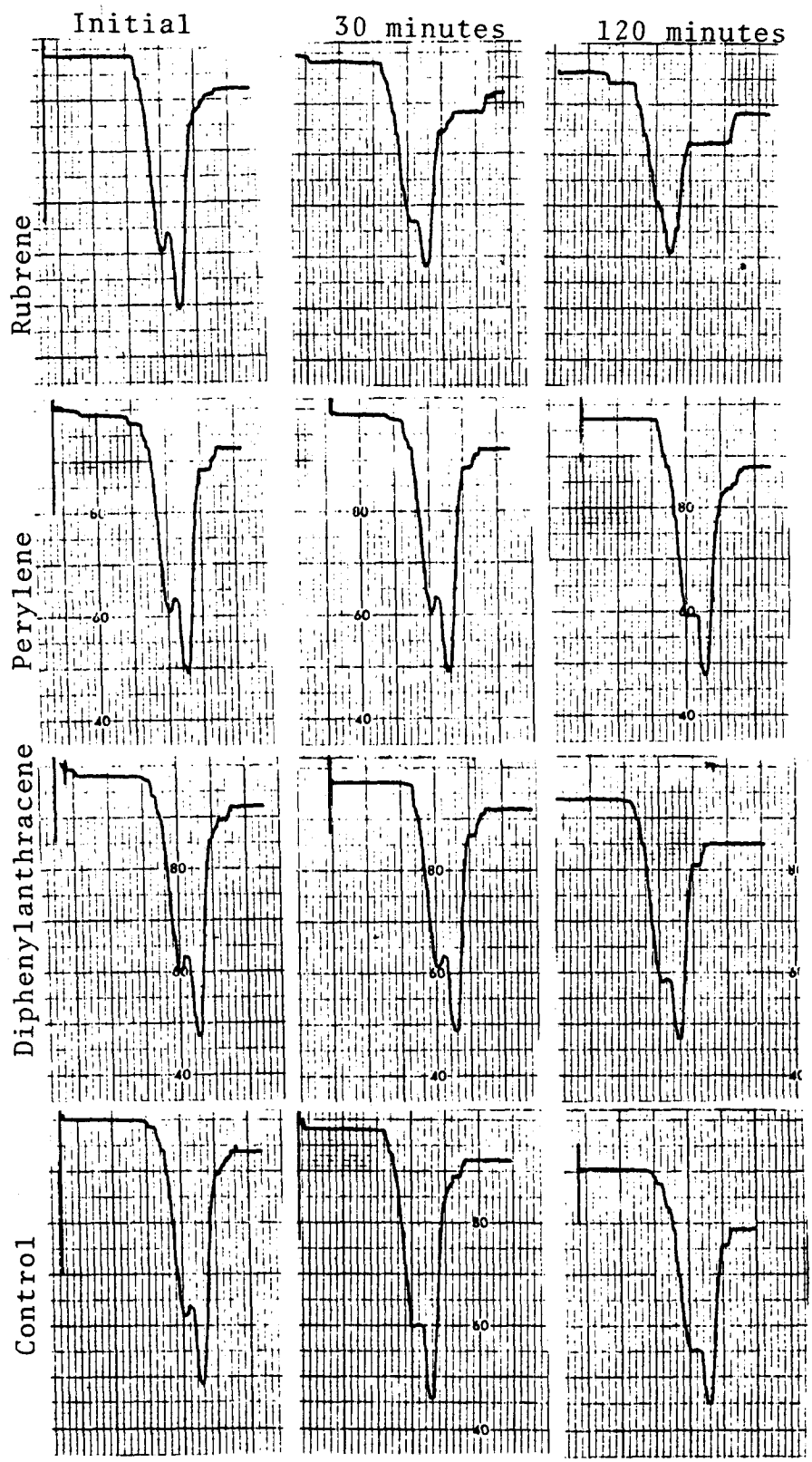


Figure 8..Reaction of trans-(8) with Aromatic Hydrocarbons

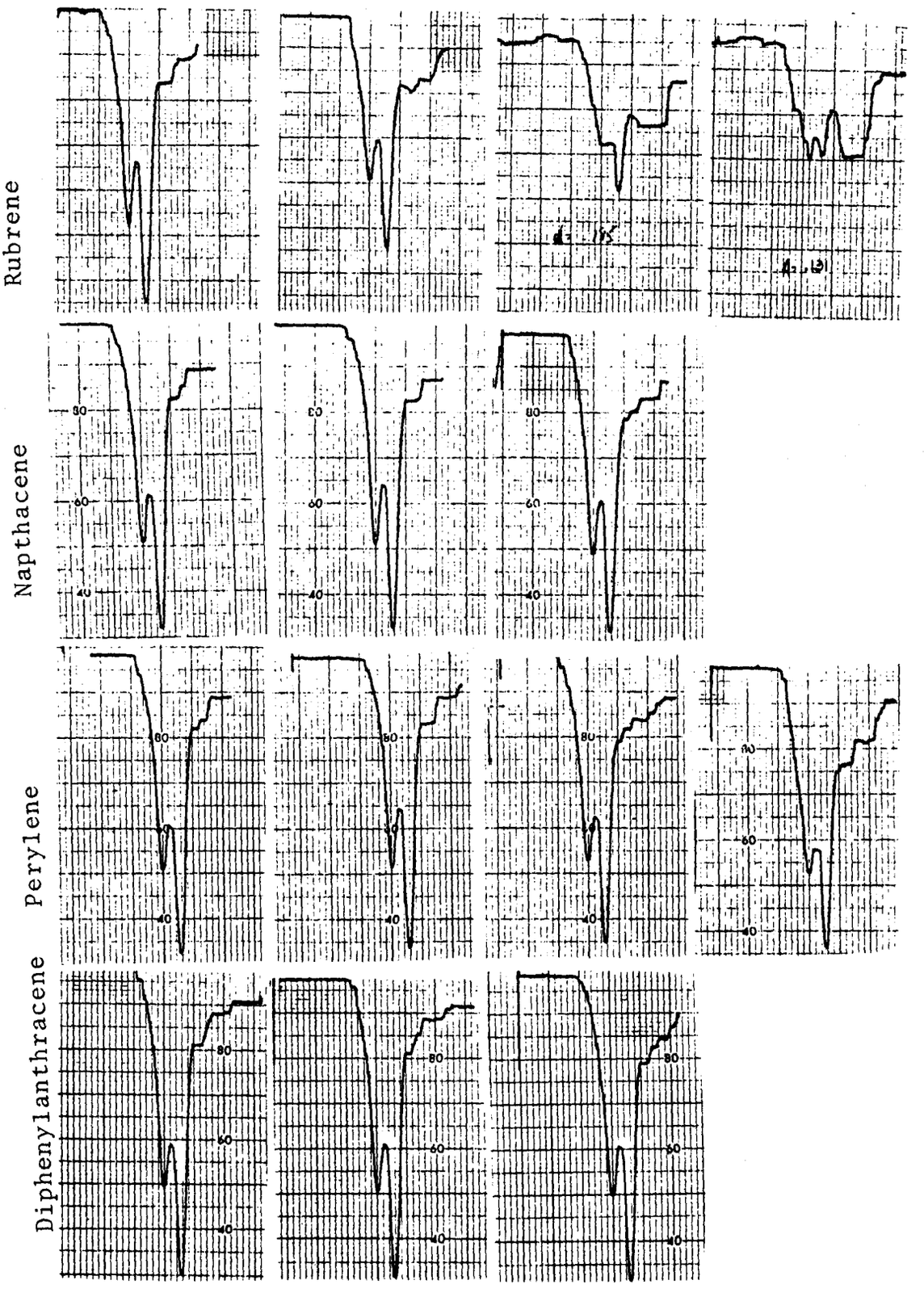


Figure 9. Reaction of Benzoyl Peroxide with Aromatic Hydrocarbons

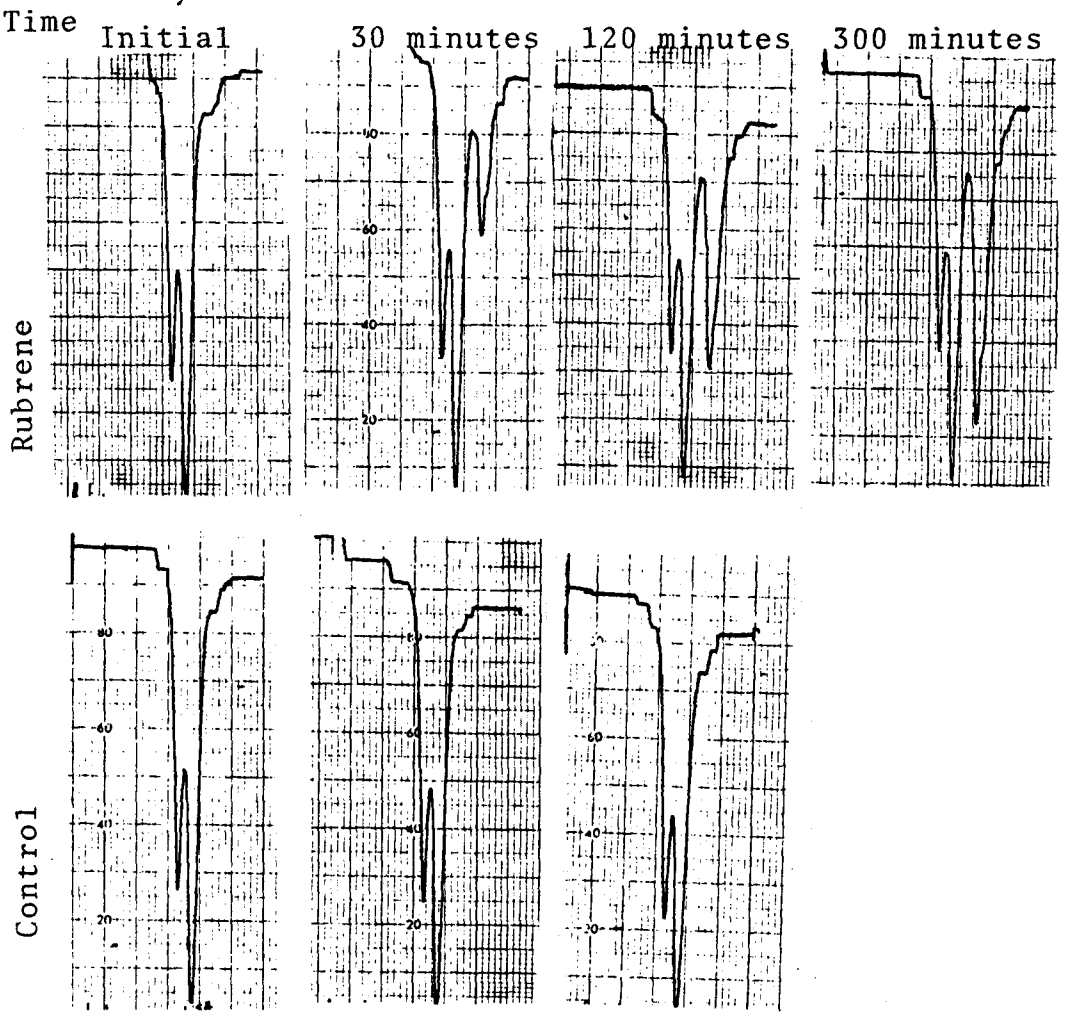


Table 46. Reaction of Diphenoyl Peroxide (12) with Rubrene[†]

1. Diphenoyl peroxide 3.06×10^{-3} M Rubrene 2.48×10^{-3} M

Time (sec)	64	68	72	76	80	84	88	98	108	118	128	148	208
Moles ($\times 10^3$) remaining	1.56	1.53	1.50	1.47	1.44	1.41	1.38	1.35	1.32	1.26	1.23	1.20	1.14

2. Diphenoyl peroxide 3.06×10^{-3} M Rubrene 2.31×10^{-3} M

Time(sec)	80	90	100	110	120	130	140	150	160	170	180	240
Moles ($\times 10^3$) remaining	2.22	2.10	2.00	1.94	1.87	1.85	1.82	1.82	1.77	1.75	1.72	1.66

3. Diphenoyl peroxide 3.06×10^{-3} M Rubrene 1.6×10^{-3} M

Time (sec)	20	30	40	50	60	80	100	120	140	160	180
Moles ($\times 10^3$) remaining	3.00	2.75	2.56	2.39	2.31	2.08	1.91	1.81	1.73	1.66	1.62

[†]Followed by infrared at 1780 cm^{-1}

oxide and rubrene reaction concentrations. Figure 10 plots the data of Table 46, ln M (M = molar concentration of peroxide remaining) versus time (seconds). Table 47 compiles the first order rate constants obtained by the method of least squares.

Thermal Decomposition of Bicyclo[3.1.0]hexanediacyl Peroxide (9).

In 30-40 mg batches, a total of 100 mg of solid peroxide (9) was heated in a vacuum until explosive decomposition occurred. The volatile products were collected into a cold trap containing enough solvent (∿ 0.5 ml) for vpc or nmr analysis. A weighed amount of n-octane was added to those samples subjected to vpc analysis.

1. Vpc Analysis of Pyrosylate.

Collection into hydrocarbon solvents of hexane, decane, cyclohexane, or benzene yielded similar vpc traces (DBT, 25°C). All peaks were identified by coinjection with authentic samples and GC-MS (molecular weight only) except methylenecyclopentene (74) which was isolated as described below. All authentic samples were commercially available except bicyclo[3.1.0]hexane (72) and bicyclo[3.1.0]hex-2-ene (73) which were independently prepared as described below.

Figure 10. Reaction of Diphenoyl Peroxide (12) with Rubrene

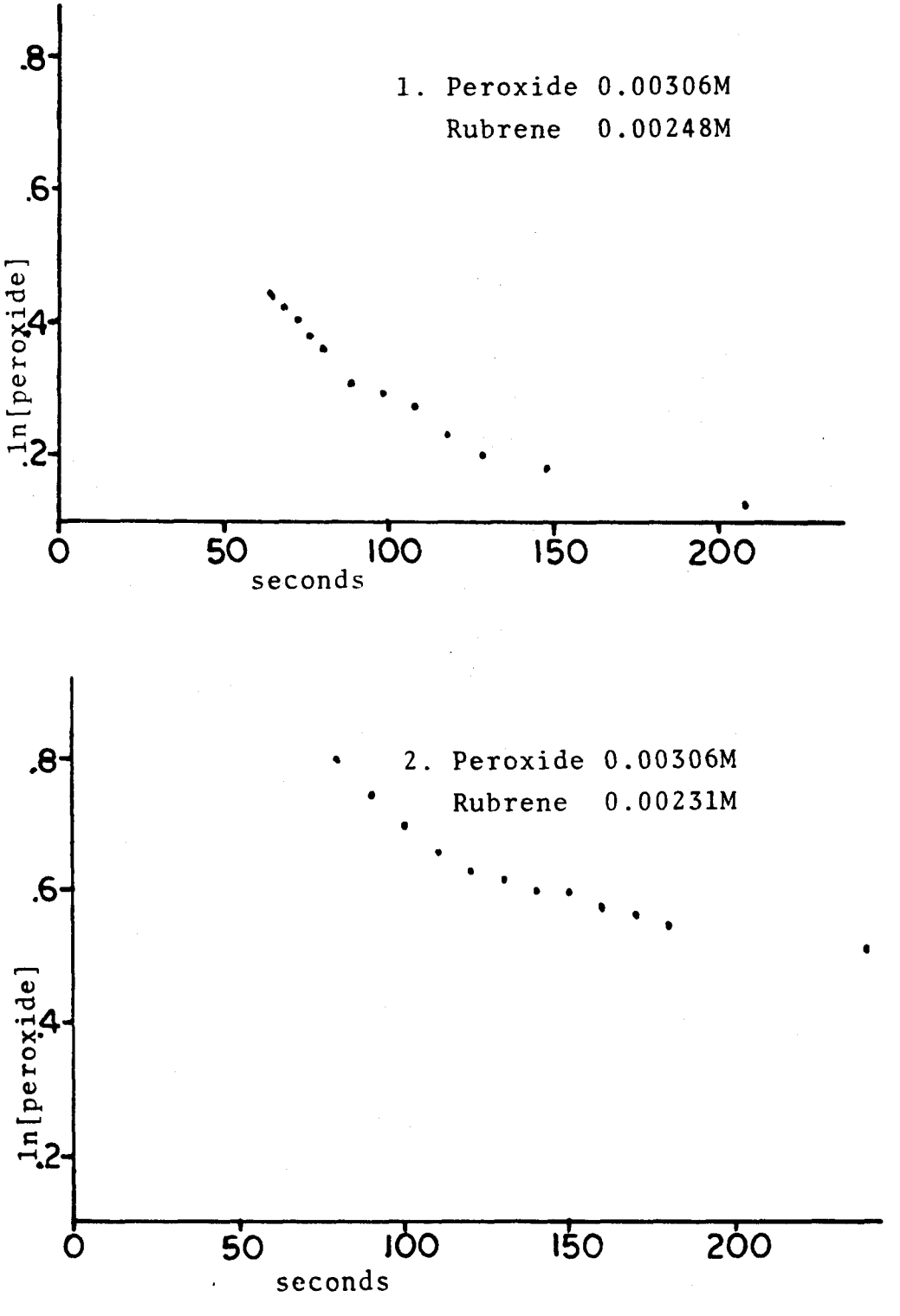


Figure 10.-continued

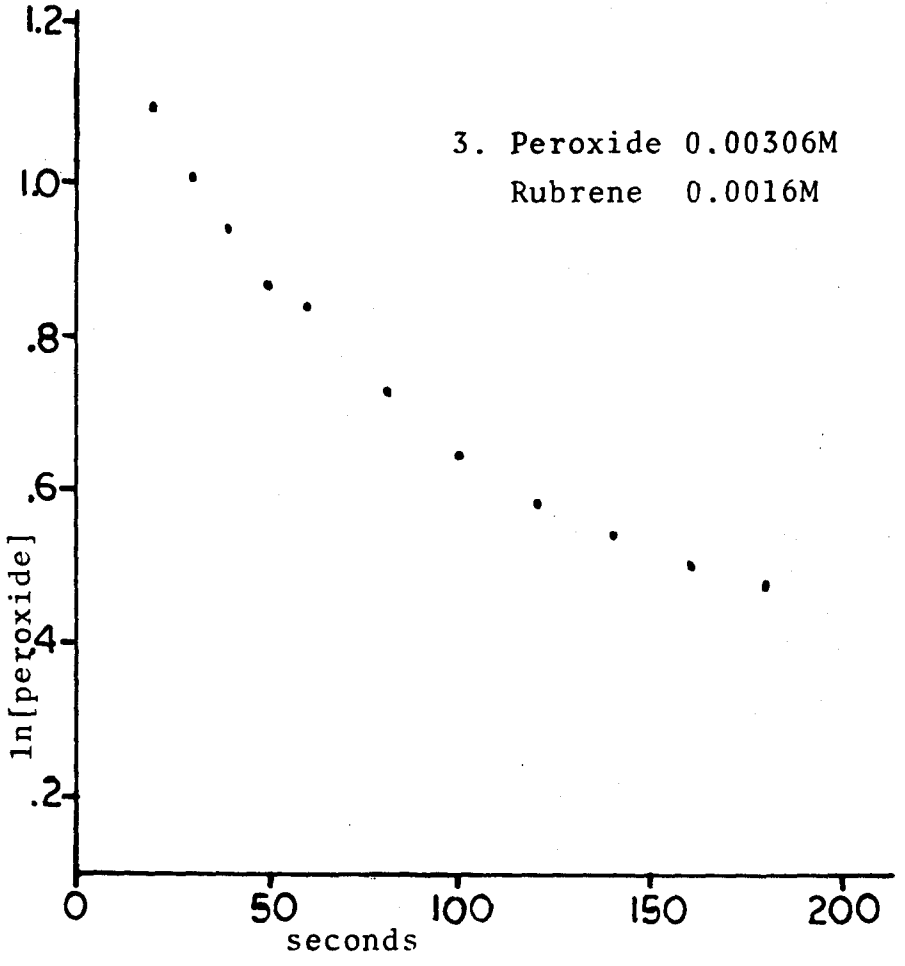


Table 46. Observed First Order and Second Order Rate Constants for the Reaction of Diphenoyl Peroxide (12) with Rubrene

	Run 1			Run 2		Run 3		
	0-80sec	0-120sec	all pts.	0-120sec	all pts.	0-80sec	0-120sec	all pts.
$k_{obs}(x10^3)$[a]	10.0	3.82	2.30	4.23	1.66	10.0	4.97	3.78
r^2[b]	1.00	0.98	0.88	0.99	0.82	0.98	0.97	0.95
k_2[c]	4.03	1.54	0.927	1.83	0.719	6.25	3.11	2.36

[a] k_{obs} calculated by the method of least squares from data in Table 46 plotted as ln M (moles remaining) versus time (seconds)

[b] r^2 = least squares fit

[c] $k_2 = k_{obs}$/concentration rubrene

Table 48 lists relative retention times and absolute yields of the products as determined by analytical vpc (DBT, 25°C) against n-octane. Also shown are the products after storage for one day at 0°C.

Preparative vpc (DBT, 25°C) allowed isolation of the largest peak (RRT=0.76 in Table 48) identified as methylenecyclopentene (74);[102] nmr (C_6D_6) δ 6.07 (d, 2, ring = C<u>H</u>), 4.87 (d, 2, methylene C<u>H</u>$_2$), and 2.31 ppm (m, 4, C<u>H</u>$_2$). Hydrogenation over platinum oxide with one atmosphere of hydrogen for 3 hr yielded only methylcyclopentane as determined by analytical vpc (DBT, 25°C).

2. <u>Hydrogenation of Pyrosylate</u>.

The crude pyrosylate (0.5 ml of n-hexane) was placed over 4 mg platinum oxide and allowed to stir 3 hr at 0°C under 1 atmosphere of hydrogen. Table 49 lists the products as determined by vpc (DBT, 25°C).

3. <u>Nmr of Pyrosylate (-30°C)</u>.

A Fourier transform nmr was taken at -30°C of the twice distilled pyrosylate in benzene-d_6, Figure 11. In addition to those peaks due to hexane (δ 1.30 and 1.00 ppm) and methylenecyclopentene (δ 6.17, 4.87, and 2.50-2.30 ppm) three additional peaks were located at δ 2.40 (multiplet, J = 4.0Hz) 1.97 (triplet, J = 4.0Hz) and 0.61 ppm (singlet). Cut and weigh integration showed the latter two peaks to be equal in size.

Figure 11. NMR (-30°C) of Pyrosylate of Peroxide (9)

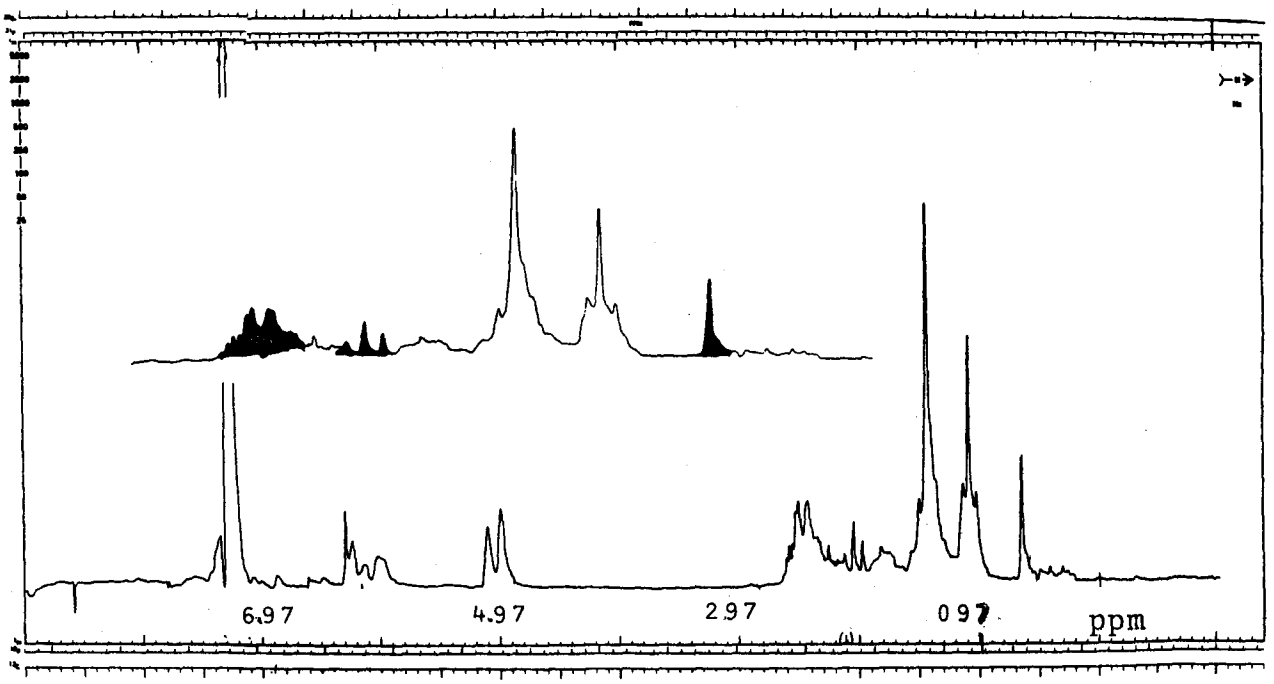


Table 48. Products from the Thermal Decomposition of Bicyclo[3.1.0]hexane diacyl Peroxide (9).[†]

Compound	RRT	% Yield Immediate analysis	% Yield Analysis after 24 hr at 0°C
Methylcyclopentane	0.23	0	0
Cyclohexane	0.33	0.35	0.39
Bicyclo[3.1.0]hexane (72)	0.45	1.9	2.0
Bicyclo[3.1.0]hex-2-ene (73)	0.49	0	0
Cyclohexene	0.51	2.0	0.35
1,3-cyclohexadiene	0.60	1.9	1.3
Methylenecyclopentane (74)	0.76	11.3	1.1
Benzene	1.00	2.3	2.3
1,4-cyclohexadiene	1.08	0	0
Octane	1.20	---	---

[†]Analyzed by vpc (DBT, 25°C) against n-octane added as internal standard.

Table 49. Products from the Hydrogenation of the Pyrosylate of (9)

Compound	Ratio product/n-octane before H_2	after H_2
Methylcyclopentane	0	0.43
Cyclohexane	0	0.038
Bicyclo[3.1.0]hexane (72)	0.035	0.040
Cyclohexene	0.031	0
1,3-Cyclohexadiene	0.023	0.019
Methylenecyclopentene	0.255	0
Benzene	0.045	0.027

Bicyclo[3.1.0]hexane (72).[100]

Zinc-copper couple was prepared by slowly adding zinc (35g, 30 mesh) into 75 ml of refluxing glacial acetic acid containing 0.5g cupric acetate. After addition was complete, the blue color of cupric acetate disappeared and a reddish-brown solid had formed, the acetic acid was decanted off. The zinc-copper couple was washed several times with glacial acetic acid and then ether. The freshly prepared couple was placed into a 250 ml three-necked round bottom flask containing 100 ml ether and 10 ml diiodomethane. Cyclopentene (20.0g, 0.29 mol) and an additional 20 ml diiodomethane (total 30 mls, 0.37 mol)

were slowly added over 2-3 hr. The reaction was allowed to gently reflux (with occasional heating from a heat lamp) for 15 hr. The ethereal solution was decanted off the zinc-copper couple, washed with cold 1N hydrochloric acid, dried (K_2CO_3), and concentrated. The remaining oil was distilled and a pure sample obtained by preparative vpc (SE-30, 120°C); nmr ($CDCl_3$) δ 1.90-1.15 (m, 8, cyclopentane $C\underline{H}_2$ and bridgehead $C\underline{H}$) and 0.5-0.0 ppm (m, 3, cyclopropane $C\underline{H}_2$).

Bicyclo[3.1.0]hex-2-ene (73).[101]

Freshly cracked cyclopentadiene (13.2g, 0.20 mol) was allowed to react in a 250 ml pressurebottle with 100 ml of a saturated ethereal solution of diazomethane (generated from 10.0g, 0.1 mol N-nitrosomethylurea) for 2 days at 25°C. The ether was removed at reduced pressure and the remaining oil distilled at 150°C (∿ 25 mm) yielding 140 mg of a sample containing dicyclopentadiene and the desired azo compound. This was pyrolyzed at 160°C for 40 min in a sealed tube. Besides dicyclopentadiene, only one major peak could be detected by analytical vpc (DBT, 25°C). This was obtained pure by preparative vpc (DBT, 100°C): nmr ($CDCl_3$) δ 5.95 (m, 1, =CH), 5.40 (m, 1, =CH), 2.50 (m, 1, $C\underline{H}$-H), 2.10 (m, 1, $C\underline{H}$-H), 1.75 (m, 1, allylic ring junction CH), 1.50 (m, 1, ring junction $C\underline{H}$), 0.85

(m, 1, cyclopropyl CH) and -0.2 ppm (m, 1, cyclopropyl CH). Hydrogenation (PtO, 1 atm H_2) in n-hexane yielded pure bicyclo[3.1.0]hexane (72).

Photolysis of Bicyclo[3.1.0]hexane diacyl Peroxide (9).

Peroxide (9) (72 mg) was placed in a nmr tube with 0.5 ml dichloromethane-d_2, and sealed in vacuo. Irradiation for 30 min at -60°C followed by 30 min at 0°C showed no decomposition of starting material by nmr.

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Abstracts of Propositions

1. A study of the mechanism of reductive elimination from metallocyclopentanes (to cyclobutanes) is proposed. Preparation of several stereochemically labelled platinum, nickel, and titanium cyclopentanes is proposed.

2. A synthesis to a new class of compound, α-carbonates (1,3-dioxetanones), is proposed. The proposed synthesis is versatile enough to allow a variety of R groups to be incorporated at C-2. A study of the decomposition of α-carbonates is proposed.

3. The preparation of several metallocyclobutanes and the study of their decomposition pathways is proposed.

4. The reduction of carbon dioxide to carbon monoxide on the surface of a metal is proposed. A catalytic cycle for the reduction of carbon dioxide to methanol is considered.

5. The study of the reaction of metal-carbenes with organic carbonyl compounds is proposed. Using electrophilic metal-carbenes, a route to "ketone metathesis" will be examined.