Syntheses and Decomposition of *meso*- and *dl*-2,3-Dimethylsuccinyl and *cis*- and *trans*-1,2-Hexahydrophthaloyl Peroxides[1,2]

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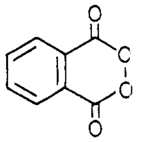
The thermal decomposition of *cis*- and *trans*-1,2-hexahydrophthaloyl peroxides (**4** and **5**, respectively) in dichloromethane affords cyclohexene in 27 and 32% yields, respectively. Similarly, the thermal decomposition of **4** and **5** in methanol affords cyclohexene (30%) and trace quantities of 1-methoxycyclohexane (**15**) and 3-methoxycyclohexene (**16**). No evidence for the generation of *trans*-cyclohexene was found. Cis and trans peroxides **4** and **5** undergo decomposition in the presence of triphenylphosphine and some aromatic hydrocarbons. Upon direct irradiation peroxides **4** and **5** afford cyclohexene in 40% yield. The thermal decomposition of *meso*- and *dl*-2,3-dimethylsuccinyl peroxides (**6** and **7**, respectively) affords *trans*- and *cis*-2-butenes in similar ratios (2.2). This is different from the reported braching ratio of triplet 2-butene (1.02). Meso peroxide **6** on thermal decomposition at 92 °C in dichloromethane affords *trans*- and *cis*-2-butenes and *threo*- and *erythro*-2,3-dimethylpropiolactones (**30** and **29**) in ratios of 2.2:1.0:0.3:0.1, respectively. *dl* Peroxide **7** on thermal decomposition at 92 °C in dichloromethane affords *trans*- and *cis*-2-butenes and *threo*- and *erythro*-2,3-dimethylpropiolactones (**30** and **29**) in ratios of 2.1:1.0:0.4:0.1. The intermediacy of rapidly equilibrating carboxy biradicals **32** and **33** or dicarboxy biradicals **34** and **35** that fragment to the same set of carboxy biradicals **32** and **33** is sufficient to explain the data. The thermal decomposition of meso and *dl* peroxides **6** and **7** in methanol affords 2-butenes as the major products and small amounts (2–4%) of methyl ethers, 2-methoxybutane (**39**) and 2-methoxy-3-butene (**38**). Irradiation of *cis*- and *trans*-2-butenes in methanol affords trace quantities of methyl ethers **38** and **39**. Meso and *dl* peroxides **6** and **7** undergo decomposition in the presence of triphenylphosphine and aromatic hydrocarbons. The relative reactivities of induced peroxide decomposition with aromatic hydrocarbons are rubrene > perylene > diphenylanthracene. *dl*-2,3-Dimethylsuccinyl peroxide (**7**) emitted faintly visible light in the dark in the presence of rubrene. Direct irradiation of meso peroxide **6** affords *trans*- and *cis*-2-butenes and *threo*- and *erythro*-2,3-dimethylpropiolactones (**30** and **29**) in ratios of 2.5:1.0:0.1:0.02. Direct irradiation of *dl* peroxide **7** affords *trans*- and *cis*-2-butenes, *threo*-**30**, and *erythro*-**29** in ratios of 1.9:1.0:0.3:0.03.

Thermal routes for the generation of electronically excited states of simple alkenes are unknown. Thermochemical estimates[4] suggest that the thermal fragmentation of succinyl peroxides may be an energy sufficient reaction to populate the π,π^* triplet of the corresponding alkene product (Scheme I).

The mechanism of the decomposition of succinyl peroxides is not known, and only a few examples of any six-membered cyclic diacyl peroxides exist.[5-8] The syntheses and decompositions of phthaloyl peroxide (1)[6a,b] and phenylmaleoyl peroxide (2)[7] were reported in 1955 and 1973, respectively.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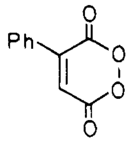
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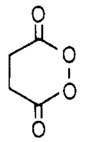
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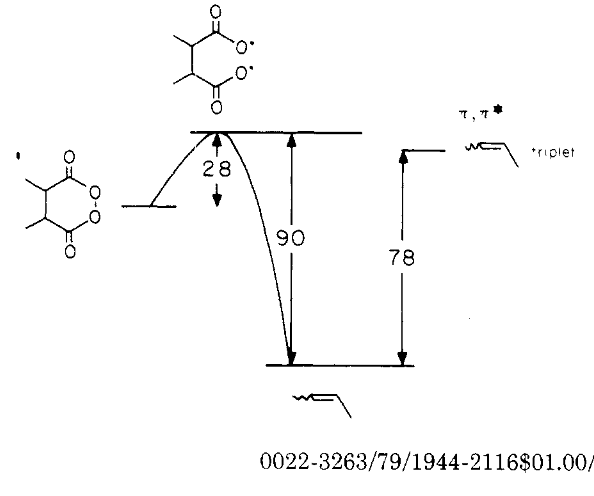
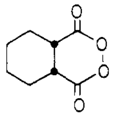
Succinyl peroxide (3) was reported in 1951, but neither spectral data nor decomposition chemistry were given.[5]

Scheme I



We describe here our recent efforts with regard to the syntheses, characterization, and thermal decomposition of *cis*- and *trans*-1,2-hexahydrophthaloyl peroxides (**4** and **5**, respectively) and *meso*- and *dl*-2,3-dimethylsuccinyl peroxides (**6** and **7**, respectively). Our initial goals were aimed at exploring (a) their ease (or difficulty) of synthesis which will bear on their suitability as precursors to alkenes by thermal or photochemical routes, (b) the stereochemistry of the decomposition products as this relates to mechanism, and (c) the induced decomposition of these six-membered cyclic peroxides by aromatic hydrocarbons.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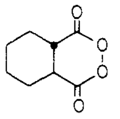
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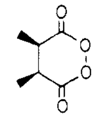
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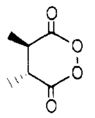
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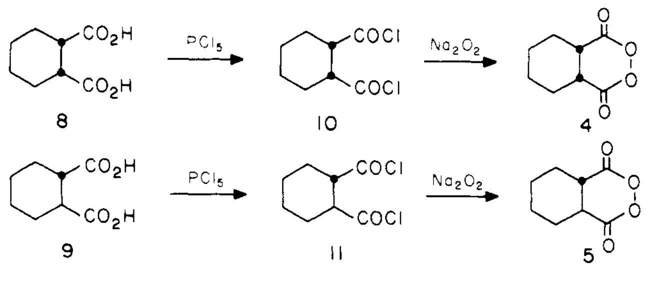
Results and Discussion

Syntheses of *cis*- and *trans*-1,2-Hexahydrophthaloyl Peroxides (4 and 5). *cis*- and *trans*-Hexahydrophthaloyl peroxides (**4** and **5**) were prepared by successive treatment of the corresponding cis and trans dicarboxylic acids, **8** and **9**, respectively (or the anhydrides), with phosphorus pentachloride and an aqueous buffered solution of sodium peroxide (Scheme II).[6b] The isomeric purities of the cis and trans diacid

Scheme II



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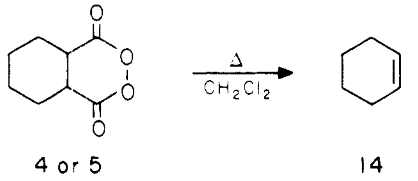
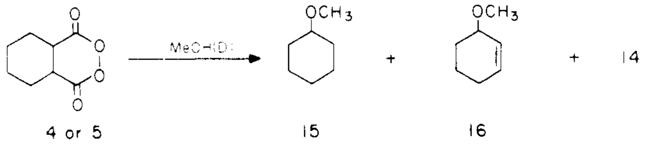
chlorides **10** and **11** were >95%, determined by analytical vapor phase chromatography (VPC) of the corresponding *cis*- and *trans*-dimethyl 1,2-hexahydrophthalates (**12** and **13**) obtained from the reaction of the diacid chlorides with methanol. The white crystalline cis and trans diacyl peroxides, **4** and **5**, were obtained in 28% yield after precipitation from *n*-hexane. *These solid peroxides decomposed rapidly and often explosively when subjected to shock or rapid heating.* Safety measures and caution should be taken when working with these potentially hazardous materials. They are well-behaved in solution and are found to be soluble in several organic solvents: chloroform, dichloromethane, benzene, tetrahydrofuran, and acetonitrile. The NMR spectra of these peroxides were consistent with their assigned structure. Typical dried solid samples contained small amounts of *n*-hexane (~12%). Two strong carbonyl stretches were observed which are characteristic of these peroxides, 1803 and 1775 cm^{-1} for the cis isomer **4** and 1800 and 1775 cm^{-1} for the trans isomer **5**, and easily distinguishes them from the corresponding anhydrides and acid chlorides. Molecular weight determination by the method of freezing point depression in benzene showed the peroxides to be monomeric.[9]

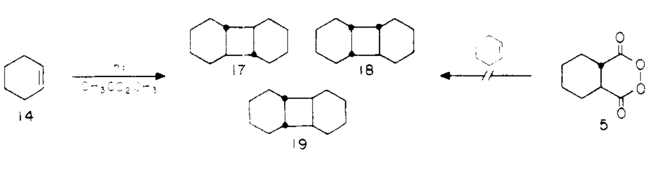
Decomposition of *cis*- and *trans*-Hexahydrophthaloyl Peroxides (4 and 5). The thermal decomposition of *cis*- and *trans*-hexahydrophthaloyl peroxides (**4** and **5**) in dichloromethane at 100 °C afforded cyclohexene (**14**) as the only volatile product in 27 and 32% yields, respectively, as determined by analytical VPC. The thermal decomposition of **4** and **5** in dry methanol at 95 °C afforded cyclohexene (**14**) as the major product (30%) and trace quantities of 1-methoxycyclohexane (**15**) and 3-methoxycyclohexene (**16**) (0.5% yield).



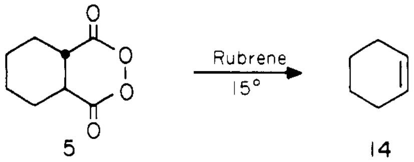


Decomposition in methanol-*O*-d_1 revealed no significant deuterium incorporation[10] as might be expected if the generation and trapping of *trans*-cyclohexene were occuring.[11]

It is known that irradiation of cyclohexene in the presence of methyl acetate affords three dimers, *trans-anti-trans*-, *cis,trans*-, and *cis-anti-cis*-tricyclo[6.4.0.$0^{2,7}$]dodecanes (**17**, **18**, and **19**, respectively).[12] In an effort to trap any transient *trans*-cyclohexene that might be generated in the hexahydrophthaloyl peroxide decompositions, the decomposition of trans peroxide **5** was carried out in neat cyclohexene. Coinjection techniques with authentic samples of the dimers on two analytical VPC columns, as well as a VPC-MS search (for *m/e* peak 164), showed no detectable trace of dimers (<1%) formed.



The reaction of peroxides **4** and **5** with triphenylphosphine or dimethyl sulfide in dichloromethane afforded the corresponding anhydrides. In the presence of some aromatic hydrocarbons[13] such as rubrene or perylene in dichloromethane



(15 °C), **4** and **5** decomposed to cyclohexene (20%). Direct irradiation of cis peroxide **4** in dichloromethane (Hanovia 450-W medium-pressure mercury arc/Pyrex) afforded cyclohexene (40%) as the only volatile product.

Syntheses of *meso*- and *dl*-2,3-Dimethylsuccinyl Peroxides (6 and 7). Diacids. A mixture of *meso*- and *dl*-2,3-dimethylsuccinic acids (**21** and **22**, respectively) was synthesized from the reaction of diethyl methylmalonate and α-bromopropionate as reported.[14] Recrystallization from concentrated HCl afforded the dimethylsuccinic diacids **21** and **22** enriched in the meso isomer **21** (>99%), mp 210 °C (lit.[14] 209 °C). Conversion of the water-soluble *dl* diacid enriched fraction to the anhydride by treatment with acetyl chloride and recrystallization from carbon tetrachloride afforded *dl*-2,3-dimethylsuccinic anhydride (**24**), mp 128 °C (lit.[14] 120–125 °C), >97% isomerically pure, analyzed by analytical VPC.

Peroxides. *meso*-2,3-Dimethylsuccinyl peroxide (**6**) was prepared by treatment of *meso*-2,3-dimethylsuccinic acid (**21**) with phosphorus pentachloride, affording the corresponding diacid chloride **27**. The freshly distilled meso diacid chloride **27** was dissolved in dichloromethane and added to an aqueous buffered solution of sodium peroxide.[6] Similarly, *dl*-2,3-dimethylsuccinyl peroxide (**7**) was prepared by successive treatment of *dl*-2,3-dimethylsuccinic anhydride (**24**) with phosphorus pentachloride and an aqueous buffered solution of sodium peroxide. The peroxides were obtained in 2–4% yields as white powders after precipitation from dichloromethane–hexane. Since *meso*- and *dl*-dimethyl succinates could be separated by analytical VPC, the isomeric purity of the meso and *dl* diacids, **21** and **22**, and the diacid chloride precursors, **27** and **28**, to the peroxides could be checked by conversion to their respective esters, **25** and **26**. Reaction of the meso and *dl* peroxides, **6** and **7**, with triphenylphosphine afforded the corresponding meso and *dl* anhydrides **23** and **24**, which could be conveniently analyzed by analytical VPC. Thus, the isomeric purity of the meso and *dl* peroxides, **6** and **7**, could be determined. Both meso and *dl* peroxides were prepared in >95% isomeric purity (Scheme III).[9]

Both peroxides were soluble in dichloromethane, chloroform, and acetonitrile and slightly soluble in tetrahydrofuran. The *dl* peroxide **7** was soluble in benzene. Both peroxides in

Scheme III

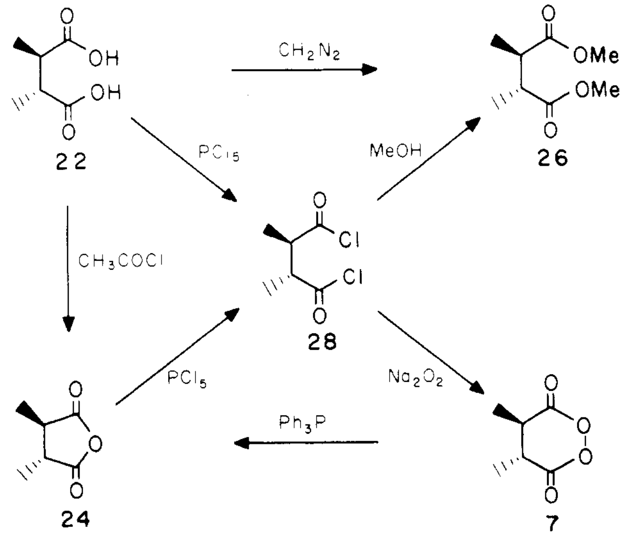


Table I. Pyrolysis of *meso*-6 and *dl*-7[a]

peroxide	temp, °C	*trans-/cis-* 2-butenes
meso-6	92	2.2
meso-6	278	2.1
meso-6	357	1.7
dl-7	92	2.2
dl-7	278	1.6
dl-7	357	1.6

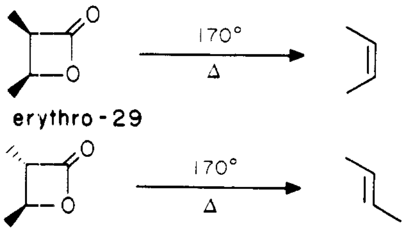
[a] Yields and ratios were determined by analytical VPC (13% DBT, 25 °C) using 2-methylbutane as an internal standard.

solid form decompose explosively when heated, and often they detonated upon drying. The peroxides were particularly difficult to get out of solution, especially the *dl* isomer, and were sometimes prepared in situ as stock solutions in dichloromethane. The NMR spectra of the peroxides are consistent with their assigned structures. Two strong carbonyl stretching frequencies are characteristic of these peroxides (meso 1810 and 1778 cm^{-1}, and *dl* 1811 and 1792 cm^{-1}). Attempts at carrying out a molecular weight determination by the method of freezing point depression in benzene were fruitless. The meso peroxide was not sufficiently soluble in benzene, and only milligram quantities of *dl* were available, insufficient to determine molecular weight cryoscopically. Their similar synthetic origin, similar infrared spectra, and similar decomposition behavior to the monomeric 1,2-hexahydrophthaloyl peroxide suggest that they may be likewise monomeric. Until improved methods of syntheses of these peroxides are developed we will have to interpret the stereochemical data that follow under the constraint that molecular weights of these very labile species are still unknown.

Synthesis of *erythro*- and *threo*-2,3-Dimethylpropiolactones (29 and 30). A mixture of *erythro*- and *threo*-2,3-dimethylpropiolactones (29 and 30, respectively) was synthesized by treatment of 3-hydroxy-2-methylbutanoic acid (31) with benzenesulfonyl chloride in ether at 25 °C for 24 h.[15]

31 29 + 30

The isomers were separated and isolated by preparative VPC. The infrared (1820 cm^{-1}) and NMR spectra were consistent with the β-lactone structure.[16] The isomeric purity of both isomers was >98% as shown by analytical VPC. β-Lactones have been shown to decompose stereospecifically with syn elimination to afford olefin products.[15] The isomers were collected into *n*-octane as they eluted from the gas chromatograph and then were pyrolyzed in a sealed tube for 3.8 h at 171 °C. The first eluting β-lactone peak afforded 99.7% pure

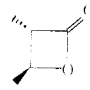
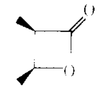


erythro-29
threo-30

trans-2-butene after pyrolysis and was assigned the threo configuration. The second eluting peak afforded 98.7% pure *cis*-2-butene after pyrolysis and was assigned the erythro configuration.

Decomposition of *meso*- and *dl*-2,3-Dimethylsuccinyl Peroxides (6 and 7). In Dichloromethane and Tetrahydrofuran. Solutions of 6 and 7 in dichloromethane or THF (10^{-3} M) were heated at 92 °C for 4 min. The reaction was complete as determined by examination of the peroxide carbonyl region (1800–1775 cm^{-1}) in the infrared. The ratios of *trans-/cis*-2-butenes are given in Table I. Yields of 2-butenes were typically between 40–60%, as determined by analytical VPC. These peroxides were also subjected to gas phase pyrolyses at 278 and 357 °C in a vacuum flow oven.

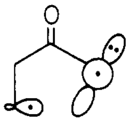
Table II. Ratios of *cis*- and *trans*-2-Butenes and *erythro*- and *threo*-2,3-Dimethylpropiolactones 29 and 30 from the Thermal Decomposition of Peroxides 6 and 7 at 92 °C[a]

			 *threo*-30	 *erythro*-29
meso-6	61	28	8	3
dl-7	60	28	10	2

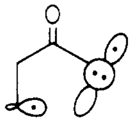
[a] Overall yields were 50–70%. Yields were determined by analytical VPC (2-butenes, 13% DBT, 25 °C; β-lactones, 10% PMPE, 90 °C) with 2-methylbutane and dodecane as internal standards.

The similarity in the stereochemistry of the *cis*- and *trans*-2-butene products suggests a common intermediate or set of intermediates. Thermochemical estimates[4] suggest that there is sufficient energy released in these fragmentations to populate the triplet state of 2-butene ($E_T \approx 78$ kcal mol^{-1}). The kinetics of the cis-/trans-photosensitized isomerization of 2-butene in the gas phase reveal a branching ratio of triplet 2-butene of 1.02.[17] The lack of correspondence for the trans/cis ratios between the benzene-sensitized triplet 2-butene (1.02) and the peroxide decomposition data presented here (2.2) demands that the triplet, if formed at all, cannot be the only intermediate in this reaction. The yields and stereochemistry of the *cis*- and *trans*-2-butenes and *erythro*- and *threo*-β-lactone products from the thermal decomposition of meso and *dl* peroxides 6 and 7 in solution at 92 °C are given in Table II. The *erythro*- and *threo*-β-lactones 29 and 30 were difficult to analyze accurately by analytical VPC due to tailing of the sensitive β-lactones on the analytical column. However, the loss of stereochemical integrity in the β-lactone products from the thermal decomposition of the peroxides 6 and 7 is high, and within experimental error we find that the erythro/threo ratios from the meso and *dl* peroxide 6 and 7 decompositions are the same. The *cis*- and *trans*-2-butenes and the *erythro*- and *threo*-β-lactones 29 and 30 were shown not to isomerize under the reaction conditions.

One explanation of the data suggests the intermediacy of carboxy biradicals 32 and 33 which decompose to 2-butenes and β-lactones in a ratio of about 8:1. One might imagine different possible electronic states of the carboxy biradicals 32 and 33, for example, 3π and 4π, having different behavior.[18]



3π

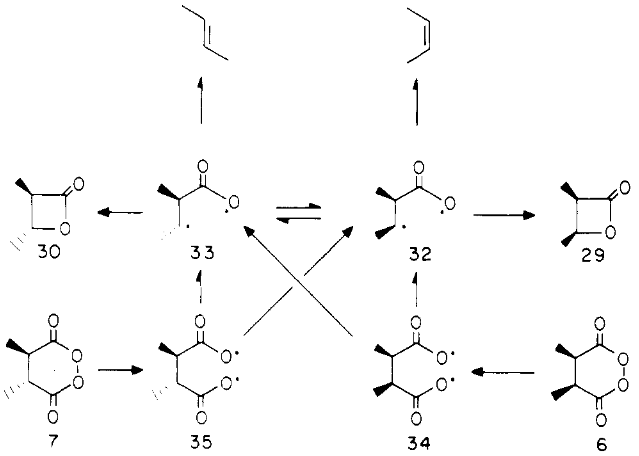


4π

For the 4π state, the cleavage and closure pathways might be more competitive with rotation than the 3π state. The relative energies of the 3π and 4π states are unknown.

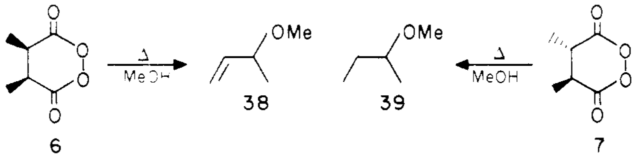
The intermediacy of rapidly equilibrating carboxy biradicals 32 and 33, with the properties k(rotation) $\gg$ k(cleavage) > k(closure), is sufficient to explain the similar product ratios from both meso and *dl* peroxides, 6 and 7 (Scheme IV).

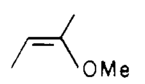
Scheme IV



However, reasonable precursors to the carboxy biradicals 32 and 33 are the meso and *dl* dicarboxy biradicals 34 and 35. If both the meso and *dl* dicarboxy biradicals 34 and 35 fragment to the same set of carboxy biradicals 32 and 33, then the carboxy biradicals 32 and 33 could also have the properties $k(\text{rotation}) \leq k(\text{cleavage}) > k(\text{closure})$. The data do not allow this distinction.

In Methanol. The thermal decomposition of meso and *dl* peroxides, 6 and 7, in methanol at 60 °C afforded 2-butenes as the major products (trans/cis ratio $\approx$2.3) and small amounts (2–4%) of methyl ethers 38 and 39. Coinjection with authentic samples and VPC–MS analysis identified these compounds as 2-methoxybutane (39) and 2-methoxy-3-butene (38). (*E*)- and (*Z*)-2-methoxy-2-butenes (40 and 41) and 2-methoxy-1-butene (42) were independently synthesized.[19] However, they were not separable from the methanol solvent under our analytical VPC conditions, and their presence or absence in the reaction mixture is unknown. The reason for the appearance of the 2-methoxybutane (39) and 2-methoxy-3-butene (38) products is unclear. One possibility is radical–cation chemistry. Kropp and co-workers[20] have shown that the direct irradiation of 2,3-dimethylbutene in methanol affords high yields of methyl ethers. Similarly, he has shown that direct irradiation of 2-methyl-2-butene in methanol affords the corresponding methyl ethers, but in lower yields. Kropp has found that the efficiency of methyl ether formation decreases with decreasing substitution on the olefin. In agreement with this, we find that irradiation of *cis*- and *trans*-2-butenes in methanol affords trace quantities of 2-methoxybutane (39) and 2-methoxy-3-butene (38).

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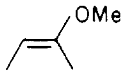
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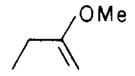
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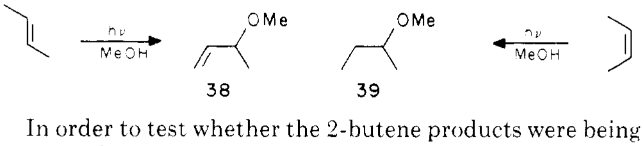
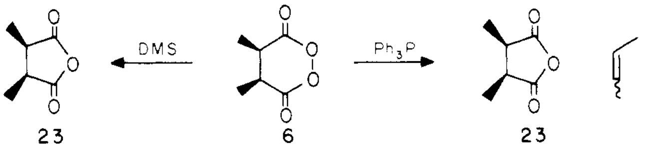


In order to test whether the 2-butene products were being converted to methyl ethers under the reaction conditions, *cis*- and *trans*-1,2-hexahydrophthaloyl peroxides (4 and 5) were allowed to decompose in the presence of a large excess of *cis*-2-butene in methanol. No methyl ethers, 38 and 39, corresponding to the reaction of 2-butene were observed. Similarly, the thermal decomposition of meso peroxide 6 in the presence of a large excess of cyclohexene in methanol produced methyl ethers 38 and 39, but did not yield any cyclohexyl methyl ethers, 15 and 16. In addition, decomposition of the 1,2-hexahydrophthaloyl peroxides 4 and 5 in the presence of freshly prepared samples of *erythro*- and *threo*-2,3-dimethylpropiolactones (29 and 30) in methanol afforded no 2-methoxybutane (39) or 2-methoxy-3-butene (38). We conclude that the methyl ethers are not being formed from subsequent transformations of 2-butene or β-lactone but apparently result from some intermediates, perhaps radical cations, generated in the cyclic peroxide fragmentation reactions.

Triphenylphosphine and Dimethyl Sulfide. Addition of excess triphenylphosphine (or dimethyl sulfide) to *meso*- and *dl*-2,3-dimethylsuccinyl peroxides (6 and 7), 0.02 M in dichloromethane, showed by infrared analysis (1775 cm^{-1}) complete disappearance of the peroxide in 20 min and appearance of carbonyl absorptions characteristic of the corresponding anhydride (1865 and 1790 cm^{-1}). Meso peroxide 6 (>99% isomerically pure) in the presence of triphenylphosphine afforded an $\sim$65% yield of 99% isomerically pure *meso*-2,3-dimethylsuccinic anhydride (23) and $\sim$46% 2-butenes (trans/cis ratio 2.1). In the reaction of meso peroxide 6 with dimethyl sulfide, formation of anhydride was the major pathway.



Aromatic Hydrocarbons. Meso and *dl* peroxides 6 and 7 underwent induced decomposition in the presence of aromatic hydrocarbons. The disappearance of peroxide was followed by infrared analysis. In a typical reaction, 0.1 M peroxide in dichloromethane at 15 °C was allowed to react with $\sim$0.04 M rubrene, perylene, or diphenylanthracene (DPA). Disappearance of the peroxide was observed with each of these aromatic hydrocarbons with apparent relative reactivities of rubrene > perylene > DPA. The *dl*-2,3-dimethylsuccinyl peroxide (7) emitted faintly visible light in a dark room in the presence of rubrene (R). This is similar to Schuster's[13] observations of light emission from diphenoyl peroxide and the proposed CIEEL mechanism. By analogy to Schuster's work,[13] a similar mechanism for the *dl* peroxide is shown in Scheme V. The relative reactivities of rubrene, perylene, and DPA with the *dl* peroxide are in the same order and direction as found by Schuster for the aromatic hydrocarbon induced decomposition of diphenoyl peroxide. Schuster was able to correlate the bimolecular one-electron transfer rate to diphenoyl peroxide with the one-electron oxidation potential of the corresponding hydrocarbons. In addition, we find that disappearance of *dl* peroxide 7 in the presence of rubrene is faster than the meso isomer 6. This suggests that one may be able to correlate differences in reduction potentials of different peroxides with differences in bimolecular rates of reduction in the presence of a single aromatic hydrocarbon.

Scheme V

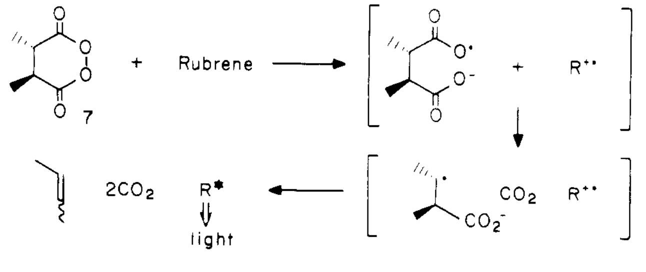
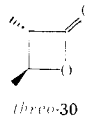
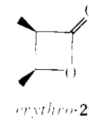


Table III. Direct Irradiation of Meso and *dl* Peroxides 6 and 7

peroxide			 *threo*-30	 *erythro*-29
meso-**6**[b]	69	28	3	0.5
dl-**7**[c]	53	39	8	0.8

[a] 0 °C, in CH_2Cl_2. [b] Absolute yields were between 43 and 48%. [c] Absolute yields were between 30 and 40%.

Photochemical. Direct irradiation of the meso and *dl* peroxides **6** and **7** (0.06–0.10 M) in dichloromethane (Hanovia 450-W medium-pressure mercury arc/Pyrex) afforded *cis*- and *trans*-2-butenes as the major products and small quantities of β-lactones **29** and **30** (Table III). The ratios did not change in the presence of added base (sodium carbonate). Controls showed that under the irradiation conditions the β-lactones **29** and **30** did not decompose or isomerize.

Summary

We have described here our initial exploratory efforts at the synthesis and characterization of the thermal, photochemical, and induced decompositions of six-membered cyclic diacyl peroxides. In general we find that the reaction of the corresponding diacid chloride with an aqueous buffered solution of sodium peroxide affords the succinyl peroxides **4–7** in low yields which are difficult to get out of solution. This provides sufficient material for mechanistic studies, but not enough for practical synthetic exploitation. Solid peroxide obtained by precipitation from *n*-hexane decomposes violently upon heating or shock. These peroxides are soluble in several organic solvents and are well-behaved in solution. Yields of alkenes from the peroxides by thermal and photochemical routes are modest (30–40%). Identical stereochemistry in the 2-butene and 2,3-dimethylpropiolactone products from the thermal decomposition of *meso*- and *dl*-2,3-dimethylsuccinyl peroxides (**6** and **7**) suggests a *stepwise* decomposition pathway involving a common intermediate or set of intermediates. No evidence for the thermal generation of electronically excited states of alkenes from the corresponding cyclic peroxide decompositions was found. Reaction of these cyclic peroxides with triphenylphosphine and dimethyl sulfide afforded stereospecifically the corresponding anhydrides. The cyclic diacyl peroxides **4–7** underwent induced decomposition in the presence of aromatic hydrocarbons with relative rates of rubrene > perylene > diphenylanthracene. The rate of disappearance of each peroxide in the presence of rubrene was dependent on the structure of the peroxide.

Experimental Section

All reactions of diacyl peroxides were carried out in glassware that had been washed with methanol–disodium ethylenediaminetetraacetic acid (EDTA), rinsed with water, and dried. Elemental analyses were performed by the Caltech analytical facility. Melting points were obtained using a Thomas-Hoover capillary melting point apparatus and are uncorrected. Proton nuclear magnetic resonance (NMR) spectra were obtained on a Varian Associates A-60A, EM-390, or XL-100 spectrometer. Carbon nuclear magnetic resonance (^{13}C NMR) spectra were obtained on a Varian Associates XL-100 spectrometer. Chemical shifts are given as parts per million (ppm) downfield from tetramethylsilane (Me_4Si) in δ units, and coupling constants are in hertz (Hz). Nuclear magnetic resonance data are reported in the following order: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), number of protons, assignment]. Infrared spectra (IR) were recorded on a Perkin-Elmer 257 grating or Beckman IR 4210 infrared spectrometer. Mass spectra were recorded on a DuPont 21-492B spectrometer. Vapor phase chromatography–spectra (VPC–MS) were obtained on a Finnegan 3200 EI mass spectrometer interfaced to a Finnegan 9500 gas chromatograph[22] or on a Hewlett Packard gas chromatograph interfaced to an EAI QUAD 300 mass spectrometer.

Table IV. VPC Columns

column designation	description
DBT	20 ft × 0.125 in., 10% dibutyl tetrachlorophthalate on 100/120 Chromosorb P A/W
Carbowax 20M	10 ft × 0.125 in., 10% Carbowax 20M on 100/120 Chromosorb W
PMPE	10 ft × 0.125 in., 10% poly-*m*-phenyl ether (6 ring) on 100/120 Chromosorb W A/W DMCS
PMPE	10 ft × 0.375 in., glass 10% poly-*m*-phenyl ether on Chromosorb W A/W DMCS
SF-96	10 ft × 0.125 in., 10% SF-96 on 100/120 Chromosorb P A/W
UCON	10 ft × 0.125 in., 10% UCON-550X on 100/120 Chromosorb W
UCON	10 ft × 0.375 in., 20% UCON-550X on 60/80 Chromosorb W

For analytical vapor phase chromatography (VPC), a Hewlett-Packard 5700A or 5720 gas chromatograph equipped with a flame ionization detector and with nitrogen carrier gas was used. The 0.125-in. packed stainless steel columns used in this instrument are listed in Table IV. Quantitative VPC analysis was accomplished using a Hewlett-Packard 3370A electronic digital integrator. For preparative VPC, a Varian Aerograph Model 920 gas chromatograph equipped with a thermal conductivity detector and with helium carrier gas was used. The 0.25- and 0.375-in. packed aluminum columns used in this instrument are listed in Table IV. Peak assignments were made by coinjection with authentic samples and/or VPC–MS analysis. Detector response for all hydrocarbons and olefins (2-butenes) was assumed to be linear. Other compounds were analyzed with respect to a weighed internal standard, and appropriate response corrections were made.

***cis*-1,2-Hexahydrophthaloyl Peroxide (4).** The freshly prepared cis diacid chloride **10** (4.88 g, 0.023 mol) obtained from the reaction of *cis*-1,2-hexahydrophthalic acid and phosphorus pentachloride was dissolved in 75 mL of dichloromethane and added dropwise at 0 °C with stirring to a solution containing 3.0 g (0.038 mol) of sodium peroxide, 3.0 g of Na_2HPO_4, and 3.0 g of NaH_2PO_4 in 75 mL of water. Stirring was continued for 3 h, 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 1.1 g (28%) of a white precipitate, the cis 1,2-peroxide **4**: IR (CH_2Cl_2) 1805 and 1780 cm^{-1} (C=O); NMR ($CDCl_3$) δ 3.10 (m, 2, CH), 2.50–1.50 (m, 8, CH_2).

***trans*-1,2-Hexahydrophthaloyl Peroxide (5).** The freshly prepared trans 1,2-diacid chloride **11** (4.12 g, 0.019 mol) obtained from the reaction of *trans*-1,2-hexahydrophthalic acid and phosphorus pentachloride was dissolved in 75 mL of dichloromethane and added dropwise at 0 °C with stirring to a solution containing 3.0 g (0.038 mol) of sodium peroxide, 3.0 g of Na_2HPO_4, and 3.0 g of NaH_2PO_4 in 75 mL of water. Stirring was continued for 3 h, 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 0.9 g (28%) of a white precipitate, the trans 1,2-peroxide **5**: IR (CH_2Cl_2) 1800 and 1775 cm^{-1} (C=O); NMR ($CDCl_3$) δ 2.90 (m, 2, CH), 2.30–1.10 (m, 8, CH_2).

***meso*-2,3-Dimethylsuccinyl Peroxide (6).** To 3.0 g of *meso*-2,3-dimethylsuccinic acid (**21**, 0.021 mol, 99.5% meso) was added 10.0 g (0.048 mol) of phosphorus pentachloride. The reaction mixture was allowed to stir at 80–90 °C for 3 h. The phosphorus oxychloride was removed at room temperature under reduced pressure. The remaining reaction mixture was added to 25 mL of ether. The precipitate was removed by filtration, and the filtrate was concentrated. This was distilled under reduced pressure to afford 2.2 g (59.2%) of *meso*-2,3-dimethylsuccinyl chloride (**27**): bp 40–50 °C (0.1 mm); IR (CH_2Cl_2) 1790 cm^{-1} (C=O); NMR ($CDCl_3$) δ 3.22 (m, 2, CH), 1.45 (d, 6, CH_3). Several drops of this freshly prepared diacid chloride (**27**) were added to 0.5 mL of methanol. The sample was shown by analytical VPC to contain the dimethyl esters, 99% *meso*-**26** and 1% *dl*-**26** (UCON, 130 °C, relative retention times 1.00 and 1.12, respectively).

The freshly prepared diacid chloride **27** (2.2 g, 0.012 mol) was dissolved in 75 mL of dichloromethane and added dropwise at 0 °C to a stirred solution of 3.0 g (0.038 mol) of sodium peroxide, 3.0 g of Na_2HPO_4, and 3.0 g of NaH_2PO_4 in 75 mL of water. Stirring was continued for 3 h, and the reaction mixture was allowed to warm to room temperature. The dichloromethane layer was separated, dried ($CaCl_2$), and concentrated. Addition of *n*-hexane afforded 65 mg (3.8%) of a white precipitate **6** which was collected by filtration: IR (CH_2Cl_2) 1810 and 1778 cm^{-1} (C=O); NMR ($CDCl_3$) δ 2.98 (m, 2, CH), 1.38 (d, 6, CH_3).

***dl*-2,3-Dimethylsuccinyl Peroxide (7).** *dl*-2,3-Dimethylsuccinic anhydride (2.7 g, 0.021 mol), recrystallized from carbon tetrachloride [mp 86–88 °C; 97.5% *dl* and 2.5% meso by analytical VPC (PMPE, 180 °C, relative retention times 1.00 and 1.30, respectively)] was added to 10.0 g (0.048 mol) of phosphorus pentachloride. The reaction mixture was allowed to stir at 80–90 °C for 3 h. The phosphorus oxychloride was removed at room temperature under reduced pressure. The remaining reaction mixture was added to 25 mL of ether. The precipitate was removed by filtration, and the filtrate was concentrated. This was distilled under reduced pressure to afford 2.9 g (78%) of *dl*-2,3-dimethylsuccinyl chloride (**28**): bp 40–50 °C (0.1 mm); IR (CH_2Cl_2) 1790 cm^{-1} (C=O); NMR ($CDCl_3$) δ 3.34 (m, 2, CH), 1.32 (d, 6, CH). Several drops of this freshly prepared diacid chloride **28** were added to 0.5 mL of methanol. The sample was shown by analytical VPC to contain the dimethyl esters. 2.2% *meso*-**26** and 97.8% *dl*-**26** (UCON, 130 °C).

The freshly prepared diacid chloride **28** (2.9 g, 0.016 mol) was dissolved in 75 mL of dichloromethane and added dropwise at 0 °C to a stirred solution of 3.0 g (0.038 mol) of sodium peroxide, 3.0 g of Na_2HPO_4, and 3.0 g of NaH_2PO_4 in 75 mL of water. Stirring was continued for 3 h, and the reaction mixture was allowed to warm to room temperature. The dichloromethane layer was separated, dried ($CaCl_2$), and concentrated. Additions of *n*-hexane afforded 40 mg (1.7%) of a white precipitate **7** which was collected by filtration: IR (CH_2Cl_2) 1811 and 1782 cm^{-1} (C=O): NMR ($CDCl_3$) δ 3.05 (m, 2, CH), 1.35 (d, 6, CH_3).

Cryoscopic Molecular Weight Determination in Benzene.[21] **(a)** *cis*- and *trans*-1,2-Hexahydrophthaloyl peroxides (**4** and **5**) were taken up in benzene (7.6 mg of **4** in 0.4483 g of benzene and 21.9 mg of **5** in 0.4777 g of benzene). Temperature was measured by an iron–constantan thermocouple. Freezing point curves were plotted by a Hewlett-Packard recorder interfaced to a millivolt meter. Calibration was performed on ferrocene. The molecular weights obtained were 195 ± 26 for *cis*-4 and 207 ± 19 for *trans*-**5** (calcd 170).

(**b**) In a second run, 19.4 mg of cis and 16.7 mg of trans peroxides 4 and **5**, respectively, were prepared in 0.9471 and 1.0189 g of benzene, respectively. Readings were taken in millivolts of the freezing point of benzene vs. ice water as determined by an iron–constantan thermocouple. Data were obtained from a digital readout millivolt meter, and the freezing point depression curves were plotted by hand. Calibration was performed on *dl*-2,3-dimethylsuccinic anhydride (**24**). The molecular weights determined were 214 ± 68 for both peroxides 4 and **5** (calcd 170).

***erythro*- and *threo*-2,3-Dimethylpropiolactones (29 and 30).** 3-Hydroxy-2-methylbutanoic acid (1.0 g, 8 mmol), obtained from the reaction of lithium diisopropylamide, propionic acid, and acetaldehyde, was taken up in 80 mL of dry ether. This was allowed to react with 1 mL (8.6 mmol) of benzenesulfonyl chloride in the presence of excess sodium carbonate at 25 °C for 24 h. The reaction mixture was filtered and concentrated to afford a yellow oil which contained both isomeric *erythro*- and *threo*-2,3-dimethylpropiolactones (4%) as shown by analytical VPC (PMPE, 80 °C, relative retention times 1.00 and 1.36). The first eluted isomer was isolated by preparative VPC (PMPE, 105 °C), collected in 100 μL of *n*-octane, sealed 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 that the only volatile products were 99.7% *trans*-2-butene and 0.3% *cis*-2-butene. Therefore, the first eluted β-lactone was assigned as *threo*-2,3-dimethylpropiolactone (**30**): IR ($CDCl_3$) 1820 cm^{-1} (C=O); NMR ($CDCl_3$) δ 4.75 (m, 1, CHOCO), 3.75 (m, 1, CHCO), 1.40 (d, 3, J = 6.0 Hz, C**H**$_3$CHO), 1.22 (d, 3, J = 7.5 Hz, C**H**$_3$CHCO); exact mass (15 eV) calcd for $C_5H_8O_2$ *m/e* 100.052, obsd *m/e* 100.052.

The second eluted isomer was isolated by preparative VPC (PMPE, 105 °C), taken up in 100 μL of *n*-octane, sealed in a base-washed 6-mm o.d. Pyrex tube, and heated to 171 °C. Analysis by analytical VPC (DBT, 25 °C) showed that the only volatile products were 98.7% *cis*-2-butene and 1.3% *trans*-2-butene. This second eluted β-lactone was assigned as *erythro*-2,3-dimethylpropiolactone (**29**): IR ($CDCl_3$) 1820 cm^{-1} (C=O): NMR ($CDCl_3$) δ 4.35 (d of q, 1, J = 7.5 Hz, CH_3C**H**COO), 1.60 (d, 3, J = 6.0 Hz, CH_3CHO), 1.45 (d, 3, J = 7.5 Hz, CH_3CHCO); exact mass (15 eV) calcd for $C_5H_8O_2$ *m/e* 100.052, obsd *m/e* 100.051.

Thermal Reactions. Cis and Trans Peroxides 4 and 5. Stock solutions of peroxides *cis*-**4**, 0.005 M, and *trans*-**5**, 0.004 M, were each prepared in dichloromethane with *n*-heptane weighed and added as an internal standard. Aliquots (100 μL) were prepared in base- and EDTA-rinsed 6-mm o.d. Pyrex tubes, sealed under vacuum, and immersed in a silicon oil bath at 98 ± 3 °C. Analytical VPC analysis (DBT, 60 °C) of the distilled products showed a 27% yield of cyclohexene from **4** and a 32% yield from **5**. 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 did show considerable absorption between 1800–1700 cm^{-1} which was not present in the starting material.

Meso and *dl* Peroxides 6 and 7. Stock solutions of peroxides *meso*-**6** and *dl*-**7** were each prepared in dichloromethane and THF at 0.001–0.006 M or 0.1–0.2 M concentrations. 2-Methylbutane was weighed and added as an internal standard. Dodecane was weighed and added as internal standard to those samples (0.1–0.2 M in dichloromethane) subjected to analyses for β-lactones **29** and **30.** All pyrolyses were carried out in degassed, sealed, and base- and EDTA-washed 6-mm o.d. Pyrex tubes.

Sample tubes were immersed in a silicon oil bath at 92 ± 3 °C for 4 min. The contents were frozen (77 K), the tubes opened, and the mixtures 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*-**29** and *threo*-**30** were determined by analytical VPC (PMPE, 90 °C). Relative retention times of *erythro*-**29,** *threo*-**30,** and dodecane are 1.00, 1.52, and 1.92, respectively (see Table II). The 2-butenes and β-lactones **29** and **30** were shown to be stable under the reaction conditions.

The vapor phase pyrolyses were carried out in a 2.8 × 30 mm cylindrical Pyrex tube with a 0.6 × 3 cm injector port with a serum cap mounted in a Hoskins type FC 303A tube furnace. The other end of the tube was connected via a 6-mm bore stopcock (A) to a high vacuum line equipped with two liquid nitrogen cooled U-shaped traps plus a small receiving tube. The temperature was measured by an iron–constantan thermocouple connected to a potentiometer. Before pyrolyses the tube was evacuated and stopcock A was closed. In a typical run 10 μL of stock solution (0.001 M peroxide in dichloromethane with 2-methylbutane as an internal standard) was injected into the pyrolysis tube through the serum cap via a gas-tight syringe. After a pyrolysis time of 5 s, stopcock A was opened and the pyrolysate was collected in the liquid nitrogen cooled traps. The hydrocarbon contents of the traps were transferred to the receiving tube which was sealed with a torch and removed for analysis. The pyrolysate tube was cooled to 77 K and opened, and the contents were immediately analyzed by analytical VPC (DBT, 25 °C).

Peroxides 4–7 in Methanol. General. A 1-mg sample of each of the peroxides **4–7** was placed in a 6-mm o.d. base- and EDTA-washed Pyrex tube, and 75–100 μL of methanol (or methanol-*O*-d_1) was added. The peroxides were not soluble in methanol. The samples were degassed, sealed under vacuum, and heated for 3 min at 97 ± 3 °C. The tubes were frozen and opened, and the contents were analyzed by analytical VPC (UCON).

Cis Peroxide 4 in Methanol. Two products eluted after methanol [UCON (80 °C) and UCON VPC–MS (80 °C)].[22] They were identified as 1-methoxycyclohexane (**15**) and 3-methoxycyclohexene (**16**), relative retention time (RRT) = 1.0 and 1.3, respectively.

Meso Peroxide 6 in Methanol. Four peaks eluted before methanol (UCON, 80 °C): *cis*- and *trans*-2-butene (RRT = 1.0), dimethoxymethane (RRT = 2.4), 2-methoxy-3-butene (**38**) (RRT = 3.0), and 2-methoxybutane (**39**) (RRT = 3.3).

***dl* Peroxide 7 in Methanol.** Five peaks eluted before methanol (UCON, 80 °C): *cis*- and *trans*-2-butene (RRT = 1.0), unidentified (RRT = 2.5), 2-methoxy-3-butene (**38**) (RRT = 3.0), and 2-methoxybutane (**39**) (RRT = 3.3).

Controls. Thermal Decomposition of Meso Peroxide 6 in Methanol in the Presence of Cyclohexene. Peroxide **6** (5.0 mg) was added to 50 μL of methanol containing 35 mg of cyclohexene in a 6-mm o.d. pyrolysis tube, and the sample was degassed, sealed in vacuo, and heated to 100 °C for 3 min. Analytical VPC analysis (UCON, 25 °C) showed 2-butenes, dimethoxymethane, 2-methoxy-3-butene, and 2-methoxybutane. However, analytical VPC analysis [UCON (80 °C) and DBT (80 °C)] showed no peaks corresponding to the cyclohexyl methyl ethers **15** or **16.**

Thermal Decomposition of Trans Peroxide 5 in Methanol in the Presence of 2-Butene. Peroxide **5** (4 mg) was placed in a 6-mm o.d. pyrolysis tube with 100 μL of methanol saturated with *cis*-2-butene, and the sample was degassed, sealed in vacuo, and heated to 100 °C for 3 min. Analytical VPC analysis (UCON, 25 °C) showed no peaks corresponding to methyl ethers **38** and **39.**

Thermal Decomposition of Cis Peroxide 4 in the Presence of Threo β-Lactone 30 in Methanol. A freshly collected sample of isomerically pure β-lactone **30** in methanol (estimated concentration of about five times that of the observed β-lactone products in peroxide **6** and **7** decompositions) was placed in a 6-mm o.d. pyrolysis tube with 4 mg of peroxide **4**, and the sample was degassed, sealed under vacuum, and heated to 100 °C for 4 min. Analytical VPC analysis (UCON, 25 °C) revealed no peaks corresponding to methyl ethers **38** or **39**. Similarly, a freshly collected sample of 80% *erythro*-**29** and 20% *threo*-**30** in methanol and 5 mg of **4** was prepared and heated as described for *threo*-**30** above. Analytical VPC analysis (UCON, 25 °C) revealed no peaks corresponding to methyl ethers **38** or **39**.

Thermal Decomposition of Trans Peroxide 5 in the Presence of *threo*-2,3-Dimethylpropiolactone (30) in Methanol. A freshly collected sample of isomerically pure β-lactone **30** in methanol with 4 mg of peroxide **5** was prepared and heated as described above. Analytical VPC analysis (UCON, 25 °C) revealed no peaks corresponding to methyl ethers **38** or **39**.

Thermal Decomposition of Trans Peroxide 5 in the Presence of Cyclohexene. The four possible dimers of cyclohexene were synthesized by procedures in the literature.[12,23] The relative retention times of cyclohexene, the cyclohexene dimers *trans-anti-trans*-tricyclo[6.4.0.0^{2,7}]dodecane (**17**), *cis,trans*-tricyclo[6.4.0.0^{2,7}]dodecane (**18**), and *cis-anti-cis*-tricyclo[6.4.0.0^{2,7}]dodecane (**19**), and dodecane (**20**) 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.

Trans peroxide **5** (90 mg 0.51 mmol) in 500 μL of cyclohexene was placed in a 7-mm o.d. Pyrex tube, and the mixture was degassed, sealed under vacuum, and heated to 100 °C for 4 min. Analytical VPC analysis (Carbowax 20 M, 115 °C) revealed one major peak after cyclohexene (RRT = 1.0). This peak, RRT = 6.3, coinjected with the trans-anti-trans dimer **17**. However, analytical VPC analysis on a different stationary phase (SF-96, 150 °C) revealed one major peak after cyclohexene (RRT = 1.0). This peak, RRT = 10.6, did not correspond to trans-anti-trans dimer **17** (RRT = 8.90). To confirm this, a VPC–MS scan[22] (Carbowax 20 M, 115 °C) on *m/e* 164 was carried out and no peaks were observed.

Reaction of Cis and Trans Peroxides 4 and 5 with Triphenylphosphine and Dimethyl Sulfide. Stock solutions of cis peroxide **4** and trans peroxide **5** (0.022 and 0.19 M, respectively, in dichloromethane) were prepared with hexane weighed in as an internal standard. Each stock solution (1 mL) was allowed to react for 1 h with either 35 mg (0.133 mmol) of triphenylphosphine or 30 μL (0.43 mmol) of dimethyl sulfide. Both reaction mixtures indicated conversion to the corresponding anhydride product: IR ($\mathrm{CH_2Cl_2}$) 1865 and 1790 cm^{-1} from *trans*-**5** and 1862 and 1790 cm^{-1} from *cis*-**4** (anhydride C═O). The volatile products were distilled. The reaction of peroxides **4** and **5** with triphenylphosphine showed cyclohexene (4–8%) as a volatile product. This was not the case in the reaction with dimethyl sulfide.

Reaction of Meso and *dl* Peroxides 6 and 7 with Triphenylphosphine and Dimethyl Sulfide. To 100 μL of stock solution of *meso*-**6** (and *dl*-**7**) (0.01 M in dichloromethane) with pentadecane as an internal standard was added 10 mg (0.038 mmol) of triphenylphosphine at 25 °C. After 1 h at 25 °C, analysis of the reaction mixture by analytical VPC (PMPE, 130 °C) indicated 2,3-dimethylsuccinic anhydride, 97.2% isomerically pure meso from **6** (70.5% yield) and 99% isomerically pure *dl* from **7** (30.2% yield).

Reaction of a stock solution of *meso*-**6** (0.028 M in dichloromethane) containing 2-methylbutane and *n*-pentadecane as internal standards with 20 mg (0.076 mmol) of triphenylphosphine or 9 μL (0.12 mmol) of dimethyl sulfide for 1 and 3 h, respectively, at 28 °C afforded *meso*-2,3-dimethylsuccinic anhydride in 65 and 28% yields (99 and 97% isomerically pure), respectively. Distillation of the volatile products from the reaction with triphenylphosphine afforded 2-butenes (36%, 68:32 trans/cis ratio) by analytical VPC (DBT, 25 °C). 2-Butenes were not found in the reaction with dimethyl sulfide.

Reaction of *cis*- and *trans*-Hexahydrophthaloyl Peroxides (4 and 5) and *meso*- and *dl*-2,3-Dimethylsuccinyl Peroxides (6 and 7) with Aromatic Hydrocarbons. Stock solutions (0.5 mL) of peroxides **4–7** (0.1–0.15 M in degassed dichloromethane) were allowed to react with 0.02 mmol each of the aromatic hydrocarbons rubrene, perylene, and diphenylanthracene. These reaction mixtures were allowed to stand in the dark in sealed vials at 22 °C. The infrared spectra at 1775 cm^{-1} were recorded at intervals of 30, 120, and 300 min to follow the disappearance of peroxide. Controls in the absence of aromatic hydrocarbon were run in all cases and showed less than 3–4% decomposition over 5 h. The analytical infrared technique was not sufficiently reliable to obtain quantitative data, but qualitatively the rate of decomposition of peroxides **4–7** increased in the presence of aromatic hydrocarbons in the order diphenylanthracene < perylene < rubrene. Moreover, the peroxides decomposed at different rates. In the presence of rubrene the rate of decomposition increased in the following direction: *cis*-**4** < *trans*-**5** < *meso*-**6** < *dl*-**7**. The *dl* peroxide **7** decomposition was sufficiently fast in the presence of rubrene that visible light from the reaction could be observed in a dark room.

Photochemical Decomposition of Peroxides 4–7. Direct Photolyses. Peroxides **4–7** were dissolved in degassed, spectral grade dichloromethane (0.06–0.10 M) with a weighed amount of *n*-heptane for *cis*-**4** and *trans*-**5** as an internal standard and a weighed amount of 2-methylbutane and dodecane as internal standards for the *meso*-**6** and *dl*-**7** series. Measured aliquots of 100 μL of these stock solutions were placed in EDTA-washed, 6-mm o.d. Pyrex tubes. These samples were degassed by one freeze–pump–thaw cycle and sealed under vacuum. Samples were kept at 77 K in the dark before and after photolysis until analysis. All samples were irradiated at 0 °C using a Hanovia 450-W lamp. The products were distilled, and yields were determined by analytical VPC analysis.

Registry No.—4, 69780.64-9; **5,** 69780-65-0; **6,** 64725-46-8; **7,** 64725-47-9; **10,** 60901-05-5; **11,** 36909-95-2; **14,** 110-83-8; **15,** 931-56-6; **16,** 2699-13-0; **17,** 51319-07-4; **18,** 51319-08-5; **19,** 29782-49-8; **20,** 112-40-3; **21,** 608-40-2; **23,** 16844-07-8; **24,** 35046-66-3; *meso*-**26,** 29800-12-2; *dl*-**26,** 29913-52-8; **27,** 64725-48-0; **28,** 64725-49-1; **29,** 69780-66-1; **30,** 69780-67-2; **38,** 17351-24-5; **39,** 6795-87-5; 3-hydroxy-2-methylbutanoic acid, 473-86-9; propionic acid, 79-09-4; acetaldehyde, 75-07-0; *trans*-2-butene, 624-64-6; *cis*-2-butene, 590-18-1; 2-methylbutane, 78-78-4; dimethoxymethane, 109-87-5; *cis*-1,2-hexahydrophthalic acid, 610-09-3; *trans*-1,2-hexahydrophthalic acid, 2305-32-0.

References and Notes

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