I. ON THE LIFETIME OF 1,4-DIRADICALS. ATTEMPTED TRAPPING OF TETRAMETHYLENE.

II. SIX-MEMBERED CYCLIC DIACYL PEROXIDES. THERMAL DECOMPOSITION OF 1,2,3,4-TETRAHYDROPHTHALOYL PEROXIDE.

Thesis by

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ABSTRACT

Part I. Thermochemical calculations suggest that the depth of the potential well for tetramethylene 1,4-diradical can be probed by trapping the intermediate with sulfur dioxide. This was attempted using N-azacyclopentylmethane sulfonamide (1) as the precursor to tetramethylene. Gas chromatographic evidence for the presence of sulfolane in the decomposition of 1 in sulfur dioxide could not be confirmed by gc/ms and results were not reproducible. It is suggested that a precursor which decomposes more cleanly than 1 will be necessary in order to get quantitative results from a trapping experiment.

Part II. 1,2,3,4-Tetrahydrophthaloyl peroxide (13) has been synthesized. Thermal decomposition of 13 gave hydrocarbon yields of 5%. No evidence was found for lactone formation, but the presence of anhydride and epoxide products suggests that bimolecular redox chemistry is occurring.

The possibility of $\pi\pi^*$ cyclohexadiene formation in the thermal decomposition of 13 is discussed. Evidence was not found which suggests that this is occurring.

Induced decomposition of 13 by rubrene resulted in emission of light consistent with chemically initiated electron exchange luminescence (CIEEL).

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Part I

ON THE LIFETIME OF 1,4-DIRADICALS. ATTEMPTED TRAPPING OF TETRAMETHYLENE.

INTRODUCTION

The mechanism for the dimerization of ethylene to form cyclobutanes has been studied extensively both experimentally[1] and theoretically. Three types of mechanisms have been considered: concerted, stepwise-ionic, and stepwise-diradical. In several cases ionic mechanisms have been indicated, notably for the dimerization of ketones[1,2] and for cycloadditions of polycyanoolefins.[3]

The least motion $[\pi_s^2 + \pi_s^2]$ concerted mechanism is "forbidden" by Woodward-Hoffmann rules.[4] An ab initio calculation by Salem of the energy surface for this pathway leads to an E_a of 156 kcal/mole.[5] This compares unfavorably with the experimental value of 62.5 kcal/mole,[6] in agreement with the Woodward-Hoffmann prediction. The pyrolysis of 7,8-cis,exo-dideuterio-cis-bicyclo[4.2.0]octane by Baldwin and Ford[7] designed to test for the Woodward-Hoffmann "allowed" $[\pi_s^2 + \pi_a^2]$ concerted pathway indicated that this pathway may be operating in part despite the severe steric constraints imposed by this transition state. A similar experiment on 6,7-dimethylbicyclo[3.2.0]heptanes led to results "strongly in favor of a diradical intermediate."[8]

The mechanism most generally evoked for the reaction involves the intermediacy of 1,4- tetramethylene diradical. A MINDO/3 semiempirical SCF MO calculation by Dewar[9] showed the lowest energy pathway between two ethylenes and cyclo-

butane to be via a 1,4 diradical. Unfortunately there has been no direct experimental evidence for its existence as an intermediate, such as the CIDNP which has been observed from diradicals in the photolysis of cyclic ketones.[10]

One approach to studying the behavior of tetramethylene has been to generate it from precursors other than ethylene and cyclobutane under conditions where these are stable and examine the product ratios. Although several substituted tetramethylenes have been generated from a host of different precursors (azo compounds,[11] diazenes,[12] ketones,[13] and sulfolanes[14]) it is difficult to compare the results of these experiments because of the different substitution, reaction conditions and temperatures involved.

Parent tetramethylene-d_2 has recently been generated thermally from the corresponding azo compound (gas phase, 439°) by Dervan and Santilli.[15] Analysis of the stereochemistry in the products (Scheme 1) affords the relative rates of rotation, cleavage, and closure shown in Table I. These can be compared with results from the thermal decomposition of cis-(and trans-)3,4-dimethyl-1,2-diazacyclohexenes (gas phase, 439°) by Dervan and Uyehara.[11b] For secondary radical centers vs primary radical centers rotation is slower and closure becomes slightly more competitive with cleavage. In the Bartlett and Porter experiment (solution phase, 145-148°) in which two tertiary radical centers are formed, the closure reaction is > 98% stereospecific.[11a]

Scheme 1

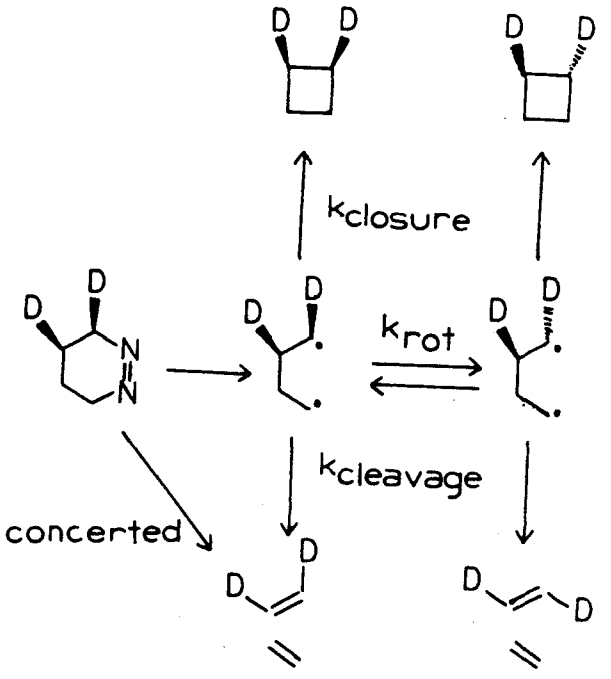


Table I. Relative Rates of Rotation, Cleavage and Closure for Variously Substituted Tetramethylenes Produced from Cyclic Azo Compounds

	 primary[a]	 secondary[a] cis	secondary[a] trans	 tertiary[b]
k_{clos}	1	1	1	1
k_{cleav}	2.2	1.8	1.4	1.1
k_{rot}	12.0	1.4	0.53	0.02

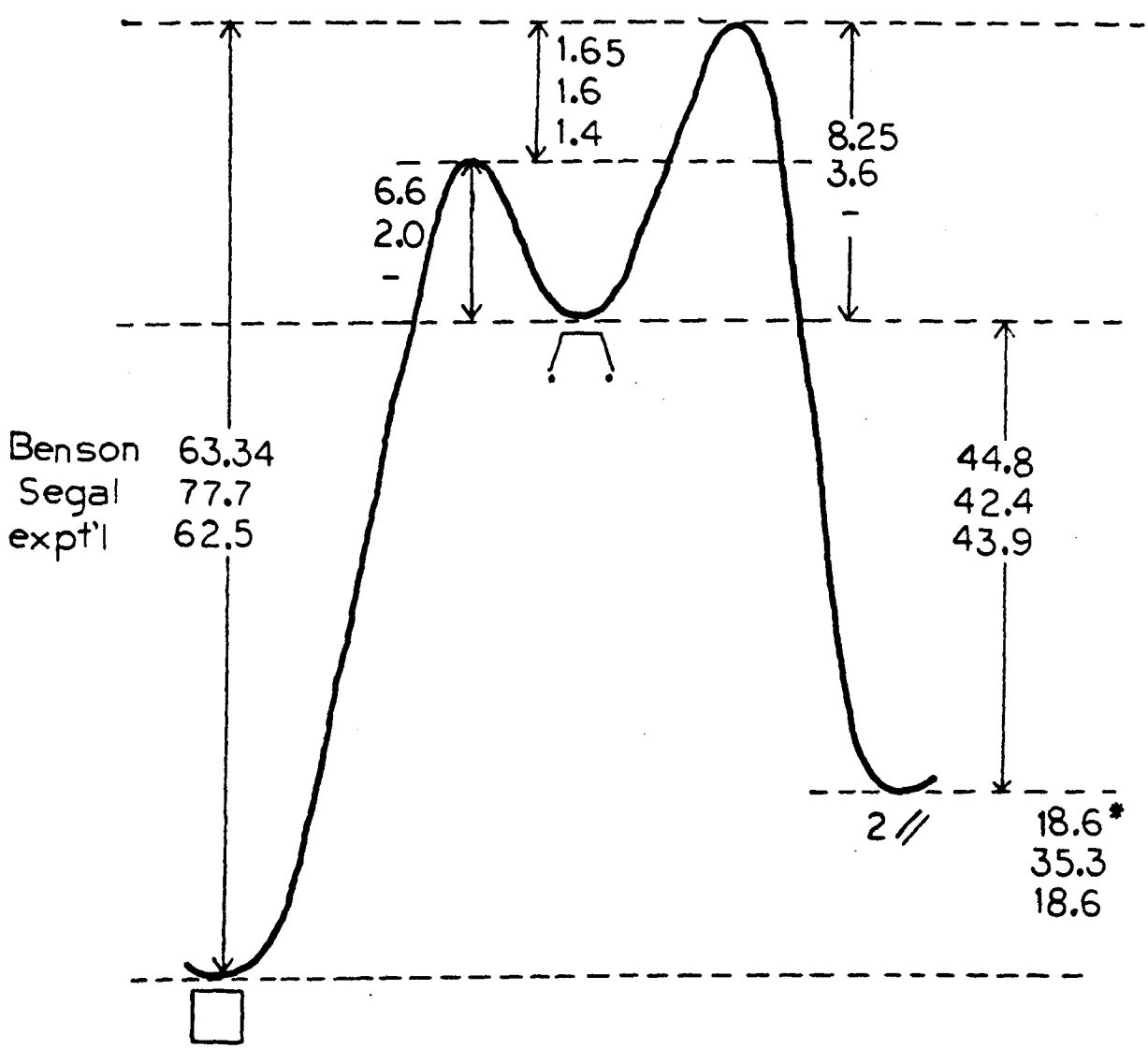
a) gas phase, 439°; Primary ref. 15, secondary ref. 11b;
b) 0.05-0.1M in benzene, 145-148°. Ref. 11a.

These elegant experiments have given us important information about the differences in energy of the transition states for rotation, cleavage, and closure in the 1,4-diradical. Unanswered is the question concerning the depth of the potential well. Theoretical calculations by both ab initio and semi-empirical methods have estimated this energy. An extended Hückel calculation by Hoffmann[16] has suggested that such a well does not in fact exist and that there is a large flat region of the potential energy surface where the ring opened C_4H_8 exists. He believes that such a flat region would be operationally indistinguishable from a true minimum.

Benson's thermochemical estimates give the energy surface shown in Figure 1.[17] Ab initio SCF calculations by Segal[18] for the same surface are also shown along with experimental values. Benson's value for the well depth is 6.6 kcal/mole while Segal's is 2.0 kcal/mole. Segal notes, however that the value for the barrier to closure is probably more in error than the others, the error being the direction of underestimation. So it is likely that 2.0 kcal/mole is a lower limit to the depth of the potential energy well.

Each of these theoretical calculations gives a value for the difference between the E_a's for cleavage and closure in close agreement with the experimental value obtained from Santilli and Dervan's data for parent tetramethylene.

Figure 1. Energy Surface for Cyclobutane ⇄ 2 Ethylene in kcal/mole.



* calculated from Benson's tables

The depth of the well for the diradical can be probed experimentally by trapping tetramethylene with sulfur dioxide to form the cyclic sulfone which is stable and well characterized. Good[20] has determined an activation energy of 3.1 kcal/mole and an A factor of $10^{7.8}$ for ethyl radical combining with sulfur dioxide. These should serve as reasonable estimates for the reaction of tetramethylene with sulfur dioxide. Rate constants and relative product ratios for cyclobutane and sulfolane calculated from Benson's and Segal's energy parameters are shown in Table II. Since Segal's E_a for closure is likely a lower limit, it appears that at worst we need to be able to see one part in 10^5, and this is obtainable with analytical vpc techniques.

The ratio of cyclobutane to sulfolane should be a function of temperature, eqn 1. Thus a plot of product ratio vs T^{-1} will give

$$\ln \frac{\square}{\text{C}_4\text{H}_8\text{SO}_2} = \ln \left(\frac{A_{closure}}{A_{capture}}\right) + \frac{E_{capt} - E_{clos}}{R} \left(\frac{1}{T}\right) \qquad (1)$$

a slope from which we can calculate E_a(closure). As the calculated values in Table II show, the change in slope is dramatic for small changes in E_a(closure). A caution should be noted that the absolute value for E_a(closure) calculated by this method is valid only if the activation energy for combination of sulfur dioxide with ethyl radical approximates that for combination with tetramethylene.

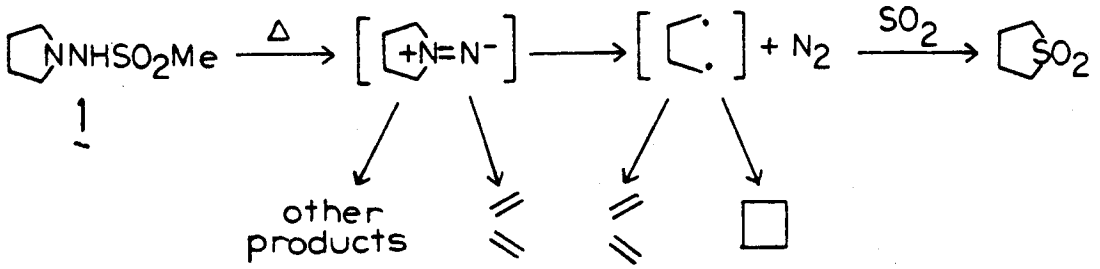
Table II. Calculated Rate Constants (sec^{-1}). (SO_2) is 15M.

		$k_{closure}$	$k_{cleavage}$	$k_{capture}$	$k_{clos}/k_{capt}(SO_2)$
Benson[a]	300°	6.3×10^{9}	9.0×10^{9}		91
	120°	4.5×10^{8}	3.3×10^{8}		24
	25°	3.1×10^{7}	1.1×10^{7}		5
Segal[b]	300°	3.5×10^{11}	5.4×10^{11}		5070
	120°	1.6×10^{11}	1.3×10^{11}		7620
	25°	7.0×10^{10}	3.0×10^{10}		11460
Good[c]	300°			4.6×10^{6}	
	120°			1.4×10^{6}	
	25°			4.1×10^{5}	

a) Ref. 17; b) Ref. 18; c) Ref. 20

1,1-Diazenes decompose thermally to afford molecular nitrogen and radicals.[21] Dervan and Uyehara[22] have pyrolyzed N-(2,3-dimethylazacyclopentyl)methanesulfonamide and shown it to give 2-butenes and 1,2-dimethylcyclobutanes as products both in the gas phase (306°, 439°) and in solution (120°). Thus N-azacyclopentylmethanesulfonamide (1) should be a reasonable precursor from which to enter the tetramethylene manifold, see Scheme 2.

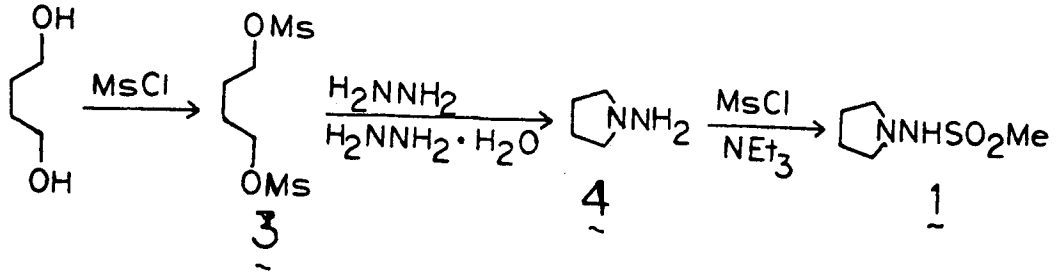
Scheme 2



RESULTS AND DISCUSSION

The sulfonamide precursor was prepared by the sequence shown in Scheme 3.[23]

Scheme 3



Gas phase pyrolysis of 1 gave ethylene and cyclobutane in a ratio (2///□) of 138 ± 16, plus 1-2% unidentified hydrocarbon products. Analysis was done by electronically integrated analytical vpc (SE-30, 25°). Sealed tube pyrolysis of 1 in diglyme at 120° also gave ethylene and cyclobutane along with a brown tar. Pyrolyses of 1 conducted neat in sulfur dioxide also led to a tarry mixture. Distilled gases were analyzed by analytical vpc (SE-30, 25°). The fraction which potentially contained the sulfolane was distilled and analyzed by analytical vpc (SE-30, 180°) or (Carbowax 20M, 180°). A solution of authentic sulfolane in dichloromethane was shown to distill under vacuum with heating, but only with about 34% efficiency. Table III shows a summary of the pyrolysis data. Pyrolysis of 1 in THF showed no sulfolane peak, as expected.

Table III. Pyrolyses of 1 in Sulfur Dioxide.

	Temp.°C	Time hrs.			
1	120	2	50.7	*	a
2	120	2	74.0	*	a
3	120	2	e	-	a
4	120	2	e	*	a,d
5	120	2	e	-	b
6	120	2	68.4	*	c
7	120	2.5	42.4	-	c
8	90	2.5	43.5	*	c
9	90	2.5	42.9	-	
10	50	17.5	102.9	-	c
11	40	24.5	71.79	-	c
12	RT	80	e	*	
13	RT	120	63.5	*	b

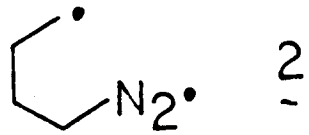
a) Sample was kept at room temperature for one day between sealing and pyrolysing. b) One equivalent of triethylamine was added to the pyrolysis solution. c) Sulfur dioxide was passed through phosphorous pentoxide. d) Sulfolane peak observed only in sample extracted from the tar. It did not appear in the distilled sample. e) Not measured. f) * = peak attributed to sulfolane appeared in the gc.

A mass spectrum of authentic sulfolane (Aldrich) was taken. GC/MS was performed on the sample from pyrolysis 4. The gc was done using a column other than that used in the original analysis so retention times could only be estimated. Two peaks occurred near the estimated retention time, neither of which were sulfolane. A 3% Carbowax 20M column was prepared that could be used for both the original analysis and the gc/ms. Of the following eight pyrolyses only two produced the sulfolane peak in the initial analysis and neither sample was large enough to analyze by gc/ms.

CONCLUSION

The gc/ms would be the definitive experiment needed to confirm our assignment of the "sulfolane peak". This would be needed in order to claim permissive evidence for trapping tetramethylene.

Two major problems still remain in the system if one hopes to investigate the depth of the potential well. First, one would have to show that sulfolane could be quantitatively distilled from the product mixture so that accurate product ratios could be obtained. Second, one would have to show that the species being trapped was in fact tetramethylene and not the diazenyl biradical 2.



The complex chemistry which occurs in the decomposition of the N-sulfonamide 1 renders it an unsuitable precursor for this study.

At present we have no suitable precursor to parent tetramethylene which would decompose cleanly at the temperatures required to work with liquid SO_2 (critical temperature 157°C).[24] The azo compound used by Santilli and Dervan requires much higher temperatures to effect decomposition.

The experimental determination of the well depth for tetramethylene 1,4-diradical remains as the last piece of data needed for a clearer picture of the behavior of this intermediate. A good experimental value for this number will be an excellent test for the theoretical methods that have been used to calculate it.

EXPERIMENTAL

General

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 spectrometer. Chemical shifts are reported as parts per million downfield from tetramethylsilane (TMS) in δ units. Magnetic resonance data are reported in the order: chemical shift; multiplicity, s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet; number of protons.

Gas chromatography-mass spectra (GC-MS) were run on a Finnegan 3200 E.I. mass spectrometer interfaced to a Finnegan 9500 gas chromatograph at the Jet Propulsion Laboratory by Ray Haack.

Analytical vapor phase chromatography (vpc) was performed on a Hewlett-Packard 5700A 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 a thermal conductivity detector. Helium was used as the carrier gas. Analytical and preparative gas chromatography columns are listed in Table IV. All 1/8" columns are stainless steel and were used for analytical work.

Table IV VPC Columns

Column Designation	Description
SE-30	10'x1/8", 30% SE-30 on 100/120 Chromosorb P
Carbowax 20M	10'x1/8", 10% Carbowax 20M on 100/120 Chromosorb W
Carbowax 20M	10'x1/8", 3% Carbowax 20M on 100/120 Chromosorb W
Carbowax 20M-GC/MS	5', 3% Carbowax 20M on 8100 mesh gas Chromosorb Q washed with terphthalic acid.
Pennwalt (preparative column)	5'x1/4", 28% Pennwalt 223 on Chromosorb P, glass column

1,4-Butanediol dimethylsulfonate (3)[23]

To 300 ml dry pyridine distilled from KOH was added 36g (0.4 mole) 1,4-butanediol. The solution was cooled to -40° with stirring under nitrogen whereupon 70 ml (0.9 mole) methanesulfonyl chloride distilled from P_2O_5 was added dropwise over forty minutes. The reaction mixture thickened and warmed but was kept below 40° with a dry ice/acetone bath. The resulting slurry was poured over 500g ice and allowed to stand at room temperature for two hours. The resultant white solid was collected by suction filtration, washed with ice water, air dried, and placed in a vacuum desiccator over P_2O_5. The yield was 84.0g (85%) colorless product: mp 116-118°; nmr ($CDCl_3$) δ 1.7-2.05 (m, 4), 3.03 (s, 6), 4.15-4.5 (m, 4).

1-Aminoazacyclopentane (4)[23]

A solution of 24.0g (97.6 mmole) 3 in 20.0 ml (0.643 mole) hydrazine hydrate and 10 ml (0.20 mole) anhydrous hydrazine was stirred with heating under nitrogen. As soon as the exothermic reaction began, heating was discontinued and the flask was cooled slightly with an ice bath. The clear solution was allowed to stir over night at ambient temperature. The solution was extracted with 4 x 30 ml anhydrous ether and the ethereal extracts concentrated

(atmospheric pressure). Vacuum distillation (2 mm, 25°) and separation by preparative vpc (Pennwalt, 150°) yielded 3.0g (0.035 mole, 36%) product. nmr ($CDCl_3$) δ 1.7-2.0 (m, 4), 2.5-2.8 (m, 4), 3.2 (s, 2).

N-Azacyclopentylmethanesulfonamide (1)[23]

To a solution of 4 (850 mg, 9.87 mmole) and triethylamine (1.51 ml, 0.109 mole) (distilled from BaO, stored over KOH) in 17 ml dichloromethane freshly distilled from P_2O_5, was added methanesulfonyl chloride (0.76 ml, 9.9 mmole) via syringe with stirring under nitrogen at -78°. The mixture was stirred for 30 minutes at -78° followed by an additional 30 minutes at room temperature. The mixture was diluted with 25 ml dichloromethane, washed once with saturated aqueous $NaHCO_3$, dried ($MgSO_4$) and concentrated (reduced pressure) to yield 1.3g yellow crystals. Recrystallization (benzene/hexane) gave 0.72g (44%) white needles: mp 76-78°; nmr (benzene-d_6) δ 1.3-1.7 (m, 4), 2.5-2.9 (m, 7), 5.7 (br s, 1).

Pyrolyses of N-Azacyclopentylmethanesulfonamide (1)

Gas Phase: Aliquots (7 μℓ) of 1 in benzene-d_6 were injected into an evacuated heated oven (200 cm^3, 440°) for 5 seconds, then collected in a liquid nitrogen cold trap. Analysis was done by analytical vpc (SE-30, RT) using gas syringe techniques.

Solution Phase: Solutions of 200 mg $\underset{\sim}{1}$ in 35 drops condensed sulfur dioxide were prepared in base-washed thick-walled tubes and sealed under vacuum following two freeze-thaw cycles. These were pyrolyzed in an oil bath outfitted with a thermostat control. Products were distilled under high vacuum, the first collection being taken without heating, the second fraction taken by heating the pyrolysis tube vigorously with a heat gun or oil bath. Analysis of the first gaseous fraction was done by analytical vpc (SE-30, RT) using gas sampling techniques. Analysis of the second liquid fraction was done by analytical vpc (Carbowax 20M, 180°).

Figure 2. Mass Spectrum of Sulfolane Obtained by gc/ms.

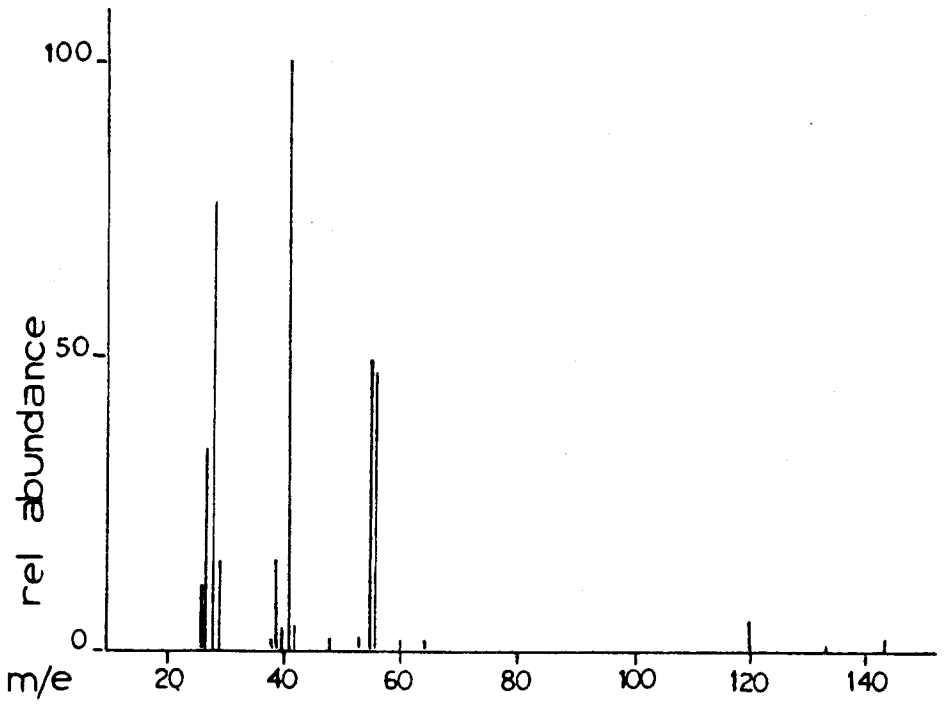
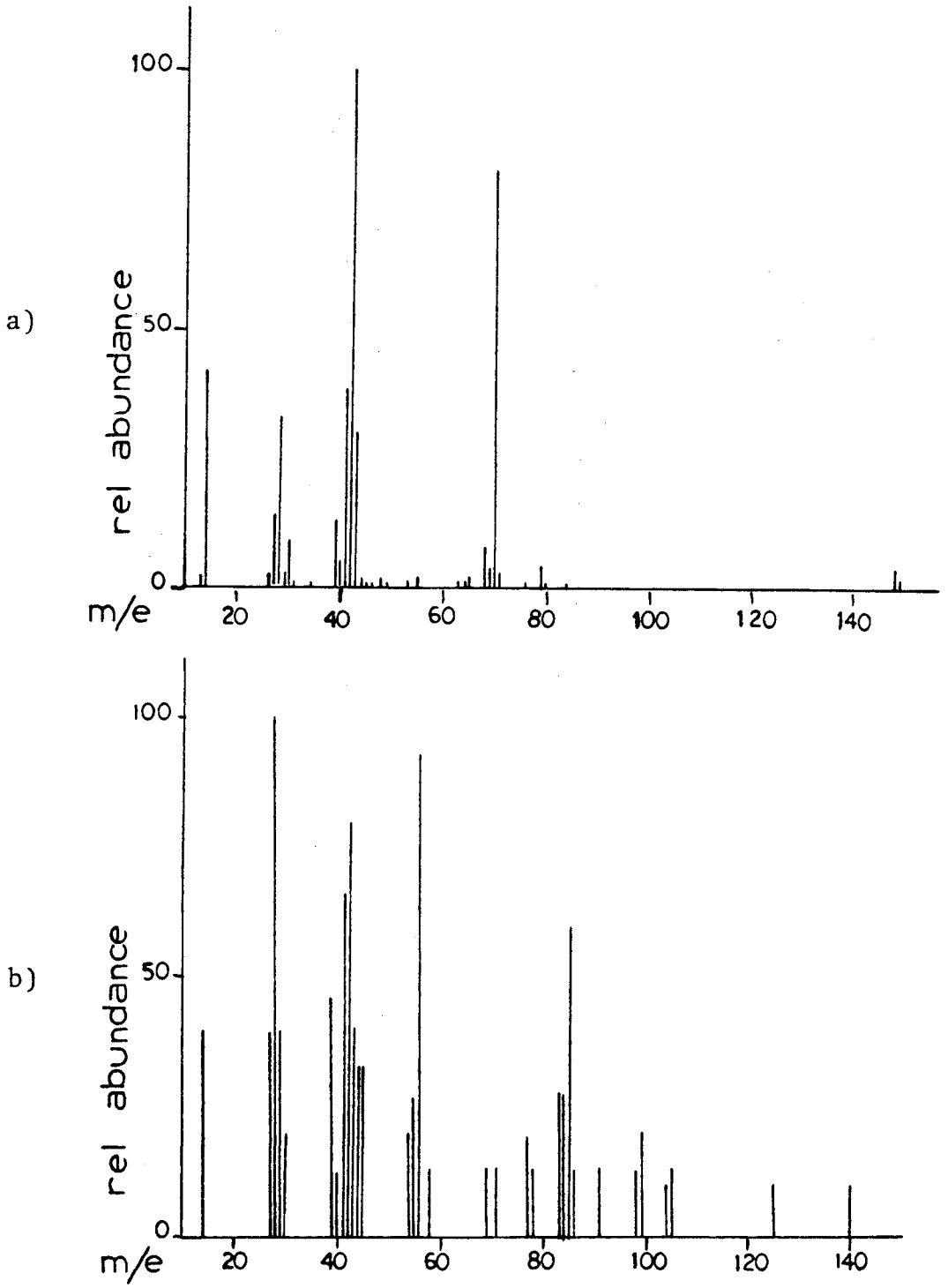


Figure 3. Mass spectral data obtained from gc/ms of pyrolysis 4. Spectrum (a) is for the larger peak whose retention time is 1.2 relative to the peak whose spectrum is shown in (b).



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Part II

SIX-MEMBERED CYCLIC DIACYL PEROXIDES.
THERMAL DECOMPOSITION OF 1,2,3,4-TETRAHYDROPHTHALOYL PEROXIDE.

INTRODUCTION

Chemiluminescence

Chemiluminescence results when an electronically excited molecule produced by a chemical reaction emits a photon upon its return to the ground state. A potentially chemiluminescent reaction must be at least exothermic enough to populate an excited state of the product. For luminescence in the visible range, 50-80 kcal/mole is required.[1] The total energy available to a system is usually considered to be the enthalpy of reaction plus the activation energy.[2]

Quantum yields for chemiluminescent reactions vary from nearly 100% in the case of bioluminescence from fireflies down to about 10^{-10}. The overall quantum yield can be considered as the product shown in equation (1),

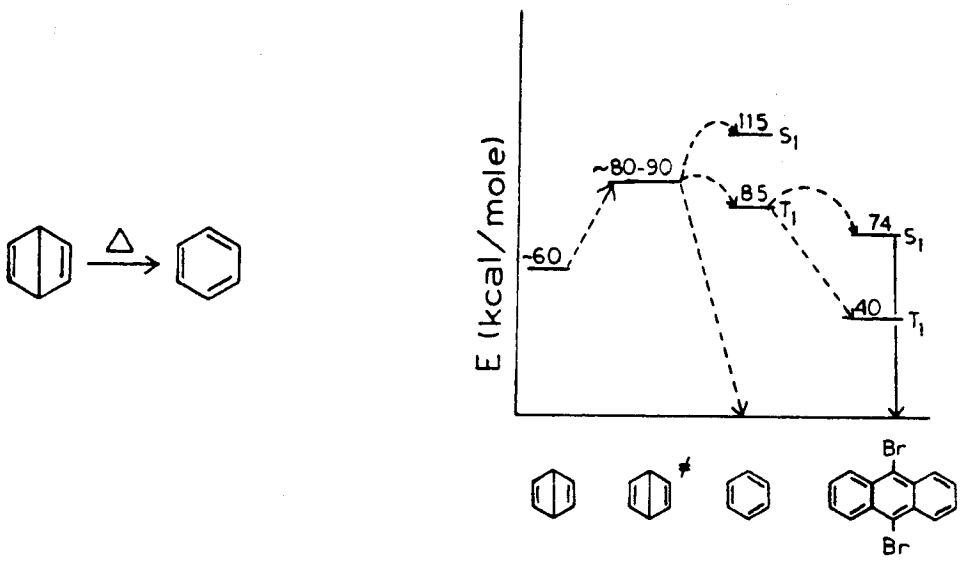
$$\phi = \phi_C \times \phi_E \times \phi_F \qquad (1)$$

where ϕ_C is the normal chemical yield of the excited molecule, ϕ_E is the number of such molecules formed in the excited state, and ϕ_F is its fluorescent efficiency.[1] This allows us to consider chemiluminescence as a two stage process consisting of a chemiexcitation step ($\phi_C \times \phi_E$) followed by a luminescence step (ϕ_F).[3] Luminescence can be enhanced by the addition of efficient fluorescers to accept the energy of the initially formed excited state product. Because of this, and because we are concerned with the initial formation of the excited state from a chemical process, our em-

phasis is on the chemiexcitation stage of chemiluminescence.

Two examples of chemiluminescent reactions seem especially pertinent to this discussion because they involve the thermal rearrangement or decomposition of a single reactant. The thermal rearrangement of Dewar benzene to benzene with the energy diagram shown in Figure 1,[4] gives chemiluminescence in the presence of fluorescent acceptors.[4]

Figure 1



Benzene triplets were shown to form with ϕ_E of 0.02% for the parent system. Substitution of Dewar benzene with chlorine was found to increase the quantum yield to 0.1%, possibly because of a heavy atom effect on spin orbit coupling.[4]

The thermal decomposition of 1,2-dioxetanes[3,5] 1 into two carbonyl fragments is a remarkably exothermic reaction. The combination of a weak O-O bond, the strain of the four-membered ring, and the ability of 1 to form two carbonyl groups in a single transition state account for the exothermicity of 80-110 kcal of its decomposition.[1,3] All of the 1,2-dioxetanes synthesized thus far have themselves been chemiluminescent, or have been able to produce chemiluminescence upon the addition of a fluorescent acceptor, see Scheme 1. The energy diagram for tetramethyl dioxetane (1, R = Me), see Figure 2, shows that both singlet and triplet acetone excited states are energetically accessible. The quantum yields, ϕ_E, for singlet and triplet $n\pi^*$ excited acetone formation are 0.5% and 50% respectively, making 1 a very efficient source of excited states.

Scheme 1

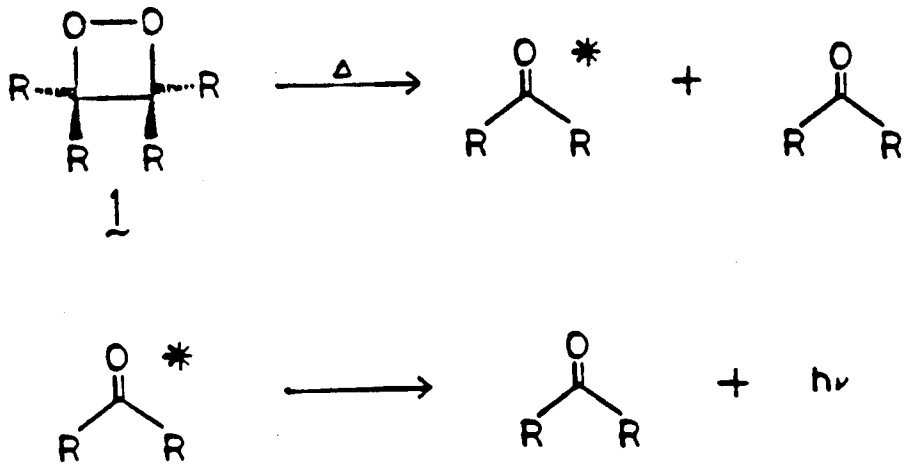
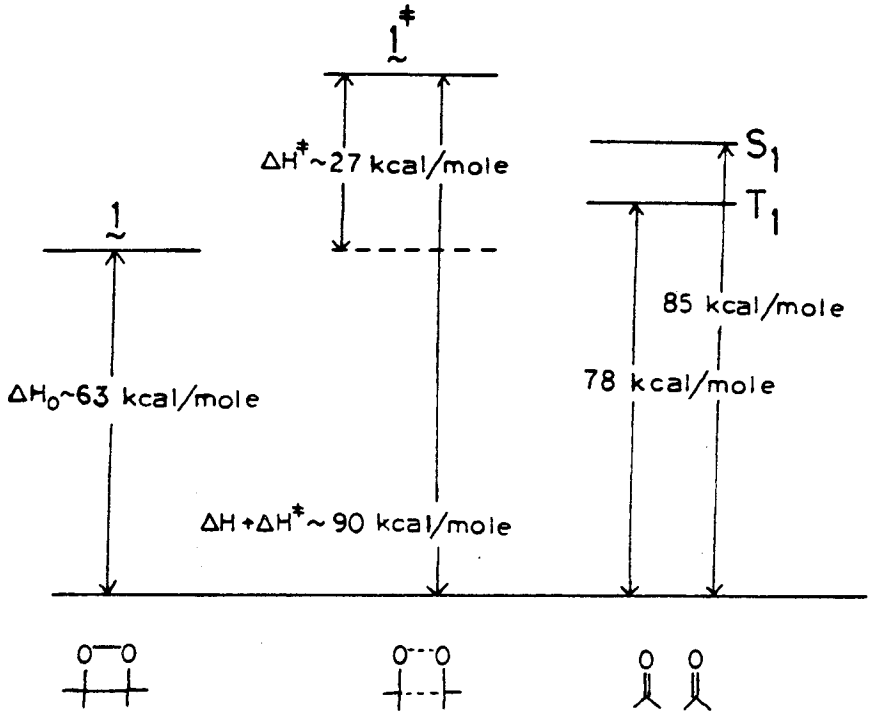


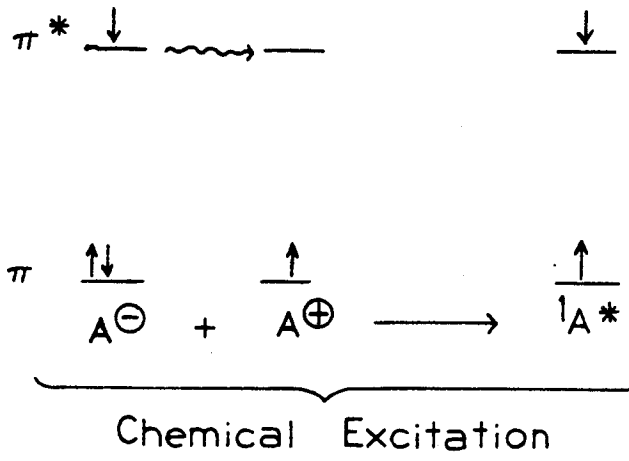
Figure 2



Another type of chemiluminescent reaction which is pertinent to our discussion is electrochemically generated chemiluminescence. This involves electron transfer from a radical anion to a radical cation to form an excited state.[1,6] These experiments are typically done using alternating current at an electrode to generate radical anions and radical cations of aromatic-hydrocarbons in the vicinity of one another which can then react. This is shown schematically in Figure 3.[6] Chemiluminescent reactions which involve electron transfer in their excitation step are relatively numerous. Both singlet and triplet products have been shown to form, depending on the energetics of the particular re-

action.

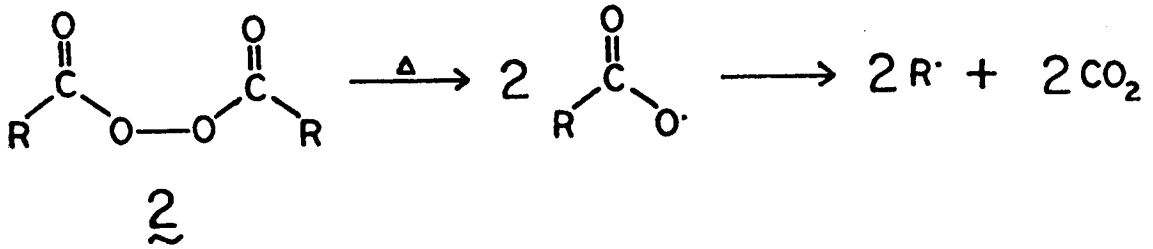
Figure 3



Diacyl Peroxides

Diacyl peroxides, 2, are well known as sources of radicals, as they decompose as shown in Scheme 2. The O-O bond dissociation energy for diacyl peroxides is typically

Scheme 2

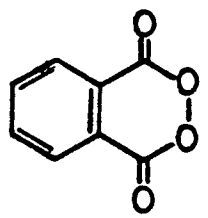


2

about 30 kcal/mole which is less than that for dialkyl peroxides (35-39 kcal/mole) or for hydroperoxides (40-43 kcal/mole).[7] Hundreds of linear diacyl peroxides have been

synthesized and characterized, and various routes for the decomposition of some of these linear peroxides have been studied in depth.[7]

A comparable amount of work on cyclic diacyl peroxides is conspicuously absent. In the six-membered ring series only the aromatic peroxides phthaloyl peroxide,[8-14] (3) and phenylmaleoyl peroxide (4),[15] have been characterized in the literature. The mechanisms of their decompositions are still not well understood.



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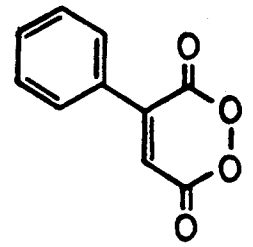
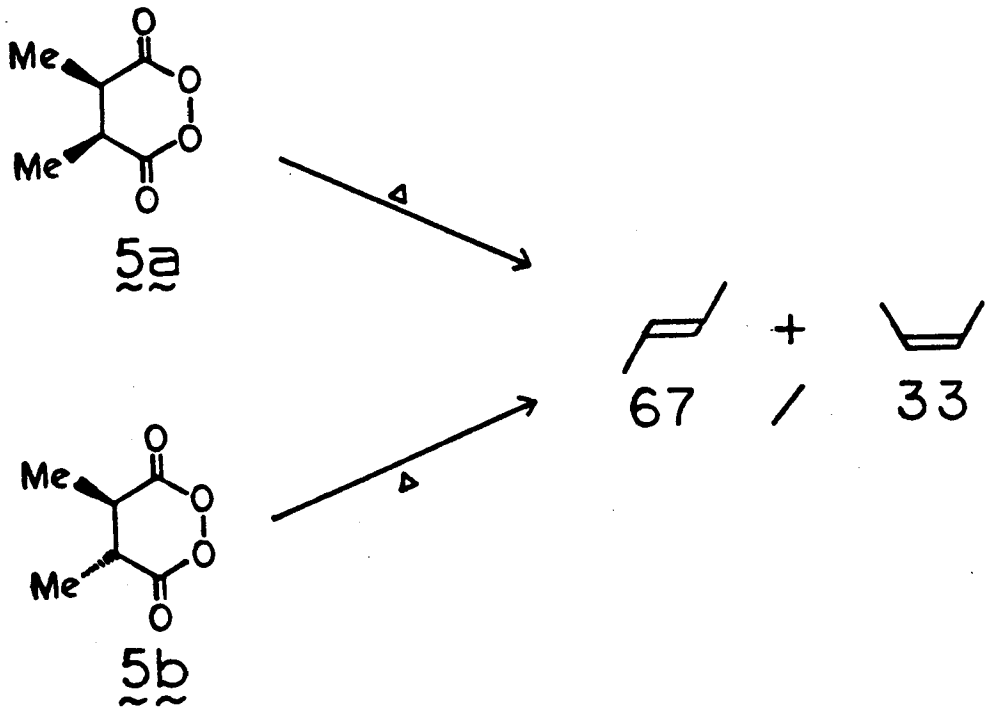
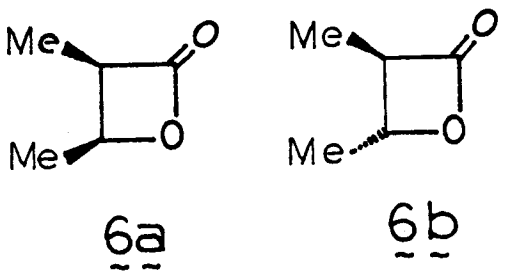


4

Recently, Jones and Dervan reported[16] the first successful synthesis and characterization of monomeric meso- and dl-2,3-dimethyl succinoyl peroxides (5a) and (5b). The thermal decomposition of these peroxides, see Figure 4, was investigated in solution and in the gas phase. Yields of 2-butenes were typically 40-60% and a constant ratio of 67/33 for trans/cis 2-butenes was observed. Minor products (< 10%) of the decomposition were the β-lactones 6a and 6b.[19]

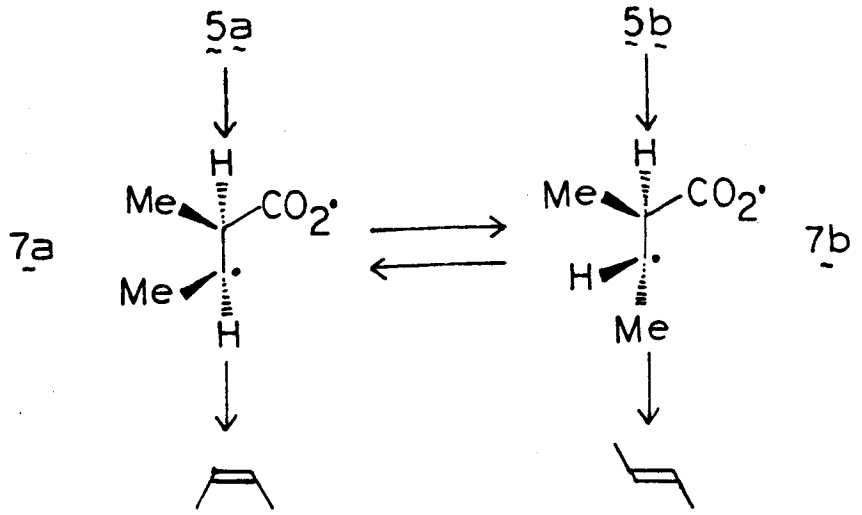
Figure 4





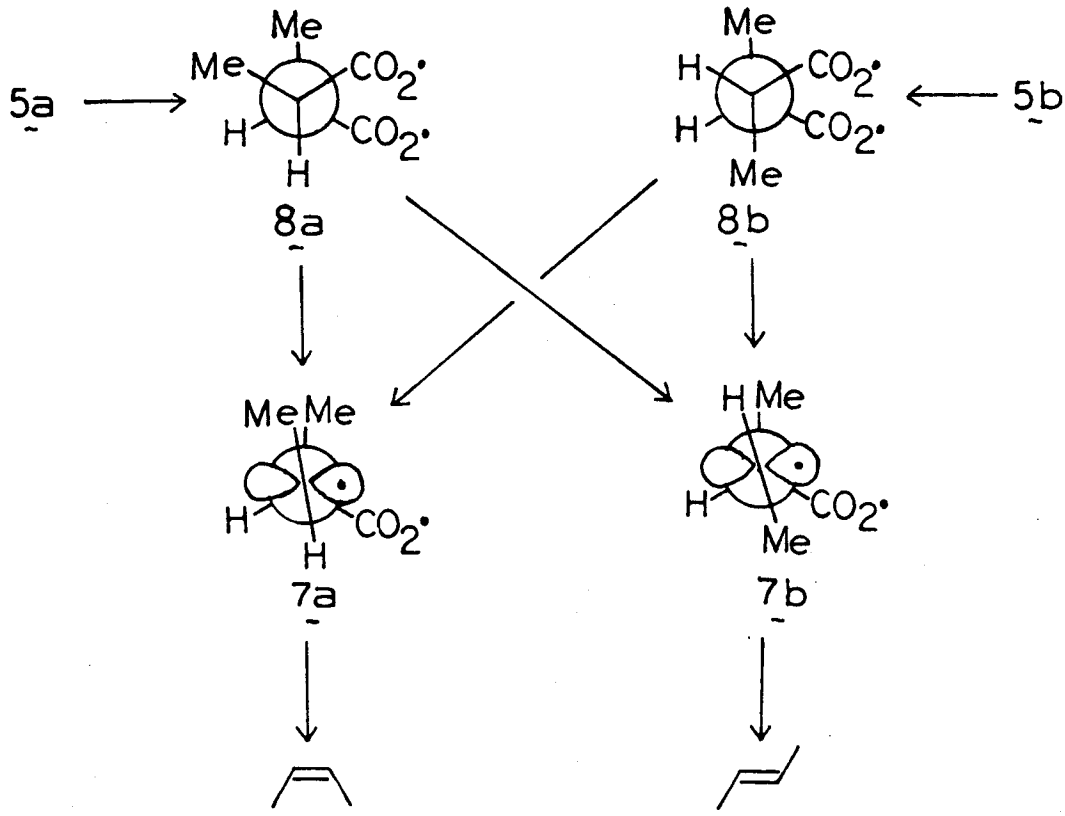
These results suggested a common intermediate in the decomposition of the two peroxides, one possibility being the carboxy diradicals, 7a and 7b, which could undergo rapid equilibrium before decarboxylation as shown in Scheme 3. Another possibility is that initial scission of the O-O

Scheme 3



bond affords bis-carboxy diradicals 8a and 8b which each give the same ratio of cis and trans carboxy diradicals 7a and 7b as shown in Scheme 4. This mechanism requires that k(rotation) for 8 be much greater than k(decarboxylation) to 7a and 7b.

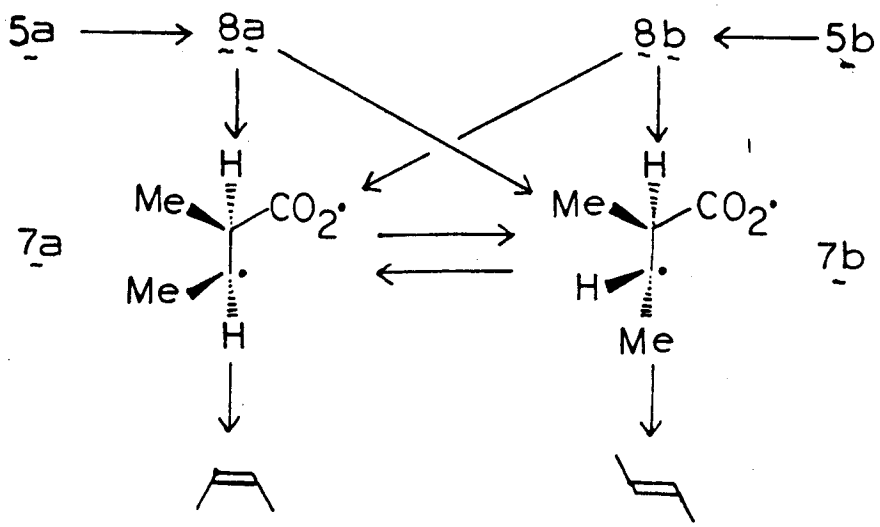
Scheme 4



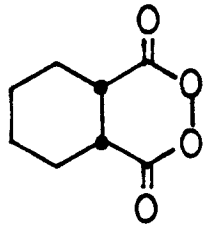
The E_a for the decarboxylation of the acetoxy radical has been estimated at 6.6 kcal/mole.[17] The highest rotational barrier in n-butane is for one methyl-methyl and two hydrogen-hydrogen interactions and has an energy barrier of 4.6 kcal/mole.[18] The lower energy barrier (2 Methyl-H, 1 H-H interactions) is 3.4 kcal/mole. In the bis-carboxy diradical the lowest energy rotational barrier involves Me-CO_2·, H-CO_2·, and Me-H interactions for 8a and 2 Me-H and 1 CO_2·-CO_2· interactions followed by 2 H-CO_2· and 1 Me-Me interactions for 8b. The highest rotational barrier involves

Me-Me, $CO_2\cdot$-$CO_2\cdot$, and H-H interactions for 8a and 1 H-H and 2 Me-$CO_2\cdot$ interactions for 8b. The rotational barriers for these intermediates are not known but it seems reasonable that they are slightly higher than those for n-butane. This would make decarboxylation competitive with rotation. If k(decarboxylation) ∿ k(rotation) then the bis-carboxy diradical mechanism shown in Scheme 4 cannot adequately explain the constant ratio of 2-butenes observed. Both mechanisms may be operating as shown in Scheme 5.

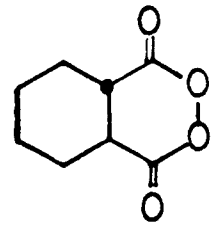
Scheme 5



Kinetic analysis showed the thermal decomposition to be first order. Rate constants measured at 48.50 were on the order of 1-4 x 10^{-4} sec^{-1}.[19] The cis and trans perhydrophthaloyl peroxides (9a) and (9b) have been synthesized by Jones. Rate constants for these peroxides at 48.5° are in



9a

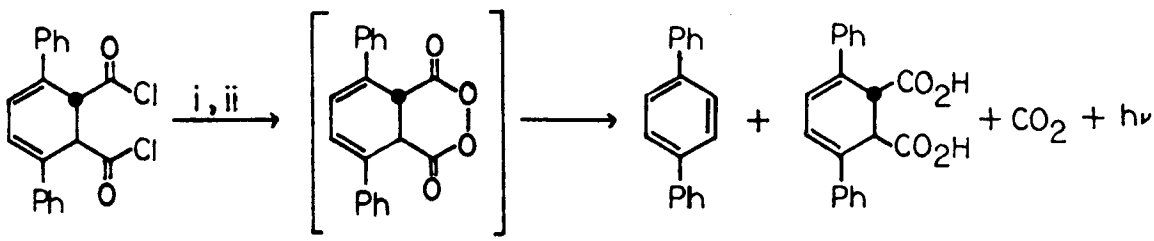


9b

the same range as those for the dimethyl succinoyl peroxides.[19]

In a recent work Schuster[21] proposed the possibility of a six-membered cyclic diacyl peroxide as an unisolated intermediate in the chemiluminescent reaction shown in Figure 5. He reports a yield of 1.5 ± 1% p-terphenyl singlet and 35 ± 10% p-terphenyl triplet for this reaction. This would be the first example of a $\pi\pi^*$ excited state aromatic resulting from a peroxide decomposition.

Figure 5



10

i. diisopropylethylamine
ii. H_2O_2

This result led to speculation whether $\pi\pi^*$ olefin might be resulting from the decomposition of 2,3-dimethyl succinoyl peroxides. A comparison of the energetics of the two reactions is shown in Table I. The decomposition of peroxide $\underset{\sim\sim}{10}$ is energy sufficient to populate either singlet or triplet p-terphenyl and the decomposition of $\underset{\sim}{5}$ is energy sufficient to populate triplet 2-butene. Thus far no experiment has been done with $\underset{\sim}{5}$ to indicate whether or not triplet butenes are in fact being formed during its decomposition.

Table I. Energy Parameters for p-terphenyl and cis-2-butene in kcal/mole

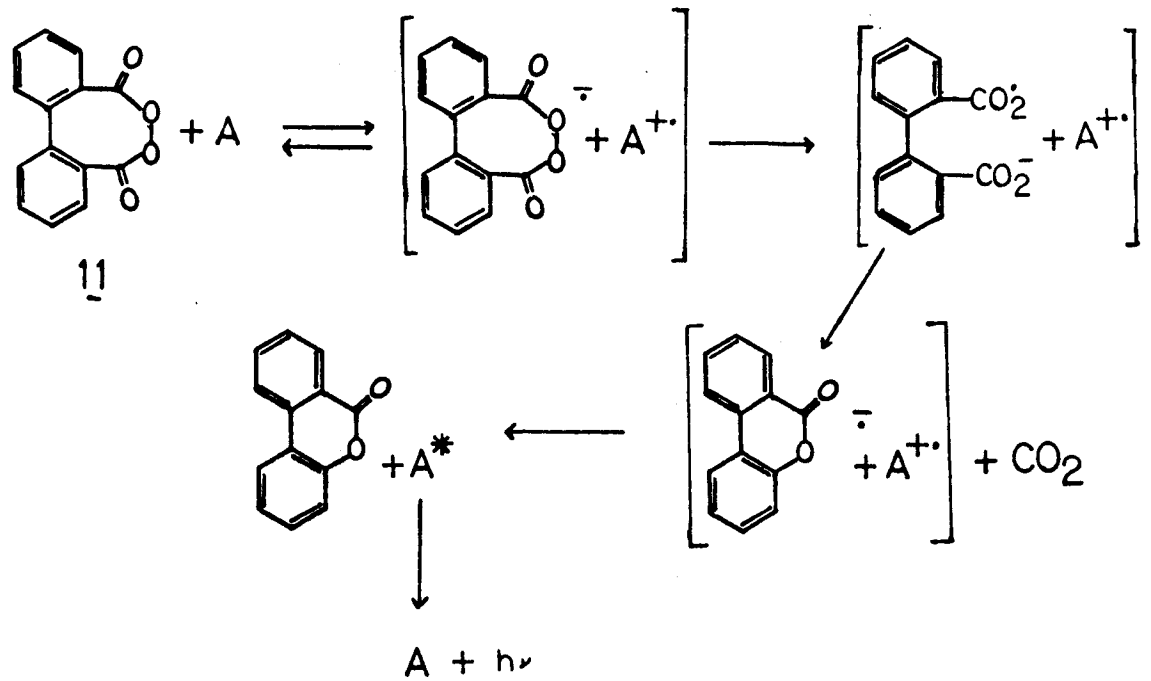
	E_S	E_T	ΔH_r [a]	$\Delta H+E_a$ [b]
p-terphenyl	90	58.3[d]	-86	-106-116
cis-2-butene	138[d]	78.2[d]	-59	-74-78

a) For the reaction: peroxide→olefin + $2CO_2$. Estimated using Benson thermochemical estimates.[20] b) Assuming an E_a of 20-30 kcal/mole.[7] c) Reference 21. d) Reference 22.

Chemically Initiated Electron Exchange Luminescence

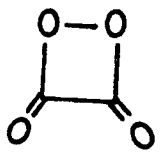
In more recent work,[23] Schuster has proposed an alternate mechanism for chemiluminescence from cyclic diacyl peroxides, which may account for the light observed from the reaction shown in Figure 5. His study of the decomposition of diphenoyl peroxide (11) in the presence of fluorescent aromatics, such as rubrene, gave evidence for the induced decomposition shown in Scheme 6. In the reaction shown in Figure 5, the product p-terphenyl could be acting as the activator.

Scheme 6



11

This mechanism is referred to as Chemically Initiated Electron Exchange Luminescence, or CIEEL. It has much in common with the well known electrochemically generated chemiluminescence,[1,6] and is analogous to a mechanism proposed by Capra[1] for the decomposition of dioxetane dione (12) in the presence of fluorescent polynuclear aromatic



12

hydrocarbons. The observed rate in the decomposition of 11 was shown to increase with increasing concentration of the acceptor, and the reciprocal of the relative chemiluminescent intensity, to increase linearly with the reciprocal of activator concentration. The rate also increased with decreasing ionization potential of the activator used.

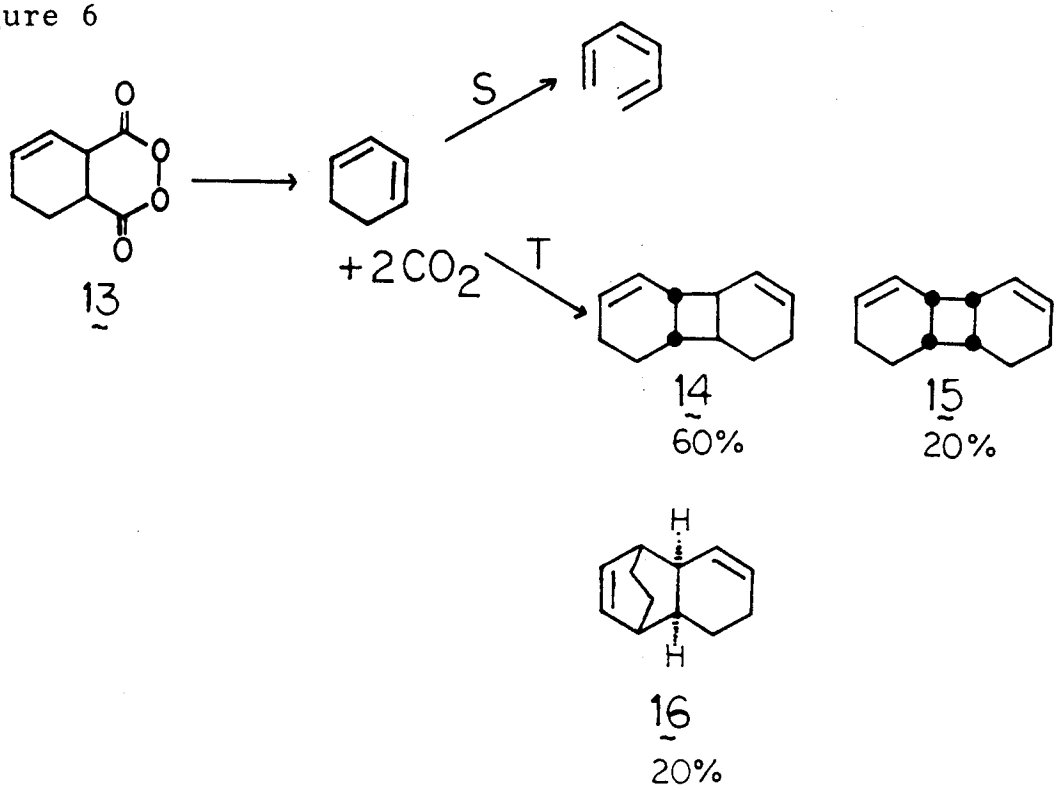
CIEEL appears to be a general phenomena. Jones has shown that addition of rubrene to solutions of 2,3-dimethyl succinoyl peroxides or of perhydrophthaloyl peroxide, increases the rate of their decomposition. Overall rates of CIEEL decomposition for peroxides 5 and 9 appeared to be slower than that observed for 11. However, the dl isomer, 5b, decomposed at a rate fast enough to allow the observance of visible chemiluminescene with the naked eye in a darkened room.[19]

The use of sensitive photon counting techniques may make it possible to monitor the chemiluminescence from the slower CIEEL decompositions.

RESULTS AND DISCUSSION

Cyclic diacyl peroxides appear to have the energetic potential for producing $\pi\pi^*$ excited state olefins. In order to investigate the possibility of these excited states being formed during peroxide decomposition, we began our study of 1,2,3,4-tetrahydrophthaloyl peroxide (13). The olefinic product of this decomposition is 1,3 cyclohexadiene whose singlet[24] and triplet[25,26] chemistries are distinct and well known, see Figure 6. Thus we will be able to look for triplet formation without using fluorescent acceptors which can induce decomposition via a CIEEL mechanism. This system has the advantage that the quantum yield for dimerization from the triplet is unity[25] and that the diacid precursor to the peroxide is a known compound.[27]

Figure 6

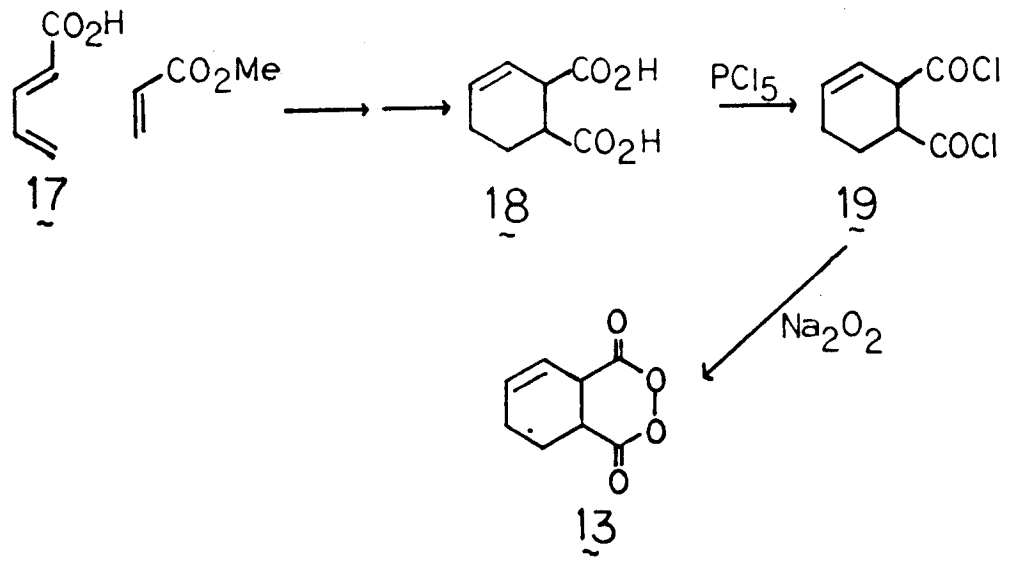


Thermochemical estimates[20] of the energy surface for the decomposition, neglecting any strain for the peroxide ring, show a $\Delta H_{reaction}$ of -61 kcal/mole. Since typical E_a's are in the range of 20-30 kcal/mole,[7] the total available energy is 82-92 kcal/mole.[28] E_T and E_S for 1,3-cyclohexadiene are respectively 52.4 and 97 kcal/mole.[22] Thus the triplet $\pi\pi^*$ state should be energetically accessible, but the singlet state most likely is not.

Syntheses

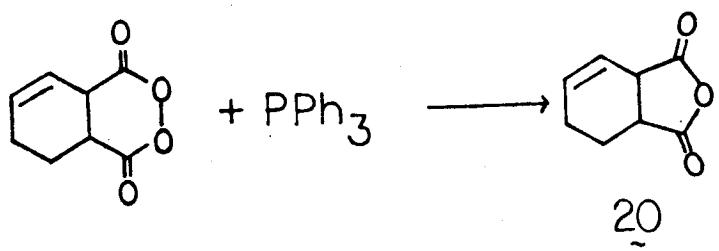
3-Cyclohexene-1,2-dicarboxylic acid (18) was prepared by the method of Lythgoe[29] via a Diels-Alder reaction of 2,4-pentadienoic acid (17)[30] and methyl acrylate, see Scheme 7. Partial separation of the cis and trans isomers

Scheme 7



of 18 was achieved by fractional crystallization. The peroxide 13 was prepared by successive treatment of 18 with phosphorous pentachloride and sodium peroxide.[8,9,16] The nmr for both diacid chloride 19 and peroxide 13 were consistent with the proposed structures. IR of the peroxide shows the characteristic double peak for ν(C=O) at 1810 and 1785 cm^{-1}, spaced 20-30 cm^{-1} apart.[5,16] Reaction of the peroxide with triphenyl phosphine[31,32] (see Figure 7) gave an IR which showed peaks for ν(C=O) at 1878 and 1806 cm^{-1}. This splitting is characteristic of an anhydride confirming the assignment of the peroxide.

Figure 7



20

Isomeric composition, see Table II, of 18 was determined by reaction with diazomethane and of the diacid chloride 19 by reaction with methanol, each to form the corresponding cis and trans dimethyl esters of 18 which were analyzed by analytical vpc (Carbowax 20M, 200°). The peroxide 13 reacted with triphenyl phosphine to give the corresponding anhydrides 20 which were analyzed for isomeric

composition by analytical vpc (PMPE, 200°). The assignment of anhydride retention times was confirmed by the conversion of the diacids 18 to the anhydrides 20 with acetic anhydride.[29] Predominant composition of the diacid samples was determined by their melting points.[27]

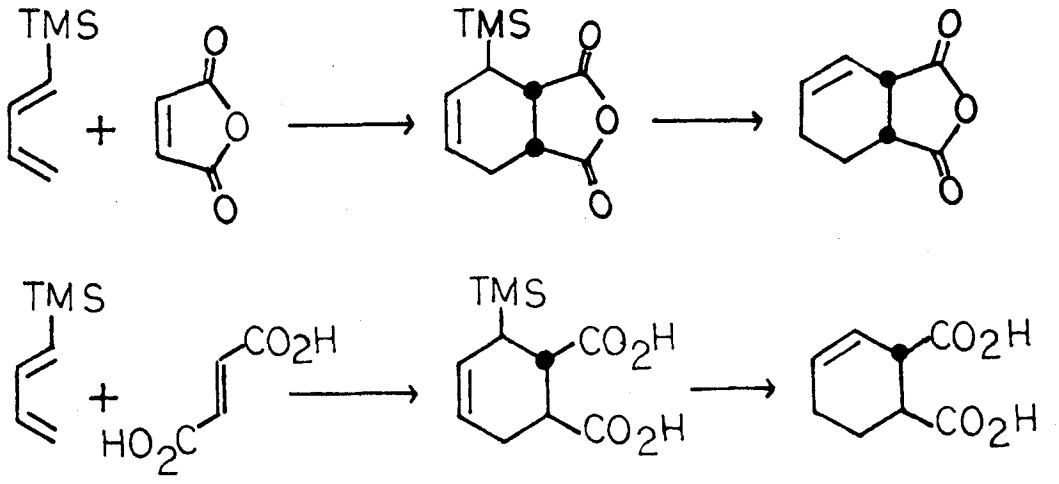
Table II. Typical Isomeric Compositions of Precursors to Peroxide 13.

		cis/trans ratio		
Diacid 18 Fraction	m.p.	Acid 18	Acid Chloride 19	Peroxide 13
"cis"	174	77/23	86/14	10/90
"trans"	210	38/62	41/59	10/90

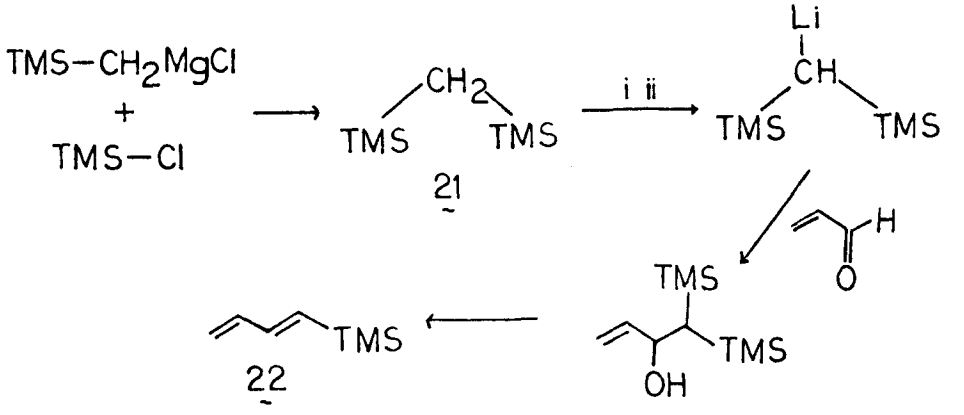
The yields of peroxide were typically low, < 10% based on the diacid. The trans-fused peroxide appears to have a faster rate of formation than does the cis-fused isomer since the former is formed predominantly from the intermediate diacid chloride, regardless of the isomeric composition of that precursor. One would not expect epimerization to occur during the peroxide forming step. This result can be rationalized if one considers that the trans configuration allows the favorable diequatorial placement of the peroxide ring.

Stereospecific syntheses of each isomer were planned via Scheme 8. The trimethylsilyl diene 22 is available through several routes.[33] We attempted the route shown in Scheme 9. The synthesis of the bis-(trimethylsilyl)methane

Scheme 8



Scheme 9



(21) appeared to be successful but initial attempts to perform the conversion to 22 were unsuccessful. Because of problems encountered in the decomposition of non-stereospecific 13, the synthesis of stereospecific diacids was not pursued further.

Thermal Decompositions

Solutions of peroxide 13, 0.12 and 0.06 M in ether, dichloromethane, and diglyme were degassed in sealed tubes and heated at 90°. The product mixture was analysed directly by analytical vpc (DBT, 80°). The major hydrocarbon products observed were benzene and 1,3-cyclohexadiene. For pyrolysis times of 5 minutes, their ratio ranged from 1.6-3.2 and appeared to be independent of peroxide concentration. It was shown that cyclohexadiene does not disproportionate under the reaction conditions in the absence of peroxide. Thermal decomposition of 13 at 108° showed hydrocarbon yields to be on the order of 5%.

A series of decompositions of 13, 0.15 M in diglyme, using n-octane as an internal standard were done to measure the yield of cyclohexadiene and benzene and to determine a mass balance for the reaction. The results are shown in Table III. It is interesting that the benzene remains relatively constant form day one to day three while the yield of cyclohexadiene rises dramatically. Hexane, from crystal-

Table III. Mass Balance Results of Pyrolysis of 13 in Diglyme at 90°.

Length of Pyrolysis Min.	Day No.	(mmole/mmole peroxide)x100% Benzene	CHD	cyclic C_6	Total	mg Hexane
10	1	1.9	1.0	0.1	3.0	0.17
	1	1.9	0.9	0.2	3.0	0.17
	2[a]	2.9	7.1	0.1	10.1	0.16
	3[b]	5.4	27.0	0.5	32.9	0.15
20	1	2.2	1.0	0.1	3.3	0.23
	1	2.2	1.0	0.1	3.3	0.21
	2[a]	2.8	1.7	0.1	4.6	0.21
	2[a]	2.6	1.4	0.0	3.9	0.20
	3[b]	2.9	1.7	0.0	4.6	0.20
40	1	1.9	0.5	0.1	2.4	0.12
	1	2.6	1.4	0.1	4.1	0.12
	1	2.8	2.5	0.0	5.3	0.12
	1	4.2	3.2	0.1	7.4	0.11
	2[a]	2.4	18.2	0.3	20.9	0.11
	3[b]	5.0	94.9	1.5	101.4	0.11

a) First night samples were kept in the freezer. b) Second night samples were kept at room temperature.

lization, which could not be removed from the peroxide, acted as a check on the internal standard, showing that there were no significant losses due to evaporation. Apparently the major portion of product formation was occurring subsequent to pyrolysis.

In an attempt to unravel this observation, we monitored the disappearance of peroxide rather than the appearance of product. This was done by IR at 40° and at 70°, by thermally quenching samples before taking their spectra. The peroxide carbonyl peaks disappeared with time and new ones began to grow in the same region, but they were not identified.

Some IR samples were subsequently analyzed by analytical vpc (PMPE, 150°), (DBT, 80°) for anhydrides and hydrocarbons, respectively. Two samples from the 40° decomposition showed both cis and trans anhydrides 20 in a ratio of 1/1.8. An additional peak with a longer retention time (1.6 relative to cis 20) appeared in relative ratios of 4.3 and 6.0 for the 48 hr sample and 72 hr sample, respectively. This peak which was not identified did not appear in any of the samples from the 70° pyrolysis. In the 70° decomposition six percent yields were obtained for all samples.

An experiment which monitored the decomposition in benzene-d_6 by NMR showed only a slight change in the spectrum upon pyrolysis. The IR spectrum of the product mixture again looked like the anhydride 20. Comparison with the IR

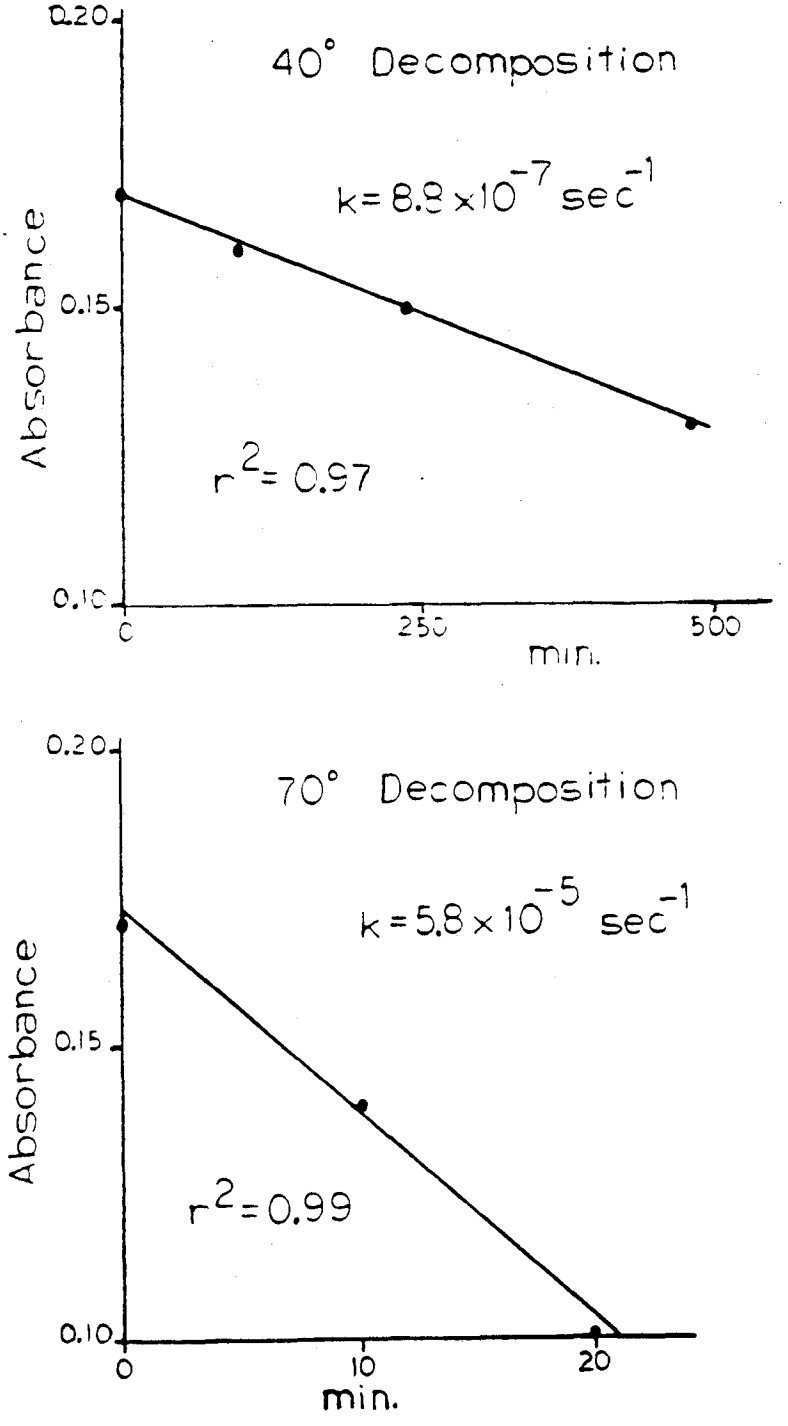
from the reaction of peroxide with triphenyl phosphine shows exactly the same absorbances (after subtracting those due to the phosphorous compounds). The pyrolysis mixture has, in addition, two peaks at 1250 and 862 cm^{-1}. These are where one would expect peaks from an epoxide, so we suspect that one reaction the peroxide undergoes is oxidation of the double bond to the corresponding epoxide, while the peroxide linkage is itself reduced to the anhydride.

The IR spectrum of anhydride purified by preparative vpc (PMPE, 180°) was taken. Interestingly it showed that the absorbance observed at 1739 cm^{-1} in both the pyrolysis and triphenyl phosphine reaction is not due to the anhydride. The identity of this peak has not been determined.

Pyrolysis of 0.05 M peroxide in benzene gave 7.5% ± 1 yield of anhydrides. Decomposition of neat peroxide in a sealed tube gave 3.9% anhydride and 6% hydrocarbon products. It is still unknown what comprises the remainder of the mass balance.

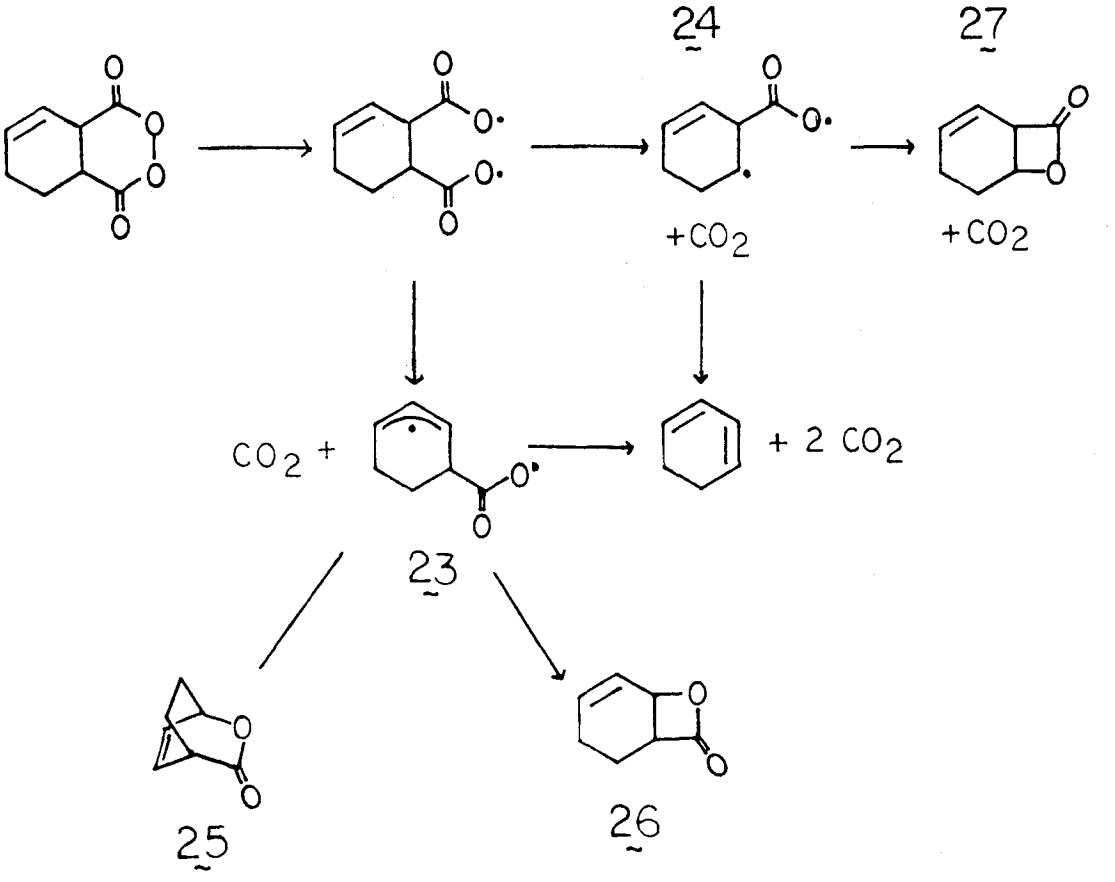
The IR experiments did allow a very rough calculation of the kinetics for the disappearance of peroxide, see Figure 8. From these plots we estimate E_a to be 30 kcal/mole and log A to be 14.8. These parameters give a half-life of 23 minutes at 90°. This is much longer than had been anticipated based on the decomposition rates observed for the dimethyl succinoyl peroxides.[19]

Figure 8. Kinetic data for disappearance of 13 obtained by monitoring IR peak at 1785 cm^{-1}.



The possibility of lactone formation as shown in Scheme 10 was considered. The carboxy diradicals 23 and 24 are analogous to intermediates proposed by Jones and Dervan,[16] formation of 23 being more favorable because

Scheme 10



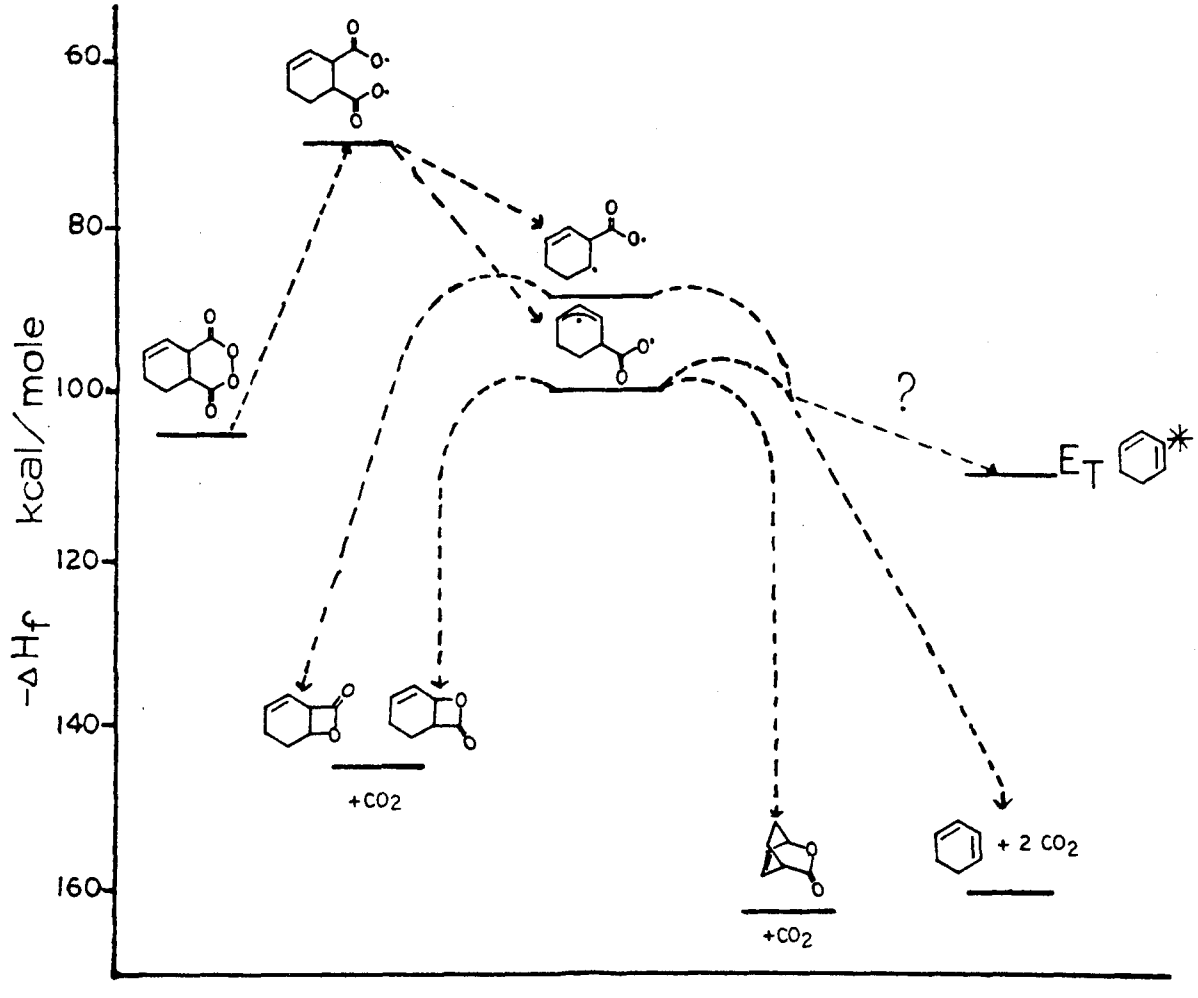
it involves cleavage of the more labile allylic carboxy group. The β-lactones, 26 and 27, would be analogous to the β-lactones observed in the decomposition of dimethyl succinoyl peroxides.[19] As can be seen from the energy diagram shown in Figure 9, the formation of less strained δ-lactone 25 is competitive energetically with formation of cyclohexadiene and presents an even more attractive alternate decomposition product.

Bicyclo[2.2.2]-3-oxaocta-5-ene-2-one (25) has recently been synthesized by Malpass and Twaddle[35] via the Diels-Alder reaction of cyclohexadiene and chlorosulfonylisocyanate. We have made the lactone by this method and have obtained IR and nmr spectra which agree with those of the authors. The compound begins to decompose at 115°[35] but we have observed it by vpc (PMPE, 140°). At this temperature other peaks, probably decomposition products are also observed. It was successfully purified by preparative vpc (PMPE, 110°) and analytical conditions found (PMPE, 110°) such that no decomposition products appeared.

Decomposition of 0.42 M peroxide 13 in CH_2Cl_2 gave no peak at the retention time of the δ-lactone, even at the most sensitive setting on the gc.

The δ-lactone was decomposed in a sealed nmr tube at 120°. Monitoring the reaction by nmr showed that it converted cleanly to cyclohexadiene and CO_2, with a first order

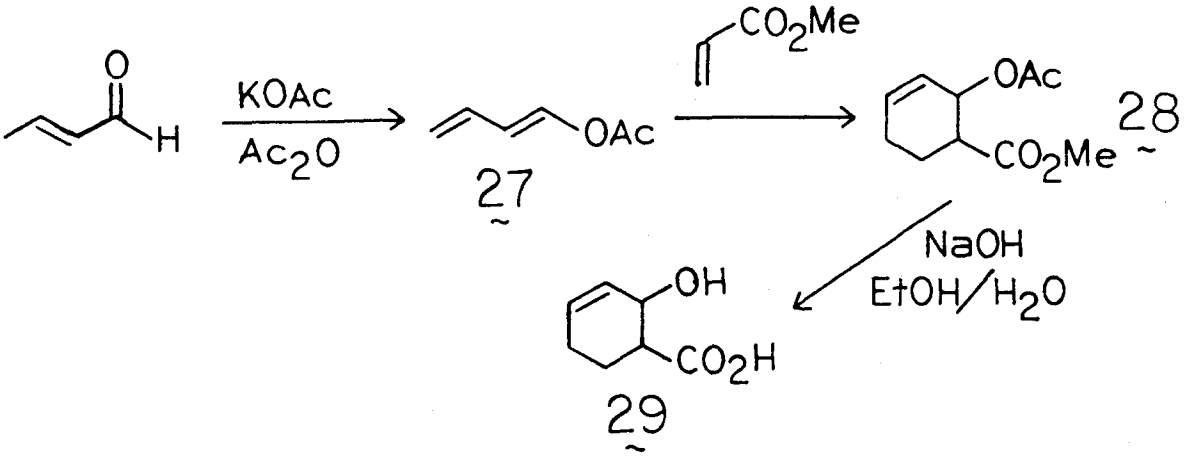
Figure 9. Estimated[20] Energy Diagram for Decomposition of 13.



rate constant of 2.92×10^{-5} sec^{-1}. Assuming an A factor of 10^{14},[20] one estimates the E_a to be 33 kcal/mole.

An attempt was made to synthesize the β-lactone 26 from the corresponding hydroxy-acid 29, which was prepared via Scheme 11. An attempt was made to convert the hydroxy-

Scheme 11



acid to the β-lactone via the method of Adam[36] using benzene sulfonyl chloride in pyridine. Analysis by analytical vpc (PMPE, 110°) showed two product peaks which were separated by preparative vpc (PMPE, 100°). Neither had an IR peak at 1830 cm^{-1} which would be characteristic of a β-lactone. Another attempt employed the method of Mageswaran[37] using methane sulfonyl chloride in Na_2CO_3/ether. This also gave two products. The IR of the crude product mixture showed no peak near 1830 cm^{-1}.

These syntheses have not been pursued further at present.

Chemically Initiated Electron Exchange Luminescence

It was observed that addition of peroxide 13 to a solution of rubrene in dichloromethane resulted in chemiluminescence which was visible to the naked eye in a dark room.

With a view toward looking at the CIEEL decomposition of the cyclic diacyl peroxides synthesized thus far in the group, an attempt was made to reproduce Schuster's[38] kinetic results with diphenoyl peroxide. Diphenoyl peroxide was synthesized by the method of Ramirez.[39] Chemiluminescence measurements were made using a MPF-4 Fluorescence Spectrophotometer.

The reaction of 5×10^{-5} M diphenoyl peroxide with 7×10^{-3} M tetracene in deoxygenated dichloromethane at 25.6° gave no light detectable by the fluorimeter, although low intensity light was visible in a dark room using 10^{-2} M peroxide with the same tetracene concentration.

The experiment was done with perylene, 5×10^{-3} M and 1×10^{-2} M, and diphenoyl peroxide, 1×10^{-3} M. Light was detected but we were at the absolute limit of the instrument sensitivity. The kinetics did not appear to be first order.

The experiment was run using rubrene as activator in the concentration range 1 to 13×10^{-4} M. Again the kinetics were not first order and the light emission monitored by

the fluorimeter appeared to decay linearly. The reason for this is not known. The results were analyzed by integrating the measured light decay and fitting it to the form $c-ce^{-kt}$ varying c so that the equation $[1-(c-ce^{-kt})c]$ gave an intercept of one, thus attempting to get the best first order plot available from the data. This resulted in a bimolecular rate constant which was about six times greater than that expected at this temperature from Schuster's data.

It is not clear why we cannot reproduce the strictly first order kinetics reported by Schuster. One possibility is the difference in peroxide concentrations used. Because the fluorimeter is not as sensitive as usual instrumentation used for monitoring chemiluminescence, we have been using peroxide concentrations on the order of 10^{-4} M or greater, whereas Schuster reports 5×10^{-5} M peroxide concentrations. It seems unlikely that this would account for the entire problem, however.

Cryoscopic molecular weight determination was performed on the peroxide, 13, giving results of 200g/mole ± 40 for one sample and 235g/mole ± 47 for a second sample. Since molecular weights have routinely been high for this and similar peroxides,[19] it was thought that they were perhaps contaminated with some polymeric peroxide.

An attempt was made to obtain pure monomeric peroxide using gel permeation chromatography which separates compounds according to molecular size. The following experi-

Table IV. Gel Permeation Chromatography

Column	Solvent	Void Vol. drops	Substance	Retention Vol. drops	% Yield
PVA-500[a]	THF	850	trans 178 mg	800-1600	4
			trans 363 mg	800-2000	
Biobeads SX-12[b] 10g	THF/CH_2Cl_2 2:1	900	cis	800-2000	
			dl anhydride[d] 305 mg	1300-1600	~100%
Biobeads SX-12 50g	"	4600	trans 369 mg	4600-6500	43%
			dl anhydride 200 mg	6300-6700	~100%
			cis 80 mg	4600-5000	
Sephadex LH-20[c] 10g	"	1450	dl anhydride 30 mg	2300-2800	
			benzoyl peroxide 120 mg	2100-2900	
			cis 103 mg	1200-2200 [2200-3100][e]	
			cis 113 mg	1200-2300 [2300-3200][e]	63%[f]
Sephadex LH-20 10g	"		cis 104 mg	1500-2500 [2800-3800][e]	
Biobeads SX-12 5g			Peak #1 from run above	1300-2600 [2800-4600][e]	
Sephadex LH-20 15g	1,2 dichloro-ethane/THF 3:1	1300	trans 18 mg	1350-1950	

a) polyvinyl acrylate with an exclusion limit of MW 300-500; b) poylstyrene with an exclusion limit of MW 400; c) a hydroxypropylated cross-linked dextran; d) dl-2,3-dimethyl-succinic anhydride; e) IR shows this peak to be other than starting material; f) based on iodometric method.

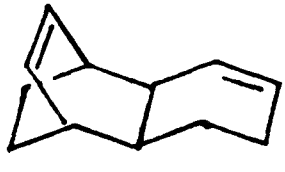
ments were done on the saturated peroxides, cis- and trans-1,2-hexahydrophthaloyl peroxide,[19] because their precursors are commercially available allowing large quantities of peroxide to be made conveniently. The results are shown in Table IV.

No successful separation was accomplished on any column tried. Peroxide consistently came out essentially at the void volume. This implies that either all peroxide is polymeric or for some other reason it is being excluded from the beads.

Cyclohexadiene Dimers

In order to be able to look for the triplet chemistry of cyclohexadiene, a sample of the photodimers 14, 15, 16 of cyclohexadiene[40] were analyzed by analytical vpc (SF-96, 130°) and retention times were measured relative to decane. Isomers 14 and 16 occurred under the same peak. The two major peaks were separated by preparative vpc (Apiezon J, 145°) and gave nmr spectra for isomers 14 and 15 identical with the literature.[41]

The thermal dimers, 16 and 30, were prepared by heating cyclohexadiene at 210° for 23 hours in a sealed tube, fol-



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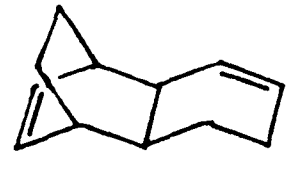

16

lowed by preparative vpc (SF-96, 150°). It is was not possible to obtain the minor isomer 16 pure without significant contamination from the major isomer 30, but the NMR and IR spectra of the combined dimers was consistent with that reported.[26] The thermal dimers gave gc retention times relative to decane which were easily distinguishable from those of the photodimers.

A 0.07 M solution of peroxide in freshly purified, dimer-free cyclohexadiene was pyrolyzed for 5 minutes at 86°. Analysis showed evidence of thermal dimers but no indication of photodimers, which would be expected were triplet chemistry occurring.

In view of the fact that the overall yield of cyclohexadiene is only a few percent in this decomposition, it is possible that even if triplet excited cyclohexadiene were being formed, the dimer concentration would be beyond our detection limit. Because of the complex nature of the chemistry that is occurring in this sytem, it has proved unsuitable for the purpose of discovering whether or not six-membered cyclic diacyl peroxides form $\pi\pi^*$ excited state triplets upon decomposition.

EXPERIMENTAL

General

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, a Varian T-60, or a Varian EM-390 spectrometer. Chemical shifts are reported as parts per million downfield from tetramethylsilane (TMS) in δ units. Magnetic resonance data are reported in the order: chemical shift; multiplicity, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; number of protons.

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

Mass spectra were performed by David Erwin on a DuPont 21-492B spectrometer.

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 the 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 chromatography columns are listed in Table V. All 1/8" columns are stainless steel; all 3/8" columns are aluminum.

Table V VPC Columns

Column Designation	Description
DBT	10'x1/8", 10% dibutyl tetrachlorophthalate on 100/120 Chrom P acid washed.
PMPE	10'x1/8", 10% poly-m-phenyl ether on 100/120 Chrom W acid washed DMCS.
SF-96	10'x1/8", 10% SF-96 on 100/120 Chrom P acid washed.
PMPE	2'x1/8", 10% poly-m-phenyl ether on 100/120 Chrom W acid washed DMCS.
AJ	5'x3/8", 35% Apiezon J on 60/80 Chrom W.
DC-550	10'x3/8", 25% silicone DC-550 on 60/80 Chrom P acid washed
SE-30	20'x3/8", 25% SE-30 on 45/60 Chrom P.
SF-96	10'x3/8", 25% SF-96 on 45/60 Chrom A.
PMPE	2'x3/8", 10% poly-m-phenyl ether on 60/80 Chrom W.
Carbowax 20M	10'x3/8", 25% Carbowax 20M on 60/80 Chrom W acid washed.

The 1/8" columns were used in analytical work. The 3/8" columns were used in preparative work.

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

Saturated ethereal solutions of diazomethane used throughout much of this work for analytical analysis were 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.

trans-2,4-Pentadienoic Acid (17)[30]

To a solution of 100g (0.96 mole) of malonic acid in 220 ml pyridine, cooled to 0°, 80 ml (2.00 mole) of acrolein were added dropwise with vigorous mechanical stirring. After reacting for three hours, the temperature was raised to 35-40° and the solution allowed to stir overnight, while evolving carbon dioxide. The solution was cooled, acidified with concentrated HCl to pH 2 and extracted with ether. The ethereal solution was dried ($MgSO_4$) and concentrated giving bright yellow sticky crystals. These were recrystallized from petroleum ether giving slightly yellowish crystals, which became whiter upon standing in air. In order to ob-

tain pure white product, it was necessary to allow the diene acid to stand in air until all yellow disappeared and product began turning brown. Recrystallization at this point led to pure white product. mp 69-72°; ir ($CHCl_3$) 1692, 1642, and 1603 cm^{-1}; nmr ($CDCl_3$) δ 5.3-7.6 (22 peaks).

cis- and trans-1,2,3,4-Tetrahydrophthalic Acid (18)[29]

A solution of 15g (0.15 mole) of trans-2,4-pentadienoic acid and 1g of hydroquinone in 100 ml (1.63 mole) methyl acrylate were refluxed for 20 hours. The cooled solution was diluted with ether and extracted with 10% sodium carbonate. The aqueous solution was acidified with concentrated HCl, extracted with ether, dried ($MgSO_4$) and concentrated to afford a thick brown oil. The monomethyl ester was hydrolyzed for five days at room temperature in 500 ml 1N NaOH. The solution was then acidified, extracted into ether, dried ($MgSO_4$) and concentrated. Fractions of crystals were collected and washed with cold ether as they appeared during solvent removal. Typically six fractions were collected, the first ones containing primarily trans-diacid (mp 210°) and later fractions containing largely cis-diacid (mp 174°). nmr (DMSO-d_6) δ 12 (s, 2), 5.7 (d, 2), 3.3 (d, 1), 2.6 (d, 1), 1.9 (br s, 4).

1,2,3,4-Tetrahydrophthalic Acid Chloride (19)

A mixture of 3.0g (0.018 mole) of diacid 18 and 8g (0.04 mole) phosphorous pentachloride was stirred until a solution formed. The solution was heated for two hours at 70-80° and $POCl_3$ and excess PCl_5 were removed by distillation at reduced pressure. (PCl_5 sublimes onto the distilling head.) Vacuum distillation yields the diacid chloride, 19, a pale yellow liquid. ir ($CDCl_3$) 1788 cm^{-1}; nmr ($CDCl_3$) δ 5.0 (d-t, 1), 4.4 (d-q, 1), 3.8-4.1 (m, 1), 3.2-3.6 (m, 1), 1.7-2.6 (m, 4).

1,2,3,4-Tetrahydrophthalic Peroxide (13)

A solution of 3.0g each of sodium phosphate monobasic and sodium phosphate dibasic in 75 ml water is cooled to 0°. To the vigrously stirring solution, 3.0g (0.038 mole) sodium peroxide is added slowly over five minutes. A solution of the diacid chloride 19 in 75 ml dichloromethane is added and the resultant solution stirred vigorously for three hours at 0°. The layers are separated and the aqueous layer washed once with dichloromethane. All organic layers are then dried ($CaCl_2$) and carefully concentrated to yield a white paste. This is taken up in a minimum of dichloromethane and added dropwise to hexane stirring in a methanol/ice bath. The crystals are collected by suction filtration. ir (CH_2Cl_2) 1810, 1785, and 1733 cm^{-1}; nmr ($CDCl_3$) δ 5.2-6.1 (br s, 1), 4.2-4.9 (m, 1), 3.9 (br s, 1), 3.3 (br s, 1), 2.1 (br s, 4).

Bis-(trimethylsilyl)methane (21)

To a rigorously dried flask, 8.8g (0.36 mole) of magnesium turnings were added under nitrogen and flamed, then 50 ml anhydrous ether was added. Ten ml of a solution of 45g (0.36 mole) trimethylsilylmethylchloride in 75 ml ether was added via a dropping funnel. With vigorous stirring the reaction began and the remaining solution was added over 2 hours. An equimolar amount of trimethylsilyl-chloride in ether solution was added over several hours with refluxing and then allowed to sit overnight under nitrogen. The reaction mixture was poured carefully over ice, extracted with ether, washed with saturated sodium chloride, and dried ($MgSO_4$). The solution was concentrated and distilled. GC analysis showed significant contamination from bis-trimethylsilyloxide. The product 21 was separated by preparative vpc (SF-96, 100°). mass spectrum (75 eV) m/e (relative intensity) 28(67), 32(11), 43(8), 45(13), 59(12), 73 (100), 132(36), 145(78), 160(19); nmr ($CDCl_3$) δ 0 (s).

Trimethylsilylbutadiene (22)[34]

The bis-trimethylsilylmethane solution in ether was used without further purification. Two ml of solution, 1 ml distilled N,N,N',N'-tetramethylethylenediamine and 20 ml anhydrous ether were mixed in a rigorously dried 25 ml 3 necked flask under argon and cooled with an ice bath.

Addition of 8.5 ml of 1.6 M n-butyllithium was followed by 3 days of stirring at room temperature. A solution of 0.9 ml acrolein in 5 ml ether was dried ($CaCl_2$) and added to the reaction mixture. After stirring for several hours the mixture was poured over ice. The aqueous layer was washed once with ether and the ethereal extracts dried (Na_2SO_4), concentrated and vacuum distilled. The products were separated by preparative vpc (SE-30, 100°) but none gave an NMR spectrum characteristic of a diene. It may be necessary to purify the bis-trimethylsilylmethane by preparative vpc prior to attempting this sequence.

Pyrolysis of Peroxide 13

Pyrolyses were done in sealed tubes on degassed samples. Pyrolysis temperatures ranged from 85-117°. Pyrex tubes were cleaned using the sequence: chromerge, distilled water, concentrated aqueous ammonia, distilled water, EDTA in methanol/water, and distilled water.

Monitoring Decomposition of 13 by IR.

A standard solution $\leq$ 0.1 M of peroxide in dichloromethane was prepared. Sample tubes were degassed and sealed with 25 μl solution per tube. The tubes were placed in a thermostated circulating bath (40°) or a thermostated oil bath (70°) and timing begun. At the appropriate intervals tubes were removed, cooled, and the IR spectra taken. To

calculate kinetic data, a baseline was chosen in each spectrum and absorbance relative to that baseline was calculated from the percent transmittance. Any vpc analyses were done subsequent to taking the spectrum.

1,2,3,4-Tetrahydrophthalic Anhydride (20)

A solution of 1 gram of 1,2,3,4-tetrahydrophthalic acid in 20 ml acetic anhydride was refluxed for 1 hr. The solvent was removed by distillation at reduced pressure and the product purified by preparative vpc (PMPE, 180°). ir (CH_2Cl_2) 1863, 1789 cm^{-1};

Bicyclo[2.2.2]3-oxaocta-5-ene-2-one (25)[35]

To a solution of 1.75 ml (0.020 mole) chlorosulfonyl-isocyanate in 50 ml freshly distilled dichloromethane, stirring under nitrgoen at room temperature, were added 2.0g (0.025 mole) of 1,3-cyclohexadiene in 10 ml dichloromethane over ten minutes via syringe. Immediately the solution turned dark purple. Over the 42 hour reaction period the solution turned successively green and orange. Concentration of the solution afforded brown crystals which were recrystallized from acetone. The resulting white crystals were dissolved in 12 ml acetone and 8 ml water. Six drops of concentrated HCl were added and the solution stirred for 45 minutes. Extraction with dichloromethane gave an orange

oil after solvent removal which was extracted with petroleum ether. This extract was concentrated to give a nearly colorless oil, which was purified by preparative vpc (PMPE, 110°), ir ($CDCl_3$) 1752, 1738 cm^- ; nmr ($CDCl_3$) δ 6.5 (m, 2), 5.2 (m, 1), 3.4 (m, 1), 1.1-2.4 (m, 4).

Butadienyl Acetate (27)[42]

A solution of 20.86g (0.21 mole) potassium acetate in 80 ml acetic anhydride was refluxed for 30 minutes under nitrogen, then 19.6g (0.28 mole) crotonaldehyde was added over 40 minutes and refluxing was continued for an additional 30 minutes. The reaction mixture was cooled, quenched with an equal volume of water and extracted with 4 x 60 ml hexane. The hexane solution was washed with water, saturated bicarbonate, and brine, then dried (Na_2SO_4). The hexane was removed by distillation and product fractionally distilled at reduced pressure. ir (CH_2Cl_2) 1753, 1658 cm^{-1}; nmr ($CDCl_3$) δ 5.0-7.5 (m, 5), 2.1 (s, 3).

Methyl 2-Acetoxy-3-cyclohexenylcarboxylate (28)

A degassed solution of 0.12g (0.001 mole) butadienyl acetate (27) in 0.9 ml (0.01 mole) methyl acrylate was heated for 24 hours in a sealed tube at 150°. The product was purified by preparative vpc (Carbowax 20M, 200°). nmr ($CDCl_3$) δ 5.6-6.2 (m, 2), 5.5 (t, 1), 3.6 (s, 3), 2.8 (m, 1), 2.0 (m, 7).

Chemiluminescence Experiments

Stock solutions of the various activators were prepared in dichloromethane, degassed by bubbling with argon, and were diluted volumetrically. Solutions were kept cold and in the dark except when in use. Stock solutions of peroxide were prepared and samples were added to the activator solution via syringe and mixed just prior to making the measurements. All measurements were made on a model MPF-4 Fluorescence Spectrophotometer.

Molecular Weight Determination of 13

Molecular weights were determined by the freezing point depression of benzene. Measurements were made using a digital millivolt meter and cooling curves were plotted by hand. A calibration curve was prepared using dl-2,3-dimethylsuccinoyl anhydride.

Gel Permeation Chromatography

Void volumes were determined using polyethylene glycol MW 811 for the PVA-500 and Biobeads SX-12 columns and using Carbowax 20M for the Sephadex LH-20 column. Analysis was done by spotting fractions on a TLC plate and spraying with Dragendorf's reagent.

Analysis for peroxide was done by spraying with a solution of potassium iodide in acetic acid/isopropanol, 1:10 by volume.

Peroxide was determined quantitatively in several runs using an iodmetric method.[43] For each chromatographic fraction to be tested a 100 μℓ sample was diluted volumetrically to 5 ml with 2:1 acetic acid/chloroform. The solution was bubbled with argon for 1 minute then 50 μℓ of 50% aqueous potassium iodide was added and bubbling continued for an additional minute. The flask was stoppered, mixed and stored in the dark for one hour before reading. Absorbance was read on a Beckman 25 UV Visible Spectrometer at 470 nm using a water blank. A standard curve was prepared using a stock solution of iodine instead of peroxide fractions.

Thermal Dimers of 1,3-Cyclohexadiene (16, 30)

1,3-Cyclohexadiene, freshly purified by preparative vpc (DC-550, 80°), was heated in a sealed, degassed tube at 210° for 23 hours. The resulting products were separated by preparative vpc (SF-96, 150°). ir ($CDCl_3$) (79/21 mixture of 30 and 16) 3020, 2930, 1645, 1615, 1440, 1377, 1258, 1179, 1168, 1073, 943, and 859 cm^{-1}; nmr ($CDCl_3$) (major isomer 30) δ 5.5-6.5 (m, 4), 1.0-2.5 (m, 12), (minor isomer 16) δ 5.0-6.5 (m, 4), 0.5-2.5 (m, 12).

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28. We need not worry about unfavorable entropic effects[2] in this case since we are going from one mole of reactants to three moles of product, which is entropically favorable by a sufficient amount.

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