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THE UNIVERSITY OF ALBERTA

STUDIES ON 1,2-DIOXETANES

BY

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A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES

AND RESEARCH

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR

DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

FALL, 1973

THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled STUDIES ON 1,2-DIOXETANES submitted by John Edward Filby, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

Karl R. Kopecky
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Fred H Wolfe

A. Paul Schaap
External Examiner

Date Fall 1973

TO MY MOTHER AND FATHER

We shall not cease from exploration
And the end of all our exploring
Will be to arrive where we started
And know the place for the first time.

T. S. Eliot

ABSTRACT

A number of β-bromo- and β-iodohydroperoxides were prepared and reactions of these compounds with silver acetate were studied. Several 1,2-dioxetanes, formed during these reactions, were isolated in 25 - 35% yields and the chemistry of these compounds was investigated.

It was found that the 1,2-dioxetanes isolated were decomposed at moderate temperatures, yielding carbonyl compounds arising from cleavage of the 1,2-dioxetane ring. A kinetic study of the thermolyses of several 1,2-dioxetanes, namely, trimethyl-1,2-dioxetane, tetramethyl-1,2-dioxetane, 1,6-dimethyl-7,8-dioxabicyclo[4.2.0]octane and 11,12-dioxa[4.4.2]propellane, was carried out. It was found that, in each case, first order kinetics was obeyed over two to three half lives. Experimental values for the energies of activation are 23.5, 25.6, 24.5 and 23.0 kcal mole^{-1}, respectively.

A section is included in this work concerning the many reported syntheses of 1,2-dioxetanes which have appeared in the literature in recent years. These reports are discussed in the light of present knowledge of dioxetane chemistry. A supposedly general synthesis of 1,2-dioxetanes <u>via</u> the ozonation of olefins was investigated in some detail; it was concluded that simple dioxetanes could not be prepared by this method.

Finally, an investigation was carried out concerning the nature and yields of the electronically excited carbonyl fragments generated on thermolysis of 1,2-dioxetanes. Luminescence measurements from

fluorescer containing solutions of tetramethyl-1,2-dioxetane 4 indicated that the yields of excited singlet and excited triplet acetone, generated by thermolysis of this compound, are 0.2% and ∿ 100%, respectively.

A possible use for 1,2-dioxetanes, as secondary liquid light standards, is discussed.

ACKNOWLEDGEMENTS

The author is deeply indebted to his research director, Dr. K. R. Kopecky, for constant encouragement and advice throughout this work. Dr. Kopecky was always available for discussion, at which times he seldom failed to introduce new and interesting ideas.

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Finally, the author wishes to thank his wife, Greta, for typing the thesis, and for the myriad other forms of assistance rendered during this research and in the preparation of this manuscript.

TABLE OF CONTENTS

PAGE

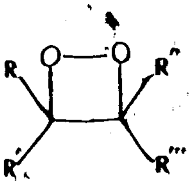
CHAPTER IV (Cont.)

LIST OF TABLES

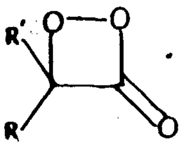
LIST OF FIGURES

INTRODUCTION

The synthesis of 1,2-dioxetanes, represented by the general structure I, has been the subject of recent intensive studies. Much of the interest in this family of high energy compounds stems from the belief that such materials are critical intermediates in many chemiluminescent reactions.



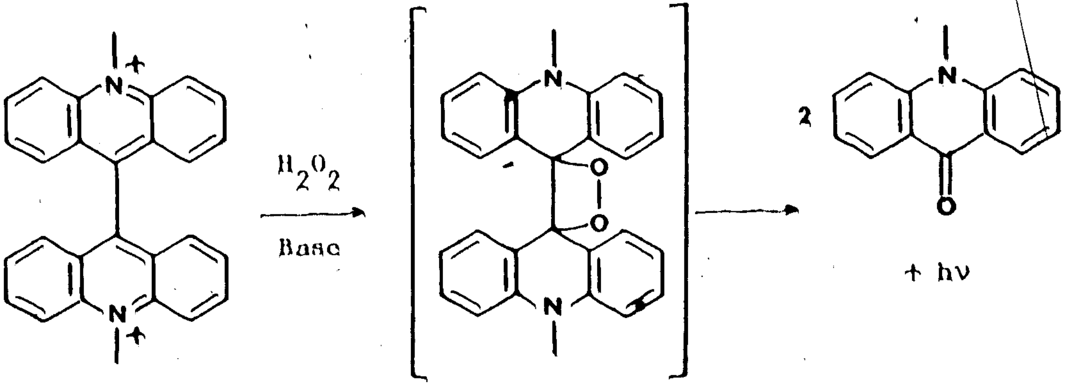
I



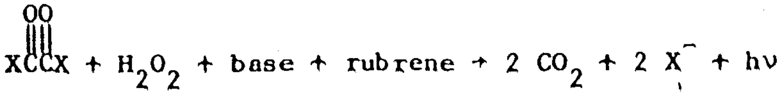
II

Chemiluminescence was observed from the compound known as lucigen as long ago as 1935; this dimethylbiacridinium salt is cleaved to N-methylacridone when treated with hydrogen peroxide and base. The reaction gives off a bright light which McCapra has shown to be emitted from the excited singlet state of the product.[1] The proposed intermediate in this reaction is the cyclic four-membered peroxide shown below.

Cleavage of the 1,2-dioxetane produces a product molecule in the excited singlet state.

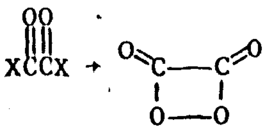


Light is also produced when oxalyl chloride or oxalate esters are treated with basic hydrogen peroxide in the presence of fluorescer molecules such as rubrene.[2] Rauhut has obtained good evidence that the critical intermediate in this reaction is the cyclic peroxide 3,4-dioxo-1,2-dioxetane, 1.



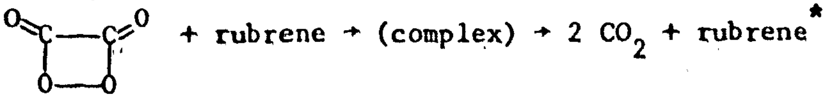
$$X\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}X + H_2O_2 + \text{base} + \text{rubrene} \rightarrow 2\,CO_2 + 2\,X^- + h\nu$$

X = Cl, O-R etc.



$$X\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}X \rightarrow$$

1

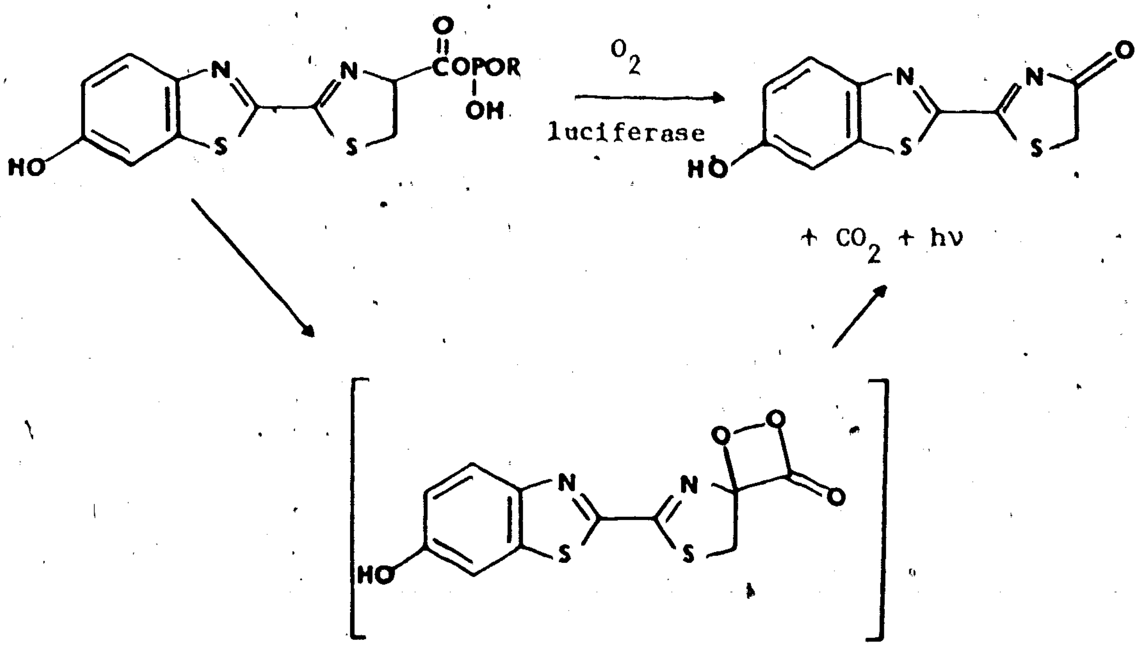


+ rubrene → (complex) → 2 CO_2 + rubrene*

1

rubrene* → rubrene + hν

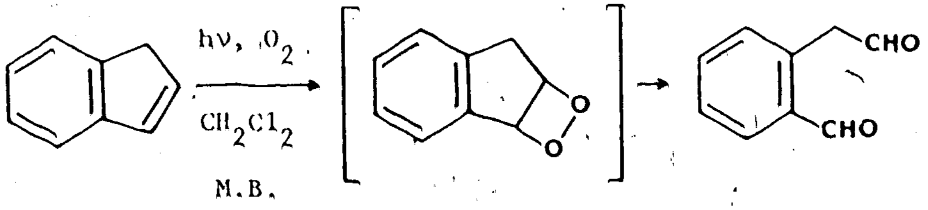
α-Peroxylactones of general structure II have been suggested as intermediates in many bioluminescent systems. Work by White,[3] McCapra[1] and others has shown that, in the presence of luciferase and oxygen, luciferin (shown below as the anhydride derivative) is converted into the amide shown and CO_2; light is emitted during the reaction. White and McCapra simultaneously suggested that light was produced by decomposition of an intermediate cyclic peroxide.



1,2-Dioxetanes have also been proposed as intermediates in reactions of singlet oxygen and related reagents with certain types of olefin to account for the cleavage products obtained. For example Rio & Bertholet[4] explained the high yields of carbonyl derivatives formed during photooxygenation of stilbene and styryl derivatives by proposing the intermediacy of 1,2-dioxetanes.

Kearns[5] proposed the intermediacy of a 1,2-dioxetane in the photooxygenation of indene to account for the high yield of homophthalaldehyde obtained when the reaction was carried out in methylene chloride, eq. [1].

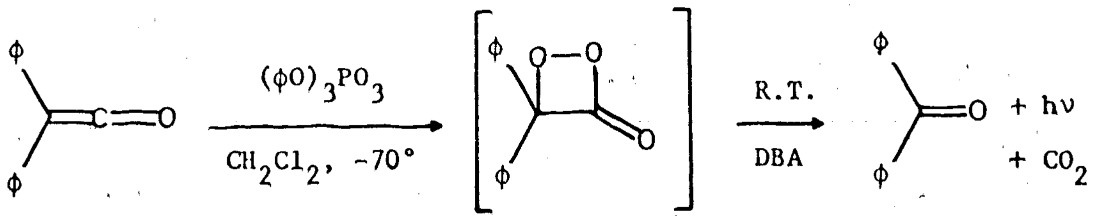
[1]



M.B. = Methylene Blue

Bollynky[6] suggested that the reaction of triphenyl phosphite ozonide with ketenes also proceeded via a 1,2-dioxetane intermediate, eq. [2].

[2]

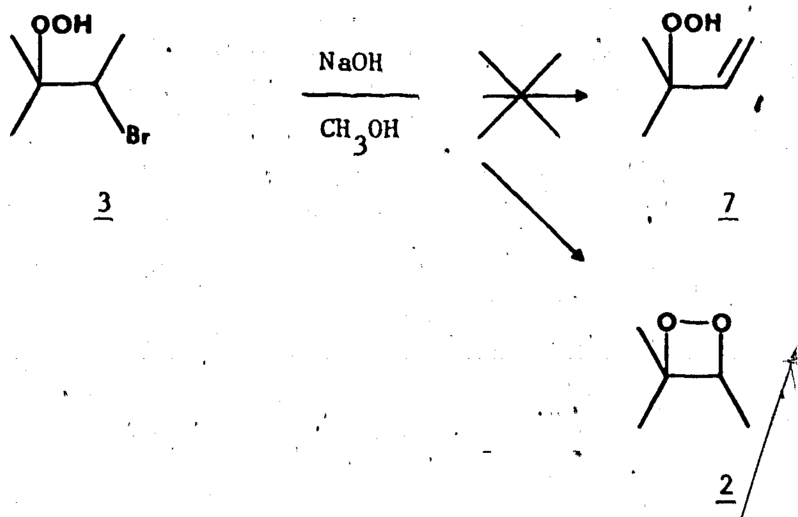


The intermediate is apparently unstable at room temperature; when the solution was allowed to warm to room temperature in the presence of dibromoanthracene (DBA) chemiluminescence was observed.

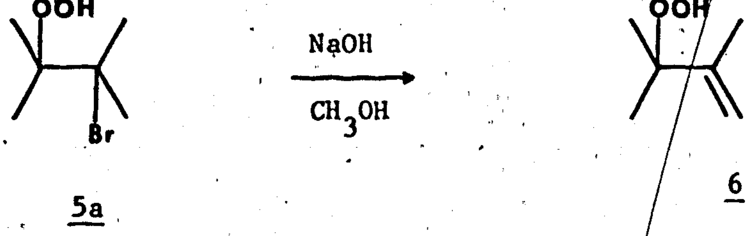
1,2-Dioxetanes have been proposed as intermediates in many other reactions too numerous to mention in this work. However, in these cases as well as in the preceeding examples the intermediates proposed appeared to be too unstable to allow their isolation, hence, no direct evidence existed then to support the proposals that such intermediates could behave in the manner suggested. However, the isolation by Mumford[7] of the first stable 1,2-dioxetane, trimethyl-1,2-dioxetane 2, and the demonstration that its decomposition was indeed chemiluminescent placed these earlier proposals on a firmer footing.

Trimethyl-1,2-dioxetane 2 was obtained as an unexpected product from the reaction of 3-bromo-2-methyl-2-butyl hydroperoxide 3 with sodium hydroxide in methanol, eq. [3].

[3]

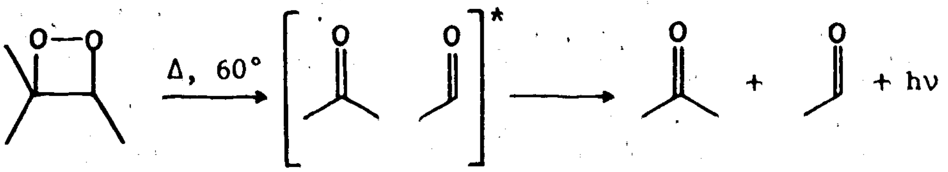


[4]



By analogy to the reaction of 3-bromo-2,3-dimethyl-2-butyl hydroperoxide 5a, eq. [4], treatment of 3 with base was expected to lead to the allylic hydroperoxide 7.[8] No trace of this product could, however, be detected and the major product was 2.

Tetramethyl-1,2-dioxetane 4 was subsequently prepared by treatment of 5a with silver acetate and it was demonstrated that both compounds could be thermolyzed at moderate temperatures to yield the corresponding carbonyl compounds.[7] Decomposition of both 2 and 4 was accompanied by light emission; the luminescence spectrum of 2 closely matched the emission spectrum of acetone suggesting that the excited singlet state of acetone is responsible for the luminescence.

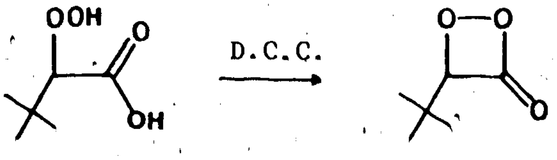


2

Since publication of this pioneering synthesis, many reports concerning the preparation and chemistry of 1,2-dioxetanes have appeared in the literature.

The highly unstable 3,3-dimethyl-1,2-dioxetane 8 was isolated by Richardson[9] using a technique similar to that described by Mumford; adapting this approach somewhat, Adam[10] reported the synthesis of the first peroxy lactone 9, eq. [5].

[5]

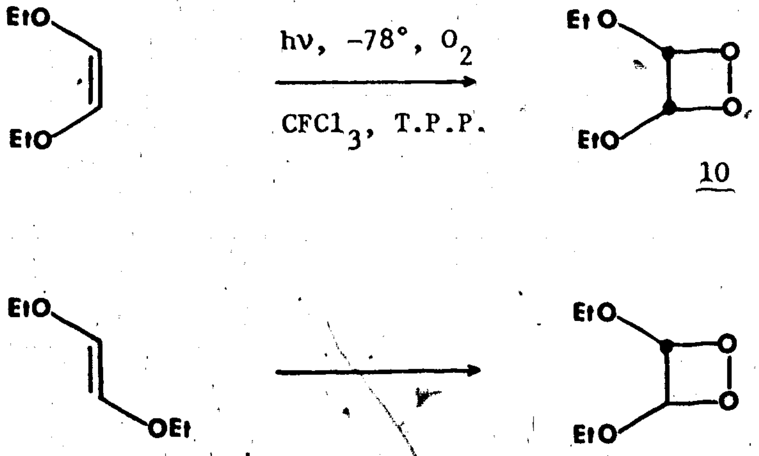


9

D.C.C. = Dicyclohexylcarbodiimide

1,2-Dioxetanes are also formed in good yields from the low temperature reaction of singlet oxygen with electron rich olefins.[11,12] This reaction appears to be limited to olefins which have no active hydrogens α to the double bond. For example, singlet oxygen adds in a stereospecific manner to <u>cis</u>- and <u>trans</u>-1,2-diethoxyethylene yielding the 1,2-dioxetanes 10 and 11,[12] eq. [6].

[6]



10

11

T.P.P. = Tetraphenylporphyrin

Triphenyl phosphite ozonide,[13] a reagent which reacts with olefins to yield products similar to those derived from photooxygenation of the olefins, also reacts with the above olefins to yield

1,2-dioxetanes. In this case, however, the reaction is non-stereospecific, both cis- and trans-olefin give rise to a mixture of 10 and 11 on treatment with the reagent.[12]

All the 1,2-dioxetanes described in this section appear to be more or less unstable at room temperature, all decompose to yield the corresponding carbonyl compounds. It has been shown that this decomposition obeys first order kinetics and activation parameters have been estimated in several cases.[9,14]

As an initial project, it was proposed to synthesize several 1,2-dioxetanes with different structural features.

The synthesis of several such compounds is described in Chapter I and the chemistry of these compounds is also described. A discussion of other preparations of 1,2-dioxetanes is presented in Chapter II. A kinetic study of the thermolysis of these compounds was also carried out and the results of this study are presented in Chapter III. Finally an investigation into the yield and nature of excited states generated on thermolysis of these compounds was also carried out. The results of this study are presented in Chapter IV.

CHAPTER I

PREPARATION AND CHEMISTRY OF 1,2-DIOXETANES

It was proposed initially to carry out a detailed study of the kinetics of decomposition of trimethyl-1,2-dioxetane, 2 and tetramethyl-1,2-dioxetane 4. These results could be compared with [illegible] Richardson's studies on the dimethyl compound to determine the influence of methyl substitution on the rates of decomposition of 1,2-dioxetanes.

Additionally, it was proposed to synthesize 1,2-dioxetanes derived from 1,2-dimethylcyclohexene 12 and $\Delta^{9,10}$-octalin 13 to examine the behaviour of bicyclic and tricyclic 1,2-dioxetanes.

Although 2 was readily accessible in good yield by the method devised by Mumford, his preparation of the tetrasubstituted dioxetane 4 gave rise to very low yields (*ca*. 5%) of product. Since we were interested in preparing tetrasubstituted-1,2-dioxetanes, the first objective then was to improve on the synthetic route leading to this class of compounds.

RESULTS AND DISCUSSION

Preparation of β-Halohydroperoxides:

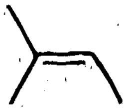
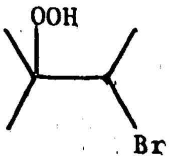
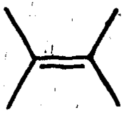
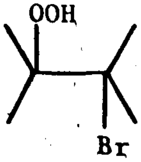
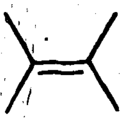
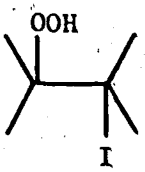
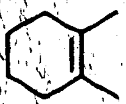
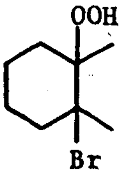
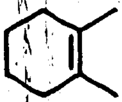
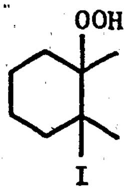
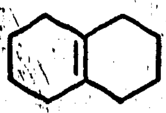
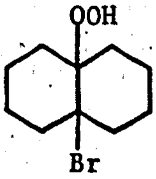
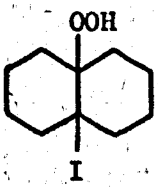
β-Halohydroperoxides were prepared according to the method of van de Sande,[8] by reaction of either 1,3-dibromo-5,5-dimethylhydantoin or the corresponding diiodo compound with olefins at -40° in the presence of excess hydrogen peroxide. Yields of halohydroperoxides prepared in this way are listed in Table I. NMR spectra of the products are reported in the experimental section.

The bromohydroperoxides 3 (derived from 2-methyl-2-butene) and 5a (derived from 2,3-dimethyl-2-butene) had earlier been prepared by van de Sande and by Mumford, respectively. Materials prepared according to procedures described by these authors showed spectral properties identical to those reported. Thus, 3 was prepared in 90% yield from the reaction of 2-methyl-2-butene with 98% hydrogen peroxide and 1,3-dibromo-5,5-dimethylhydantoin (DBH) at -40°. Iodometric analysis of this sample indicated a purity of 94% based on the active oxygen content. In a similar manner 5a was prepared in 95% yield from 2,3-dimethyl-2-butene.

The corresponding iodohydroperoxide, 5b, was synthesized by a similar procedure using 1,3-diiodo-5,5-dimethylhydantoin (DIH) in place of the dibromo compound. The product, a faintly pink solid, was found to undergo spontaneous decomposition at room temperature; for this reason large quantities of 5b were not isolated in a pure state but were stored as solutions in ether or CCl_4. A small sample

TABLE I

Preparation of β-Halohydroperoxides

Starting Olefin	Halogen Source	Halohydroperoxide	Yield %
	DBH[a]	 3	84
	DBH	 5a	95
	DIH	 5b	80
	DBH	 14a	94
	DIH	 14b [b]	-
	DBH	 15a	85
	DIH	 15b	88

of 5b was recrystallized from heptane, white crystals so obtained melted at 32 - 35° with some decomposition.

Iodometric titration of this sample indicated a purity of 97.8%. White crystals of 5b could be stored at -10° for a few days.

1,2-Dimethylcyclohexene 12 was prepared from 2-methylcyclohexanol as outlined in the experimental section.

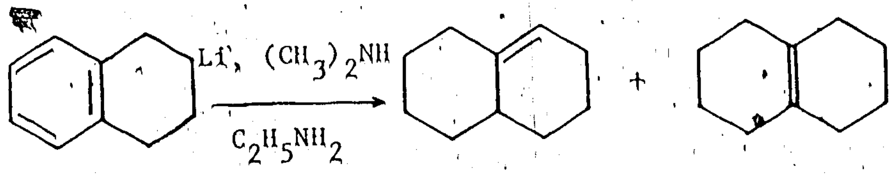
The bromohydroperoxide of 1,2-dimethylcyclohexene had also been prepared, but not isolated, by van de Sande.[8] Best yields of this material were obtained when freshly distilled olefin was used; the product, a colourless, viscous oil, solidified at -10°. A small sample of this material was recrystallized with difficulty from pentane, m.p. 44 - 46°. Iodometric analysis showed a purity of 97.2%.

The corresponding iodohydroperoxide 14b, was obtained as a highly unstable, yellowish oil from the reaction of 12 with hydrogen peroxide and DIH. The oil so obtained solidified at -10° but decomposition was rapid, even at this temperature. Recrystallization of a small sample from pentane at low temperatures yielded a yellow powder, m.p. 54 - 55°.

Iodometric analysis of this material was carried out but high values (greater than 110% of the theoretical active oxygen content) were found for the active oxygen content. It seems probable that liberation of iodine from the iodohydroperoxide 14b or from the iodohydrin produced after reduction gives rise to these high values.

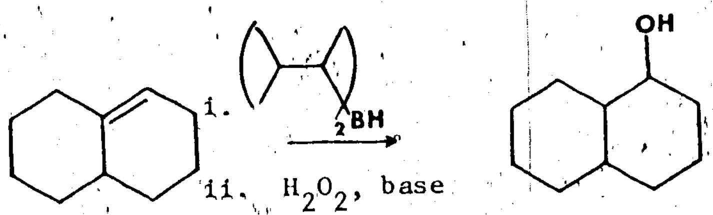
$\Delta^{9,10}$-Octalin 13 was prepared by modifying the procedure of Benkeser,[15] eq. [7].

[7]



∿ 30% 16 ∿ 70% 13

[8]



The original procedure called for naphthalene as starting material, the yield of product, however, could be doubled without increasing the scale of the reaction if tetralin was used as starting material. Separation of the desired $\Delta^{9,10}$-isomer was achieved by the hydroboration reaction developed by Benkeser, eq. [8]. The extremely bulky borohydride reagent adds only to the less hindered 16, oxidation of this adduct yielded an alcohol from which unreacted 13 could easily be separated by distillation.

9-Bromo-10-hydroperoxy-trans-decalin 15a was prepared in high yield from 13 by the usual methods. Recrystallization of the crude product from heptane yielded white crystals, m.p. 114 - 115°; iodometric analysis indicated the presence of 99.7% of the theoretical active oxygen content. 9-Hydroperoxy-10-iodo-decalin 15b was prepared and purified using a similar procedure; white crystals of product, m.p. 105° (decomp.) were unstable at room temperature but could be stored for weeks at -10° without appreciable decomposition. Iodometric analysis of a purified sample indicated a purity of 98.7%.

Since both 15a and 15b could readily be purified by recrystallization, in subsequent preparations of these materials impure $\Delta^{9,10}$-octalin was used, the hydroboration purification step being omitted.

Preparation of 1,2-Dioxetanes:

Trimethyl-1,2-dioxetane 2 was prepared according to the method of Mumford.[7] Tetramethyl-1,2-dioxetane 4 was obtained in reasonable yield (ca. 30%) by reaction of bromohydroperoxide 5a with a large excess of silver acetate; the best solvent for the reaction was found to be methylene chloride. Thus, a solution of 5a in methylene chloride was added rapidly to a slurry of silver acetate powder in methylene chloride stirred at room temperature. Reaction was rapid under these conditions and the mixture was filtered after a few minutes to give a clear yellow solution containing the dioxetane. After work up the dioxetane was freed from side products by low temperature sublimation followed by low temperature crystallization from pentane.

Reaction of iodohydroperoxide 5b under the same conditions resulted in a similar yield of 4, but this material was less convenient to use.

As we shall see later, the reaction was highly sensitive to solvent effects, methylene chloride or chloroform as solvent were equally effective but the former was chosen for its greater volatility and hence ease of removal.

Experiments with other silver salts such as silver benzoate, silver trifluoroacetate and silver tosylate were carried out but yields of dioxetane from these experiments were inferior.

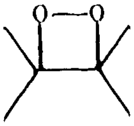
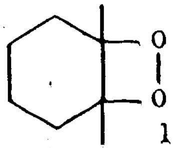
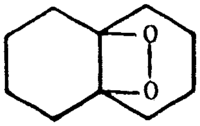
1,6-Dimethyl-7,8-dioxabicyclo[4.2.0]octane 17 and 11,12-dioxa-[4.4.2]propellane 18[16] were prepared in a similar manner from the analagous halohydroperoxides. Bromohydroperoxides 14a and 15a were found to be quite unreactive towards silver ion under the reaction conditions; in particular, 15a was extremely unreactive towards silver ion and very low yields of the 1,2-dioxetane 18 were obtained.

However, good yields of both 17 and 18 could be obtained from the reaction of the corresponding iodohydroperoxides 14b and 15b with silver ion, see Table II.

Isolation of 17 was achieved by the same low temperature sublimation and crystallization techniques used in the preparation of 4; 18, however, was too involatile (and too unstable) to be purified by these means. Isolation of 18 was achieved by low temperature chromatography on silica gel followed by low temperature crystallization. Spectral data together with analysis of the 1,2-dioxetanes prepared are given in the experimental section.

TABLE II

Preparation of 1,2-Dioxetanes

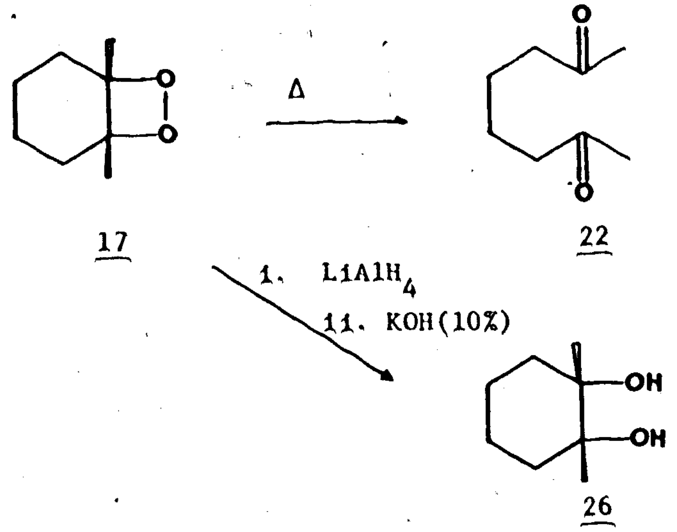
Starting Material	Product	Isolated Yield (%)
5a	 4	∿ 30%
5b	4	∿ 30%
14a	 17	∿ 15%
14b	17	∿ 25%
15a	 18	a
15b	18	∿ 35%

a - low, not determined.

Characterization of 1,2-Dioxetanes:

1,2-Dioxetanes were characterized by iodometric analysis (see experimental section), by their thermal decomposition to yield carbonyl compounds and by reduction to the corresponding cis-diols. These reactions are illustrated in eq. [9] using 17 as an example.

[9]



Thus 17 decomposed either on heating, or on standing for extended periods at room temperature yielding octane-2,7-dione 22 as the only product. This decomposition was accompanied by a faint bluish chemiluminescence which could be observed in a dark room. The decomposition of 17 could also be followed readily by NMR spectroscopy, Figure 1. The NMR spectrum of the starting material showed signals at τ8.6 (s) for the methyl protons and τ7.9 to 8.7 for the ring protons. These signals gradually disappeared on standing and were replaced by a new methyl absorption at τ7.87 (s) together with other signals characteristic of dione 22.

Product isolated from this decomposition was identical in all

Figure 1a. NMR spectrum (CCl_4) of 1,6-dimethyl-7,8-dioxabicyclo[4.2.0]octane 17.

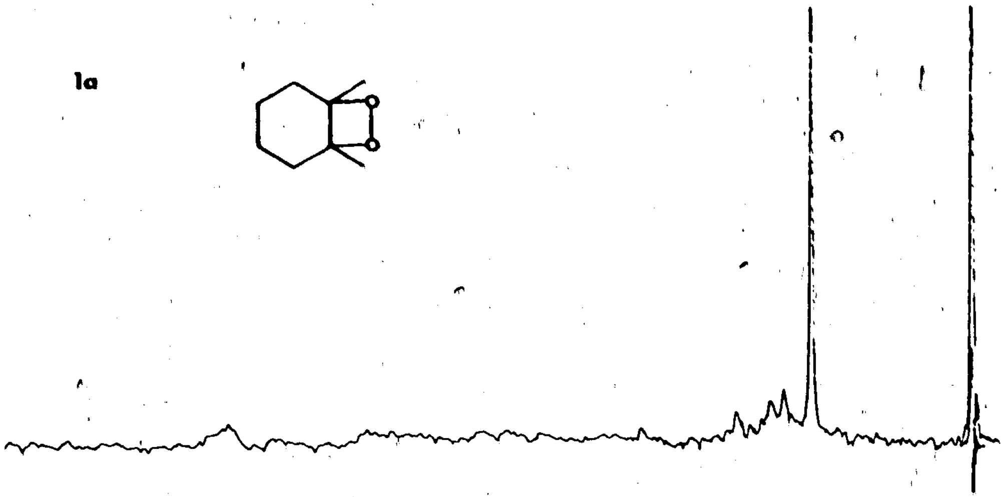
Figure 1b. NMR spectrum of a solution of 17 in CCl_4 after ∿ 72 hours at room temperature.

Figure 1c. NMR spectrum (CCl_4) of authentic octane-1,7-dione 22.

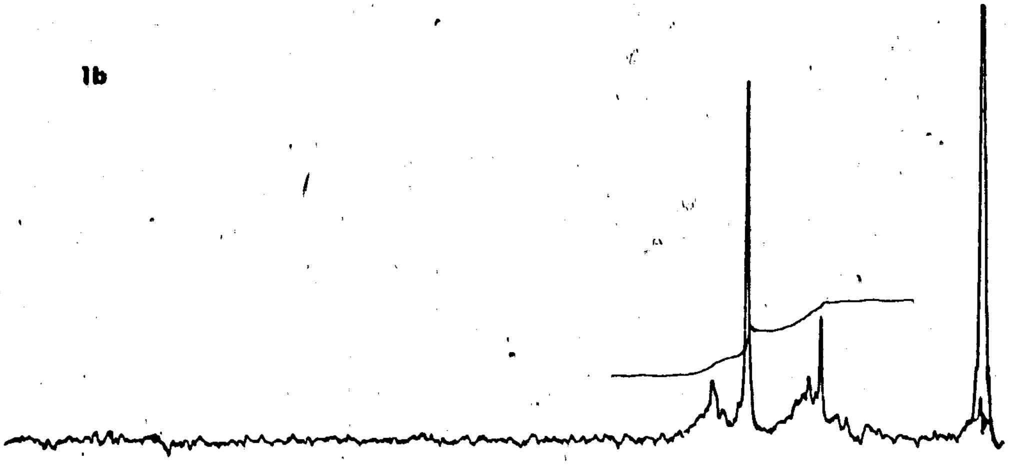
Figure 2a. NMR spectrum (CCl_4) of 11,12-dioxa[4.4.2]propellane 18.

Figure 2b. NMR spectrum of a solution of 18 in CCl_4 after ∿ 48 hours at room temperature.

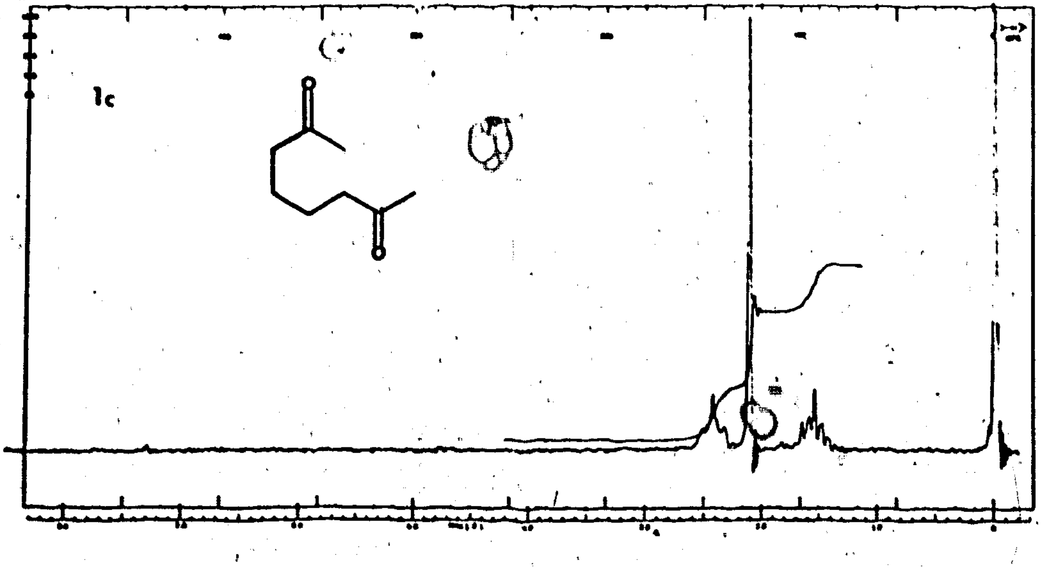
1a



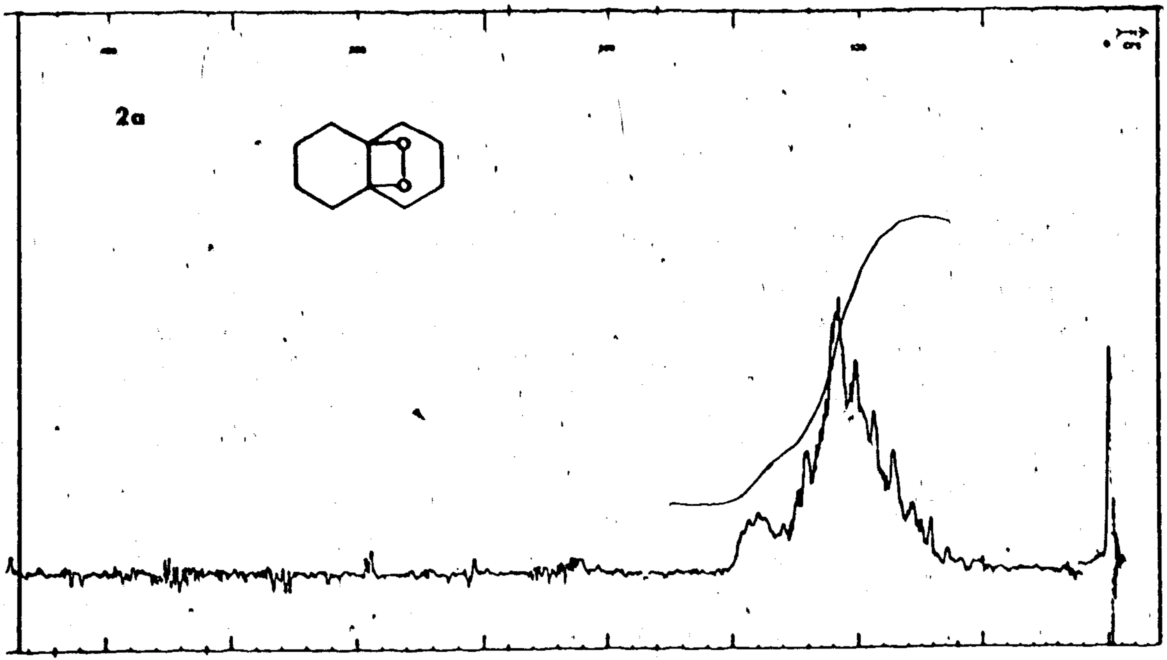
1b



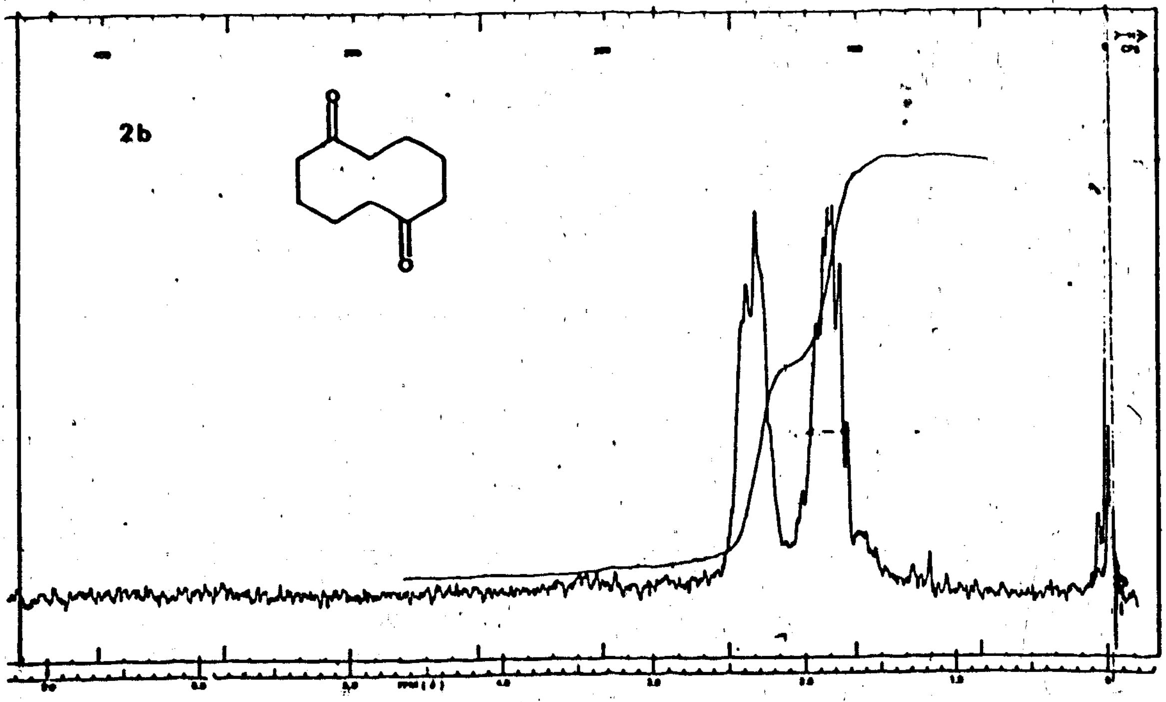
1c



2a



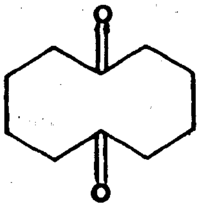
2b



respects with a sample of authentic 22 prepared by an unambiguous route.

Reduction of 17 was achieved by adding a solution of the dioxetane in ether to a slurry of $LiAlH_4$ in ether, stirred at -78°. The yield of *cis*-diol so obtained was ∿ 100%. A sample of this material, recrystallized from benzene, showed spectral properties (NMR, IR) identical to those of authentic material.

In a similar fashion, a solution of 18 in heptane, on standing at room temperature for several days, deposited crystals of pure cyclodecane-2,6-dione 24 as the only product. Dione so obtained was found to be identical in all respects to an authentic sample of 24. NMR spectra of dioxetane 18 and the decomposition product derived from this material, 24, are shown in Figure 2.



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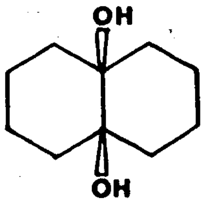
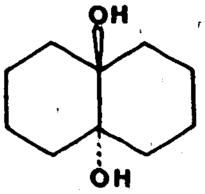


25



27

cis-9,10-Dihydroxydecalin 25 was obtained in 98% yield (as estimated by titration with $Pb(OAc)_4$ solution) from the reduction of 18. A sample of isolated diol, recrystallized from benzene, did not depress the melting point of an authentic sample of 25, however, a marked depression was observed for a mixture of recovered 25 with a sample of *trans*-9,10-dihydroxydecalin 27.

It had earlier been demonstrated that the decomposition of $\underline{4}$ yielded acetone as the only product, but no reduction experiments with $\underline{4}$ had been carried out. Reduction of $\underline{4}$ was carried out using the same technique described earlier to yield a quantitative amount of pinacol. Material so obtained showed spectral properties (NMR, IR) identical to those of authentic material.

UV Spectra of 1,2-Dioxetanes:

UV-visible spectra of some 1,2-dioxetanes are presented in Figure 3. All compounds of this class isolated to date are yellow in colour and this is reflected in the UV-visible spectra, all of which display tails stretching into the visible region. All the compounds show absorption maximum between 275 - 280 nm, ε 25 - 30.

A comprehensive spectral examination of organic peroxides has not been carried out probably due to the lack of distinctive peroxide absorptions. It is proposed that overlapping lone pair orbitals of the two adjacent oxygen atoms lead to low energy bonding and high energy antibonding orbitals π_{00} and π^*_{00} which are correspondingly filled with electrons in the ground state.[17] Thus the lowest energy electronic transition in simple peroxides can be characterized by $\pi^*_{00} \rightarrow \sigma^*_{00}$.

Simple alkyl peroxides show only weak, nearly structureless absorptions below 400 nm. For example, di-tert.-butyl peroxide shows an inflection at $\sim$ 250 nm, $\varepsilon \sim 7$.[17]

The electronic structure of 1,2-dioxetanes is likely distorted

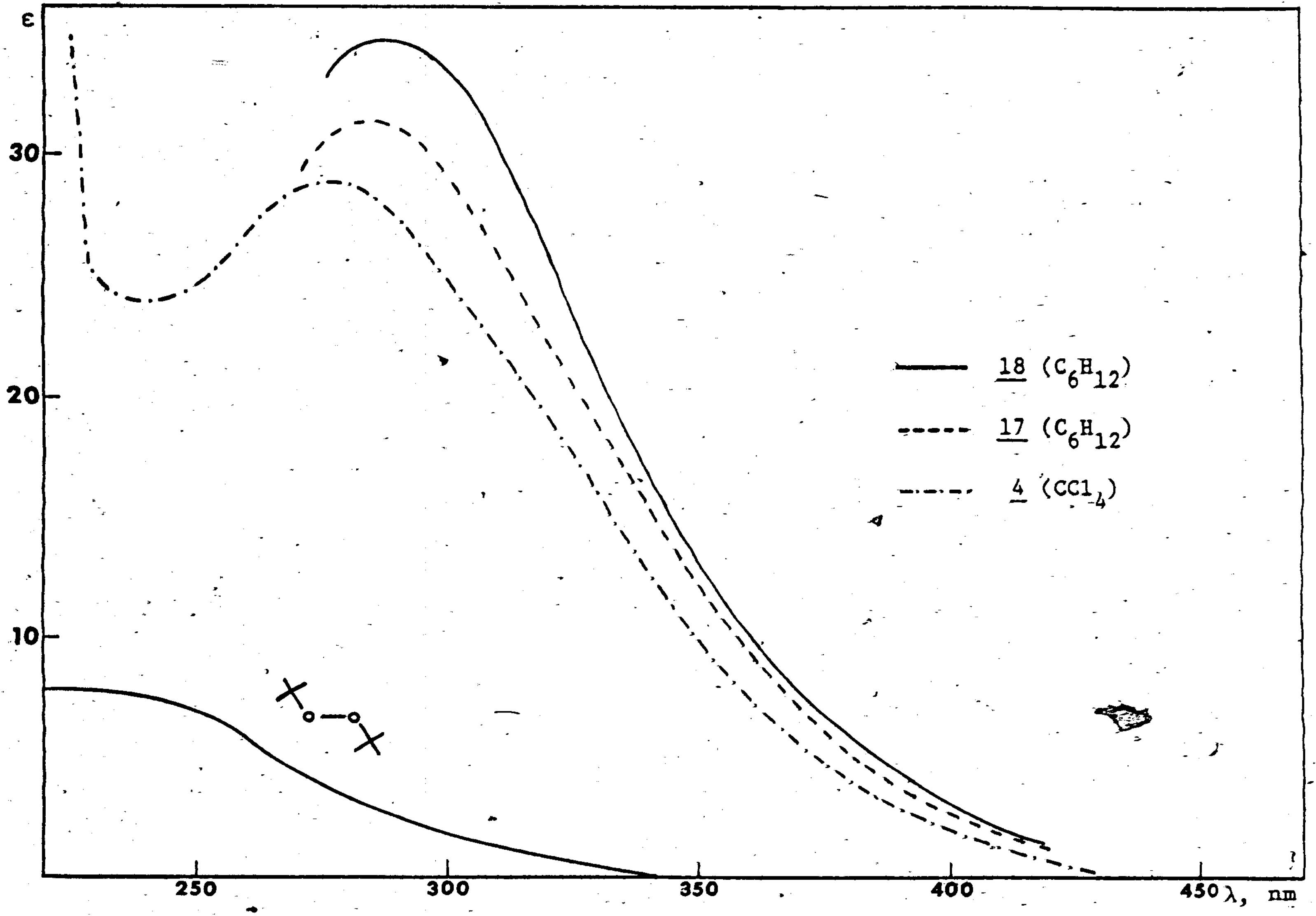
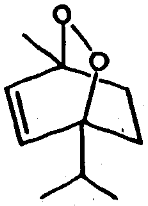


Figure 3. Ultraviolet-Visible Spectra of 1,2-Dioxetanes

by the strain effects caused by the four-membered ring and this seems to be reflected in their UV spectra as increased ε values and absorptions at higher wavelengths.

The peroxide linkage in endoperoxides should also be somewhat distorted, although this distortion would not be expected to be as severe as that in 1,2-dioxetanes. In accordance with this, ascaridole, shown below, appears to be a faintly yellow oil.

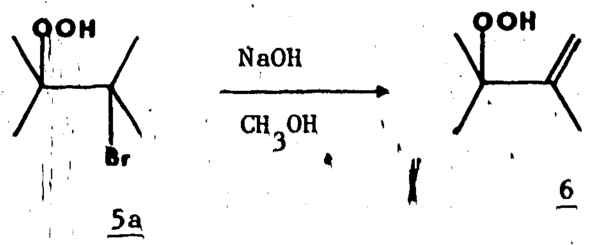


To ensure that the absorption spectra recorded were actually those of the 1,2-dioxetanes and were not due to the decomposition products (carbonyl compounds absorb in the same region), solutions of 1,2-dioxetanes prepared for spectral measurement were analyzed for peroxide content before and after the spectra were recorded. Decomposition of samples during the short time required to record the spectra was found to be negligible.

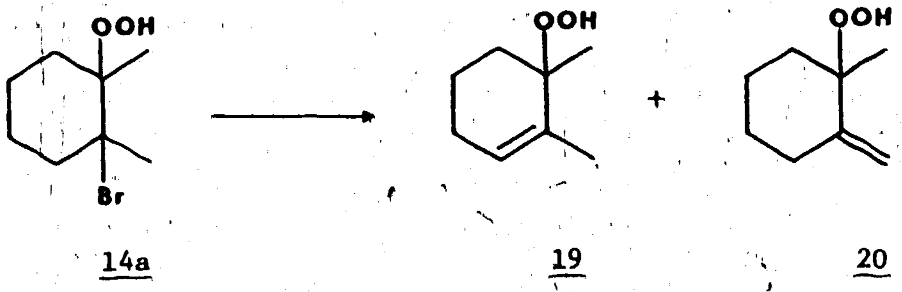
Reactions of Halohydroperoxides with Base:

van de Sande demonstrated that the β-bromohydroperoxides 5a and 14a were converted in good yield to the corresponding allylic hydroperoxides on treatment with methanolic sodium hydroxide,[8] eq. [10] and eq. [11].

[10]



[11]

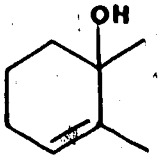


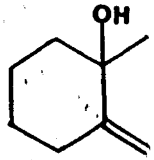
Similar results were obtained using the corresponding chlorohydroperoxides but yields of the allylic hydroperoxides were somewhat less.

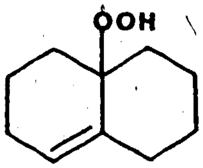
Treatment of the iodohydroperoxide 5b with base under the same conditions resulted in an almost quantitative yield of allylic hydroperoxide 6. Similarly, reaction of 14b under the same conditions yielded the isomeric allylic hydroperoxides 19 and 20 in the same ratio ($\sim$ 5:95) as that observed by van de Sande.[8]

Spectral properties of 19 and 20 had not previously been reported so that it was necessary to reduce the mixture of these materials to the corresponding allylic alcohols 29 and 30 the spectra of which were reported by van de Sande.[8]

10-Hydroperoxy-$\Delta^{1,9}$-octalin 23 was prepared in high yield, *ca.* 80%, by the reaction of either 15a or 15b with sodium hydroxide in methanol. Material isolated showed spectral properties identical to those reported by Foote for a sample prepared by photooxygenation of $\Delta^{9,10}$-octalin.[18]


29

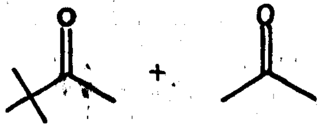

30


23

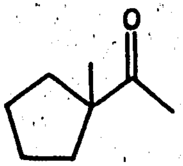
Reaction of β-Halohydroperoxides with Silver Acetate:

Treatment of either bromo- or iodohydroperoxides with silver acetate resulted in mixtures of products; in addition to the ring closure reaction leading to 1,2-dioxetane formation, products arising from elimination and rearrangement reactions were also observed, eq. [12] to eq. [14]. Secondary products, derived from decomposition of the dioxetanes were usually also observed.

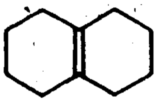
[12] 5a,b $\xrightarrow[CH_2Cl_2]{AgOAc}$ 4 + 6 +



[13] 14a,b $\longrightarrow$ 17 + 19 + 20 + 22 +


21

[14] 15a,b $\longrightarrow$ 18 + 23 + 24 +



13

Reaction of 5a and 5b, then, with silver acetate under conditions described earlier resulted in a mixture containing tetramethyl-1,2-dioxetane 4 ($\sim$ 30%), allylic hydroperoxide ($\sim$ 55%) and pinacolone ($\sim$ 15%). The latter product distilled over with 4 when this product was sublimed from the reaction mixture, and was isolated from mother liquors after crystallization of 4. The NMR spectrum of isolated material showed absorptions at τ7.95 (s) and τ8.9 (s) in the ratio 1:3. The yield of pinacolone was determined as the 2,4-dinitrophenylhydrazine derivative.

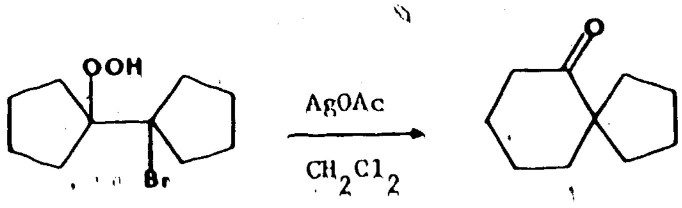
The residue obtained after sublimation of 4 was found to be almost pure 3-hydroperoxy-2,3-dimethyl-1-butene 6, identical in all respects with an authentic sample prepared from reaction of 5a with sodium hydroxide.

A similar mixture of products was obtained from the reaction of 14a and 14b with silver acetate. Again the rearranged product, 1-acetyl-1-methylcyclopentane 21, distilled over during sublimation of the dioxetane 17 and was isolated from the mother liquor after crystallization of this latter compound. Isolated 21 was identified by comparison of its spectral properties with those of authentic material prepared by the method of Hart.[19] The semicarbazone derivative was prepared from isolated 21, m.p. 138 - 141°, reported 141°.[20] The yield of 21 (as a percentage of total product) from iodohydroperoxide 14b, as estimated from the weight of semicarbazone derivative, was ∿ 20%.

The residue, after removal of 17 and 21, consisted largely of the allylic hydroperoxides 19 and 20. These were identified by a comparison of an NMR spectrum of the residue with a spectrum of material obtained by reaction of 14a with sodium hydroxide. TLC analysis of the residue also indicated the presence of small quantities of the dione 22. The yield of allylic hydroperoxide (as a percentage of total product) from 14b, as estimated by iodometric titration, was ∿ 50%.

The major product isolated from chromatography of mixture obtained from the reaction of 15b with silver acetate, eq. [14], was the allylic hydroperoxide 23. The yield of this product, as estimated by iodometric titration, was *ca.* 50%. Small amounts of the diketone 24 were also isolated from the column (*ca.* 2%) but no trace of the expected rearrangement product, spira[4.5]decan-6-one 32, could be detected either by TLC or by VPC. This product is formed in high yield from the reaction of bromohydroperoxide 31, eq. [15], with silver acetate.[21]

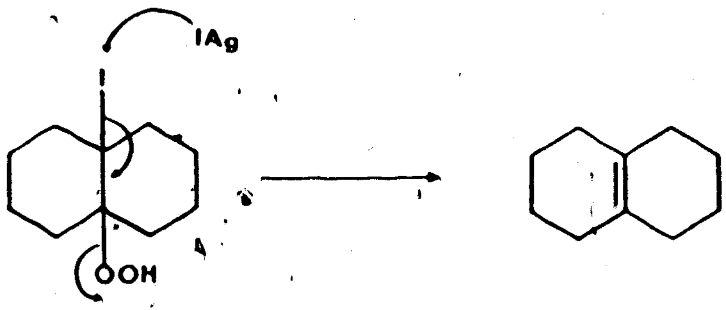
[15]



31 32.

The small amount of $\Delta^{9,10}$-octalin (~ 1%) isolated from the chromatography could possibly arise via an E_2 elimination from the iodohydroperoxide, eq. [16]. This material was identified by its R_f value on silica gel and from its NMR spectrum.

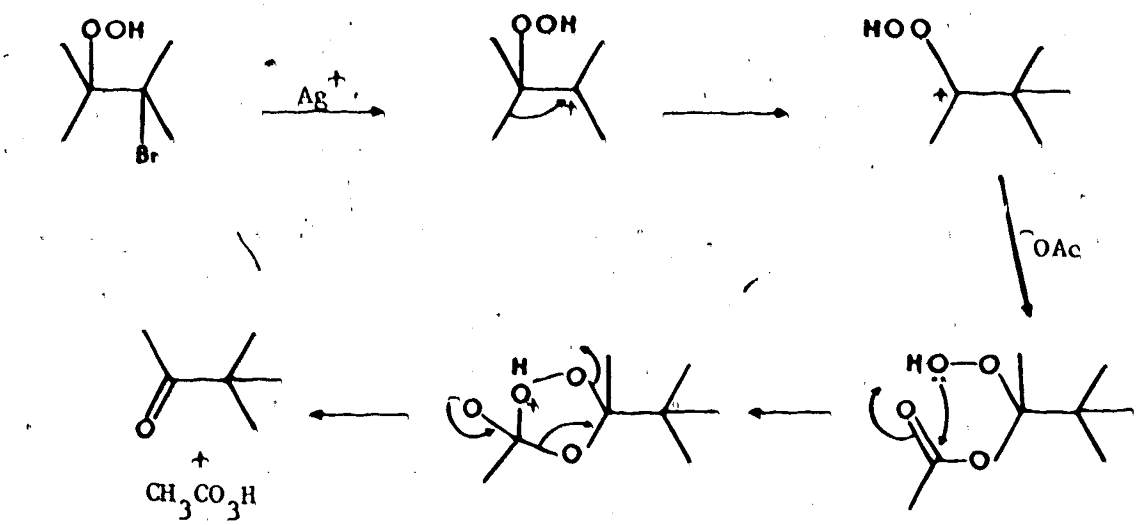
[16]



Pinacol-Type Rearrangements of Halohydroperoxides:

Rearrangement products obtained from the reaction of halohydroperoxides with silver salts resemble "semi-pinacol" rearrangement products derived from the reaction of iodohydrins with mercury salts.[22] However, in the former case, rearrangement is accompanied by a cleavage of the peroxide linkage. A possible mechanism for this rearrangement is shown in eq. [17].

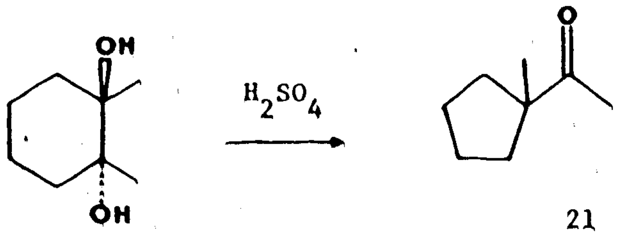
[17]



1-Acetyl-1-methylcyclopentane 21, obtained from rearrangement of 14a or 14b, is also obtained in the pinacol rearrangement of trans-1,2-dimethylcyclohexane-1,2-diol,[23] eq. [18]. This suggests a trans configuration for the halogen and hydroperoxy groups of 14a,b since pinacol rearrangement of the cis-diol gives 2,2-dimethylcyclohexanone,[23] eq. [19].

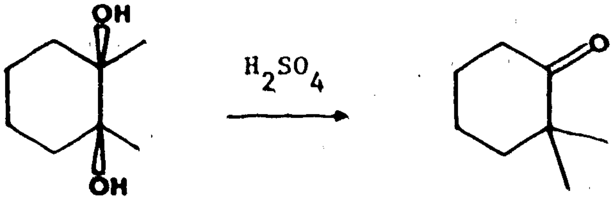
The differences in behaviour of these isomeric diols are best explained by reference to Newman projections (see diagram). In the cis-isomer the hydroxyl group and the migrating methyl group can attain a trans-diaxial configuration and migration of the methyl group can readily occur. In the trans-isomer no potential migrating group can attain a trans-diaxial configuration with respect to the hydroxyl groups. The carbon atoms of the ring, however, bear a *trans* relationship to the hydroxyl groups and rearrangement to the ring-contracted product 21 can occur.

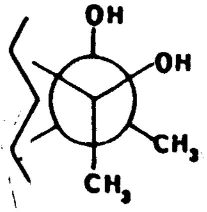
[18]



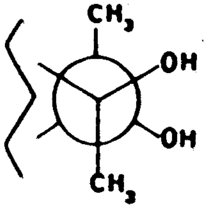
21

[19]



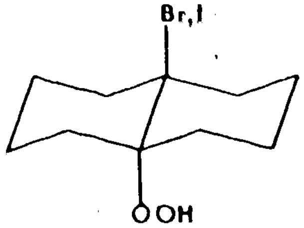


cis



trans

Perhaps a similar explanation can account for the lack of formation of the spiroketone 32 from 15a or 15b. If compounds 15a and 15b have a *trans* configuration, then the carbon atoms of the ring cannot bear a *trans* relationship to the halide leaving group.

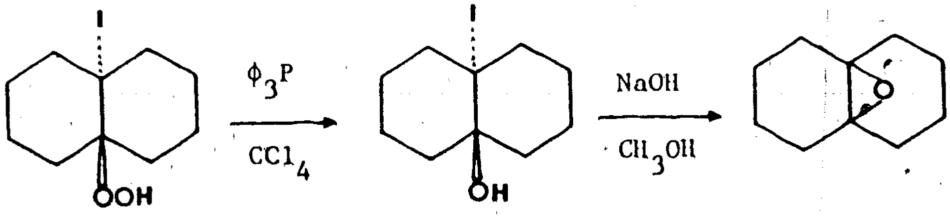


15a,b

Now, rearrangement of 9,10-dihydroxy-trans-decalin to 32 does occur but heating is necessary to achieve this reaction.[24] It is possible that conditions in the reaction of 15a or b with silver ion are mild enough to prevent such a rearrangement.

Confirmation of the trans configuration of 15b comes from the sequence of reactions shown in eq. [20].

[20]

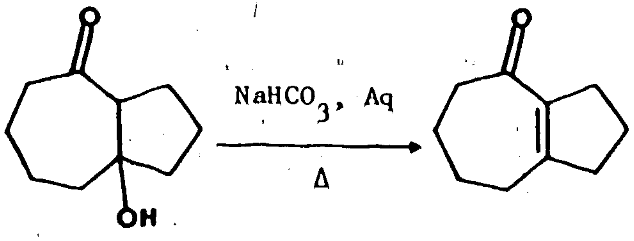


15b 28 33.

Reduction of alkyl hydroperoxides by phosphines is known to proceed with retention of configuration at the alkyl carbon,[25] thus, the iodohydrin obtained for this reduction, 28, necessarily has the same configuration as the starting material. This product reacted almost instantaneously with sodium hydroxide in methanol at 0° yielding the epoxide 33 indicating a trans relationship of the hydroxyl and iodo groups.

Under certain conditions an unusual rearrangement product, 7-hydroxy[5.3.0]decane-2-one 34 was obtained from the reaction of either 15a or 15b with silver acetate.

[21]



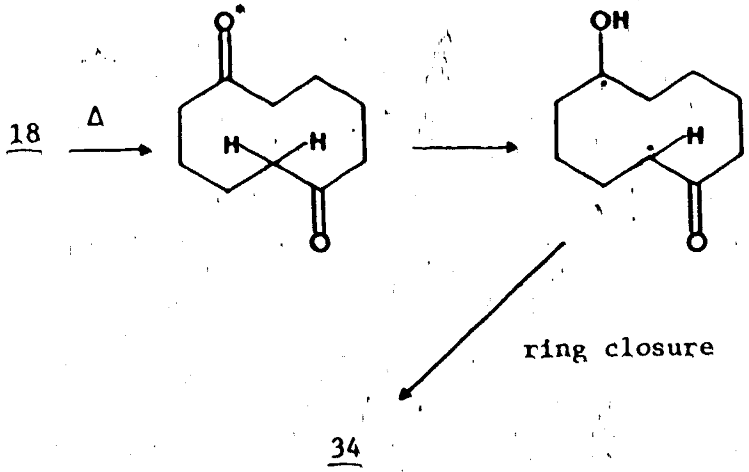
34 35

This product seemed to be formed when only a slight excess of silver acetate was used in the reaction. The structure of 34 was shown from spectral data and by its facile conversion to the known compound 35,[26] eq. [21]. The IR spectrum (CCl_4) showed absorptions at 3600 (s) and 3480 (b) for the hydroxyl group and a strong carbonyl absorption at 1700 cm^{-1}; the NMR spectrum ($CDCl_3$) showed absorptions at τ6.85 (broad triplet, 1H) for the methine proton, τ7.5 (broad, 2H) for the protons adjacent to the carbonyl group and an exchangeable proton at τ8.6.

It was assumed that 34 was formed via an internal aldol condensation of cyclodecane-2,6-dione 24. Accordingly, control experiments were carried out by stirring pure samples of the dione 24 and the 1,2-dioxetane 18 with mixtures containing silver acetate, silver iodide and acetic acid in methylene chloride solution. In neither case could any of the cyclized product be detected. It is worth noting though, that 34 was only occasionally formed during the reactions of halohydroperoxides 15a and 15b with silver ion, perhaps conditions for its formation were not met in the control experiments.

A second possibility, that 34 could arise *via* a photocyclization reaction, eq. [22], was also investigated.

[22]



No 34 was observed, however, when solutions of the dioxetane 18 were heated alone, or in the presence of silver acetate. The only product detected in both cases was the dione 24.

Attempts to prepare 34 by direct photolysis of 24 were also unsuccessful. Photolysis experiments were carried out using a medium pressure mercury lamp and an immersion well apparatus equipped with a Pyrex filter. Complex mixtures of products obtained from the photolysis experiments were not examined in detail but in no case could any of the desired cyclized product 34 be detected.

Subsequent experiments did indicate that 24 is cyclized under mild acidic conditions to yield 34. Silica gel appears to be acidic enough to effect this transformation; small quantities of 34 were isolated during preparative layer chromatography of mixtures containing 24. It was shown that no cyclized product was present in the mixture before chromatography. Cyclization of 24 to 34 could also be readily achieved by treatment of the dione with methylene chloride to which a small quantity of HI had been added. Under these conditions the elimination product, 35, was also formed. Both 34 and 35 were identified by TLC analysis on silica gel plates.

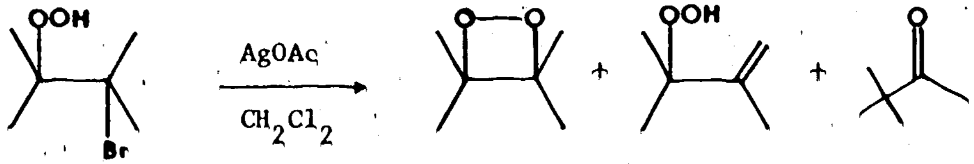
The IR spectrum ($CHCl_3$) of 34 shows both free and hydrogen-bonded hydroxyl stretching bands at 3600 (s) and 3480 (b) cm^{-1}, respectively. The ratio of the intensity of the higher wavenumber band to that of the lower increases as the concentration of 34 is decreased, suggesting that intra-molecular hydrogen-bonding is unimportant for this compound.[27] It was not possible, then, to assign a cis or trans configuration for the ring-juncture of this compound.

Solvent Effects in the Reactions of β-Halohydroperoxides with Silver Acetate:

Solvent effects appear to be very important in the reactions of halohydroperoxides studied; best yields of 1,2-dioxetanes were obtained in solvents such as chloroform or methylene chloride. If, however, the reactions were carried out in hydroxylic solvents such as methanol or 2-propanol only trace amounts of dioxetane were formed. For example, the only product formed from the reaction of 15b with silver acetate in methanol appeared to be the allylic hydroperoxide 23, no 1,2-dioxetane 18 could be detected.

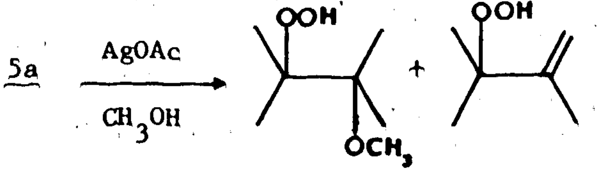
A similar effect was noted in the reaction of 5a with silver acetate, eq. [23] and eq. [24].

[23]



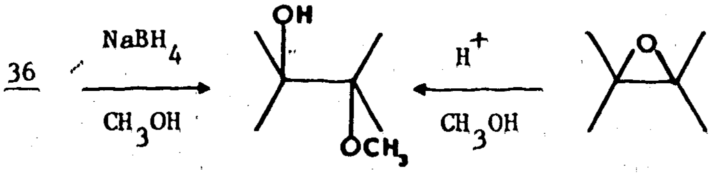
5a 4 6

[24]



36 6

[25]

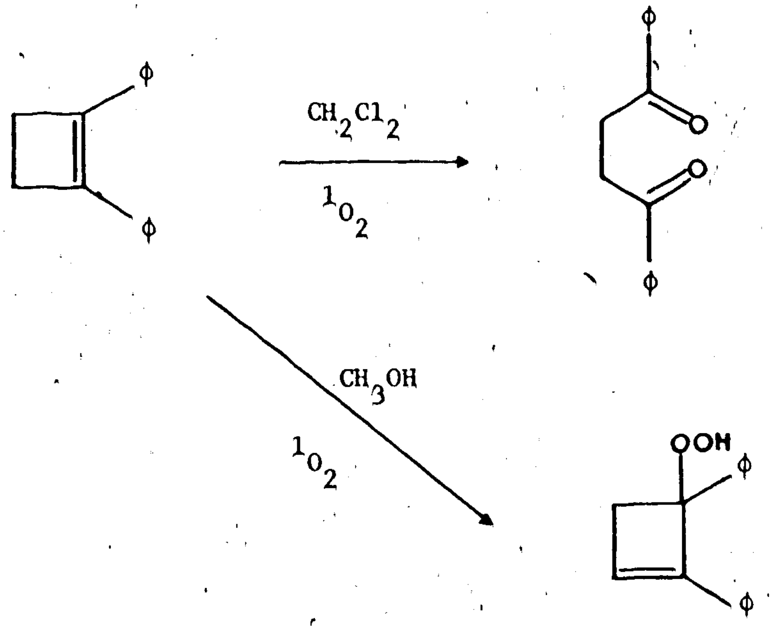


37 38

In methanol solution the substitution product, 3-methoxy-2,3-dimethyl-2-butyl hydroperoxide 36, and allylic hydroperoxide 6 were formed in approximately equal amounts. Identification of 36 was made on the basis of its NMR spectrum (CCl_4) which showed absorptions at τ8.93 (s), 8.87 (s) and 6.84 (s). Confirmation of the structure was obtained by reduction of the reaction mixture with $NaBH_4$, the NMR spectrum of this reduced sample showed absorptions at τ8.81, 8.86 and 6.76. Signals at these positions were observed for a sample of 3-methoxy-2,3-dimethyl-2-butanol 37 prepared from 2,3-dimethyl-2,3-epoxybutane 38, eq. [25].

The similarity between base catalyzed elimination reactions of β-halohydroperoxides and the photooxygenation of olefins has already been noted.[8] It is interesting that certain photooxygenations show solvent effects remarkably similar to those observed in reactions of β-halohydroperoxides with silver salts,[28] eq. [26].

[26]



Cleavage products observed in this and other reactions may or may not arise <u>via</u> 1,2-dioxetane intermediates; this subject is discussed more fully in Chapter II.

<u>Reduction of 1,2-Dioxetanes by Phosphines:</u>

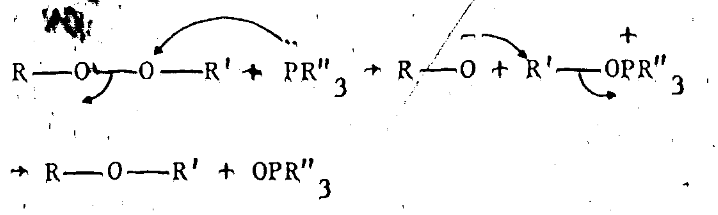
The chemistry of 1,2-dioxetanes is dominated by their thermal instability, this makes it difficult to assess the chemical reactivity of the peroxide linkage in these compounds.

All classes of peroxides react with tertiary phosphines, but different classes of peroxides react at vastly different rates.

This difference in reactivity forms the basis of an analytical procedure for the determination of different classes of peroxides.[29] The more reactive peroxides such as hydroperoxides or diacyl peroxides usually react rapidly at room temperature but the more sluggish dialkyl peroxides often require extended reaction at elevated temperatures before reaction occurs.

The generally accepted mechanism[30] for the reduction of peroxides by phosphorus compounds involves initial nucleophilic attack on oxygen, eq. [27], followed by a displacement of oxygen.

[27]



$$R{-}O{-}O{-}R' + PR''_3 \rightarrow R{-}\overset{-}{O} + R'{-}\overset{+}{O}PR''_3$$

$$\rightarrow R{-}O{-}R' + OPR''_3$$

Di-t-alkyl peroxides, however, normally react at elevated temperatures by initial cleavage of the peroxide bond to give products arising from free radical reactions; thus, thermolysis of dicumyl peroxide leads to a good yield of dicumyl, Scheme I.

Scheme I

$$RO{-}OR \rightarrow 2RO\cdot$$

$$RO\cdot + PR'_3 \rightarrow RO{-}\dot{P}R'_3$$

$$RO{-}\dot{P}R'_3 \rightarrow R\cdot + OPR'_3$$

$$2R\cdot \rightarrow RR$$

$$R = \phi C(CH_3)_2$$

The usual reason given for this is that the peroxide oxygen atoms of such compounds are sterically hindered by the bulky tertiary alkyl groups and nucleophilic attack on oxygen is not possible. (The oxygen atoms in t-butyl peroxide, for example, have been compared to the α carbon atom of neopentyl halides.)[30]

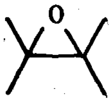
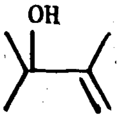
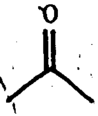
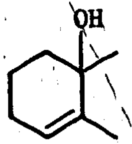
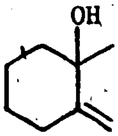
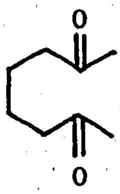
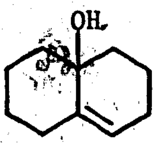
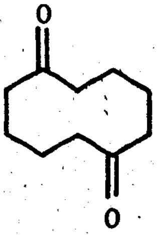
Since the peroxide linkage of 1,2-dioxetanes does not appear to be sterically hindered one would expect rapid reaction of these materials with tertiary phosphines and this is in fact the case. The three 1,2-dioxetanes studied react almost instantaneously with triphenyl- or tri-n-butylphosphine at 0° in CCl_4 solution. The reaction products (Table III) were identified by comparison of spectra with those of authentic materials and by comparison of VPC or TLC behaviour with authentic materials. Relative yields of products were determined by integration of the NMR spectra.

The products would appear to arise via an ionic mechanism as given in eq. [27]. However, the displacement reaction leading to an ether linkage can only occur where, after the initial displacement by phosphorus, free rotation about the C-C bond of the 1,2-dioxetanes is possible, eq. [28]. Thus, only 4 gives rise to the expected epoxide product, eq. [28], 17 and 18 give products arising from elimination reactions, eq. [29].

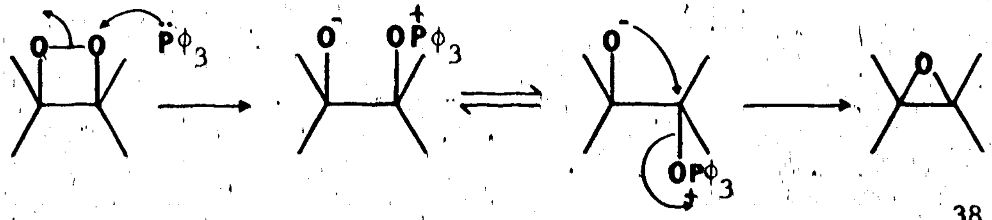
In each reaction studied, a small amount of cleavage product was observed; this is not surprising, since the reaction of phosphines with 1,2-dioxetanes seems to be fairly exothermic.

TABLE III

Reaction of 1,2-Dioxetanes with Triphenylphosphine

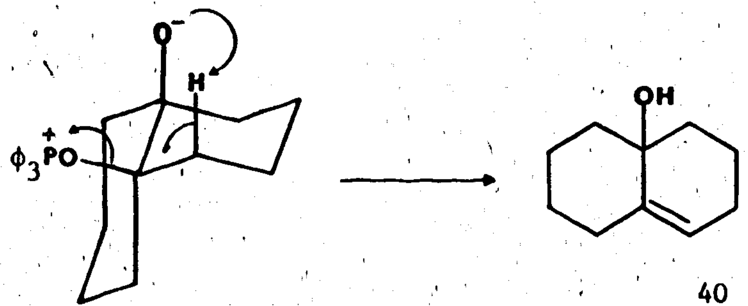
Dioxetane	Product	Approximate % Yield
4	 38	85
	 39	10
		5
17	 29	70
	 30	20
	 22	10
18	 40	-
	 24	-

[28]



38

[29]



40

The less nucleophilic trisubstituted phosphites, for example, triphenyl phosphite, triethyl phosphite and trimethyl phosphite, do not react (at least, at room temperature) with the dioxetanes studied indicating that the peroxide linkage in these materials is perhaps not exceptionally reactive. Hydroperoxides, diacyl peroxides and some dialkyl peroxides react readily with phosphites; diethylperoxide, for example, is reduced even at low temperature by triethyl phosphite yielding diethyl ether.[31]

Stability of Tetramethyl-1,2-dioxetane Under Acidic and Basic Conditions:

Earlier attempts to prepare 4 by treatment of 3-bromo-2,3-dimethyl-2-butyl hydroperoxide, 5a, with silver perchlorate or silver fluoroborate were unsuccessful, acetone was the only product detected in these reactions.[8] It was thought that the reason for the failure of these reactions was that any dioxetane formed during the reaction was decomposed rapidly by the strong acids ($HClO_4$ etc.) also formed during the reaction.[7] Surprisingly, 4 was found to be quite stable in the presence of strong acids; the rate of decomposition of 4 in CCl_4 solution containing CF_3CO_2H (0.1 M) was only about twice the rate in CCl_4 alone. The only product detected from the decomposition of 4 in acid solution was acetone.

The stability of 4 to basic conditions was also investigated by stirring the dioxetane in a methanolic solution of sodium hydroxide. Approximately 5% of starting material was isolated from this reaction mixture even after three days at room temperature, this suggests that 4 is not attacked by base. Again, the only product detected from this reaction was acetone.

It has already been shown that the thermolysis of 1,2-dioxetanes leads exclusively to cleavage products. Additionally, 1,2-dioxetanes are not rearranged in the presence of acids or bases. It seems unlikely then, as has been suggested,[5] that 1,2-dioxetanes are intermediates in photooxygenation reactions of olefins which lead to formation of allylic hydroperoxides.

EXPERIMENTAL

Melting points and boiling points recorded are uncorrected. Refractive indexes were measured using a Bausch and Lomb Abbe-3L Refractometer. Infrared spectra were recorded on Perkin-Elmer Model 421 and Model 337 spectrophotometers. UV spectra were recorded using Cary 15 and Bausch and Lomb recording spectrophotometers. ^1H NMR spectra were determined using Varian analytical spectrometers, Models HA-100, A-60 and A56/60 with tetramethylsilane (TMS) as internal standard. ^{13}C NMR spectra were recorded using a Bruker HFX 10 spectrometer. VPC analysis was carried out on Aerograph 202 and A-90-P3 gas chromatographs. Mass spectra were obtained on an A.E.I. MS-2 mass spectrometer.

All preparations and reactions of β-halohydroperoxides were carried out behind shields and peroxidic compounds were estimated iodometrically using the method of Organic Syntheses.[32] Solutions and solvents were dried over anhydrous magnesium sulphate unless otherwise noted. Removal of solvents was achieved using a rotary evaporator unless stated otherwise.

3-Bromo-2-methyl-2-butyl Hydroperoxide 3:

This material was prepared according to the method devised by van de Sande.[8] To 50 ml of dry ether at -40° was added 98% hydrogen peroxide (17.0 g, 0.5 mole), addition was made slowly such that the temperature did not rise above -35°. 2-Methyl-2-butene (7.0 g, 0.1 mole) was then added in one portion followed by 1,3-dibromo-5,5-

dimethylhydantoin (14.3 g, 0.05 mole) added in small portions. After addition was complete the mixture was allowed to stir at -40° for a further 15 minutes, after which time the cooling bath was removed and the contents of the flask allowed to warm quickly to ca. 10°. When the mixture became homogeneous it was extracted several times with water (4 x 50 ml), the organic layer was then dried and solvent was removed at room temperature.

The crude product, 17.5 g of a colourless oil, contained 95% of the theoretical oxygen content as determined by iodometric titration; the overall yield was 90%.

The NMR spectrum (CCl_4) showed absorptions at τ1.4 (broad, D_2O exchangeable), τ5.56 (quartet, J = 7 Hz) for the methine proton, τ8.32 (doublet, J = 7 Hz) for the single methyl group and τ8.63 and τ8.72 for the non-equivalent gem-dimethyl groups. This spectrum was identical to that obtained by Mumford.[7]

Trimethyl-1,2-dioxetane 2:

Trimethyl-1,2-dioxetane was prepared from bromohydroperoxide 3 by the procedure outlined by Mumford.[7] A solution of sodium hydroxide (0.4 g) dissolved in 1 ml H_2O and 3 ml of methanol was added slowly to a solution of 3 (1.8 g) stirred in methanol (6 ml) at 0°. After ca. 100 minutes the mixture was extracted with iso-pentane (3 x 25 ml), the combined extracts were dried and solvent was removed evaporatively at room temperature. The residue, a yellow oil, was purified by distillation under high vacuum (5μ) at room temperature. A colourless forerun was discarded. Finally, two low temperature (-78°) crystallizations from iso-pentane yielded crystals of pure 2, m.p. 4 - 7°. Iodometric titration showed 100% of the theoretical active oxygen content.

The NMR spectrum (CCl_4) was identical to that reported by Mumford.[7]

3-Bromo-2,3-dimethyl-2-butyl Hydroperoxide 5a:

The procedure described for the preparation of 3 was used to prepare 5a from 8.4 g (0.1 mole) of tetramethylethylene, 14.3 g (0.05 mole) of the DBH, and 17.0 g (0.5 mole) of 98% hydrogen peroxide in 50 ml ether.

In this way 19.1 g of a crude 5a, a white solid, was obtained. Iodometric titration indicated 98% of the theoretical amount of active oxygen. The NMR spectrum (CCl_4) showed absorptions at $\tau 1.85$ (broad, D_2O exchangeable), $\tau 8.56$ (s) and $\tau 8.19$ (s) in good agreement with the spectrum described by van de Sande.[8]

3-Iodo-2,3-dimethyl-2-butyl Hydroperoxide 5b:

This material was prepared using a procedure similar to that described for 5a but 1,3-diiodo-5,5-dimethylhydantoin (20 g, Arapahoe Chemicals) was used in place of the dibromo compound. The mixture was stirred for 30 minutes at -40° to ensure complete reaction before being allowed to warm to 0 - 10°. The mixture was extracted with water (3 x 50 ml) and then with several portions of dilute sodium thiosulphate solution until the colour of iodine was discharged.

Solvent was removed to low volume but, because of the sensitive nature of solid 5b, care was taken not to evaporate to dryness. CCl_4 (30 ml) was then added and the solution again evaporated to low volume. This process was repeated several times to obtain a concentrated solution of 5b in CCl_4. This solution was normally discoloured by traces of free iodine. The yield of crude product was estimated as 80% by iodometric titration.

A sample of 5b was purified by recrystallization from heptane to yield white needles, m.p. 32 - 35° (decomp.). Solid 5b was unstable at room temperature, decomposing spontaneously after an induction period of several minutes. Iodometric titration showed 97.8% of the theoretical active oxygen content. The NMR spectrum (CCl_4) showed absorptions at τ1.48 (s, 1H, D_2O exchangeable), τ7.95 (s, 6H) and τ8.50 (s, 6H).

Tetramethyl-1,2-dioxetane 4:

This compound was prepared in reasonable yield by the following procedure:

2-Bromo-2,3-dimethyl-3-butyl hydroperoxide (4 g) in methylene chloride (20 ml) was added rapidly to a rapidly stirred slurry of silver acetate (12 g) in methylene chloride (80 ml). After 15 minutes the silver salts were filtered off and the organic layer, pale yellow in colour, was washed with water (1 x 30 ml) followed by sodium carbonate (10%, 30 ml). Removal of solvent after drying with

$MgSO_4$ yielded a bright yellow oil. Volatile materials were distilled from this oil under high vacuum (5μ) and room temperature; a little iso-pentane was added to the distillate and the solution cooled to −78°. The yellow crystals of 2 which formed were filtered off and dried by pressing between filter papers. The yield of crude material was 0.7 g (30%).

Pure material was obtained by sublimation at room temperature and at 5μ. Material so obtained had active oxygen content as determined by iodometric titration of 98.7%, m.p. (sealed tube) 73 − 76°.

The ^1H NMR spectrum of 4 (CCl_4) showed a single absorption at τ8.49. The ^{13}C NMR spectrum (acetone-d_6) showed absorptions at 89.33 for the tertiary carbon atoms and 23.55 for the methyl carbon atoms; these values are reported as ppm downfield from TMS.

Reduction of Tetramethyl-1,2-dioxetane 4:

The same general procedure was adopted for the reduction of all peroxidic materials; thus, reduction of 4 was carried out by slowly adding a solution of the dioxetane (0.12 g, freshly sublimed) to a slurry of $LiAlH_4$ (0.2 g) in ether (10 ml) stirred at −78°. The mixture was stirred at this temperature for 20 minutes and then allowed to warm to room temperature. Excess $LiAlH_4$ was then decomposed by the addition of KOH solution (10%) until a clear solution was formed. The granular precipitate was filtered off and washed several times with ether; the washings were combined with the filtrate and solvent was evaporated yielding white crystals (0.14 g) of pinacol.

The NMR spectrum ($CDCl_3$) showed absorptions at τ8.72 (s) and τ8.32 (b) in the ratio 3:1 (expected ratio 6:1) indicating that some water of crystallization was also present; taking this factor into account, the yield of pinacol was ∿ 100%. A sample of isolated pinacol recrystallized from benzene showed spectral properties (IR, NMR) identical to those of authentic material.

2,3-Dimethyl-3-hydroperoxy-1-butene 6 from 5b:

A solution of 5b (0.25 g, recrystallized from heptane) in methanol (2 ml) was added to a solution of sodium hydroxide (0.05 g) in methanol (5 ml) stirred at 0°. After 10 minutes the solution was diluted with water (30 ml) and extracted with methylene chloride (3 x 10 ml); the combined extracts were dried and solvent was evaporated yielding a small quantity of colourless oil (∿ 0.1 g). The NMR spectrum (CCl_4) showed absorptions at τ1.58 - 1.8 (b), τ5.1 - 5.2 (m), τ8.25 (m) and τ8.70 (s). This spectrum was identical to that reported for 6.[8]

1,2-Dimethylcyclohexene 12:

2-Methylcyclohexanone, prepared by oxidation of 2-methylcyclohexanol,[33] (230 g) was added to a solution of methylmagnesium iodide (two moles) in dry ether (two litres) contained in a three litre flask. After addition was complete, the mixture was heated under reflux for a further 15 minutes, the reaction was then worked up with NH_4Cl solution. The residual oil obtained by evaporation of solvent was mixed with orthophosphoric acid (30 ml) and heated to reflux temperature for two hours. Distillation of the mixture through a Vigreux column yielded a mixture of olefins containing ∿ 65% of the desired product together with 30% of isomeric 2,3-dimethylcyclohexene and a small quantity of 2-methylmethylenecyclohexane.

12 was separated from this mixture by distillation using a Nestor-Faust annular teflon spinning band column. The NMR spectrum of material boiling at 134 - 136° (710 mm) showed absorptions at τ8.4 (s) for the methyl protons and a broad absorption at τ8.1 for the ring protons; no trace of olefinic protons between 4 - 6 could be detected. Reported b.p. 134 - 136°.[20]

$\Delta^{9,10}$-Octalin 13:

Tetralin (100 g) was dissolved in a mixture of ethylamine (500 ml) and dimethylamine (400 g) contained in a three-necked flask fitted with a magnetic stirrer and a Dewar-type dry-ice condenser. The mixture was stirred briefly and lithium ribbon (23 g) cut into small pieces was added. The mixture was stirred for 14 hours after which time the solvent was allowed to evaporate. The residue was then cooled in an ice bath and water (200 ml) was slowly added. The precipitated lithium salts were filtered off and washed with ether (4 x 50 ml); the filtrate was also extracted with ether (4 x 50 ml). Combined ether washings and extracts were dried, concentrated and the residue was distilled under reduced pressure to yield a mixture of $\Delta^{9,10}$-octalin (∿ 70%) and $\Delta^{1,9}$-octalin (∿ 30%). The combined yield was 98 g, b.p. 70 - 78° at 10 mm.

Separation of the $\Delta^{9,10}$-isomer was achieved using the method of Benkeser.[15] Sodium borohydride (4.7 g) and 2-methyl-2-butene (23.1 g) dissolved in anhydrous tetrahydrofuran (200 ml) were stirred together in a one litre, three-necked flask fitted with a reflux condenser, stirrer and a mercury trap. Boron trifluoride-etherate (23.5 g) in THF (22 ml) was added, followed by the crude octalin mixture (20 g), added over a period of 10 minutes. The mixture was then stirred for 3.5 hours. Water (50 ml) was then added dropwise followed by NaOH solution (3 N, 35 ml), added over 10 minutes, and hydrogen peroxide (30%, 35 ml), added over 45 minutes. The mixture was stirred for five hours at 44 - 45°. On cooling, the organic layer was separated off, washed several times with water and concentrated after drying over $MgSO_4$. Distillation of the residue under reduced pressure yielded <u>13</u> (14 g), b.p. 75 - 77° at 14 mm, reported b.p. 75 - 77° at 14 mm.[15] The NMR spectrum (CCl_4) showed two broad absorptions centred at τ8.25 and τ8.54. No olefinic absorptions could be detected.

<u>2-Bromo-trans-1,2-dimethylcyclohexyl Hydroperoxide 14a:</u>

The procedure described for the preparation of <u>3</u> was used to prepare <u>14a</u> from 11.0 g (0.1 mole) of 1,2-dimethylcyclohexene <u>12</u>. The yield of crude <u>14a</u>, a colourless oil, was 21.8 g, 97.5%. Iodometric analysis indicated 96.8% of the theoretical active oxygen content. The crude product solidified on standing at -10°. A small sample of this material was recrystallized with difficulty from pentane at -78°, m.p. 44 - 46°. The NMR spectrum (CCl_4) showed absorptions at τ8.2 and 8.52 for the methyl protons and a broad absorption between τ7.8 and 8.7 for the ring protons. The peroxidic hydrogen was not visible but D_2O exchange indicated the presence of an exchangeable hydrogen. The IR spectrum (CCl_4) showed bands at 3500 (s) and 3400 (b); also at 855 and 925 cm^{-1}.

2-Iodo-trans-1,2-dimethylcyclohexyl Hydroperoxide 14b:

This compound was prepared by the standard methods for preparation of halohydroperoxides. The yield of 14b from 11.0 g pure olefin 12 was 24 g, 89%. Initially, the sample was obtained as a yellowish oil but the sample solidified on standing at -10°; recrystallization of some of the material from heptane yielded fine, pale yellow crystals, m.p. 54 - 55° with some decomposition. The material was found to be fairly unstable even at -10° although it could be stored at -78°, probably indefinitely. At room temperature, the crystals appear to decompose spontaneously. A satisfactory analysis of this material could not be obtained by iodometric titration; titrations were much higher than expected, probably due to elimination of iodine from the compound. A typical analysis indicated 120 - 130% of the theoretical active oxygen content. The NMR spectrum ($CDCl_3$) showed absorptions at τ2.41 (m, D_2O exchangeable), τ7.82 and τ8.33 for the methyl protons. The ring protons appear as a broad band between τ7.8 and τ8.5.

9-Bromo-10-hydroperoxy-trans-decalin 15a:

The procedure described for the preparation of 3 was used to prepare 15a from 13.6 g pure $\Delta^{9,10}$-octalin (0.1 mole). The yield of product, recrystallized from heptane, was 21.3 g, 85%. White crystals of 15a melted at 114 - 115° without decomposition, iodometric analysis showed a purity of 99.7%. The NMR spectrum ($CDCl_3$) showed absorptions at τ2.8 (b, D_2O exchangeable) for the hydroperoxy group and broad absorption at τ8.28 and 8.5 for the ring protons.

The mass spectrum of 15a did not show a parent peak, major fragments were observed, however, at 231, 233, (loss of OH) and at 215, 217 (loss of OOH). The base peak appeared at 135 ($C_{10}H_{15}$).

9-Hydroperoxy-10-iodo-trans-decalin 15b:

The procedure used to prepare 5b was used to prepare a sample of 15b from 13.6 g (0.1 mole) of pure $\Delta^{9,10}$-octalin, 20 g (∿ 0.05 mole) of 1,3-diiodo-5,5-dimethylhydantoin and 17 g, (0.5 mole), 98% hydrogen peroxide in 80 ml of dry ether. The crude product, a faintly pink solid, was recrystallized from heptane yielding 26 g (88%) of white crystals, m.p. ∿ 105° (decomp.). Iodometric analysis indicated the presence of 98.7% of the theoretical active oxygen content.

The NMR spectrum ($CDCl_3$) showed absorptions at τ3.1 (s, D_2O exchangeable) for the hydroxyl proton and τ8.1 (b), τ8.4 (b) for the ring protons. The IR spectrum (CCl_4) showed major absorptions at 3540, 2940, 2860, 1460, 1450, 1435, 1350, 1320, 1295, 1255, 1180, 980, and 825 cm^{-1}.

The mass spectrum did not show a parent ion, minor fragments were observed at 278, 261; major fragments at 169 (-I), 152 (-I,OH) and 135 ($C_{10}H_{15}$). The crystals of 15b decomposed rapidly at room temperature but could be stored at -10° for several weeks.

cis-1,6-Dimethyl-7,8-dioxabicyclo[4.2.0]octane 17:

Using the same procedure as was employed in the preparation of tetramethyl-1,2-dioxetane 4, a solution of 14b (3 g) in methylene chloride (20 ml) was added fairly rapidly to a slurry of silver acetate (6 g) in methylene chloride (80 ml). At each addition the mixture turned, first red, and then yellow; reaction occurred almost instantaneously at room temperature. Five minutes after addition was complete, the mixture was filtered rapidly through "Celite" and the resulting solution worked up in the usual fashion to yield a yellow oil (1.3 g). The oil was distilled at low pressure (5μ) and the volatile materials dissolved in iso-pentane; repeated crystallization of this solution at -78° yielded the product 17, 0.35 g (25%), m.p. 48 - 50°. Iodometric analysis of this product indicated a purity of 99.2%.

The ^1H NMR spectrum ($CDCl_3$) showed absorptions at τ8.6 (s) for the methyl protons and τ7.9 to 8.7 for the ring protons. The ^{13}C NMR spectrum (acetone-d_6) showed absorptions at 22.909 for the methyl carbon atoms, 88.337 for the carbon atoms connected to oxygen and 34.412 and 19.608 for the carbon atoms of the ring. All values are reported in ppm downfield from TMS.

The molecular weight, as determined by osmometry, was 134, required, 142.

The UV spectrum (cyclohexane) showed a broad maximum at 285 nm, ε = 30. The spectrum showed a tail out to 420 nm.

The IR spectrum (CS_2) showed absorptions at 870, 882, 910, 1050, 1180, 1205, 1380, 2850, and 2900 cm^{-1}. An absorption at 1700 cm^{-1} was also observed due to decomposition of the sample to diketone; this absorption increased in intensity if the sample was left in the beam of the spectrometer.

11,12-Dioxa[4.4.2]propellane 18:

A solution of 9-hydroperoxy-10-iodo-trans-decalin 15b, (2 g, freshly recrystallized from heptane) in methylene chloride (20 ml) was added fairly quickly to a rapidly stirred slurry of silver acetate (5 g) in methylene chloride (80 ml). After stirring for five minutes the mixture was filtered through "Celite" and the filtrate washed once with sodium bicarbonate solution (10%, 20 ml) and once with water (20 ml). After drying over $MgSO_4$, solvent was removed evaporatively to yield a yellow oil (∿ 1.2 g).

This residual oil was dissolved in pentane and immediately transferred to a column of silica gel (12 g) maintained at -50° by means of a cooling jacket. The yellow band due to dioxetane was eluted rapidly with pentane containing ~~0.5%~~ ether; fractions collected were stored at -78°. After some time, crystals of 18 deposited from several of the fractions, supernatant liquid was decanted off and the crystals redissolved in iso-pentane and transferred to a glass ampoule. The ampoule was cooled until crystallization was complete and solvent was removed at 5μ using a high vacuum apparatus to give crystals of pure 18 (0.14 g, 12%), m.p. 34 - 36°.

Iodometric analysis of the pure material indicated 100.7% of the theoretical active oxygen content.

The total yield of dioxetane isolated from the chromatography was obtained by combining all dioxetane containing fractions; these combined fractions were made up to 100 ml and a 5 ml aliquot was titrated by the usual iodometric method. Since it was extremely difficult to pipette solutions of pentane at -78°, the aliquot was obtained by simply filling a 5 ml volumetric flask. The yield of dioxetane was 37%.

2-Methylene-1-methylcyclohexyl Hydroperoxide 20, From Reaction of 14b with Base:

A solution of 2-iodo-trans-1,2-dimethylcyclohexyl hydroperoxide 14b (2.0 g, crude) in methanol was treated with a solution of sodium hydroxide (2.0 g) in methanol (50 ml) using a procedure similar to that outlined in the previous experiment. The NMR spectrum of the colourless oil obtained after work-up showed absorptions at τ2.38 (b, D_2O exchangeable), τ5.1 (m), τ7.52 - 8.7 for the ring protons and τ8.59 (s). These absorptions are consistent with the structure 20. A small signal was also observed at τ5.35 (b); this was assumed to be due to the presence of the isomeric 3-hydroperoxy-2,3-dimethylcyclohexene 19.

Reduction of the mixture with $LiAlH_4$ using the same procedure adopted for the reduction of 4 yielded a colourless oil, the NMR spectra (CCl_4) of which showed absorptions at τ5.15 (m), τ5.39 (m), τ7.6 - 8.6 and τ8.7 (s). This spectrum compares well with that obtained by van de Sande[8] for 2-methylene-1-methylcyclohexanol. The spectrum also showed a small absorption at τ4.7 presumably due to the isomeric 3-hydroxy-2,3-dimethylcyclohexene.

Distillation of the mixture, obtained by reaction of 14b with base, under high vacuum yielded essentially pure 20, n_D^{25} = 1.4840. Analysis: calculated for $C_8H_{14}O_2$; C 67.57, H 9.93; found, C 67.37, H 9.95.

10-Hydroperoxy-$\Delta^{1,9}$-octalin 23:

A solution of 9-bromo-10-hydroperoxy-trans-decalin 15a (1.25 g) in methanol was stirred with a solution of NaOH in methanol as described in the reaction of 5b with base. Evaporation of solvent after work-up, and recrystallization of the residue from Skelly B, yielded white crystals of 23 (0.8 g, 89%), m.p. 58 - 59°, reported m.p. 60°.[11] The NMR spectrum ($CDCl_3$) showed absorptions at τ3.15 (b, D_2O exchangeable), τ4.4 (b) and a broad multiplet between τ7.7 - 8.9. This spectrum was in excellent agreement with that observed by Foote.[18]

Reaction of the corresponding iodohydroperoxide 15b under the same conditions yielded 23 in 95% yield.

1-Acetyl-1-methylcyclopentane 21:

i. From 1,2-Dimethylcyclohexene 12:

Using the method developed by Hart,[19] trifluoroacetic anhydride (15.3 g) was added slowly to a suspension of hydrogen peroxide (98%, 1.7 ml) in methylene chloride (20 ml) stirred at 0°.

The solution so obtained was added dropwise over a period of 20 minutes to a solution of 12 (6.6 g) in methylene chloride (100 ml) stirred at 0 - 8°. A solution of boron trifluoride-etherate (50%, 8.3 ml) was added simultaneously. After addition was complete the mixture was stirred for a further 15 minutes after which 35 ml of water was added. The organic layer was filtered off and washed several times with saturated $NaHCO_3$ solution.

The product, a colourless oil, was obtained by distillation of the residue after removal of solvent; product boiling at 50 - 52° 12 mm was collected, reported b.p. 51 - 51.5°, 12 mm. n_D^{25} = 1.4458, reported n_D^{25} = 1.4458.[20]

The NMR spectrum ($CDCl_3$) showed absorptions at τ8.75 (s), τ8.79 (s) and τ8.0 - 8.5 for the ring protons in the ratio 3:3:8.5, expected ratio 3:3:8. The semicarbazone of 21 was prepared, m.p. 138 - 141°; reported m.p. 140 - 141°.[20]

ii. From Reaction of 14b with AgOAc:

A sample of the yellow distillate obtained in the preparation of 17 was allowed to stand at room temperature until the yellow colour had completely faded (three to four days).

The now colourless oil was dissolved in methanol (2 ml) and then added to a solution of semicarbazide hydrochloride (1 g) and sodium acetate (1.5 g) in 2 ml of water and 3 ml of methanol.

A white precipitate which formed immediately was filtered off and identified (mixed m.p. with semicarbazone derivative of authentic 22 218 - 220°) as the semicarbazone of 22. The filtrate deposited white crystals on standing at -10° which were recrystallized from methanol/water, m.p. 138 - 141°; mixed m.p. with semicarbazone of authentic 21, 138 - 141°.

Octane-1,7-dione 22:

i. From cis-1,2-Dimethylcyclohexane-1,2-diol 26:

A small amount of cis-diol 26 (0.5 g) was stirred with lead tetraacetate (2.2 g) in dry benzene. After three hours ethylene glycol (∿ 1 ml) was added to destroy excess reagent and the precipitated lead diacetate was filtered off. The benzene layer was washed several times with water (3 x 10 ml) and dried over $MgSO_4$. Removal of solvent yielded 0.5 g of a white solid 22. The m.p. after recrystallization from Skelly B was 43 - 44°, reported m.p. 44 - 45°.[34] The NMR spectrum ($CDCl_3$) showed absorptions at τ7.57 (broad triplet), τ7.87 (s) and τ8.46 (broad quintuplet) in the ratio 2.1:3.0:1.9, expected ratio 2:3:2. The semicarbazone derivative was prepared, m.p. 219 - 220°.

ii. From 1,7-Octadiyne:

1,7-Octadiyne (Columbia Chemicals, 3 g) in methanol (15 ml) was heated under reflux for 15 minutes with a solution of yellow mercuric oxide (1 g) dissolved in 10% sulphuric acid (10 ml). The mixture was poured into 10% Na_2CO_3 solution (50 ml) and extracted with ether (50 ml). Removal of solvent after drying over $MgSO_4$ yielded 4.1 g of crude solid. Recrystallization from Skelly B yielded beautiful white plates (3.5 g, 87.5%), m.p. 43 - 44°.

iii. From Decomposition of 17:

A solution of pure, recrystallized 17 (0.1 g) in pentane was allowed to stand at room temperature for five days. The solution was then allowed to stand overnight at -10°. Crystals of 22 were deposited from this solution. The product was filtered off and the spectral properties (NMR, IR) of isolated material were found to be identical to those of authentic octane-1,7-dione 22. The yield of product obtained in this way was 0.1 g.

cis-1,2-Dimethylcyclohexan-1,2-diol 26:

i. From 1,2-Dimethylcyclohexene 12:

Pure cis-diol was prepared according to the method of Criegee;[35] 1,2-dimethylcyclohexene 12 (0.45 g) was stirred together with osmium tetroxide (1 g) in dry ether (40 ml) for one hour. The mixture was then allowed to stand overnight after which time the solvent was allowed to evaporate. A solution of sodium sulphite (20 g) in a mixture of ethanol (25 ml) and water (100 ml) was then added and the solution heated under reflux for two hours. The hot solution was then filtered and the residue was washed twice with hot ethanol. The washings were added to the filtrate which was heated on a steam bath to remove the ethanol. The aqueous residue, after cooling, was extracted with methylene chloride (4 x 10 ml). Evaporation of the solvent after drying yielded 0.7 g of crude 26. Recrystallization from benzene yielded white crystals (0.55 g), m.p. 40 - 41°, reported m.p. 38 - 39°.[20] The NMR spectrum ($CDCl_3$) showed absorptions at τ8.86 (s), τ8.1 - 8.9 for the ring protons and an exchangeable proton at τ7.65 in the ratio 3:4:1.

ii. From Reduction of 17:

Using a procedure identical to that used for the reduction of tetramethyl-1,2-dioxetane 4, 17 (0.1 g) was reduced with $LiAlH_4$ yielding 0.11 g of 26. The NMR spectrum of the crude material indicated that some water of crystallization was present. The ratio of hydroxylic protons to the remaining protons was 1:3.7 instead of the expected value 1:7. Hydrate water was removed by repeated evaporation of the sample with portions of benzene. Isolated material was recrystallized from benzene to yield white crystals, m.p. 39 - 40°. These did not depress the m.p. of a sample of authentic 26; the mixed m.p. was 38 - 40°.

9,10-Dihydroxy-*cis*-decalin 25:

i. From $\Delta^{9,10}$-Octalin:

Using the method of Criegee,[35] $\Delta^{9,10}$-octalin (0.55 g) was treated with osmium tetroxide (0.1 g). After hydrolysis and work-up as described earlier the crude product was recrystallized from benzene to yield white crystals (0.6 g) of 25, m.p. 88 – 89°, reported m.p. 90°.[35] The NMR spectrum (CCl_4) showed a broad absorption at τ8.45, and an exchangeable proton at τ8.1 (s) in the ratio 7.7:1.

ii. From Reduction of 18:

A solution of 18 in pentane was added very slowly to a slurry of $LiAlH_4$ (1 g) in ether (50 ml) stirred at -78°. After addition was complete, the solution was allowed to warm to room temperature and stirred for a further 20 minutes. Excess reagent was then destroyed by the addition of KOH solution (10%); insoluble salts were filtered off and washed several times with ether. Combined washings and filtrate were concentrated using a rotary evaporator and the residue was repeatedly evaporated with portions of dry benzene to ensure removal of water present as the hydrate. Finally, the residue was dissolved in benzene and made up to 25 ml; 5 ml of this solution was analyzed for diol content using lead tetraacetate solution. The yield of diol was found to be 98%, based on the dioxetane content of the pentane solution. The remaining sample was concentrated whereupon white crystals deposited. Isolated [illegible] showed spectral properties (NMR, IR) identical to those of [illegible] material; the yield of isolated cis-diol was 74%.

Cyclodecane-1,6-dione 24:

i. From 25:

9,10-Dihydroxy-cis-decalin 25 (0.6 g) was stirred with lead tetraacetate (2.2 g) in dry benzene (10 ml). After two hours excess reagent was decomposed by the addition of ethylene glycol (1 ml). Precipitated lead salts were filtered off and the filtrate washed several times with water. The solution was dried and solvent was removed evaporatively. The residue was recrystallized from Skelly B yielding white plates of <u>24</u> (0.55 g), m.p. 98 - 99°, reported m.p. 98 - 99°.[26] The IR spectrum ($CHCl_3$) showed major bands at 2920, 1705, 1435, 1370, 1140, and 1110 cm^{-1}. The NMR spectrum (CCl_4) showed two broad absorptions of equal intensity centred at τ7.75 and τ8.2.

ii. <u>Large Scale Preparation:</u>

Larger quantities of <u>24</u> were prepared according to the method of Suhk Dev.[26]

Formic acid (98%, 83 ml) and hydrogen peroxide (30%, 32 ml) were stirred together keeping the temperature at 45° - first by cooling, then by warming - while $\Delta^{9,10}$-octalin (28.4 g) was added dropwise over a period of half an hour. The mixture was stirred for six hours at 45° then allowed to stand overnight at room temperature.

Sodium chloride (60 g) and water (200 ml) were then added and the mixture was allowed to stand overnight. The solid formate ester was then filtered off and was hydrolyzed by adding it to an ice cold solution of sodium hydroxide (16 g in 30 ml H_2O). The mixture was stirred at 0° for 30 minutes and then at 75 - 80° for a further 20 minutes. Finally, the mixture was diluted with water (150 ml) and the white crystals which precipitated out were filtered o[illegible]. The yield of crude <u>trans</u>-diol <u>28</u> was 29 g.

The trans-diol so obtained was dissolved in dry benzene (80 ml) and an equivalent amount of lead tetraacetate was added. The mixture was stirred at room temperature for two hours and then heated under reflux for a further half an hour. Ethylene glycol was then added to destroy excess reagent and the mixture was allowed to stand overnight. The precipitated lead salts were filtered off and the benzene layer washed as in the previous preparation. Evaporation of solvents yielded 25 g of crude dione.

7-Hydroxybicyclo[5.3.0]decane-2-one 34:

i. From 15b:

Silver acetate (9 g) was added slowly, over a period of 30 minutes to a solution of iodohydroperoxide 15b (15 g) in methylene chloride (100 ml) stirred at 0 to -10°.

Stirring was continued at this temperature for a further four hours after which the mixture was filtered through "Celite" to remove the silver salts. The filtrate was washed with 10% sodium bicarbonate solution (3 x 50 ml) and then dried over $MgSO_4$. Removal of the solvent under vacuum yielded a yellow oil (7.8 g). This oil, on standing at -10° for several days, deposited white crystals (∿ 2 g) which were filtered off and recrystallized twice from heptane, m.p. 96 - 97°. Calculated for $C_{10}H_{16}O_2$; C 71.34, H 9.59; found, C 71.09, H 9.52.

The IR spectrum (CCl_4) showed major bands at 3600 (s), 3480 (b), 2940, 2880 (shoulder), 1700, 1450 (s), 1350 (b), 1170 (b), and

895 (s).

The NMR spectrum ($CDCl_3$) showed absorptions at τ7.85 (broad triplet) for the methine proton, τ7.5 (b) for the protons adjacent to the carbonyl group and τ7.5 - 8.5 for the ring protons. An exchangeable proton was visible at τ8.6. The mass spectrum of the sample showed a parent peak at 168; major fragments were observed at 150, 111, 108, 107, 95, 84, 81, 68, and 67.

ii. From Cyclodecane-1,6-dione 24:

A solution of 24 (0.2 g) in methylene chloride (2 ml) was absorbed on silica gel G (3 g) and the mixture was allowed to stand overnight at room temperature. The silica gel was then extracted repeatedly with ether. Evaporation of the extracts yielded a white solid which was shown by TLC analysis to contain starting material 24 and a compound with an R_f value similar to that of 34. This material was isolated by preparative TLC on silica gel using Skelly B/ether (10:1) as eluent and its spectral properties (NMR, IR) were found to be identical to those of authentic 34.

Bicyclo[5.3.0]dec-1,7-ene-2-one 35:

Cyclodecane-1,6-dione 24 (0.2 g) was heated under reflux with a saturated solution of sodium bicarbonate (20 ml). After one hour the mixture was cooled and extracted with methylene chloride (2 x 10 ml). Evaporation of solvent, after drying over $MgSO_4$, yielded a yellow oil (∿ 0.1 g). The crude product was purified by chromatography on silica gel, fractions were eluted with Skelly B/ether

(10:1). Isolated 35, a faintly yellow oil, had n_D^{25} = 1.5251, reported n_D^{25} = 1.5260.[26]

The NMR spectrum ($CDCl_3$) showed two broad absorptions at τ7.13 – 7.8 and τ8.0 – 8.5 with well defined peaks at τ7.4, 7.55 and τ8.15, 8.2 and 8.25.

The IR spectrum (CCl_4) showed major bands at 2940, 2870, 2840, 1640 (intense, broad), 1450, 1430, 1380, 1350, 1335, 1260, and 1050.

The semicarbazone derivative of this material was prepared, the m.p. after recrystallization from methanol/water was 188 – 190°.

A small quantity (0.2 g) of the hydroxy-ketone 34 was heated with aqueous sodium bicarbonate solution under the same conditions. The crude product obtained after work-up showed an NMR spectrum identical to that of 35. The total product was stirred with a solution of semicarbazide hydrochloride (0.1 g) and anhydrous sodium acetate (0.15 g) in aqueous methanol (5 ml). The mixed m.p. of a sample of the product (recrystallized from methanol) with a sample of the semicarbazone of authentic 35 was 188 – 190°.

Spiro[4.5]decane-6-one 32:

This compound was prepared using a procedure identical to that employed for the preparation of 1-acetyl-1-methylcyclopentane 21. In this way the yield of crude product from $\Delta^{9,10}$-octalin (8 g) was 7.1 g. Pure material was obtained by chromatography of a small sample (0.2 g) of crude material on silica gel, fractions were eluted with Skelly B/ether mixture (10:1).

The IR spectrum (neat) of purified material showed a strong absorption at 1700 cm^{-1}. The semicarbazone derivative was prepared, m.p. 188 - 190°, reported m.p. 187 - 190°.[19]

2,3-Epoxy-2,3-dimethylbutane 38:

A solution of m-chloroperbenzoic acid (4.8 g) in methylene chloride (30 ml) was cooled to 0° and a solution of tetramethylethylene (1.7 g) in methylene chloride (20 ml) was added slowly so that the temperature did not rise above 25°. After one hour most of the precipitated m-chlorobenzoic acid was filtered off. Excess reagent was destroyed by shaking the filtrate with sodium sulphite solution (10%) until the washings gave a negative test with starch/iodide paper. The filtrate was then washed several times with saturated sodium bicarbonate solution. The solution was then dried and fractionated using a 10" Vigreux column to yield 1.6 g (80%) of 38, b.p. 87 - 90°, n_D^{25} = 1.3938. Reported b.p. 90 - 90.5°, n_D^{25} = 1.4010.[37] The NMR spectrum (CCl_4) showed a sharp singlet at τ8.78.

9,10-Epoxy-cis-decalin 33:

i. From $\Delta^{9,10}$-octalin

Using a procedure identical to that employed for the preparation of 38, the epoxide of $\Delta^{9,10}$-octalin 33 was prepared in 93% yield from 2.7 g of the olefin. The product, a faintly yellow oil, showed a band at 840 cm^{-1} in the IR spectrum.

The NMR spectrum (CCl_4) showed two broad absorptions of equal intensity centred at τ8.35 and τ8.62. $\underline{n}_D^{25}$ = 1.4839, reported $\underline{n}_D^{20}$ = 1.4847.[100]

ii. From 9-Hydroxy-10-iodo-*trans*-decalin 15b:

A solution of triphenylphosphine (0.1 g) in CCl_4 (2 ml) was added to a solution of 9-hydroperoxy-10-iodo-*trans*-decalin 15b (0.1 g) in CCl_4 (3 ml) stirred at 0°. No attempt was made to remove the phosphorus compounds from solution after reaction. The NMR spectrum of the solution showed a broad absorption between τ7.6 - 8.4. Solvent was then removed evaporatively and the residue containing the crude iodohydrin 15b was dissolved in methanol (2 ml). 1 N sodium hydroxide solution was then added (1 ml) and the solution was stirred for 10 minutes. Water was added (20 ml) and the mixture was extracted with CCl_4 (3 x 5 ml); this extract was dried and concentrated. The NMR spectrum of the extract showed absorptions at τ8.35 and 8.62, the position and appearance of these signals were identical to those of 9,10-epoxy-*cis*-decalin 33. TLC analysis on silica gel plates showed that isolated material had an R_f value identical to that of authentic 33 using several solvent systems.

3-Methoxy-2,3-dimethyl-2-butanol 37:

2,3-Epoxy-2,3-dimethylbutane 38 (0.2 g) was mixed with methanol (∿ 0.1 g) in a test tube. One drop of trifluoroacetic acid was added and the solution was mixed thoroughly. Water (5 ml) and CCl_4 (5 ml) were then added and the organic layer was separated off and dried. The NMR spectrum of the solution showed absorptions at τ6.76 (s), τ7.25 (b, D_2O exchangeable), τ8.81 and 8.86.

3-Methoxy-2,3-dimethyl-2-butyl Hydroperoxide 36:

Bromohydroperoxide 5a (2 g) was treated with silver acetate in methanol solution using the same procedure as was employed in the preparation of 4. The NMR spectrum (CCl_4) of the reaction mixture after work-up showed signals at τ8.89 (s), 8.33 (m) and 5.22 (b), these were due to the alkylic hydroperoxide 6. Additional signals were also present at τ8.93 (s), 8.87 (s) and 6.84 (s); the ratio of signals at τ6.84 to those at τ8.89 and 8.87 was ∿ 1:4, suggesting the presence of 36. A hydroperoxy absorption was also observed at τ1.5 (m).

The residue was dissolved in methanol (20 ml), and the solution was stirred at 0°. $NaBH_4$ (1 g) was added and the mixture was stirred at 0° for 20 minutes, then heated under reflux for a further 15 minutes. Water was added (50 ml) and the solution was extracted with methylene chloride (4 x 5 ml). Evaporation of solvent after drying yielded a colourless residual oil. The NMR spectrum of this oil ($CDCl_3$) showed absorptions at τ5.0 (m), 5.25 (m), 8.22 (m) and 8.67 characteristic of the allylic alcohol 39. Signals characteristic of 37 were also present. Integration of the methyl signals indicated that the ratio of 39:37 was ∿ 1:1.

Reduction of 1,2-Dioxetanes by Triphenylphosphine:

A solution of 4 (0.04 g, freshly recrystallized from pentane) in CCl_4 (1 ml) was added dropwise to an ice cold solution of triphenylphosphine (0.1 g) in CCl_4 (25 ml). The yellow colour of the dioxetane was discharged immediately and the NMR spectrum of the resulting solution showed a very strong absorption at τ8.78. The major product of the reaction was assumed to be tetramethylethylene oxide; this was confirmed by VPC analysis on FFAP. The major product from the reaction had a retention time both at 30° and 60° identical to that of authentic epoxide.

A small absorption at τ7.9 in the NMR spectrum of the solution was attributed to acetone; absorptions at τ8.9 (s), τ8.25 (d), τ5.4 and τ5.1 (broad signals) indicated the presence of 2-methyl-3-hydroxy-1-butene, 39. Relative yields of products were determined by integration of the respective methyl signals.

In a similar manner 17 (0.04 g) was reduced with triphenylphosphine (0.08 g) in CCl_4 solution. The NMR spectrum of the resulting solution showed broad absorptions at τ4.12 and at τ5.05 and 5.27 together with signals at τ8.3 (d) and τ8.7 (s) indicating the presence of the isomeric, allylic alcohols 29 and 30. Integration of the olefinic signals gave the relative yields of these two materials. A small signal at τ8.65 (s) was attributed to the cleavage product, octane-2,7-dione 22. The presence of this material was confirmed by TLC on silica gel plates, eluting with ether/Skelly B 1:5.

In the same way, 18 (0.1 g) was reduced to yield a solution whose NMR spectrum showed a broad absorption between τ7.3 and τ8.7, together with a small signal at τ4.55 (broad). The IR spectrum of the solution showed a broad absorption at 3600 cm^{-1} and a small carbonyl absorption at 1700 cm^{-1} probably due to some cleavage product, cyclodecane-1,6-dione 24.

The major component present was shown to be 10-hydroxy-$\Delta^{1,9}$-octalin 40 by comparison of spectra with that of authentic material and by its behaviour on TLC. The minor component was identified as 24 by its R_f value on silica gel plates using several solvent systems.

10-Hydroxy-$\Delta^{1,9}$-octalin 40:

This material was prepared from 10-hydroperoxy-$\Delta^{1,9}$-octalin 23 by reduction with $LiAlH_4$ in the usual manner. The NMR spectrum (CCl_4) showed absorptions at τ4.55 (b) for the olefinic proton and τ7.5 - 8.6 for the remaining protons.

Reaction of Tetramethyl-1,2-dioxetane 4 with Base:

A solution of the dioxetane 4 (1 g) in methanol (100 ml) containing sodium hydroxide (1.5 g) and benzene (2.6 g) was stirred at room temperature in a flask protected from light. After 72 hours the solution was worked up by the addition of water (50 ml) and the solution was then repeatedly extracted with pentane. Solvent was removed by distillation through a Vigreux column and the residue was examined by VPC; (dinonyl phthalate at 70° and FFAP at temperatures between 50 - 100°) the only product detected was acetone. Yellow crystals were deposited when the residue was cooled to -10°. These were shown to be unreacted starting material on the basis of an NMR spectrum (CCl_4) which showed a sharp singlet at τ8.49.

CHAPTER II

OTHER PREPARATIONS OF 1,2-DIOXETANES

When this work was well in progress, several syntheses of compounds reported to be 1,2-dioxetanes appeared in the literature. Certain features of these compounds, however, did not appear to be fully compatible with the structures assigned them; for this reason it was felt that these reports warranted separate discussion.

A reportedly general synthesis of 1,2-dioxetanes from ozonation of olefins was investigated in some detail and is also discussed in this section.

DISCUSSION

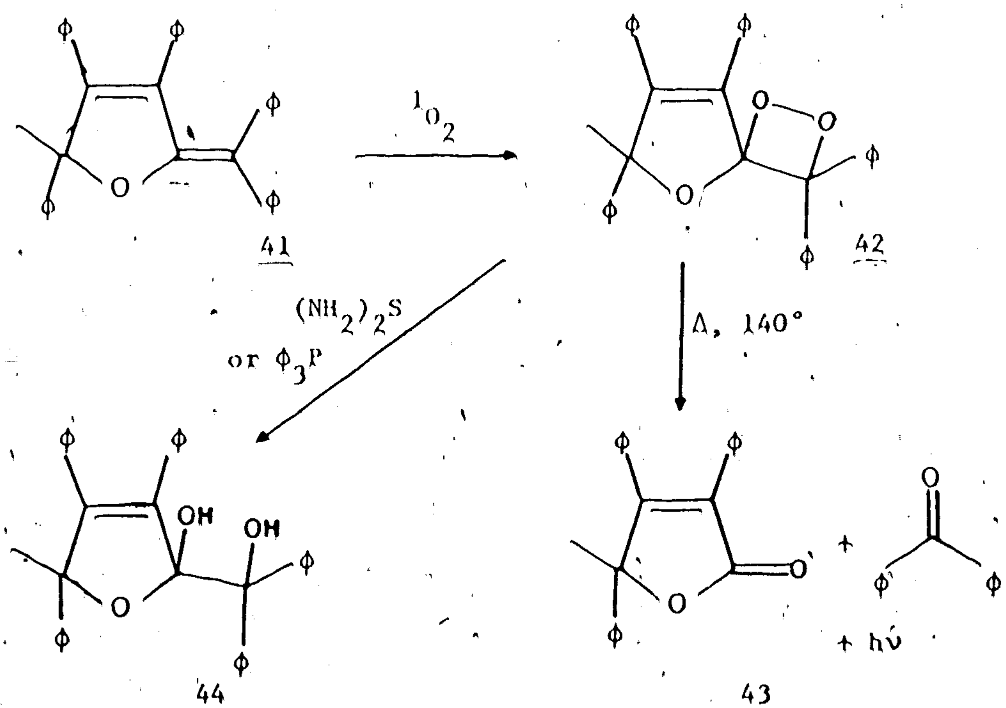
Formation of 1,2-Dioxetanes *via* Photooxygenation of Olefins:

The reactions of many olefins, particularly those with phenyl substituents, with singlet oxygen yield products arising from cleavage of the double bond. As discussed in Chapter I, it is believed that many of these reactions proceed *via* 1,2-dioxetane intermediates; more recently, several such intermediates were reportedly isolated in excellent yields.

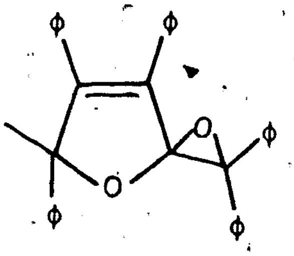
Basselier and Le Roux[38] reported that photooxygenation of the furan derivative 41 led to a peroxidic material which they formulated as the 1,2-dioxetane 42. This material, isolated in 80% yield, was characterized by reduction to the diol 44 and by thermolysis to the lactone 43 as shown in Scheme II. The product, 42, was reported to be thermally stable at room temperature but was decomposed at 140° yielding the lactone 43 and benzophenone in 84 and 86% yields, respectively. The decomposition was reported to be violent at this temperature and was accompanied by a blue luminescence. The reason for the exceptional thermal stability of 42 compared with other 1,2-dioxetanes such as 4 is not obvious.

The reaction of 42 with acidified KI solution to liberate iodine, and the reduction of 42 by thiourea to yield the diol 44 are consistent with the assigned structure. However, it is not obvious how reduction of 42 with triphenylphosphine can lead directly to the diol 44. The reduction of 1,2-dioxetanes by organic phosphines has been discussed earlier; organic peroxides normally react with phosphines to yield products arising from oxygen abstraction reactions.

Scheme II



The expected product from the reduction of 42 is, of course, the epoxide 45.



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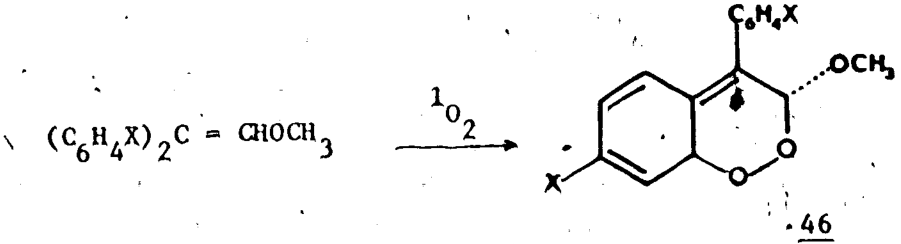
It is possible, of course, that this compound is, in fact, formed during the reduction and is converted to the diol during work-up.

Finally, the physical characteristics of 42 are inconsistent with the assigned structure; isolated material was reported to be a white solid in contrast to other 1,2-dioxetanes which are yellow. It has been demonstrated that this colour is not due to impurities[39] and it appears to be a general characteristic of 1,2-dioxetanes.

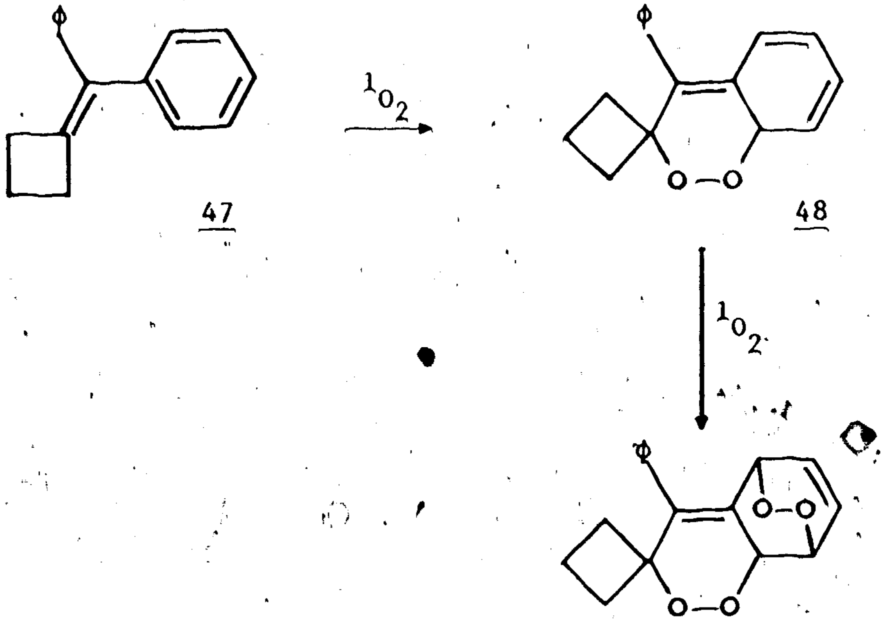
Foote[40] has carried out much excellent work on the photooxygenation of similar materials and recently reported the isolation of unusual products, 46, from photooxygenation of substituted 1,1-diphenyl-2-methoxyethylenes, eq. [30].

[30]



The product arises via a 1,4-addition of singlet oxygen to the styryl moiety. Similar 1,4-adducts have been isolated by other workers,[41] eq. [31].

[31]



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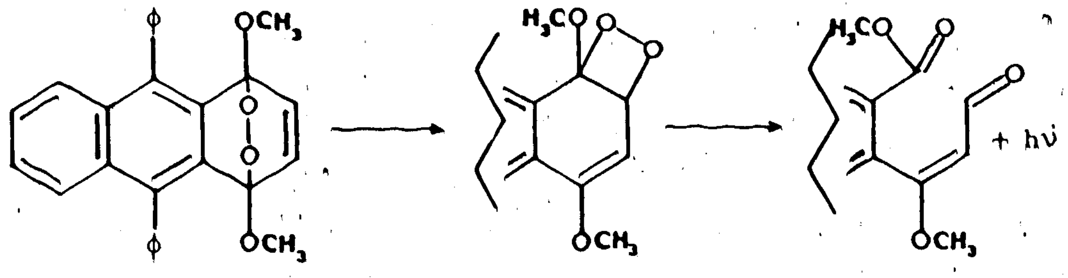
The possibility exists that the product, 42, formulated as a 1,2-dioxetane, is in fact a 1,4-adduct with a structure similar to that of 46 or 48. Examples of thermal rearrangements of 1,4-adducts to 1,2-dioxetanes are known; for example, Wilson[42] has obtained good evidence that the *endo*-peroxide 50, eq. [32], is rearranged on heating to give the 1,2-dioxetane intermediate shown. Cleavage of this intermediate leads to light emission.

[32]



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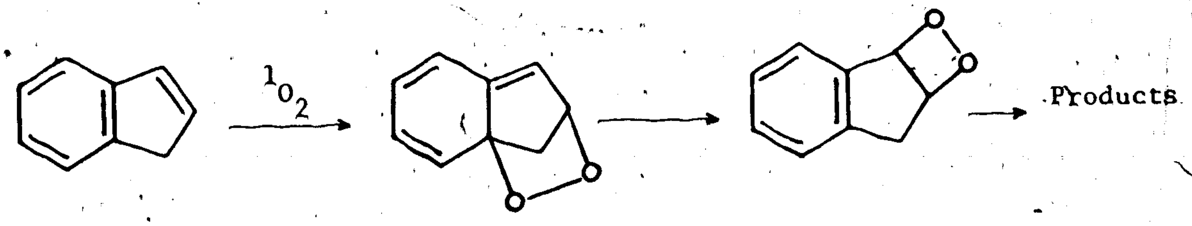
A similar rearrangement could explain the chemiluminescence observed by Basselier during the thermolysis of 42 at elevated temperatures.

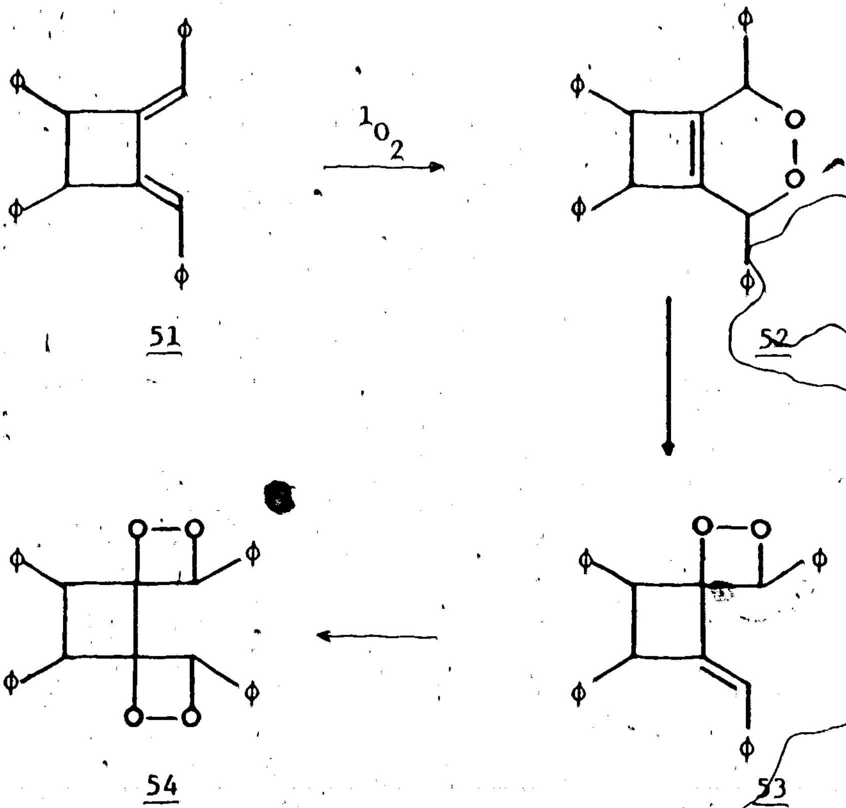
Foote[40] also suggested that homophthalaldehyde formed during photooxygenation of indene (see Chapter I) arose via cleavage of a 1,2-dioxetane which was formed by rearrangement of the initially formed 1,4-adduct, eq. [33].

[33]



The synthesis of a 1,2-dioxetane formed by ~~rearrangement~~ of a 1,4-adduct has recently been reported,[43] Scheme III. The initially formed 1,4-adduct, 52, obtained from the photooxygenation of the cyclobutane derivative 51 was reported to be unstable in the presence of even trace amounts of protic solvents. Rearrangement of this 1,4-adduct gave rise to a second peroxidic compound, formulated as the 1,2-dioxetane 53. Prolonged photooxygenation of 51 or 53 led to the formation of a di-adduct which was formulated as the bis-1,2-dioxetane 54.

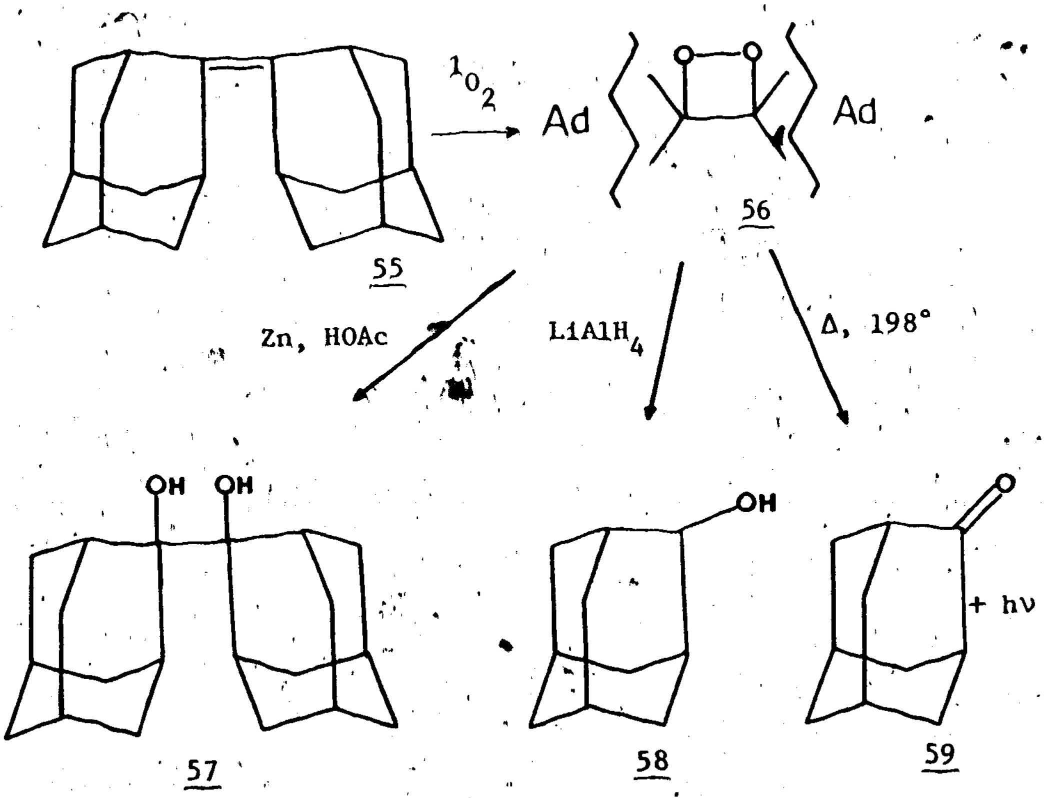
Scheme III



Both 53 and 54 appear to have a high thermal stability and can be heated to their melting points (180 and 181°, respectively) without decomposition. This stability is remarkable in view of the behaviour of other 1,2-dioxetanes such as the tetramethyl derivative 4. However, evidence for the structures assigned to 53 and 54 is not compelling; reduction of 53 was reported to yield the corresponding diol but this diol was not well characterized. A more reasonable expl[illegible]on for the observed facts is that the mono-adduct 53 has a structure similar to that of other 1,4-adducts isolated such as 48, eq. [31]. This adduct could then add a second mole of oxygen to yield a di-adduct of structure similar to that of 49.

Another remarkably stable 1,2-dioxetane, 56, was reportedly isolated in 85% yield from the photooxygenation of adamantylideneadamantane 55,[44] Scheme IV.

Scheme IV



The product 56 was a solid which melted, apparently without decomposition, at 163 - 164°. Decomposition did, however, occur when the product was heated to reflux temperature in ethylene glycol (198°) and this decomposition was accompanied by chemiluminescence.

Adamantanone 58, the only product detected from the decomposition, was isolated in 80% yield. 56 was reportedly inert to sodium borohydride but could be reduced to the diol 57 upon reaction with zinc and acetic acid. The reaction of 56 with $LiAlH_4$ is difficult to explain; in view of the high thermal stability of this material it is not clear why reaction with $LiAlH_4$ should lead to cleavage products. Otherwise, however, this material appears to have been well characterized. It is worth noting though, that treatment of cyclopentylidenecyclopentane with triphenyl phosphite ozonide gives rise to a product which, although certainly not a 1,2-dioxetane, decomposes at elevated temperatures with simultaneous emission of light.[21]

Very recently, Kearns[46] reported the synthesis of a comparatively simple 1,2-dioxetane 60 from the photooxygenation of 2,5-dimethyl-2,4-hexadiene, eq. [34].

[34]

60

The spectral properties reported for 60 appear to fit the assigned structure.

Formation of 1,2-Dioxetanes From Ozonation of Alkenes:

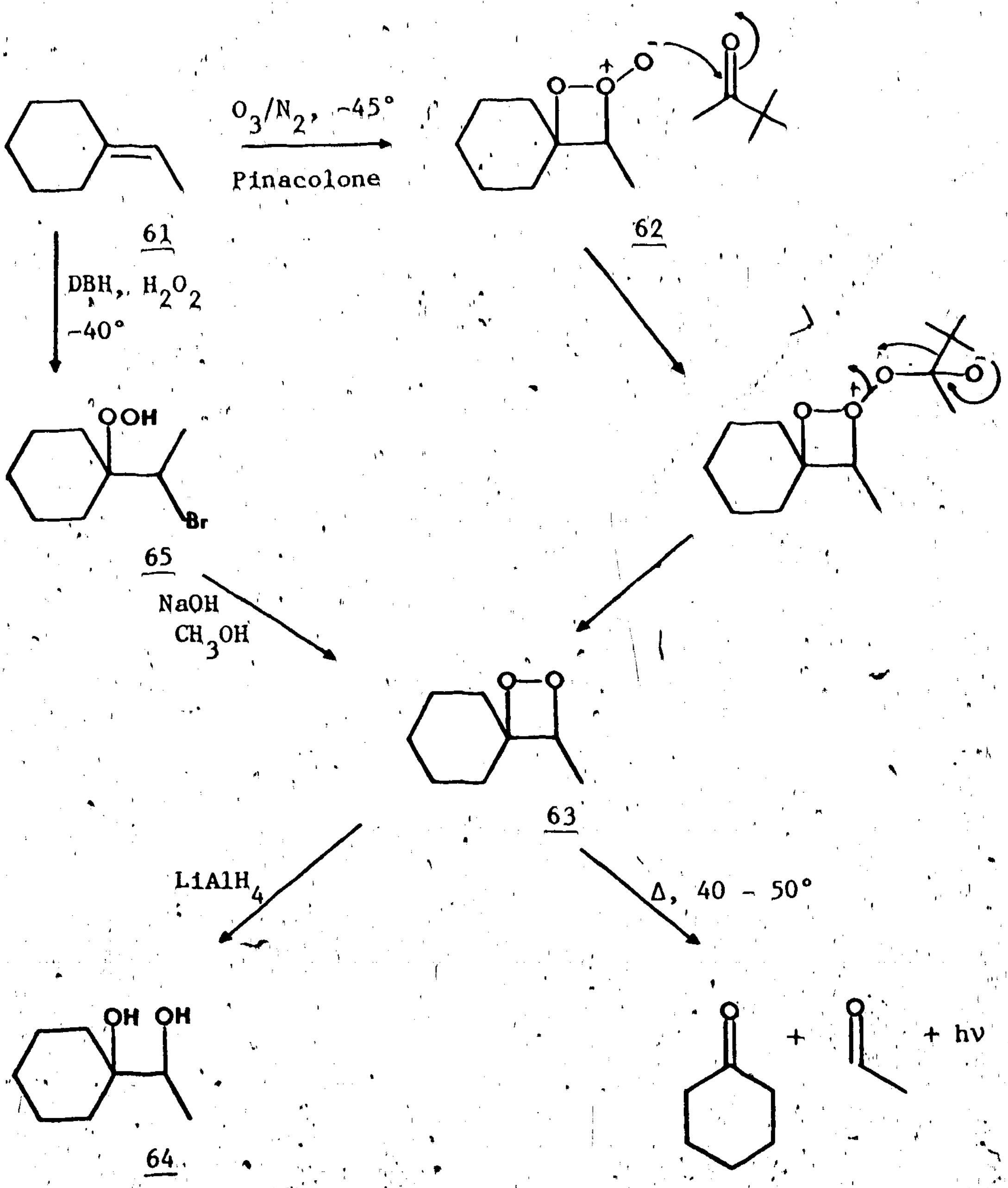
Recent reports by Story indicated that cleavage products rather than normal ozonides were formed on ozonation of alkenes in certain aldehydic or ketonic solvents. Cleavage products were assumed to arise from decomposition of intermediate 1,2-dioxetanes and it was subsequently claimed that, if the ozonation was carried out in pinacolone, these intermediates could be isolated in good yields. The isolation of several simple 1,2-dioxetanes by this method was reported; in particular, the isolation, in 50 - 75% yield, of 1,2-dioxa-3-methylspiro[3.5]nonane 63 was reported,[47] Scheme V.

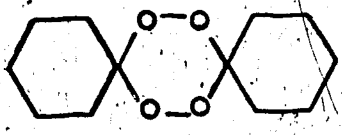
It was claimed that the key Staudinger "Molozonide" intermediate 62 was reduced by pinacolone yielding the dioxetane; this mechanism was supported by the detection of an equivalent amount of t-butyl acetate in the reaction mixture after ozonation was complete.

63 was reported as a colourless, fairly stable oil which could be decomposed by thermolysis at 170° yielding cyclohexanone and acetaldehyde. This decomposition was accompanied by a flash of blue luminescence. Further characterization of this material was achieved by its reduction to the diol 64 on treatment with $LiAlH_4$.

Because this method was described as a general synthetic route to 1,2-dioxetanes it was thought that an investigation of this work would be a worthwhile exercise; the simple one-step reaction described represented a marked improvement over the present synthetic

Scheme V


O_3/N_2, -45°
Pinacolone
61
62
DBH, H_2O_2
-40°
OOH
Br
65
NaOH
CH_3OH
63
LiAlH$_4$
Δ, 40 - 50°
OH OH
64
+ hν



66

route to simple derivatives of this class of compounds. Additionally, the material isolated by Story was apparently a remarkably stable compound and it was not clear why the properties of <u>63</u> should differ from those of other simple 1,2-dioxetanes.

It was decided firstly to prepare a sample of <u>63</u> by a "conventional" route and to investigate its properties.

RESULTS

"Conventional" Synthesis of 1,2-Dioxa-3-methylspiro[3.5]nonane, 63:

Synthesis of 63 was carried out by the usual methods described in Chapter I and is outlined in Scheme V. 1-(1-Bromoethyl)-cyclohexyl hydroperoxide 65 was prepared in 95% (crude yield) from the reaction of ethylidenecyclohexane 61 with DBH and 98% hydrogen peroxide at -40°. Reaction of 61 at this temperature was quite sluggish, necessitating reaction times of several hours. The product 65, a colourless oil which solidified when stored at -10°, was shown to contain 96.2% of the theoretical active oxygen content. This product was subsequently purified by way of the DABCO complex by Lockwood. Pure material was a low melting solid, m.p. $\sim$ 45°.[48]

Treatment of 65 with sodium hydroxide in methanol gave a yellow solution from which the dioxetane, a bright yellow oil, was isolated in ca. 15% yield. Isolated material was purified by several low temperature distillations under high vacuum; purified material contained 97.8% of the theoretical active oxygen content as estimated by iodometric titration.

The NMR spectrum of 63 (CCl_4) showed absorption at τ4.92 (quartet, J = 6.5 Hz) for the methine proton, τ8.67 (doublet, J = 6.5 Hz) for the methyl group and τ7.8 - 8.9 for the ring protons. When a solution of 63 was allowed to stand at room temperature for several days these absorptions disappeared and were replaced by a pattern typical of cyclohexanone; the solution at this point was colourless.

Light emission could readily be observed at 50 - 60° from a solution of the compound (5 ml) in pinacolone to which a few drops of 9,10-dibromoanthracene (DBA) had been added. Reduction of 63 with $LiAlH_4$ by the usual method yielded a quantitative amount of the diol 64. The NMR spectrum of this material ($CDCl_3$) showed a clean quartet at τ6.42, J = 7 Hz, an exchangeable absorption at τ7.4, a doublet at τ8.84, J = 7 Hz and a broad absorption between τ8.2 - 8.9. The UV-visible spectrum of 63 has also been measured[48] and is very similar to the spectra of other dioxetanes reported in Chapter I.

The properties of 63 then do not appear to differ significantly from those of other 1,2-dioxetanes described in Chapter I.

Ozonolysis of Ethylidenecyclohexane 61:

The ozonolysis was carried out using carefully purified pinacolone as solvent. The solution was stirred at -45° and a slow stream of O_3/N_2 was bubbled through the solution until ozonolysis was complete (as evidenced by a blue colouration of the solution). At this point close to the theoretical one mole equivalent of O_3 had been absorbed. The solvent was then removed by vacuum distillation; the distillation flask was maintained at 0 - 5° during the distillation to avoid any decomposition of unstable products and the distillate was collected in a cold trap at -78°.

The residue so obtained consisted of white crystals suspended in a colourless, viscous oil.

A small portion of this mixture was separated by filtration.

The NMR spectrum (CDCl$_3$) of the colourless oil showed a multiplet centred at τ4.82 and very broad absorptions at τ7.5 - 9.2. No doublet could be observed at high field. The NMR spectrum (CDCl$_3$) of the white crystals (recrystallized from heptane) showed a fairly broad absorption between τ7.5 to τ8.8. No absorptions were present below τ7.5.

The IR spectrum of the oil showed a broad absorption at 3500 cm^{-1} and the compound readily liberated iodine from acidified KI solution indicating the presence of a peroxy group. The NMR spectrum indicated that D$_2$O exchange had occurred although no exchangeable peak could be observed. However, this is frequently the case with hydroperoxy compounds. Thin layer chromatography on silica gel indicated the presence of at least two peroxidic products.

The IR spectrum of the crystals showed no absorptions characteristic of hydroperoxy or carbonyl groups, the compound liberated iodine very slowly from an acidified solution of potassium iodide. This product was shown to be the dimeric peroxide <u>66</u> on the basis of mixed melting points. The m.p. of isolated material was 129 - 130°, reported m.p. 129 - 130°. The mixed m.p. of isolated material together with authentic <u>66</u> was 128 - 129°.

A sample of the oil separated from the ozonolysis mixture was reduced according to the general procedure for reduction of peroxides described earlier. The NMR spectrum of the reduced product resembled that of cyclohexanol, no trace of the expected diol 64 was detected by TLC analysis or by VPC analysis (QF1 at 90°).

Finally, solvent distilled from the mixture after ozonolysis was analyzed by VPC (Carbowax 20M, 75°) for the presence of t-butyl acetate; none could be detected, even if the solvent was carefully fractionated using a Nestor-Faust spinning band apparatus before analysis. Inspection of pinacolone solutions containing known amounts of t-butyl acetate indicated that 1% of acetate was easily detectable by this method. This is a surprising result in view of the earlier report but has since been confirmed independently by other groups.[49,50]

Chemiluminescence from Ozonolysis Mixtures:

A few drops of a saturated solution of DBA in benzene were added to a portion of the pinacolone solution (10 ml) immediately after ozonolysis and the solution was warmed to 100° in a dark room; no light emission was observed. Light emission was also tested for using a spectrofluorometer with a heated cell compartment; again no emission was observed. If however, a small quantity of pure dioxetane 63 (ca. 3 mg) was added to the solution, a bright chemiluminescence was readily observed.

When the oil obtained from ozonation of 61 was plunged into an oil bath at 170°, a violent reaction occurred with simultaneous emission of a flash of blue light. The NMR spectrum of the residue obtained after this treatment showed absorptions similar to those of cyclohexanone. Analysis of this residue by VPC (FFAP, 80°) indicated that cyclohexanone had been formed in the decomposition. The dimeric peroxide <u>66</u> was stable at 170° and melted without decomposition.

Ozonation of <u>61</u> was also carried out in both commercial and purified samples of pinacolone, using crude ozone/air and crude ozone/N_2 as well as pure ozone/N_2 mixtures. Colourless oils containing varying amounts of white solid were invariably obtained and, although these samples were not investigated in detail, it was shown that none of these samples contained any of the 1,2-dioxetane <u>63</u>.

As a control experiment a small sample of pure <u>63</u>, <u>ca</u>. 0.2 g, was ozonized in pinacolone containing ethylidenecyclohexane (50 ml) at −45° for 10 minutes. A portion of this solution, when heated to 60° in the presence of added DBA exhibited a bright luminescence indicating that the 1,2-dioxetane was stable to the reaction conditions.

CONCLUSIONS

It seems evident that the compound isolated by Story from the ozonation of 61 is not the 1,2-dioxetane 63.

Luminescence measurements using a spectrofluorometer can easily detect 1,2-dioxetanes at a concentration of 10^{-4} M; since none could be detected in the ozonolysis mixtures the maximum yield of 1,2-dioxetane starting with 0.25 M olefin is only 0.04%.

Whilst it is difficult to disprove the presence of 63 as a transient intermediate in the ozonolysis of ethylidenecyclohexane, control experiments indicate that 63 is stable under the reaction conditions and is therefore probably not formed at all during the ozonolysis.

The ozonation of ethylidenecyclohexane has been investigated in some detail by Lockwood[48] who found that, while the nature of the solvent did indeed affect the nature of the products derived from the ozonation of 61, there was no evidence to suggest a direct interaction of solvent with any intermediate formed during the ozonolysis. Ozonation of 61 in dimethyl ether yielded a mixture of products similar to that obtained when the reaction was carried out in pinacolone solution.

It was also reported that ozonolysis of 9,9'-bifluorenylidene in pinacolone solution yielded a 1,2-dioxetane.[51] These experiments have since been repeated by Criegee[52] who isolated only the corresponding dimeric peroxide.

Samples of impure allylic hydroperoxides prepared in these laboratories have also been shown to undergo chemiluminescent decomposition at elevated temperatures. This property has been observed for samples prepared by photooxygenation of olefins,[45] by reaction of β-halohydroperoxides with base and from the reaction of triphenyl phosphite ozonide with olefins.[21] The nature of the impurities leading to luminescence has not been established but it has been shown that pure samples of allylic peroxides do not show this property.

Interestingly enough, peroxidic materials isolated by Kohler[54] from the autoxidation of enols were reported to decompose with a flash on heating. These peroxides were originally formulated as 1,2-dioxetanes but are now known to be α-hydroperoxyketones.

EXPERIMENTAL

Pinacolone:

Pinacolone as received from Aldrich contained as much as 5% impurity. Analysis by VPC (Carbowax 20M, 70°) showed the presence (ca. 3%) of a volatile material having a retention time close (but not identical) to that of t-butyl acetate. On evaporation of a sample of the material a heavy residue (ca. 2%) was obtained.

The material was purified by drying over anhydrous potassium carbonate (this also removed any acidic impurities) followed by fractional distillation. A fraction boiling between 102 and 103° was collected for use in the ozonolysis experiments.

Ozone/Nitrogen Mixtures:

Mixtures of pure ozone in nitrogen were prepared according to a method described in the literature.[55] The O_3/O_2 mixture generated by a Welsbach ozone generator was absorbed on silica gel (Fischer 12 - 20 mesh) contained in a "U" tube which was immersed in a bath at -78°. When ozone breakthrough occurred the tube was flushed for several minutes with pure, dry nitrogen. A mixture of pure ozone and nitrogen was obtained by slowly removing the "U" tube from the cooling bath while flushing the tube with dry nitrogen.

Ozonolysis of Ethylidenecyclohexane:

Ethylidenecyclohexane (1.4 g) was added to pure pinacolone (50 ml) in a 250 ml, three-necked flask fitted with a thermometer, an inlet tube and an outlet tube leading to a flask containing acidified KI solution. The solution was stirred magnetically and cooled by means of a chlorobenzene/dry ice bath to -45°. The flask was flushed with dry N_2 for 10 minutes and then a slow stream of O_3/N_2 was introduced through the inlet tube. Ozonolysis was continued until a blue colouration appeared in the solution, simultaneously the flask containing KI solution began to darken rapidly.

Uptake of O_3 was estimated by passing the remaining O_3 in the tube through two gas-washing bottles in series containing acidified KI solution. The contents of the exhaust gas flask were added to the solution of iodine obtained and the combined solutions were made up to one litre. 25 ml aliquots of this solution were titrated with standard $Na_2S_2O_3$ solution. The total O_3 absorbed on the silica gel was then determined by saturating the same tube with ozone and passing the total contents through acidified KI solution. 85% of the theoretical quantity of O_3 was found to be absorbed in the reaction.

The solvent was removed by vacuum distillation; evaporation from the distillation flask was sufficient to cool the solution to below 5°. In this way most of the pinacolone could be removed. The distillate was collected in a cold trap at -78°.

Pinacolone-free samples were obtained by repeated evaporation of the mixture with CCl_4 at the rotary evaporator.

Reductions with $LiAlH_4$:

A solution of the peroxidic material to be reduced (0.5 g) in ether (10 ml) was added very slowly to a slurry of $LiAlH_4$ (0.7 g) in ether (50 ml) stirred at -40°. When addition was complete the mixture was allowed to warm up and then stirred at reflux temperature for 30 minutes. At this time the solution was cooled to 0° and a solution of KOH (10%) was added slowly until the ether layer became clear. The ethereal solution was then filtered and solvent removed to yield the reduced products.

1-(1-Bromoethyl)-cyclohexylhydroperoxide 65:

This compound was prepared in 95% yield by the methods described in Chapter I. Iodometric analysis of the crude product, a colourless oil, showed 96.2% of the theoretical active oxygen content. The NMR spectrum ($CDCl_3$) showed absorptions at τ5.5 (quartet, J = 7 Hz), τ8.3 (doublet, J = 7 Hz) and τ8.0 - 8.6 for the ring protons. Traces of another constituent (possibly the dibromide) were also present, as evidenced by a small absorption at τ7.9 (doublet).

1,2-Dioxa-3-methylspiro[3.5]nonane 63:

To a solution of bromohydroperoxide 56 (2.2 g) in methanol (6 ml) was added slowly a solution of NaOH (0.44 g) in H_2O (1 ml) and methanol (3 ml). The solution was stirred at 0° for 50 minutes and then CCl_4 (10 ml) and water (10 ml) were added. The CCl_4 layer was separated off and dried over $MgSO_4$, solvent was removed under reduced pressure at room temperature. The bright yellow residue was then fractionated under high vacuum (5μ) at room temperature, a colourless forerun was discarded. The yellow distillate, 0.2 g, 14% was further purified by a second distillation and iodometric analysis indicated 97.8% of the theoretical active oxygen content.

Cyclohexanone Diperoxide 66 and 1-(1-Hydroxyethyl)-cyclohexanol 64:

Authentic samples of these materials were prepared by Mr. P. A Lockwood.

Chemiluminescence Studies:

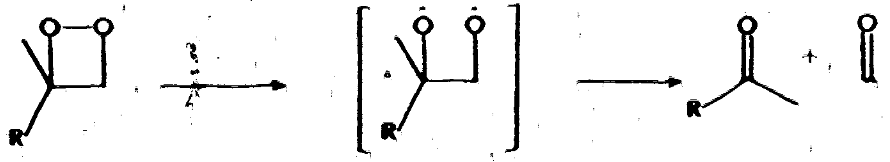
Chemiluminescence studies were carried out using a Turner 430 spectrofluorometer with the xenon lamp off. The cell compartment was heated by means of an external water bath.

CHAPTER III

THERMAL DECOMPOSITION OF 1,2-DIOXETANES

Several reports concerning mechanisms for the thermal decomposition of 1,2-dioxetanes have appeared in the literature. The possibility of a one-step "concerted" mechanism has been suggested by Kearns[56] although no evidence for this process was presented. The work of Richardson and O'Neal,[57] however, has shown that the activation parameters for the decomposition of 3,3-dimethyl-1,2-dioxetane 8 and 3-methyl-3-phenyl-1,2-dioxetane 67 are experimentally indistinguishable. This data was interpreted as evidence for a two-step mechanism with formation of a biradical intermediate as the rate determining step, eq. [35].

[35]



R = CH_3, 8

R = C_6H_5, 67

In a concerted mechanism the phenyl group would be expected to interact differently than the methyl with respect to the developing carbonyl bond.

These authors also showed that calculated activation parameters, based on such a two-step mechanism, were in good agreement with their experimental data.[58] Additionally, these authors have reported calculated activation parameters for several other 1,2-dioxetanes including the trimethyl and tetramethyl derivatives 2 and 4. It was of interest therefore, to measure activation parameters for these, and other, compounds and to compare the experimental and calculated values.

RESULTS AND DISCUSSION

Rates of Decomposition of 1,2-Dioxetanes:

Trimethyl-1,2-dioxetane 2 and tetramethyl-1,2-dioxetane 4 were decomposed in CCl_4 solution by immersion in a thermostatted bath. At least 10 minutes were allowed to elapse to enable the solutions to attain thermal equilibrium, then aliquots were withdrawn at suitable intervals and estimated for peroxide content by iodometric titration. It was found that the decomposition of both 2 and 4 exhibited first-order kinetics during two - three half-lives. Some decompositions with 4 were also carried out by sealing solutions of the dioxetane in glass ampoules. The glass ampoules were immersed in a water bath and, at suitable intervals, ampoules were withdrawn from the bath for estimation of peroxide content. This method did not appear to offer any advantage over the first method discussed.

Rate constants for the first order decomposition of 2 and 4 were estimated graphically using the formula of eq. [36],

$$[36] \qquad \mathrm{Log}\ C_t = \mathrm{Log}\ C_o - \frac{k_d t}{2.303}$$

where C_o is the initial concentration of dioxetane and C_t the concentration at time, t. By plotting the left hand side of the eq. [36] against time, a straight line of slope $k_d/2.303$ was obtained.

An example of the data obtained for the decomposition of 2 at 39.8° is shown in Table IV and Table V shows similar data for the decomposition of 4 at 40.0°. Infinity titres ($t = \infty$) were

TABLE IV

Decomposition of Trimethyl-1,2-dioxetane 2 in CCl_4 at 39.8°

Aliquot: 1 ml
Titrant: $Na_2S_2O_3$ (0.0123 M)

Run B 6

Time (s)	Titration (ml)	C_t (M)	$-\text{Log}_{10}\ C_t$
0	9.175	0.1135	0.9450
1800	9.025	0.1060	0.9747
3600	8.125	0.0946	1.0231
5400	7.70	0.0891	1.0501
7200	7.325	0.0811	1.0910
9000	6.775	0.0776	1.1101
18000	4.15	0.0484	1.3149
27000	2.75	0.0316	1.5000
~ 90000 (∞)	0.5		
Blank	0.2		

From graph, $k_d = 4.71 \times 10^{-5}\ s^{-1}$

TABLE V

Decomposition of Tetramethyl-1,2-dioxetane 4 in CCl_4 at 40°

Aliquot: 1 ml

Titrant: $Na_2S_2O_3$ (0.02 M)

Run C1

Time (s)	Titration (ml)	C_t (M)	$-Log_{10}$ C_t
0.0	14.35	0.143	0.8432
360	13.9	0.139	0.8570
720	13.5	0.135	0.8697
1440	12.9	0.129	0.8894
3024	11.05	0.1105	0.9568
5148	9.6	0.096	0.0177
8424	7.675	0.0675	1.1149
11232	6.325	0.06325	1.1959
18000	3.825	0.03825	1.4100
∿ 43200 (∞)	0.2		
Blank	0.2		

From graph, $k_d = 7.26 \times 10^{-6}\ s^{-1}$

determined by taking aliquots from the solutions of dioxetanes after a period of at least six half-lives. First order plots of the data presented in Tables IV and V are shown in Figure 4. The rate constants for 2 and 4 at all the temperatures recorded are presented in Table VI.

The decomposition of 17 and 18 was followed by recording the chemiluminescence decay of solutions of these compounds. The luminescence from dilute solutions of these dioxetanes was too faint to be measurable with any degree of accuracy with the available apparatus. Luminescence however, was considerably enhanced if fluorescers such as 9,10-dibromoanthracene (DBA) were present. It has been demonstrated that the presence of such fluorescers does not affect the rate of decomposition of dioxetanes in aerated samples.[14]

Solutions of 17 and 18 dissolved in benzene saturated with DBA were sealed into glass cuvettes and placed in the heated cell compartment of a Turner 430 spectrofluorometer. After the solutions reached the temperature of the pre-heated cell compartment, the intensity of chemiluminescence decayed with first-order kinetics.

It has been shown for other 1,2-dioxetanes that the chemiluminescence decay rate does in fact measure the rate of disappearance of 1,2-dioxetane.[14,59] The relative intensity (I_t) of chemiluminescence for a solution of 1,2-dioxetane is proportional to the concentration of dioxetane and the rate constants for the first-order decomposition of 17 and 18 could be estimated graphically by plotting Log I_t against time.

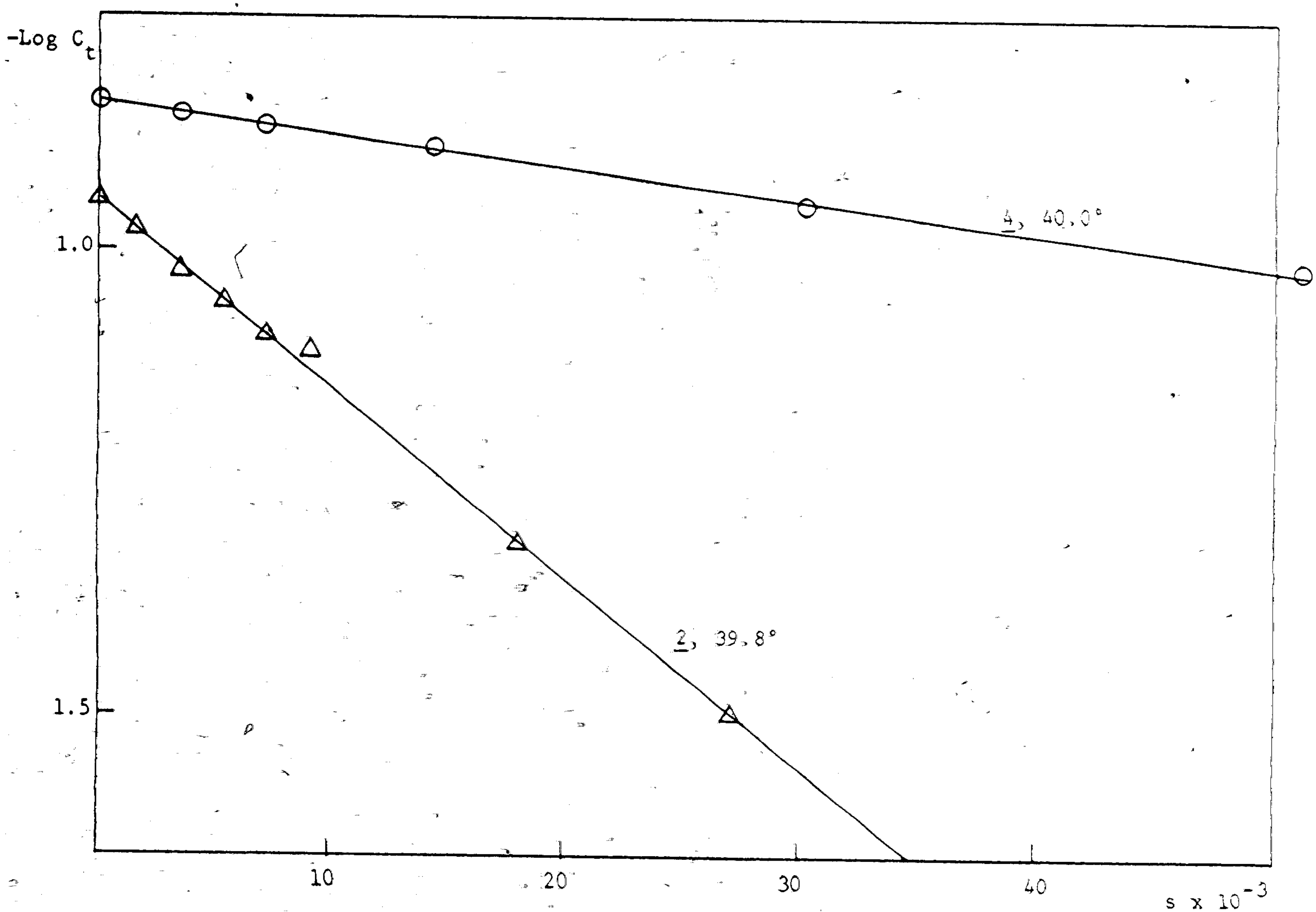


Figure 4. Rates of Decomposition of 1,2-Dioxetanes in CCl_4

TABLE VI

Rate Constants for Decomposition of 2 and 4 in CCl_4

Compound	Temp. (°C)	Method	Rate Constant x 10^6 (s^{-1})
2	60.1	1	484
2	60.1	1	461
2	60.1	1	461
2	60.1	1	478
2	39.8	1	47.1
2	39.8	1	46.0
2	39.8	1	47.9
4	50.0	1	26.2
4	50.0	1	26.7
4	50.0	1	26.6
4	50.0	1	26.4
4	50.0	1	26.9
4	60.0	1	87.4
4	60.0	1	87.5
4	60.0	1	87.4
4	40.0	1	7.26
4	40.0	1	7.26
4	52.0	2	49.7

1 = Iodometric

2 = Chemiluminescence decay

Examples of the data obtained from the decomposition of 17 and 18 are presented in Tables VII and VIII, respectively. Infinity readings were taken after at least 10 half-lives had expired; data presented is corrected for this reading. First-order plots of the data presented in Tables VII and VIII are shown in Figures 5 and 6, respectively.

In order to check the accuracy of the method employed in these studies, the rate of decomposition of 4 was also followed by this method; the rate constant derived by this method is in reasonable agreement with those obtained earlier by iodometric methods. It was also possible to follow the decomposition of 17 by an NMR method; the rate of disappearance of the methyl signal of 17 and the rate of appearance of the methyl signal of octane-1,7-dione 22 could both be easily followed. Rate constants derived from this method were in good agreement with those derived from the chemiluminescence decay methods.

Additionally, the rate of decomposition of 18 was followed by iodometric methods. Again, rate constants derived from chemiluminescence decay measurements and from the iodometric studies were in reasonable agreement. Solutions of dioxetanes free from DBA or other fluorescers were, of course, used for rate determinations by both NMR and iodometric methods. The rate constants for the decomposition of 17 and 18 are presented in Table IX.

The chemiluminescence decay rates for degassed samples of 4, 17 and 18 showed marked acceleration over the rate observed for

TABLE VIII

Decomposition of cis-1,6-Dimethyl-7,8-dioxabicyclo[4.2.0]octane 17 in Benzene at 37.0°

Run 11

Time (s)	Meter Reading (I_t)	Log I_t	Scale
1800	27.8	1.444	x 300
3600	26.0	1.415	x 300
5400	23.4	1.371	x 300
7200	20.8	1.318	x 300
9000	18.9	1.276	x 300
10800	16.9	1.228	x 300
12600	15.4	1.187	x 300
14400	13.9	1.143	x 300
16200	12.3	1.090	x 300
18000	11.0	1.041	x 300
20100	9.9	0.996	x 300
22400	8.9	0.949	x 300
24200	7.4	0.869	x 300
35000	4.0	0.602	x 300
36800	3.4	0.531	x 300
38600	3.1	0.491	x 300
∿ 120000 (∞)	0.2		

From graph, k = $6.17 \times 10^{-5}\ s^{-1}$

TABLE VIII

Decomposition of 11,12-Dioxa[4.4.2]propellane 18 in Toluene at 29.68°

Run 15

Time (s)	Meter Reading (I_t)	Log I_t	Scale
600	18.4	1.2648	x 30
1200	16.0	1.2041	x 30
1800	14.1	1.1492	x 30
2400	12.6	1.1003	x 30
3000	11.3	1.0531	x 30
3600	10.0	1.000	x 30
4200	9.1	0.9590	x 100
4800	8.0	0.9031	x 100
5400	7.0	0.8451	x 100
6000	6.3	0.7993	x 100
6600	5.6	0.7482	x 100
7200	5.1	0.7076	x 100
7800	4.5	0.6532	x 100
8400	4.0	0.6021	x 100
9000	3.6	0.5563	x 100
9600	3.2	0.5051	x 100
10200	2.9	0.4624	x 300
11400	2.35	0.3711	x 300
12000	2.1	0.3220	x 300
12600	1.95	0.2788	x 300
13200	1.70	0.2304	x 300
∿ 80000 (∞)	0.1		x 300

From graph, k = $1.89 \times 10^{-4}\ s^{-1}$

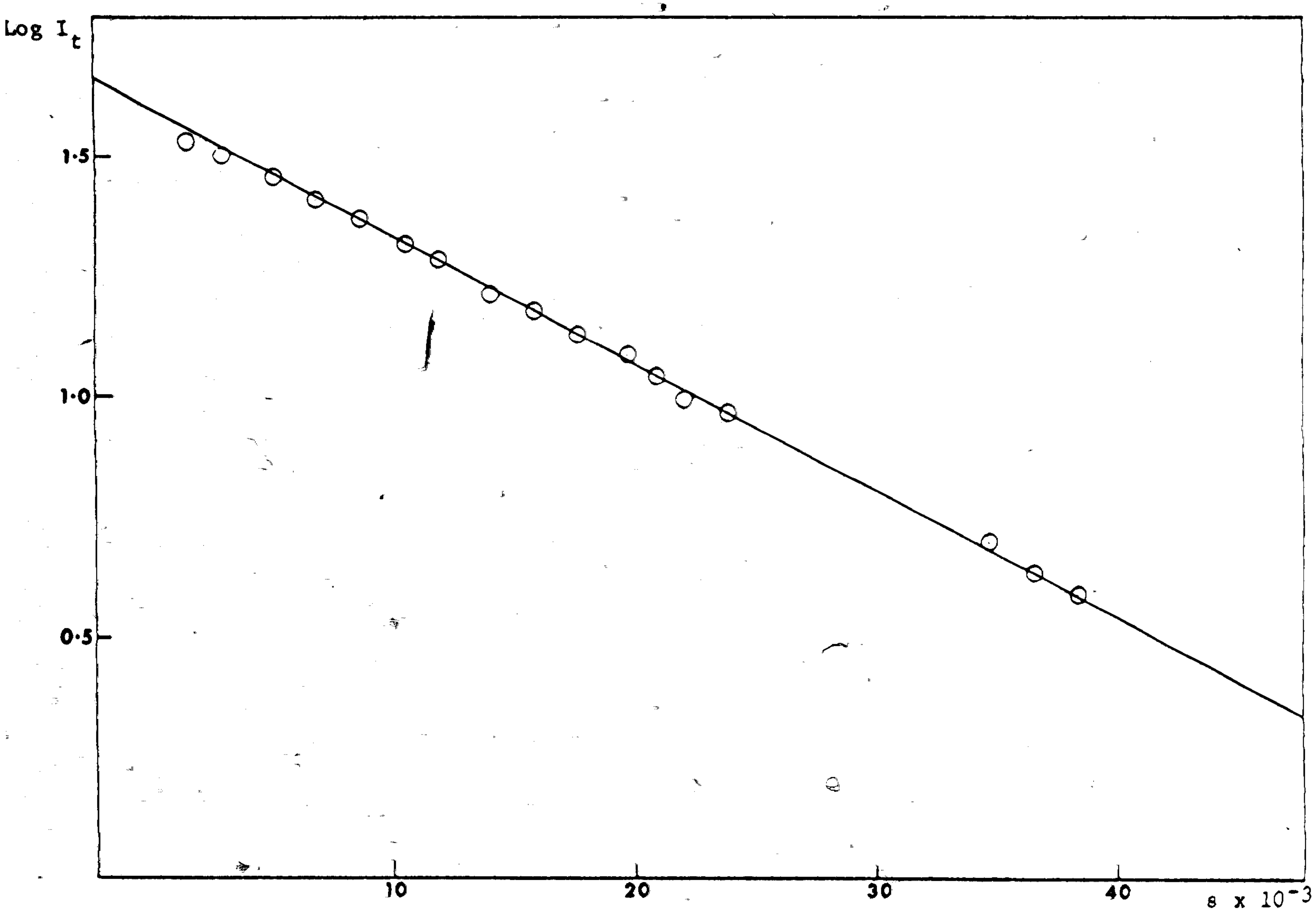


Figure 5. Rate of Decomposition of 17 at 37° in Benzene

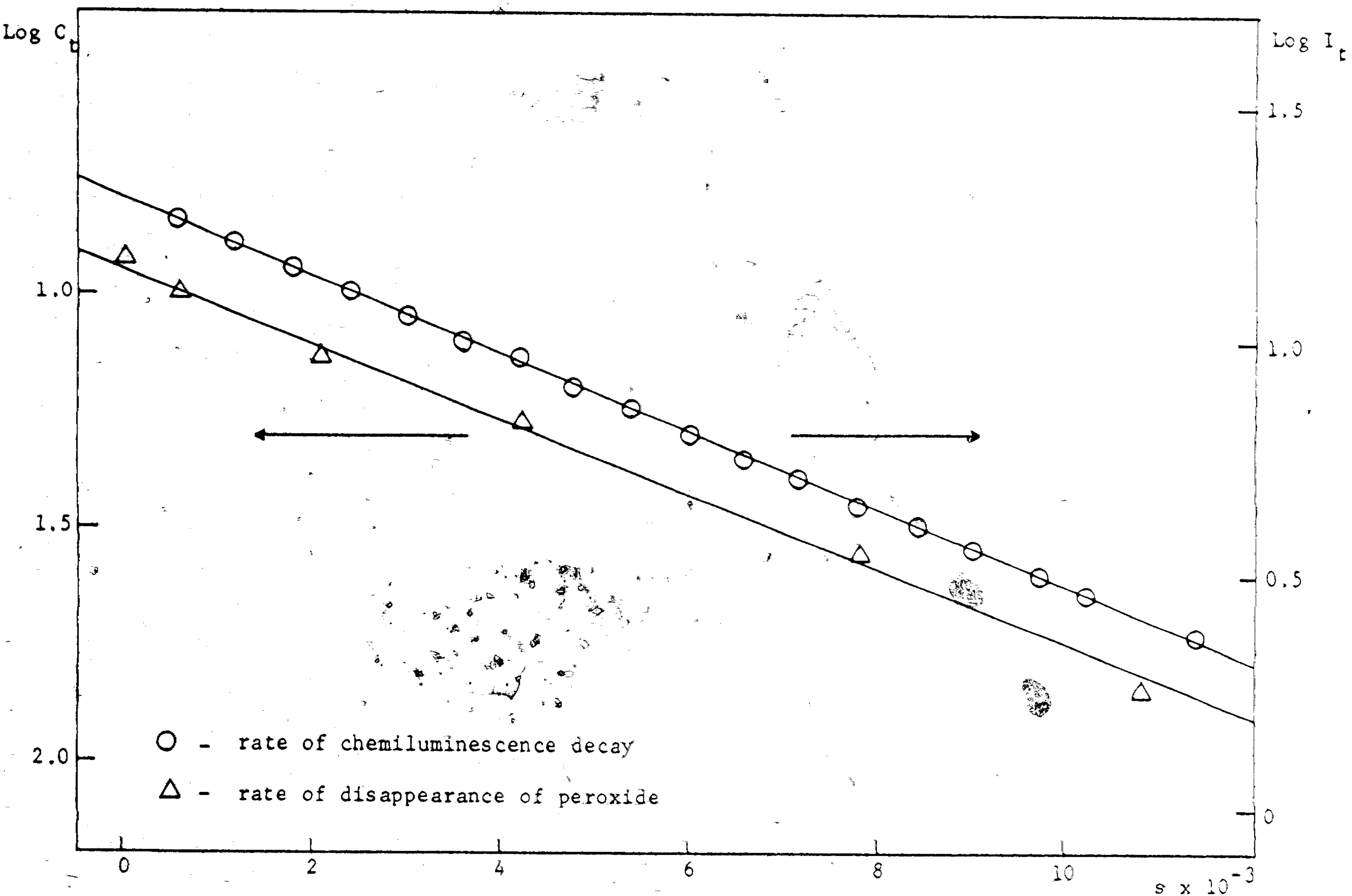


Figure 6. Rate of Decomposition of 18 at 29.68° in Toluene

TABLE IX

Rate Constants for Decomposition of 17 and 18

Compound	Temp. (°C)	Initial Concentration (M)	Method	Solvent	Rate Constant x 10^5 (s^{-1})
17	52.0	0.3	2	C_6H_6	39.5
17	52.0	0.2	2	C_6H_6	41.5
17	52.0	0.2	2	C_6H_6	39.8
17	52.0	0.2	2	C_6H_6	40.0
17	50.0	0.1	3	CCl_4	42.5
17	59.4	0.15	2	C_6H_6	97.5
17	59.4	0.3	2	C_6H_6	97.5
17	59.4	0.5	2	C_6H_6	99.5
17	59.4	0.2	2	C_6H_6	105.0
17	37.0	0.2	2	C_6H_6	6.17
17	37.0	0.3	2	C_6H_6	6.23
17	37.0	1.15	2	C_6H_6	5.95
18	29.68	0.05	2	Toluene	20.7
18	29.68	0.005	2	Toluene	18.9
18	29.68	0.01	2	Toluene	19.0
18	29.68	0.12	2	Toluene	17.7
18	29.68	0.025	1	Toluene	17.5
18	10.01	0.01	1	Toluene	1.32
18	10.01	0.002	2	Toluene	1.42
18	10.01	0.005	2	Toluene	1.36

1 - Iodometric

2 - Chemiluminescence decay

3 - NMR

aerated samples. For example, the half-life of a degassed solution containing 10^{-2} M 4 and 10^{-4} M DBA was only 20 minutes at 45°. Additionally, samples containing a high concentration (greater than ca. 0.1 M) of dioxetane showed non-linear first-order rate plots. An initial rate acceleration was observed before the rate of decomposition settled down to a "normal" value. Difficulties were also experienced in obtaining reproducible rates at high temperatures. For example; the rate of decomposition of 18 at 50.0° was too fast to be followed with any degree of accuracy by the method employed. These results are in keeping with those observed by Wilson; it appears that 1,2-dioxetane is decomposed by excited fluorescer (triplet) if oxygen (a very efficient triplet quencher) is absent. This induced decomposition of 1,2-dioxetanes is discussed more fully in Chapter IV.

Activation Parameters:

From the rate data of Table IX and also Table VI the energies of activation for the thermal decomposition of 1,2-dioxetanes were calculated using the eq. [37].[53]

$$[37] \qquad E_A = \frac{4.567\, T_2 T_1 (\text{Log } k_2 - \text{Log } k_1)}{T_2 - T_1}$$

Enthalpies and entropies of activation were calculated from eq. [38] and eq. [39] respectively.

$$[38] \qquad \Delta H^{*} = E_A - RT$$

$$[39] \qquad \frac{\Delta S^{*}}{4.576} = \text{Log } k_d - 10.753 - \text{Log } T + \frac{E_A}{4.576\ T}$$

Data calculated from these equations is presented in Table X together with data on the dimethyl-1,2-dioxetane 8.

The data calculated for the trimethyl-1,2-dioxetane 2 and tetramethyl-1,2-dioxetane 4, together with data obtained by Richardson[57] for the dimethyl compound 8, suggests that increasing substitution of the 1,2-dioxetane ring by methyl groups tends to stabilize the system. The experimental value for the energy of activation for the thermal decomposition of 4 (25.6 kcal mole^{-1}) is somewhat larger than the value of 24.7 kcal mole^{-1} calculated for this compound on the basis of a two-step biradical mechanism. Initially it was thought that 18 might prove to be quite a stable compound since thermal decomposition of this material yields a cyclodecane derivative. Formation of ten-membered rings is usually an unfavourable process since these materials are quite strained due to transannular CH interactions.[60]

The energy of activation for the decomposition of 18 can be calculated using the method of O'Neal and Richardson.[58] If it is assumed that the reaction takes place by a biradical mechanism in which fission of the peroxide linkage is the rate-determining step (eq. [35]), then E_A, the energy of activation for the process, is given by eq. [40].

TABLE X

Activation Parameters for the Thermal Decomposition of 1,2-Dioxetanes

Compound	E_A[a] (kcal mole^{-1}) Estimated	E_A[a] (kcal mole^{-1}) Experimental	Temp. (°C)	ΔH^* (kcal mole^{-1})	ΔS^* (e.u.)
8	22.9	22.9[b]			
2	–	23.5±0.5	40.0	23.0±0.5	-5±1
4	24.7[a]	25.6±0.3	40.0	25.0±0.3	-2±1
17	22.5	24.5±1.0	37.0	24.4±1.0	+1±2
18	22.2	23.0±0.6	29.7	22.4±0.6	-1.5±1

a - errors estimated by substituting extreme values of k_1 and k_2 into eq. [37].

b - reference 58.

$$[40] \qquad E_A = \Delta H_f^\circ\ (\text{biradical}) - \Delta H_f^\circ\ (\text{dioxetane}) + E_{-1}$$

E_{-1} is the activation energy for ring closure of the biradical. ΔH_f° (b) and ΔH_f° (d) may be calculated by group additivity methods.[61,62] Thus, ΔH_f° (d) for 18 consists of the group contribution shown below

$$8[C(H)_2(C)_2] + 2[O(O)(C)] + 2[C(O)(C)_3]$$

$$= 8(-4.95) + 2(-4.5) + 2(-6.6)$$

A correction must be made for the strain energy inherent in the four-membered ring. In their thermochemical calculations, Richardson and O'Neal[58] used a value of 26.0 kcal mole^{-1} for the strain energy of the 1,2-dioxetane ring; this value must be added to the heat of formation of the dioxetane.

The difference between the calculated heats of formation of cis- and trans-decalin is 1.6 kcal mole^{-1};[61] since 18 contains a cis-decalin system, this value must also be added to the heat of formation.

Each oxygen atom in the dioxetane ring is axial with respect to one of the cyclohexane rings of the decalin system and therefore has two gauche interactions with the ring. This leads to a total of four gauche (oxygen) interactions, each at 0.3 kcal mole^{-1}, which must also be added to the heat of formation of 18.

It seems unlikely that additional corrections must be made to take into account the rigidity of the propellane system. The ring correction given in tables for bicyclo[4.1.0]heptane is 28.9 kcal mole^{-1}, only 1.3 kcal greater than the strain energy of cyclopropane (27.6 kcal mole^{-1}).[61] The 1.3 kcal difference is easily accounted for by gauche interactions of the cyclopropane ring with the cyclohexane ring suggesting that the rigidity imposed in bicyclic systems does not significantly alter the strain energy. The heat of formation of 18 is given by:

$$\Delta H_f^\circ\ (18) = -61.8 + 26.0 - 1.2 + 1.6$$

$$= -33 \text{ kcal mole}^{-1}$$

Similarly, ΔH_f° (biradical) is made up of the group contribution shown below.

$$8[C(H)_2(C)_2] + 2[C(\dot{O})(C)_3]$$

The correction for a cis-decalin system must also be added to the heat of formation of the biradical, as must a correction for the four gauche oxygen interactions. A fifth interaction between the two oxygen atoms must also be added in the case of the biradical. Thus, the heat of formation of the biradical derived from 18 is:

$$\Delta H_f^\circ\ (b) = -22.4 + 1.6 + 1.5$$

$$= 19.3 \text{ kcal mole}^{-1}$$

Using a value of 8.5 kcal for E_{-1}, the energy of activation for the decomposition of 18 is:

[illegible] $-19.3 + 33 + 8.5$

[illegible] $22.2\ \mathrm{kcal\ mole}^{-1}$

Again, this value is a little lower than the experimental value of 23.0 kcal mole^{-1}. Similar calculations for the decomposition of 17 lead to a value of 23.2 kcal mole^{-1} for the energy of activation for this process. This value is again less than the experimental value of 24.5 kcal mole^{-1}.

EXPERIMENTAL

Solvents:

CCl_4 was dried over anhydrous potassium carbonate and redistilled. Benzene was purified by shaking with concentrated H_2SO_4 until the acid layer was colourless. The solvent was then washed several times with water and then with saturated sodium bicarbonate solution; after drying over $MgSO_4$ the benzene was distilled from sodium. Toluene (MCB spectro grade) was used as received.

Rates of Disappearance of Peroxide:

Method A: Solutions of 1,2-dioxetane in CCl_4, contained in a pear shaped flask fitted with a Leibig condenser, were immersed in a thermostatted bath and swirled to enable thermal equilibrium to be quickly reached. It was shown that the temperature of the solution reached bath temperature in less than eight minutes. Aliquots (1 ml) were withdrawn at suitable intervals for iodometric analysis.

Method B: Samples (ca. 2 ml) of solutions of dioxetane were transferred to glass ampoules by means of a syringe and the ampoules were sealed under vacuum. The samples were placed in a thermostatted bath and, at suitable intervals, ampoules were withdrawn from the bath and quenched at -78°. Before estimation the ampoules were placed in a bath at 25° for 30 minutes. Each ampoule was then broken open and an aliquot withdrawn for peroxide estimation as before.

Rates of Chemiluminescence Decay:

Chemiluminescence decay methods were carried out using a Turner Model 430 spectrofluorometer with the xenon lamp source turned off. The 60 nm emission monochromator bandwidth was selected to maximize sensitivity.

Method A: Samples were prepared by dissolving either purified or crude dioxetane in benzene (2 ml) saturated with DBA at room temperature (∿ 10^{-2} M). The samples were sealed into pyrex cuvettes which were placed in the heated cell compartment of the spectrofluorometer. Readings were taken at the emission maximum of DBA of 450 nm at suitable intervals. The cell compartment of the instrument was heated by water circulated from a thermostatted bath. The cell temperature was checked before and after each kinetic run was carried out.

Method B: The cell compartment supplied with the instrument had a very inefficient temperature control system. An improved system was designed consisting of a pyrex cell, path length 10 cm, with a fused outer jacket for temperature control. One end of the cell was silvered and sample was introduced through a wide tube entering the middle of the cell. The 10 ml capacity of the cell greatly enhanced the light emission and enabled studies to be made on dilute solutions of dioxetanes.

Samples were prepared by adding solutions of dioxetanes (in toluene) (1 ml) to a solution of DBA in toluene (10^{-2} M). Toluene was used as solvent to minimize evaporation losses. The mixture was mixed and poured into the modified cell compartment. Readings were taken as before. In both method A and method B, the cell temperature was measured by direct insertion of a thermometer into the liquid filled cell or cuvette.

Rate of Disappearance of 17 by NMR Spectroscopy:

A solution of 17 (0.1 g, recrystallized) in CCl_4 contained in a sealed NMR tube was placed in the heated probe of a Varian HA 100 instrument. The concentration of 17 present at any time was monitored by comparing the height of the integration signal for the methyl protons of 17 to the total integral, since this did not change during the experiment.

CHAPTER IV

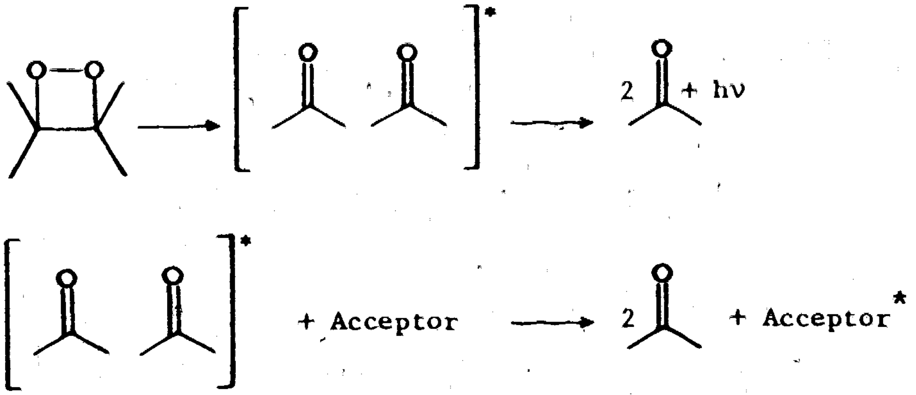
FORMATION OF ELECTRONICALLY EXCITED STATES FROM CLEAVAGE OF 1,2-DIOXETANES

INTRODUCTION

The observation of chemiluminescence during thermal decomposition of 1,2-dioxetanes indicates that at least some of the products generated are formed in an electronically excited state.

When dioxetanes are decomposed thermally in the presence of fluorescer, a more intense, different coloured luminescence matching the fluorescence spectrum of the fluorescer is observed.[7] This enhanced luminescence in the presence of fluorescer molecules such as biacetyl, DBA, diphenylanthracene (DPA) and rubrene demonstrates that energy released in the cleavage of 1,2-dioxetanes can be transferred to suitable acceptor molecules present in the system. A possible mode of energy transfer is shown in Scheme VI.

Scheme VI



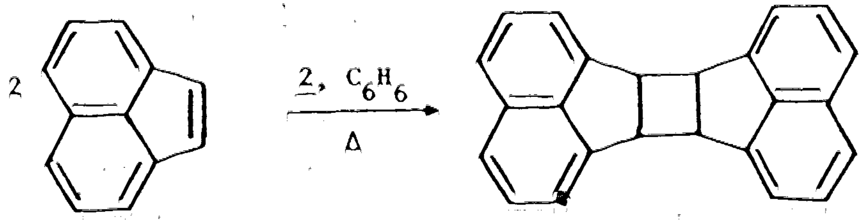
$$\text{Acceptor}^{*} \longrightarrow \text{Acceptor} + h\nu$$

$$\text{Acceptor}^{*} \longrightarrow \text{Acceptor}$$

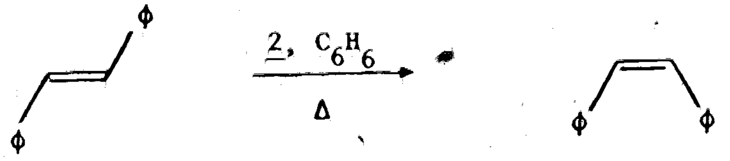
This scheme, as written, implies formation of an eximer on decomposition of the 1,2-dioxetane 4. Formation of this eximer may or may not occur, however, the excited state generated in the decomposition can itself emit light or transfer its energy to an acceptor molecule. The excited acceptor may then, depending on the structure, emit light or undergo a photochemical transformation.

This latter phenomenon of "Photochemistry without Light" was first investigated by White[63] who utilized the energy available from the decomposition of 2 to initiate several photochemical reactions, eq. [41] to eq. [43].

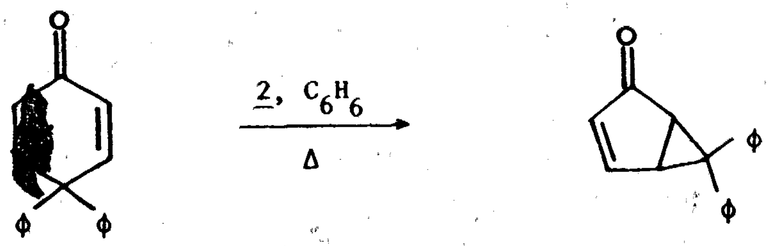
[41]



[42]

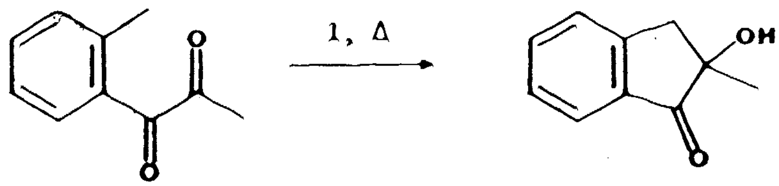


[43]

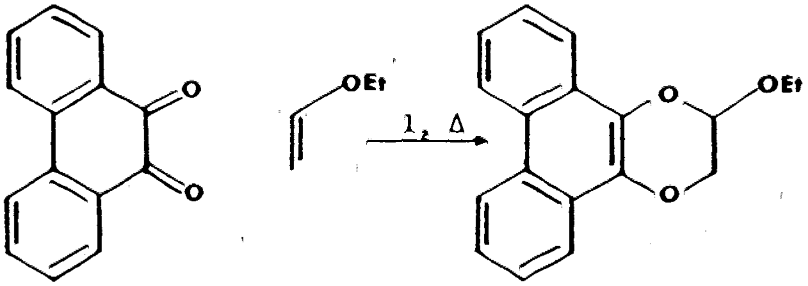


Ullman[64] has also carried out similar transformations using the dioxetane-dione 1, eq. [44] and eq. [45].

[44]



[45]



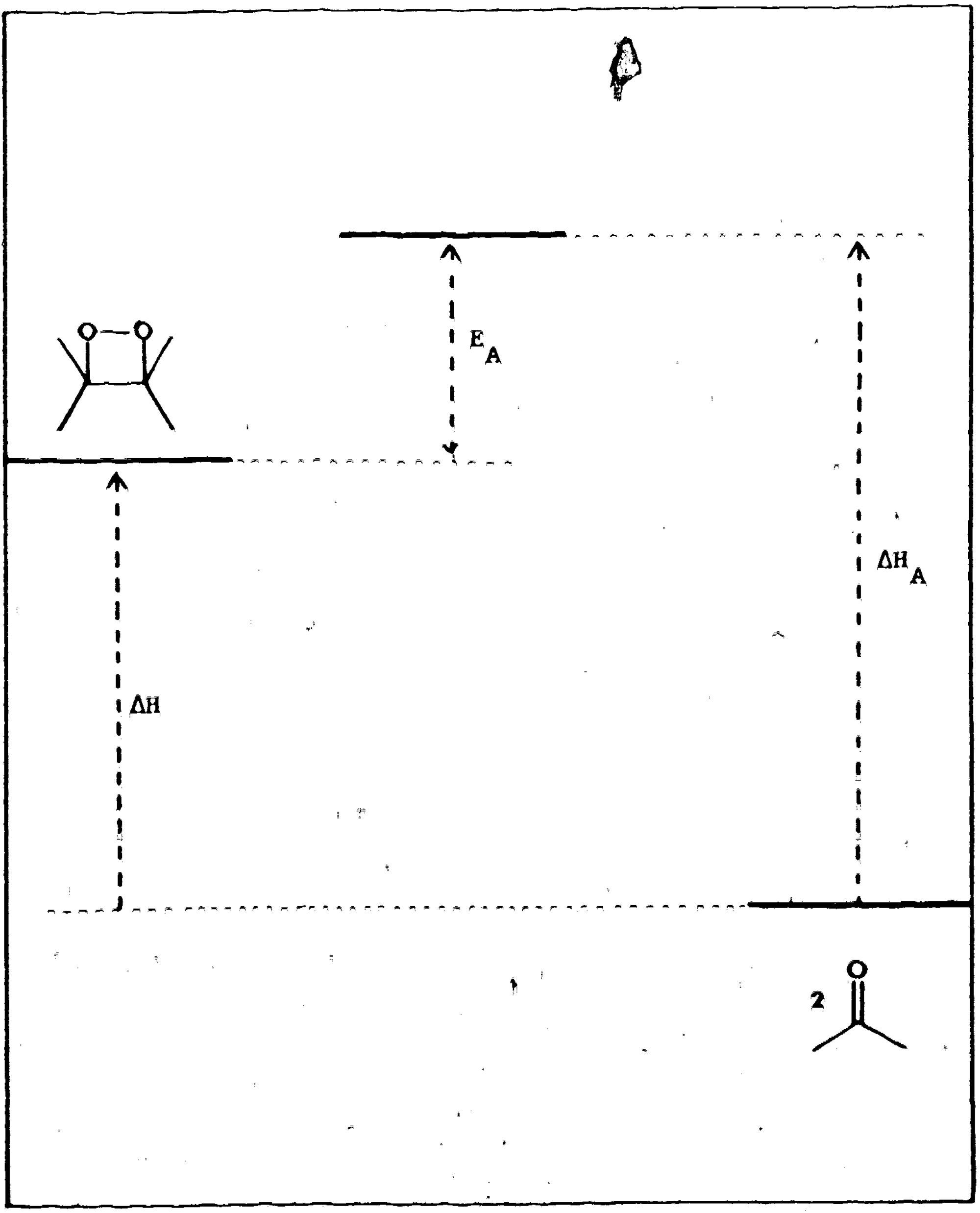
Yields of photoproducts from all these reactions were very low, about 5% at best based on the initial quantities of 1,2-dioxetane.

Figure 7 shows, schematically, the energy available for the decomposition of 1,2-dioxetanes. The energy released on decomposition of trimethyl-1,2-dioxetane 2 (ΔH_A) has been calculated from eq. [46].[7]

[46] $$\Delta H_A = \Delta H_f^\circ \text{ (products)} - \Delta H_f^\circ \text{ (reactant)} - E_A$$

ΔH_f° for the dioxetane was calculated from Benson's group additivity method; such calculations indicated that the transition state for

Figure 7. Energy Available (ΔH_A) from Decomposition of 1,2-Dioxetanes



decomposition of dioxetane lies 88 kcal above the ground state of products. The first excited singlet state of acetone is estimated at ∿ 84 kcal above the ground state;[65] thus, sufficient energy is released on decomposition of 1,2-dioxetanes to generate one excited acetone molecule per molecule of dioxetane decomposed.

A problem which has received much recent attention is the question of the efficiency at which excited states are generated. In other words, does each dioxetane molecule yield one excited state upon decomposition? The indications are that this is not the case; the low yields of photoproducts obtained in eq. [41] to eq. [45], imply that the energy available for cleavage of 1,2-dioxetanes is very inefficiently utilized.

Estimates of the efficiency at which excited states are generated from thermal cleavage of various 1,2-dioxetanes vary and some reports are apparently contradictory. White[63] estimated a yield of 4% of excited states capable of sensitizing the isomerization of trans-stilbene, eq. [42], from decomposition of 2. Similarly for the photoaddition of ethyl vinyl ether to phenanthraquinone, eq. [45], Ullman[64] calculated a chemical sensitization efficiency of 4% for the dioxetane dione 1.

However, Wilson[14] suggested that decomposition of cis-diethoxy-1,2-dioxetane 10 gave rise to excited formate in quantitative yield. This estimate was made on the basis of light emission measurements made when the dioxetane was decomposed in the presence of fluorescer molecules with known fluorescence efficiencies (DBA and DPA). White[66] also made light emission measurements for trimethyl-1,2-dioxetane 2 in the presence of an europium complex fluorescer. Under these conditions, he estimated a 14% yield of excited states from the decomposition of this compound. He also claimed that light emission from 10 under the same conditions was less than 1% of that from the trimethyl compound.

These varying estimates of excited state production suggest the interesting possibility that perhaps the structure of 1,2-dioxetanes can influence the efficiency at which excited states are generated.

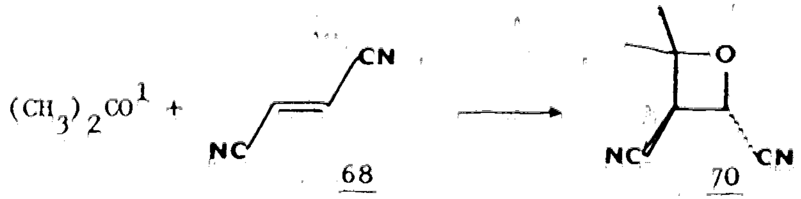
The photoproducts observed in eq. [41] and [43] are characteristic of triplet photochemistry, implying that energy transfer in these systems occurs from triplet excited acetone. Additionally, the chemiluminescence yields of both 8 and 10 are markedly greater with 9,10-dibromoanthracene (DBA) than with 9,10-diphenylanthracene (DPA), in spite of the much higher fluorescence efficiency of the latter.[14] This also implies involvement of triplet excited states, whose energy DBA is more capable of converting into singlet energy than is DPA, because of the increased spin-orbit coupling and mixing of singlet and triplet states due to the heavy atoms.[67]

Triplet states were at first assumed to arise via intersystems crossing from initially formed singlet states. However, Wilson could find no evidence for formation of singlet formate from 10.

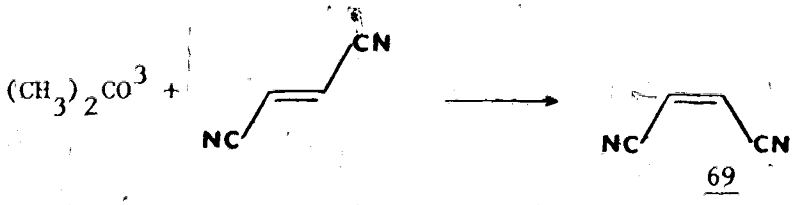
Direct evidence for the formation of singlet states is, of course, observable in the luminescence spectrum of 2 which matches the fluorescence spectrum of acetone. Also, light emission from firefly luciferin and from lucigen (see Chapter 1) occur from the singlet state of the products formed. Light emission from the luciferin/luciferase system is very efficient, *ca.* 90%, making this probably the most efficient chemiluminescent system.

Turro[68] devised a very elegant method for the estimation of both singlet and triplet acetone formed by decomposition of tetramethyl-1,2-dioxetane 4. *trans*-Dicyanoethylene 68 yields completely different products with singlet and triplet acetone, namely the oxetane 70 and *cis*-dicyanoethylene 69, respectively, eq. [47] and eq. [48].

[47]



[48]



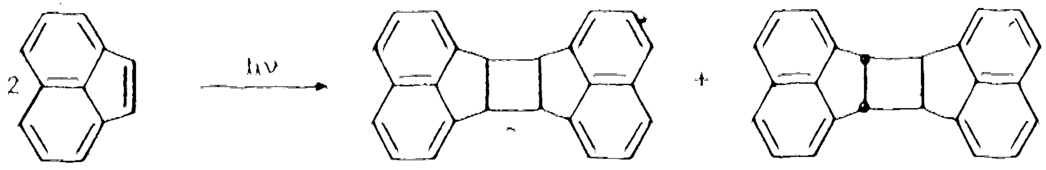
Knowledge of the limiting quantum yields for these reactions allowed measurement of the limiting yields of singlet and triplet acetone, by extrapolation of a plot of the yields of 69 and 70 (formed in the presence of decomposing 4) to infinite concentration of 68. At this point all the singlet acetone could be trapped before intersystems crossing occurred. From these experiments the yield of singlet acetone was estimated at 0.3%, while that of triplet acetone was ~ 50%.

It seems possible, then, that structural effects influence not only the yield, but also the nature of the excited states formed in the decomposition of 1,2-dioxetanes.

RESULTS AND DISCUSSION

Photolysis of acenaphthylene 71 gives rise to a mixture of *cis*- and *trans*-cyclobutane derivative dimers, eq. [49].

[49]



71 72 73

The structures of these dimers are well established,^{69} and there is considerable evidence that, whilst acenaphthylene in the singlet excited state gives rise almost exclusively to the *cis*-isomer 72, triplet excited acenaphthylene leads to a mixture of dimers containing 70 - 85% of the *trans*-isomer 73.^{70,71} The exact composition of the mixture depends upon the solvent used. The products of the reaction possess absorption maxima in the ultraviolet at 219 and 225 nm, respectively; hence, the composition of mixtures of 72 and 73 is easily determined by UV spectroscopy.

Thus, examination of the yields and composition of products formed by decomposition of 1,2-dioxetanes in the presence of suitable concentrations of 71, provides an indication of the relative yields and nature of excited states generated in the thermolysis of these materials.

It was proposed to carry out thermolysis of 1,2-dioxetanes 4, 17 and 18 in the presence of acenaphthylene to determine if any differences existed in the yields and nature of the excited states formed.

Acenaphthylene was purified according to the method of Schenck,[71] by recrystallization of the picrate derivative. Pure samples of cis- and trans-dimers were also prepared in order to check the spectral characteristics of these materials. The preparation and purification of these materials is described in the experimental section.

Benzene solutions containing dioxetane and acenaphthylene, contained in glass ampoules, were degassed by several freeze-thaw cycles at 5μ and the ampoules were sealed. Thermolysis of 1,2-dioxetanes was achieved by immersing the ampoules in a water bath at 95 - 100° for 15 minutes. A bright yellow emission of brief duration (∿ 5 - 10 s) was observed during this thermolysis from solutions containing high concentrations of 1,2-dioxetanes (∿ 1.0 M). The source of this emission is unclear since acenaphthylene is reported to be nonfluorescent.[70] Perhaps the emission occurs from an eximer of acenaphthylene. Eximer emission has been observed from solutions containing high concentrations of aromatic molecules; usually such emissions are observed at longer wavelengths than the normal fluorescence spectrum.[73] This emission was not observed from solutions containing concentrations of 1,2-dioxetane of 0.1 M or less.

The cyclobutane derivative dimers 72 and 73 were separated from starting material by preparative TLC on silica gel using cyclohexane as solvent. The yields of products and the composition of the dimer mixtures so obtained were determined by UV spectroscopy according to the method of Cowan and Drisko.[70] The results of these experiments are presented in Table XI.

To check the efficiency of the product isolation procedure employed in these experiments, a solution containing weighed quantities of the cis- and trans-acenaphthylene dimers (cis:trans ∿ 0.3) was analyzed by UV spectroscopy and then subjected to the same preparative TLC and extraction procedure. The solution so obtained showed the same spectral distribution as that of the starting solution although the optical density of recovered material was somewhat diminished, indicating that the cis-trans ratio of products had not changed during the procedure but ∿ 5% of material had been lost. The product yields quoted in Table XI are corrected for this small loss of material.

Dimer-containing solutions, as extracted from the preparative TLC plates were invariably reddish-brown coloured indicating that some impurities (possibly oxidation products of acenathhylene) were present. To ensure that these materials were not interfering with the UV analysis, control experiments were carried out by heating solutions containing only acenaphthylene under the same conditions of the dioxetane thermolysis experiments. The samples were then chromatogrammed on silica gel plates as before. Small quantities of brown material, having the same R_f value as that of the products 72 and 73, were extracted from the plate after elution with cyclohexane; this material showed a small absorption between 219 and 225 nm, having an equal optical density at both points. The effect of such

TABLE XI

Sensitized Dimerization of Acenaphthylene in Benzene at ~ 98°

Dioxetane	Concentration (M)	$\Phi_{App} \times 10^2$	cis:trans ratio
4	0.1	2.4	0.05
4	0.1	2.3	0.15
4	1.0	2.9	0.02
4	1.0	3.1	0.08
17	1.0	2.9	0.07
17	0.1	2.5	0.12
18	1.0	1.8	0.12
18	0.1	1.4	0.08

Acenaphthylene concentration = 1.0 M.

Φ_{App} = Moles of product per mole of dioxetane decomposed.

impurities then, is to raise the apparent cis:trans ratio of the products obtained in the dioxetane thermolysis experiments.

It was unnecessary to apply a correction for these impurities in the case of solutions containing appreciable quantities of dimers, such as were obtained from the thermolysis of solutions 1.0 M in dioxetane. A small correction was applied, however, to the yield and cis:trans ratio of products from experiments using 0.1 M dioxetane.

The optical density of solutions derived from thermolysis of solutions 10^{-2} M in dioxetane, however, was of the same order as the blank, making yield determinations impossible.

The apparent quantum yields Φ_{App} (moles of product per mole of dioxetane decomposed) of products derived from the thermolysis of dioxetanes 4, 17 and 18 are all quite low, between $1 - 3 \times 10^{-2}$. 18 however, appears to give rise to consistently lower yields of photoproducts than do the other 1,2-dioxetanes studied.

The ratio of products 72 and 73 formed during the photolysis of acenaphthylene is highly solvent dependent. From the triplet sensitized photolysis of acenaphthylene in benzene solution, Schenck isolated a mixture containing 85% of the trans-dimer, 73 (cis:trans ratio, 0.17).[71] Analysis of the products isolated from the dioxetane sensitized dimerization of acenaphthylene (Table XI) indicated that, in each case, the mixture of dimers isolated contained > 85% of the trans-isomer, 73. This suggests that the dimerization proceeds via transfer of triplet energy from excited carbonyl fragments. White reached a similar conclusion based on experiments in which he utilized the energy available from the thermolysis of trimethyl-1,2-dioxetane to sensitize the dimerization of acenaphthylene.[63]

An outline of the reactions leading to the dimerization of acenaphthylene in these experiments is shown in Scheme VII.

Scheme VII

$$D \longrightarrow K^* \qquad (i)$$

$$K^* + A \longrightarrow A^* + K \qquad (ii)$$

$$A^* + A \longrightarrow AA \qquad (iii)$$

$$A^* \longrightarrow A \qquad (iv)$$

The multiplicity of the excited ketone (K^*) generated by decomposition of dioxetane (D) is not specified. A and AA represent acenaphthylene and acenaphthylene dimer, respectively. On the basis of a similar scheme, White[63] formulated an expression for the apparent quantum yield Φ_{App}, for the dioxetane sensitized isomerization of trans-stilbene, eq. [50],

$$[50] \qquad \Phi_{App} = \Phi_{D\to K^*}\, \Phi_{ET}\, \Phi_{Photo}$$

where $\Phi_{D\to K^*}$ is the efficiency at which dioxetane cleaves to yield excited states, Φ_{ET} the quantum yield for the energy transfer step (ii) and Φ_{Photo} is the photochemical yield for the sensitized photolysis of A. It is not possible to obtain a value for $\Phi_{D\to K^*}$ from the experiments with acenaphthylene, since Φ_{Photo} for acenaphthylene is not known.

White estimated a value of 0.04 for $\Phi_{D\to K^*}$ for the sensitized isomerization of trans-stilbene; it is possible that this low value indicates that other reactions are also occurring, Scheme VIII.

Scheme VIII

$$D + A^* \longrightarrow K^* + K + A \qquad (v)$$

$$K^* + D \longrightarrow K^* + 2K \qquad (vi)$$

$$A + K^* \longrightarrow \text{oxetane} \qquad (vii)$$

Reactions (v) and (vi) are photoinduced decompositions of the dioxetane and tend to reduce the concentration of dioxetane without increasing the number of excited states formed.

It was found (Chapter III) that the rates of chemiluminescence decay of degassed solutions of dioxetanes containing DBA showed marked acceleration over those of aerated samples. This effect had previously been noted by Wilson, who also observed that the chemiluminescence yields from degassed samples were less than those of aerated samples.[14] These observations were explained by assuming that triplet DBA, excited via energy transfer from triplet carbonyl, sensitizes the decomposition of dioxetane, (v) in Scheme VIII. In aerated samples, however, triplet DBA is efficiently quenched by dissolved oxygen.

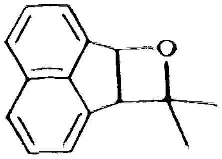
Reaction (vi) can also account for the initial rate accelerations observed for concentrated solutions of dioxetanes. Induced decomposition of dioxetane by excited carbonyl fragments is quite likely when high concentrations of dioxetane are present.

Clearly, then, for maximum chemical sensitization efficiencies, low concentrations of dioxetane and high concentrations of acceptor molecules are required. Unfortunately, it was found that dioxetane concentrations of less than 0.1 M were impractical in these experiments with acenaphthylene as substrate. Small amounts of impurities formed during the isolation of products tended to mask the spectrum of the dimers formed when only small amounts of dimers were present.

When olefins are used as acceptor molecules another reaction, the Paterno-Büchi reaction,[65] is also possible (vii) Scheme VIII. This reaction, as it is normally carried out, is probably not feasible in the case of acenaphthylene since it would be impossible to photolytically excite most ketones in the presence of acenaphthylene. Ketones are excited at ∿ 310 nm and acenaphthylene would absorb very strongly at this wavelength.

Clearly, though, excited carbonyl fragments generated in situ by decomposition of 1,2-dioxetanes are capable of undergoing photocyclization additions to olefins. Turro has, in fact, demonstrated this reaction.[68]

Rates of intersystems crossing are relatively slow for aliphatic ketones so that these molecules can undergo reactions from both singlet and triplet excited states.[74] In general, oxetane formation can arise from the addition of either singlet or triplet excited carbonyl compounds with olefins. However, in cases where the triplet energy of the carbonyl compound is higher than that of the olefins (and this is often the case for simple aliphatic ketones), oxetane formation is inefficient compared to energy transfer. For some such cases low yields of oxetanes are still observed, and these products are believed to arise from addition of carbonyl in the singlet excited state.[75] Any oxetane products arising from the thermolysis of 1,2-dioxetanes in the presence of acenaphthylene, then, would almost certainly be formed by addition of ketone in the excited singlet state. A search was made for products arising from Paterno-Büchi reactions such as the oxetane 74.



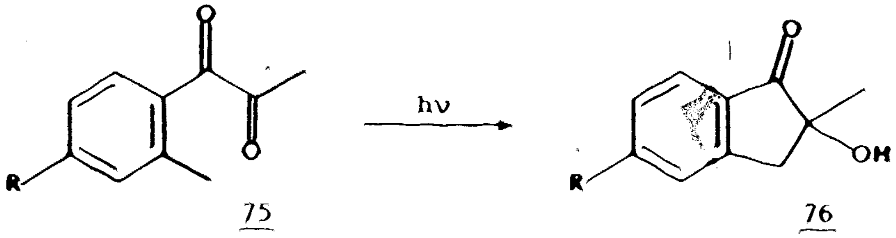
74

The remaining part of the preparative TLC plate, after separation of the portion containing the dimers 72 and 73, was extracted with benzene and the concentrated extract analyzed by VPC. Carbowax 20M and SE30 columns were used at various conditions for the analysis but only acenaphthylene could be detected.

Photocyclization of 1-(2,4-Dimethylphenyl)propane-1,2-dione 75b:

The triplet sensitized reaction of 1-(o-tolyl)-propane-1,2-dione 75a is reported to proceed with a quantum yield of 0.8,[76] eq. [51]. The high quantum yield for this reaction makes 75a an attractive choice of substrate for chemical sensitization reactions. It was decided to carry out chemical sensitization experiments with this material to check the results of the experiments with acenaphthylene.

[51]

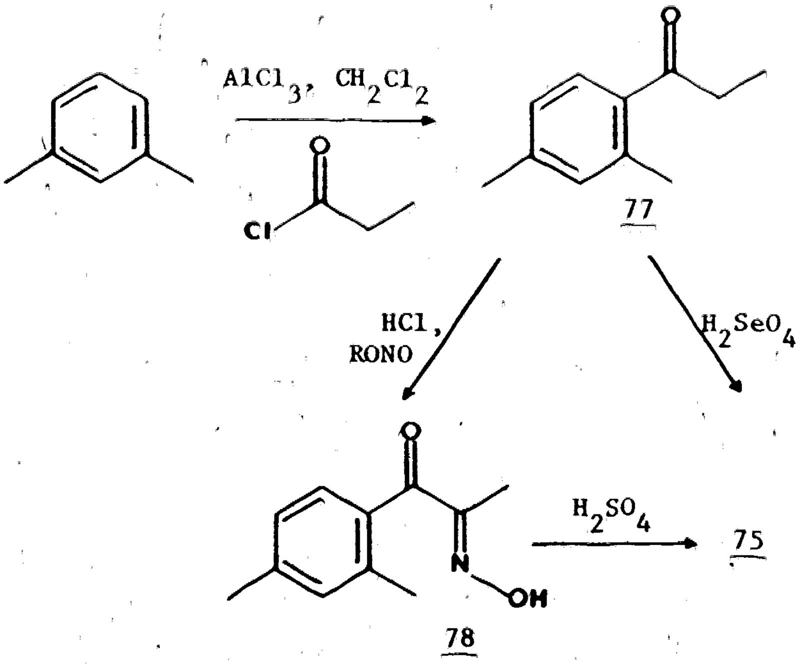


a, R = H

b, R = CH_3

Since methods for the synthesis of 75a seemed somewhat tedious,[64,77] it was decided to prepare 75b instead since a comparatively simple route to this compound could readily be envisaged, Scheme IX.

Scheme IX



The presence of a p-methyl group should not affect the photochemical properties of 75.

The selenium dioxide oxidation[78] of dimethylpropiophenone proved difficult; although some of the desired product was found (as observed by NMR spectroscopy and by the bright yellow colour), large amounts of starting material remained in the mixture and these could not be separated by distillation.

An alternative route, via the α-oximidoketone 78, proved more successful. Although subsequent hydrolysis of this oxime proceeded in poor yield, the product could easily be separated from starting material by filtration. The product was purified by vacuum distillation.

An alternative procedure for the hydrolysis of oximes using lead tetraacetate[79] was tried, but a complex series of reactions occurred and no identifiable products were obtained.

Best yields of the dione 75b were obtained when the hydrolysis of the oxime was carried out in the presence of sodium bisulphite.[80]

Chemical sensitization experiments using 75b as a substrate were carried out using the same techniques employed in the acenaphthylene experiments. Yields of the cyclized product 76b were estimated by VPC analysis on FFAP at 190°, using anisyl alcohol as an internal standard. Relative peak areas for product and standard were measured using a planimeter. Apparent quantum yields of photoproducts derived from these experiments are shown in Table XII.

Using eq. [50], and assuming that Φ_{Photo} for this system is

TABLE XII

Sensitized Photocyclization of 75b in Benzene Solution

Dioxetane	Concentration (M)	Temperature (°C)	Acceptor Concentration (M)	$\Phi_{App} \times 10^2$
4	1.7	∿ 100	0.7	6.6
17	1.35	∿ 95	0.7	1.1
18	0.9	∿ 60	0.7	0.4
4	1.0	∿ 100	1.0	5.1
18	1.0	∿ 100	1.0	0.9

Φ_{App} = Moles of product per mole of dioxetane decomposed.

0.8; the value of 6.6×10^{-2} for tetramethyl-1,2-dioxetane 4 corresponds to a value of 0.08 for $\Phi_{D\rightarrow K^*}$. (Under the conditions of the experiment, $\Phi_{ET} = 1$.) This value, while still low, is somewhat higher than values obtained by White[63] and Ullman[64] from similar experiments. Again, as observed in the acenaphthylene experiments, chemical sensitization using 18 seems to lead to lower apparent quantum yields of product.

Thermolysis of cis-1,6-Dimethyl-7,8-dioxabicyclo[4.2.0]octane 17:

The yields of photoproducts obtained in earlier experiments were all fairly low, possibly because quantum yields for product formation in these reactions depended on several steps, eq. [50].

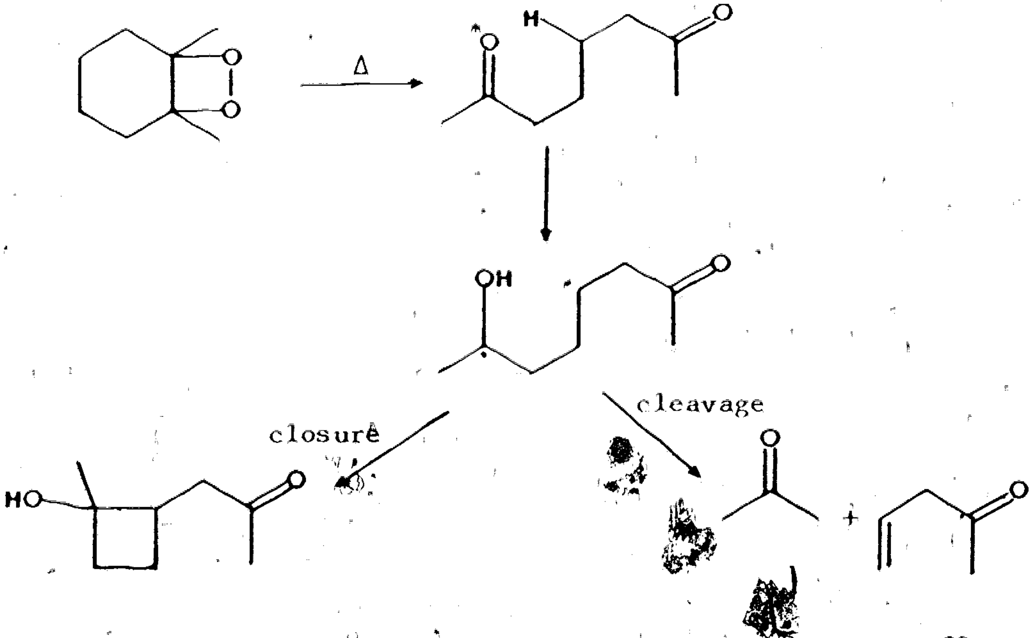
A more direct way of measuring yields of excited states derived from thermolysis of 1,2-dioxetanes would be to design a system in which the excited carbonyl fragments generated on thermolysis could themselves undergo photochemical reaction.

Excited octane-2,7-dione 22 formed by decomposition of 17 is capable of undergoing Norrish type II cleavage[81] to yield acetone and the unsaturated ketone 80, Scheme X.

This type of cleavage is observed in the mass spectra of 22; major fragments at 84 ($P-(CH_3)_2CO$) and 58 ($P-CH_2{:}CHCH_2COCH_3$). However, quantum yields for this type of cleavage in aliphatic systems are usually quite small (~ 0.1).[82] Nevertheless, it was felt that even trace amounts of acetone formed would be detectable by VPC.

Pure 17 for thermolysis experiments was purified by two recrystallizations from iso-pentane followed by sublimation; solutions of this material at concentrations varying from 1.0 M to 10^{-2} M in various solvents were degassed and sealed into glass ampoules. Thermolysis experiments were carried out by immersing the ampoules in boiling water for ∿ 10 minutes, after which time the ampoules were cooled, broken open, and the contents analyzed by VPC using FFAP and dinonyl phthalate columns.

Scheme X



80

The initial choice of solvent for the thermolysis, carbon tetrachloride, proved to be an unfortunate one. Degassed solutions of 17 in CCl_4 darkened appreciably on heating at 100° and, on standing, deposited oily droplets. The major product from the reaction, isolated by preparative TLC on silica gel, was found to be 1-acetyl-2-methylcyclopentene 79. This material was identified by its spectral properties and by comparison with authentic material.

This same product also arose from the direct photolysis of octane-2,7-dione in CCl_4 solution; it almost certainly arises from an acid catalyzed condensation of 22 brought about by traces of HCl formed by photolysis of solvent.

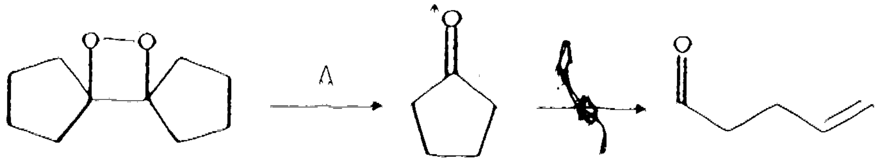
Numerous solutions of 17 in various hydrocarbon solvents were prepared and subjected to thermolysis under the usual conditions; however, careful analysis of the solutions after reaction failed to reveal the presence of acetone. VPC traces of the solutions sometimes showed two to three small peaks but no peaks larger than 1/3000 the area of the peak due to 22 were observed.

Samples of purified 22 were subjected to thermolysis experiments under the same conditions as were used for the thermolysis of 17. VPC analysis of these solutions usually showed small peaks at retention imes similar to those observed in solutions from the thermolysis of 7 indicating that, probably, these peaks were due to impurities.

Direct photolysis experiments were also carried out on 22 by hotolyzing solutions of the diketone in cyclohexane for varying eriods of time. VPC analysis of the resulting mixtures indicated he presence of complex mixtures; small amounts of acetone could, owever, be detected.

It would appear then, that Norrish type II cleavage is not a major photochemical reaction of octane-2,7-dione. Since little is nown about the photochemistry of 22 perhaps dioxetane 82 would be a etter choice for the purposes of observing direct photochemistry from excited carbonyl fragments, eq. [52].

[52]



82 81

The quantum yield for formation of 4-pentenal 81 from photolysis of cyclopentanone at 313 nm is 0.37.[83] Turro has utilized this system to carry out actinometry experiments.[84]

Effects of Fluorescer Concentration on Chemiluminescence Quantum Yields:

Reactions leading to fluorescence from a solution containing dioxetane and fluorescer are represented by Scheme XI.

Scheme XI

$$D \xrightarrow{k_1} K^* + K \qquad (i)$$

$$K^* + A \xrightarrow{k_2} A^* + K \qquad (ii)$$

$$K^* \xrightarrow{k_3} K \qquad (iii)$$

$$A^* \xrightarrow{k_4} A \qquad (iv)$$

$$A^* \xrightarrow{k_5} A + h\nu \qquad (v) \quad \text{Chemiluminescence}$$

A mechanism such as Scheme XI leads to the expression outlined in eq. [53],[14]

$$[53] \qquad \frac{1}{\Phi_{ch}} = \frac{1}{\Phi_f} + \frac{k_3}{k_2\Phi_f}\,\frac{1}{[A]}$$

where Φ_f is the fluorescence efficiency of A, and Φ_{ch} is the chemiluminescence quantum yield. Since the chemiluminescence intensity R is proportional to the quantum yield, a plot of 1/R *versus* the reciprocal fluorescer concentration should be a straight line.

The chemiluminescence intensity was measured from solutions of dioxetane containing various concentrations of fluorescer. Tables XIII and XIV show the results of light emission measurements from solutions of tetramethyl-1,2-dioxetane *4* in the presence of DPA and DBA, respectively.

Samples for these studies were prepared using techniques previously described in the kinetics section (Chapter III). Cell temperatures were adjusted so that the rate of decomposition of dioxetane was very slow and an essentially constant flux of photons was obtained. Figure 8 is a plot of the data obtained with tetramethyl-1,2-dioxetane *4* in the presence of DBA and DPA.

The plot of $1/R_{rel}$ *versus* $1/[A]$ for DBA is linear in the range 10^{-4} to 10^{-2} *M* fluorescer indicating that the fluorescence of DBA occurs *via* excitation by one species of excited state.[14] The markedly enhanced light intensity from solutions containing DBA over those containing DPA is indicative that excitation is occurring *via* energy transfer from triplet carbonyl.[14,67]

The slope of the DPA plot is approximately the same as that of DBA in the range 10^{-4} - 2×10^{-4} *M* fluorescer indicating that, in

TABLE XIII

Chemiluminescence Yields from Tetramethyl-1,2-dioxetane 4

Added Fluorescer: DPA　　　**Dioxetane Concentration:** 0.011 M

Temperature: 45°　　　**Solvent:** Toluene

Fluorescer Concentration [A] (M)	1/[A]	Reading (R)	1/R
10^{-4}	10,000	0.45	2.2
2×10^{-4}	5,000	0.5	2.0
10^{-3}	1,000	1.1	0.91
2×10^{-3}	500	2.65	0.38
5×10^{-3}	200	3.8	0.26
8×10^{-3}	125	5.85	0.17
10^{-2}	100	6.75	0.15
2×10^{-2}	50	9.1	0.11
6×10^{-2}	17	5.5	0.20
0.1	10	2.5	0.4

TABLE XIV

Chemiluminescence Yields from Tetramethyl-1,2-dioxetane 4

Added Fluorescer: DBA | Dioxetane Concentration: 0.011 M

Temperature: 45° | Solvent: Toluene

Fluorescer Concentration [A] (M)	$\frac{1}{[A]}$	Reading (R)	1/R
10^{-4}	10,000	8.3	0.12
10^{-3}	1,000	60	0.017
2×10^{-3}	500	94.5	0.011
5×10^{-3}	200	130	0.0077
8×10^{-3}	125	137	0.0073
10^{-2}	100	138	0.00725
5×10^{-2}	20	104	0.014
10^{-4a}	10,000	8.5	0.12
10^{-3a}	1,000	78	0.013

a - sample degassed

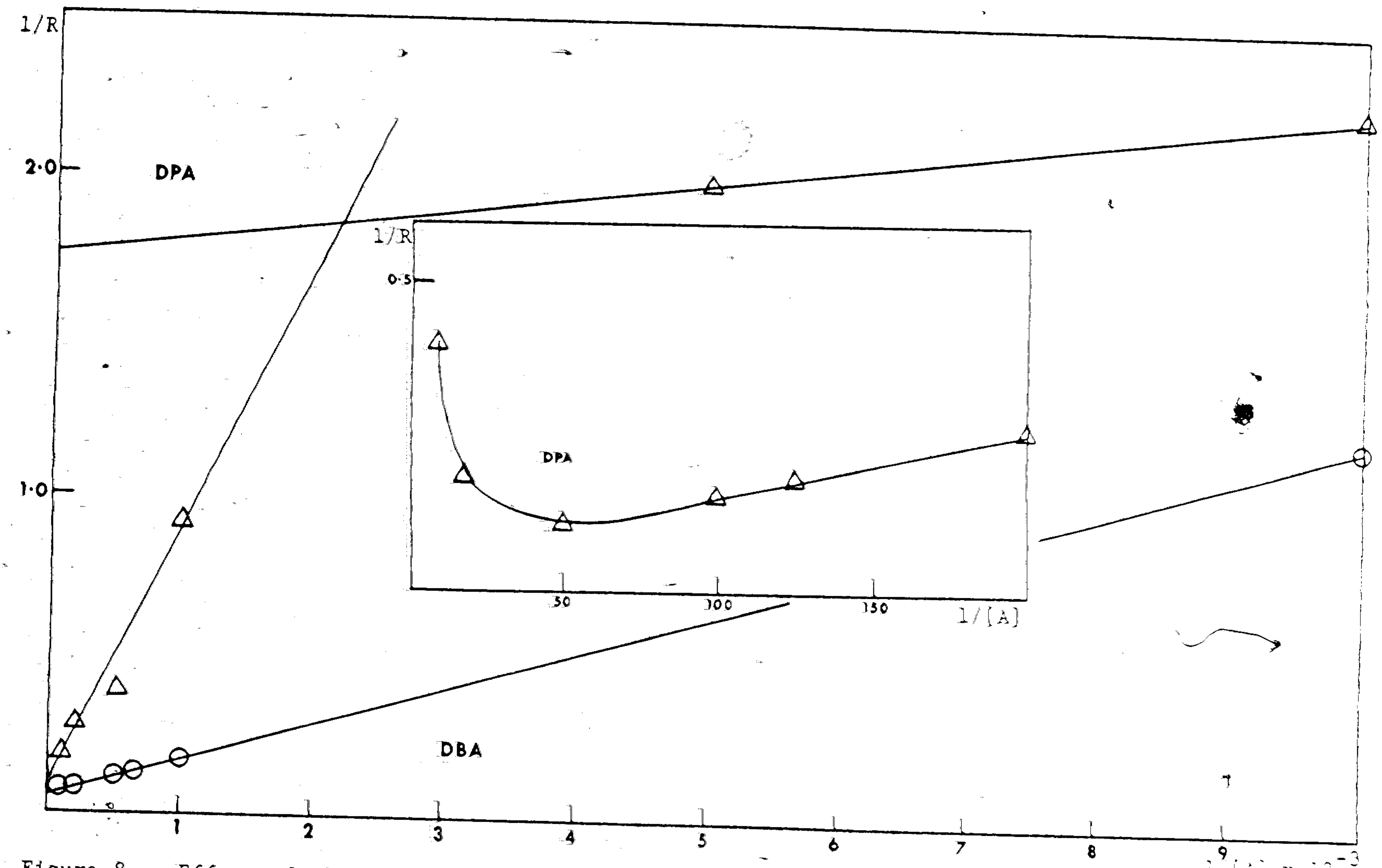


Figure 8. Effect of Fluorescer Concentration [A] on the Relative Intensity of Chemiluminescence from 4 (Dioxetane Concentration, 10^{-2} M)

this concentration range, excitation is occurring via energy transfer from the same excited species, namely triplet carbonyl.[14]

However, at higher concentrations of DPA, > 10^{-3} M, a change in the slope is observed implying that a different species of excited state, singlet carbonyl, is being intercepted. Since DPA is very inefficient at converting triplet energy to singlet, at these concentrations the majority of the fluorescence from this material occurs via excitation by singlet carbonyl. These results contrast with those of Wilson[14] who observed no change in slope of a similar light intensity plot from solutions containing cis-diethoxy-1,2-dioxetane 10 in the presence of DPA. It was inferred that, even at a fluorescer concentration of 0.1 M, excitation of DPA occurred solely via energy transfer from triplet formate.

These results are, however, open to some question since concentration quenching (self quenching) severely reduces the light intensity from solutions containing high (> 10^{-2} M) concentrations of DBA or DPA (see inset in Figure 8). This effect can be observed visually; solutions of DPA at concentrations below 10^{-2} M appear bluish and have a definite fluorescent appearance. At higher concentrations the solutions appear yellow and lack this fluorescent appearance.

Thus, readings taken by Wilson at 0.1 M fluorescer concentration have little significance. Additionally, no readings were taken at low concentrations of DPA. Hence, there is insufficient data to infer that the plot of reciprocal light intensity against reciprocal fluorescer concentration shows no change in slope.

Quantum Yields:

Estimates of the chemiluminescence quantum yields from solutions of 1,2-dioxetanes were made by comparing the intensity of emitted light, R, with that of a luminol light standard. I, the number of photons emitted per ml per second was calculated from eq. [54],[85]

$$[54] \qquad I = \frac{RL}{\int_0^\infty R'dt}$$

where R is the spectrofluorometer reading for the dioxetane sample, R' the reading for the light standard, and L the number of photons emitted per ml from the light standard. One ml of luminol solution having an optical density of 1.0 at the absorption maximum of 360 nm is reported to emit 9.75 ± 0.7 x 10^{14} photons.[86]

Figure 9 shows a typical plot of light intensity versus time for a 10 ml sample of the light standard, using the same cell as was used for the chemiluminescence measurements with 1,2-dioxetanes. The value of $\int_0^\infty R'dt$ (the average of four such plots) was 1240 (arbitrary units).

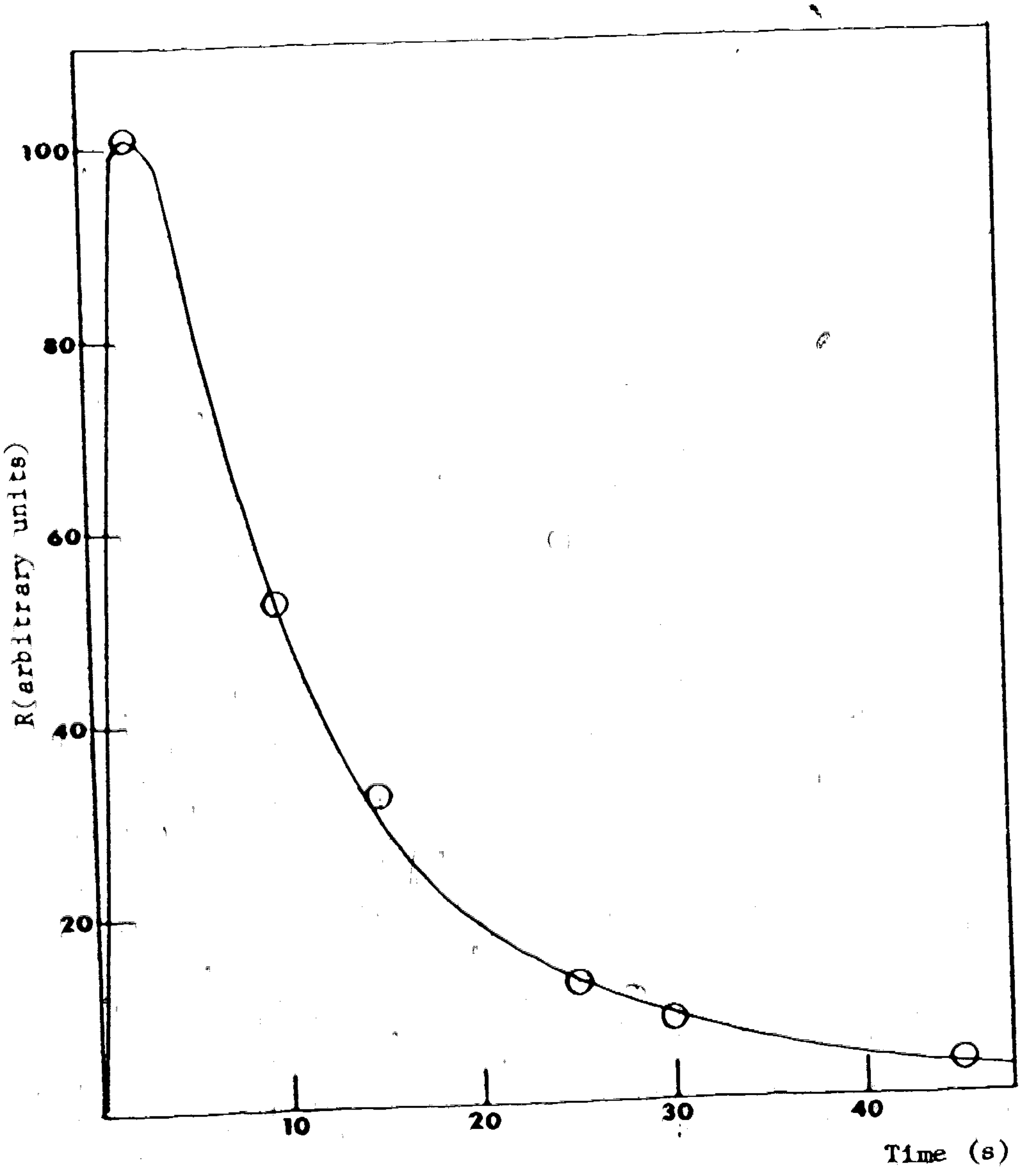
The number of photons emitted per molecule Φ_{ch} is given by eq. [55], where k_d is the first-order rate constant for decomposition of

$$[55] \qquad \Phi_{ch} = \frac{I}{k_d\ [D] \times 6.023 \times 10^{23}}$$

dioxetane and [D] the concentration of dioxetane in one ml of solution.

Chemiluminescence intensities of solutions containing 1,2-dioxetane and fluorescer are shown in Table XV. Two factors tend to

Figure 9. Emission from Luminol Light Standard



reduce the fluorescence intensity of these samples; i, quenching of fluorescence by dioxetane and; ii, quenching of fluorescer by dissolved oxygen. It has been shown that 1,2-dioxetanes quench the fluorescence of molecules such as biacetyl[87] and DPA,[14] however, at the low concentration of dioxetane used during these experiments, this quenching effect is quite small (< 10%).[14]

Quenching of fluorescence by dissolved oxygen is more important, especially when the fluorescer molecule is DPA. Wilson has demonstrated that the fluorescence of an aerated solution containing DPA is ∿ 20% weaker than that of a degassed sample.[14] Oxygen does not effectively quench fluorescence from solutions containing DBA because the lifetime of the singlet excited state of this compound is much shorter than that of DPA.[73]

Table XV also shows the number of photons emitted per molecule, Φ_{ch}, from four 1,2-dioxetanes in the presence of fluorescers. The values of Φ_{ch} for solutions containing DPA include a correction for the effects of quenching by dissolved oxygen.

Φ_{ch} for a solution containing dioxetane and fluorescer is given by eq. [56].

$$[56] \qquad \Phi_{ch} = \Phi_{D\to K^*} \Phi_{Et} \Phi_f$$

Extrapolation of the plot representing the quenching of singlet excited acetone by DPA in Figure 8 should lead to a value for the quantum yield of singlet excited acetone from 4. Thus, $\Phi_{D\to K^*}$ becomes $\Phi_{D\to {}^1K}$. At infinite concentration of DPA all excited singlet

TABLE XV

Chemiluminescence Yields from 1,2-Dioxetanes in Toluene Solution

Dioxetane	Concentration (M, x 10^3)	Fluorescer (at 10^{-2} M)	Temperature (°C)	Reading (R)	k_d (s^{-1}, x 10^5)	Φ_{ch} x 10^3
2	1.52	DPA	40.0	0.9	4.7	0.32
2	1.52	DBA	40.0	35.0	4.7	9.6
4	10.8	DPA	45.0	6.75	1.41	1.12
4	10.8	DBA	45.0	138	1.41	22.3
17	0.89	DPA	26.0	0.5	1.40	0.76
17	0.89	DBA	26.0	11.5	1.40	15.7
18	8.85	DPA	24.0	0.65	8.5	0.02
18	8.85	DBA	24.0	39.0	8.5	1.95

states are quenched and so $\Phi_{Et} = 1$. The corrected fluorescence reading, R, at this point is 15.0.

Substitution of this value into eq. [54] leads to:

$$I = \frac{15 \times 0.015 \times 9.75 \times 10^{14}}{1240} = 1.77 \times 10^{11} \text{ photons ml}^{-1} \text{ s}^{-1}$$

At 45°, $k_d[D] \times 6.023 \times 10^{23}$ is $1.41 \times 10^{-5} \times 0.0108 \times 10^{-3} \times 6.023 \times 10^{23}$, i.e. 9.17×10^{13} molecules ml^{-1} s^{-1}, and therefore, $\Phi_{ch} = 1.93 \times 10^{-3}$ photons molecule^{-1}. Substitution of this value into the modified eq. [56] leads to $\Phi_{D\rightarrow{}^1K} = 1.93 \times 10^{-3}$ since Φ_f for DPA is ∿ 1.0.[73]

A value for the quantum yield of triplet excited acetone from 4 may be estimated by extrapolation of the plot representing quenching of triplet excited acetone by DPA in Figure 8. The quantum yield of chemiluminescence, under these conditions, is given by eq. [57].

$$[57] \qquad \Phi_{ch} = \Phi_{T\rightarrow S}\, \Phi_{D\rightarrow{}^3K}\, \Phi_f$$

where $\Phi_{T\rightarrow S}$ is the efficiency at which transfer of energy from triplet excited acetone leads to singlet excited DPA. An estimate of this efficiency is ∿ 10^{-4}.[14] At an infinite concentration of DPA, the corrected value of Φ_{ch} is 9.3×10^{-5} photons molecule^{-1}. This leads to a value for $\Phi_{D\rightarrow{}^3K}$ of 0.93.

These results are in good agreement with those of Turro,[68] who estimated the yields of singlet excited acetone and triplet excited acetone formed on thermolysis of 4 at 0.3% and 50%, respectively.

The quantum yield for the formation of triplet acetone can also be calculated from the light emission measurements using DBA as fluorescer. The chemiluminescence quantum yield from a solution of 4 containing 10^{-2} M DBA is 22.3×10^{-3} photons molecule^{-1}.

Substitution of this value into eq. [57] leads to:

$$\Phi_{D \to {}^3K} = \frac{22.3 \times 10^{-3}}{\Phi_{T \to S}\ \Phi_f}$$

Φ_f for DBA at 20° is 0.1;[88] however, it is probable that the fluorescence efficiency of this compound has a negative temperature coefficient similar to that of 9,10-dichloroanthracene (DClA).[89] The corrected value for Φ_f at 45° is 0.065.[14] According to Vassil'ev's figures,[67] the rate constant for energy transfer from a triplet carbonyl to singlet DBA is $\sim 3 \times 10^8\ M^{-1}\ s^{-1}$, i.e. about 100 times slower than the allowed, diffusion-controlled triplet-triplet transfer. This suggests that the value of $\Phi_{T \to S}$ is $\sim 10^{-2}$,[14] however, substitution of this value in eq. [57] leads to a value of ∿ 30 for $\Phi_{D \to {}^3K}$. Since the maximum of excited states that can be generated from decomposition of a 1,2-dioxetane molecule is one, this value is clearly impossible.

More recent experiments[90] indicate that the value for $\Phi_{T \to S}$, obtained from Vassil'ev's data, is too low and that the correct value for this quantum yield is 0.3. Substitution of this value into eq. [57] leads to a value of 1.06 for $\Phi_{D \to {}^3K}$; this is a much more reasonable result and is in good agreement with results obtained by other workers.[68]

From calculations based on Vassil'ev's figures, Wilson concluded that thermolysis of cis-diethoxy-1,2-dioxetane 10 led to a quantitative yield of triplet excited formate.[14] However, if it is assumed that the correct value for $\Phi_{T\to S}$ is 0.3, Wilson's experimental results lead to a value of 0.03 for $\Phi_{D\to {}^3K}$ in the case of dioxetane 10.

This value is more reasonable since it is in agreement with her quantum yield of chemiluminescence from solutions of 10 containing DPA (see Table XVI); furthermore, this value is also in agreement with observations by White,[66] who demonstrated that the chemiluminescence quantum yield from 10 was much smaller than that from trimethyl-1,2-dioxetane 2.

Plots of 1/R versus 1/[A], similar to those shown in Figure 8, for solutions of 18 containing DBA and DPA (Figure 10), enable $\Phi_{D\to {}^1K}$ and $\Phi_{D\to {}^3K}$ to be calculated for this compound. The extrapolated values of R for the plots representing quenching of singlet and triplet ketone are 1.12 and 0.34, respectively (both values corrected for the effect of quenching by dissolved oxygen). These values lead to values for $\Phi_{D\to {}^1K}$ and $\Phi_{D\to {}^3K}$ of 2.9×10^{-5} and 8.8×10^{-2}, respectively.

These results do show convincingly that decomposition of 18 leads to a lower yield of excited states than does decomposition of 4. The yield of triplet ketone formed by decomposition of 18 is less than one tenth of that derived by thermolysis of 4. This lower yield of excited states could perhaps be explained on the basis of "eximer" formation as outlined in Scheme VI. Decomposition of 18 could yield a very tight "intramolecular eximer" in which two carbonyl fragments

TABLE XVI

Yields of Excited Carbonyl Fragments from Thermolysis of 1,2-Dioxetanes

xetane	Fluorescer	$\Phi_{D\to{}^1K} \times 10^3$	$\Phi'_{D\to{}^3K}$
2	DPA	0.39	—
2	DBA	—	0.457
4	DPA	1.93	0.93
4	DBA	—	1.06
17	DPA	0.97	—
17	DBA	—	0.748
18	DPA	0.03	0.088
18	DBA	—	0.065
10	DPA	—	0.03
10	DBA	—	0.07[a]

[a] Calculated from the data in reference 14, using a value of 0.3 for $\Phi_{T\to S}$.

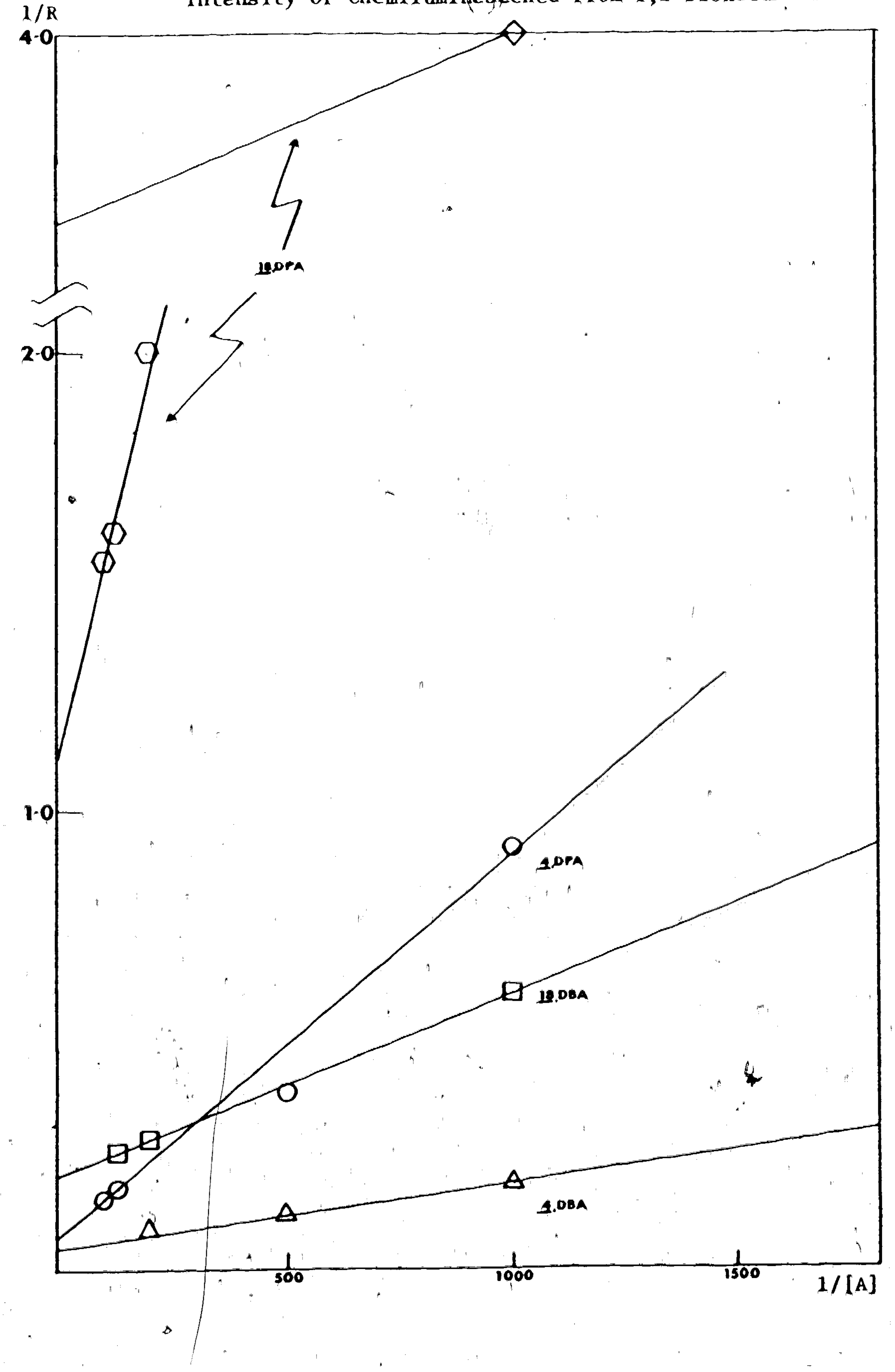
are held together by the framework of the molecule. Energy transfer from such a complex may be less efficient than from an isolated excited ketone.

However, plots of 1/R versus 1/[A] for solutions of 18 with DBA and DPA show the same sort of behaviour as was observed for tetramethyl-1,2-dioxetane 4. Figure 10 shows plots for solution of 18 and 4 in the presence of both DPA and DBA. The close similarity of the behaviour of 18 and 4 suggests that similar excited states are being intercepted by fluorescer in both cases. Eximer formation, then, cannot account for the low yield of excited states generated on thermolysis of 18.

The slopes of both the DBA and DPA plots in the case of 18 are steeper than the corresponding plots derived from thermolysis of 4; a factor of two to three in relative slope for both fluorescers.

The slopes of the plots in Figure 10 represent k_3/k_2 (Scheme III). Since the plots derived from decomposition of 18 are steeper than the corresponding plots for 4, this suggests that excited states generated by thermolysis of 18 have shorter lifetimes than the corresponding excited states of acetone and, hence, less will be intercepted by added fluorescer. This would, of course, reduce the chemiluminescence yield from 18, but this factor alone is insufficient to account for the extremely low chemiluminescence yield for this compound. Even at infinite concentration of DPA, where all excited singlets are quenched, the extrapolated yield of photons is still only 0.03 x 10^{-3} photons per molecule.

Figure 10. Effect of Fluorescer Concentration [A] on the Relative Intensity of Chemiluminescence from 1,2-Dioxetanes.



The yields of excited triplet and excited singlet carbonyl fragments generated during thermolysis of 2 and 17 were also estimated. These values, together with the results for 4, 18 and 10, are shown in Table XVI. It was assumed, for the purposes of these calculations, that thermolysis of 17 and 18 led to excited states having equal lifetimes; a similar assumption was made concerning the lifetime of excited states generated by thermolysis of 2 and 4.

CONCLUSIONS

The results of the chemiluminescence experiments confirm earlier suggestions[68] that cleavage of 1,2-dioxetanes leads directly to triplet excited carbonyl fragments. The results listed in Table XVI indicate that thermolysis of 4 and 17 lead to similar yields of excited state products; somewhat lower yields of excited state products are generated during thermolysis of 2 and 18. In particular, the yield of singlet excited ketone derived from 18 appears to be exceedingly small.

Turro[91] has proposed what he terms a "diabatic pericyclic" mechanism for the decomposition of 1,2-dioxetanes, in order to explain the high yields of triplet excited states formed during thermolysis of these materials. This mechanism may loosely be described as a "concerted" mechanism. However, if it is accepted that triplet excited ketone can add, perhaps by a two-step mechanism, to an olefin (the Paterno-Büchi reaction) yielding an oxetane; then there seems no reason why the reverse reaction, yielding triplet ketone, should not occur in the case of 1,2-dioxetanes. There is some evidence for a two-step biradical mechanism in the thermal decomposition of 1,2-dioxetanes, (see Chapter III).

The driving force for formation of triplet excited products could be the lower energy of these excited states compared with the corresponding singlet states. The energy of the lowest triplet state of acetone, for example, is ∿ 76 kcal mole^{-1} compared with ∿ 84 kcal mole^{-1} for the lowest singlet state.[65]

The energy available from the decomposition of 1,2-dioxetanes (ΔH_A) appears to influence the yields of excited states formed. The available energy is made up of the enthalpy change during the reaction (ΔH°_r) plus the energy of activation E_A, Figure 7. The energies available from the decomposition of 2 and 4 have been calculated using group additivity methods similar to those described earlier.[61] A similar approach enables values for the energy available from decomposition of 17 and 18 to be calculated. For example, the energy available from thermolysis of 18 is:

$$\Delta H^\circ_f(\underline{24}) - \Delta H^\circ_f(\underline{18}) - E_A$$

ΔH°_f for 18 has already been calculated at -33 kcal mole^{-1}.

$$\Delta H^\circ_f(\underline{24}) = 8[C(H)_2(C)_2] + 2[C(O)(C)_2] + \text{ring correction}$$

The ring correction value for cyclodecane is not listed in Benson's tables but ring corrections have the same value as the ring strain energy for ring sizes from six to nine.[61] A reasonable value for the ring correction for cyclodecane, then, is +13 kcal mole^{-1}. However, the ring strain in cyclodecane-1,6-dione 24 is probably less than this, since the presence of two sp^2 centres redu[illegible] transannular CH interactions.[60] Space-filling models show that, although 24 is quite a "crowded" molecule, it is certainly less crowded than cyclodecane itself. Studies by Turner[92] on the heats of hydrogenation of cyclic alkynes indicate that cyclodecene, a compound with two adjacent sp^2 centres, is less strained than cyclodecane.

The value of 13 kcal is therefore a maximum value for the ring strain of 24; the actual value must lie somewhere between 0 and 13. The minimum value for the heat of formation, then, is given by:

$$\Delta H_f^\circ(\underline{24}) = 8(-4.95) + 2(-31.5) + 13 = -89.6 \text{ kcal mole}^{-1}$$

The minimum value for ΔH_A from thermolysis of 18 is therefore $-89.6 + 33.0 - 22.9 = -79.6$ kcal mole^{-1}. The available energy must clearly be greater than this, since this value is insufficient to allow formation of singlet excited states, and singlet excited states are observed during thermolysis of 18.

Table XVII lists values for the energies available from the thermolysis of 1,2-dioxetanes. The results listed in Tables XVI and XVII indicate that there is a relationship between the available energy and the yield of excited states generated by thermolysis of 1,2-dioxetanes.

Further support for this relationship is found in results obtained from the photolysis of 1,2-dioxetanes. The direct photolysis of 4 is reported to proceed with a quantum yield of 1.0.[39] It was found that the yield of singlet acetone formed during photolysis was much higher than that formed from the thermolysis. Furthermore, the yield of singlet excited acetone was found to increase as the energy of the excitation light was increased; excitation of 4 with 366 nm light resulted in a 10% yield of singlet acetone whereas excitation at 240 nm led to a 35% yield of singlet excited product. In other words, the yield of singlet acetone was influenced by the amount of

TABLE XVII

Available Energy from Thermolysis of 1,2-Dioxetanes

Dioxetane	$(H_r^\circ - E_A)$ (kcal mole^{-1})
4	93.42
2	89.3
17	94.3
18	79.6 - 92.6

energy supplied to the system.

1,2-Dioxetanes as Light Standards:

The calibration of photocubes in instruments such as spectrofluorometers is usually a tedious procedure.[86] Liquid light standards (secondary standards) provide the most convenient method for this calibration since these standards duplicate the geometry of the cells or cuvettes used for experimental determinations. However, the two types of liquid light standard available suffer from many disadvantages. The luminol light standard described earlier is particularly difficult to use. Although the light output from this system is quite high, the emission is of very brief duration (see Figure 9) and considerable dexterity is necessary to obtain reproducible light emissions.

The radioactive light standard described by Hastings[93] gives an essentially constant flux of photons but such standards necessarily have very low intensities. The light emission from such standards is, in fact, too low to be of use in the calibration of less sensitive instruments.

A solution of dioxetane containing a fluorescer may provide an attractive alternative secondary light standard. The number of photons emitted from a solution of 4 containing a known concentration of DBA could be determined by absolute methods.[86] This solution would then be an extremely convenient secondary light standard.

Solutions of 1,2-dioxetanes emit an essentially constant flux of photons at moderate temperatures (25 - 45°) and the intensity of this emission is much higher than that of the radioactive light standards. Solutions containing 1,2-dioxetanes may be stored at -10° for months without appreciable deterioration, however, deterioration does not affect the usefulness of the standard. In practice, it would merely be necessary to estimate the concentration of dioxetane in the standard emitted and the temperature of the instrument. The number of photons emitted ml^{-1} s^{-1} from the standard could then be calculated.

EXPERIMENTAL

M.C.B. spectrograde toluene, Fisher spectrograde cyclohexane and benzene were used without further purification. DBA was used as supplied by Aldrich Chemical Co.; DPA was kindly supplied by Dr. K. R. Kopecky and was recrystallized from toluene before use.

Acenaphthylene 71:

Acenaphthylene received from Aldrich was dark in colour, m.p. 80 - 85°. It was first recrystallized from ethanol with decolourizing charcoal. A solution of recrystallized material (13 g) in hot ethanol (400 ml) was slowly added to a solution of picric acid (24 g) in boiling ethanol (1,000 ml). The mixture was heated on a steam bath until the solution was completely clear, then allowed to cool at room temperature. The beautiful pale-orange needles of picrate derivative that precipitated were filtered off and recrystallized from ethanol. The yield of pure derivative was 25 g (78%). Crystals of the picrate derivative were decomposed by stirring with dilute ammonia solution; the bright yellow hydrocarbon which was filtered off was washed repeatedly with dilute NH_3 solution until the washings were colourless. Finally, the hydrocarbon obtained in this way was recrystallized from ethanol to yield 8.9 g (70%) of yellow crystals, m.p. 91 - 92°, reported m.p. 92 - 93°.[71]

Acenaphthylene Dimers 72 and 73:

A solution of acenaphthylene, purified via recrystallization of the picrate, (8 g), in cyclohexane (200 ml) was photolyzed for 72 hours using a 200 W medium pressure mercury lamp equipped with a Pyrex glass filter in an immersion well apparatus. After 72 hours the photolysis was by no means complete; nevertheless, the solution was removed from the photolysis vessel which was then rinsed twice with boiling benzene. The solution plus washings were evaporated to dryness and the residue was washed twice with hot cyclohexane to remove unreacted acenaphthylene yielding ∿ 4 g of mixed dimers. *cis*-Dimer was obtained by boiling the residue with cyclohexane; the solution was decanted from the residue and allowed to cool. The crystals which deposited from this solution were filtered off, dissolved in benzene, and a saturated solution of picric acid in benzene was added. Splendid, deep red crystals of the picrate formed when the solution was allowed to stand for a few hours. These were filtered off, recrystallized from benzene, and decomposed with ammonia solution in the usual fashion. The hydrocarbon so obtained was recrystallized from cyclohexane (using activated charcoal) to yield white prisms of the *cis*-dimer, m.p. 231 - 232°. Pure *trans*-isomer was obtained by repeatedly extracting a portion of mixed dimers with hot cyclohexane; the residue after extraction was recrystallized several times from benzene solution to yield fine white needles of *trans*-dimer, m.p. 320 - 321°.

Samples of 72 and 73 for UV analysis were prepared in the fashion of analytical samples. All glassware was washed with concentrated sulphuric acid, rinsed thoroughly with distilled water, dried in an oven and cooled in a vacuum dessicator. Glassware used for weighing was thereafter handled only with clean tongs.

cis-Dimer **72**: $\epsilon^{219} = 1.44 \times 10^{5}$, $\epsilon^{225} = 7.75 \times 10^{4}$; reported $\epsilon^{219} = 1.27 \times 10^{5}$, $\epsilon^{225} = 6.60 \times 10^{4}$.[10]

trans-Dimer **73**: $\epsilon^{219} = 7.50 \times 10^{4}$, $\epsilon^{225} = 1.22 \times 10^{5}$; reported $\epsilon^{219} = 7.38 \times 10^{4}$, $\epsilon^{225} = 1.19 \times 10^{5}$.[70]

Dioxetane Sensitized Dimerization of Acenaphthylene:

Pure, crystalline samples of **4** and **17** were used in these experiments; samples of **18** used contained 5 - 10% impurity (chiefly the dione **24**) and were estimated for dioxetane content immediately before use. Samples for the sensitization experiments were prepared by dissolving appropriate quantities of dioxetane and acenaphthylene in benzene. One ml samples of solutions containing 0.1 M dioxetane were prepared; samples containing concentrations of dioxetane of 0.1 M and 10^{-2} M were made up to 10 ml. Blank samples were prepared by dissolving appropriate quantities of acenaphthylene in benzene; both one ml and 10 ml samples were prepared.

The solutions were transferred to scrupulously cleaned pyrex ampoules and were degassed by six freeze-thaw cycles at 5μ. The sealed ampoules were then heated at 95 - 100° in a water bath for 15 minutes to allow complete thermolysis of the 1,2-dioxetanes. Emission of a bright yellow light was observed during the thermolysis of solutions containing concentrations of dioxetane ∿ 1.0 M.

The ampoules were then allowed to stand at ∿ 8° for several days until the majority of the products 72 and 73 had precipitated. The precipitated dimers were filtered off and washed with ice cold pentane to remove all traces of acenaphthylene.

The filtrate was applied to a silica gel preparative TLC plate which was eluted in the dark using cyclohexane. Two such elutions were usually required to separate acenaphthylene from the dimers formed which were visualized under UV light as a purple line close to the bottom of the plate.

Silica gel containing absorbed product was carefully scraped from the plate, transferred to a soxhlet thimble and extracted for eight hours with boiling benzene. The extract was evaporated to dryness, then cyclohexane (10 ml) was added and the mixture again evaporated. This procedure was repeated three times to remove all traces of benzene from the extract. The residues so obtained were extracted repeatedly with boiling cyclohexane. Combined extracts were filtered and, after cooling, were combined with the precipitated dimers and made up to 100 ml. These solutions were then diluted to give solutions suitable for analysis by UV spectroscopy.

The optical density of the blank (10 ml) sample, A^{219} 0.297, A^{225} 0.293, was of the same order as those samples prepared from solutions containing 10^{-2} M dioxetane. For example, the optical density of a sample prepared from a solution containing 10^{-2} M 4 was; A^{219} 0.32, A^{225} 0.34. For this reason, data from solutions containing 10^{-2} M dioxetane was not included in the results. The blank absorbance was subtracted from the absorbance of samples prepared for solutions containing 0.1 M dioxetane; corrections were unnecessary for samples prepared from solutions containing 1.0 M dioxetane. A correction was added to the optical density of all samples, however, to allow for the loss of sample (5%) during work-up.

A typical sample was analyzed as follows:

Sample 13: 0.1 M 4; sample size, 10 ml.

Diluted 1 × 50 ml	O.D. = A^{225} 0.67, A^{219} 0.525
After subtracting blank correction	O.D. = A^{225} 0.61, A^{219} 0.465
After adding correction for material loss	O.D. = A^{225} 0.64, A^{219} 0.49

2,4-Dimethylpropiophenone 77:

This compound was prepared by modifying the procedure of Nightingale and Carton.[94]

Anhydrous $AlCl_3$ powder (68 g) was added slowly, with stirring, to a cooled solution of propionyl chloride (46 g) in methylene chloride (100 ml). The clear solution so obtained was decanted from the small amount of residue and was added dropwise to an ice cold, stirred solution of m-xylene (60 g) in methylene chloride (100 ml). After addition was complete the solution was heated under reflux for a further 60 minutes and then poured slowly into ice water (500 ml). The organic layer was washed several times with dilute sodium hydroxide solution and then with water. The organic layer was dried over $MgSO_4$ and the solvent removed evaporatively.

Distillation of the residue yielded 75 g (92%) of colourless oil, b.p. 112°, 10 mm; reported b.p. 112°, 10 mm.[94]

The NMR spectrum ($CDCl_3$) showed absorptions at τ2.43 (d, J = 8 Hz, 1H), τ2.96 (b, 2H), τ7.14 (quartet, J = 7 Hz, 2H), τ7.51 (s, 3H), τ7.7 (s, 3H), and τ8.84 (triplet, J = 7 Hz, 3H).

Selenium Dioxide Oxidation of 77:

Selenous acid (2.6 g) was dissolved in dioxane (12 ml) stirred at 50 - 55°. 28 (2.25 g) was added and the mixture was stirred at reflux temperature for four hours. Most of the selenium was then filtered off and the solvent removed by distillation. Distillation of the residue yielded a mixture of product containing starting material and other selenium containing compounds.

The NMR spectrum of the product showed absorptions at τ8.84 (triplet) and τ7.14 (quartet) indicating the presence of starting material.

Dimethyl-iso-nitrosopropiophenone 78:

This compound was prepared according to a procedure described in the literature.[95] To a 500 ml, three necked flask fitted with stirrer and reflux condenser was added a solution of 77 (32.4 g) in dry ether (150 ml). Dry HCl gas was passed into the stirred solution while freshly distilled iso-amyl nitrite (24 g) was added from a tap funnel at such a rate that the ether refluxed gently. Addition was complete after four hours; the solution was stirred for a further 30 minutes and then allowed to stand overnight. The ether layer was then extracted with 10% NaOH solution (5 x 30 ml) and the combined extracts were poured into a mixture of concentrated HCl (40 ml) and ice (60 g). The crude yellow material was recrystallized (toluene) to yield 30.2 g of white crystals (87%), m.p. 104 - 105°.

The NMR spectrum ($CDCl_3$) showed absorptions at τ1.3 (D_2O exchangeable), τ2.7 - 3.1 for the aromatic protons, τ7.67 (s), τ7.72 (s) and τ7.9 (s) for the methyl groups.

The mass spectrum showed a parent peak at 191 and major peaks at 174, 133 and 105 corresponding to loss of OH, $CH_3C{:}NOH$ and $CH_3C{:}NOH{:}CO$, respectively.

Calculated for $C_{11}H_{13}NO_2$: C 69.09, H 6.85, N 7.33; found, C 69.31, H 6.96, N 7.49.

The IR spectrum ($CHCl_3$) showed major bands at 3240 (b), 2910 (s), 1660 (s), 1640 (s), 1600 (s), 1450 (b), 1300 (s), 1190 (s), 1010 (m), 870 (s), 825 (s), 755 (s), and 740 (s) cm^{-1}.

1-(2,4-Dimethylphenyl)propane-1,2-dione 75b:

Hydrolysis of the oxime 78 was attempted using a procedure described in the literature.[96] Dimethyl-iso-nitrosopropiophenone 78 (25 g) was added to 10% H_2SO_4 (250 g) contained in a one litre flask arranged for steam distillation. Distillation was continued until the residue was clear and colourless. The distillate (approximately four litres) was saturated with NaCl and extracted with ether until the extracts were colourless. The combined extracts were dried over $MgSO_4$ and solvent was removed.

The bright yellow oil so obtained deposited white crystals which were found to be unchanged 78. These were filtered off and the yellow oil redistilled (b.p. 85 - 89° at 0.2 mm). The yield was very low (3.5 g).

The product, a bright yellow oil, solidified at -10°.

The NMR spectrum ($CDCl_3$) showed an AB system at τ2.42 (J = 7 Hz) and τ2.92; half of this system was partially obscured by the other aromatic proton at τ2.86. The methyl absorptions appeared at τ7.47, τ7.51 and τ7.64.

Mass spectrum showed a parent peak at 176 and major peaks at 133 and 105 corresponding to loss of CH_3CO and $CH_3CO{:}CO$, respectively.

Reaction of 78 with Lead Tetraacetate:

A procedure has been reported for the hydrolysis of oximes using the above reagent;[79] it was decided to investigate this reaction using the compound 78.

78 (3.6 g) dissolved in acetic acid (15 ml) was added to a stirred suspension of lead tetraacetate (2 g) in acetic acid (15 ml) at 70°. No nitrogen was evolved, the colour steadily darkened and no identifiable products could be obtained on work up.

Reaction of 78 with Sodium Bisulphite:

Sodium bisulphite (16 g) was added to a solution of 78 (1.9 g) dissolved in 50% aqueous ethanol (25 ml) and the mixture was heated under reflux for two hours. At this time only a trace of the starting material 78 could be detected by TLC on silica gel. The ethanol was distilled off and the residue diluted with water (25 ml); HCl

(50%) was then added to decompose the excess bisulphite reagent and the solution was extracted with methylene chloride (3 x 10 ml). After removal of solvent, the product 75b was redistilled under vacuum. The yield of 75b was 1 g (59%).

2-Hydroxy-2,5-dimethylindan-1-one 76b:

Using the procedure of Bishop and Hamer,[77] a solution of 75b (0.5 g) in hexane (500 ml) was irradiated in a one litre flask. The solution was stirred magnetically under an atmosphere of nitrogen and irradiation, carried out using a G.E. "Sunlamp", was continued until the yellow colour of the dione had faded. Solvent was removed at the rotary evaporator to yield a yellow oil which deposited white crystals when allowed to stand at -10° for several days. The m.p. after recrystallization from heptane was 84 - 85°.

The NMR spectrum ($CDCl_3$) showed absorptions at τ2.29 and 2.80 (AB system, J = 8 Hz) and τ2.70 for the aromatic protons. Other absorptions appeared at τ6.8 (m), τ7.66 (s) and τ8.57 (s). The mass spectrum showed a parent peak at 176 and a major fragment at 158 ($P-H_2O$). For $C_{11}H_{12}O_2$: calculated C 75.0, H 6.82; found, C 74.98, H 6.84.

Energy Transfer Experiments Using 75b:

The procedure used was the same as that employed in the acenaphthylene studies. A mixture of 0.06 g of 75b and 0.1 g of 2 (freshly sublimed) was made up to ca. 0.5 ml with dry benzene; the sample was degassed by three freeze-thaw cycles at 5μ and sealed. During the heating at 98° a green fluorescence was observed, presumably corresponding to emission from the diketone.

The yield of product (76b) was estimated by VPC on FFAP at 190° using anisyl alcohol as internal standard. The instrument was calibrated by injecting mixtures of 76b and anisyl alcohol at known concentrations. Peak areas were measured using a planimeter.

Thermolysis of 17 in CCl_4:

A sample of pure, resublimed 17 (0.0312 g) dissolved in CCl_4 (0.5 ml) was degassed by four freeze-thaw cycles at 5μ and sealed into a scrupulously cleaned pyrex ampoule. The ampoule was then placed in boiling water for 15 minutes; during this heating period the sample was observed to darken slightly. The sample was removed from the heating bath and allowed to stand at -10°; after several hours at this temperature the sample darkened appreciably and deposited oily droplets. Analysis of this solution by VPC (FFAP 50 - 110°) revealed that no acetone had been formed. TLC (silica gel plates eluted with ether/Skelly B 1:10) showed that a new compound, with a higher R_f value than diketone 22, had been formed.

The experiment was repeated using a larger sample of [illegible]08 g) in CCl_4 (1 ml); the reaction product was isolated by p[illegible]e TLC on silica gel using ether/Skelly B as eluent. The product, a yellow oil, showed spectral characteristics identical to those of 1-acetyl-2-methylcyclopentane, 79. The semicarbazone derivative of this compound was prepared, m.p. 220°, some decomposition at 214°; mixed m.p. with a sample of semicarbazone from authentic 79, 218 – 220°, some decomposition at 215°.

A blank experiment was carried out by heating a sample of diketone 22 (0.2 g) in one ml of CCl_4 (sample degassed as before) at 100°. No darkening of the solution occurred and no new products could be detected by TLC.

A sample of 22 (0.01 g) in CCl_4 (1 ml) was degassed and sealed into a quartz ampoule. The ampoule was irradiated using a 200 W medium pressure mercury lamp; after only 15 minutes the solution had darkened in colour and a dark brown flocculent precipitate was observed. Examination of the mixture by TLC as before showed the presence of a new compound with R_f value the same as that of 79.

1-Acetyl-2-methylcyclopentene 79:

Diketone 22 (0.5 g) was stirred at 60 – 70° for 40 minutes in acetic acid (25 ml) containing one ml of concentrated sulphuric acid. The mixture was then poured into ice water (100 ml); the mixture was neutralized with sodium bicarbonate and extracted several times with methylene chloride. A yellow oil, containing crystals of unreacted 22, was obtained after drying the sample over $MgSO_4$ and evaporative removal of solvent. The unsaturated ketone 79 was purified by column chromatography on silica gel using Skelly B/ethyl acetate 10:1 as eluent.

The NMR spectrum ($CDCl_3$) showed absorptions at τ7.75 (s), τ7.85 (poorly resolved doublet) and broad absorptions at τ7.1 - 7.7 and τ8.0 - 8.5. The UV spectrum (C_6H_{12}) showed λ_{max} 245 nm, ε ∿ 1450 in good agreement with the assigned structure.[97] The semicarbazone of this material was prepared and recrystallized from methanol, m.p. 218 - 221°; reported m.p. 221°.[98]

Thermolysis of 17 in Hydrocarbon Solvents:

Samples of 17 for these experiments were recrystallized twice from iso-pentane prior to use. Solutions of 17 were sealed into glass ampoules after degassing by three freeze-thaw cycles at 5μ. Usually a blank experiment was run at the same time, substituting pure octane-1,7-dione 22 for the dioxetane.

Samples were heated at ∿ 100° for 15 minutes and then analyzed by VPC on an FFAP column using a variety of conditions. No acetone could be detected and the only peak observed was found to be that of diketone 22.

Photolysis of Octane-1,7-dione 22:

Pure, resublimed 22 (0.15 g) was dissolved in spectrograde cyclohexane (1 ml) and the solution was sealed into an ampoule after degassing by the usual techniques. Samples prepared in this way were suspended a short distance from a 200 W medium pressure mercury lamp and photolyzed for periods of time from two - 72 hours. After ca. 12 hours secondary photolysis appeared to occur extensively, but a fairly clean mixture was obtained after five hours. TLC analysis of this mixture on silica gel revealed that most of the starting material was unchanged. VPC analysis of this mixture on FFAP revealed that a small amount of acetone had been formed. This was confirmed by mixed injection techniques using a variety of column conditions.

Chemiluminescence Quantum Yields:

Measurements were made using the same 10 cm cell with fused outer jacket described in the kinetics section. Samples were prepared by adding toluene solutions containing 1,2-dioxetanes (1 ml) to solutions of the fluorescer in toluene (10 ml). The solutions were mixed thoroughly and poured into the cell. The cell was placed in the instrument and readings at the fluorescence maximum of 450 nm were taken, using 60 nm slitwidth, at one minute intervals until 10 minutes had expired.

Calibration of Spectrofluorometer:

Luminol (0.18 g), prepared by the method of Fieser,[99] was dissolved in DMSO (dried over CaH) and the solution made up to 10 ml. One ml of this solution was dissolved in 100 ml of dry DMSO to prepare a 10^{-4} *M* solution. The optical density of this solution at 350 nm was 0.775. Two ml of this solution was diluted to 100 ml and this solution (O.D., 0.015) was used immediately for the calibration experiments. 10 ml of this solution and one ml of a saturated solution of potassium-t-butoxide in t-butyl alcohol were simultaneously injected through a septum into the cell of [illegible] spectrofluorometer. A plot of the light intensity reading at the emission maximum 484 nm[86] *versus* time was made; in this way the total light emitted was recorded. This experiment was repeated several times and an average value for the integrated light output was obtained.

Values obtained for the total integrated light output, as measured by a planimeter, were 6.2, 6.6, 6.0 and 5.8 square inches; where one square inch ≡ 200 relative units.

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