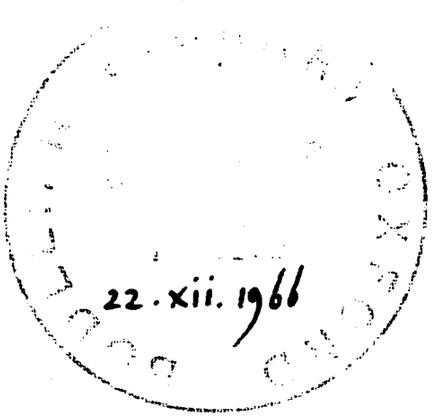
SOME STUDIES IN ORGANIC PHOTOCHEMISTRY

by

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A Thesis submitted for the Degree of
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Brasenose College,
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Wo viel Licht ist, ist starker Schatten.

-GOETHE.

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CONTENTS

Page

INTRODUCTION 1

References 10
Diagrams (i) to (xliv)

PART I. DISCUSSION 14

Section I. THE PHOTOCHEMISTRY OF THE SYSTEM: DIMETHYL MALEATE/ DIMETHYL FUMARATE/ACETONE

Chapter I General Discussion

A) The absorption of ultraviolet light in this system ... 14
B) Charge-transfer absorption 15
C) On the nature of the exciting radiation employed ... 16
D) Preliminary irradiations. Photochemical products ... 16
E) General principles of a mechanistic investigation ... 20
F) The first series of photokinetic experiments 22
G) The second series of photokinetic experiments 24
H) The photochemistry of oxetanes 28
I) The third series of photokinetic experiments 30
(a) A critique of the experimental method
(i) Apparatus (1) The reactor 30
(2) The lamp 33
(b) Reaction product analysis
(i) Apparatus 37
(ii) Estimation of chromatogram peak areas 39
(c) General experimental approach 39
(d) Errors 40
(e) The possibility of cyclobutane formation 44
(f) Experimental data
(i) General observations 45
(ii) Analysis of data 47
(iii) The relative proportions of incident light absorbed by the various components 57
(iv) The effect of oxygen 59
J) Energy levels
(a) General 60
(b) A summary of previous measurements of the energy levels of dimethyl maleate, dimethyl fumarate and acetone 62
(c) Means of measuring triplet energy levels 63
(d) Measurements 66

Tables

Page

Chapter 2 Theoretical Discussion

A) Introduction 70
B) Comparisons of rates using borosilicate apparatus with rates using quartz apparatus 70
C) A comparison of the f(0.23M)q case with the fb case ... 71
D) A comparison of the mq and mb cases 76
E) The effect of varying the concentration of dimethyl fumarate 80
F) Summary 83
G) On the possible natures of the excited states 83

Section II. THE PHOTOCHEMISTRY OF ACETOXIME

A) Introduction 90
B) Acetoxime/cyclohexene system
(a) General 90
(b) Mechanism 93
C) Other systems 98

Section III. IRRADIATIONS INVOLVING ALDEHYDES

A) General 99
B) Propionaldehyde, propionaldehyde/styrene and related irradiations 100
C) Propionaldehyde/dimethyl maleate irradiation 101
D) Acetaldehyde/dimethyl maleate irradiation 102
E) Propionaldehyde / methyl crotonate irradiation 102
F) Propionaldehyde/cyclohexene irradiation 103
G) Crotonaldehyde/dimethyl maleate irradiation ... ...
H) Correlation between the peroxide induced and photochemical reactions 104

PART II. EXPERIMENTAL

General 107

Section I THE PHOTOCHEMISTRY OF THE SYSTEM: DIMETHYL MALEATE/ DIMETHYL FUMARATE/ACETONE 111

Section II THE PHOTOCHEMISTRY OF ACETOXIME 138

Section III IRRADIATIONS INVOLVING ALDEHYDES 147

REFERENCES 156

DIAGRAMS I - XIX

FIGURES I - XLI

ABSTRACT i

INTRODUCTION

Photochemistry is concerned with the processes attending the electronic redistribution resulting from the absorption of visible or ultraviolet radiant energy by a molecule. These processes depend on the physical environment of the substance irradiated.[1] For example, fragmentation products are less evident in the liquid phase than in the gas phase photolysis of acetone,[2] and this has been attributed both to the more rapid collisional deactivation of the excited state occurring in liquids and to the Franck-Rabinowitsch 'cage' effect of the surrounding liquid molecules preventing the primary fragmentation products from recoiling rapidly from each other thus enhancing their chance of recombination.[3] Much effort has been expended in reaching an understanding of gas phase photochemical reactions and the interested reader is directed to the numerous reviews on the subject.[4] The whole of the work described in this thesis concerns liquid phase reactions.

A second factor bearing on the observed photochemistry of a molecule is the nature of the excited state produced. A large number of excited states of any molecule exist but only few are important photochemically, for, not only must a state be formed, but it must exist long enough to react. By virtue of electronic spin, two series of singly excited states of diamagnetic molecules exist. These are designated 'singlet' and 'triplet' states and between the two series radiative transitions are 'forbidden'. The ground state of a diamagnetic molecule having singlet character, the lowest excited singlet state is most commonly encountered

photochemically unless non-radiative singlet→triplet conversion from the excited singlet to the lower energy longer-lived triplet state is possible when this state dominates the photochemistry of the molecule.[5] Excited states may be further described in terms of their orbital configurations. Thus (σ,π^*), (n,π^*) and (π,π^*) states are frequently encountered and correspond to the excitation of an electron from a σ orbital, a non-bonded (n) orbital or a delocalised π orbital to a higher energy π orbital. The (n,π^*) and (π,π^*) states will be considered frequently in the context of this work and the reader is referred to reviews for a fuller elementary discussion of the basic concepts involved.[6] Further aspects of this subject will be developed in Discussion, Section I of this thesis.

Since each excited state of a molecule corresponds to a different electronic distribution, each has a distinctive chemistry of its own.[7] Thus the $^3(\pi,\pi^*)$ state of 9-anthraldehyde (i) has been postulated as the state responsible for the photodimerisation reaction (i → ii), whereas the $^3(n,\pi^*)$ state is thought to be involved in oxetane formation when the substance is irradiated in 2-methylbut-2-ene (i → iii).[4,8] It is not always easy to discover the state involved in a photoreaction since this may not correspond to the state excited owing to the possibility of internal conversion between states.[9] Added complications exist because, not only is energy transferable between different states of the same chromophore, but it may be transferred between isolated chromophores within a molecule[10a] or even between different molecules.[10b] Either singlet or triplet energy may be transferred between molecules although different

rules govern the mode of transfer in the two cases.[11,15]

Although much of the published work in photochemistry is descriptive, certain efforts have been directed towards a unified understanding of the subject on the basis of the fundamental process involved.[12,13,14,15,23]

In view of the volume of photochemical literature, it is proposed here to review selectively only those aspects of photochemistry pertinent to the investigations described in this thesis. These investigations have been concerned with the photochemistry of unsaturated systems, absorbing as they do in a spectral region particularly convenient for experimentation.

The simplest photochemical reaction involving the C=C chromophore is that of cis↔trans isomerisation. In the first excited (π,π^*) state, an electronic distribution is produced having lowest energy in the perpendicular form (iv), named by Hammond[15] a 'phantom' state. Much work has been directed towards reaching an understanding of the mechanism of cis↔trans photoisomerisation. Both singlet and triplet mechanisms have been observed thermally,[16] and there is reason to believe that both occur photochemically. Hammond and co-workers[15] have examined the composition of the photostationary state of the cis↔trans isomerisation reaction of the stilbenes (v), the 1,2-diphenylpropenes (vi), the piperylenes (vii) and ethyl fumarate/ethyl maleate (viii) in the presence of various triplet sensitizers (i.e. compounds which absorb the incident radiation, and having rapidly and efficiently degraded from the excited singlet states first produced to their triplet states, pass on their triplet excitation energy to the substance investigated). The composition

of the photostationary state was found to vary with the triplet energy of the sensitizer used and from the 'chemical spectrum' so obtained, Hammond inferred the triplet excitation energies of the cis- and trans- isomers investigated. To explain the puzzling results obtained at low sensitizer energies, the possibility of energy transfer directly to the low energy 'phantom' triplet state was invoked.

There is evidence that the singlet state mechanism is important in certain systems.[18] However more detailed investigations reveal that in certain cases the mechanism may be more complicated. Thus it has been shown that the cis↔trans photoisomerisation reaction of stilbene probably involves neither the lowest excited singlet nor the lowest excited triplet states but a higher energy triplet level.[17]

This photoisomerisation reaction is not confined to the C=C system but is observed in N=N[18] and C=N[19,20] systems also. One particularly interesting example of this reaction is the cis↔trans isomerisation of dibenzoylcyclopropane (ix).[21] Photosensitization experiments indicate that the cyclopropane triplet energy is ~87kcal/mole above the ground state [22] (that of ethylene is ~82kcal/mole).

Excited singlet-state aldehydes and ketones have been found to degrade very rapidly and efficiently to their lower-energy triplet states. The well known photochemical hydrogen abstracting properties of the oxygen atom of ketones has been correlated with the nature of this triplet level. Thus it has been shown that $^3(n,\pi^*)$ benzophenone is responsible for the formation of benzpinacol when benzophenone is irradiated in the presence of benzhydrol,[23] (x → xi). This mechanism has been extended to other

hydrogen abstracting reactions of ketones.[24] It has been suggested that, in those cases where the hydrogen abstracting reaction is suppressed, the lack of reactivity is due to the lowest energy and longest-lived triplet state having (π,π^*) rather than (n,π^*) character.[25] A recent investigation has drawn attention to the close similarity which exists between the hydrogen abstracting reactions of $^3(n,\pi^*)$ ketones and those of alkoxy radicals.[26]

The irradiation of aldehydes or ketones in the presence of olefins has been found frequently to result in the production of oxetanes. Thus benzaldehyde irradiated in 2-methylbut-2-ene yields the oxetane (xii). This irradiation was performed in 1909 by Paterno and Chieffi[27] in their pioneer work on this reaction. It was not until 1954 that the reaction again received attention. Büchi and co-workers[28] found that only one (xii) of the two possible oxetanes (xii, xiii) was formed and suggested the following two-step mechanism involving attack of excited carbonyl compound on ground state olefin.

a) Attack of the oxygen of the excited benzaldehyde (xiv) on the C=C bond of the olefin in such a way as to give the more stable diradical intermediate (xv, not xvi).

b) Ring closure of the diradical (xv) to give the oxetane (xii).

Since this work was performed a large number of oxetane forming reactions have been observed. Bradshaw[29] has noted the formation of oxetanes from cyclohexene and terminal olefins with a variety of ketones and has rationalised his data in terms of the Büchi mechanism. Oxetanes have been observed in systems involving maleic anhydride, maleonitrile,

fumaronitrile[30] and quinones.[31] Irradiations involving dienes and p-benzoquinone have been found to yield the spiropyran (xvii)[32] in a reaction analogous to the oxetane-forming reaction of monoölefins. A formally related reaction is the photoaddition of monoölefins to o-quinones to give dioxanes[33] (xviii→xix). Oxetanes are produced in irradiations involving fluoroaldehydes and fluoroketones with fluoro-olefins,[34] and oxetenes (xxi) have been postulated as intermediates in reactions involving acetylenes[35] (xx→xxii). Intramolecular oxetane formation has also been recorded. Work initiated by Srinivasan[36a] has been developed by Yang[36b] on the internal oxetane formation of γ,δ-unsaturated ketones (xxiii→xxiv and xv). Aromatic aldehydes commonly yield oxetanes with olefins but this is much rarer with alkyl aldehydes, although examples do exist.[28,37] Crotonaldehyde has also been observed to form oxetanes.[38] Examples do exist of related apparently thermal reactions leading to the production of oxetane,[39] but the possibility that these reactions are light induced cannot be ruled out on the basis of the published accounts.

Although examples of the photochemical production of oxetanes are numerous, it is only recently that any advance has been made towards understanding the mechanism of their formation. Arnold and co-workers[40] have noted a close correlation between the ability of ketones to form oxetanes when illuminated with olefins and their power to abstract hydrogen photochemically. This suggested that the same $^3(n,\pi^*)$ state of the ketone was required for both reactions. It has recently been postulated that the $^1(n,\pi^*)$ state should exhibit similar reactivity but

that its short life is the factor preventing its detection in the cases investigated.[52] Arnold also reported that if the olefin in the olefin/ketone system irradiated possessed a lower triplet energy than that of the ketone, no oxetanes were formed but rather products derived from the olefin alone were observed. This is evidence that excited olefin produced by triplet-energy transfer from the ketone is not able to initiate the oxetane forming reaction.

Yang[41] has since extended this investigation by correlating the oxetane reaction with phosphorescence data. He showed that oxetane is produced efficiently if the $^3(n,\pi^*)$ state is the lowest excited state of the ketone. Oxetanes are formed in poor quantum yield when the $^3(\pi,\pi^*)$ state has lowest energy but evidence was advanced to suggest that the reaction observed might be that of an upper $^3(n,\pi^*)$ state.

Other products besides oxetanes have also been observed when ketones are irradiated with olefins. Thus, de Mayo[53] investigated the irradiation of acetone in cyclohexene and observed, besides the formation of the allylic substitution product (xxvi), the alcohol (xxvii) which he believed may have been produced by attack of a second excited acetone molecule on the oxetane first formed. The stereospecific formation of the ketone (xxix)[54] by irradiating acetone with norbornylene (xxviii) is the latest example to be described of a reaction first recorded by Kharasch.[55]

One other mode of photoaddition of carbonyl compounds to olefins merits special note. It has been stated that rare examples exist of alkyl aldehydes reacting with olefins to give oxetanes. More commonly saturated

ketones are obtained. Thus Kharasch[56] has observed that when acetaldehyde is irradiated with 1-octene, 2-decanone is produced (xxx→xxxi). Carbon monoxide and methane were evolved during the radiation and biacetyl was isolated from the reaction mixture. A radical chain mechanism[56,53] has been suggested for this reaction.

$$RCHO + h\nu \rightarrow R\cdot + \cdot CHO$$

$$R\cdot + RCHO \rightarrow RH + R\dot{C}O$$

$$R\dot{C}O + R'_2C{=}CR'_2 \rightarrow RCOR'_2C{-}\dot{C}R'_2$$

$$RCOR'_2C{-}\dot{C}R'_2 + RCHO \rightarrow \underline{RCOR'_2C{-}CHR'_2} + R\dot{C}O$$

$$RCOR'_2C{-}\dot{C}R'_2 + R'_2C{=}CR'_2 \rightarrow \text{polymer}$$

$$R\dot{C}O \rightarrow R\cdot + CO$$

$$R\cdot + RCHO \rightarrow RH + R\dot{C}O$$

$$2R\dot{C}O \rightarrow RCOCOR$$

The formation of 1:1 photoadducts between olefins and carbonyl compounds has few parallels in other branches of photochemistry. The formation of cyclobutanes from olefins in light, although formally analogous to the oxetane reaction, in fact differs considerably for the important (n,π^*) states are lacking in olefins. The literature dealing with the photochemical formation of cyclobutanes is extensive.[42,43]

Very few cases are known of the photoreactions of $n\rightarrow\pi^*$ analogues of carbonyl compounds yielding products corresponding to oxetanes. For the general photochemistry of molecules containing the C=N and N=N chromophores, the reader is directed to two reviews.[44] Syn↔anti-

photoisomerisation, analogous to the cis↔trans isomerisation reaction is known.[19,20] The photochemical conversion of nitrones to oxaziranes (xxxii→xxxiii)[45,46] is believed to be a singlet state reaction[19] and is but one example of a more general photochemical reaction[47] (xxxiv→xxxv).

There is evidence[48] that the thermally unstable material (xxxvii) is formed when a pyrazolenine (xxxvi)is irradiated by a reaction apparently similar to that producing oxetane from carbonyl compounds and olefin. The 1,2-diazetidine (xxxix) has been postulated[49] as an intermediate in the photochemical formation of azocompounds and olefins from Schiff's bases (xxxviii→xl) and the thietane (xlii) has been invoked to explain photochemical products obtained from thiobenzophenone and olefin (xli→xliii).

A related cyclic intermediate (xliv) has been postulated in the photoreaction of nitrobenzene with olefin[51]

The purpose of the work described in this thesis was threefold.

Firstly, it was considered valuable to extend the study of the mechanism of oxetane formation with ketones from olefins to α,β-unsaturated esters to observe whether the modification of theenergy levels of the molecule produced by the ester group affects the mode of the reaction.

Secondly the study of the photochemistry of C=X/C=C systems (where 'X' is a heteroatom) was extended from ketones to oximes to note any differences in behaviour attending the variation of X.

Thirdly an investigation of the photochemistry of aldehyde/olefin mixtures was conducted in order to discover the nature of the photochemically active excited species produced.

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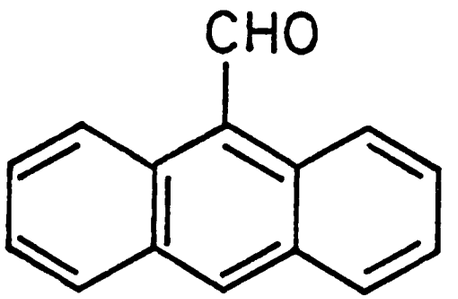
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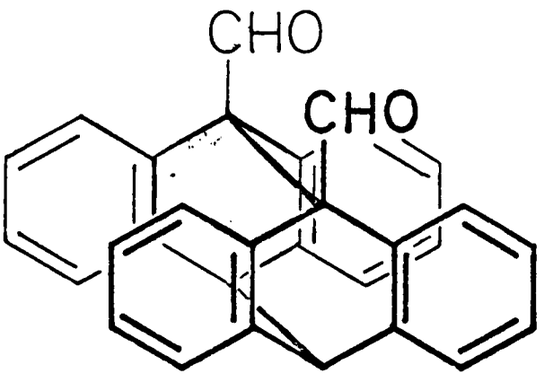
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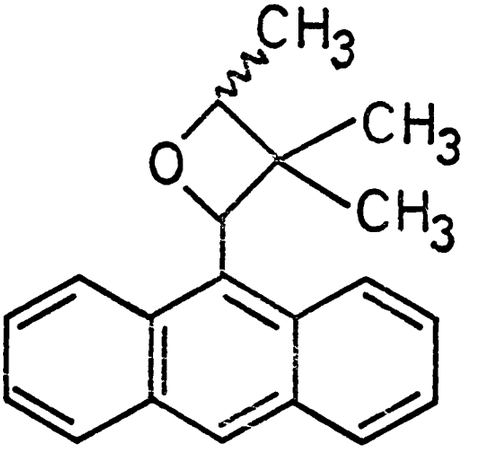
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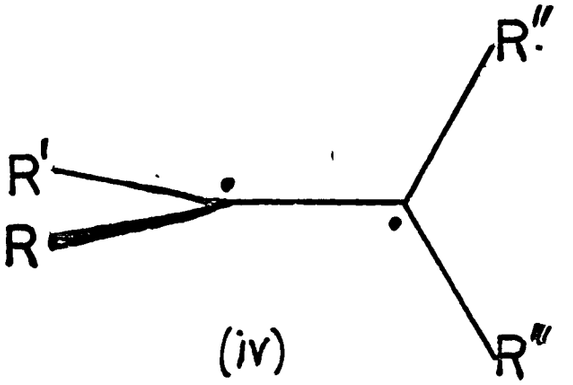
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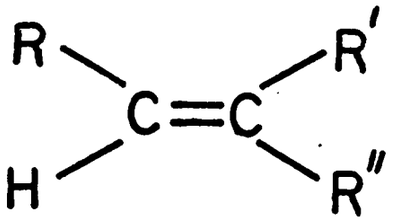
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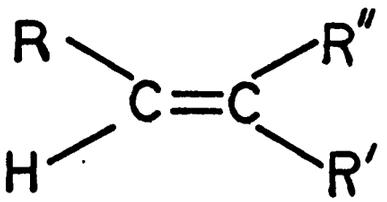
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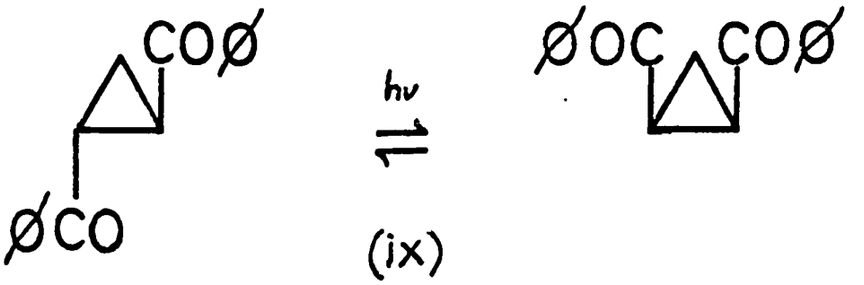
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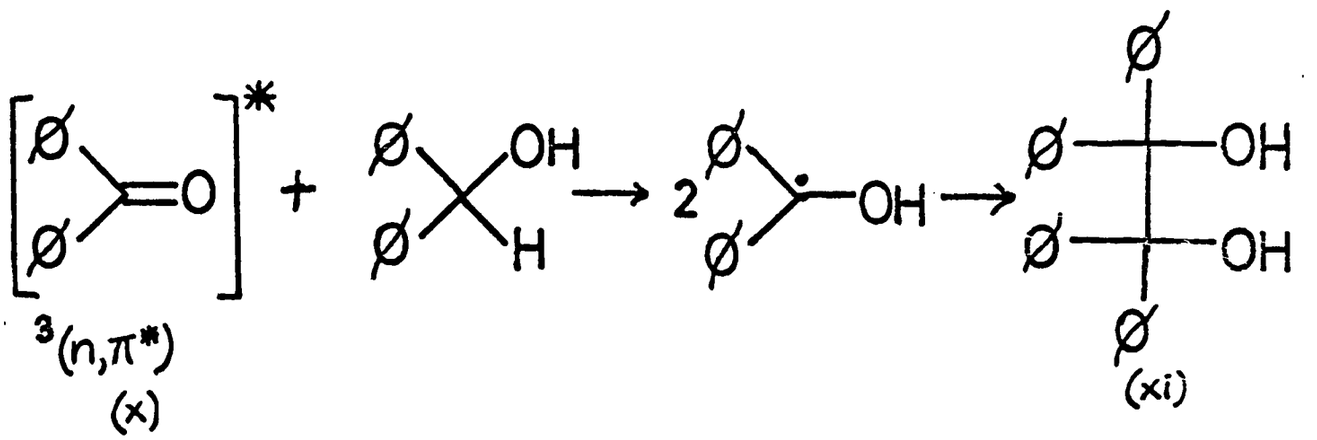
⇅ hν



	R	R′	R″
(v)	Ø	Ø	H
(vi)	Ø	Ø	CH_3
(vii)	CH_3	$CH{=}CH_2$	H
(viii)	$CO_2C_2H_5$	$CO_2C_2H_5$	H

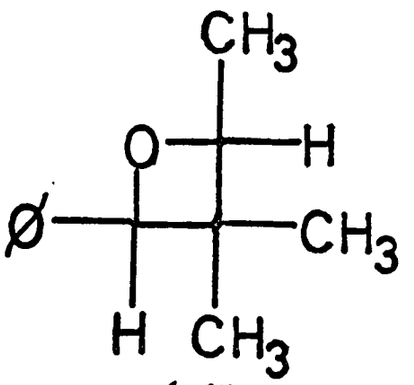


(ix)

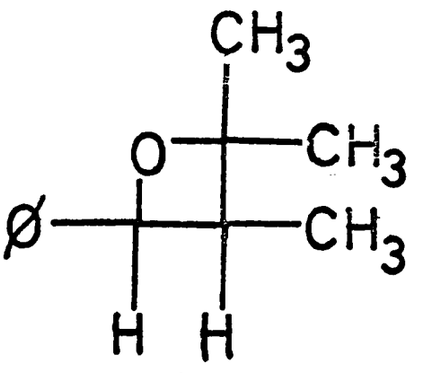


$^3(n,\pi^*)$
(x)

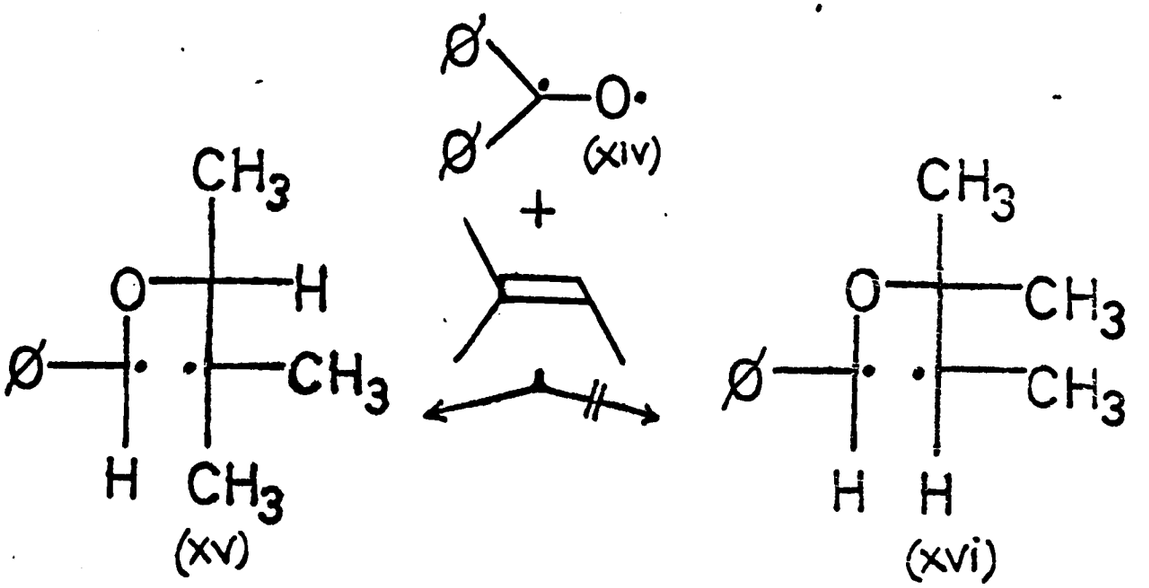
(xi)



(xii)



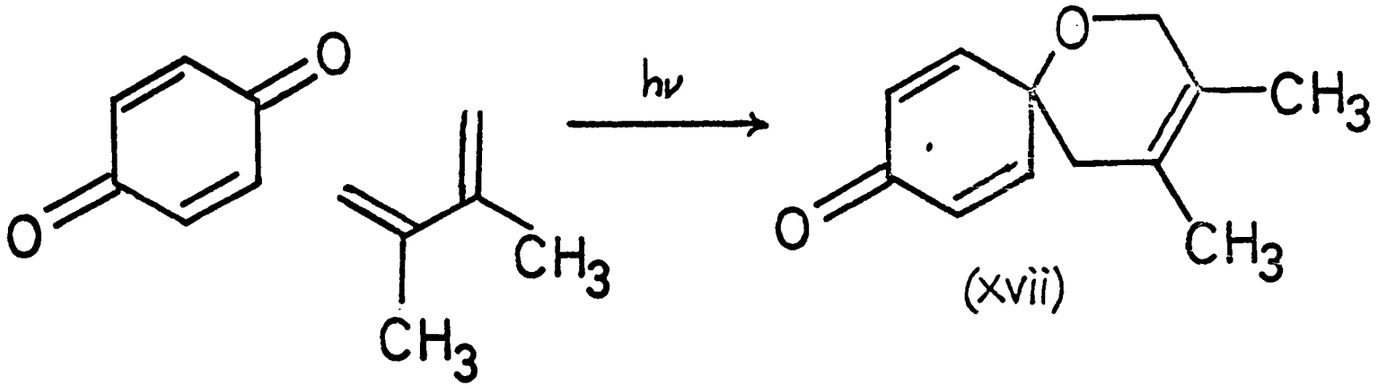
(xiii)



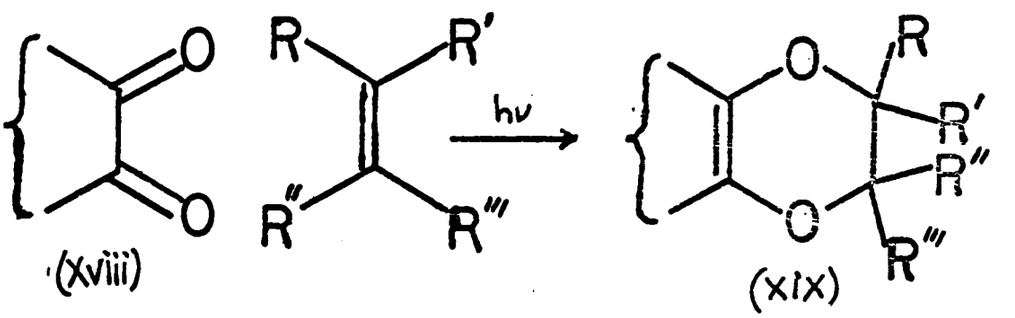
(xiv)

(xv)

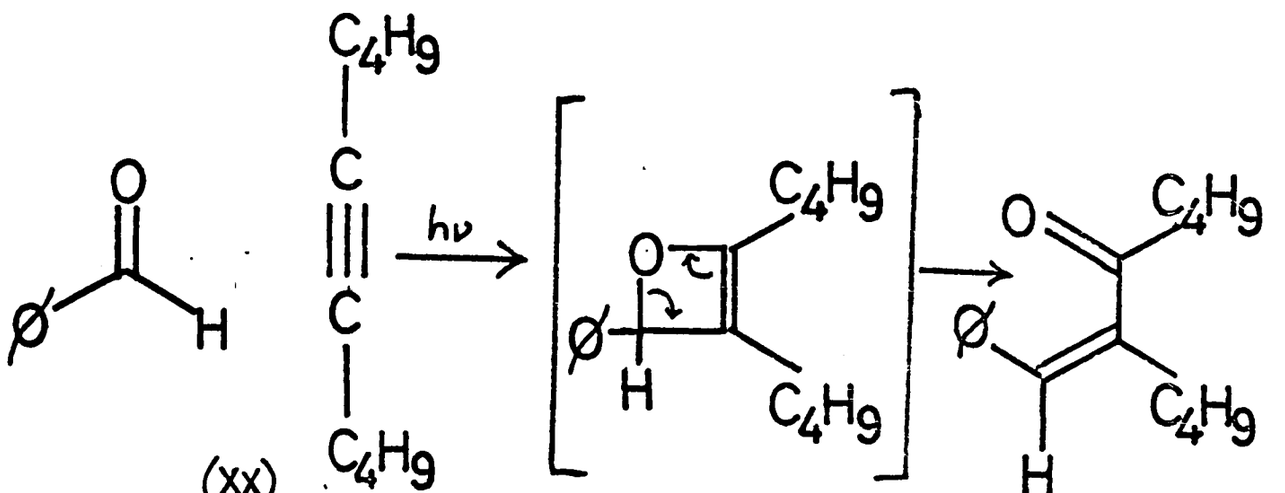
(xvi)



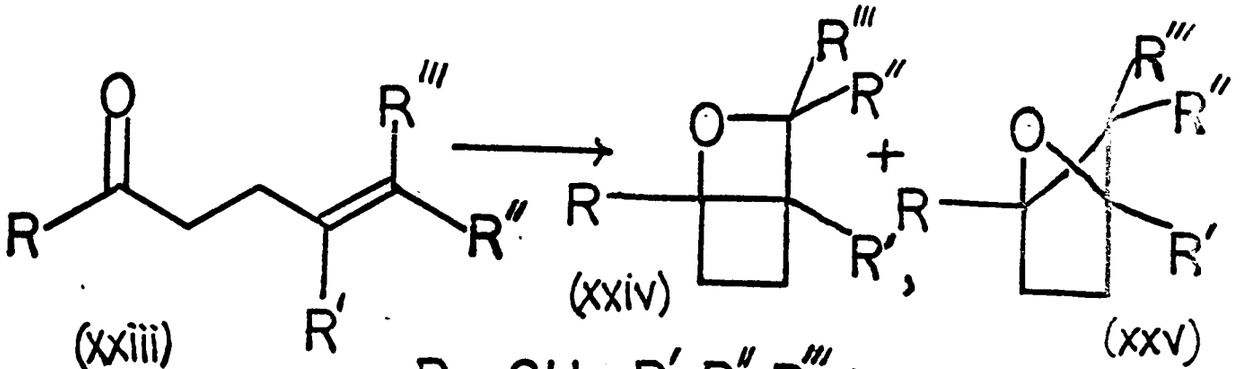
(xvii)



(xviii) (xix)

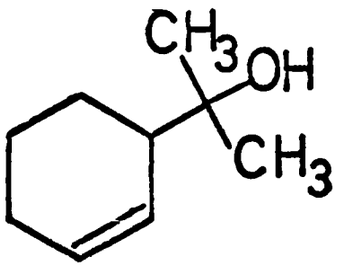


(xx) (xxi) (xxii)

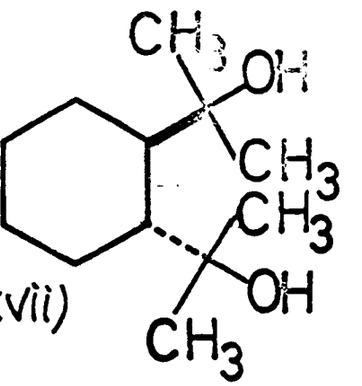


(xxiii) (xxiv) (xxv)

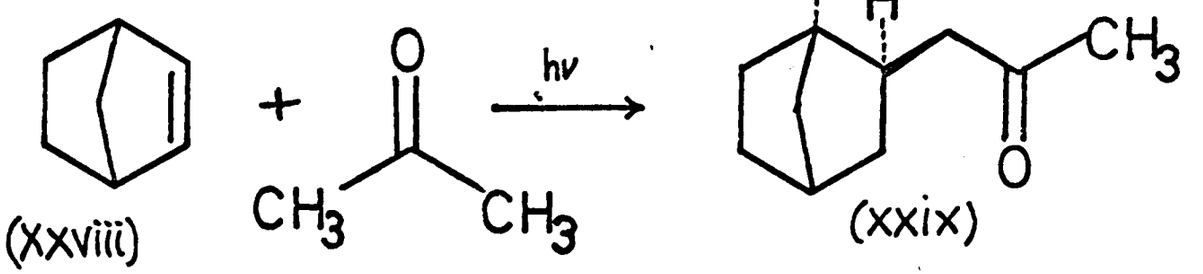
$R = CH_3$; $R', R'', R''' = H$ or CH_3.



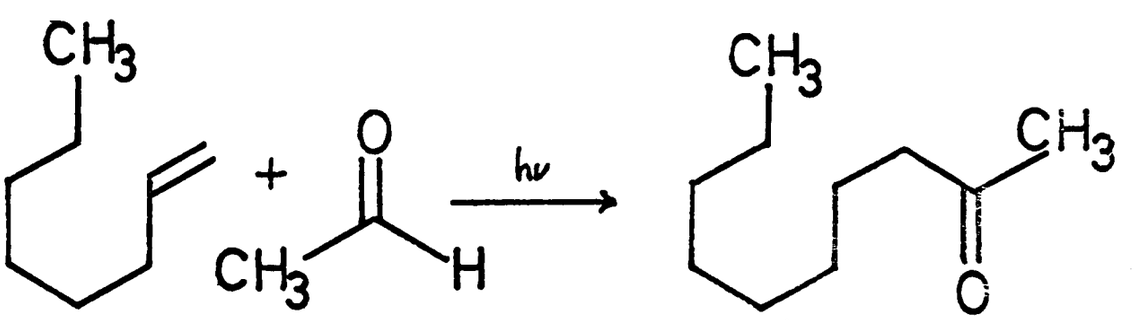
(xxvi)



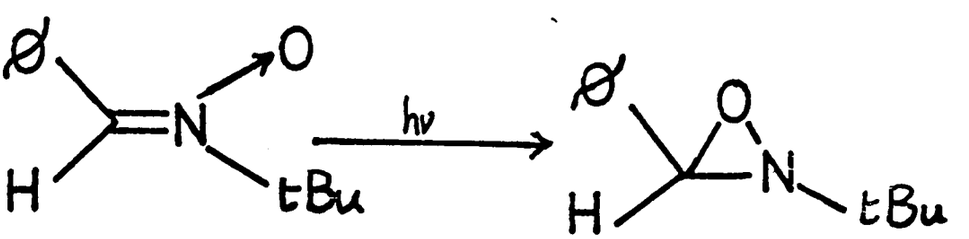
(xxvii)



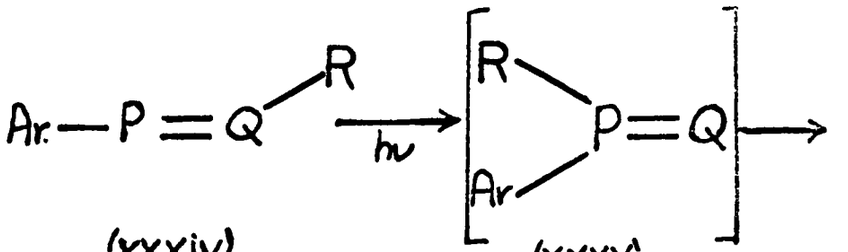
(xxviii) (xxix)



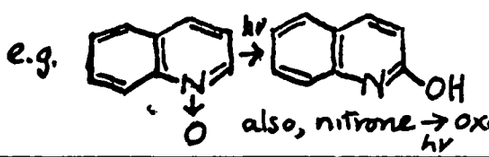
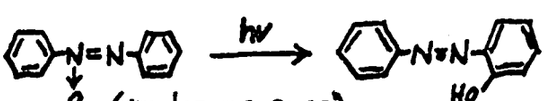
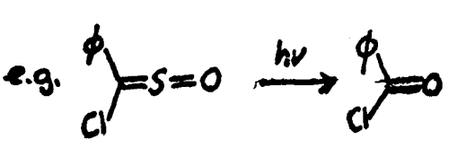
(xxx) (xxxi)

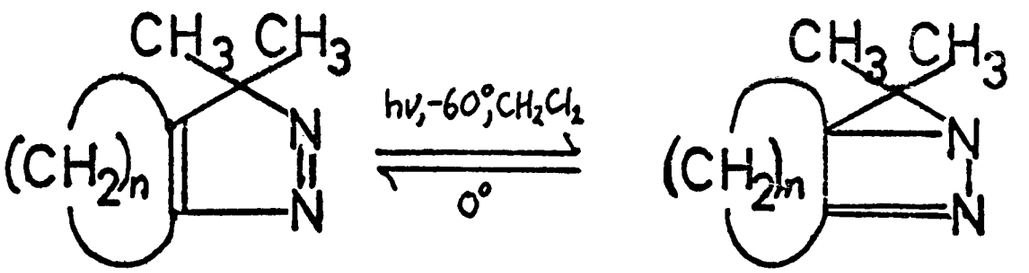


(xxxii) (xxxiii)

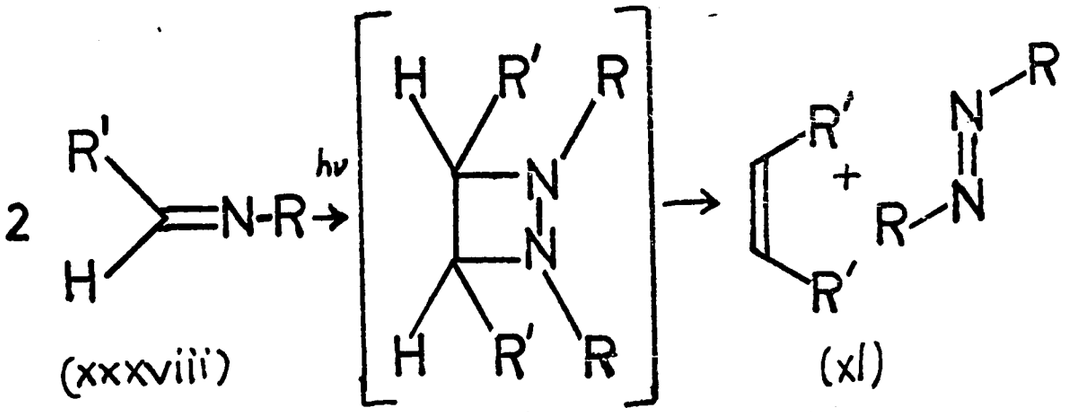


(xxxiv) (xxxv)

P	Q	R
C—H	N	O—H
e.g. $\phi CHNOH \xrightarrow{h\nu} \phi CONH_2$		
C—H	$\overset{+}{N}$—C	$\bar{O}$
e.g.  also, nitrone $\xrightarrow{h\nu}$ oxaziranε.		
N	$\overset{+}{N}$—C	$\bar{O}$
e.g.  (vinylogous case)		
C—Cl	$\overset{+}{S}$	$\bar{O}$
e.g. 		



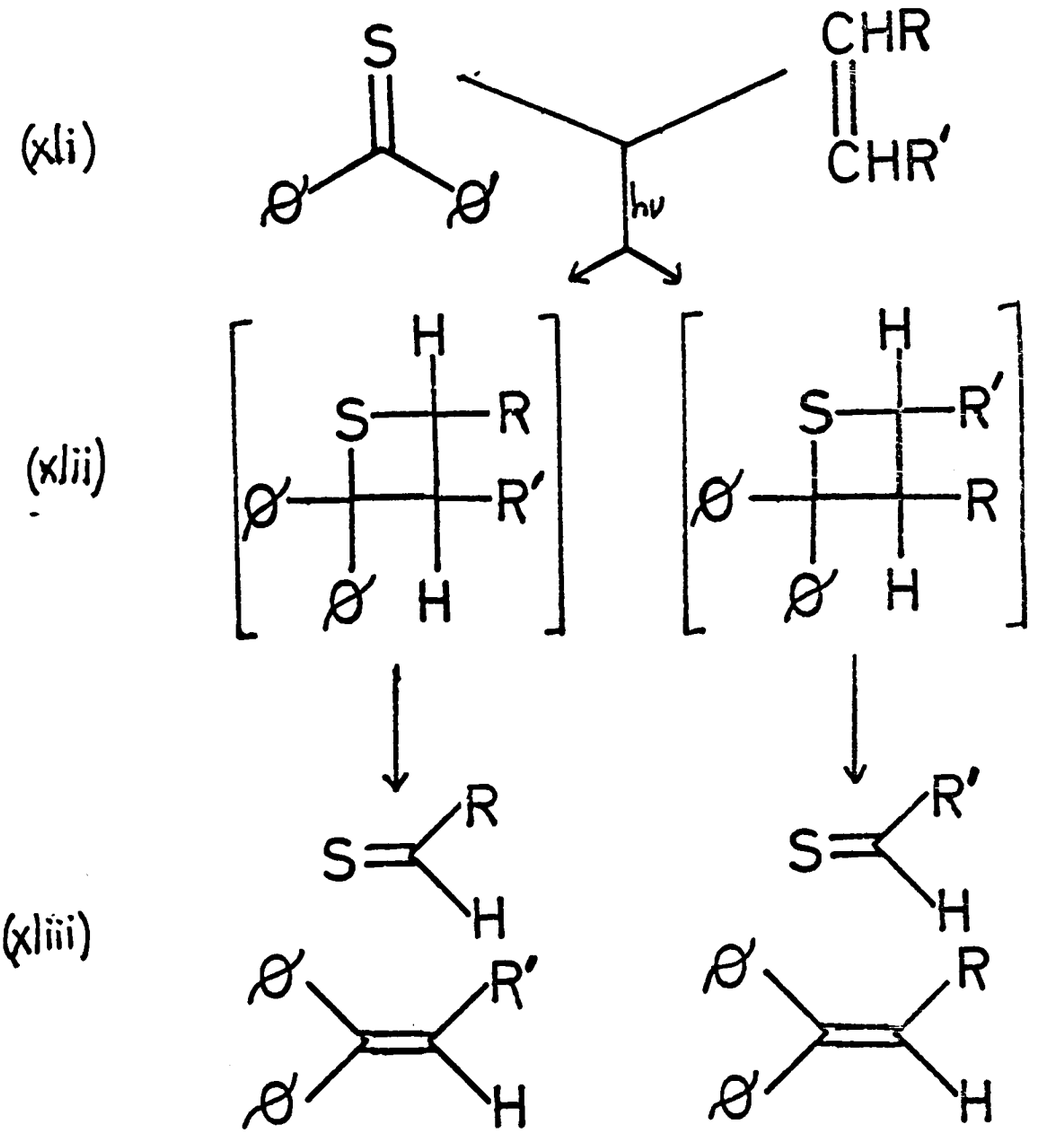
(xxxvi) n = 4, 5. (xxxvii)



(xxxviii) (xxxix) (xl)

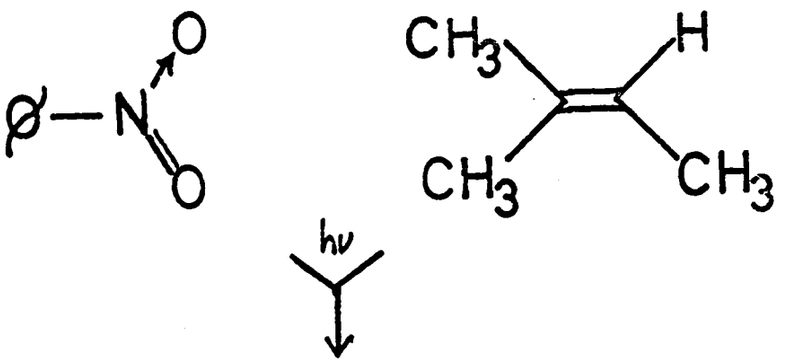
R , C_6H_5-

R′ , p$(CH_3)_2N$-C_6H_4-

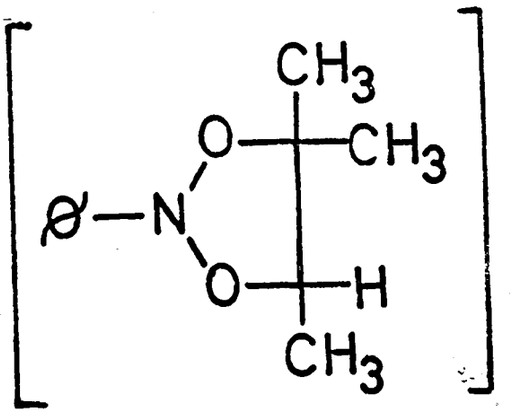


(xli) (xlii) (xliii)

R	CH_3	OR	H
R′	CH_3	OR	C_4H_9



(xliv)



Many products.

PART ONE - DISCUSSION

Section I

THE PHOTOCHEMISTRY OF THE SYSTEM: DIMETHYL MALEATE/DIMETHYL FUMARATE/ACETONE

Chapter 1: General Discussion

A) The absorption of ultraviolet light in this system

The ultraviolet absorption spectra of acetone, of dimethyl maleate and of dimethyl fumarate have been recorded by N.A. Sörensen.[1] The absorption bands measured in hexane solution have the following characteristics.

	$\lambda_{max}(m\mu)$	$\log\epsilon_{max}$
dimethyl fumarate	208.7	4.5160
dimethyl maleate	192.76	4.3404
acetone	186.36	3.069
acetone	274.68	1.146

W.D. Closson, S.F. Brady, E.M. Kosower and P.C. Huang have examined the ultraviolet spectra of a series of α,β-unsaturated esters.[2] In every case examined, solvent shift experiments revealed that the intense absorption in the region of 200 $m\mu$ wavelength is due to an electronic $\pi \rightarrow \pi^*$ transition of the unsaturated ester. In a number of cases examined, a weak shoulder was also observed on the long wavelength side of this peak and this was ascribed to an $n \rightarrow \pi^*$ transition of the molecule. Thus, with diethyl fumarate and diethyl maleate, the following observations were made.

	Solvent	λ_{max} (mμ)	ϵ_{max}	Description
diethyl fumarate	isooctane	260	~250	Shoulder; $n \rightarrow \pi^*$
diethyl fumarate	isooctane	209.8	17000	$\pi \rightarrow \pi^*$
diethyl fumarate	water	211.5	17500	$\pi \rightarrow \pi^*$
diethyl maleate	isooctane	193.7	11700	$\pi \rightarrow \pi^*$
diethyl maleate	water	195.5	11500	$\pi \rightarrow \pi^*$

The $n \rightarrow \pi^*$ absorption was only observed with diethyl fumarate in a non-polar solvent. In all other cases it was thought to be submerged in the intense $\pi \rightarrow \pi^*$ absorption band. As no evidence was forthcoming concerning the $n \rightarrow \pi^*$ transition of diethyl maleate even in non-polar solvents, it was concluded that the energy separation between the singlet-singlet $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions was probably smaller in diethyl maleate than in diethyl fumarate.

The 274.68 mμ band of acetone has long been known to result from and $n \rightarrow \pi^*$ transition. A comprehensive review of the ultraviolet spectra of molecules containing non-bonded (n) electrons has been given by J.W. Sidman.[3]

B) Charge-transfer absorption[4]

Approximately 0.2M solutions of dimethyl maleate and of dimethyl fumarate in acetone respectively were examined spectrophotometrically in a 0.1 mm cell balanced against a 0.1 mm cell containing pure acetone. No spectral evidence was obtained at wavelengths greater than 240 mμ to indicate the possibility of charge-transfer complex formation.

C) On the nature of the exciting radiation employed

All irradiations conducted in the present work were performed using a 500 watt medium pressure mercury arc. Information concerning the relative output of radiant energy at various wavelengths from a typical lamp of this kind is given in Table I. The photochemical reactors employed with this light source were constructed of quartz or of borosilicate glass. The quartz apparatus permitted all light of wavelength greater than 200 mμ to enter the irradiated solution whereas the borosilicate glass apparatus was opaque to light of wavelength less than 280 mμ. The variation of transmission properties with wavelength of a 4 mm. thickness of quartz and of a 4 mm. thickness of borosilicate glass are represented graphically in Figure I.

The data given in Table I and in Figure I are based on information supplied by the manufacturers of the apparatus concerned.

At the concentrations employed in the photochemical investigation of the system: dimethyl maleate/dimethyl fumarate/acetone, incident radiation is absorbed both by the unsaturated ester and by acetone if quartz apparatus is used, whereas if borosilicate glass apparatus is used only about 1% of the incident light absorbed by the solution directly excites the unsaturated ester. The use of borosilicate apparatus also reduces considerably the total rate of absorption of light energy by the system relative to irradiations conducted in quartz. For a more detailed examination of this question, see page 57.

D) Preliminary irradiations. Photochemical products

An approximately 0.2M deoxygenated acetone solution of dimethyl

fumarate was irradiated for 18 hours using quartz apparatus and the crude irradiation product was examined by gas chromatography. The chromatogram indicated the formation of a single major product with a retention time considerably in excess of that of dimethyl fumarate. The product peak accounted for ~80% of the total peak area of the entire chromatogram.

Peaks of small amounts of six other components including dimethyl maleate and a trace of dimethyl fumarate were also observed on the chromatogram.

The major component was isolated by preparative gas chromatography of the irradiation product. Molecular weight determinations using a mass spectrometer indicated the material to be a 1:1 adduct of dimethyl fumarate to acetone. Because the parent peak was weak, the molecular weight was confirmed osmometrically. Elemental analyses further confirmed this formulation. The absence of hydroxyl absorption and the presence of strong absorption bands at 1043, 1022 and 975 $cm.^{-1}$ in the infrared spectrum[5] as well as the absence of ketonic absorption in the ultra-violet spectrum suggested that the material was an oxetane adduct. This was confirmed by an examination of the n.m.r. spectrum.

P.W. Grubb obtained an oxetane from the irradiation of maleic anhydride in acetone.[6] This he hydrolysed and methylated to give authentic 2,2-dimethyl-cis-3,4-dimethoxycarbonyloxetane,(I). This was found to have spectral properties very similar to, but different from, those of the oxetane produced in the dimethyl fumarate/acetone irradiation. The retention times of the two oxetanes on the analytical gas chromatograph

also differed, Grubb's material being somewhat more firmly held on the column.

However Grubb's compound was found to have retention times on a number of gas chromatography columns which were identical with those of one of the minor photoproducts of the dimethyl fumarate/acetone irradiation. This minor component was only isolated when the Model 770 F and M preparative gas chromatograph was commissioned by this laboratory. It was then found to be identical in all respects with Grubb's compound. It was postulated that the major product from the irradiation of dimethyl fumarate in acetone was the stereoisomeric oxetane, namely 2,2-dimethyl-trans-3,4-dimethoxycarbonyloxetane,(II).

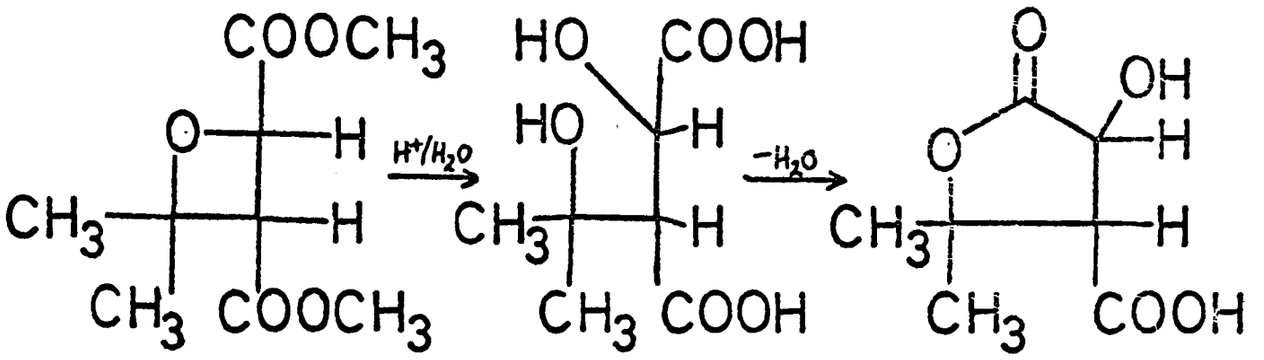
The n.m.r. spectra of these compounds are recorded in Table II.

Equilibration experiments using sodium methoxide in dry methanol conducted on Grubb's compound and on the oxetane obtained from the dimethyl fumarate/acetone irradiation confirmed that these two compounds were stereoisomers. Whether the known cis-oxetane diester or the postulated trans-oxetane diester were used, a mixture of the two oxetanes in the constant ratio

90% supposed trans-oxetane diester : 10% cis-oxetane diester

was obtained.

The supposed trans-oxetane was also hydrolysed using concentrated aqueous hydrochloric acid to give a lactone, thought to be 3-hydroxy-5,5-dimethyl-γ-butyrolactone-4-carboxylic acid,(III), presumed to be formed by the route



The following additional preliminary irradiations were also conducted, using solutions of approximately the same concentration irradiated for the same length of time. In each case the product was examined by gas chromatography.

(a) Dimethyl maleate irradiated in acetone using quartz apparatus. The trans-oxetane diester, the cis-oxetane diester, dimethyl maleate and at least three other components were present in the crude product. The ratios of concentrations of these compounds were much as in the dimethyl fumarate/acetone/quartz case, the trans-oxetane diester greatly predominating. This can be rationalised on a number of bases, one of which is that the known photochemical cis ↔ trans isomerisation reaction led to the same photostationary ratio of dimethyl maleate : dimethyl fumarate very rapidly in comparison with the rate of the oxetane forming reaction, both when dimethyl maleate and when dimethyl fumarate were irradiated in acetone. This was particularly likely in the case of quartz irradiations since here the unsaturated ester molecules absorbed a considerable proportion of the incident radiation.

(b) i) Dimethyl maleate irradiated in acetone using borosilicate glass apparatus.

ii) Dimethyl fumarate similarly irradiated.

In both these cases, the photoreactions were much slower than in the quartz cases. This was expected since the total active flux transmitted by borosilicate glass is much less than is transmitted by quartz. However, the occurrence of cis↔trans isomerisation of the unsaturated ester was observed to the extent that the major component in the reaction product from both borosilicate irradiations was dimethyl maleate, dimethyl fumarate being present only to about one fifth of this amount. The trans-oxetane diester was the only major long retention-time product together with a very little material of slightly longer retention-time. In contrast with the products of the quartz irradiations, no other minor components were observed on the gas chromatograms.

E) General principles of a mechanistic investigation

Any detailed mechanistic examination of this system is complicated by the fact that even when borosilicate apparatus is used, two different photochemical reactions occur simultaneously, namely the photochemical cis↔trans isomerisation of the unsaturated ester and the photochemical formation of oxetane. By considering the inter-relation of these two reactions it was hoped to obtain insights into the mechanism of each reaction. The possibility of the formation of cyclobutane derivatives by the photochemical dimerisation of maleic or fumaric ester had also to be considered.

Because of the cis↔trans photoisomerisation reaction of the

unsaturated ester, it is likely to be difficult to interpret data obtained from a study of the reaction mixture after a significant irradiation time, since, at times after the lamp has been switched on, the photochemistry exhibited by the system is that of mixtures of varying proportions of dimethyl maleate and dimethyl fumarate in acetone. Additionally there are complications because the cis- and trans-oxetane diesters themselves are unstable to differing extents under the irradiation conditions used (see page 28).

Other difficulties attending any quantitative investigation of a photochemical reaction involve the effects of the progressive formation of polymer film on the reactor walls cutting down light transmission to the solution and also possible effects following any significant warming of the solution by absorbed radiation which might occur in spite of the cooling techniques employed. Both these effects are likely to be more important when quartz apparatus is used than when borosilicate glass apparatus is employed.

In any detailed examination of reaction mechanism, it is important to know whether the reaction products investigated are produced by a single reaction or by a secondary reaction from a primary photoproduct.

A technique was employed to overcome these difficulties and which would determine whether a photoproduct was formed directly or by a secondary reaction from a primary photoproduct, provided that this primary photoproduct had more than a transitory existence in the reaction solution.

The technique was to examine the photochemistry of the system at time

zero; at the instant the lamp was switched on. At time zero, no change had taken place. No cis↔trans photoisomerisation had occurred. No polymer film had formed. No warming of the solution had taken place. At time zero, rates of secondary reactions were zero.

The method was to follow the reaction progress with time and to extrapolate back to find the reaction rates at time zero. Further insights could sometimes be obtained by considering the situation at times other than time zero, but such information was always likely to be very difficult to interpret.

Three series of experiments were undertaken. Although much effort was expended on the first two series of experiments, the main value of these experiments was not in the results obtained from them but in the development of an experimental technique. The final series of experiments, although open to some criticism, were of a kind on which a quantitative rather than a purely qualitative consideration of the mode of the photochemical reactions investigated could be based.

Brief mention is now made of the first two series of photokinetic experiments:-

F) The first series of photokinetic experiments

Only two experiments were conducted. A deoxygenated 0.22M solution of dimethyl maleate in acetone was irradiated in one case using a quartz reactor and in the other using apparatus of identical geometry but constructed of borosilicate glass. The irradiations were continued to in excess of 20 hours. The first sample was taken after 15 minutes irradiation and thereafter each sample was taken at very roughly twice

the irradiation time of the previous sample so that eight or nine samples in all were taken. In order to take a sample from the reactor the lamp was switched off and about 1 ml. of sample taken, after which the irradiation was recontinued. Each sample was examined using a Pye argon gas chromatograph but because of the very different retention times of the maleic and fumaric esters on the one hand and the oxetane diesters on the other, the samples were analysed twice, once using a low temperature to estimate the unsaturated esters and secondly using a higher column temperature to estimate the oxetane diesters. In this way well-formed resolved peaks were obtained. Peak areas were estimated by triangulation and rates of change of peak area ratios were taken as a measure of rates of change of concentration ratios of compounds under the influence of light.

Some of the results of this investigation are represented graphically in Figures II and III. The following observations are based on this data.

(a) Plots of the ratio of

$$\frac{\text{trans-oxetane diester peak area}}{\text{sum of unresolved peak areas of unsaturated esters in some chromatogram}}$$

against irradiation time are represented in Figure II. In the quartz case this function has an unambiguous positive gradient at time zero. In the borosilicate glass case, within experimental error, this function is zero up to an irradiation time of five hours when it begins to rise steeply, but its gradient is always less by a factor of more than ten than that in the quartz case.

It appears that dimethyl maleate did not form trans-oxetane diester with acetone when borosilicate glass apparatus was used, whereas when quartz apparatus was used, it did. The oxetane formed in the borosilicate irradiation seems to have been formed by some secondary process, possibly via initial photoisomerisation to dimethyl fumarate which then reacted further to form oxetane.

(b) Similar behaviour is observed from the cis-oxetane diester, although it was always present in smaller concentration than the trans-oxetane diester.

(c) Plots of the ratio $\frac{\text{dimethyl maleate peak area}}{\text{dimethyl fumarate peak area}}$ against irradiation time are represented in Figure III. The isomerisation of dimethyl maleate to dimethyl fumarate reached a photostationary state after between one and two hours irradiation in the quartz case and about two and a half hours irradiation in the borosilicate glass case. This indicates that the excited state of acetone probably photosensitized the cis$\leftrightarrow$trans isomerisation of the unsaturated ester.

In the borosilicate glass case, this photostationary ratio remained constant at a value of 5 even up to an irradiation time of twenty-two hours. This stability of the photostationary ratio contrasts with its slow reduction in the quartz case.

G) The second series of photokinetic experiments

A more extensive survey of the reaction was implemented with the following improvements in technique.

(a) Absolute concentrations were estimated from the chromatogram

traces by selecting a marker which gave a well-formed peak at a convenient retention time and by making each sample up to a standard concentration in this marker after it was removed from the reactor.

For these experiments 2-methylquinoline was found to be a suitable marker.

All solutions were examined gas chromatographically without further manipulation, such as warming to evaporate off some of the solvent, as this could possibly have changed the concentration ratios in the sample.

(b) More frequent samples were taken at shorter irradiation times.

(c) Each solution irradiated was maintained deoxygenated and well stirred by passing a stream of nitrogen through the solution during the experiment.

(d) It was important that the level of solution in the reactor remained constant during the irradiation. Diminution in volume could be caused by evaporation of acetone as well as by the loss which occurred as samples were taken. The evaporation of acetone was greatly accelerated by the nitrogen stream maintained through the solution during irradiation. In order to minimise this the nitrogen was first saturated with acetone vapour before being led to the reactor.

The remaining small diminutions in solution volume occurring as samples were taken was offset by adding antibumping chips in the well of the reactor. This had the advantage of maintaining the absorbing surface area of solution presented to the lamp constant without varying solution concentration. This practice was abandoned in the final series of experiments as it was thought that the inhibition to efficient mixing presented

by having antibumping chips in the reactor was a potential source of considerable error even though the nitrogen stream through the solution was so directed to minimise this effect.

Irradiations were conducted using quartz and borosilicate glass apparatus, in each case conducting two experiments, one starting with 0.22M dimethyl maleate in acetone and the other starting with 0.22M dimethyl fumarate. A fifth experiment using 0.58M dimethyl fumarate in acetone was conducted using the quartz apparatus.

The results from this examination are represented graphically in Figures IV-XII. The following observations are based on this data.

(a) Using borosilicate glass apparatus.

(i) Dimethyl fumarate/acetone irradiation.

The trans-oxetane diester was formed from time zero whereas cis-oxetane diester was not observed until the reaction had progressed for five hours. The rate of formation of cis-oxetane diester was then observed to increase progressively with irradiation time. Thus, the cis-oxetane diester was not a primary photoproduct of this irradiation.

The dimethyl fumarate concentration decreased rapidly at first, less rapidly later, reaching a constant value after about twelve hours irradiation.

(ii) Dimethyl maleate/acetone irradiation. Isomerisation to dimethyl fumarate proceeded from time zero but the initial rate of formation of oxetane was very small. At no stage during the entire irradiation was there more than a very little oxetane present.

(b) Using quartz apparatus.

(i) 0.22M Solution of dimethyl fumarate in acetone was irradiated. Photoreaction was much more rapid than when borosilicate glass apparatus was used. Photochemical cis↔trans isomerisation to reach a photo-equilibrium between maleic and fumaric esters was complete in approximately 45(x2) minutes. Thereafter the concentrations of both maleic and fumaric esters fell rapidly until, after about 12 hours, neither were present in the reaction mixture.

The trans-oxetane diester concentration rose rapidly initially but after about 30(x2) minutes irradiation, at which time the isomerisation to dimethyl maleate was nearing photoequilibrium, the rate of formation of oxetane became smaller. After 12 hours irradiation when the last traces of maleic and fumaric esters were finally consumed, the concentration of the trans-oxetane diester ceased to increase and began to fall steadily and was still decreasing at 40 hours irradiation time. This demonstrates the photosensitivity of the oxetane in acetone solution.

The cis-oxetane diester concentration also increased very rapidly in concentration up to about 10 hours irradiation time when it also reached a maximum value and began to decrease somewhat. The cis-oxetane diester appeared to be formed from time zero but because of the extremely rapid photoisomerisation of dimethyl fumarate to dimethyl maleate and because of the paucity of measurements at short irradiation times it was not possible to be certain that there was not an initial time lag of some minutes in the formation of the cis-oxetane diester which would indicate that it was formed by a secondary reaction. More detailed experiments in

the final series show that this is in fact the case.

(ii) 0.58M Solution of dimethyl fumarate was irradiated in acetone. In this case, a very obvious time lag of about 1 hour occurred before cis-oxetane diester was produced whereas the trans-oxetane diester was produced from time zero.

(iii) Dimethyl maleate/acetone irradiation. Both cis- and trans-oxetane diesters appear to be formed from time zero. In no case examined was the cis-oxetane diester produced at a rate which was more than a fraction of the rate of formation of the trans-oxetane diester in the same experiment.

H) The photochemistry of oxetanes

The reverse reaction of the photochemical oxetane forming reaction, namely the photodecomposition of oxetanes to olefins and ketones under the influence of short wavelength ultraviolet light, is known.(7)

Although the oxetane diesters produced in the system investigated have weak tail absorptions in the wavelength region of the irradiation employed in these experiments (see Figure XXXIX), the fraction of the incident radiation absorbed by them is likely to be small. However there is evidence that the oxetanes were not stable under the irradiation conditions used (see page 27).

Two crude experiments were devised to investigate the significance of this effect. Deoxygenated 0.049M acetone solutions of the trans-oxetane diester and cis-oxetane diester respectively were irradiated in a small water-cooled quartz reactor. Samples were taken from time to time and examined gas chromatographically.

(a) trans-Oxetane diester/acetone irradiation.

Although after two hours irradiation a little short-retention time material was observed to have been formed, the major component of the mixture was the trans-oxetane diester. After ten hours irradiation some trans-oxetane was still present although a large number of other components were also observed, the major peaks being at short retention time. Peaks corresponding in retention time to those of dimethyl maleate, dimethyl fumarate and a very small peak corresponding to the cis-oxetane diester were observed. Retention time data does not constitute proof of identity however. The dark appearance of the final product indicated some reaction had taken place to compounds not expected to be observable on the gas chromatogram. When the excess acetone was removed, the final product had a smell resembling that of acetoin. Its infra-red spectrum exhibited strong hydroxyl and carbonyl bands but treatment with Brady's reagent yielded only a very small amount of a derivative melting with decomposition over the range 251-254°.

(b) cis-Oxetane diester/acetone irradiation.

The cis-oxetane diester was observed to decompose to a large number of products, but much more rapidly than the trans-oxetane diester. After fifteen minutes irradiation, considerable quantities of the cis-oxetane diester were still present in the reaction mixture but after two hours irradiation it had almost all been destroyed. No peak which could be attributed to the formation of trans-oxetane diester was ever observed in this irradiation.

Thus, under the conditions used, the oxetanes are both unstable, possibly being attacked by excited acetone, and a large number of products are formed. The trans-oxetane diester is considerably more stable than the cis-oxetane diester, but even this is not so unstable that the photokinetic data on rates of its formation at time zero are likely to be in error.

I) The third series of photokinetic experiments

To this point, experiments gave a general impression of the overall photochemistry of the system under investigation. The third series of photokinetic experiments was devised to obtain reliable quantitative information concerning the photochemistry of the system at time zero.

(a) A critique of the experimental method.

(i) The Apparatus.

(1) The reactor.

In view of the poor geometry of the reactor available when these experiments were undertaken, it is surprising that consistent results were obtained at all. Efficient mixing of the irradiated solution is required during photochemical kinetic experiments. This is because molecules activated by the ultraviolet light are not distributed evenly throughout the body of the solution (unless the solution is light saturated) but are concentrated in the surface layers of the solution adjacent to the lamp. Because of the short lifetimes of the excited states produced by light, agitation makes no significant difference to this distribution but it does prevent the production of those concentration gradients within the solution which would arise from the accumulation of reaction products in

the region of the lamp and the associated formation of local concentrations of unused starting material in regions remote from it. Such concentration gradients would add greatly to the practical difficulties of sampling and to the interpretation of data at any time other than at time zero. Large concentration gradients would tend to make for large random errors in the final concentration-time plot. Even so, the concentration gradient of excited states which must inevitably exist in the region of the lamp must make detailed interpretations of photokinetic experiments more difficult.

The reactor employed is represented in Figure XIIIa. Two probes, one of borosilicate glass and one of quartz were available. The reactor construction was such that at any instant the bulk of the solution was in a region below the lamp, the lamp itself being surrounded by a thickness of solution of only 3.9 mm. As most of the light absorbed by the system was absorbed in the first fraction of a millimetre of solution, this arrangement provided a pathlength sufficient to absorb virtually all the light of photoactive wavelengths, but it could possibly have hindered efficient mixing of the solution.

All solutions were refluxed and finally cooled under nitrogen to deoxygenate them prior to irradiation. In order to ensure the exclusion of oxygen during the irradiation, dry oxygen-free nitrogen was bubbled continuously and rapidly through the reaction mixture from a source in the well of the reactor. This had the added advantage of providing efficient mixing of the solution to the extent that no effects which could be attributed to poor mixing were noted in the final data.

Many difficulties attending a photokinetic examination are considerably reduced if attention is restricted to an interpretation of the effects observed at time zero (see page 21). In this way any gradual monotonic changes in rate occurring during the course of the reaction as the result of side effects such as an increase in the, temperature of the reaction mixture owing to the proximity of the lamp or a formation of polymer film on the reactor walls cease to be a source of error. This is because the irradiation is commenced under standard conditions and because data obtained at times during the irradiation are used only to extrapolate back to time zero, so that any progressive changes in reaction conditions although altering the form of the concentration-time curves at times after the initiation of irradiation cannot vary the gradients of these functions at time zero. Even so, measures were taken to eliminate such changes as much as possible so that some insights could be obtained from an examination of the system at non-zero irradiation times. Thus, in all irradiations conducted with this apparatus, the cooling system was made as efficient as possible and measures were taken to prevent the progressive fall in the solution level in the reactor during irradiation. Because of the poor design of the reactor, a significant fall in the solution level could result from a small reduction in volume of the solution. Two reasons are advanced for this diminution in solution volume.

(A) Evaporation of acetone accelerated by the rapid stream of nitrogen passed through the solution. To alleviate this, the nitrogen used was saturated with acetone vapour by being passed through two acetone wash-bottles before being passed into the reactor.

(B) Progressive reduction in solution volume as samples were taken at intervals during the course of the irradiation. To counter this, after a sample had been taken, the volume of the solution was made up to a set mark on the reactor with acetone.

The importance of these corrections is not primarily associated with small changes in concentration as occur, for example, when acetone evaporates from the solution, but results from the reduction in the absorbing surface area presented to the lamp as the solution volume is reduced.

(2) The lamp.

The lamp used in these irradiations was a 500 watt Hanovia medium pressure mercury arc. Its age was about 220 hours running time initially. Information concerning the light transmission of the probes used and concerning the light output of a typical lamp at various wavelengths has already been presented (see Table I and Figure I).

In earlier experiments, calculations of reaction rates have been based on measurements of concentrations at a series of irradiation times and it has been assumed that, within narrow limits, the rate of production of ultraviolet energy by the lamp has been constant with time. Experiments now to be discussed have shown that this is not a valid assumption.

A photo-monitoring device was constructed using a photocell sensitive to ultraviolet and blue light and for which a linear response with incident light intensity over a considerable working range is claimed. This cell was mounted behind a filter of such a kind that the monitor was only sensitive to ultraviolet light of wavelengths 230 mμ - 420 mμ (see

Figure XIV). Light was directed into the monitor via a long tube fitted with a variable iris by means of a diffusing surface of magnesium oxide. This is illustrated in Figure XVa. The purpose of these accessories was to add a degree of control over the use of the photomonitor and to minimise the effect of small changes in the position of the arc within the apparatus with respect to the photomonitor as well as to provide a uniform and less intense illumination of the photocell surface. Magnesium oxide was considered to be a suitable material for use as an ultraviolet diffusing surface as spectral measurements performed on an aqueous solution of magnesium chloride revealed no absorption at wavelengths greater than 215 mμ.

The photocell was connected via a portable amplifier to a recorder and fluctuations in ultraviolet light output with time were recorded. In all following discussions, the assumption is made that the percentage fluctuation in output at any wavelength in the ultraviolet region is independent of the value of that wavelength; that is, when a fluctuation in output occurs, that all the ultraviolet lines are affected to the same extent.

On switching on the lamp, a monitor trace of the kind shown in Figure XVI was obtained. Two features were at once apparent.

(A) The lamp required time to achieve full ultraviolet output.

(B) The full output varied with time in a step-like fashion.

Fifty experiments were conducted over a period of a week using a lamp of age 150 hours running time in order to discover the mode and range of variations in the ultraviolet light output of the lamp. The lamp used

was of an identical model to that used in the photokinetic experiments. During this series of measurements, the relative positions of the component pieces of apparatus remained unchanged. The parameters investigated were

(A) the maximum recorder deflection produced by the lamp immediately after the initial warming-up period. This is designated 'h'.

(B) the time elapsing after switching on before this state was reached. This is designated 't'.

(C) the time elapsing after switching on the lamp before a recorder deflection of $\frac{h}{2}$ was reached. This is designated 'T'.

(D) $\frac{'A'}{B}$, where A is the integrated area under the recorder trace during the first five minutes of the lamp being switched on and where B is the area under the same trace during the second five minutes. These areas were estimated by cutting out the pieces of paper in question and taking their weights as being proportional to their areas. An analysis of the reliability of this method is given on page 131.

(E) the time elapsing between switching the lamp off in a previous experiment and switching it on again for the experiment under consideration. This is designated 'n' and is taken as infinite for values in excess 30 minutes.

(F) the root mean square mains voltage, 'V'.

An analysis of the data led to the following conclusions.

(A) 'h' does not depend on 'n' (from experiments 51-58) but a correlation exists with mains voltage 'V'. Although the lamp was fed from the mains via a transformer designed to reduce the influence of mains

voltage fluctuation on lamp output, a variation of ± 18% was observed in 'h' while 'V' varied by ± 2.4%. These figures are based on data from experiments 27-50, and these results are represented graphically in Figure XVII. From this, even allowing for experimental error, a positive correlation is deduced between 'h' and 'V'.

(B) When 'n' is infinite, 't' lies between 3.5 minutes and 5.3 minutes. 't' is not a precisely definable quantity as is seen from an examination of Figure XVI. Instead 'T', a quantity which could be measured with greater precision was observed. If $n = \infty$, T = 3.53 minutes with a standard deviation of 5.7%. 'T' was found to depend on 'n' (see Figure XVIII) but to be independent of 'V'.

(C) When 'n' is infinite, $\frac{'A'}{B}$ was found to be 0.462 with a standard deviation of 7.5%, so that, if the reaction velocity is proportional to the intensity of light used, then the first 5 minutes of irradiation are equivalent to only 2.3 minutes of subsequent irradiation from the standpoint of chemical change produced, all other factors being constant.

$\frac{'A'}{B}$ showed a dependence on 'n'. This is represented in Figure XIX.

(D) A crude examination of the influence of the relative disposition of the pieces of apparatus used in these experiments on the recorder deflection, 'h', showed that 'h' was very sensitive indeed to this factor. An account of this examination is given on page 122.

From these the following more general conclusions were drawn.

(A) In photokinetic experiments, it is advisable to monitor the light output of the source used and in calculations to use in place of the quantity time, the quantity $\int Idt$ where I is 'the intensity of the

output of the lamp at any instant' and t is 'time'. The total area under the photomonitor trace is a measure of this quantity and can be used as a basis for calculating corrected rates of reaction provided that

(i) the relative geometrical disposition of the appartus used remains constant.

(ii) the rate of the reaction studied is proportional to the light intensity. This is not always so.(8)

(B) Gross errors arise if the lamp is switched off for samples to be taken at intervals of the order of ten minutes or less, and if no photomonitor is used. It is advisable not to switch the lamp off while taking samples especially if short irradiation times are used.

(b) Reaction product analysis.

Gas chromatography was considered to be the most reliable and speedy means of accurately analysing the mixtures of compounds produced photochemically since,with it, it is possible to estimate with precision over over a very wide range of concentrations complex mixtures of substances with the minimum of preliminary manipulation. Although more rapid than other methods for analysing the particular mixtures encountered in this study, the method was extremely time-consuming.

(i) The Apparatus. In earlier experiments a Pye Argon gas chromatograph was used. This had the following disadvantages.

(1) This chromatograph is fitted with a β-ray detector. Such detectors are extremely sensitive. However, for quantitative work they are of doubtful reliability.

Thus, (A) for a given compound, the detector exhibits a linear relationship between chromatogram peak area and mass of compound passing

through the detector at one detector voltage setting only, and even the value of this voltage varies with column temperature.[9] In the second series of photokinetic experiments, a consistent difference in peak-area ratios was obtained using such a chromatograph depending on whether the measurements were conducted using a column temperature of 100° or 150°.

(B) The detector sensitivity is temperature dependent.

(C) Trace amounts of water vapour and even the air peak itself have been found to have an effect on the detector characteristics.[9]

From these considerations it follows that attempts to use β-ray detectors for quantitative work necessitate much preliminary calibration of the instrument and the use of elaborate precautions against error.

(2) The high thermal capacity of the instrument was a hindrance to the analysis of the mixtures which contained components of widely differing retention times.

All further experiments were conducted using a Perkin-Elmer F11 gas chromatograph. The advantages of this instrument are numerous.

(A) Utilisation of a flame-ionisation detector. Such detectors give a linear and reproducible concentration response provided they are not overloaded.

(B) Incorporation of a temperature programming device, making it possible to estimate with precision each component of a mixture in one estimation, even though the components may differ greatly in retention characteristics.

(C) Incorporation of an attenuator of very wide range, facilitating the estimation of compounds present in a mixture in widely differing

concentrations.

(ii) The estimation of chromatogram peak areas

Peak area estimation by triangulation is only satisfactory for well-formed symmetrical broad peaks. In the third series of photokinetic experiments, peak areas were estimated by cutting out the peak, noting the attenuator setting at which it was recorded and taking a value for its area as equal to its weight x the attenuator setting value. The mass of material represented by a peak is given by the area so calculated x a calibration factor specific to the compound estimated which is determined in a separate experiment.

Provided the chromatograph was not overloaded and the peaks were not too small, this method of estimating peak areas was found to be as precise as is claimed for estimations using a planimeter (see page 131).

(c) General Experimental Approach

Six experiments were conducted, two using quartz probes and two using borosilicate glass probes. With each probe, 0.23 M deoxygenated acetone solutions of dimethyl maleate and of dimethyl fumarate respectively were irradiated. With the quartz probe, two additional experiments were conducted using 0.025 M and 0.47 M solutions of dimethyl fumarate in acetone.

In each case the photomonitor was incorporated and samples taken more frequently than in the previous series of experiments. The photomonitor and screen were so placed that that light which was monitored was that which came directly from the lamp without first passing through the irradiated solution. To achieve this the lamp was not inserted to its

full extent into the probe and the diffusing screen placed above the irradiation apparatus (see Figure XVb).

1 ml. samples were taken from time to time during each irradiation without first switching off the lamp. A constant volume of marker solution, in this case a standard solution of methyl salicylate in acetone, was added to each sample which was then analysed gas chromatographically without further manipulation. A typical gas chromatogram of this kind is represented in Figure XX. It was previously verified that, under the conditions employed in the gas chromatograph, the components were thermally stable.

During irradiation precautions were taken to keep the solution deoxygenated and well-mixed and care was taken to keep the level of the solution in the reactor constant.

(d) Errors

Errors were of three types.

(i) Errors which gradually and monotonically increased as the irradiation proceeded. As was explained on page 32, these errors had no significance with regard to an estimation of rates of formation at time zero.

(ii) Errors introduced between experiments and which are important when the results of one irradiation are compared with those of another. In comparing results obtained in different irradiations, but within the same series of irradiations, that is, within either the quartz series or the borosilicate glass series, it must be assumed that

1) the ~~quartz~~ probe had the same transmission properties

initially in the two irradiations compared. This was probably so if the apparatus was cleaned thoroughly between irradiations.

2) the same light flux emitted by the lamp caused the same monitor recorder deflection in each case.

It has been noted that this deflection is very sensitive to the relative positioning of the component pieces of apparatus. Since partial dismantling was necessary between experiments to clean the apparatus, an elaborate system of markings and rigid supports was devised to enable the apparatus to be reassembled reproducibly and to prevent the introduction of error at this point. However no further check was instituted to verify that this was so, as it was difficult to see how such a check could be incorporated.

The ratio $\frac{\text{integrated area under the photomonitor trace}}{\text{irradiation time}}$ was found to vary from experiment to experiment but to remain within the observed range of fluctuations of light output of the lamp (see pp.35,47). This was only so for comparisons within the quartz series of experiments or within the borosilicate glass series. For comparisons between the two series of irradiations this ratio was greater than could be accounted for on the basis of lamp output fluctuation. The origin of these variations was the very slightly different geometries of the borosilicate probe and the quartz probe and the different optical properties of these two materials although conditions were designed to minimise these effects by, for example, sampling light for the photomonitor from above the reactor.

The only possible means of comparing rates between the two series of

experiments is to ignore lamp fluctuations and to compare rates calculated not on the basis of integrated light intensity units as recorded by the photomonitor, but on the basis of the quantity 'time'. This introduces the possibility of error of up to ± 20%. Such an error is only introduced if rates are compared. If ratios of rates are compared between the two series, rates calculated on the basis of integrated light intensity units can be compared with precision.

3) the solution presents the same absorbing surface area to the lamp in the irradiations compared.

(iii) Random experimental error of concentration determinations during one irradiation. Random error arises from the following causes.

(a) Random error in preparing each sample for chromatographic analysis. 1 ml. (or 2 ml.) of reaction mixture was taken from the reactor and 50λ (or 100λ) of marker solution added to it. The error in preparing the marker solution itself did not contribute to the random error but did contribute to the absolute error of all points determined using that marker solution.

The 2 ml. standard flasks used to make up samples were assigned an error of ± 0.04 ml. by the manufacturers. Arbitrarily the micropipette used to add marker to the sample was assigned the same percentage error.

(b) Random error in peak weighing. An investigation showed that peak areas of the order of one square inch could be estimated to a precision of ~1.3% by this means.

(c) Other sources, such as error in the attenuator settings of the gas chromatograph, were ignored. The various attenuator settings were

only comparable to $\frac{1}{2}$% or to 1% (see page 124), so this was not strictly correct. However, the complications following a consideration of such factors are very great and for the purposes of a crude estimation of random error were not considered.

An estimation of random experimental error in concentration determinations during one irradiation

Let 'D' represent the compound being estimated and 'M' represent the marker.

Then peak-ratio of D =

$$\left(\frac{\text{weight of peak produced by D}}{\text{weight of peak produced by M on the same chromatogram}}\right) \times \left(\text{ratio of attenuation factors}\right)$$

Also, concentration of D = (concentration of M) x (peak ratio of D) x (calibration factor). If $\sigma(x)$ is the standard deviation of a quantity x and $\bar{x}$ is the mean value of that quantity

$$\frac{\sigma^2(\text{peak ratio})}{(\overline{\text{peak ratio}})^2} = \frac{\sigma^2(\text{peak weight D})}{(\overline{\text{peak weight D}})^2} + \frac{\sigma^2(\text{peak weight M})}{(\overline{\text{peak weight M}})^2}$$

$$+ \frac{\sigma^2(\text{volume sample taken})}{(\overline{\text{volume sample taken}})^2} + \frac{\sigma^2(\text{volume marker added})}{(\overline{\text{volume marker added}})^2} \text{ approximately}$$

~~if $(\overline{\text{peak weight D}}) \sim (\overline{\text{peak weight M}})$~~

So $\frac{\sigma(\text{peak ratio})}{(\overline{\text{peak ratio}})} = 3.4 \times 10^{-2}$, using the data presented.

The reasonableness of this value was checked by drawing in by eye a smooth curve through the scatter of points representing the variation of fumarate

concentration during the irradiation of dimethyl maleate in acetone using the borosilicate probe (see page 126) and calculating from first principles the value of this ratio from the scatter of points about the curve. In all cases random error was assumed to be limited to concentration determinations. The other variable, the integrated light intensity value, was assumed to have no random error. This was not strictly true but was considered to be a reasonable assumption in view of the crude assessment of random error required and of the very great complications following any inclusion of this factor. On this basis, it was calculated that

$$\frac{\sigma(\text{peak ratio})}{(\text{peak ratio})} = 2.3 \times 10^{-2}$$

for the case examined, using the equation,

$$\sigma(\text{peak ratio}) = \sqrt{\frac{\sum^{n} (x-x_T)^2}{n}}$$

where $(x-x_T)$ was the distance parallel to the concentration axis of the point from the curve and n was the number of points considered.

(e) The possibility of the photochemical formation of a tetramethoxycarbonylcyclobutane

The photochemical dimerisation of derivatives of maleic and fumaric acid is a well known reaction.[10] In the case of maleic anhydride there is evidence that it is photosensitized by acetone.[6] In the case of fumaronitrile irradiated in acetone no cyclobutane has been observed.[6,11]

A sample of cis-trans-cis-1,2,3,4-tetramethoxycarbonylcyclobutane (IV) was obtained during investigations of the photochemistry of dimethyl

maleate/azobenzene mixtures (see page 132). The retention time of this compound was determined gas chromatographically. The final products from each of the irradiations of the third photokinetic series were then examined. No peaks of retention time even roughly approximating to that of the cyclobutane were observed and so it was concluded that no cyclobutane was produced in this system.

An irradiation of the tetramethoxycarbonylcyclobutane in acetone showed that this compound is stable under the irradiation conditions used even when an irradiation time of 48 hours is employed.

(f) Experimental data

The unprocessed data are set out in Table V, page 125, and represented graphically in Figures XXI-XXXIII. The data were processed in the form of 'peak ratios'. Calibrations to convert these to 'concentrations' were performed subsequently. For convenience, irradiation time is represented by the symbol 't', and integrated light intensity by 'T'.

(i) General observations

(1) The overall forms of the curves are in general agreement with those obtained in the second photokinetic series, except that in the third series, shorter irradiation times were used.

(2) An examination of the data revealed that determinations of the large excess of starting material, particularly at short irradiation times, were erratic. The manufacturers of the chromatograph advised that this was due to overloading the detector. In certain cases, these measurements could be improved by a careful adjustment of gas pressures. The chromatographic analyses were not repeated using more dilute samples

to determine the time variation of excess starting material concentration as the only value of this would have been to provide a material balance check and this could usually be performed at longer irradiation times in any case (see page 55 of this thesis).

(3) At very long irradiation times, random error in the determinations increased considerably.

(4) From the irradiation of dimethyl fumarate in acetone using a borosilicate glass probe, no peak corresponding to cis-oxetane diester was observed before t = 10 hr. 27 min. Only very small amounts of this compound were present at t = 16 hr. 36 min.

(5) Only very small amounts of oxetane were formed from the irradiation of dimethyl maleate in acetone using a borosilicate glass probe. Before t = 1 hr. 27 min., determinations were within experimental error of zero.

(6) From an examination of the irradiation of dimethyl fumarate in acetone using a quartz probe the following points emerged.

(A) In the 0.23M case, there was a slight lag in the formation of the cis-oxetane diester. This was of the order of 15 minutes and had not been unambiguously detected in the second kinetic series of experiments.

(B) In the 0.47M case, there was a lag of the order of 1 hour before the cis-oxetane diester was formed.

(C) In the 0.025M case, small concentrations of products not obtained in other irradiations were observed. Thus sample 18 (page 130) was found to produce six new peaks on the gas chromatogram. That side reactions played an important part in the photochemistry of this dilute

system is apparent from a material balance investigation (see page 55).

The identification and estimation of the peak due to cis-oxetane diester was complicated by the presence of other peaks of similar dimensions and retention times in this irradiation. The data given in Table V for this compound are believed to represent the most likely concentration-irradiation time dependence. However, on any basis, the rate of formation of cis-oxetane diester at time zero was very small indeed.

(7) During the course of an irradiation, the average value for the ratio $\frac{\text{integrated area under the photomonitor trace}}{\text{irradiation time}}$ was found to have the values:-

Borosilicate probe

dimethyl fumarate irradiation	0.435	Ratio $\frac{0.435}{0.358} = 1.214$
dimethyl maleate irradiation	0.358	

Quartz probe

dimethyl fumarate irradiation	
0.025M case	0.659
0.23M case	0.813
0.47M case	0.69
dimethyl maleate irradiation	0.627

and lie within the range $0.720 \pm 12.9\%$

(ii) Analysis of data

(1) A note on nomenclature

In order to distinguish between the various rates of formation the following arbitrary nomenclature is employed.

m ≡ dimethyl maleate

f ≡ dimethyl fumarate

t ≡ trans-oxetane diester

c ≡ cis-oxetane diester

q ≡ irradiated using a quartz probe

b ≡ irradiated using a borosilicate glass probe

A concentration-irradiation time curve is described thus:-

a first letter representing the substance being irradiated in acetone followed by the initial molarity of that substance in brackets, if this is necessary to define the irradiation considered;

a second letter representing the type of probe used;

a third letter representing the compound of which the rate of formation is described.

Thus f(0.23M)qt represents the concentration-irradiation time curve for the trans-oxetane diester when a 0.23M solution of dimethyl fumarate in acetone was irradiated using a quartz probe.

All rates were calculated on the basis of arbitrary integrated light intensity units ('T' units) and not on the basis of irradiation time.

(2) The gradient at time zero

(A) General

For reasons of time, only one determination of each concentration estimated was usually made. The points determined exhibited scatter about a simple curve. Since only one determination had been made and since there was no a priori expectation of the form of the concentration-time curves, it was not possible to eliminate the chance that the physical reality was

a curve passing through all the points determined. However, an analysis of the experimental method showed that the determinations possessed random error. It was considered that the most likely representation of the physical reality would be the simplest curve consistent with the expected magnitude of this random error. Curves with numerous inflections were not expected even though these would fit the data more closely than the simpler curve.

An examination by eye of the concentration-time curves showed that in many cases these curves could only be approximated by a straight line over a very short range from time zero. In such cases a linear fit would lead to an unreliable determination of the gradient at the origin. Computer techniques were invoked in order to fit higher order curves and so to make use of contributions from points over a greater range.

The experimental data were processed by an English Electric KDF9 computer under the control of programme A1000 of the Mercury Autocode Library. This is a polynomial least squares fit programme.

Not all the experimental data were submitted to the computer. Those which were submitted are marked with asterisks in Table V. The criteria for excluding data were

(a) Data such as the fb cases with $T > 2.0$, where, over very long irradiation times, the random error in determinations had increased considerably.

(b) Data such as the mbc and mbt cases where the random error was of the order of the value of the determination.

(c) Data such a fbf, mbm and f(0.23M)qf where because the column was

overloaded with respect to the component considered, highly erratic and unreliable results were obtained.

(d) Where, as in f(0.025M)qm and mqf the curve was in two distinct sections. Then only the first section of the curve was submitted to the computer.

(e) Data, such as mqf (point 6), mbf (point 10, point 16) where gross errors were observed in isolated points.

The remaining data was submitted to the computer unweighted. Coefficients of least squares fit polynomials of increasing order up to a maximum order specified, together with the coefficients of the associated orthogonal polynomials and the residual sum of squares for each fit were calculated.

(B) On the means of choosing which order fit provides the best representation of the physical reality to which the data approximates and on the means of deciding whether even the best fit is satisfactory.

Polynomials of the form $y = A + Bx + Cx^2 + \ldots$, where x represented the integrated light intensity value and y the corresponding peak ratio, and of order up to degree five (except for the mqf and f(0.025M)qm cases where only six points were submitted and where the maximum degree was taken as three) were fitted to the data. The curve selected was the lowest order curve consistent with the determinations and the estimated random errors.

From the computer print-out, M, the sum of the residuals for each fit was calculated. From an analysis of the experimental procedure, σ, the standard deviation in the determinations was estimated roughly (see

page 43). From this the quantity $\chi^2 = \frac{M}{\sigma^2}$ was calculated, and from this the probability of a given polynomial fit, p, was estimated from tables.(12) This quantity is a measure of whether the scatter of points from the fitted curve is commensurate with the estimated random error in the points themselves. 'p' values between 0.05 and 0.95 were acceptable.

The curve selected was the lowest order curve with an acceptable 'p' value. In certain cases no fit tried was acceptable, and so other means were used to estimate the gradient at time zero.

In those cases where an acceptable polynomial fit was obtained, the gradient of the curve at time zero was the coefficient of 'x' of the polynomial fitted and the standard deviation in this quantity was given by the formula

$$\sigma(\text{coeff of } x) = \sqrt{\sigma_n^2 \sum_{o}^{i=n} \frac{b_i^2}{D_i}}$$

where n is the order of the fitted polynomial,

b_i is the coefficient of x in the i^{th} order orthogonal polynomial,

D_i is the divisor of the i^{th} order orthogonal polynomial,

σ_n is the standard deviation of the points from the fitted polynomial,

σ_n is calculated from the formula

$$\sigma_n = \frac{\text{sum of the residuals of fitted polynomial}}{\text{degree of freedom of that polynomial}}$$

Note: As explained on page 44 , the simplification was made in these

calculations and was implicit in the computer programme used that random error is confined to y, the peak ratio, and is excluded from x, the integrated light intensity term.

(C) Processed data

The results given in Table VI were obtained by applying these methods to the curves in turn.

(D) Cases where a satisfactory polynomial fit was not obtained

(a) f(0.23M)qm. 15 points were fed to the computer but this failed to give a satisfactory result. By eye, the first seven points, including the origin are nearly collinear. These seven points were taken and the gradient of the least squares straight line through them calculated using the standard formula

$$m = \frac{\Sigma xy - \frac{(\Sigma x)(\Sigma y)}{n}}{\Sigma(x^2) - \frac{(\Sigma x)^2}{n}}$$

A very rough estimate of the error in this gradient was obtained from an examination of the calculated error in the points by assuming the standard deviation in the gradient covers the range of gradients obtained by joining the points $(x_7+\sigma_7, y_7)$ and $(x_7-\sigma_7, y_7)$ to the origin where x_7 and y_7 are the co-ordinates of the seventh point and σ_7 is the calculated standard deviation in x_7.

On this basis, gradient at the origin = 2.11 Tunits^{-1}

σ(gradient) = 0.07 Tunits^{-1}

(b) f(0.47M)qc. This function has a very small gradient at the origin. Poor computed values were obtained because of the large interval between the origin and the second point and because the origin was not weighted in the computer programme.

From the graph (see Figure XXXI), the six points up to T = 0.8679 appear to be approximately collinear. A least squares fit to these points would give an estimate of the maximum gradient of the curve at the origin.

This procedure gave a line of gradient 0.000532 $Tunit^{-1}$.

(c) f(0.025M)q

No computer determination of this series was successful. This was probably due to the very rapid photoisomerisation to dimethyl maleate which led to a photoequilibrium with a preponderance of maleate within ten minutes irradiation time. All the concentration-irradiation time curves, including that representing the rate of oxetane formation exhibited a very different character after ten minutes irradiation from that at time zero. This was not satisfactorily dealt with by the computer procedure adopted when points of irradiation times up to four hours were submitted.

Approximate methods for obtaining an estimate of the gradient at time zero using only the first four determinations including that at time zero, that is, those determinations undertaken within the first fifteen minutes irradiation, were investigated.

f(0.025M)qt. A quadratic was fitted through the origin and the mid-points of the second and third and of the third and fourth points. The gradient of this quadratic at the origin is 0.1136 $Tunits^{-1}$. The residual

of the second point is 0.000015, the curve passing above the point. It was difficult to estimate the error in the gradient. A rough estimate was ~0.013 Tunits^{-1}. It is extremely unlikely that the gradient is greater than 0.17 Tunits^{-1}. This is the gradient of the line joining the point (x_2,y_3) to the origin where x_i,y_i are the co-ordinates of the i^{th} point, the first point being at time zero.

After the initial period and within the range T = 0.2695 to T = 1.0990, the curve is approximately linear with a least squares gradient of 0.0240 Tunits^{-1}. All but one point have residuals of less than 5×10^{-4} from this line.

f(0.025M)qm. A cubic was fitted through the first four points. Its gradient at the origin is 3.305 Tunits^{-1}. The error in this quantity is uncertain. It is extremely unlikely that the gradient is less than 2.55 Tunits^{-1}, which is the gradient of the line joining the first point to the origin.

f(0.025M)qf. The co-ordinates (x_m,y_m) of the mid-points of each consecutive pair of the first four points were calculated. The gradient of the peak-ratio/irradiation time function at x_m was assumed to be that of the chord joining the points of which (x_m,y_m) was the mid-point.

A plot of gradient, thus obtained, against x was found to be approximately ~~col~~linear. Extrapolation to x = 0 (i.e. time zero) gave a gradient of the original function at time zero of -2.95 Tunits^{-1}. The estimated error in this quantity if the method is valid is < 0.1 Tunits^{-1}.

(3) Calibration

Calibration experiments were performed on standard solutions of

dimethyl maleate, dimethyl fumarate and the cis- and trans-oxetane diesters containing methyl salicylate marker. From these experiments it was calculated that a peak ratio of unity in the photokinetic experiments corresponded to the following concentrations.

Compound	Molarity	σ
dimethyl maleate	0.113M	0.001M
dimethyl fumarate	0.123M	0.002M
trans-oxetane diester	0.0916M	0.0035M
cis-oxetane diester	0.126M	0.010M

(4) Summary of data

Using these calibration constants, the gradients at time zero were converted to units of gm.mol./li./Tunit. Data are summarised in Table VIIa.

(5) Material balance

As explained on page 45 , it was not possible to obtain a reliable measure of the rate of decay of starting material at time zero, so that it was not possible to check that the rate of decay of reactant was in accord with the rate of formation of products at time zero.

A material balance check was conducted not at time zero but at some later stage in the reaction when all the reaction components' concentrations could be estimated with some reliability. The concentration values taken were usually found by drawing smooth curves through the scatter of points and reading off values from this. In the system investigated, provided no side reactions had occurred, the sum of the molarities of maleate, fumarate and oxetanes should be constant with irradiation time.

(A) f(0.23M)q

T	0	0.25	0.50
m	0	0.061	0.116
f	0.23	0.161	0.112
t	0	0.010	0.018
c	0	0	0
Σ	0.23	0.232	0.246

(B) f(0.47M)q

T	0	0.6	1.4
m	0	0.121	0.228
f	0.47	0.286	0.135
t	0	0.032	0.061
c	0	0	0
Σ	0.47	0.439	0.424

(C) f(0.025M)q

T	0	0.4	0.8	1.6	2.0
m	0	0.0205	0.0167	0.0118	0.0093
f	0.025	0.0024	0.0020	0.0015	0.0012
t	0	0.0012	0.0022	0.0039	0.0044
c	0	0	0	0	0
Σ	0.025	0.0241	0.0209	0.0172	0.0149
m/f	0	8.54	8.35	7.85	7.75

No significant side reactions played a part in the f(0.23M)q case. Some side reaction possibly occured in the f(0.47M)q case. If this did occur, the new product has been shown not to be cyclobutane (page 44 of this thesis). A very significant side-reaction occurred in the f(0.025M)q case. Whatever the products, the magnitude of this effect is much greater than could be accounted for by the new compounds giving peaks on the gas chromatogram (see page 46).

In the fb, mb and mq cases, no confident gas chromatographic estimations of the starting material concentration could be made from the

available data. Some attempt to obtain a rough material balance check was made in the cases of fb and mb.

(D) fb		(E) mb	
Sample No.	6	Sample No.	6
m	0.218	m	0.209
f	0.005	f	0.005
t	0.001	t	0
c	0	c	0
Σ	0.224	Σ	0.214M

Initial concentration of fumarate = 0.23M.

Initial concentration of maleate = 0.23M.

(iii) The relative proportions of the incident light at time zero absorbed by the various components of the reaction mixture.

Absorption spectra are known to exhibit solvent shifts.[39] Since the irradiations were conducted in acetone solution, calculations were based on absorption spectra recorded in a solvent of similar solvent shift properties to acetone. Ethanol was selected as a suitable solvent since the spectrum of pure acetone examined using 0.1 mm cells exhibited λ_{max} = 272.5 mμ whereas a dilute ethanolic solution of acetone in 1 cm. cells exhibited λ_{max} = 272 mμ.

Spectra in ethanolic solution were recorded. Calculation revealed that the system absorbed completely all light of wavelength less than 320 mμ wavelength emitted by the lamp. Light of 334 mμ and longer wavelengths was only absorbed to a negligible extent.

Calculations of relative absorption were based on the measured spectra

using the formula:-

The fraction of the total number of photons absorbed by the mixture A + B, which are absorbed by A =

$$\frac{\sum_{n=200m\mu}^{n=320m\mu} \frac{i_n f_n}{E_n} \frac{\epsilon_{A,n} C_A}{\epsilon_{A,n} C_A + \epsilon_{B,n} C_B}}{\sum_{n=200m\mu}^{n=320m\mu} \frac{i_n f_n}{E_n}}$$

where C_A and C_B are the concentrations of components A and B in gm.mol./li.

$\epsilon_{A,n}$, and $\epsilon_{B,n}$ are the extinction coefficients of components A and B at wavelength n mμ.

i_n is the power in watts of the emitted line at wavelength n mμ.

f_n is the fraction of incident light transmitted by the probe (total thickness of glass = 4 mm) at wavelength n mμ.

E_n is the magnitude in ergs of a quantum of wavelength n mμ.

The results of this investigation are recorded in Table VIIb.

The interpretation of the kinetic data presented depends on the solution not being light saturated. A typical lamp of the kind used emits 69.75×10^{18} photons/sec. within the spectral range of the lines from 200 mμ to 335 mμ.* This means that 1 einstein of radiation in this

---

* Calculated on the basis of figures given in Table I.

range is emitted in 2.4 hours. By considering a more extreme case that was encountered in any of the photokinetic experiments and by grossly over-estimating the life-time of the excited states produced, (in this case estimating 5 sec.), it was shown that light saturation even with respect to the most dilute component in the 3.9 mm thickness of solution surrounding the lamp could not occur.

(iv) The effect of oxygen

In every irradiation of this series, measures were taken to exclude oxygen from the solution. An experiment was devised to test whether the trace amounts of oxygen remaining in solution in spite of deoxygenation had a significant effect on the data. It seemed likely from a study of the form of the concentration-time curves that any effect extended over the whole range of irradiation-time and was not confined to an initial period only, such as might be expected if the oxygen, although quenching the reaction initially was rapidly and irreversibly removed by a photo-oxidation process.

A rigorous investigation of this matter would have been very involved. A rough check was provided by irradiating three solutions of the same concentration of dimethyl fumarate in acetone in three pyrex glass test-tubes, using identical irradiation conditions. The solutions differed only with regard to degassing procedure.

Solution A had had oxygen slowly bubbled through it for five minutes prior to the test-tube being sealed.

Solution B had been similarly treated, but using 'white spot' nitrogen.

Solution C had been rigorously degassed to a pressure of 10^{-4} mm of

mercury at liquid air temperatures.

After the irradiation, sample A was slightly yellow. Samples B and C were clear. Gas chromatographic analysis revealed that the concentrations of the components of the mixtures produced photochemically were identical within the limits of accuracy of the experimental method. No cyclobutane was observed to have been formed in any of the solutions examined. It was concluded that small amounts of oxygen were not likely to have a significant effect of the photochemistry of this system and that the results of the photokinetic experiments could be treated with some confidence.

J) Energy levels. (a) General

In order to rationalise photochemical data, it is important to have a knowledge of the relative energy levels of the compounds irradiated. Two fundamental problems attend any attempts to investigate these levels. The following discussion concerns molecules with diamagnetic ground states.

(i) The lowest electronic triplet states of molecules are frequently but not inevitably the chemically significant excited states because they are the longest lived of the electronically excited species.[13a,b] Such a state, as well as being of lower energy than any other triplet state, also has a lower energy than any excited singlet state. This arises because the orbital wave function of the triplet state exhibits a probability density distribution which results in lower coulombic repulsions between electrons than is the case with the singlet state of the same orbital electron configuration. Non-radiative intersystem-crossing from an excited singlet state to the lower energy triplet state is often efficient for

(n,π^*) states.[14] However, transition from the triplet state to the ground (singlet) state is a comparatively slow process. Radiative transitions to the ground state are forbidden as the spin functions of the two states are orthogonal and intersystem crossing is not efficient by virtue of the considerable energy separation between the ground state and the first excited triplet state. A comparison of the radiative lifetimes of phosphorescent states in solution at room temperatures and in rigid media at liquid air temperatures shows that collisions between molecules and thermal vibrations greatly facilitate the deactivation process.[15]

Whereas data concerning the excited singlet energy levels of molecules can be derived from an investigation of their ultraviolet spectra, such an examination rarely yields information about their triplet levels because singlet-triplet transitions are highly forbidden.

Information concerning triplet energy levels has been obtained from phosphorescence measurements,[16] or by perturbing the system such that singlet-triplet absorption more easily occurs.

(ii) Because of the Franck-Condon principle, the absorption maxima observed in spectra usually correspond to energies of transition between different electronic states each having different vibrational energies. The chemically significant quantity required for calculations is the energy of the 0,0 transition, that is, the energy of the transition between the ground and excited electronic states neither possessing quanta of vibrational energy. The energy of the 0,0 transition is significant because the excess vibrational energy of newly formed excited electronic state is extremely rapidly degraded[17] and so plays no part in photo-

chemical reactions. The energy of the 0,0 transition might be very far removed from that of the absorption maximum. Thus, although 1,3-butadiene exhibits in intense sharp $\pi \rightarrow \pi^*$ absorption with λ_{max} = 210 mμ, there is some evidence that the 0,0 band occurs at a wavelength > 253.7 mμ, and possibly even at about 320 mμ.[18] It is not always easy to determine the energy of a 0,0 band.

(b) A summary of previous measurements of the energy levels of dimethyl maleate, dimethyl fumarate and acetone.

Some data on the singlet levels is implicit in the ultraviolet spectral data given on page 14 of this thesis. No indication of the position of the 0,0 band is provided.

i) Acetone[19]

The singlet-singlet $n \rightarrow \pi^*$ 0,0 transition of acetone is known to have an energy of 79 kcal/mol. (362 mμ). Acetone has been observed to phosphoresce but nothing is known for certain of the magnitude of the singlet → triplet $n \rightarrow \pi^*$ 0,0 transition. R.E. Rebbert and P. Ausloos have supposed it to be in the range 70-79 kcal/mol. (409-362 mμ).

ii) Dimethyl maleate and dimethyl fumarate

The triplet energies of the diethyl esters have been investigated by G.S. Hammond and co-workers.[20] No reliable data was forthcoming. No phosphorescence was observed and the absorption spectra of 1.2M solutions of the esters in ethyl iodide in 10 cm. cells (see page 64 of this thesis) yielded only structureless 'tails'. On this very inadequate basis, Hammond supposed the singlet-triplet excitation of diethyl maleate to lie between 72 and 77 kcal/mol. (397-372 mμ) and that of diethyl

fumarate between 61 and 67 kcal./mol. (469-427 mμ).

From a further investigation of the variation of composition of the photostationary state of the photosensitized cis↔trans isomerisation reaction as a series of different photosensitizers of known triplet energies were used, Hammond suggested that the vertical excitation energy of diethyl maleate lies higher than that of diethyl fumarate, and further, that the 0,0 singlet-triplet transition of diethyl fumarate lies at 61 kcal/mol. (469 mμ). To explain his data he additionally invoked the possibility of non-Franck-Condon excitation to a non-planar triplet state which he called a 'phantom triplet'.

By studying the mechanism of thermal cis → trans isomerisation of dimethyl maleate to dimethyl fumarate, J.L. Magee and co-workers have indicated that the phantom triplet state has an energy $\leq$ 26.5 kcal/mol. above the ground state of maleate (or 32.5 kcal/mol. above that of fumarate).[21]

(c) Means of measuring triplet energy levels

In order to clarify the photochemical data obtained, an investigation of the triplet energy levels of dimethyl maleate, dimethyl fumarate and acetone was undertaken. Absorption methods were pursued. Emission methods were not investigated.

(i) General

Singlet-triplet transitions are forbidden because the spin wave functions of the two states are orthogonal. That singlet-triplet transitions are observed, albeit weakly, is because spin-orbit interaction lends the triplet level a small amount of singlet character.

It is known from a study of atomic spectra that spin-orbit coupling increases with the atomic number of the atom so that quite intense singlet → triplet absorptions are observed in the spectra of heavy atoms. Similarly, the presence of heavy atoms in an organic molecule tends to increase the intensity of singlet → triplet absorption. Thus an enhanced singlet-triplet transition probability has been associated with the substitution of heavy halogen atoms in aromatic systems.[22] A closely related effect is the collisional perturbation of spin-orbit coupling which leads to the enhancement of singlet-triplet absorption when a substance is dissolved in a solvent containing an heavy atom. Thus M. Kasha has ascribed the yellow coloration produced on dissolving α-chloronaphthalene in ethyl iodide to an enhancement of the singlet-triplet absorption of the solute.[23] Perturbations produced by highly charged species and by paramagnetic ions have also been observed to enhance singlet-triplet absorption.[24]

Oxygen has been observed to enhance singlet-triplet absorption in proportion to the pressure of oxygen used. Following the initial observation of the oxygen enhancement of the singlet-triplet absorption of benzene,[25] D. Evans has developed and extended the method in a series of papers.[26] Nitric oxide has been observed to behave in a similar way to oxygen.

The oxygen perturbation causes enhancement of the singlet-triplet transition, and it has been confirmed in those cases where triplet energies can be measured by other means that the enhanced 0,0 bands are not shifted in wavelength. In oxygen perturbation experiments, as well as

singlet-triplet bands, new intense featureless absorptions are also frequently observed at shorter wavelengths. These are ascribed to charge transfer transition from the perturbed molecule to oxygen. The charge transfer bands can be distinguished from singlet-triplet bands as the former are sensitive to solvent shift effects whereas the latter are very insensitive.[27]

Two mechanisms have been put forward to account for the phenomenon of oxygen perturbation.[28] It has been shown that the effect is not merely one of perturbation by the inhomogeneous magnetic field in the region of the paramagnetic oxygen molecule.[29] Both current theories consider the singlet-triplet enhancement to be associated with the formation of a complex between oxygen and the molecule studied. The modification of the energy levels of such a molecule by oxygen are shown in Figure XXXIV.[28] Charge transfer bands also arise. Hoijtink suggested that the singlet-triplet enhancement arose from the states ^3G and ^3F, that is that the intensity is 'stolen' from the singlet-singlet transition of the organic molecule, whereas Murrell and Mulliken suggest that the ^3CT and ^3F interaction is more important, that is, that the intensity is 'stolen' from the charge-transfer absorption.

A further method of considerable significance to the measurement of triplet energy levels is that of electron impact spectroscopy. Excitation arising from electromagnetic radiation will only lead to electronic transitions from the ground state to certain excited states, other transitions being 'forbidden'. It has long been known that a beam of electrons can be used in place of light to cause electronic energy transitions in atoms and

molecules,[30] but in this case optically forbidden transitions are allowed. Thus, since the electrons in the exciting beam possess spin, singlet-triplet transitions are readily induced.[31] A. Kuppermann and L.M. Raff have recently built a spectrometer on this principle and investigated the spectra of a number of molecules including ethylene.[32] The method employed is to direct a monoenergetic beam of electrons at a sample in the form of a low pressure gas and to measure the spectrum of energies of the scattered electrons. The spectra observed were in good agreement with energy level data obtained in other ways. With ethylene two optically forbidden bands were observed. It was possible to distinguish between spin forbidden and symmetry forbidden optical transitions by noting the effect of varying theenergy of the incident electron beam.

(ii) Measurements

(1) The methyl iodide method

An ultraviolet spectral examination of concentrated solutions of dimethyl maleate in methyl iodide was conducted. No absorption was noted at wavelengths greater than 360 mμ below which wavelength the solvent itself absorbed.

(2) Oxygen perturbation

Oxygen perturbation experiments were conducted using apparatus on loan from D.F. Evans. Two concentrated chloroform solutions of the substance investigated in 5 cm. cells were introduced into the two beams of a spectrophotometer. The two solutions were identical in all respects except that one was saturated with oxygen at a pressure of 1800-2000 lb./sq.in.

Singlet-triplet absorption occurs at longer wavelengths than the

corresponding singlet-singlet band. Observations of the singlet-triplet absorption were complicated by the fact that in most of the cases examined, the enhanced singlet-triplet band, as well as being extremely weak, was also only slightly separated from the intense singlet-singlet absorption.

(A) Chloroform used as a solvent, was not transparent at wavelengths below 255 mμ. Under oxygen pressure, a new absorption was observed between 255 mμ and 300 mμ. No other absorption was observed at wavelengths up to 650 mμ.

(B) Dimethyl fumarate. A very weak absorption was observed . This is represented in Figure XXXV. The oxygen induced absorption tailed to ~440 mμ. An absorption maximum was observed at 343 mμ, ε = 0.024. No fine structure was apparent apart from a slight hump at ~ 362 mμ. Measurements at shorter wavelengths than 330 mμ were uncertain and at shorter wavelengths than 320 mμ impossible owing to the onset of singlet-singlet absorption.

(C) Dimethyl maleate. A very weak absorption was observed. This is represented in Figure XXXVI. An absorption maximum was observed at 332-335 mμ, ε = 0.023. It was not possible to be absolutely confident that this corresponded to a true maximum owing to the onset of singlet-singlet absorption. The singlet-triplet band exhibited no fine structure apart from a slight hump at ~ 370 mμ. The absorption tailed to ~ 405 mμ.

(D) Methyl crotonate. Absorption was more intense and occurred at shorter wavelengths than with dimethyl maleate and dimethyl fumarate. Some fine structure was evident (see Figure XXXVII). The absorption tailed to 386 mμ. Absorption maxima were at 339 mμ, ε = 0.094; 328.5 mμ, ε = 0.141;

319 mμ, ε = 0.163 and 311 mμ, ε = 0.169. The onset on singlet-singlet absorption made an investigation of singlet-triplet absorption at wavelengths shorter than 300 mμ impossible.

No solvent shift experiments were undertaken, but it was considered unlikely that the oxygen enhanced absorptions of dimethyl maleate, dimethyl fumarate and methyl crotonate described were charge transfer bands, since although the carbon-carbon double bond of crotonate is more electron rich than that of maleate or fumarate, the crotonate absorption lies at shorter wavelengths. This is not expected for a charge-transfer band. The greater intensity of the singlet-triplet absorption in the crotonate case is in accord with the theory of Mulliken and Tsubomura.[28]

Oxygen has been used to catalyse the thermal cis → trans isomerisation of dimethyl maleate.[33] Since the perturbed spectra of maleate and fumarate were repeatable reproducibly over a period of about ½ hour it was judged that any isomerisation reaction was so slow as to be without consequence in these measurements.

(E) Maleic anhydride. Only tail absorption was observed in the region 360 mμ - 420 mμ. At shorter wavelengths, the singlet-triplet absorption was obscured by the intense singlet-singlet band.

(F) Acetone. Very weak tailing occurred to approximately 390 mμ. Below 350 mμ more intense absorption occurred. At 332.5 mμ, ε ~ 0.0050. However no reproducible data could be obtained. Measurements at shorter wavelengths than 332 mμ were not possible owing to singlet-singlet absorption.

(G) Acetoxime. Oxygen perturbation methods failed because of the

intervention of a very rapid irreversible oxidation reaction.

(3) Electron Impact Spectroscopy

Professor Kuppermann is in the process of investigating the energy levels of dimethyl maleate, dimethyl fumarate and acetone on a newly constructed high resolution electron impact spectrometer. It is hoped that data from these experiments will be available in time to be submitted as an appendix to this thesis.

Table I

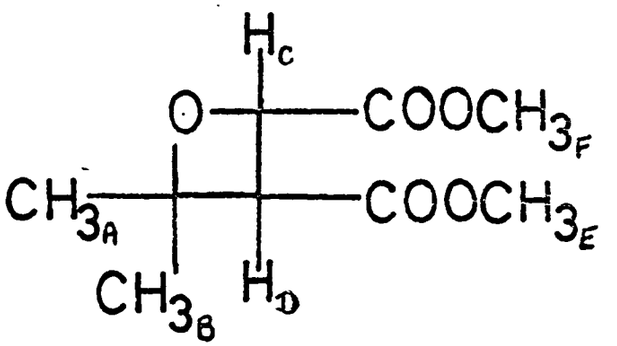
Absolute output in watts at different wavelengths for each 100 watts loading on the lamp of a typical medium pressure mercury arc in quartz operating at about 800 mm. internal pressure.

Wavelengths in mμ	Intensity in watts
235	0.12
238	0.23
240	0.21
246	0.09
248	0.53
254	0.68
258	0.08
260	0.11
264	0.14
265	0.98
270	0.23
275	0.17
280	0.55
289	0.26
292	0.11
297	0.74
302	1.42
313	2.72
334	0.37
366	4.30
391	0.06
405	1.14
406	0.24
436	2.10
492	0.06

Table II

Spectral Properties of the oxetane diesters

I) Nuclear magnetic spectra, recorded in CCl_4 solution



proton	cis-oxetane diester		trans-oxetane diester		Integrated peak area
A	8.45 τ	singlet	8.47 τ		3
B	8.60 τ	singlet	8.67 τ		3
A-B separation	9.0 c.p.s.		12.0 c.p.s.		
C	5.11 τ	doublet	4.94 τ		1
D	6.26 τ	doublet	6.49 τ		1
J_{CD}	9.0 c.p.s.		6.9 c.p.s.		
E,F	6.26 τ, 6.33 τ		6.23 τ,	6.25 τ	3,3

II) Mass spectra. $\frac{m}{e}$ values > 50 are given. Relative intensities are given in brackets. (Only those peaks are recorded with relative intensity > 0.5).

trans-oxetane diester. 202(0.08); 145(3.1); 143(1.6); 142(0.55); 116(0.7); 115(10.0); 114(2.2); 113(6.8); 85(1.2); 84(0.85); 83(8.7); 82(0.9); 73(1.2); 59(2.1); 58(1.0); 55(1.3); 53(0.7).

cis-oxetane diester. 202(0.05); 145(1.8); 143(2.0); 141(0.95); 116(0.7); 115(9.4); 114(3.6); 113(7.5); 112(0.7); 99(0.75); 98(0.6); 85(0.85); 84(0.9); 83(10.0); 82(1.5); 74(1.7); 73(2.6); 71(1.0); 70(2.2); 69(0.8); 59(3.8); 58(1.3); 57(1.0); 56(0.6); 55(3.1).

For Table III, see page 120.

Table IV, see page 121.

Table V, see page 125.

Curve	Order of fit taken	No. of points submitted to computer	Gradient calculated ($Tunits^{-1}$)	Standard deviation of gradient ($Tunits^{-1}$)	σ^2 for this fit	σ^{2*} of points based on an analysis of experimental method
mqt	1	26	0.0349	0.0012	1.32×10^{-5}	1.4×10^{-5}
mqc	2	20	0.00398	0.00023	3.35×10^{-7}	1.4×10^{-7}
mqf	2	6	0.454	0.05	1.29×10^{-4}	0.56×10^{-4}
mbf	3	23	0.2431	0.0085	4.61×10^{-6}	5.76×10^{-6}
f(0.23m)qt	3	16	0.600	0.027	3.63×10^{-5}	3.00×10^{-5}
f(0.23m)qc	2	11	0.0011	0.0009	1.46×10^{-7}	1.85×10^{-8}
f(0.23m)qf	3	18	-1.60	0.14	1.09×10^{-3}	0.83×10^{-3}
f(0.47m)qt	2	18	0.643	0.013	1.35×10^{-4}	1.96×10^{-4}
f(0.47m)qm	4	20	1.77	0.17	3.00×10^{-3}	2.60×10^{-3}
fbt	2	24	0.0417	0.0017	1.47×10^{-6}	0.72×10^{-6}
fbm	1	21	0.1432	0.0023	2.75×10^{-5}	1.16×10^{-5}

Table VI

* σ^2 values given here are based on the expression $\frac{\sigma(\text{peak ratio})}{(\overline{\text{peak ratio}})} = 3.4 \times 10^{-2}$ derived on page 43 . In certain cases, such as fbt, f(0.23M)c, the apparently poor fit results from poor estimation of this quantity as inspection of the graphical plot shows.

In all cases not listed in this table, the method employed failed to provide a satisfactory polynomial fit.

Table VIIa

Rates are given in units of gm.mol./li./Tunit.

Standard deviations are given in brackets.

Irradiation	mq*	fq			mb	fb
Initial concentration of maleate/fumarate ($gm.mol.li^{-1}$)	0.23	0.025	0.23	0.47	0.23	0.23
Initial rate of formation of:						
a) dimethyl maleate	-	0.37	0.239 (0.008)	0.20 (0.02)	-	0.0162 (0.0003)
b) dimethyl fumarate	0.167 (0.018)	-0.36 (0.01)	-	-	0.030 (0.001)	-
c) trans-oxetane diester	0.00959 (0.00033)	0.0104 (0.0012)	0.0550 (0.0025)	0.0590 (0.0012)	~0	0.00382 (0.00016)
d) cis-oxetane diester	0.00151 (0.00009)	~0	~0 [$<1.8 \times 10^{-4}$ (1.1×10^{-4})]	0 [$<6.7 \times 10^{-5}$]	~0	0

* correction has been made in this case for the different amplifier setting in the photomonitor circuit (see page 127) so that the mq data given in this table is directly comparable with the fq data.

Table VIIb

Irradiation	mq	fq	fq	fq	mb	fb
Initial concentration of dimethyl maleate/ dimethyl fumarate (gm.mol./li.)	0.23	0.025	0.23	0.47	0.23	0.23
Fraction of total number of photons absorbed by the system at time zero which are absorbed by:						
i) maleate/fumarate	0.11	0.024	0.14	0.67	0.0026	0.0150
ii) acetone	0.89	0.976	0.86	0.33	0.997	0.985

It was also calculated that within the wavelength range 200 mμ - 320 mμ, the total number of photons emitted by the lamp in unit time which are transmitted by the borosilicate glass probe):(number transmitted by the quartz probe) other factors remaining constant is 0.273 : 1.000.

For Table VIII, see page 71.

Table IX, see page 81.

Chapter 2: Theoretical Discussion

A) Introduction

In the general section, the measurements of rates of reaction have been discussed with particular emphasis on the reliability of the data obtained. The implications of this data are now considered. Although it is very apparent that much further photokinetic work is required to arrive at a full understanding of the photochemistry of this system, certain general deductions can be made. In this section it is shown that the data provides very strong evidence that oxetanes are formed in this system primarily by the action of excited maleate or fumarate on ground state acetone. In every other photochemical case so far investigated, oxetanes are formed by the action of excited ketone on ground state olefin.[34] Further there is evidence that the transitory states of maleate and fumarate responsible for oxetane formation differ from those involved in photochemical cis↔trans isomerisation. Finally some further tentative suggestions are made concerning the mechanism of these reactions.

For a note on the nomenclature employed in this section, see page 47. The data are set out in Tables VI and VII.

B) Comparisons of rates using borosilicate apparatus with rates using quartz apparatus

For a full discussion of the principles involved in making these comparisons, see page 41 of this thesis. In summary, it has been shown that although ratios of rates of formation can be compared between the two series of irradiations, rates themselves, calculated on the basis of

integrated light intensity units, cannot be compared. The best that can be achieved is to compare rates calculated on the basis of irradiation time units. However, the possibility of error of up to ± 20% exists in these comparisons.

The data presented in Table VIII are rates based on irradiation time units, and calculated from the data given in Tables VI and VII.

Table VIII

Rate of formation (standard deviations, taking no account of lamp fluctuations, are given in brackets) at time zero in gm.mol./li./hr.

Case	mq	mb	f(0.23m)q	fb
dimethyl maleate	-	-	0.194 (0.006)	0.00704 (0.0001)
dimethyl fumarate	0.105 (0.011)	0.0107 (0.0004)	-	-
trans-oxetane diester	0.00604 (0.00021)	0 (<0.0001)	0.0447 (0.0020)	0.00166 (0.00007)
cis-oxetane diester	0.00095 (0.00006)	0 (<0.0001)	0	0

C) A comparison of the f(0.23M)q case with the fb case

(a) The rates of formation of cis-oxetane diester at time zero in both cases are zero. In the fb case, no cis-oxetane diester was formed even after 8 hr. irradiation. In the f(0.23M)q case, cis-oxetane diester

was present after about 40 min. irradiation when its rate of formation had increased to about 0.0009 gm.mol./li./Tunit.

In the f(0.23M)q case, a photostationary ratio of maleate:fumarate was reached after about one hour's irradiation (0.75-1.00 Tunits). At T = 1.75, the ratio of concentrations of maleate:fumarate was 5.58. In the fb irradiation, no photostationary ratio was attained during the course of the irradiation.

In a comparison of rates of formation at time zero between the f(0.23M)q and fb cases, concentration effects are not considered since they are identical in each case, the initial concentration of dimethyl fumarate being the same in both cases.

(b) Consider the following possibilities for oxetane formation.

(i) That oxetane was formed by the reaction

$$F + A^* \rightarrow \text{oxetane}$$

and by no other reaction, where 'F' and 'A' represent dimethyl fumarate and acetone and * indicates and unspecified state of electronic excitation.

On this basis, the rate of oxetane formation in the quartz case at time zero can be calculated from the rate observed in the borosilicate case. The rate in the quartz case should be given by the expression

$\frac{0.00166}{0.273} \times \frac{0.86}{0.985}$ gm.mol./li./hr. within the limits of error of $\pm$ 20%,

where 0.00166 gm.mol./li./hr. is the rate of oxetane formation at time zero in the borosilicate case,

0.273 is the factor correcting for the reduction in light energy transmitted per unit time in the absorbing region of the solution

when the quartz probe is replaced by the borosilicate glass probe, and 0.86 and 0.985 are the fractions of absorbed incident light which directly excite acetone in the quartz and borosilicate cases respectively.

The actual rate of formation of oxetane in the quartz case could exceed this value if the energy transfer reaction

$$F^* + A \rightarrow F + A^*$$

also occurred. If this occurred with 100% efficiency, the maximum possible rate of oxetane formation in the quartz case would be

$$\frac{0.00166}{0.273} \times \frac{1}{1} = \underline{0.0061} \text{ gm.mol./li./hr.}$$

The observed value in the quartz case was 0.0447 gm.mol./li./hr.,* over seven times the maximum predicted value. This is strong evidence that the reaction

$$F + A^* \rightarrow \text{oxetane}$$

was not the main contributor to the oxetane forming reaction.

(ii) That oxetane was formed by the reaction

$$F^* + A \rightarrow \text{oxetane.}$$

On this basis, in a similar way, the rate of oxetane formation in the borosilicate case can be calculated from that observed in the quartz case.

Assume at first that F* was not also produced by the energy transfer reaction

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* In this and subsequent comparisons, standard deviations are not quoted for the quantities compared. Reference to Table VIII shows that a consideration of these standard deviations does not alter the conclusions reached.

$$F + A^* \rightarrow F^* + A.$$

The expected rate of oxetane formation in the borosilicate case is given by the expression

$$0.0447 \times 0.273 \times \frac{0.015}{0.14} = \underline{0.00131} \text{ gm.mol./li./hr.}$$

Assume now that the energy transfer reaction occurred with 100% efficiency. On this basis, the expected rate is

$$0.0447 \times 0.273 = \underline{0.0122} \text{ gm.mol./li./hr.}$$

The observed rate of oxetane formation in the borosilicate case was $\underline{0.00166}$ gm.mol./li./hr. Within the limits of a $\pm$ 20% possible error of comparison, this is very good evidence in favour of the mechanism

$$F^* + A \rightarrow \text{oxetane}$$

without a significant contribution from the reaction

$$F + A^* \rightarrow F^* + A.$$

(c) Consider the following possibilities for dimethyl maleate formation.

(i) That maleate was formed by the reaction

$$F + A^* \rightarrow A + M$$

alone and that the energy transfer reaction

$$F^* + A \rightarrow F + A^*$$

occurred with 100% efficiency.

On this basis, the maximum possible initial rate of maleate formation by reaction with excited acetone is calculated from the borosilicate case to be

$$\frac{0.00704}{0.273} \times \frac{1}{1} = \underline{0.0258} \text{ gm.mol./li./hr. in the quartz case.}$$

The observed rate was 0.194 gm.mol./li./hr. in the quartz case, which is over seven times the maximum predicted. This is strong evidence that the reaction $F + A^* \rightarrow M + A$ is not the main contributor to the isomerisation reaction.

(ii) That maleate was formed by the reaction

$$F^* \rightarrow M.$$

Assume at first that F^* was not also produced by the energy transfer reaction

$$F + A^* \rightarrow F^* + A.$$

Expected rate of maleate formation in the borosilicate case is given by the expression

$$0.194 \times 0.273 \times \frac{0.015}{0.14} = \underline{0.0057} \text{ gm.mol./li./hr.}$$

Assume now that the energy transfer reaction occurred with 100% efficiency. On this basis, the expected rate is

$$0.194 \times 0.273 = \underline{0.053} \text{ gm.mol./li./hr.}$$

The observed rate of maleate formation in the borosilicate case was 0.00704 gm.mol./li.

Within the $\pm$ 20% possible error of these comparisons, this is a good indication that the data favours the mechanism

$$F^* \rightarrow M$$

and that the contribution from the energy transfer reaction

$$F + A^* \rightarrow F^* + A$$

was negligible.

(d) The quartz and the borosilicate irradiations differ in that in the quartz case, 14% of the absorbed incident light led to direct excitation of the fumarate, whereas this occurred with only 1.5% of the absorbed incident light when a borosilicate probe was used. Also the total rate of reaction, that is the rate of formation of maleate plus the rate of formation of oxetane, was 14.7 times greater when a quartz probe was used than when a borosilicate glass probe was employed.

Yet under these widely different conditions of reaction, the fraction of the total reaction leading to oxetane was constant. Thus in the borosilicate case, the ratio

$$\frac{\text{initial rate of formation of oxetane}}{\text{initial rate of formation of oxetane + initial rate of formation of maleate}} = 0.187.$$

In the quartz case, this ratio = 0.191.

Since ratios of rates and not rates themselves are here compared, these ratios can be compared with a high degree of precision.

(e) All the evidence presented very strongly suggests that both oxetane and maleate were formed from excited fumarate and that excited acetone had little part in these processes, whether by direct reaction or by energy transfer to fumarate.

D) A comparison of the 'mq' and 'mb' cases

(a) The initial rate of formation of cis- and trans-oxetane diesters in the borosilicate case was approximately zero. An examination of Figure XXIV shows that the initial rates of formation were less, very

probably much less, than 0.0002 and 0.0003 gm.mol./li./Tunits respectively.

(b) In any comparison of rates of formation at time zero between the mb and mq cases, concentration effects are not considered since they were identical in each case, the initial concentration of dimethyl maleate being the same in both cases.

(c) As with the fumarate case previously considered, the ratios

$$\frac{\text{initial rate of formation of oxetanes}}{\text{initial rate of formation of oxetanes + initial rate of formation of fumarate}}$$

were calculated.

In the quartz case this ratio was 0.0623; in the borosilicate case, ~ 0 (maximum possible value, 0.0167, from Figure XXIV).

(d) Consider the following possibilities for oxetane formation.

(i) that oxetane was formed by the reaction

$$M + A^* \rightarrow \text{oxetane} \qquad \text{alone.}$$

The minimum expected rate of oxetane formation in the borosilicate case consistent with this mechanism was calculated from the quartz data (assuming that the energy transfer reaction

$$M^* + A \rightarrow M + A^*$$

occurred with 100% efficiency) to be

$$0.00699 \times 0.273 = \underline{0.00191} \text{ gm.mol./li./hr.}$$

This is much greater than the observed rate which was less than 0.0002 gm.mol./li./hr.

(ii) that oxetane was formed from the reaction

$$M^* + A \rightarrow \text{oxetane}$$

alone. Assuming no energy transfer reaction of the kind

$$M + A^* \rightarrow M^* + A$$

the initial rate of formation of oxetane in the borosilicate case was calculated from the quartz case to be

$$0.00699 \times 0.273 \times \frac{0.0026}{0.11} = \underline{0.000045} \text{ gm.mol./li./hr.}$$

This is in accord with the observations that the rate was less than 0.0002 gm.mol./li./hr.

Thus, there is good evidence that oxetane was formed by the reaction

$$M^* + A \rightarrow \text{oxetane}$$

without a significant contribution from the reaction

$$M + A^* \rightarrow M^* + A.$$

Note: The reaction M + A* → oxetane might also have occurred. This investigation merely shows that if it did, it was a very slow reaction in comparison with the reaction M* + A → oxetane. The reaction M + A* → oxetane was expected to be a slow reaction since it is likely to proceed by attack of the electron deficient oxygen atom of excited acetone on the electron deficient C=C double bond of ground-state maleate. Oxetanes were formed very slowly during the mb irradiation. When measurable quantities were first observed in the irradiation mixture, the ratio of cis- to trans-oxetane diester was much greater than would have been expected from the other experimental data, notably the mq case. This might be connected with the participation of the slow reaction of excited acetone observable only when the reaction of excited maleate was suppressed by the use of

borosilicate apparatus.

(e) The ratio of rates of formation of cis-oxetane diester to trans-oxetane diester in the mq case was 1 : 6.35. This is evidence for the intervention, a least in part, of a triplet state reaction.[35]

(f) Consider the following possibilities for fumarate formation.

(i) that fumarate was formed by the reaction

$$M + A^* \rightarrow F + A$$

alone. The maximum expected rate in the quartz case consistent with this mechanism was calculated from the borosilicate data, by assuming that the energy transfer reaction

$$M^* + A \rightarrow M + A^*$$

occurred with 100% efficiency, to be

$$\frac{0.0107}{0.273} = \underline{0.0392} \text{ gm.mol./li./hr.}$$

The observed rate was 0.1053 gm.mol./li./hr.

This is 2.68 times the expected value. Even considering the $\pm$ 20% possible error in these comparisons, the isomerisation reaction rates cannot be accounted for on the basis of the reaction

$$M + A^* \rightarrow F + A \qquad \text{alone.}$$

(ii) that fumarate was formed by the reaction

$$M \xrightarrow{h\nu} M^* \rightarrow F.$$

alone. The rate of isomerisation in the borosilicate case was derived on this basis from the quartz data as

$$0.105 \times 0.273 \times \frac{0.0026}{0.11} = \underline{0.00068} \text{ gm.mol./li./hr.}$$

The observed rate in the borosilicate case was 0.0107 gm.mol./li./hr. Thus

the isomerisation reaction rates cannot be accounted for on the basis of the reaction

$$M \xrightarrow{h\nu} M^* \rightarrow F$$

alone. The data was however in accord with the occurrence of two reactions

$$\left.\begin{aligned} M + h\nu &\rightarrow M^* \rightarrow F \\ M + A^* &\rightarrow F + A \end{aligned}\right\}$$

leading to fumarate. The second reaction presumably involved an energy transfer step

$$M + A^* \rightarrow M^* + A \rightarrow F + A,$$

otherwise, it is not easy to see why the fumarate → maleate reaction was not similarly advanced by the presence of excited acetone.

(g) The evidence presented strongly suggests that both oxetane and fumarate were formed from excited maleate. Excited acetone, however, photosensitized the formation of fumarate, although it had no significant effect on the oxetane forming reaction. This led to different values of the ratio

$$\frac{\text{initial rate of formation of oxetanes}}{\text{initial rate of formation of oxetanes + initial rate of formation of fumarate}}$$

in the quartz and borosilicate cases. If the assumption that excited maleate is responsible for both reactions is valid, this indicates that different excited states of maleate are involved in the two reactions.

E) <u>The effect of varying the concentration of the dimethyl fumarate</u>

Irradiations of acetone solutions of dimethyl fumarate were performed using three different concentrations of fumarate. In all cases, quartz

apparatus was used.

The limited investigation conducted revealed the great complexity of the photochemistry of this system. Much more work is required before definitive statements can be made. However, some suggestions are made which could account for the observations presented in a qualitative fashion.

The results of the examination are recorded in Table IX.

Table IX

Initial fumarate concentration.	0	0.025M	0.23M	0.47M
Rate of formation of maleate.	0	0.37	0.239	0.20
Rate of formation of trans-oxetane diester.	0	0.0104	0.0550	0.0590
Sum of rates of formation of maleate and oxetane.	0	0.38	0.294	0.26
$\frac{\text{Rate of formation of trans-oxetane}}{\text{Sum of rates of formation of maleate and oxetane.}}$	-	0.0274	0.187	0.227

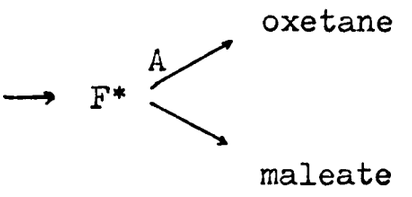
Rates are in units of gm.mol./li./Tunit.

(a) The concentration of acetone was so great, it being also the solvent, that it was regarded as constant from experiment to experiment.

(b) The total reaction, that is the sum of the oxetane and maleate forming reactions, was reduced as fumarate concentration was increased over the range examined, in spite of the fact that the percentage of the incident absorbed light absorbed directly by dimethyl fumarate increased

from 2.4% at 0.025M to 14% at 0.23M and 67% at 0.47M fumarate concentration. This is unexpected since it was shown by comparing the f(0.23M)q and fb cases that only that light absorbed directly by dimethyl fumarate led to reaction. The observed decrease in total reaction rate could be explained in terms of the onset of some efficient self-quenching process as the initial fumarate concentration was increased. The material balance examination (see page 55 of this thesis) eliminated the possibility of gross side reactions.

(c) The very different concentration dependences of the two reactions is not explicable in terms of a common intermediate reacting in two ways thus



for, since acetone was present in large excess, the rates of the two reactions are given by the equations

$$\text{Rate of formation of oxetane} = k_o [F^*]$$

$$\text{Rate of formation of maleate} = k_m [F^*]$$

and since any concentration quenching effects only influence the value of $[F^*]$, the ratio

$$\frac{\text{rate of formation of oxetane}}{\text{rate of formation of maleate}} = \frac{k_o}{k_m}$$

would be constant with fumarate concentration. This was not observed.

There is therefore some evidence for the participation of more than

one excited state of fumarate in the photochemistry of this system. This is an attractive hypothesis in view of the previous conjecture that two excited states are involved in the photochemistry of maleate (page 80).

F) Summary

The supposed mechanistic implications of this data could be rationalised in terms of the energy-level diagram given in Figure XXXVIII.

G) On the possible natures of the excited states

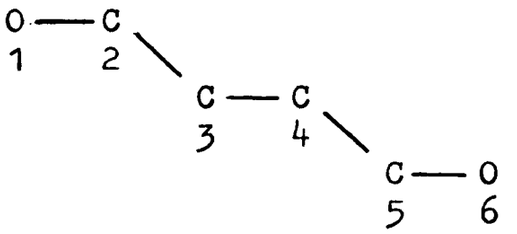
The energy level diagram presented in Figure XXXVIII, although being in no way proven, is put forward as one possible way of correlating the observed data.

Some attempt is now made to relate these energy levels with known states of the molecules. Molecules of the kind studied here are known to exist in both singlet and triplet energy states and in both (n, π^*) and (π, π^*) excited states. Spectral data on energies of transitions to these states has been presented on pages 14 and 67 of this thesis. Speculations are complicated by total lack of knowledge of the positions of 0,0 bands.

In view of the hydrogen-abstracting properties of acetone under the influence of light,[37] properties usually associated with the (n, π^*) carbonyl state, and in view of the ease and efficiency with which ^{1}(n, π^*) states of carbonyl compounds degrade to their lowest triplet states,[14,36] A* (Figure XXXVIII) is probably a ^{3}(n, π^*) state.

If A* is a triplet state, M_I^{*}† is also, for M_I^* singlet has an higher energy than the $^3(n, \pi^*)$ state of acetone. It is not possible to deduce from the data presented whether there is also a singlet state of maleate involved in isomerisation or whether the singlet states when formed degrade to $^3M_I^*$ before isomerising.

Spectral measurements[2] indicate that the $^1(n, \pi^*)$ and $^1(\pi, \pi^*)$ states of maleate are probably of very similar energy. Since the singlet triplet splitting is frequently much greater for (π, π^*) states than for (n, π^*) states,[38] this would tend to indicate that $^3M_I^*$, the lowest triplet state of maleate, is a $^3(\pi, \pi^*)$ state. It is interesting to note that the central bond order of the $^3(\pi, \pi^*)$ state is probably much lower than that of the $^3(n, \pi^*)$ state. Thus a zero order L.C.A.O. calculation of the orbitals of the π-electron system



using the approximate values of $\alpha + 2\beta$ for the oxygen Coulomb integral and $\beta\sqrt{2}$ for the C-O resonance integral revealed a C(3) - C(4) total bond order of 1.63 for the (n, π^*) state and 1.24 for the (π, π^*) state. It is not unreasonable to infer that the (π, π^*) state of maleate is more likely to readily isomerise to fumarate than is the (n, π^*) state.

Whether maleate or fumarate was irradiated in acetone, the main

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† For nomenclature M_I^* and M_O^*, see Figure XXXVIII.

product was the thermodynamically more stable trans-oxetane diester. This suggests that the reaction involves a triplet intermediate although the small amount of cis-oxetane diester obtained only when maleate was irradiated might suggest some singlet state reaction.[35] It is proposed that this $^3M_o^*$ state might correspond with the other expected triplet state of maleate, namely the $^3(n, \pi^*)$ state.

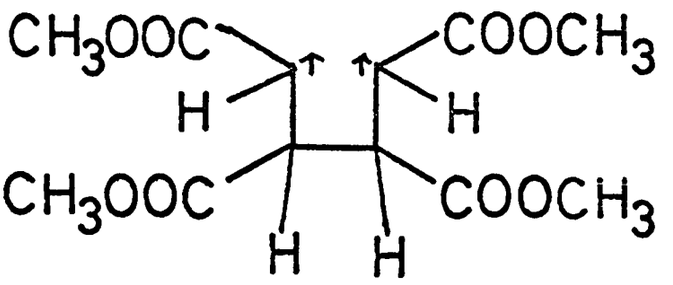
Zero order calculations suggest that the C(3) - C(4) bond of the (n, π^*) state of maleate/fumarate is electron rich, whereas that of the (π, π^*) state is electron deficient. If the $^3M_I^*$ state is a $^3(\pi, \pi^*)$ state, it is difficult to understand why it should not form an oxetane by reaction with ground state acetone, except by analogy with all other photochemical oxetane forming reactions whose mechanisms have been investigated and in which it is known that oxetanes are not formed by reaction of excited olefin with ground state ketone. But if this is so, it is even more difficult to see how the (n, π^*) state of fumarate could react with ground state acetone to give oxetane for here there is the added factor that the electron rich oxygen of ground state ~~of~~ acetone would less readily attack the electron rich C(3) - C(4) bond of (n, π^*) maleate than the electron deficient C(3) - C(4) bond of (π, π^*) maleate.

Let us assume that an analogous situation with regard to order and reactivity of energy levels exists for fumarate. This includes the assumption that the oxetane forming reaction involves a triplet state of fumarate. The stereochemistry of the oxetanes formed from maleate indicate that a triplet state of maleate is probably responsible for oxetane formation, at least in part. However the stereochemistry of the

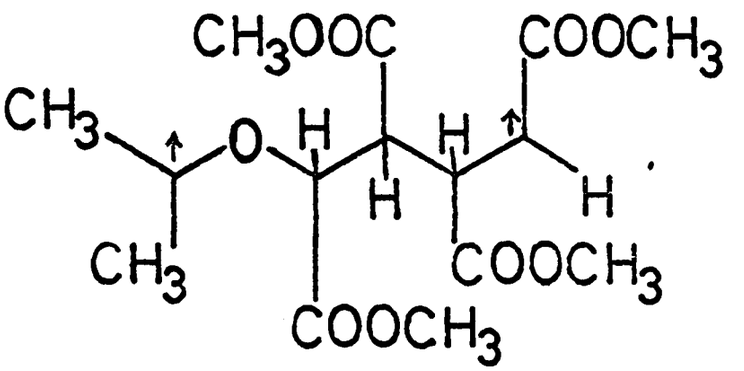
oxetanes formed from fumarate are accounted for on the basis of either a singlet reaction or a triplet reaction. There is no evidence either way. The only basis for the tentative assumption that triplet fumarate is involved in oxetane formation is by analogy with the maleate case. Table IX shows that the oxetane forming reaction comprises an increasing fraction of the total reaction and the isomerisation reaction a decreasing fraction of the total reaction as fumarate concentration increases. A qualitative explanation is suggested if, as was thought reasonable in the maleate case, the $^3(n, \pi^*)$ state has an higher energy than the $^3(\pi, \pi^*)$ state and if the formation of oxetane requires the participation of a ground state molecule of fumarate so that if the $^3(n, \pi^*)$ state does not encounter a ground state fumarate molecule during its short life, it decays to $^3(\pi, \pi^*)$ fumarate and isomerises. The likelihood of the $^3(n, \pi^*)$ state encountering a ground state fumarate molecule increases, and so its likelihood of decaying to a $^3(\pi, \pi^*)$ state decreases with increasing fumarate concentration. (n, π^*) Fumarate, which is electron rich at C(3) and C(4) is more likely to interact readily with electron deficient ground state fumarate than is (π, π^*) fumarate which is also electron deficient.

In all these considerations, it is difficult to see why the interaction of $^3(n, \pi^*)$ fumarate with ground state fumarate should not lead to cyclobutane formation, especially in view of the formation of cyclobutane when maleic anhydride is irradiated in acetone.[6] This reaction was shown to be photosensitized by acetone. However the case investigated is not unique. Fumaronitrile irradiated in acetone forms no cyclobutane.[11]

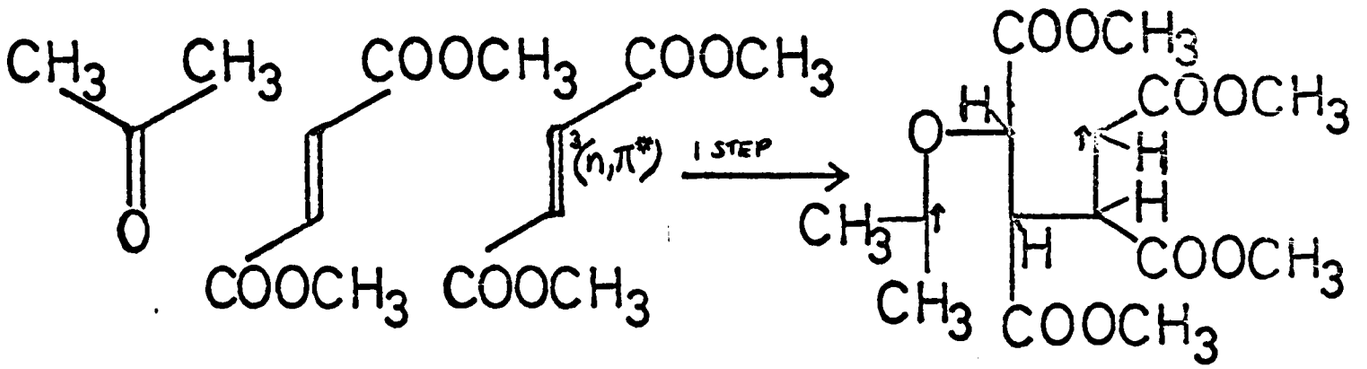
The mechanism suggested and the non-formation of cyclobutane could be reconciled if the reaction is a triplet reaction. Under these circumstances any reaction of $^3(n, \pi^*)$ fumarate with ground state fumarate would lead to the formation of the intermediate diradical



which cannot ring close until spin inversion occurs. The radical centres are electron deficient centres in virtue of the adjacent methoxycarbonyl groups. The diradical exists in a solution of acetone, and since acetone bears electron rich oxygen, there is likely to be a competing reaction with the ring closing reaction giving

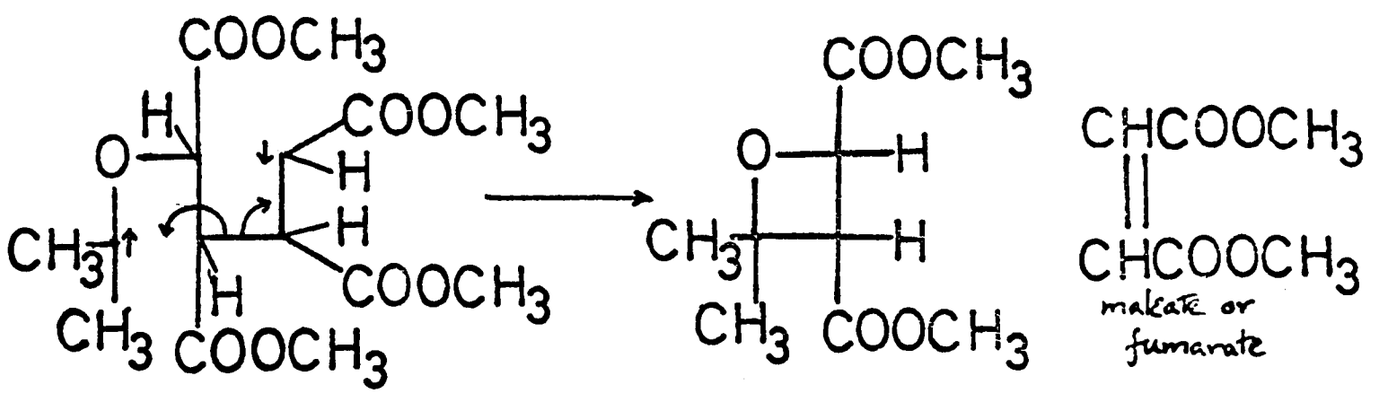


A much more likely first step would be the concerted addition reaction

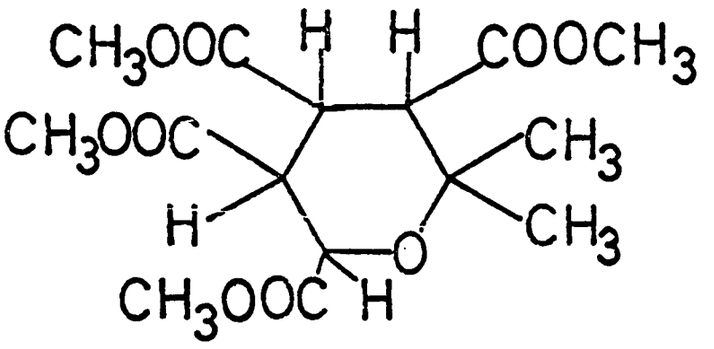


This is not as unlikely a mechanism as it might appear, for of all the acetone molecules solvating a ground state fumarate molecule, there is likely to be one in approximately the right position at any instant to undergo the concerted reaction if an $^{3}(n, \pi^*)$ fumarate molecule should approach. This concerted mechanism provides a thermodynamically more favourable route for the formation of the first C-O bond between a fumarate residue and ground state acetone than any other mechanism considered here. Little is known about the stereochemistry of concerted free radical reactions, but it seems possible that the reaction might proceed by a <u>trans</u> addition mechanism[40] so that the two radical centres once formed would be remote from each other.

Oxetane might be formed from this intermediate diradical by a substitution reaction of the kind



Fumarate provides a good leaving group and this step is expected to be exothermic. The formation of a certain amount of the compound



is expected if this mechanism is valid.

It is realised that very little evidence exists to substantiate this mechanism in detail. The mechanism is suggested merely as one means of attempting to correlate the many puzzling aspects of this reaction. Clearly much further work is required in order to reach a full understanding of the mechanism of the photochemical formation of oxetane from acetone and maleate/fumarate.

As one step in this direction, the results of electron impact spectroscopic investigations are awaited eagerly as it is hoped that these will lead to a knowledge of the triplet energy levels of the molecules concerned. The oxygen-perturbation measurements which were conducted to this end were inconclusive. They could be rationalised on the basis of the energy level scheme postulated if the main peak corresponding to a transition to a $^3(n, \pi^*)$ state and the side hump to a $^3(\pi, \pi^*)$ state. However the spectra were not good and no information of the position of 0,0 bands could be obtained.

It is hoped to be able to submit the electron impact spectra of these compounds as an appendix to this thesis if they are measured in time.

Section II

THE PHOTOCHEMISTRY OF ACETOXIME

A) Introduction

Acetoxime absorbs short wavelength ultraviolet light of wavelength less than 250 - 260 mμ. This absorption has been examined.[44,45] An ethanolic solution of acetoxime has been found to exhibit absorption having $\lambda_{max} \sim 190$ mμ ($\log \epsilon = 3.70$), similar to the acetone $\lambda_{max} = 186$ mμ band. Solvent shift experiments showed that this band of acetoxime is $\pi \rightarrow \pi^*$ in nature. No absorption corresponding to the $n \rightarrow \pi^*$ acetone band has been observed. Optical rotatory dispersion methods have failed to detect such an $n \rightarrow \pi^*$ transition in conjugated oximes.[46]

B) Acetoxime/cyclohexene system

(a) General

(i) A deoxygenated solution of acetoxime dissolved in cyclohexene was irradiated for 9 hr. in a quartz vessel. Spectral measurements showed that under the conditions used acetoxime was responsible for more than 70% of the absorption of the solution.

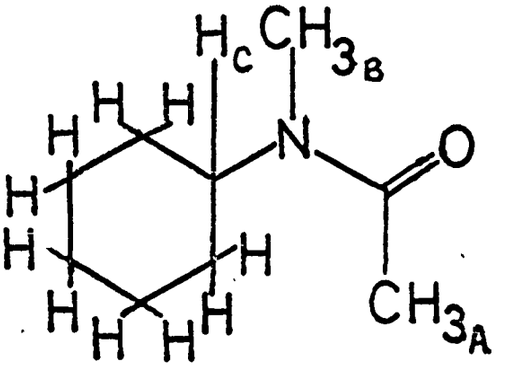
(ii) A solution of the same composition containing additionally a little benzophenone was irradiated under identical conditions. In this case, benzophenone absorption accounted for nearly all the absorption of the solution.

The crude products of these irradiations were yellow liquids. On examination by gas chromatography, the product of the irradiation conducted in the absence of benzophenone was found to consist of three major

and a large number of minor components. The largest chromatogram peak occurred at short retention time. Two closely separated moderately-sized peaks were observed at longer retention time. The product of the sensitized irradiation yielded an identical chromatogram save that the short retention time peak was even more dominant and that an additional peak was present at longer retention time. The benzophenone peak was also observed having a very long retention time.

Attempts were made to separate the major components of the crude photoproduct of the first irradiation. Neither column chromatography nor preparative thin-layer chromatography resolved the mixture of the two long retention time products. Both components were eluted together from a silica-gel column in ethyl acetate. Similarly preparative thin-layer chromatography gave a mixture of the two components. However the main short retention time product was easily separated on a silica gel column and was identified as bicyclohex-2-enyl (V).

The long retention time irradiation products were finally resolved using preparative gas chromatography. Some difficulty was encountered because of the thermal instability of certain of the components of the crude mixture. Again bicyclohexenyl was isolated. The first of the longer retention time products to be eluted from the column was identified as a 1:1 adduct of cyclohexene and acetoxime, namely N-acetyl-N-methyl-cyclohexylamine (VI). Elemental analyses and molecular weight determinations were in accord with this formulation. The infrared spectrum exhibited amide absorption at 1630 $cm.^{-1}$, but no N-H band was observed. The n.m.r. spectrum was interpreted on the following basis.



13 protons	τ = 7.9 to 9.0	Broad, largely structureless absorption band characteristic of the cyclohexyl group.
	τ = 8.02	Singlet. Protons of methyl group (A).
3 protons	τ = 7.17 τ = 7.25 separation 4.8 c.p.s.	Two singlets. Protons of methyl group (B), split by virtue of limited rotation about C-N amide bond.(48)
1 proton	τ = 6.4 τ = 5.7	Two very broad absorptions. Proton $H_{(C)}$. The analogous proton in the related compound (VII) absorbs in two very broad bands at τ = 5.85 and τ = 6.35.(49)

Further, a sample of authentic N-acetyl-N-methylcyclohexylamine was prepared by acetylation of commercially available N-methylcyclohexylamine and was found to have infrared and n.m.r. spectra identical with those of the photochemically produced material.

The second longer retention time product was found to be N-acetyl-N-methylcyclohex-2-enylamine (VIII). The infrared spectrum was very similar to that of N-acetyl-N-methylcyclohexylamine apart from bands at 3020 and 720 $cm.^{-1}$ associated with the unsaturation of the cyclohexene ring and the n.m.r. spectrum was also similar apart from a complex system of broad absorptions between τ = 4 and τ = 5 corresponding to the two vinyl protons. In addition, this compound was reduced by hydrogen in the presence

of Adam's catalyst to give a compound of identical mass spectrum and infrared spectrum to N-acetyl-N-methylcyclohexylamine.

N-acetyl-N-methylcyclohex-2-enylamine (VIII) was distinguished from its isomer N-acetyl-N-methylcyclohex-3-enylamine (IX) by an examination of the mass spectrum. Cyclohexene derivatives undergo the well-authenticated retro-Diels Alder fission in a mass spectrometer[50] and this was used diagnostically. The observation of a much stronger peak at $\frac{m}{e}$ = 125 than at $\frac{m}{e}$ = 99 was taken as evidence of the allylic substitution of the cyclohexene (see p. 141). Allylic substitution was also expected on general grounds.[51]

In this reaction, the total yield of 1:1 acetoxime/cyclohexene photo-adducts was of the order of 2% (based on acetoxime) from a 9 hr. irradiation.

Mixtures of the two amides obtained by thin-layer or column chromatography exhibited a carbonyl infrared absorption at 1730 $cm.^{-1}$ in addition to the bands expected. The intensity of this band showed that the carbonyl compound responsible was present as a significant impurity. No reaction with Brady's reagent nor with Girard's reagent T was observed. The origin of this absorption was not examined further.

(b) Mechanism

Two possible mechanisms for the photoreaction between acetoxime and cyclohexene were investigated.

The reaction probably involved a triplet excited state since it was photosensitized by benzophenone, a well-known triplet-transfer agent. Since the triplet energy of benzophenone is 68.5 kcal./mol.[52] and that of an olefin is of the order of 82 kcal./mol.,[53] any triplet transfer

presumably involved acetoxime. No determinations have been made of the triplet energies of such oximes but it is quite possible that they lie lower than 68.5 kcal./mol.

(i) One possible mechanism involves two steps.

(1) Photoisomerisation of acetoxime to N-methylacetamide (X).

(2) Photochemical addition of N-methylacetamide to cyclohexene to produce the observed products.

This mechanism is favoured by the recent observation of the photochemical transformation of aryl aldoximes to amides.(54)

The hypothesis was tested by irradiating solutions of N-methylacetamide in cyclohexene for 30 hr. both in the presence and in the absence of benzophenone. Like acetoxime, N-methylacetamide exhibits tail absorption at wavelengths < 250 mμ so that when benzophenone was present most of the reaction proceeded via the excited state of benzophenone. The liquid N-methylacetamide being rather insoluble in cyclohexene, the two components were kept well mixed by the passage of a rapid nitrogen stream through the liquid during irradiation.

The crude irradiation products possessed the same characteristic smell as the product of the acetoxime/cyclohexene irradiation and gas chromatography revealed them to be complex mixtures of photoproducts. However no N-acetyl-N-methylcyclohexylamine nor N-acetyl-N-methylcyclohexenylamine had been produced. Because of the complex nature of these and other chromatograms obtained during these investigations, retention times of components of two mixtures could only be compared reliably by running mixed chromatograms, that is a chromatogram of the mixture of the

two samples. This method was found to be superior to a comparison of absolute retention times between chromatograms.

Although this observation indicated that the acetoxime-cyclohexene adducts were not formed by a direct addition of N-methylacetamide to cyclohexene, a possibility existed that acetoxime might catalyse the addition in some way, possibly as a photosensitizer. To investigate this possibility cyclohexanone oxime was used since it was assumed that whereas the electronic nature of its oxime group would closely resemble that of acetoxime yet any products derived from its own reaction would be likely to differ in retention time from those of the acetoxime-cyclohexene adducts.

Twenty hour irradiations of cyclohexanone oxime in cyclohexene solution in the presence and in the absence of N-methylacetamide were conducted and the products again examined by gas chromatography. The chromatograms obtained were identical at longer retention times whether or not N-methylacetamide was present in the irradiation mixture. Very large peaks corresponding to cyclohexanone oxime and bicyclohexenyl were observed but no N-acetyl-N-methylcyclohexylamine nor N-acetyl-N-methyl-cyclohexenylamine were detected.

As a final experiment, the photoisomerisation reaction of acetoxime to N-methylacetamide was studied. Initial experiments were conducted irradiating cyclohexane and acetonitrile solutions of acetoxime. This approach was soon abandoned for fear of involving the solvent in the photochemistry of the system. Thus in cyclohexane solution after only one hour's irradiation at least six short retention time products were

observed. In acetonitrile solution, however, only one short retention time product was observed. This was formed very slowly over a period of 21 hr. and had a retention time on a vpc column identical with that of N-methylacetamide.

Further irradiations were conducted on solid acetoxime. A first experiment showed that of 99% of the acetoxime remained unchanged after 6 hours irradiation, so irradiation was continued over a period of 3 days. Approximately 25% by weight of the final product were extracted with organic solvents, the residue being a red water-soluble gum. An examination of the well defined infrared spectrum of the worked-up extracts provided no evidence for significant concentrations of N-methylacetamide.

However, gas chromatography of these materials using two different columns showed that one of the major peaks had retention times exactly equal to those of N-methylacetamide. It is likely either that N-methylacetamide was a minor component of these distillates, the major component not being observed on the chromatogram, or else that the major component decomposed in the chromatograph to produce some N-methylacetamide.

The products of these irradiations were found to decompose on keeping and were not investigated further.

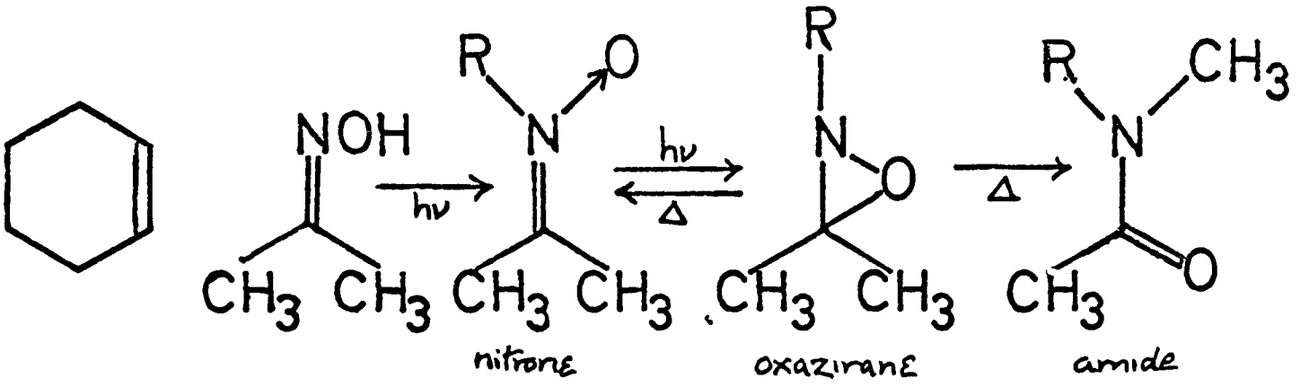
Conclusion. The mechanism postulated is unlikely because of

(1) the non-formation of 1:1 adducts of N-methylacetamide-cyclohexene in the presence of light.

(2) the very poor conversion of acetoxime to N-methylacetamide by light.

(ii) The photochemical isomerisation of nitrones to oxaziranes has

been investigated.[55] Since oxaziranes are thermally unstable yielding nitrones and amides, a possible mechanism for the photoaddition of acetoxime to cyclohexene is suggested. This is outlined in the scheme



R = cyclohexyl or cyclohexenyl.

It was proposed to examine the formation of amide from nitrone and not, at this point, to examine the formation of nitrone from oxime.

The mechanism seems somewhat unlikely in view of recent investigations indicating that the photo-reaction of nitrones yielding oxaziranes is a singlet state reaction,[56] since gas chromatography has indicated that the reaction proceeded in the presence of benzophenone, a triplet sensitizer.

Published work on the photochemistry of nitrones largely concerns arylnitrones so an attempt was made to estimate the speed and efficiency of the photo-reaction of alkyl nitrones such as are postulated as intermediates in the system under investigation. Preliminary experiments were conducted on N-methyl-α,α-dimethylnitrone (XI). Samples of the free base and the hydrochloride were prepared according to the method of O. Exner.[57] Irradiation of crystals of the hydrochloride for up to 18 hr. produced no N,N-dimethylacetamide although another product was very

slowly formed. When the free base was irradiated however, a gas chromatogram peak corresponding in retention time to that of the expected N,N-dimethylacetamide was observed. This formed very slowly so that after 9 hr. irradiation it was present in the crude mixture in very small amount, being only one of at least four photoproducts. After 20 hr. irradiation the peak had disappeared and the major product of the irradiation was a red water-soluble gum.

Conclusion. In view of the very slow and very inefficient nature of the photoisomerisation of the alkyl nitrone studied, it is unlikely that the mechanism postulated could make a significant contribution to the reaction under consideration.

Further investigations of the possible mechanism of this reaction were precluded by reason of the limited time available.

C) Other systems

Irradiations were conducted on the propionaldoxime/cyclohexene system. No progress was made towards isolating the products of this reaction by virtue of their apparent instability.

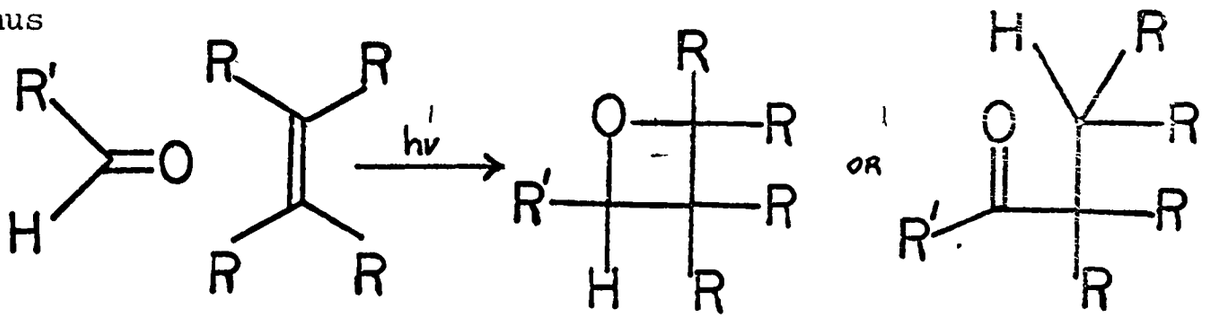
Irradiations were also conducted on the acetoxime/dimethyl maleate system. Under the conditions used the maleate accounted for all the incident light absorbed by the system. No products derived from acetoxime were observed although fumarate and the cis-trans-cis-1,2,3,4-tetramethoxycarbonylcyclobutane, both derived from the maleate, were noted.

Section III

IRRADIATIONS INVOLVING ALDEHYDES

A) General

Aldehydes add to olefins in the presence of light in one of two ways. Either oxetanes are formed or Kharasch addition takes place, thus



The current understanding of these reactions is reviewed in the introduction. The factors governing which mode of photoaddition takes place are not fully known. Aromatic and conjugated aldehydes, if they react, form oxetanes. No case is known of a conjugated aldehyde undergoing Kharasch addition. However, Kharasch addition is the usual mode of photoaddition of non-conjugated aldehydes to olefins. If the postulated mechanism of Kharasch addition[58] is valid, this difference in behaviour might be associated with the differing abilities of the two classes of aldehyde to initiate the Kharasch chain, thus,

$$RCHO + h\nu \rightarrow R^{\bullet} + {}^{\bullet}CHO$$

$$R^{\bullet} + RCHO \rightarrow RH + R\dot{C}O$$

A factor bearing on this is the relative strengths of the aldehydic C-H bonds.[59] It is further suggested that the relative energies of the $^3(n,\pi^*)$ and $^3(n,\sigma^*)$ states of the different aldehydes might be an

important factor, the first state being expected to be involved in oxetane formation[34] and the second in the Kharasch reaction.[60]

However exceptions to any simple rule occur. Evidence is accumulating that certain non-conjugated aldehydes under some circumstances form oxetanes[61,62] whereas under other conditions Kharasch addition occurs.[63] A low $\frac{\text{aldehyde}}{\text{olefin}}$ mole ratio is usually employed for oxetane formation, but this ratio is not so low that a chain mechanism such as is postulated for the Kharasch addition could not be effective. In one case this ratio was as high as 1:1 but oxetane was the only product identified.[34c] So, although there is strong circumstantial evidence in favour of the postulated mechanism of the Kharasch reaction (see Introduction), this does not fully explain the whole of aldehyde/olefin photochemistry. There is no direct evidence that the acyl radical is the species responsible for Kharasch addition nor is it known how the two modes of addition are inter-related.

In this work a number of substituted olefins have been irradiated in dilute solution in propionaldehyde. In some cases this has involved irradiating systems similar to those irradiated elsewhere.[58,62,63] Propionaldehyde exhibits a weak $n\rightarrow\pi^*$ absorption at λ_{max} = 272 mμ tailing to $\lambda \sim 330$ mμ. All irradiations (except one) were conducted using pyrex apparatus so that, except where crotonaldehyde was involved, light absorption led only to the excitation of the $n\rightarrow\pi^*$ transition of propionaldehyde.

B) Propionaldehyde, propionaldehyde/styrene and related irradiations

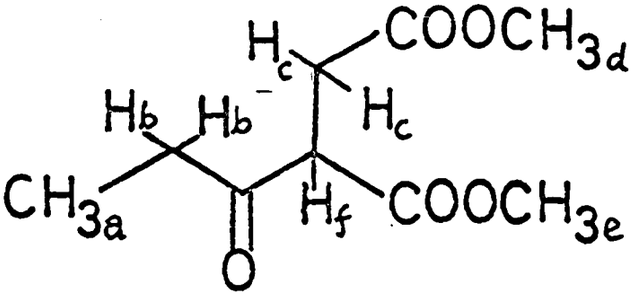
When propionaldehyde was irradiated alone for 4 hr., a small amount of material possessing hydroxyl and carbonyl infrared absorption yet not

reacting with Brady's solution was produced. A similar product, presumably also derived from the propionaldehyde alone, was obtained on irradiating a propionaldehyde/styrene mixture. The lack of significant adduct formation from styrene mirrors the observation that aldehyde does not add to styrene in the presence of peroxide.(64) It is interesting that no oxetane formation was noted although its formation in this system has been reported by other workers.(62) The conditions used for the production of oxetane differed in that a low $\frac{\text{aldehyde}}{\text{styrene}}$ ratio ($\sim$ 0.25) was employed. It is not stated what range of wavelengths of light was used in that irradiation. Attempts to resolve the complex mixture produced in the propionaldehyde/styrene irradiation described in this work met with little success.

Irradiations of ethyl vinyl ketone, crotonaldehyde and benzene in propionaldehyde yielded results analogous to those obtained with the styrene irradiation. (In the crotonaldehyde case, a considerable proportion of the absorbed incident radiation was absorbed by propionaldehyde.)

C) Propionaldehyde/dimethyl maleate irradiation

The propionaldehyde/dimethyl maleate irradiation led to the formation of a compound, identified as the 1:1 Kharasch adduct (XII) in 92% yield. This formulation was in accord with elemental analysis and molecular weight determinations. The presence of ketonic carbonyl was evident from an examination of the infrared and ultraviolet spectra and the ester carbonyl absorption was also evident in the infrared. The n.m.r. spectrum was also rationalised on the basis of this structure, thus



a	τ = 8.95 (triplet, J = 6.9 cps)		3 protons
b	τ = 7.33 (quartet, J = 6.9 cps)	}	4 protons
c	τ = 7.17 (doublet, J = 7.2 cps)	}	
d, e	τ = 6.37, 6.29 (singlets)	}	7 protons
f	τ = 6.10 (triplet, J = 7.2 cps)	}	

This was further confirmed by acid hydrolysis followed by loss of carbon dioxide from the β-ketoacid generated. The 4-oxohexanoic acid produced was identified as its methyl ester (XIII).

D) Acetaldehyde/dimethyl maleate irradiation

Acetaldehyde was similarly irradiated with dimethyl maleate and the 1:1 adduct formed in 70% yield characterised as the Kharasch addition product (XIV). The n.m.r. spectrum was interpreted in a fashion analogous to that of the propionaldehyde adduct. However the protons marked * are not exactly equivalent in this case (τ = 7.23 and 7.18).

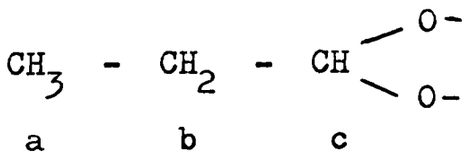
E) Propionaldehyde/methyl crotonate irradiation

Gas chromatography of the propionaldehyde/methyl crotonate product showed that it consisted of only one component, identified as the Kharasch adduct, methyl 3-methyl-4-oxohexanoate (XV). No methyl 2-ethyl-3-oxopentanoate (XVI) was formed. It was possible to distinguish

between these two structures by hydrolysis. The acid isolated was thermally stable and so unlikely to be a β-ketoacid.

F) Propionaldehyde/cyclohexene irradiation

The propionaldehyde/cyclohexene irradiation produced a mixture of compounds which were separated using preparative gas chromatography. On this occasion the recovery was poor so that only three of the components could be investigated. One compound isolated in amount after distillation sufficient only to obtain an infrared spectrum exhibited absorption characteristic of hydroxyl, vinyl hydrogen, and a cis-substituted carbon-carbon double bond. This material might possibly be 1-cyclohex-2'-enylpropan-1-ol (XVII) isolated by de Mayo (58). A second component isolated was 2,4,6-triethyl-1,3,5-trioxan (XVIII), identified by the absence of hydroxyl and carbonyl absorption and by the presence of ether absorption in the infrared. The n.m.r. spectrum could be rationalised on the basis



a	$\tau = 9.05$	
		$J_{ab} = 7.5$ cps
b	$\tau = 8.30$	
		$J_{bc} = 5.0$ cps
c	$\tau = 5.25$	

and the formulation was confirmed by analysis and molecular weight determinations.

A third component was ethylcyclohexyl ketone (XIX), the Kharasch adduct, identified on the basis of spectral data and of the m.p. of its 2,4-dinitrophenylhydrazone.

Some propionic acid was present in the irradiation product. This was almost certainly produced in work up. A little may have formed thermally during the irradiation owing to inadequate deoxygenation.

No bicyclohex-2-enyl was isolated from this irradiation. A second 4 hr. irradiation was conducted after deoxygenation. An examination of the gas chromatogram of the product showed neither bicyclohexenyl nor cyclohexanone. It has been suggested[58] that the presence of dissolved oxygen suppresses the formation of bicyclohexenyl by the reaction of cyclohexenyl radicals with oxygen to give a peroxide which degrades to cyclohexanone. This does not appear to be the reason for the non-formation of bicyclohexenyl in this case.

G) Crotonaldehyde/dimethyl maleate irradiation

A dilute deoxygenated solution of dimethyl maleate was irradiated in crotonaldehyde (mole ratio 1:10) for 2.5 hr using a pyrex reactor. Examination of the product revealed no photochemical reaction at all had occurred.* As expected, no Kharasch reaction occurred, but neither had oxetane formed nor had any product derived by energy transfer to maleate (e.g. tetramethoxycarbonylcyclobutane).

H) Correlation between the peroxide-induced and photochemical reactions

Having investigated a number of Kharasch reactions, an attempt was made to correlate the photochemical addition of aldehydes to substituted olefins with the peroxide induced reaction. As explained earlier, anomalous behaviour of aldehydes in certain cases in relation to the

---

* A small quantity (30 mg.) of crotonic acid had formed.

oxetane forming reaction leads to a questioning the nature of the excited species produced during aldehyde irradiations. In as far as a close correlation is found between the photochemical and peroxide induced reactions this is evidence that the same intermediate, the acyl radical, is responsible for both reactions.

Dilute propionaldehyde solutions containing a mixture of compounds found to undergo the photochemical Kharasch reaction were accurately prepared. To one solution peroxide was added. The other solution was irradiated. The reactions were controlled so that only a small concentration of the adduct would be formed compared with the initial concentration of unsaturated material. When the reaction was terminated, the solutions were examined by gas chromatography (for a typical chromatogram, see figure XLI). Absolute concentrations were estimated by adding a marker (naphthalene) to the reaction product solutions and by making up a calibration solution (solution B). The quantities $\frac{A}{B}$, where A was the final concentration of Kharasch adduct derived from an unsaturated compound, initial concentration of reactant B, were compared.

The following $\frac{A}{B}$ mole ratios were calculated

Unsaturated compound	Photoreaction	Ratio	Peroxide reaction	Ratio
Cyclohexene	$\leq$ 0.0010	0.017 to	$\leq$ 0.00037	0.024 to
Methyl crotonate	0.0118	0.202 to	0.00392	0.250 to
Dimethyl maleate	0.0583	1.000	0.0157	1.000

The close resemblance of the relative reactivities of these compounds together with the observation that those compounds not undergoing the

photochemical Kharasch reaction, do not undergo the peroxide-induced reaction is strong evidence that the same (nucleophilic) species, namely the acyl radical, is responsible for both reactions. The correlation of this reaction with the oxetane reaction remains a mystery.

No dimethyl fumarate was formed in the course of the photochemical reaction. This is evidence that the attack of acyl radicals on maleate is not reversible.

PART TWO - EXPERIMENTAL

GENERAL

A) Materials

Acetone used in irradiations was ANALAR grade, produced by Hopkins and Williams Ltd.

Dimethyl maleate was prepared by the method of Linstead and Whalley.[42] The purity of the final product, b.p. 100-102°C/2 cm. was confirmed by gas chromatography.

Dimethyl fumarate was prepared by the method of Jeffery and Vogel,[43] and recrystallised from benzene. For spectral measurements, samples were further resublimed.

Nitrogen used in irradiations was 'white spot' grade, further purified by treatment in turn with alkaline pyrogallol, concentrated sulphuric acid and anhydrous calcium chloride.

B) Melting points were determined using a Kofler block and were corrected.

C) Microanalyses were performed by Drs. Weiler and Strauss.

D) Ultraviolet spectra were recorded using a Cary spectrometer, model 14M-50, unless otherwise stated.

E) Infrared spectra were recorded using a Perkin-Elmer, model 237, grating spectrometer unless otherwise stated.

F) Nuclear magnetic resonance (n.m.r.) spectra were recorded using a Perkin-Elmer model R10 60 mc./sec. spectrometer and are recorded in τ values (ppm.) relative to an internal marker of tetramethylsilane.

G) Mass spectra were recorded using an A.E.I. model MS9 mass spectrometer.

H) Gas Chromatography

(a) Analytical. The following abbreviations are used.

(i) '30% L' representing 30% 'apiezon L' plus 3.7% sodium hexanoate on 'embracel'

(ii) '5% ppa' representing 5% polypropenyl adipate on 'embracel'

(iii) '15% carbowax' representing 15% carbowax 6,000 on 'embracel' packed in 4 ft. x $\frac{3}{16}$ in. glass columns and operated under a head pressure of 10 lb./sq.in. of argon carrier gas in a Pye Argon Chromatogram, (catalogue number 12001) incorporating a β-ray ionisation detector and used at a detector voltage of 1250 volts.

(iv) 'polyglycol' representing 15% polypropylene glycol LB-550x on 85% chromosorb W (60-80 mesh) packed in a 2 metre x $\frac{1}{4}$ in. outside diameter stainless steel column, used in conjunction with a Perkin-Elmer F11 gas chromatograph incorporating a flame-ionisation detector. A head pressure of nitrogen carrier gas of 10 lb./sq.in. was employed.

(b) Preparative. The following abbreviations are used.

(i) '30% L' representing 30% 'apiezon L' plus 3.7% sodium hexanoate on 'embracel',

packed in a 300 cm. x $\frac{3}{8}$ in. copper column used in conjunction with a chromatograph constructed by A. Thompson and incorporating a flame-ionisation detector and an electrostatic precipitator.

(ii) '15% carbowax' representing 15% carbowax 6,000 on 60-100 mesh embracel,

packed in a 16 ft. x $\frac{3}{4}$ in. stainless steel column used in conjunction with a model 770 F. and M. preparative gas chromatograph and using a

carrier gas of 10% hydrogen in nitrogen.

I) Irradiation Apparatus

(a) Light Sources.

(i) An Hanovia 500 watt medium-pressure mercury arc used in conjunction with an Hanovia U.V.S. Model 500/A transformer. Full details concerning the output of such a lamp are given on page 33 of this thesis.

(ii) An Hanovia 125 watt medium-pressure mercury arc.

(b) Photochemical reactors.

(i) Reactor A. A 250 ml. capacity reactor manufactured by Engelhard Hanovia and consisting of a central hollow water-cooled probe of quartz or borosilicate glass inside which the lamp was suspended and which in turn was introduced into a larger vessel holding the reaction mixture. This apparatus is represented in Figure XIIIa.

(ii) Reactor B. A quartz apparatus consisting of two separate annular quartz chambers of 80 ml. and 20 ml. capacity and separated from the centrally placed lamp by a layer of cooling water. This apparatus is represented in Figure XIIIb.

(iii) Reactor C. A small quickfit flask fitted with condenser. The lamp was placed some distance below the flask. The transmission properties of the material of the flask are very similar to those of borosilicate glass given in Figure I.

Reactors A and B were used in conjunction with the 500 watt lamp. The Reactor C was usually used with the 125 watt lamp.

Solutions were deoxygenated by refluxing for 20 min. while nitrogen was bubbled through the solution, and then cooling under nitrogen.

The deoxygenated solution was then transferred to the reactor, which had been flushed with nitrogen previously, by applying a nitrogen pressure to the liquid in the deoxygenation flask. Using reactor C, the reaction mixture could be deoxygenated in the reactor itself.

In certain cases, deoxygenation was conducted by bubbling nitrogen through the solution to be irradiated but without refluxing.

During irradiation an atmosphere of nitrogen was maintained above the liquid in the reactor.

Section I

THE PHOTOCHEMISTRY OF THE SYSTEM DIMETHYL MALEATE/DIMETHYL FUMARATE/ACETONE

A) Preliminary irradiation

A deoxygenated solution of dimethyl fumarate (9 g.) in acetone (280 ml.) was irradiated in reactor A using a quartz probe for 18 hr. Evaporation of the solvent gave a yellow oil (11 g.). Analytical gas chromatography (30% L column, 100° and 150°) revealed components of the following retention times.

Column temperature	100°	150°	subsequently identified as
Retention times (min.)	4.2 (w)		
	5.7 (w)		
	9.0 (s)	2.8 (m)	dimethyl maleate
	11.7 (m)	3.1 (Shoulder)(w)	dimethyl fumarate
	20.5 (w)	5 (w)	
	49.5 (vs)	10.4 (s)	trans-oxetane diester
	71 (w)	13.8 (w)	cis-oxetane diester

(w, m, s indicates weak, medium and strong chromatograph signals).

The oil (2.4 g.) was dissolved in acetone (2.6 g.) and samples (0.8 ml.) were injected on a small preparative gas chromatograph (30% L, 150°). The major long retention-time peak was collected in a U-tube immersed in a Drikold-acetone bath. The fraction collected (4 separations) was bulb distilled, 78-92° (air bath temperature)/0.1 mm, and identified as 2,2-dimethyl-trans-3,4-dimethoxycarbonyloxetane (II).

(Found: C, 52.67; H, 7.01; M.W. 202 (mass spectrometer), 209 (± 4%) (osmometer). $C_9H_{14}O_5$ requires C, 53.46; H, 6.977%; M.W. 202.1.)
ν (liquid film), 2987, 2957, 2850 (C-H stretch); 1760, 1740 (ester C=O stretch); 1460; 1437 (C-H deformation); 1380, 1369 (gem. dimethyl); 1330 (tert C-H deformation); 1255; 1215, 1170 (ester C-O stretch); 1077, 1043, 1022, 975 (oxetane ring) $cm.^{-1}$. N.m.r. and mass spectra, see Table II. Ultraviolet spectrum, see Figure XXXIX.

The 13.8 min. r_t analytical chromatogram peak (30% L, 150°) had a retention time equal (± 1%) to that of authentic 2,3-dimethyl-cis-3,4-dimethoxycarbonyloxetane supplied by P.W. Grubb.

B) Epimerisation of 2,2-dimethyl-3,4-dimethoxycarbonyloxetanes

2,2-Dimethyl-trans-3,4-dimethoxycarbonyloxetane (100 mg.) in dry methanol (1 ml.) containing sodium methoxide (40 mg.) was heated for 24 hr. in a sealed tube in a methanol vapour jacket. The contents of the tube were examined by gas chromatography. P.W. Grubb repeated the experiment with a sample of authentic 2,2-dimethyl-cis-3,4-dimethoxycarbonyloxetane obtained by esterifying the irradiation product of maleic anhydride/acetone.

Identical chromatograms were obtained indicating a mixture of 90% trans- and 10% cis- oxetane diester.

C) Oxetane hydrolysis

A mixture of conc. hydrochloric acid (8 ml.) and 2,2-dimethyl-trans-3,4-dimethoxycarbonyloxetane (310 mg) was heated to 100° for 2 hr. Excess acid was neutralised with sodium carbonate until the solution was only faintly acid. Continuous ether extraction yielded a colourless solid (170 mg.), which crystallised from ethyl acetate as plates, m.p. 163-167°

(decomp) identified as 3-hydroxy-5,5-dimethyl-γ-butyrolactone-4-carboxylic acid (III), (lit. (11) m.p. 165-7° (decomp)). (Found: C, 47.88; H, 6.06; M.W., 170 (± 3%) (osmometer). Calc. for $C_7H_{10}O_4$ C, 48,26; H, 5.78%; M.W. 174.2). ν (nujol) 3420 (hydroxyl O-H stretch); ~ 3000 (broad, carboxylic acid O-H stretch); 1770 (γ-lactone C=O stretch and carboxylic acid monomer C=O stretch); 1710 (carboxylic acid dimer C=O stretch); 1390; 1380 (gem. dimethyl); 1265; 1195; 1180; 1160; 1115; 950 $cm.^{-1}$. N.m.r. (D_2O) τ = 8.46 (6 protons, gem. dimethyl); τ = 6.45 (1 proton, doublet, J = 7.3 cps.); τ = 5.23 (HOD peak); τ = 4.80 (1 proton, doublet, J = 7.3 cps.).

D) Other preliminary irradiations

Using the technique described on page 111, the following solutions were irradiated for 18 hr.

(a) Dimethyl maleate (5.5 g.) in acetone (280 ml.) using a borosilicate glass probe.

(b) Dimethyl maleate (5.5 g.) in acetone (280 ml.) using a quartz probe.

(c) Dimethyl fumarate (9.0 g.) in acetone (280 ml.) using a borosilicate glass probe.

A qualitative description of the gas chromatographic analyses of the crude products of these irradiations is given in the discussion section.

E) First series of photokinetic experiments

(a) Dimethyl maleate (9 g.) in acetone (280 ml.) was irradiated in reactor A using a quartz probe. The lamp was switched off from time to time, a small sample of reaction mixture taken, and the irradiation

recommenced. Samples were taken at 15, 30 min, 1 hr, 2 hr. 2 min., 4 hr. 17 min., 6 hr. 6 min., 8 hr. 11 min., 10 hr. 14 min. and 27 hr. 47 min. irradiation time.

(b) An identical solution was irradiated under identical conditions save that a borosilicate probe was employed. Samples were taken at similar irradiation times.

Samples from both irradiations were examined by gas chromatography (30% L, 100° and 150°). Peak areas were estimated by triangulation and peak ratio-irradiation time data are represented graphically in Figures II and III.

F) Second series of photokinetic experiments

A marker solution of 2-methylquinoline (300 λ) in acetone (total volume 5 ml.) was prepared. 2-Methylquinoline (British Drug Houses Ltd.) gave only one peak on the gas chromatogram (r_t = 34 min., 30% L, 150°) and was not further purified.

General experimental technique was as in the first series of photokinetic experiments except that

(i) a rapid stream of nitrogen saturated with acetone vapour was bubbled through the solution from a source in the well of the reactor. The nitrogen stream was introduced via the side-arm of the reactor by means of a polythene tube weighted at its far end with a glass fitting.

(ii) 1 ml. samples were taken during the irradiation, the lamp being first switched off. Marker solution was added to the sample (50 λ per ml. sample) and the irradiation recommenced. Newly prepared marker solution was used for each irradiation.

(iii) Small changes in solution level in the reactor were corrected by adding antibumping granules to the well of the reactor.

The following solutions were irradiated.

(a) Using a quartz probe

(i) Dimethyl fumarate (9.0400 g.) in acetone (284 ml.)

(ii) Dimethyl maleate (9.4499 g.) in acetone (297 ml.)

(iii) Dimethyl fumarate (24.9851 g.) in acetone (297 ml.)

(b) Using a borosilicate glass probe

(i) Dimethyl fumarate (9.4488 g.) in acetone (297 ml.)

(ii) Dimethyl maleate (9.4502 g.) in acetone (297 ml.)

Samples were analysed as in the first series of photokinetic experiments and peak ratio-irradiation time data are represented graphically in Figures IV - XII.

Marker solution (50 λ per ml. sample) was added to

(a) dimethyl maleate (0.4822 g.) and dimethyl fumarate (0.5565 g.) in acetone (50 ml.)

(b) cis-oxetane diester (10 mg.) and trans-oxetane diester (9.9 mg.) in acetone (1 ml.);

and the resulting solutions examined by gas chromatography. A peak ratio to marker of unity under the conditions of the second photokinetic series was found to correspond to the following concentrations.

Compound	
dimethyl maleate	0.042 M
dimethyl fumarate	0.031 M
trans-oxetane diester	0.055 M
cis-oxetane diester	0.062 M.

G) Isolation of 2,2-dimethyl-cis-dimethoxycarbonyloxetane

The aggregate of the crude products from all the irradiations performed on maleate/fumarate/acetone, including those from the third series of photokinetic experiments was distilled. The 108-160°/2 cm. fraction (8.5 g.) was resolved into its components using a model 770 F and M preparative gas chromatograph. (Column; 15% carbowax at 150°, rising at the rate of 0.5°/min. after injection to 170°. Carrier gas; 10% hydrogen in nitrogen. Gas pressure drop across column, 22 lb./sq.in. Injection temperature; 195°. A water coolant was used in the traps.) The mixture was injected neat in amounts varying from 0.25 ml. to 1.2 ml.

The following separation was achieved.

Trap	Weight collected	Identified as	Purity (gas chromatography, ppa, 100°)
1	0.0087 g.	dimethyl fumarate	-
2	0.6894 g.	dimethyl maleate	-
3	2.8194 g.	trans-oxetane diester	~ 3% dimethyl maleate
4	0.1132 g.	(see below)	~ 3% trans-oxetane diester
bypass	1.2222 g.	-	-

The contents of trap 4 were distilled, b.p. 65-70° (air bath temperature)/ 0.1 mm. and identified as 2,2-dimethyl-cis-3,4-dimethoxycarbonyloxetane (I), identical in all respects with that obtained by P.W. Grubb.[6] (Found: C, 53.57; H, 6.67; M.W., 202 (mass spectrometer). Calc. for $C_9H_{14}O_5$, C, 53.46; H, 6.977%; M.W., 202.1). ν (CCl_4) 2960, 2940 (C-H stretch); 1745, 1740 (ester C=O stretch); 1450; 1432 (C-H deformation); 1370, 1360 (gem. dimethyl); 1285; 1197; 1163 (ester C-O stretch); 1080, 1035, 970 (oxetane ring) $cm.^{-1}$. N.m.r. and mass spectra, see Table II.

H) Photochemistry of oxetanes

Solutions of trans-oxetane diester (993 mg.) in acetone (100 ml.) and cis-oxetane diester (66.3 mg.) in acetone (5.18 g.) were introduced separately into the two compartments of the quartz reactor B. Rough deoxygenation was provided by bubbling nitrogen through the solutions for 15 min. The solutions were then irradiated with the 500 watt lamp. Samples taken at 15 min., 30 min., 1 hr. 2 min., 2 hr. and 10 hr. irradiation time were examined by gas chromatography (ppa, 100° and 125°). The results of this examination are given in the discussion section.

Evaporation of acetone from both the final irradiation products gave brown oils. A sample (61.8 mg.) from the trans-oxetane diester irradiation yielded a red derivative (8.4 mg.) on treating with Brady's reagent. The derivative m.p. 251-254° (decomp)(for which no solvent suitable for recrystallisation was found) had the composition C, 44.05; H, 3.66; N, 18.00%.

The final irradiation products had very similar infrared spectra. That from the cis-oxetane diester irradiation exhibited ν*(liquid film) 3420 (hydroxyl), 2980 (C-H), 1740 (ester C=O), 1465, 1380 $cm.^{-1}$.

I) Third series of photokinetic experiments

(a) Photomonitor

This was constructed from the following component parts.

(i) A Rank Cintel QVA 39S photocell, which is a vacuum photocell with an antimony-caesium electrode mounted in a quartz envelope. The spectral response curve, which has only been determined at wavelengths greater than 250 $m\mu$, was supplied by the manufacturers and is given in

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* Recorded using a Unicam SP800 spectrophotometer.

Figure XIV.

(ii) A 1.9 mm. thickness of Chance OX7 glass. The transmission properties of this are represented in Figure XIV.

(iii) A model 37B portable electrometer manufactured by Electronic Instruments Ltd., setting used x3. The batteries were checked from time to time between experiments.

(iv) An A.E.I./Sunvic model 10S recorder; response time ~ 2 sec.

(b) An examination of the light source. (i) General

The lamp investigated was a 500 watt Hanovia medium pressure mercury arc. Its age was 150 hr. running time. It was connected to a mains supply through an Hanovia U.V.S. model 500/A transformer.

The lamp was mounted rigidly and vertically in a clamp. An asbestos surface $5\frac{1}{2}$ in. x $5\frac{1}{2}$ in., coated with magnesium oxide from burning magnesium in its proximity in air, was mounted rigidly vertically about 1 ft. from the lamp. The laboratory was protected from stray ultraviolet light by means of a cardboard screen some distance from the lamp. Shiny metal was not used.

The photocell and associated circuitry were assembled by A. Thompson and housed in a small box fitted with the Chance glass window. To this was attached a 1 ft. 6 in. tube fitted at its far end with a variable iris. The photocell was connected via the electrometer amplifier to the recorder which during experiments was set to run at a chart speed of 30 in./hr.

The photomonitor tube was arranged in such a way that only light diffusing from the magnesium oxide surface entered the photomonitor. No

light was allowed to enter the photomonitor directly from the lamp and the apparatus was so arranged that no shadow was cast on the magnesium oxide surface. Figure XVa represents the overall experimental arrangement.

In a preliminary experiment, amplifier settings and iris aperture were varied to give a trace of optimum dimensions. Thereafter these parameters were maintained constant during the series of experiments. Care was taken not to disturb the geometry of the apparatus during the period of the experiments. In some experiments, the root mean square mains voltage was recorded by means of an apparatus constructed for the purpose by A. Thompson. When connected to a 10mV. model 10S A.E.I./Sunvic recorder, the deflection range observed on the recorder scale represented a mains voltage range of 200-250 V.

(ii) Results of the examination.

Definitions of the parameters symbolised h, t, T, V, n, are given on page and are represented diagrammatically in Figure XVI. In the following tables, h, t, and T are given in cm. as read directly from the chart. A chart speed of 30 in./hr. was used so that a distance of 1 cm. measured along the chart represents a time interval of 0.787 min. V is the average value of the r.m.s. mains voltage during the experiment. Minimum precision in measuring V, $\pm$ 0.5 V.

Table III

Time of starting experiment	Experiment Number	h(cm)	t(cm)	T(cm)	$\frac{A}{B}$	V	n (minutes)
Tues. 31st Aug.							
2.15 p.m.	1	8.1	5.2	3.65	0.4443		∞
6.45 p.m.	2	9.1	5.1	3.6	0.4663		∞
7.25 p.m.	3	8.75	5.1	3.6			∞
9.15 p.m.	4	9.0	5.6	3.7	0.4561		∞
10.50 p.m.	5	8.6	4.75	3.5	0.4489		∞
11.05 p.m.	6	8.65	4.2	2.95	0.5540		~ 8
Wed. 1st Sept.							
10.20 a.m.	7	8.2	5.9	3.6			∞
2.00 p.m.	8	7.9	6.2	3.75			∞
7.10 p.m.	9	8.8	5.3	3.5	0.4601		∞
9.40 p.m.	10	9.1	4.8	3.5			∞
11.35 p.m.	11	8.35	5.3	3.65	0.4505		∞
Thurs. 2nd Sept.							
10.30 a.m.	12	7.45	5.6	3.72	0.4255		∞
1.00 p.m.	13	8.15	6.7	4.07			∞
5.20 p.m.	14	7.7	6.0	3.85	0.4274		∞
9.20 p.m.	15	8.6	4.9	4.3	0.4829		∞
Fri. 3rd Sept.							
12.25 p.m.	16	7.75	5.95	3.8			∞
3.20 p.m.	17	7.8	5.3	3.6			∞
4.41 p.m.	18	7.6	6.0	3.6			∞
5.13 p.m.	19	8.0	5.4	3.55			∞
6.19 p.m.	20	8.9	5.4	3.4			∞
8.32 p.m.	21	8.7	4.9	3.3			∞
10.58 p.m.	22	8.6	4.7	3.3			∞
11.53 p.m.	23	8.6	4.8	3.4			∞
Sat. 4th Sept.							
2.11 p.m.	24	8.4	5.0	3.3			∞
3.55 p.m.	25	8.75	4.9	3.4			∞
4.05 p.m.	26	8.9	5.1	2.4			4
4.31 p.m.	27	9.1	4.7	3.3	241.5		20
4.45 p.m.	28	9.2	5.0	2.9	242.2		9.5
5.07 p.m.	29	9.0	4.7	3.15	241.2		17
5.20 p.m.	30	9.2	4.5	3.1	241.0		12
5.35 p.m.	31	9.1	4.9	2.7	241.7		6.5
6.17 p.m.	31A	9.0	5.1	3.1	240.5		∞
9.32 p.m.	32	8.9	4.8	3.3	241.5		∞
10.50 p.m.	33	8.9	4.5	3.3	241.5		∞
11.00 p.m.	34	9.0	4.0	2.7	241.7		5.5
11.17 p.m.	35	9.1	4.7	2.7	242		6

Table III (Cont'd)

Time of starting experiment	Experiment Number	h(cm)	t(cm)	T(cm)	$\frac{A}{B}$	V	$\frac{n}{(minutes)}$
Sun. 5th Sept.							
1.14 p.m.	36	9.0	5.0	3.35	243.5		∞
10.20 p.m.	37	8.8	5.1	3.3	241.2		∞
Mon. 6th Sept.							
9.55 a.m.	38	8.1	5.1	3.5	237		∞
11.31 a.m.	39	8.1	5.0	3.5	237.5		∞
12.44 p.m.	40	8.6	5.2	3.4	240		∞
2.50 p.m.	41	8.0	5.1	3.5	236.7		∞
4.15 p.m.	42	8.0	5.3	3.5	236		∞
6.08 p.m.	43	8.8	5.0	3.5	241		∞
6.15 p.m.	44	8.7	4.2	2.6	237.7		3
7.34 p.m.	45	8.4	5.4	3.5	238.5		∞
Tues. 7th Sept.							
10.09 a.m.	46	6.6	5.8	3.85	234.5		∞
11.08 a.m.	47	6.8	5.7	3.7	234		∞
12.10 p.m.	48	6.4	6.2	3.9	232		∞
2.59 p.m.	49	7.2	5.9	3.7	234		∞
4.20 p.m.	50	7.5	5.3	3.6	234		∞

In experiments 51-58, a slightly different arrangement of apparatus was employed, so h values are not comparable with those from previous experiments. T values are comparable.

Table IV

Experiment Number	h(cm)	T(cm)	$\frac{A}{B}$	n(min.)	V = 233±3 V.
51	9.4	3.7	0.4448	∞	
52	9.2	2.0	0.6587	2	
53	9.5	2.6	0.6020	3	
54	9.4	2.9	0.5565	4	
55	9.6	3.05	0.5416	5.4	
56	9.7	3.2	0.5167	7	
57	9.8	3.4	0.4855	10	
58	9.7	3.8	0.4239	24	

h Values of h are plotted against V in Figure XVII, using data from experiments 27-50. Precision in measuring mains voltage was greater than

$\pm$ 0.5 V. h was measured to < 0.1 cm.

Observed h values lie within the confines 7.8 cm. $\pm$ 18%, with the corresponding V values within the confines 237.7 V $\pm$ 5.7 V (or 2.4%).

t When n = ∞, t values ranged between 4.5 cm. and 6.7 cm., that is 3.5 min. and 5.3 min.

T When n = ∞, T values exhibited a standard deviation of 0.2 cm. about a mean of 3.53 cm., that is 0.16 min. (or 5.7%) about a mean of 2.8 min. This was deduced from the forty-one experiments up to experiment 50 with n = ∞.

$\frac{A}{B}$ Mean value 0.462; standard deviation, 0.035, determined from ten experiments with n = ∞. Ratios of areas B to A were determined by weighing. For an analysis of the precision of this method, see page 131. In this case, the weights representing areas of A and B ranged between 120 and 550 mg. Weighings were reproducible to $\pm$ 0.2 mg.

n The effects of variation of n on T and $\frac{A}{B}$, deduced from experiments 51-58 are shown graphically in Figures XVIII and XIX.

To estimate the order of the effect of the change in h following a change in the relative geometrical arrangement of monitor, screen and lamp, the following operations were performed.

Series A	h	% increase in h
(a) initial arrangement	7.5 cm.	-
(b) rotation of monitor about a vertical axis 4° towards the screen from the initial position	10.9 cm.	+ 45.4%
(c) rotation of monitor about a vertical axis 4° away from the screen from the initial position	6.4 cm.	- 14.7%

Series B	h	% increase in h
(a) initial arrangement	9.3 cm.	
(b) movement of monitor 2.2 cm. away from screen without rotation	8.7 cm.	- 6.5%

Series C

Movement of lamp, maintained vertical, within a circle of radius 2 cm. from its original position;

h varies from 7.7 cm. to 12.1 cm.

(c) Irradiations

The technique was similar to that described for the second series of photokinetic experiments. Reactor A was filled exactly to a fixed mark with thoroughly deoxygenated solution. Nitrogen, saturated with acetone vapour was bubbled through the solution in the reactor continuously from a source in the well of the reactor. The initial temperatures of the solutions to be irradiated were in all cases save one (see page 129) within the range 16-19°. The temperature of the solution during irradiation was moderated by the passage of cooling water through the hollow probe.

A photomonitor was incorporated. As Figure XVb shows, the lamp was not fully inserted into the probe during irradiation and the diffusing surface sampling light for the photomonitor was somewhat above the reactor. An elaborate system of rigid clamps and marks was devised to ensure that the apparatus could be partially dismantled after each irradiation and reassembled for the next irradiation with the minimal change in geometry. The reactor was surrounded by a cardboard screen during irradiations.

Shiny metal surfaces were avoided.

At intervals during an irradiation, samples were taken from the side arm of the reactor without extinguishing the lamp. The time at which a sample was taken was noted both on a stopwatch and by causing the photomonitor pen to jump. The solution level in the reactor was made up to the fixed mark by adding acetone after each sample was taken. A lamp of 220 hours running age and a photomonitor chart speed of 6 in./hr. were used.

Marker solution (50 λ of a solution of methyl salicylate* (2000 λ) in acetone (total volume 10 ml.)) was added to each sample (1 ml.) from the irradiation mixture. The prepared solutions were then examined by gas chromatography without further manipulation. Samples (10 μl.) were injected on a polyglycol column in a Perkin-Elmer F11 gas chromatograph (column temperature 125° for ~ 18 min. (dimethyl maleate and dimethyl fumarate peaks) followed by rapid rise to 160°). A typical chromatogram is represented in Figure XX. Attenuator controls were adjusted to give the largest on-scale peaks possible. The attenuation factor range of the chromatograph used extended over the range x1 to x5 x 10^5. This large range was divided into three smaller ranges. Attenuation factors are claimed to be comparable to within 0.5% within a small range and to 1.0% between ranges.

Peak areas were estimated by cutting out the peak from the chart

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* Methyl salicylate (Harrington Bros.) was found to be sufficiently pure (by gas chromatography) for use without further treatment.

paper and weighing. Peak ratios to marker, i.e.

$$\frac{\text{weight of a given peak x attenuation factor at which it was recorded}}{\text{weight of marker peak on same chromatogram x its attenuation factor}}$$

were calculated.

The quantity 'T' representing the integrated light output of the lamp from the instant it was switched on was taken as the weight in grams of the area of chart paper under the photomonitor trace. A rough correlation of this quantity with irradiation time was also calculated. Data from these experiments are given in Table V. Data marked with an asterisk was submitted for analysis by computer.

No attention is here given to precision apart from ensuring that the derived data is calculated to a greater precision than that to which the initial measurements were made. A detailed analysis of error is given on page 40 .

The results are given in the order the experiments were performed.

Table V

(i) Borosilicate irradiations.

(a) Dimethyl fumarate (0.23M) in acetone. Up to T = 2.0, on average, 0.435 T units = 1 hr. irradiation.

Sample Number	T	Peak ratios: Dimethyl maleate	Dimethyl fumarate	trans-oxetane diester	cis-oxetane diester
0	0	0*	1.829	0*	0
1	0.0388	0.0048*	1.520	0.00229*	0
2	0.0826	0.0113*	1.603	0.004146*	0
3	0.1255	0.0156*	1.506	0.006698*	0
4	0.1687	0.0274*	1.682	0.008368*	0
5	0.2217	0.0355*	1.708	0.01108*	0
6	0.2728	0.0456*	1.778	0.01363*	0
7	0.3098	0.0497*	1.609	0.01546*	0
8	0.3458	0.0525*	1.563	0.01707*	0

Table V (Cont'd)

Sample Number	T	Peak ratios: Dimethyl maleate	Dimethyl fumarate	trans-oxetane diester	cis-oxetane diester
9	0.4136	0.0524*	1.398	0.01572*	0
10	0.4506	-	0.926	0.0169*	0
11	0.4961	0.0652*	1.5215	0.0205*	0
12	0.5705	0.0901*	1.592	0.0247*,0.0230*	0
13	0.6427	0.0910*	1.527	0.0274*,0.0281*	0
14	0.7263	0.1092*	1.519	0.02999*	0
15	0.8028	0.1051*	1.392	0.0316*	0
16	0.8990	0.1259*	1.370	0.0349*	0
17	0.9888	0.1382*	1.406	0.0393*	0
18	1.1047	0.1650*	1.363	0.0431*	0
19	1.2932	0.1885*	1.289	0.0491*	0
20	1.5712	0.2321*	1.343	0.0602*	0
21	1.7766	0.2501*	1.188	0.0642*	0
22	2.3016	0.3761	1.248	0.0743	0
23	2.9006	0.5312	1.101	0.1081	0
24	3.4325	0.5499	0.9182	0.1141	0
25	3.8872	0.6824	0.9404	0.1325	0
26	4.7526	0.8074	0.7767	0.1380	0.000699
27	5.2894	0.8177	0.6972	0.1611	0.000298
28	5.6968	0.878,0.917	0.6480,0.6818	0.1479	(0.00100 (0.0076
29	7.4409	1.161	0.4868,0.4328	0.2141,0.2159	(0.00134 (0.00146

(b) Dimethyl maleate (0.23M) in acetone.

On average, 0.358 Tunits = 1 hr. irradiation.

Sample Number	T	Peak ratios: Dimethyl maleate	Dimethyl fumarate	trans-oxetane diester	cis-oxetane diester
1	0	2.0844	0*	0	0
2	0.0342	1.8835	0.0121*	0	0
3	0.0858	1.9933	0.0222*	0	0
4	0.1140	1.9465	0.02657*	0	0
5	0.1434	1.9915	0.0343*	0	0
6	0.1708	1.847	0.0393*	0	0
8	0.2386	1.699	0.05204*	0	0
9	0.2874	1.774	0.05744*	0	0
10	0.3204	1.578	0.0516	0	0
11	0.3575	1.862	0.06834*	0	0
12	0.4089	1.751	0.07368*	0	0

Table V (Cont'd)

Sample Number	T	Peak ratios: Dimethyl maleate	Dimethyl fumarate	trans-oxetane diester	cis-oxetane diester
13	0.4579	1.704	0.08058*	0	0
14	0.5121	1.677,1.715	(0.0876*,0.0879* (0.0840*	(0.00138,0.00124 (0.00138	0.00062
15	0.5758	1.598,1.679	0.0871*,0.0894*	-	0.00077
16	0.6220	1.686	0.1039	0.00106	0.00099
17	0.6784	1.655	0.09878*	0.00348	-
18	0.7804	1.579	0.1071*	-	0.00085
19	0.8603	1.869	0.1105*	0.00324	0.00067
20	0.9451	1.592	0.1124*	0.00473	0.00079
21	1.0606	1.594	0.1174*	0.00426	0.00099
22	1.2811	1.647	0.1355*	0.00522,0.00700	(0.00172 (0.00149
23	1.4703	1.622	0.1410*	0.00729	0.00097

(ii) Quartz irradiations.

(a) Dimethyl maleate (0.23M) in acetone.

On average, 1.88 Tunits = 1 hr. irradiation. During this experiment alone a different photomonitor amplification factor was used. To compare this experiment with the others, T values must first be divided by a factor of 3.

Sample Number	T	Peak ratios: Dimethyl maleate	Dimethyl fumarate	trans-oxetane diester	cis-oxetane diester
1	0	1.398,1.714	0*	0*	0*
2	0.1210	1.392	0.0638*	0.0008*	0
3	0.2836	1.393,1.788	0.1241*	(0.00770* (0.00863*	0
4	0.4325	1.317,1.413	0.1446*	(0.01096* (0.01343*	0.001941*
5	0.5722	1.702	0.1963*	0.01930*	0.002804*
6	0.7786	1.320	0.1587	0.02155*	0.002938*
7	0.9448	1.500	0.2323*	0.03176*	0.004426*
8	1.1336	1.542,1.619	0.2147	(0.03707* (0.04176*	0.004619*

Table V (Cont'd)

Sample Number	T	Peak ratios: Dimethyl maleate	Dimethyl fumarate	trans-oxetane diester	cis-oxetane diester
9	1.2986	1.459	0.2174	0.04602*	0.005233*
10	1.4788	1.593	0.2221	0.05330*	0.005546*
12	1.7418	1.474	0.2175	0.06456*	0.007553*
13	1.9855	1.468,1.445	0.2065	(0.07133*	
				(0.0706*	0.006965*
14	2.5308	1.382	0.2106	0.09271*	0.009772*
15	2.9922	1.504,1.423	0.2011	(0.1003*	(0.01009*
				(0.1047*	(0.01209*
16	3.5523	1.432,1.366	0.1989	(0.1307*	
				(0.1212*	0.01353*
17	4.1389	1.287	0.1988	0.1478*	0.01566*
18	4.6438	1.321	0.1983	0.1686*	(0.01627*
					(0.01598*
19	5.5153	1.365	0.1914	0.1905*	0.01842*
20	6.2065	1.242	0.1864	0.2111*	0.0202*
21	7.1175	1.289	0.1728	0.2422*	0.02362*

(b) Dimethyl fumarate (0.23M) in acetone.

On average, 0.813 Tunits = 1 hr. irradiation.

Sample Number	T	Peak ratios: Dimethyl maleate	Dimethyl fumarate	trans-oxetane diester	cis-oxetane diester
1	0	0*	1.6782*	0*	0*
2	0.0496	0.1082*	1.6418*	0.0273*	0
3	0.1129	0.2539*	(1.542*	0.0551*	0
			(1.525*		
4	0.1809	0.3723*	1.392*	0.0826*	0
5	0.2767	0.6060*	(1.307*	0.1317*	0.000638*
			(1.249*		
6	0.3948	0.8115*	1.116*	0.1707*	-
7	0.4848	1.003*	0.9586*	0.1972*	0.000856*
8	0.6117	1.124*	0.7298*	0.2252*	0.00174*
9	0.6779	1.291*	(0.6435*	0.2515*	0.00255*
			(0.6378*		
10	0.7609	1.360*	0.5369*	0.251*	0.0026*
11	0.8288	1.340*	0.4133*	0.268*	0.00363*
12	0.9709	(1.4058*		(0.281*	0.00331*
		(1.3711*	0.2948*	(0.268*	0.00363*
13	1.1070	1.4140*	0.2792*	0.285*	-

Table V (Cont'd)

Sample Number	T	Peak ratios: Dimethyl maleate	Dimethyl fumarate	trans-oxetane diester	cis-oxetane diester
14	1.2869	1.404*	0.2290*	0.308*	0.00638*
15	1.5313	-	0.2666*	0.332*	0.00832*
16	2.0092	1.3478	0.1940	0.325	0.00962
17	2.4576	1.2491	0.1754	0.345	0.01309
18	2.9609	1.2528	0.1787	0.391	0.01714
19	3.5916	1.2442	0.1724	0.457	0.01917

(c) Dimethyl fumarate (0.47M) in acetone.

On average, 0.69 Tunits = 1 hr. irradiation.

The solution was warmed to approximately 22° initially to prevent the dimethyl fumarate crystallising out. During the irradiation no fumarate crystallised out.

Sample Number	T	Peak ratios: Dimethyl maleate	Dimethyl fumarate	trans-oxetane diester	cis-oxetane diester
1	0	0*	-	0*	0*
2	0.0406	0.0757*	3.2373	0.02385*	0
3	0.1078	0.1730*	3.1944	0.0623*	0
4	0.1716	0.2957*	3.0825*	0.0967*	0
5	0.2432	0.4904*	3.3116	0.1603*	0
6	0.3010	0.4502*	2.533	0.1783*	0
7	0.3876	0.6998*	2.8625	0.2268*	0
8	0.4744	0.8674*	2.7442	0.2756*	0.000814*
9	0.5573	1.0496*	2.4645	0.3213*	0.001219*
10	0.6327	1.1709*	2.2564	0.3504*	0.000667*
11	0.7191	1.1838*,1.2152*	(2.0856 (2.1360	(0.3897* (0.3734*	(0.00094* (0.00078*
12	0.8679	1.4682*	1.9015	0.4697*	0.001046*
13	1.0939	1.7306*	1.4653	0.5502*	0.002482*
14	1.2573	1.9435*	1.2792	0.6375*	0.00664*
15	1.5513	2.1130*	0.9068	0.6814*	0.00658*
16	2.0892	2.478*	0.5405	0.7838*	0.00997*
17	2.5314	2.300*	0.3956	0.8267*	0.01189*
18	2.9802	2.279*	0.3604	0.8484*	0.01934*
19	3.3486	2.3864*	0.3688	-	0.02517*

Table V (Cont'd)

(d) Dimethyl fumarate (0.025M) in acetone.

On average, 0.659 Tunits = 1 hr. irradiation.

Sample Number	T	Peak ratios: Dimethyl maleate	Dimethyl fumarate	trans-oxetane diester	cis-oxetane diester
1	0	0*	0.22096*	0*	0
2	0.0355	0.09038*	0.13173*	0.003606*	
3	0.0767	0.1483*	0.06039*	0.006000*	
4	0.1415	0.1969*	0.03110*	0.007048*	
5	0.2052	0.1951*	0.02409*	0.01095*	
6	0.2695	0.2009*	0.02483*	0.01052*	0.0002348
7	0.3311	0.1935	0.02265*	0.01284*	0.0003037
8	0.4029	-	0.01966*	0.01439*	0.000365
9	0.4827	-	-	0.01404*	-
10	0.6097	0.1569	0.01905*	0.01851*	0.0005127
11	0.6967	0.1520	0.01840*	0.02120*	0.000748
12	0.8092	0.1474	0.01730*	0.02337*	0.000955
13	0.9382	0.1438	(0.01682*	(0.02719*	(0.001168
			(0.01677*	(0.02828*	(0.001046
14	1.0990	0.1334	0.01645*	0.02939*	0.001143
15	1.3546	0.1202	0.01464*	0.03579*	0.001493
16	1.5451	0.1068	0.01374*	0.04369	0.001398
17	1.9382	0.0864	0.00990*	0.04642*	0.002300
18	2.6580	0.0273	0.00430*	0.05964*	0.002758

(d) Calibration

A marker solution of methyl salicylate (200 λ) in acetone (5 ml.) was prepared. Solutions of dimethyl maleate (1.0313 g.) in acetone (total volume, 250 ml.), dimethyl fumarate (1.0738 g.) in acetone (total volume, 250 ml.) and redistilled trans-oxetane diester (138.9 mg.) with redistilled cis-oxetane diester (16.1 mg.) in acetone (total volume, 10 ml.) were made up.

Marker solution (50 λ aliquots) was added to two samples (1 ml.) of

the oxetane solution. Marker solution (2.5 ml. aliquots) was added to samples (100 ml.) of the maleate and fumarate solutions.

These solutions were examined by gas chromatography in the same way that the photokinetic samples were examined. The following results were obtained

Sample	Mean peak ratio to marker	Standard deviation in peak ratio	Number of determinations	Molarity represented by a peak ratio of unity under the photokinetic conditions
dimethyl maleate	2.637	0.022	3	0.113 ± 0.001M
dimethyl fumarate	2.533	0.047	3	0.123 ± 0.002M
trans-oxetane diester	0.748	0.028	9	0.0916 ± 0.0035M
cis-oxetane diester	0.0633	0.0057	11	0.126 ± 0.01M

(e) An analysis of the precision of estimating areas of peaks by weighing

Twenty-five identical rectangles (1.3 in. x 1.0 in.) were cut from recorder chart paper as used with a Leeds Northrup Speedomax H recorder. The mean weight was 32.4 mg./sq.in. The standard deviation was 0.4 mg./sq. in., that is 1.2% of the mean.

A similar experiment was conducted with twenty-five rectangles (2.0 in. x 1.0 in.) cut from Sunvic 10 in. H1030 recorder chart paper. This brand of chart paper was used in the photokinetic experiments. The mean weight was 34.1 mg./sq.in. The standard deviation was 0.4 mg./sq.in., that is 1.2% of the mean.

The reproducibility of area estimations using a planimeter is ordinarily of the order of 1.5%.

(f) Tetramethoxycarbonylcyclobutane

(i) Preparation

Azobenzene (1.1 g.) in dimethyl maleate (63.3 g.) was deoxygenated and irradiated for 21 hr. in quartz reactor B. A colourless solid formed during the irradiation. This was filtered off, washed with ether and recrystallised from ethanol to give colourless needles (2 g.), m.p. 144-146° identified as cis-trans-cis-1,2,3,4-tetramethoxycarbonylcyclobutane (IV), (lit. (41) m.p. 144-5°) (Found: C, 49.88; H, 5.596; M.W. 288 (mass spectrometer). Calc. for $C_{12}H_{16}O_8$, C, 50.0; H, 5.59%, M.W. 288.3) ν ($CHCl_3$) 2955, 2850 (C-H stretch); 1745 (ester C=O stretch); 1440; 1375 (methyl C-H deformation); 1300; 1032 (cyclobutane ?) $cm.^{-1}$. N.m.r. ($CDCl_3$) τ = 6.30 (singlet, ester methyl); τ = 6.23 (singlet, tertiary hydrogen). Integrated peak areas not precise as peaks are very close together. Approximate integrated peak area ratio 2.24:1.

Other aspects of this irradiated are not pursued here.

(ii) Possible formation in the system dimethyl maleate/dimethyl fumarate/acetone.

Samples (10 μl) of the final products from each of the irradiations of the third series of photokinetic experiments were examined by gas chromatography (polyglycol column, 200°, attenuation factor X20). No peak of retention time of the order of that of cis-trans-cis-1,2,3,4-tetramethoxycarbonylcyclobutane (57 min.) was observed. Chromatograms were run for > 90 min. but no peaks of retention time > 10 min. were found.

(iii) Photostability

A sample of cis-trans-cis-1,2,3,4-tetramethoxycarbonylcyclobutane

(0.104 g.) in acetone (9.6 ml.) was irradiated in reactor C using a 125 watt lamp. Gas chromatography (polyglycol, 200°) of samples taken after 1 day and 2 days irradiation revealed only one peak (r_t = 57 min.) corresponding to the cyclobutane. Using a lower column temperature (170°), a very small amount of short retention time material (r_t = 2.8 min.) was observed in the 2 day irradiation product. Under these conditions, dimethyl maleate has a retention time of 4.5 min.

(g) The effect of oxygen

Three identical pyrex test-tubes (1.5 cm. diameter) were selected. One was incorporated in the apparatus represented in Figure XL.

Resublimed dimethyl fumarate (1.343 g.) in acetone (41 ml.) was added to each of the three tubes to an identical depth (4.4 cm.). The solutions were further prepared thus.

Oxygen was bubbled slowly through one solution for five minutes, after which the tube was immediately sealed.

A second tube was similarly treated using nitrogen.

The third solution in the specially constructed apparatus was rigorously degassed. The tap, greased with high vacuum grease, was closed and the tube cooled to liquid air temperatures. The apparatus was connected to a rotary pump and, maintaining the tube in the liquid air, the tap was opened and the apparatus evacuated. The tap was then closed and the tube removed from the liquid air bath and allowed to warm to room temperature slowly. Care was taken to ensure that, on warming, the solution did not bump and so come into contact with the greased surface of the tap. While it was warming and when it had reached room temperature

the tube was vigorously shaken. The whole process was then repeated a further three times and then three more times, using a mercury diffusion pump. Finally the pressure of gas over the frozen acetone solution had been reduced to 10^{-4} mm. This represented adequate degassing.

Irradiation was commenced as soon as possible after degassing. The three tubes, mounted vertically each at a distance of 19.5 cm. from vertically mounted 500 watt lamp, were irradiated for 5 hr. 25 min.

Marker solution (50 λ aliquots of a solution of methyl salicylate (1000 λ) in acetone (5 ml.)) was added to two samples (1 ml.) from each tube. The prepared samples were examined by gas chromatography.

The following analytical data represent mean values of a number of determinations. Precision ~ 10%.

	Oxygenated solution	Nitrogenated solution	Degassed solution
dimethyl maleate	0.033M	0.031M	0.030M
trans-oxetane diester	0.0056M	0.0052M	0.0056M
cis-oxetane diester	0	0	0
tetramethoxycarbonylcyclobutane	0	0	0

J) Triplet energy level measurements

(a) Methyl iodide method

Concentrated solutions (up to 30% by volume) of dimethyl maleate in methyl iodide were examined in 1 cm. cells using an SP800 Unicam spectrophotometer. No absorption was observed at $\lambda > 360$ mμ. At $\lambda < 360$ mμ, methyl iodide absorption obscured the spectrum.

(b) Oxygen perturbation method

General

The high pressure cell (capacity ~ 20 ml, path length 5 cm.), manufactured by The Research and Industrial Instruments Company was loaned by D.F. Evans.

Chloroform (May and Baker, 'Reagent' grade) was used as solvent in all experiments. A concentrated solution of the substance examined was introduced into the pressure cell (filled to 0.8 capacity only) and into an ordinary 5 cm. balance cell. The area above the meniscus in the pressure cell was blacked out with tape and the cell fitted with an $\frac{1}{8}$ in. needle valve (type 584300) manufactured by F.J. Hone and Co. Ltd. The two filled cells were balanced against each other in a spectrophotometer and a spectrum recorded. The oxygen cell was then removed from the spectrophotometer and saturated with oxygen at a pressure of 1700-2000 lb./sq.in. over a period of fifteen minutes. The early stages of oxygen solution could be followed by virtue of the changing refractive index of chloroform. When saturated with oxygen the cell was reintroduced into the spectrophotometer and a second spectrum recorded. Finally pressure in the cell was released and when most of the oxygen had come out of solution, a third spectrum was recorded. This confirmed that the change in spectrum recorded on oxygenation was not due to the irreversible formation of oxidation products.

(i) Dimethyl maleate, dimethyl fumarate and acetone

Spectra recorded using a Unicam SP800 spectrophotometer fitted with a scale expander. Calibration was confirmed using a standard holmium

filter. Absorbance values were read as deflections of a Leeds Northrup recorder and were reproducible to within 0.0015 of an absorbance unit. The spectrophotometer was used manually.

Dimethyl maleate

Redistilled dimethyl maleate (7.1650 g.) in chloroform solution (50 ml.) was examined at an oxygen pressure of 2000 lb./sq.in. The spectrum was recorded twice and average absorbance values taken. The oxygen-enhanced absorption is recorded in Figure XXXVI. Slit widths (not recorded on the SP800 spectrophotometer) were recorded on a Unicam SP500 spectrophotometer, and are given in Figure XXXVI. This spectrophotometer was examined with a view to recording oxygen-enhanced spectra also, but it was found to be unsuitable. Oxygen enhanced absorption measurements at large slit widths are unreliable owing to the possibility of stray light effects.

Dimethyl fumarate

The spectrum of resublimed dimethyl fumarate (7.2287 g.) in chloroform solution (50 ml.) was examined at an oxygen pressure of 1800 lb./sq.in. The oxygen-enhanced spectrum is recorded in Figure XXXV.

Acetone

The spectra of solutions of ANALAR acetone (5.1, 10 and 20 ml.) in chloroform (total volume 50 ml.) were examined. The results obtained are described on page 68.

(ii) Other substances

Other spectra were recorded automatically using a Unicam SP800 spectrophotometer without a scale expander.

Maleic anhydride

Maleic anhydride was recrystallised from chloroform. No oxygen enhancement was observed using a 1 M solution. Weak oxygen-enhanced tailing (360-420 mμ) was observed using a saturated solution.

Acetoxime

Acetoxime was recrystallised from chloroform. Oxygen (1800 lb./sq.in., 5 mins.) led to the irreversible formation of oxidation products, absorbing at $\lambda < 550$ mμ.

Methyl crotonate

Methyl crotonate used contained < 2% crotonic acid. Methyl crotonate (4.91 g.) in chloroform (50 ml.) was examined under an oxygen pressure of 1800 lb./sq.in. The oxygen-enhanced spectrum is recorded in Figure XXXVII.

Chloroform

The oxygen-enhanced spectrum is described on page 67.

Section II

THE PHOTOCHEMISTRY OF ACETOXIME

A) General

Acetoxime used was recrystallised from petroleum (b.p. 60-80°).

Cyclohexene was passed through a column packed with Spence (Grade H) alumina, refluxed over sodium wire in an atmosphere of nitrogen for 12 hr. and fractionally distilled before use.

N-Methylacetamide was supplied by Hopkins and Williams Ltd.

Irradiations were conducted using reactor B (quartz).

B) Cyclohexene/acetoxime irradiation

(a) A volume (50 ml.) of a solution of acetoxime (10 g.) in cyclohexene (70 g.) was introduced into one compartment of reactor B. Benzophenone (0.5 g.) was dissolved in the remainder of this solution and the resulting solution introduced into the other compartment. After nitrogen had been bubbled through the solutions *in situ* for 15 min., they were irradiated for 9 hr. using a 500 watt lamp. Gas chromatography (ppa, 125°) revealed in both products many minor components, $r_t < 4$ min., with a large peak at $r_t \sim 3$ min., and significant peaks at $r_t = 17.7$ min. and 20.0 min. (the former being 3 times the size of the latter). A third component, $r_t = 23.1$ min. was observed in the benzophenone irradiation product. The benzophenone peak was observed at a much longer retention time.

(b) The product from the irradiation conducted in the absence of benzophenone, was examined. Cyclohexene and acetoxime were removed

(to 100°/3 cm.) leaving a brown liquid (3.5 g.), a portion (820 mg.) of which was separated on a silica-gel column (Whatman SG.31 silica gel (130 g.)), thus.

(i) A liquid (280 mg.) was eluted in 98% petroleum, (b.p. 60-80°)/2% benzene and after distillation 50-70° (air bath temperature)/0.1 mm, identified as bicyclohex-2-enyl (V).

(Found: C,88.86 ; H, 11.23; M.W., 162 (mass spectrometer). Calc. for $C_{12}H_{18}$, C, 88.8; H, 11.17%; M.W. 162.3) ν_{max}(liquid film) 3010 (vinyl C-H stretch); 2925, 2855, 2835 (C-H stretch); 1448, 1432 (CH_2,C-H deformation); 1140; 900 (six-membered ring); 715; 695 (cis-C=C) $cm.^{-1}$. Mass spectrum, $\frac{m}{e}$ = 81 ($C_6H_9^+$, intense). $Br_2|CCl_4$ was decolorised and the tetrabromide, m.p. 155-158° (lit.(47) 157°; (58) mixture of two bromides m.p. 158-160° and 191.5-192.5°) was precipitated on adding acetic acid.

(ii) Acetoxime (10 mg.) was eluted in the ether fractions.

(iii) An oil (63 mg.) was eluted by ethyl acetate. After distillation, b.p. 55-75° (air bath temperature)/0.05 mm., gas chromatography (ppa, 125°) showed this to be a mixture of the two components r_t 17.7 and 20.0 min. An identical mixture was obtained by extracting the thin-layer chromatography band, r_f = 0.25 (unbaked Kieselgel H/ether). $\nu(CS_2)$, 3000, 2915, 2840, 1730 (weak), 1640, 1310, 1295, 1150, 1105, 1005, 970 $cm.^{-1}$

(c) A second irradiation (18 hr.) of acetoxime (35 g.) in cyclohexene (245 g.) was performed using reactor A fitted with a quartz probe. The fraction (7 gm.) b.p. 40-100°/0.25 mm. was collected leaving a red tar (3 gm.). The distillate was redistilled and the fraction b.p. 90-160°/2.5 cm. collected. A portion (2 ml.) was subjected to preparative gas

chromatography using a model 770 F and M chromatograph. (Column, 15% carbowax at 150° rising to 170° at 0.5°/min. Carrier gas; 10% hydrogen in nitrogen; Gas pressure drop across column, 22 lb./sq.in. Injection temperature; 195°. An ice-water coolant was used in the traps.) The mixture was injected neat in 0.25 ml. amounts. Three fractions were collected and distilled.

	weight collected	b.p. (air bath temperature)/0.1 mm.
Trap 1	0.4113 g.	35-65°
Trap 2	0.1211 g.	58-80°
Trap 3	0.1133 g.	60-85°
Bypass	0.2301 g.	-

The traps were found to contain single components contaminated with impurities to ~ 1% (ppa, 125°).

Trap 1 contained bicyclohex-2-enyl having identical infrared spectrum and gas chromatogram with that obtained by column chromatography.

Trap 2 contained a liquid, identified as N-acetyl-N-methylcyclohexylamine (VI) (Found: C,68.98 ; H,11.36 ; N, 9.26 ; M.W., 155 (mass spectrometer). Calc for $C_9H_{17}ON$, C, 69.6; H, 11.04; N, 9.02%, M.W. 155.2) ν ($CHCl_3$) 2930, 2855 (CH_2, C-H stretch); 1630 (tert. amide C=O stretch); 1455 (CH_2, C-H deformation); 1410; 1320; 1160; 1110; 1020 (6-membered ring), 890 $cm.^{-1}$ ν (CS_2), 1260, 1240 $cm.^{-1}$ additionally. N.m.r., see discussion section.

N-methylcyclohexylamine (0.9 g.) in acetic anhydride (4 ml.) was heated to 100° for 30 min., just neutralised with aq. sodium carbonate and

made faintly acid with dil. hydrochloric acid. Ether extraction and distillation, 70-90° (air bath temperature)/0.1 mm., yielded a liquid (0.62 g.) having an infrared spectrum and gas and thin-layer chromatographic properties identical with those of the contents of trap 2.

Trap 3 contained a liquid identified as N-acetyl-N-methylcyclohex-2-enylamine (VIII) (Found: C,68.32 ; H, 10.54 ; N, 9.29 ; M.W. 153 (mass spectrometer). $C_9H_{15}ON$ requires C, 70.55; H, 9.87; N, 9.14%; M.W., 153.2). ν ($CHCl_3$) 2930, 2855 (CH_2, C-H stretch); 1625 (tert. amide C=O stretch); 1402; 1310; 1140; 1015 (6-membered ring) $cm.^{-1}$ ν (CS_2) 3020 (vinyl C-H stretch); 720 (cis-C=C) $cm.^{-1}$.

N.m.r. (CCl_4)

τ = 7.7 - 9.2	broad absorption)	9 protons
τ = 8.00	singlet)	
τ = 7.31) separation, 7.8 cps.	singlet)	3 protons
τ = 7.18)	singlet)	
τ = 6.5	very broad)	1 proton
τ = 5.7	very broad)	
τ = 3.0-4.0	complex, broad.	2 protons

Mass spectrum included: ($\frac{m}{e}$ value followed by relative intensity)

54 (0.25, $C_4H_6^+$), 81 (3.9, $C_6H_9^+$), 99 (0.55, $C_5H_9ON^+$), 125 (1.85, $C_7H_{11}ON^+$); 153 (10.0, molecular ion).

A sample (45 mg.) of the liquid from trap 3 in ethanol was shaken with hydrogen gas in the presence of Adam's catalyst. Filtration and distillation gave a liquid (40 mg.), b.p. 60-90°(air bath temperature)/0.1 mm. having infrared and mass spectra identical with those of N-acetyl-N-methylcyclohexylamine.

C) N-Methylacetamide/cyclohexene irradiations (reactor B)

Because of the limited solubility of N-methylacetamide in cyclohexene, the mixtures to be irradiated separated into two layers. Deoxygenation was achieved by bubbling nitrogen through the liquids for 1 hr. before irradiation and the components were maintained well mixed by continuing the nitrogen stream during irradiation. The following irradiations were conducted.

(a) N-Methylacetamide (2 g.) with cyclohexene (20 ml.) for 18 hr.

(b) N-Methylacetamide (9 g.) plus benzophenone (3 g.) with cyclohexene (80 ml.) for 18 hr.

(c) Cyclohexanone oxime (7.6 g.) in cyclohexene (40 ml.) for 18 hr.

(d) Cyclohexanone oxime (1.9 g.) plus N-methylacetamide (1 g.) in cyclohexene (10 ml.) for 18 hr.

The products from these irradiations were brown liquids possessing the same characteristic sweet smell as the crude product from the cyclohexene/acetoxime irradiation. Some solid had formed in the irradiation involving benzophenone.

Gas chromatography of crude products; (i) carbowax, 150°

Irradiation	(a)	(b)
	r_t = 7 min.	r_t = 7 min. (large bicyclohexenyl peak)
	At least 7 minor components,	
	r_t < 8.5 min.	r_t < 8.5 min.
	No further peaks (apart from very small ones), r_t < 1.5 hr.	r_t = 44 min. (large peak)
		1 hr. 34 min. (benzophenone peak).

(N.B: N-acetyl-N-methylcyclohexylamine exhibited r_t = 32 min.(carbowax,150°), N-acetyl-N-methylcyclohexenylamine exhibited r_t = 36.5 min. (carbowax, 150°)).

Irradiations (c) and (d). Chromatograms identical with each other, (mixed chromatogram). A minor product had a retention time equal to that of N-acetyl-N-methylcyclohexylamine (mixed chromatogram).

(ii) ppa, 120°.

Irradiations (c) and (d). Chromatograms identical.

r_t = 2.4 min. (large bicyclohexenyl peak)

r_t = 5.3 min. (large cyclohexanone oxime peak)

r_t = 8.0, 12.7, 17.3, 21.3 min. (unidentified)

Numerous very small peaks, particularly at r_t < 5.0 min.

No peaks at retention-time equal to that of N-acetyl-N-methylcyclohexylamine (19.7 min.) (mixed chromatogram).

(Note: From this point a second carbowax column was used, so that absolute retention times given after this point are not directly comparable with those presented earlier.)

D) Acetoxime irradiation

(i) Acetoxime (2.3 g.) in a small volume of ether was applied slowly to the inner surface of a compartment of reactor B. In this way the reactor wall was coated with solid acetoxime as the ether evaporated. The reactor was flushed with nitrogen and irradiation (3 days) commenced. Petroleum (b.p. 60-80°) extraction of the red oil produced yielded a yellow liquid (0.20 g.) possessing a complex gas chromatogram (polyglycol, 80°). Benzene eluted a fraction (31 mg.) of this liquid when a sample

(115 mg.) was applied to a wash-column of cellulose (standard grade Whatman cellulose powder in benzene). On distillation, 60-90° (air bath temperature)/0.1 mm., the purified sample exhibited ν (CCl_4) 2980, 2930, 1747 (very sharp), 1695 (sharp, intense), 1500, 1380, 1300, 1240, 1030, 660 $cm.^{-1}$. Gas chromatogram (carbowax, 150°) revealed two significant components. The peak at r_t = 3.7 min. (90% total peak area of chromatogram) corresponded to N-methylacetamide (mixed chromatogram).

The red oil from the acetoxime irradiation was further extracted with ether giving a liquid (0.36 g.), b.p. 60-90° (air bath temperature)/0.1 mm., having an infrared spectrum identical with that of the purified petroleum extract and a gas chromatogram (carbowax, 150°) identical apart from a large peak, r_t = 7.5 min.

The purified petroleum and ether extracts were further examined by gas chromatography (ppa, 100°) and were again found to exhibit peaks at retention time corresponding to N-methylacetamide (r_t = 8.5 min., mixed chromatogram).

The residue from the acetoxime irradiation was a red gum (~ 2 g.), readily soluble in water.

(d) Irradiation of N-methyl-α,α-dimethylnitrone (XI).

(i) The hydrochloride and the free base were prepared by the method of O. Exner.[57] Free base exhibited ν* (liquid film), 2960, 2880 (CH_3, C-H stretch), 1620 (C=N stretch); 1385 (CH_3, C-H deformation), 1208 (N-O stretch) $cm.^{-1}$.

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* Recorded on a Unicam SP200 spectrophotometer.

Hydrochloride crystals (140 mg.) were introduced into reactor B and the apparatus flushed with nitrogen. Samples were taken after 1 hr. and 18 hr. irradiation time, and were examined by gas chromatography (carbowax, 100°). Only one large peak (r_t = 4.1 min.) was present although a very small peak (r_t = 6.5 min.) corresponding in retention time to N,N-dimethylacetamide was observed. Much red polymer was formed.

(ii) Free base (350 mg.) was introduced into reactor B and the apparatus flush with nitrogen. Samples were taken at 30 min, 1 hr, 3 hr, 9 hr. and 20 hr. irradiation time. The 20 hr. product was only soluble to a very limited extent in acetone or ether, the residue being a red water-soluble gum. Irradiated samples were examined by gas chromatography (carbowax, 100°). A small peak corresponding to N,N-dimethylacetamide (r_t = 6.5 min.) was observed formed at irradiation time 30 min. At irradiation time 9 hr., new peaks, r_t = 8.7 and 12.0 min. larger than the supposed N,N-dimethylacetamide peak, were observed. At irradiation time 20 hr., the peak r_t = 8.7 min. alone was observed.

The peak ascribed to N,N-dimethylacetamide corresponded exactly in retention time to authentic N,N-dimethylacetamide on two different columns (carbowax, 100°; ppa, 100°; mixed chromatograms).

E) Other irradiations

(a) Propionaldoxime/cyclohexene

A typical irradiation of this system was conducted thus.

Cyclohexene (2.4 g.) and propionaldoxime (7.6 g.) were irradiated in reactor B for 2 hr. Evaporation under water vacuum yielded a brown oil (0.28 g.). Gas chromatography (carbowax, 150°) showed that although many

components were present, one, ($r_t \sim 2$ x that of bicyclohexenyl) dominated the chromatogram. All attempts to isolate this component met with failure.

(b) Acetoxime/dimethyl maleate

Acetoxime (11.5 g.) in dimethyl maleate (59 g.) were irradiated for 3.6 hr. A colourless solid (1.3 g.) precipitated during the irradiation was identified as cis-trans-cis-1,2,3,4-tetramethoxycarbonylcyclobutane (IV) by comparison of its infrared spectrum with that of the authentic material. Distillation of the liquid yielded only dimethyl maleate plus dimethyl fumarate, acetoxime and a little cyclobutane.

Section III

IRRADIATIONS INVOLVING ALDEHYDES

A) General

Propionaldehyde was supplied by British Drug Houses Ltd. and was redistilled.

All irradiations (except one) described in this section were performed using reactor C. Heat from the lamp caused the propionaldehyde solutions to reflux during irradiation (propionaldehyde, b.p. 49°). Solutions were degassed *in situ* prior to irradiation and an atmosphere of nitrogen was maintained during irradiation.

B) Propionaldehyde/dimethyl maleate irradiation

Dimethyl maleate (10 g.) in propionaldehyde (57 ml.) were irradiated for 8 hr. using a 500 watt lamp. On evaporating down under water vacuum, a colourless solid (14 g.) was obtained which crystallised from petroleum (b.p. 40°-60°)/benzene, as plates, m.p. 54-56°, b.p. 87-110° (air bath temperature)/0.1 mm. identified as dimethyl propionylsuccinate (XII), (yd., 92% conversion of dimethyl maleate) (Found: C, 53.73; H, 7.02; M.W., 202 (mass spectrometer). $C_9H_{14}O_5$ requires C, 53.8; H, 6.97%; M.W., 202.2). ν (CCl_4) 2980, 2955, 2900, 2845 (C-H stretch); 1755, 1750 (ester C=O stretch); 1730 (ketonic C=O stretch); 1442; 1415; 1165 (ester C-O stretch) $cm.^{-1}$ $\lambda_{max}(Et_2O)$ 266 mμ (ϵ, 64.1); tail absorption $\lambda < 245$ mμ. N.m.r. (CCl_4), τ = 8.95 (triplet, J = 6.9 cps.); τ = 7.33 (quartet, J = 6.9 cps.); τ = 7.17 (doublet, J = 7.2 cps.); τ = 6.37 (singlet); τ = 6.29 (singlet); τ = 6.10 (triplet, partly obscured by τ = 6.29 peak,

J = 7.2 cps.). Relative peak areas (τ = 8.95) 3 protons; (τ = 7.33 plus τ = 7.17) 4 protons; (τ = 6.37 plus τ = 6.29 plus τ = 6.10) 7 protons. A deep red coloration slowly formed on treating an ethanolic solution with aqueous ferric chloride (β-keto ester).

C) Hydrolysis of dimethyl propionylsuccinate

Dimethyl propionylsuccinate (986 mg.) (obtained from the irradiation of dimethyl maleate with propionaldehyde) in distilled water (10 ml.) and conc. hydrochloric acid (5 ml.) was heated on a water bath for 6 hr. Ether extraction, bulb distillation and passage through a wash column (silica gel in benzene/2% ether) yielded a liquid (100 mg.) distilling 70-100° (air bath temperature)/0.1 mm., identified as methyl 4-oxohexanoate (XIII) (Found: C, 58.00; H, 8.50; M.W., 144 (mass spectrometer). Calc. for $C_7H_{12}O_3$, C, 58.25; H, 8.39%; M.W., 144.2) ν (CS_2) 2970, 2940, 2895, 2830 (C-H stretch); 1745 (ester C=O stretch); 1723 (ketonic C=O stretch); 1355; 1205, 1170, 1140 (ester C-O stretch) 1110 $cm.^{-1}$ ν (CCl_4) 1440 $cm.^{-1}$ (C-H deformation) additionally. Semicarbazone, m.p. 147-149° (lit, 142°(65)) (Found: N, 20.98. Calc. for $C_8H_{15}O_3N_3$, N, 20.89%)

D) Acetaldehyde/dimethyl maleate irradiation

Dimethyl maleate (9.5 g.) in acetaldehyde (290 ml.) was irradiated for 12 hr. using a 500 watt lamp. This irradiation was conducted using a water-cooled quartz vessel fitted with a reflux condenser. On evaporating down under water-vacuum and distilling the residue, an oil, b.p. 85-100° (air bath temperature)/0.1 mm. (8.9 g.) was obtained and identified as dimethyl acetylsuccinate (XIV) (yd. 70% based on conversion of dimethyl maleate) (Found: C, 51.49; H, 6.60. Calc. for $C_8H_{12}O_5$, C, 51.1; H, 6.38%)

ν (liquid film), 3000, 2955, 2845 (C-H stretch); 1740 (ester C=O stretch); 1720 (ketonic C=O stretch); 1435; 1360; 1265; 1160 (ester C-O stretch) $cm.^{-1}$ N.m.r. (CCl_4) τ = 7.70 (singlet, 3 protons) τ = 7.23 (doublet, J = 7.0 cps.); τ = 7.18 (doublet, J = 7.0 cps.)(τ = 7.23 plus τ = 7.18, 2 protons); τ = 6.34 (singlet); τ = 6.26 (singlet); τ = 6.12 (triplet, partly obscured by τ = 6.26 peak. J = 7.0 cps.) (τ = 6.34 plus τ = 6.26 plus τ = 6.12, 7 protons). A purple coloration was slowly formed on treating an acetone solution with ferric chloride (β-keto ester).

E) Propionaldehyde/methyl crotonate irradiation

Redistilled methyl crotonate (7.9 g.) in propionaldehyde (100 ml.) was irradiated for 7 hr. using a 500 watt lamp. On evaporating down under water vacuum, a residue (3.0 g.) was obtained. On distillation, the fraction boiling 100-145° (air bath temperature)/0.2 mm. (0.9 g.) was found to consist of a single component (gas chromatography, ppa, 100°, r_t = 9.5 min.), identified as methyl 3-methyl-4-oxohexanoate (XV) (Found: C, 61.12; H, 8.91; M.W., 158 (mass spectrometer). $C_8H_{14}O_3$ requires C, 60.63; H, 8.91%; M.W., 158.19) ν ($CHCl_3$) 2965, 2940, 2870 (C-H stretch); 1725 (ester C=O stretch); 1715 (ketonic C=O stretch); 1460; 1440 (C-H deformation); 1410; 1377; 1350; 1275; 1175 (ester C-O stretch); 1105, 1000, 975 $cm.^{-1}$ $\lambda_{max}(Et_2O)$ 276 mμ (ε = 28.8); tail absorption λ < 240 mμ. No coloration produced by ferric chloride. Semicarbazone, M.P. 123-124° (Found: C, 50.35; H, 7.93; N, 19.80; M.W., 215 (mass spectrometer). $C_9H_{17}O_3N_3$ requires C, 50.20; H, 7.95; N, 19.52%; M.W., 215.25).

F) Hydrolysis of the photoproduct of the propionaldehyde/methyl crotonate irradiation

Methyl 3-methyl-4-oxohexanoate (141 mg.) (obtained from the propionaldehyde/methyl crotonate irradiation) in distilled water (10 ml.) with conc. hydrochloric acid (5 ml.) was heated on a water bath for 6 hr. Ether extraction and bulb distillation yielded 3-methyl-4-oxohexanoic acid (114 mg.) b.p. 80-110° (air bath temperature)/0.1 mm. (Found: C, 56.5; H, 8.43; M.W., 144 (mass spectrometer); $C_7H_{12}O_3$ requires C, 58.25, H, 8.38%, M.W., 144.17) ν (liquid film) ~ 3000 (broad absorption, carboxylic acid O-H stretch); 2975, 2940, 2880 (C-H stretch); 1713 (C=O stretch, carboxylic acid dimer); 1465 $cm.^{-1}$ N.m.r. ($CDCl_3$) τ = 8.95 (triplet, J = 7.8 cps.); τ = 8.84 (doublet, J = 9.0 cps.) (τ = 8.95 plus τ = 8.84, 6 protons); τ = 6.95 to τ = 7.8 (complex, 5 protons); τ = 0.2 (~ 1 proton, acidic proton).

G) Propionaldehyde/cyclohexene irradiation

(a) Cyclohexene (20 g.) in propionaldehyde (44 g.) was irradiated for 4 hr. using a 500 watt lamp and reactor C. The irradiation was repeated and the products from the two irradiations combined and distilled. The fraction boiling 40-120°/2.5 cm. (5.1 g.) was collected and resolved by preparative gas chromatography using a model 770 F and M preparative gas chromatograph. (Column; 30% L at 100° for 48 min. after injection followed by a temperature rise (10°/min.) to 150°. Carrier gas; 20% hydrogen in nitrogen. Injection temperature; 220°. An ice-water coolant was used in the traps.) The mixture (0.25 ml. fractions) was injected neat. The following fractions were collected and distilled.

	Weight collected	b.p. (air bath temperature/3 cm.)	
Trap 1	0.4817 g.	40-80°	pure components (analytical gas chromatography)
Trap 2	0.0790 g.	60-70°	
Trap 3	0.3147 g.	70-110°	
Trap 4	0.1988 g.	40-80°	
Bypass	0.1191 g.		

Trap 1 contained propionic acid (by comparison of infrared spectrum and gas chromatographic retention time with authentic material).

Trap 2 contained a liquid (r_t = 2.0 min, polyglycol, 150°). ν (liquid film) 3320 (associated O-H stretch); 3020 (vinyl C-H stretch); 2930, 2830 (CH_2, C-H stretch) 1653 (C=C stretch); 1455; 1440 (CH_2, CH_3 C-H deformation); 1163, 1138 (alcohol C-O stretch); 1060, 960 (six-membered ring); 900; 730 (cis-sub. C=C) cm.$^{-1}$ ν ($CHCl_3$) 3590 (free O-H stretch) cm.$^{-1}$ additionally. Substance probably 1-cyclohex-2'-enylpropan-1-ol (XVII) (isolated by de Mayo et. al.)[58]

Trap 3 contained a liquid (r_t = 1.6 min, polyglycol, 150°), identified as 2,4,6-triethyl-1,3,5-trioxan (XVIII). (Found: C, 61.72; H, 10.24; M.W., 174 (mass spectrometer). Calc. for $C_9H_{18}O_3$, C, 62.00; H, 10.42%; M.W., 174.2) ν ($CHCl_3$) 2975, 2940, 2880, 2840 (C-H stretch); 1472, 1465 (CH_2, CH_3 C-H deformation); 1365 (CH_3); 1320; 1170; 1100; 1040, 1025 (ether C-O stretch), 970, 920 cm.$^{-1}$ N.m.r. ($CDCl_3$), τ = 9.05 (triplet, J = 7.5 cps, 9 protons); τ = 8.30 (quartet, J = 7.5 cps., each peak further split to a doublet J = 5.0 cps., 6 protons); τ = 5.25 (triplet, J = 5.0 cps, 3 protons).

Trap 4 contained a liquid (r_t = 4 min, polyglycol, 150°) identified

as ethylcyclohexyl ketone (XIX) (Found: C, 75.22; H, 11.11; M.W., 140 (mass spectrometer). Calc. for $C_9H_{16}O$, C, 77.05; H, 11.50%; M.W., 140.2) ν ($CHCl_3$) 2940, 2860 (C-H stretch); 1710 (ketonic C=O stretch); 1465, 1455 (C-H deformation); 1380 (CH_3); 1150; 978 (six-membered ring) $cm.^{-1}$ N.m.r. ($CDCl_3$), τ = 8.96 (triplet, J = 7.8 cps. CH_3); τ = 7.60 (quartet, J = 7.8 cps. CH_2); τ = 7.9 to 9.1 (broad structureless absorption, cyclohexyl). 2,4-Dinitrophenylhydrazone, m.p. 148-150° (lit. (58) m.p. 149-151°).

(b) Cyclohexene (13 g.) in propionaldehyde (26.5 g.) was deoxygenated by bubbling nitrogen through the solution for 15 min., then irradiated for 4 hr. in reactor C using a 500 watt lamp. Volatile material was removed (to 70°/atm. pressure) and the residue examined by gas chromatography. No 3,3'-bicyclohexenyl (V) (r_t = 9.8 min, polyglycol, 150°) nor cyclohexanone (r_t = 1.4 min, polyglycol, 150°) was observed (mixed chromatogram).

H) Propionaldehyde/styrene irradiation

Styrene (1.97 g.) in propionaldehyde (144 g.) was deoxygenated by bubbling nitrogen through the solution for 1 hr, then irradiated for 4 hr, in reactor C using a 500 watt lamp. Volatile material was removed under a water vacuum. The residue (2.8 g.) was distilled. The fraction, b.p. 105-150° (air bath temperature)/0.1 mm. exhibited ν* (liquid film), 3400, 2900, 2850, 1710, 1460, 1380, 1100, 765, 705 $cm.^{-1}$ Gas chromatography (carbowax, 150°) revealed two components (r_t = 3.0 min. (small peak);

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* Recorded using a Unicam SP200 spectrophotometer.

r_t = 3.5 min.). Thin layer chromatography (unbaked Kieselgel H/ether) revealed a complex mixture. Undistilled crude irradiation product (1.9 g.) was subjected to column chromatography (Whatman SG31 silica gel (100 g.)).

(a) A liquid (30 mg.) eluted in benzene/10% ether exhibited ν* (liquid film) 2930, 2870, 2820, 1450, 1410, 1255 (sharp, intense), 1090 (intense), 1020 (intense), 865, 800 (intense) $cm.^{-1}$.

The material pyrolysed on attempted distillation.

(b) A liquid (660 mg.) eluted in ether gave ν_{max} (liquid film) 3400 (associated O-H stretch); 2965; 2935; 2875 (CH_3 and CH_2, C-H stretch); 1720 (weak, C=O stretch) 1465, (C-H deformation) 1410; 1380 (CH_3); 1348; 1230; 1150; 1115; 1080; 1015; 970 $cm.^{-1}$ ν_{max} ($CHCl_3$) 3660 (free O-H stretch) $cm.^{-1}$ additionally. Mass spectrum = highest significant peak at $\frac{m}{e}$ = 98. Gas chromatograph (carbowax, 125°), two components (r_t = 6.2 min. (small peak); r_t = 8.5 min.).

No significant reaction was observed with Brady's reagent and the C=O infrared absorption was not removed by bicarbonate solution extraction.

I) Propionaldehyde irradiation

Propionaldehyde (28 g.) was deoxygenated and irradiated in reactor C for 4 hr. using a 500 watt lamp. Removal of volatile material (propionaldehyde and some propionic acid) under water vacuum left a residue (90 mg.), which distilled at > 100° (air bath temperature)/0.1 mm. giving an oil (50 mg.) (Found: C, 60.48; H, 8.99%) ν* (liquid film), 3470, 2960, 2930, 2870, 1705, 1460, 1380, 1100, 960 $cm.^{-1}$ Gas chromatograph (carbowax, 100°),

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* Recorded using a Unicam SP200 spectrophotometer.

two components (r_t = 18.5 min. and 20 min.).

The following irradiations were also conducted (reactor-C)

(a) Ethyl vinyl ether (9 g.) in propionaldehyde (82 g.) for 2 hr.

(b) Benzene (11 g.) in propionaldehyde (35 g.) for 4 hr.

(c) Crotonaldehyde (3.1 g.) in propionaldehyde (17.4 g.) for 1.5 hr.

The products of these irradiations yielded material having infrared and gas chromatographic properties identical to those of the material obtained by irradiating propionaldehyde alone.

J) A Comparison of the light induced and peroxide induced reactions

Solutions A, B and C were prepared thus.

Solution A. Dimethyl maleate (1.4408 g.), methyl crotonate (1.0009 g.) and cyclohexene (0.8213 g.) in redistilled propionaldehyde (24.82 g.) were irradiated in reactor C for 50 min. with a 125 watt lamp 3 in. from the flask, the solution having been partially degassed by bubbling nitrogen for 5 min. prior to irradiation. Solution A was a sample (10 ml.) of the irradiated liquid to which resublimed naphthalene (0.1020 g.) had been added.

Solution B. Dimethyl maleate (8.3 mg.), methyl crotonate (7.8 mg.) ethylcyclohexyl ketone (8.6 mg.), methyl 3-methyl-4-oxohexanoate (10.1 mg.), dimethyl propionylsuccinate (9.9 mg.) and resublimed naphthalene (11.5 mg.) were dissolved in acetone (total volume, 1 ml.). This was Solution B.

Solution C. Dimethyl maleate (1.4995 g.), methyl crotonate (0.9694 g.) and cyclohexene (0.8240 g.) were dissolved in redistilled propionaldehyde (25 g.). The solution was flushed with nitrogen, benzoyl peroxide (32 mg.) was added and the solution was heated on a water bath for 6 hr. A sample

(10 ml.) of the resulting solution was taken and resublimed naphthalene (0.0897 g.) added. This was solution C.

Solutions A, B and C were examined by gas chromatography using a Perkin-Elmer F11 gas chromatograph (polyglycol, 60° rising rapidly to 100° after the methyl crotonate peak, then to 125° before the naphthalene peak and finally to 150° for the dimethyl propionylsuccinate peak. See Figure XLI .) Peak areas were estimated by cutting out and weighing. Average (of 3 determinations) peak-ratios to marker (naphthalene) were calculated. (For a full discussion of these methods, see Section I of this thesis.)

Solution	A	B	C
methyl crotonate	1.35	0.4(0.1)	1.4
ethylcyclohexyl ketone	$\leq$ 0.00185	0.482(0.004)	0.012(0.003)
dimethyl maleate	1.24	0.301(0.009)	1.44
methyl 3-methyl-4-oxohexanoate	0.026(0.002)	0.386(0.013)	0.101(0.006)
dimethyl propionylsuccinate	0.0928(0.0025)	0.212(0.007)	0.31(0.02)

(Number in brackets is a measure of the spread of values obtained, i.e. 0.386(0.013) indicates 0.386 is the average of 3 values within the range 0.399 to 0.373.)

The chromatograph was over-loaded with respect to crotonate and maleate (solutions A and C) see page 45. No dimethyl fumarate was present in Solution A (mixed chromatogram).

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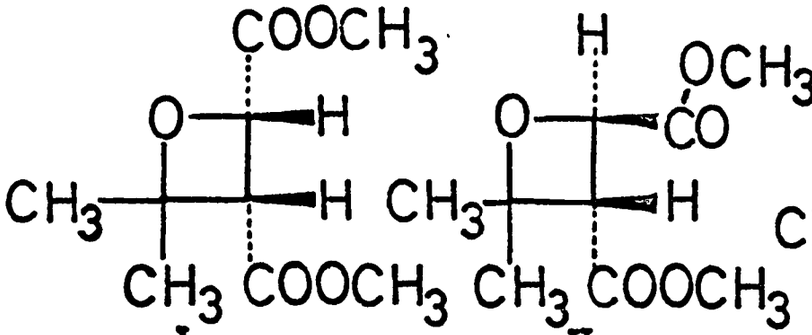
62. H. Sakuri, K. Shima, and I. Aono, Bull. Chem. Soc. Japan., 1965, 38, 1227.

63. T.M. Patrick, J. Org. Chem., 1952, 17, 1009.

64. M.S. Kharasch, W.H. Urry and B.M. Kuderna, J. Org. Chem., 1949, 14, 248.

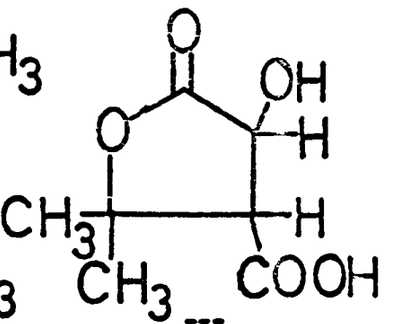
65. H.T. Taylor, J., 1958, 3922.

STRUCTURAL DIAGRAMS I - XIX

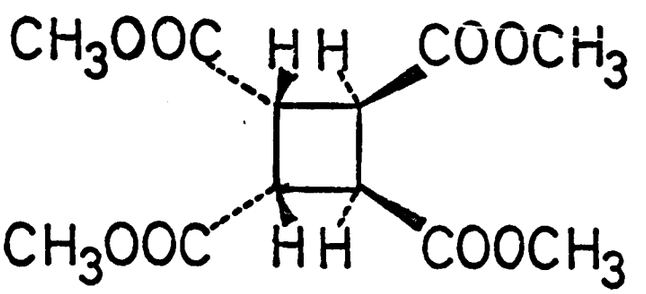


I

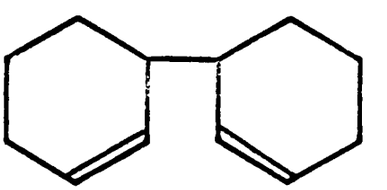
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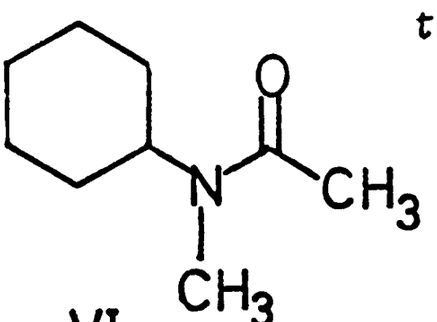
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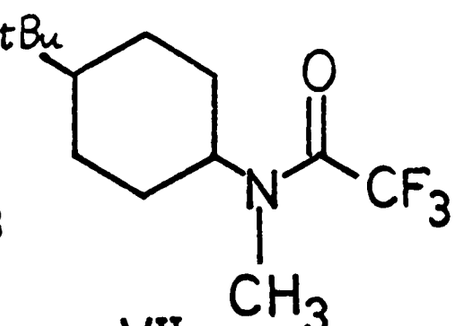
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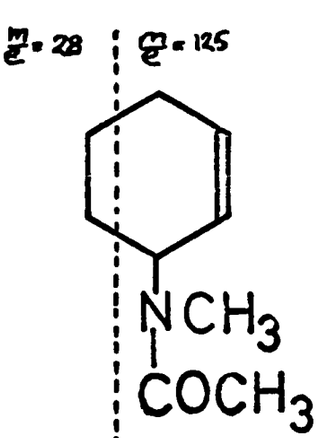
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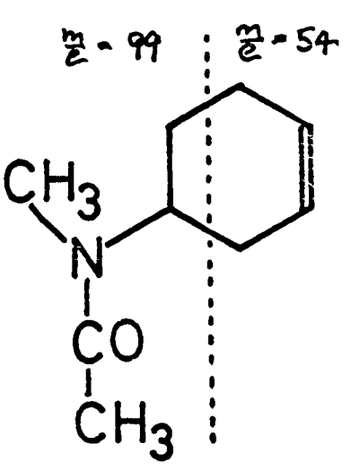
VI



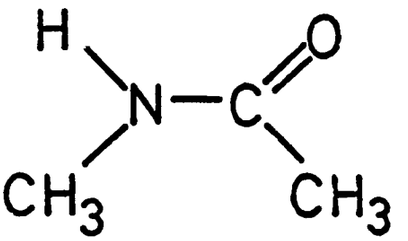
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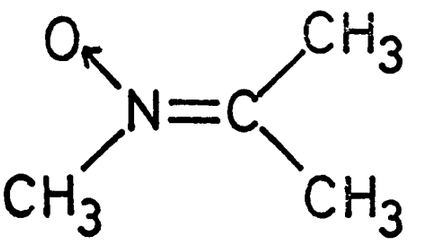
VIII



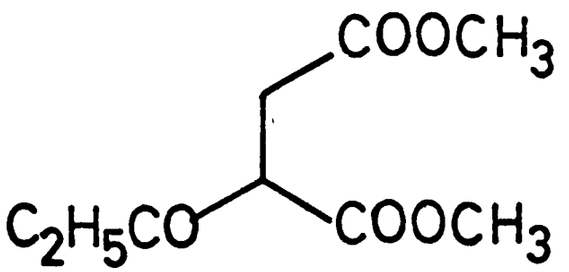
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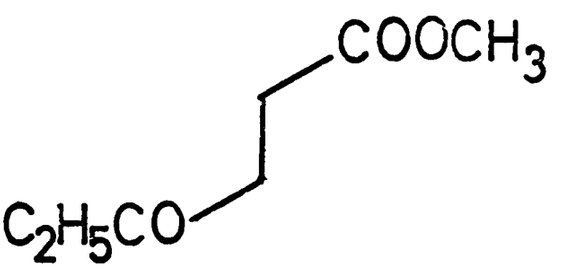
X



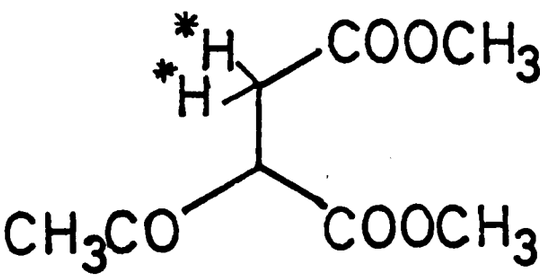
XI



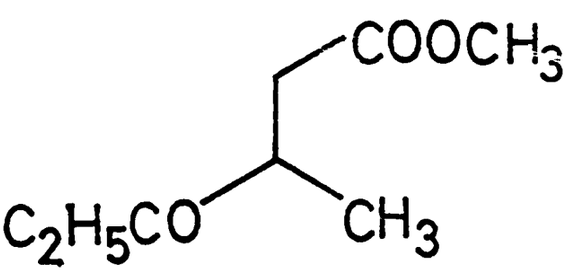
XII



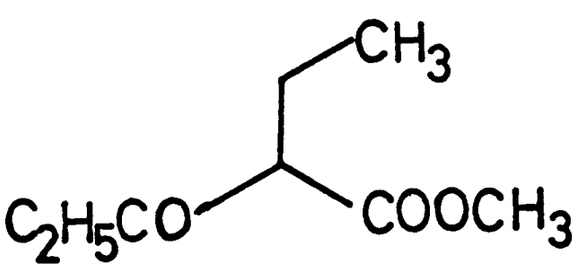
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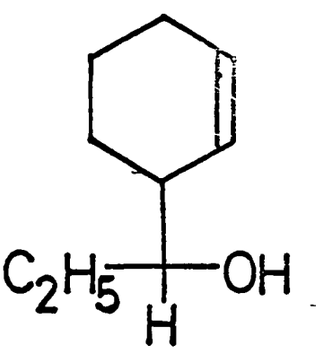
XIV



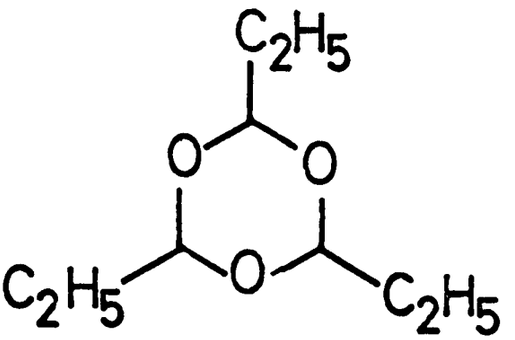
XV



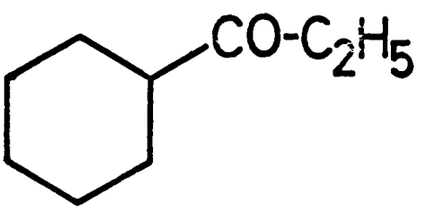
XVI



XVII



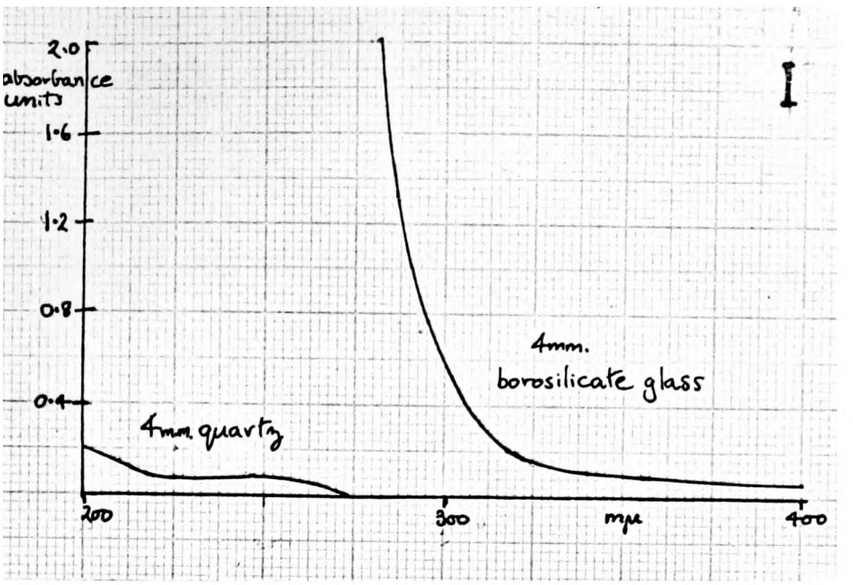
XVIII

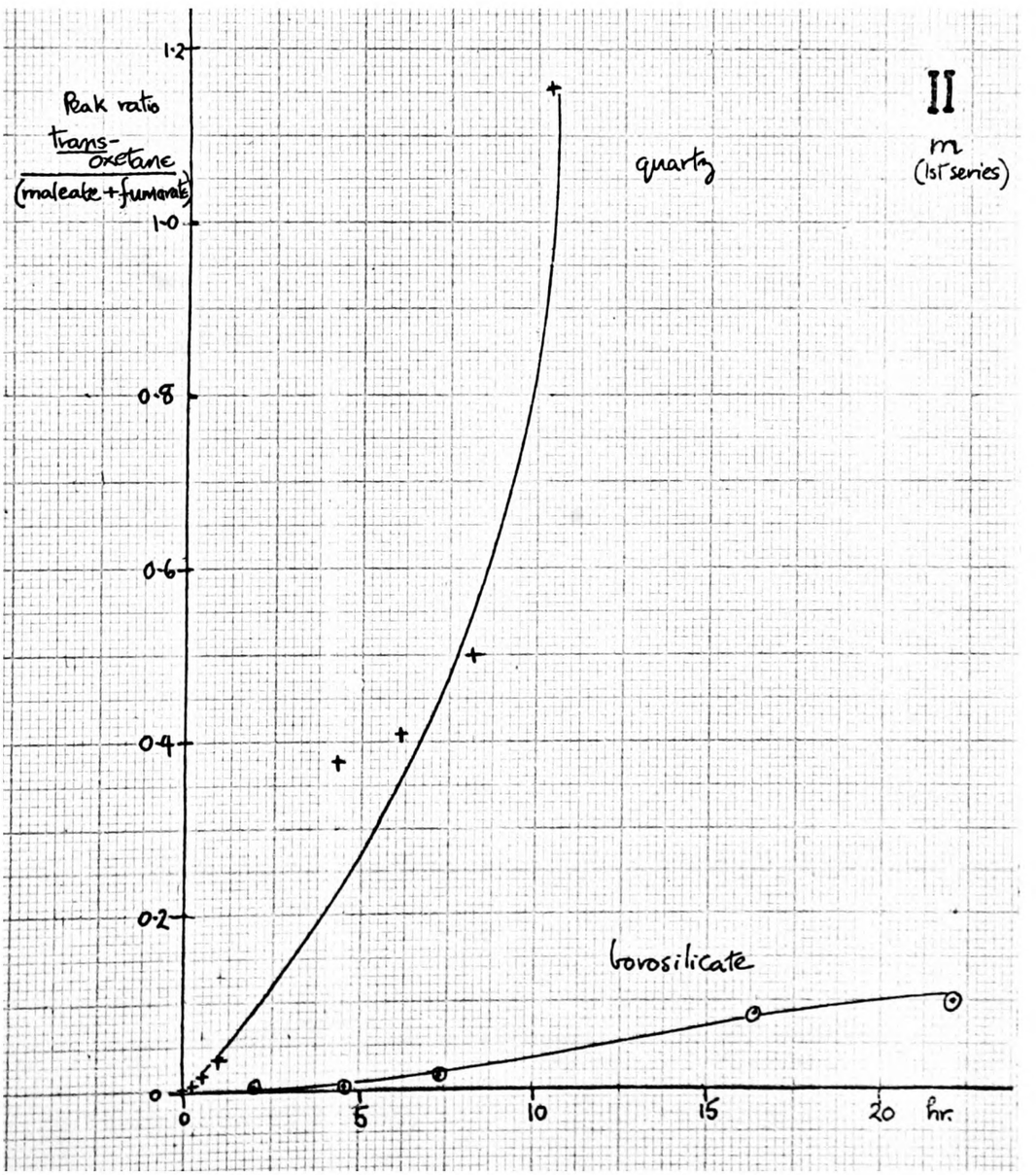


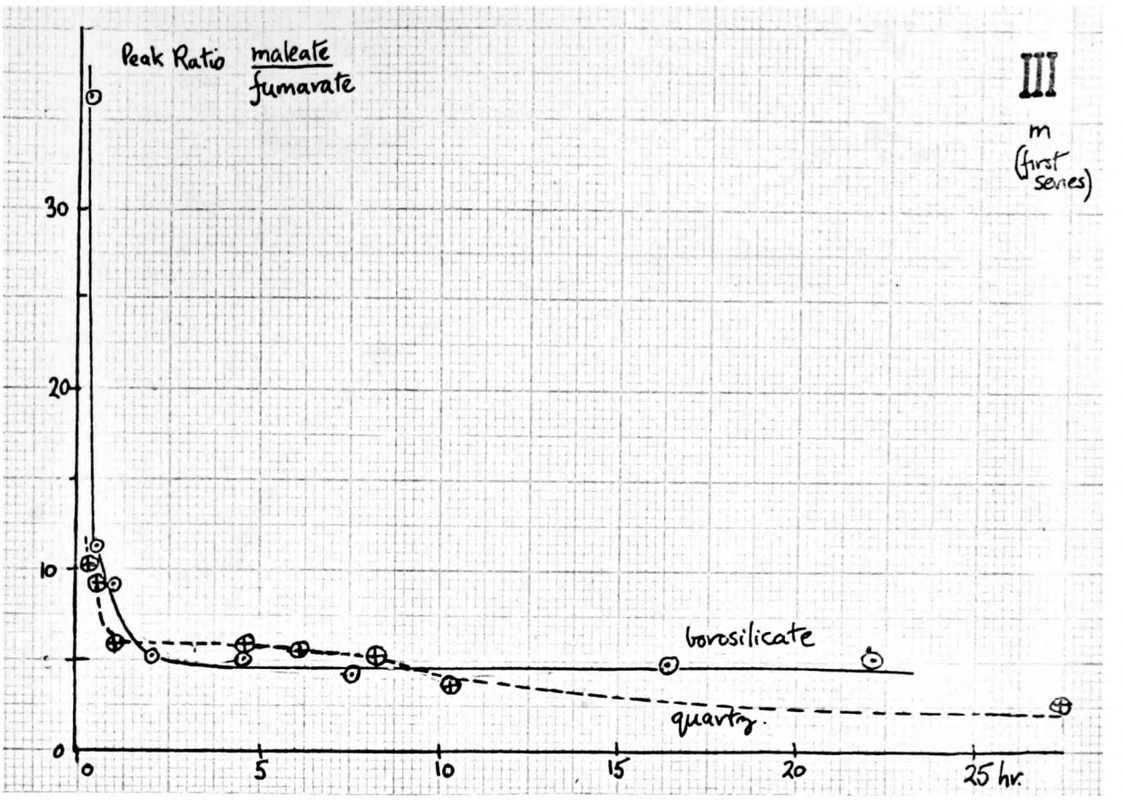
XIX

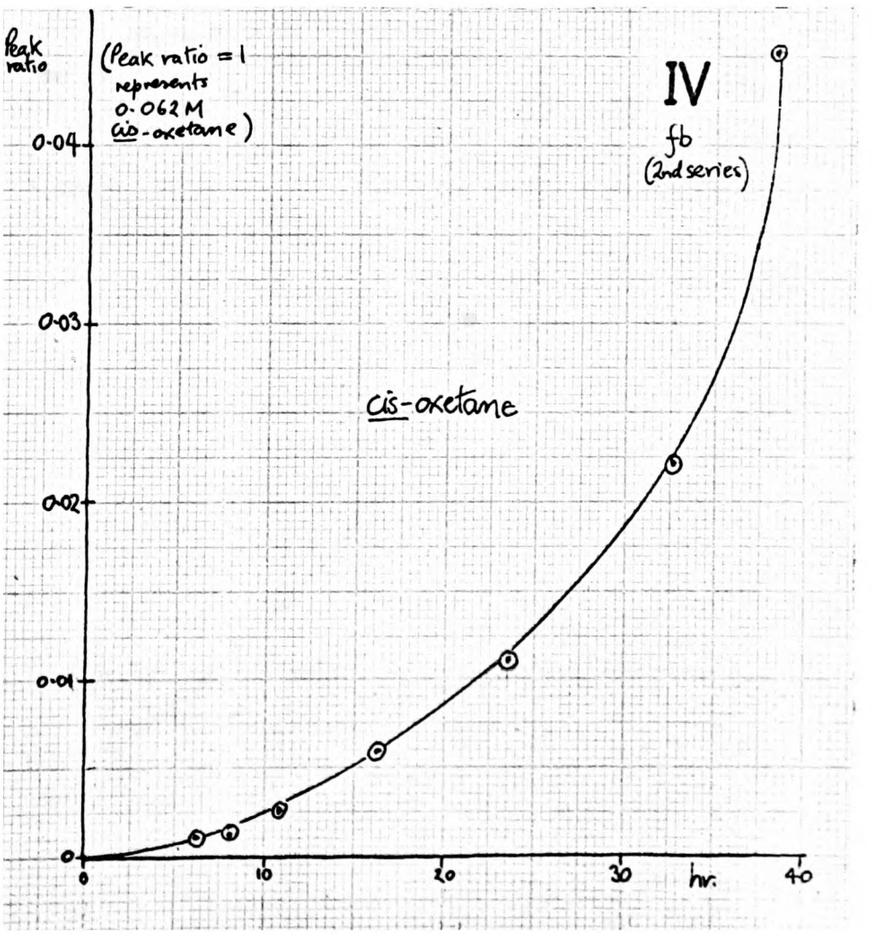
FIGURES I - XLI

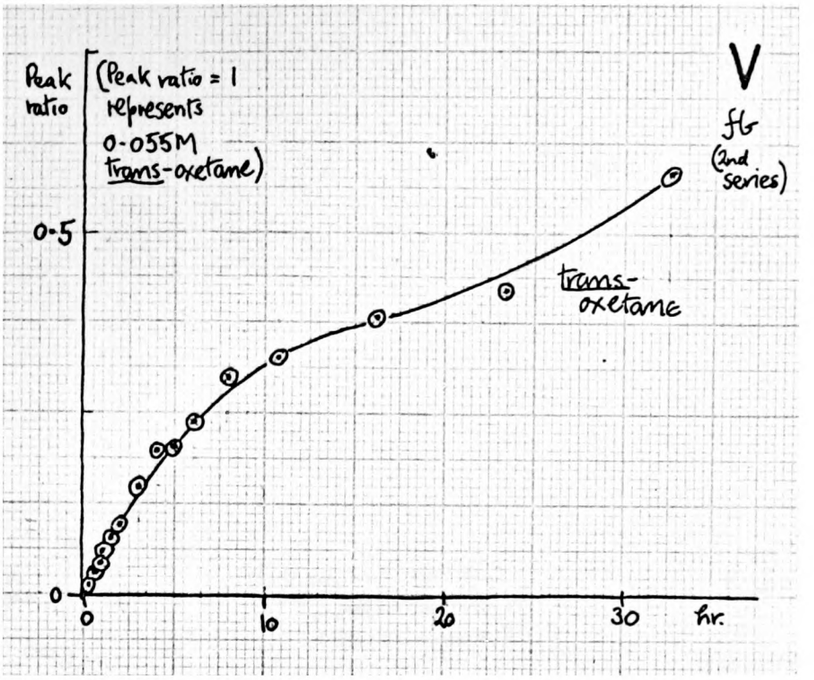
In those figures representing the variations in concentration with time of the components of the irradiated system dimethyl maleate/dimethyl fumarate/acetone, the irradiation considered is given after the figure number using the convention described on page 47 with a note indicating whether this is a member of the first, second or third photokinetic series.

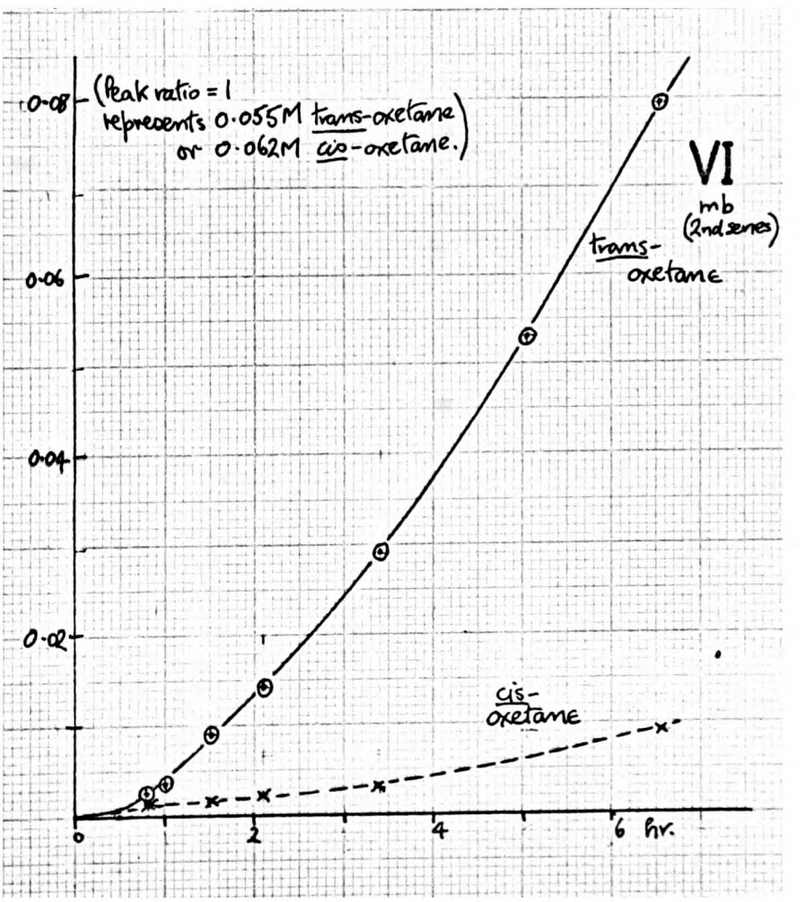

I
2·0
absorbance units
1·6
1·2
0·8
0·4
4mm. borosilicate glass
4mm. quartz
200
300
mμ
400

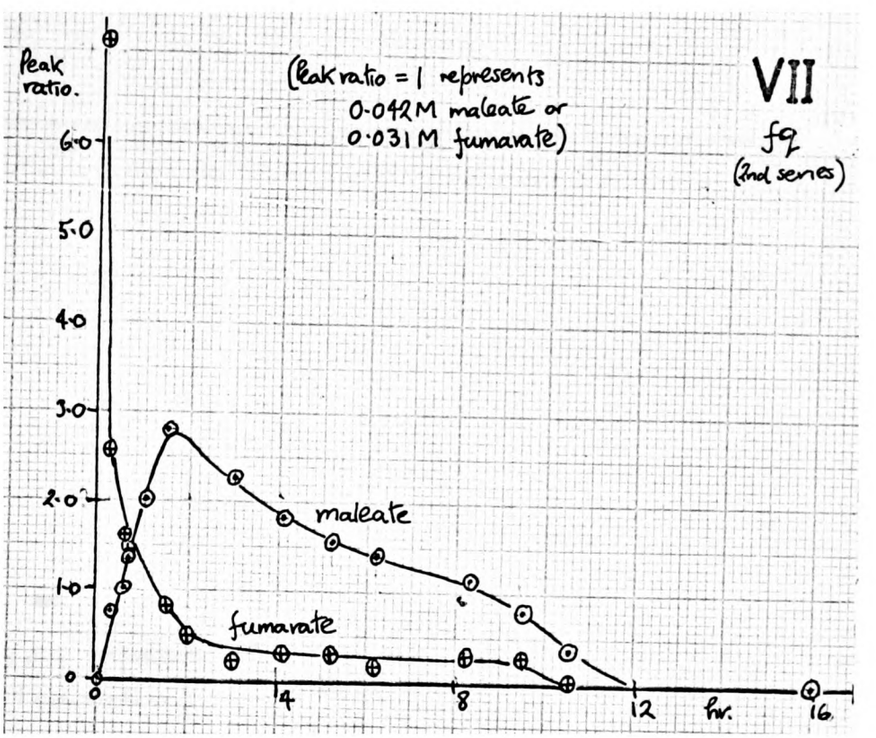

II
m
(1st series)
Peak ratio
trans-oxetane / (maleate + fumarate)
1·2
1·0
0·8
0·6
0·4
0·2
0
quartz
borosilicate
0
5
10
15
20 hr.

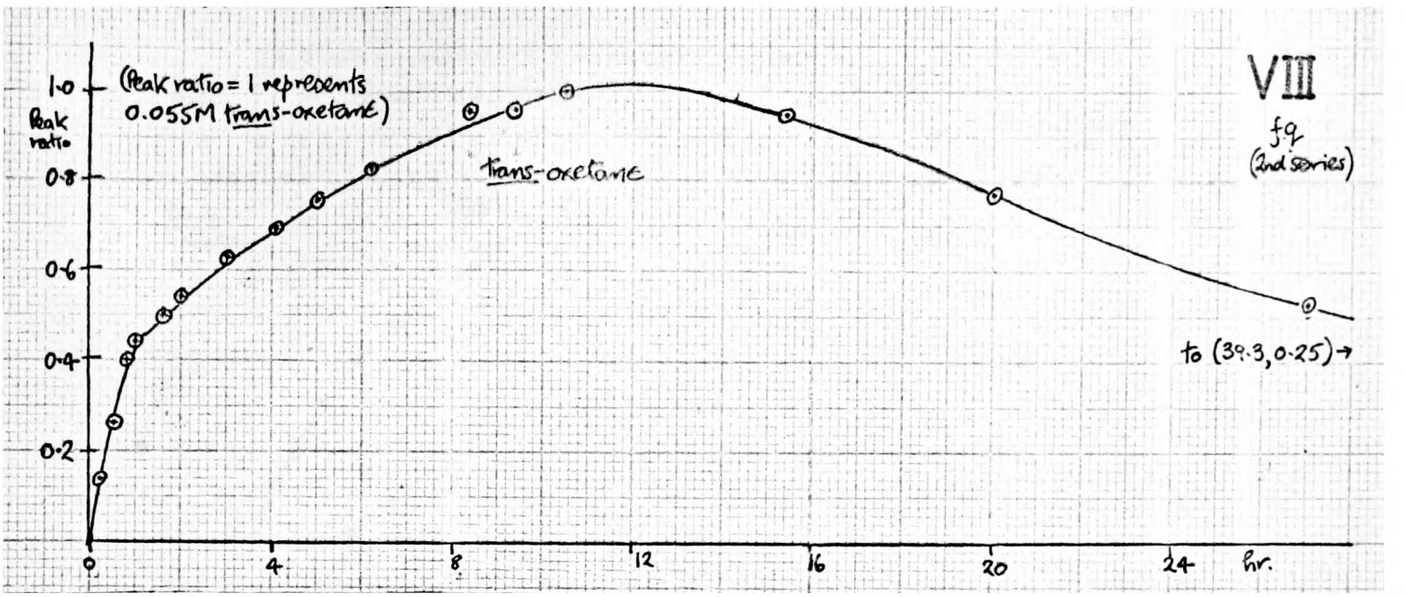

Peak Ratio maleate / fumarate
III
m
(first series)
30
20
10
0
0
5
10
15
20
25 hr.
borosilicate
quartz.

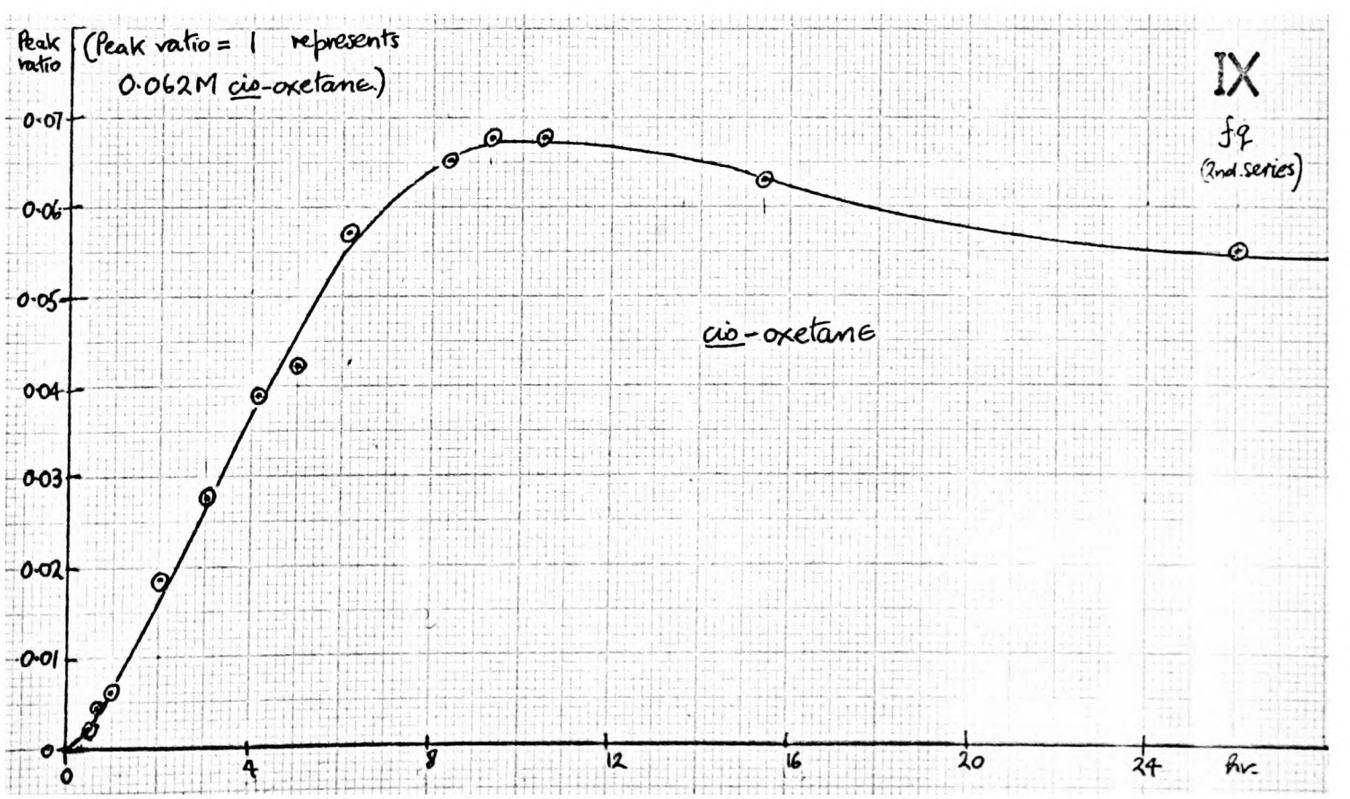

Peak ratio
(Peak ratio = 1 represents 0·062 M cis-oxetane)
IV
fb
(2nd series)
0·04
0·03
0·02
0·01
0
cis-oxetane
0
10
20
30
hr.
40

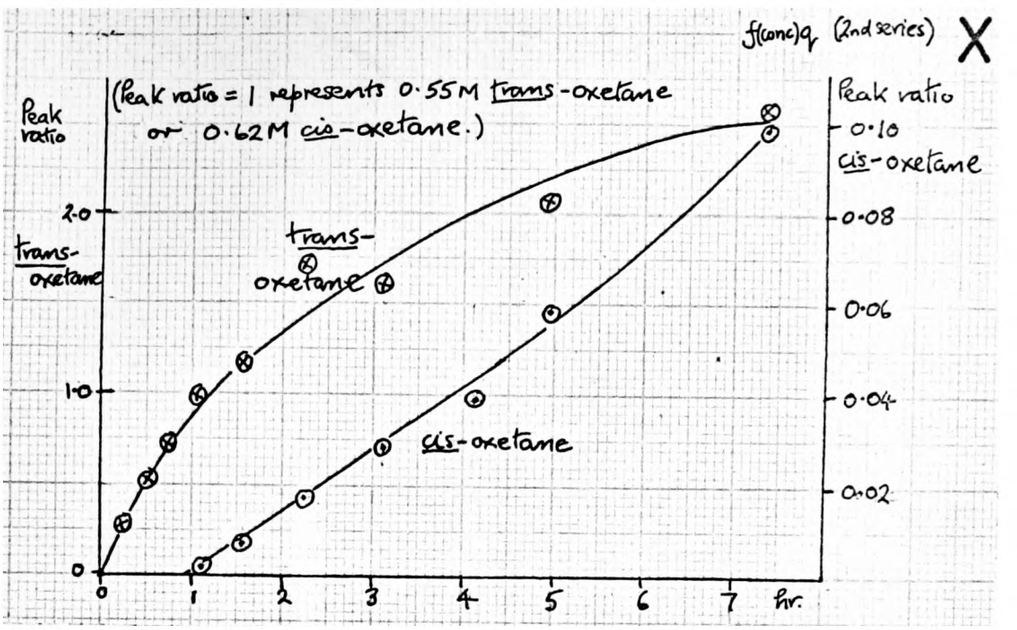

Peak ratio
(Peak ratio = 1 represents 0·055M trans-oxetane)
V
fig (2nd series)
0·5
0
trans-oxetane
0
10
20
30
hr.

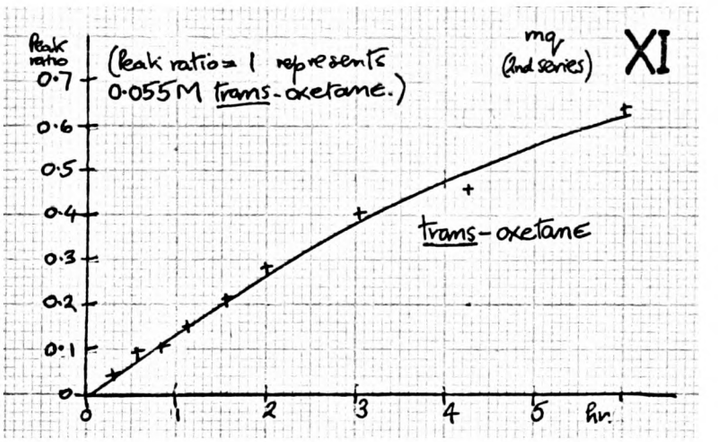

0·08
(Peak ratio = 1 represents 0·055M trans-oxetane or 0·062M cis-oxetane.)
VI
mb (2nd series)
0·06
trans-oxetane
0·04
0·02
cis-oxetane
0
2
4
6 hr.

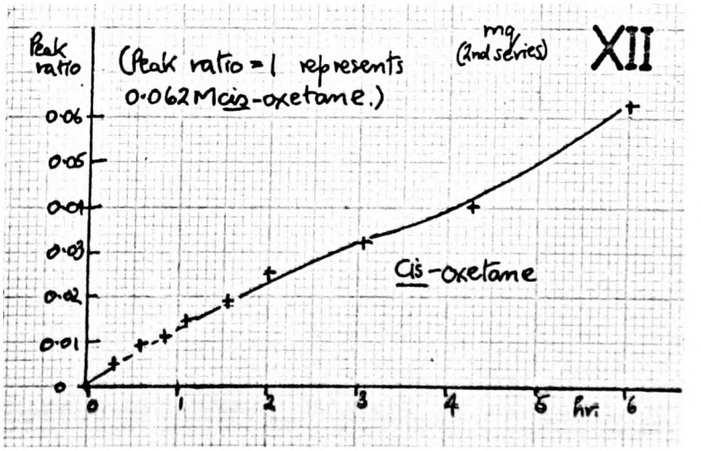

Peak ratio.
(Peak ratio = 1 represents 0·042 M maleate or 0·031 M fumarate)
VII
fq
(2nd series)
6·0
5·0
4·0
3·0
2·0
1·0
0
maleate
fumarate
0
4
8
12
hr.
16

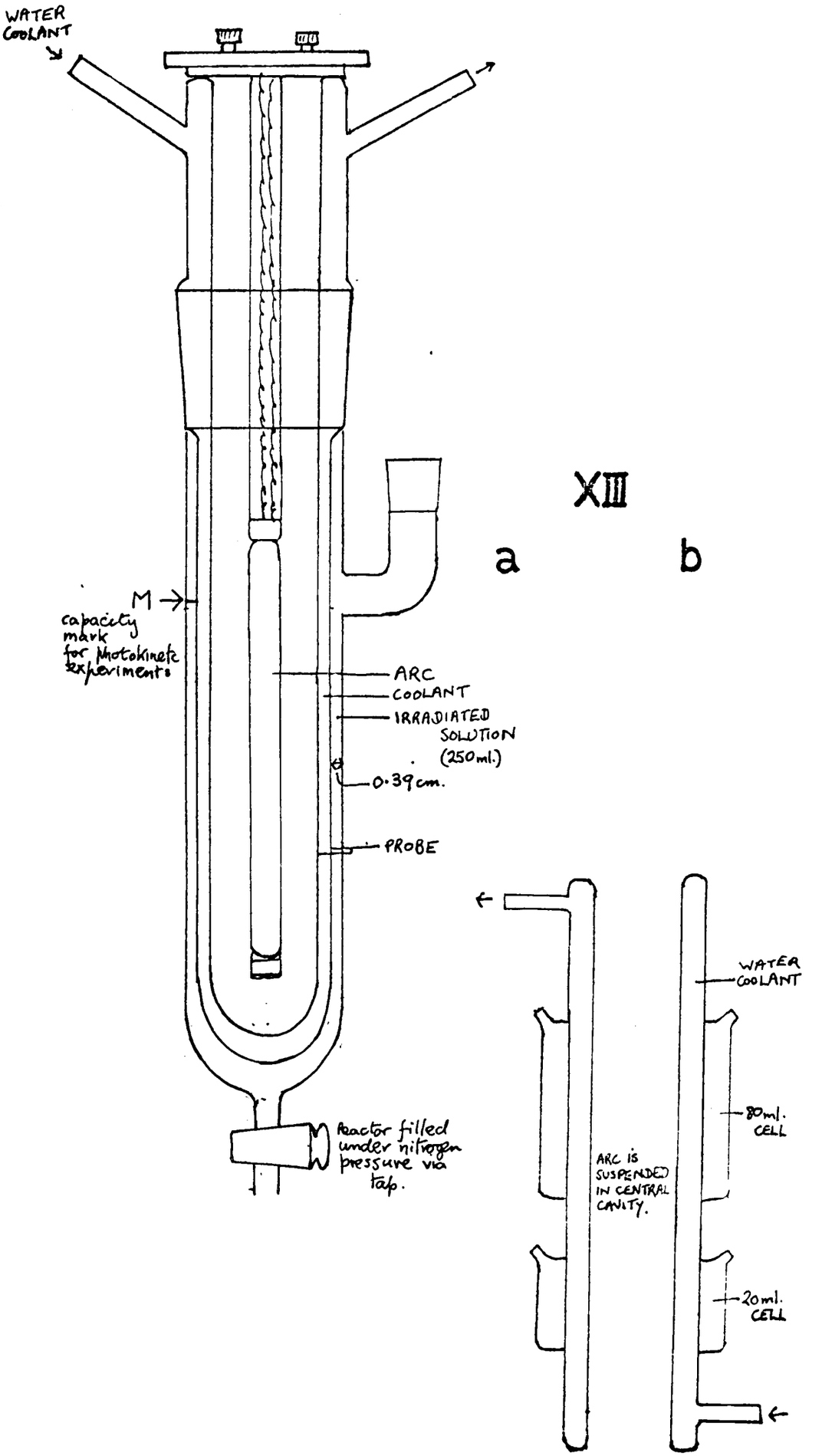

(Peak ratio = 1 represents
0.055M trans-oxetane)
Peak ratio
1.0
0.8
0.6
0.4
0.2
trans-oxetane
VIII
fq
(2nd series)
to (39.3, 0.25) →
0
4
8
12
16
20
24
hr.


Peak ratio
(Peak ratio = 1 represents
0.062M cis-oxetane)
0.07
0.06
0.05
0.04
0.03
0.02
0.01
cis-oxetane
IX
fq
(2nd series)
0
4
8
12
16
20
24
hr.

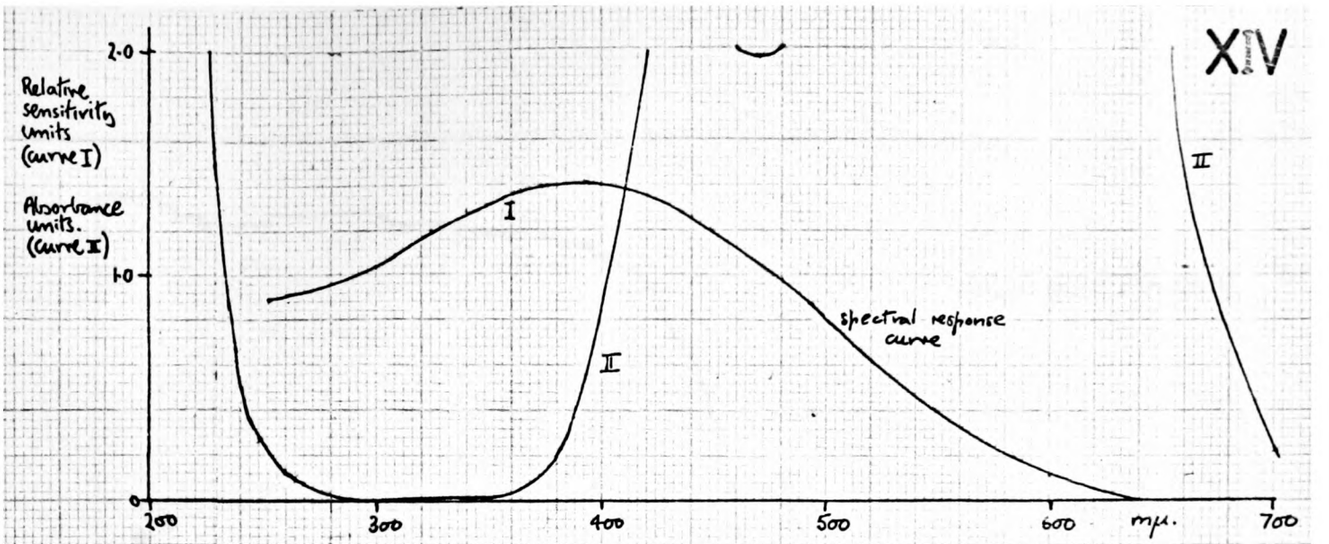

f(conc)q (2nd series)
X
(Peak ratio = 1 represents 0·55M trans-oxetane or 0·62M cis-oxetane.)
Peak ratio
trans-oxetane
Peak ratio
cis-oxetane
trans-oxetane
cis-oxetane
2·0
1·0
0
0·10
0·08
0·06
0·04
0·02
0 1 2 3 4 5 6 7 hr.


Peak ratio
(Peak ratio = 1 represents 0·055M trans-oxetane.)
mq (2nd series)
XI
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0
trans-oxetane
0 1 2 3 4 5 hr.


Peak ratio
(Peak ratio = 1 represents 0·062M cis-oxetane.)
mq (2nd series)
XII
0·06
0·05
0·04
0·03
0·02
0·01
0
cis-oxetane
0 1 2 3 4 5 hr. 6

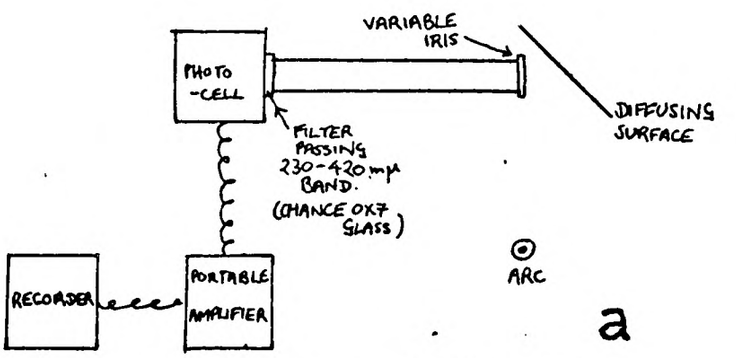

WATER COOLANT
M
capacity mark for photokinetic experiments
ARC
COOLANT
IRRADIATED SOLUTION (250ml.)
0·39cm.
PROBE
Reactor filled under nitrogen pressure via tap.
XIII
a
b
WATER COOLANT
80ml. CELL
ARC IS SUSPENDED IN CENTRAL CAVITY.
20ml. CELL

XIV



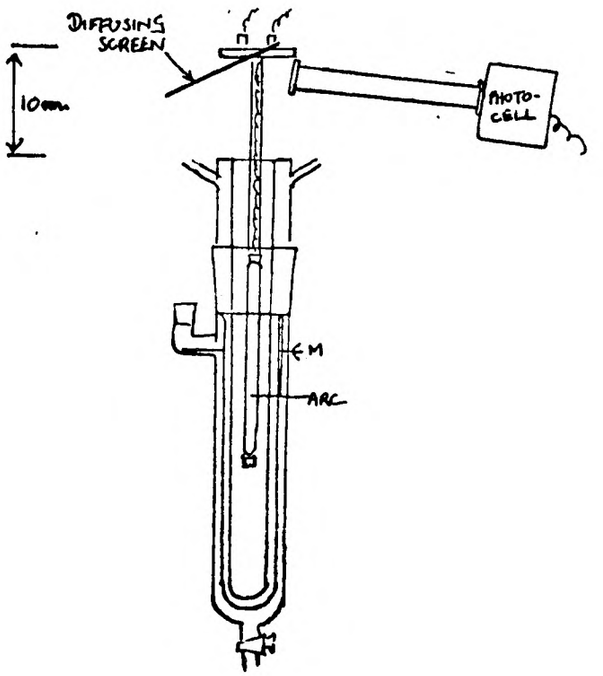
I Spectral response curve of a Rank Cintel QVA 395 photocell

II Absorption of 1·9mm. thickness of Chance OX7 glass.

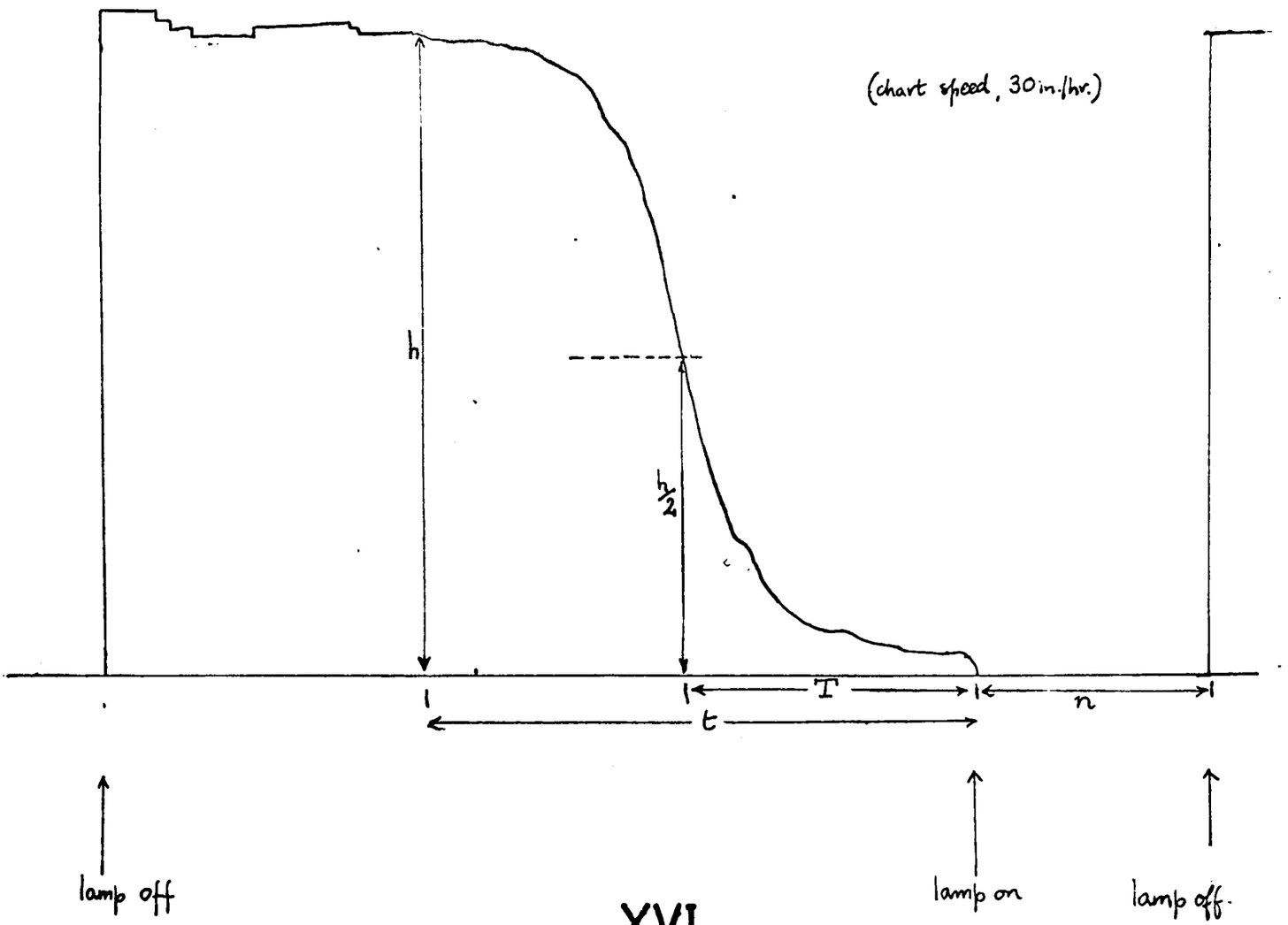


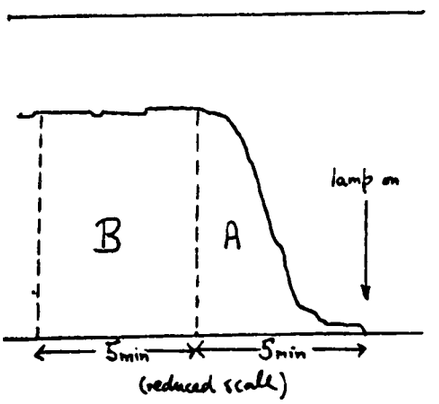
a

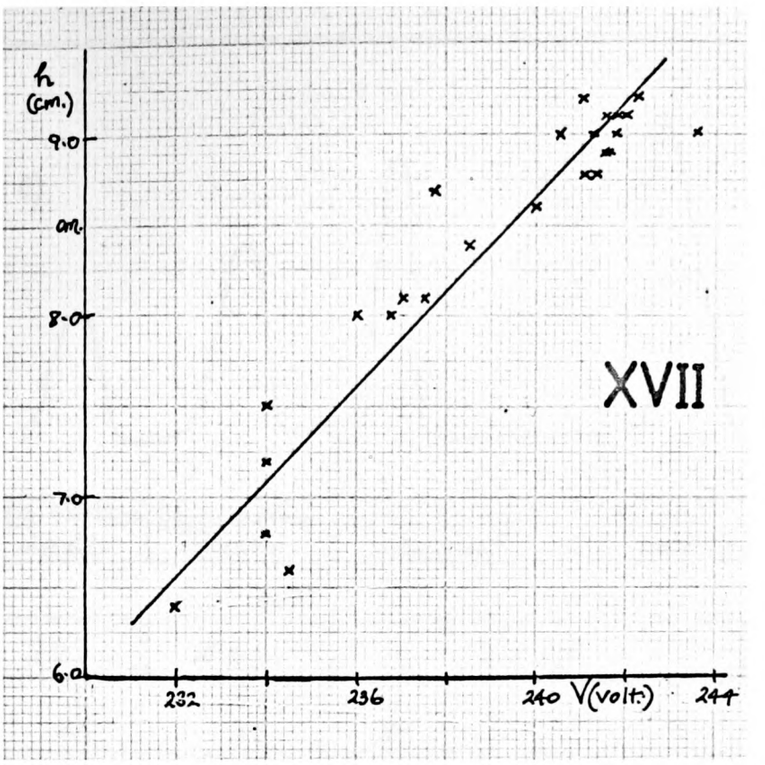
XV

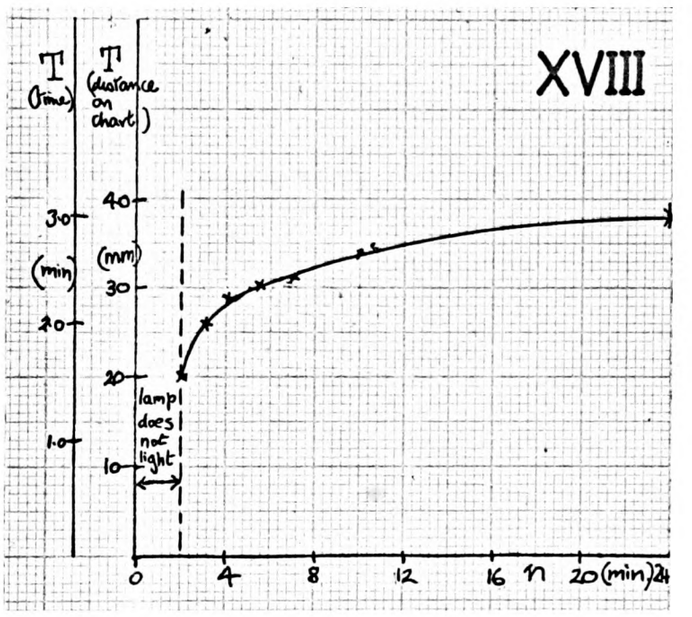


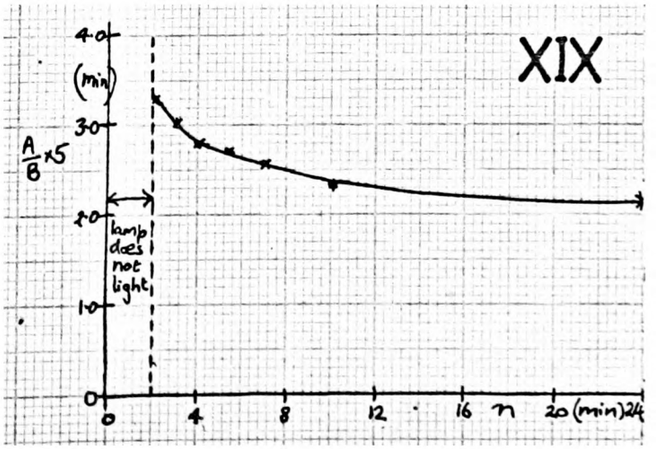
b


(chart speed, 30 in./hr.)
h
h/2
T
n
t
lamp off
lamp on
lamp off


B
A
lamp on
5min
5min
(reduced scale)


h
(cm.)
9.0
8.0
7.0
6.0
232
236
240
V(volt.)
244
XVII

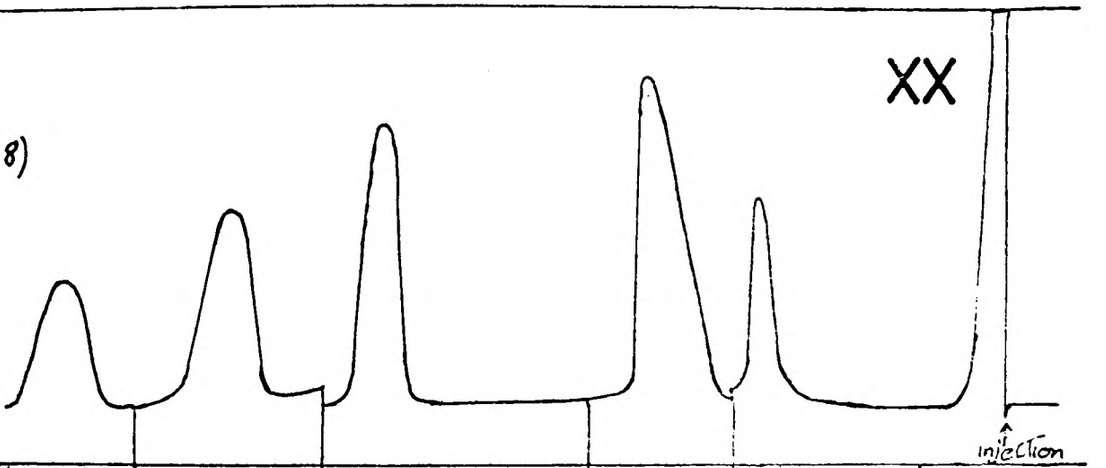

T
(time)
T
(distance on chart)
40
30
(mm)
30
(min)
20
20
1.0
10
lamp does not light
0
4
8
12
16
20(min)24
XVIII


4.0
(min)
30
A/B x5
20
lamp does not light
1.0
0
0
4
8
12
16
20(min)24
XIX

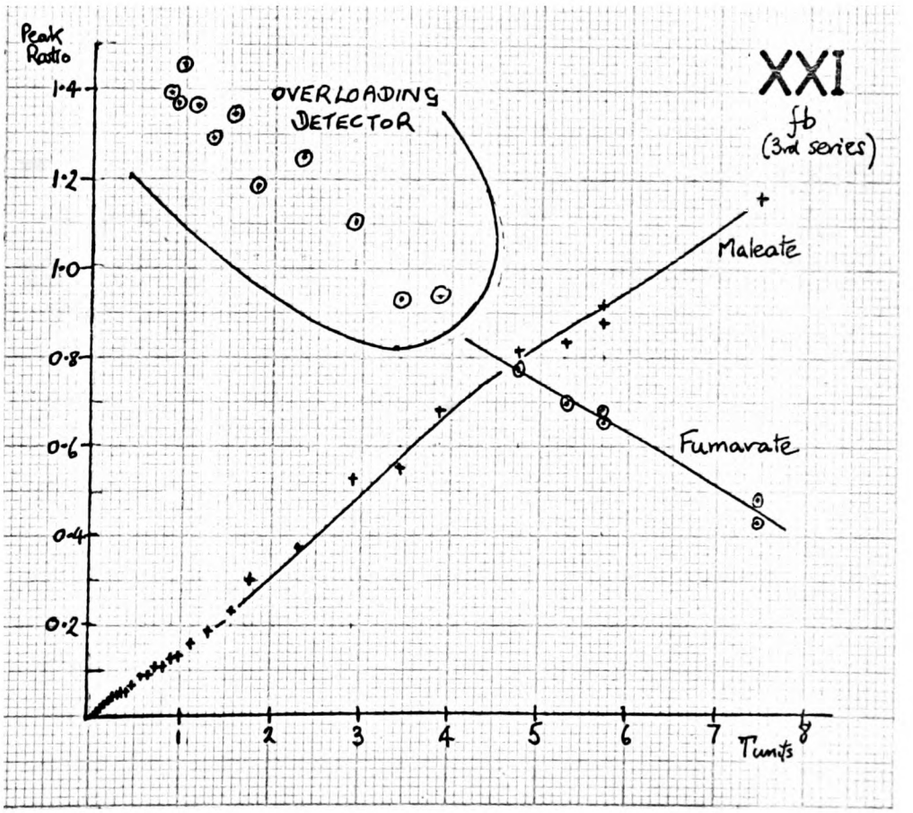
(Polyglycol.)

mq (sample 8)

XX



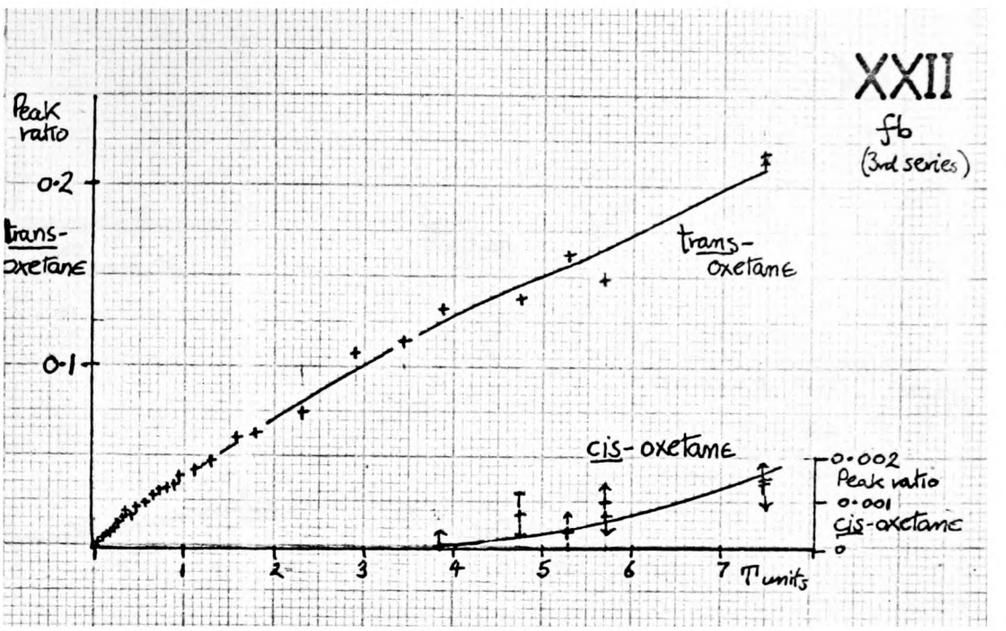
COMPOUND	cis-oxetane diester	trans-oxetane diester	methyl salicylate (marker)	dimethyl maleate	dimethyl fumarate	solvent
COLUMN TEMP.	160°			125°		
ATTENUATOR FACTOR	2 x 1	10 x 1	2 x 10^2		50 x 1	
RETENTION TIME (min)	45	37	29	16	12	0

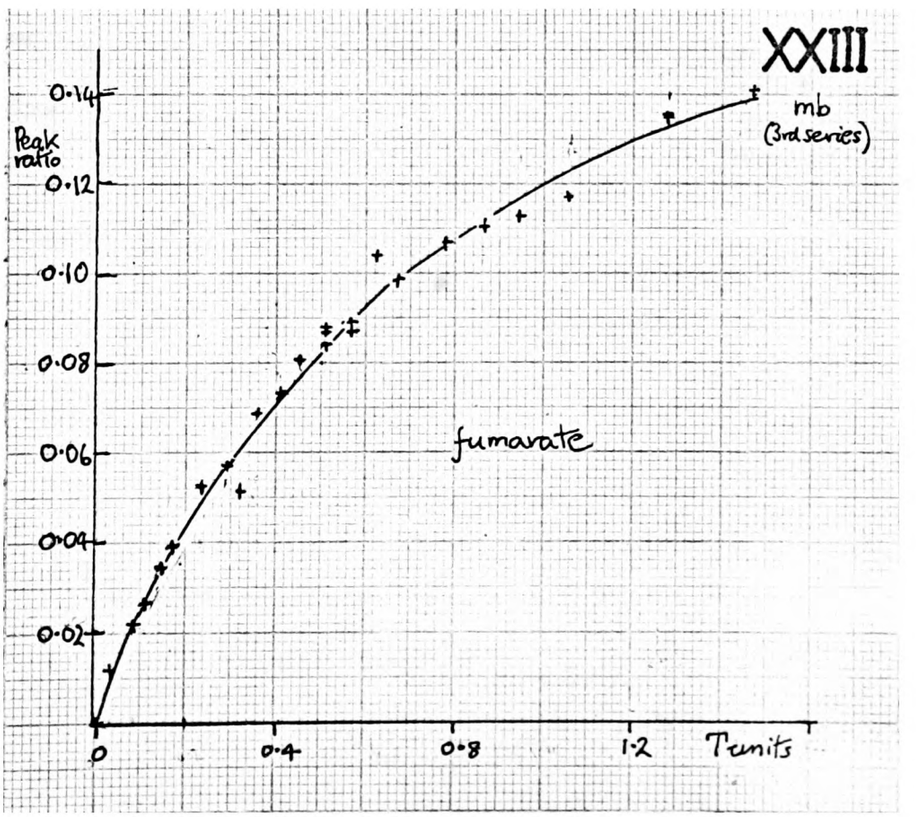


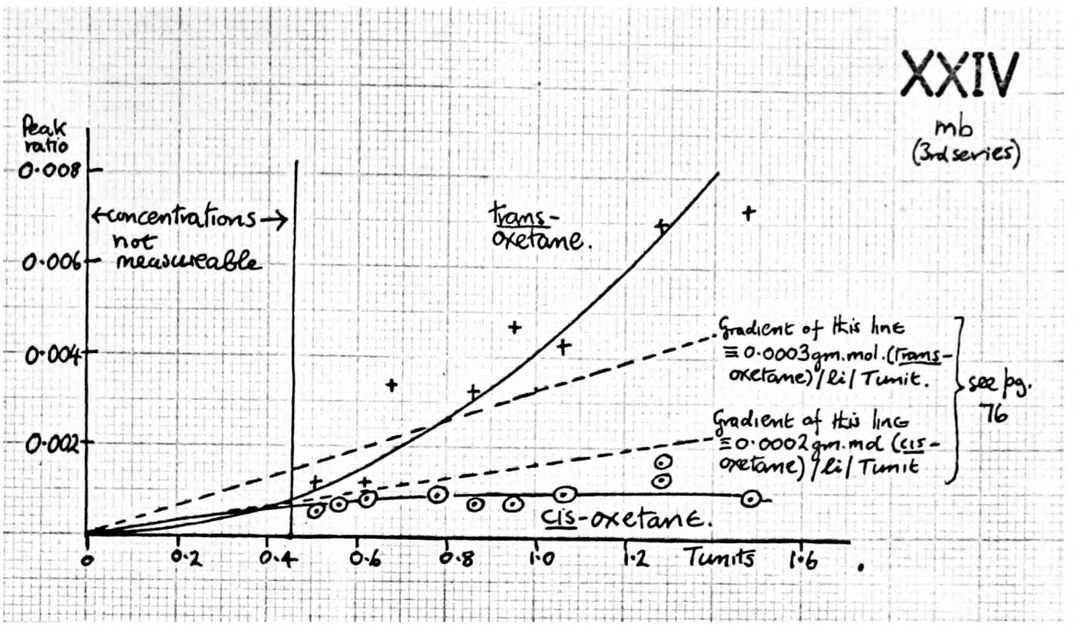
XXI

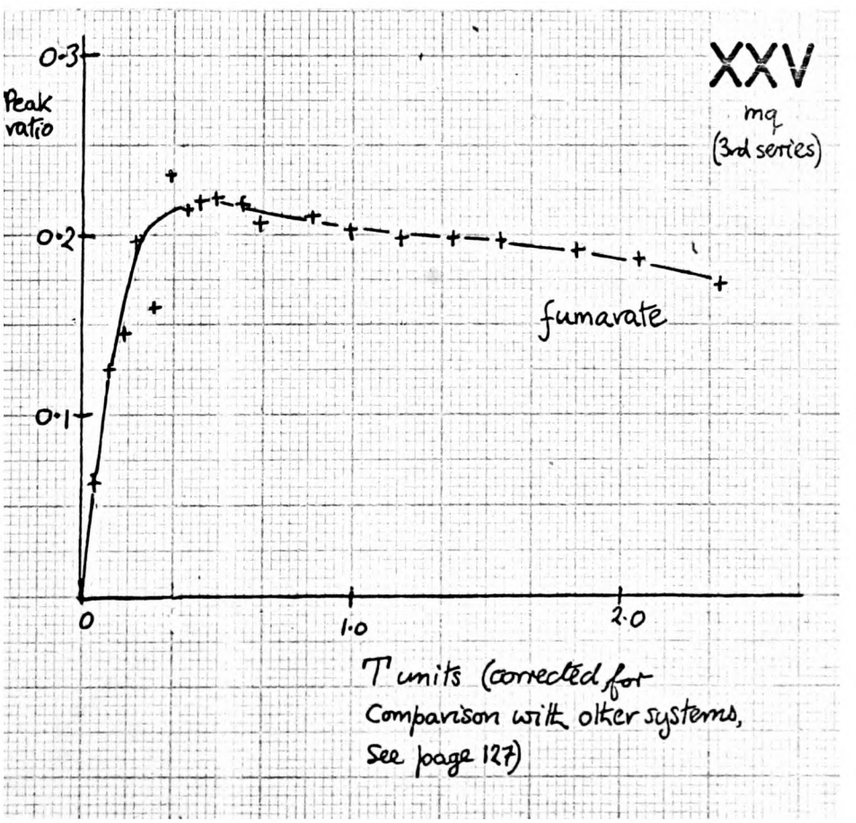
fb

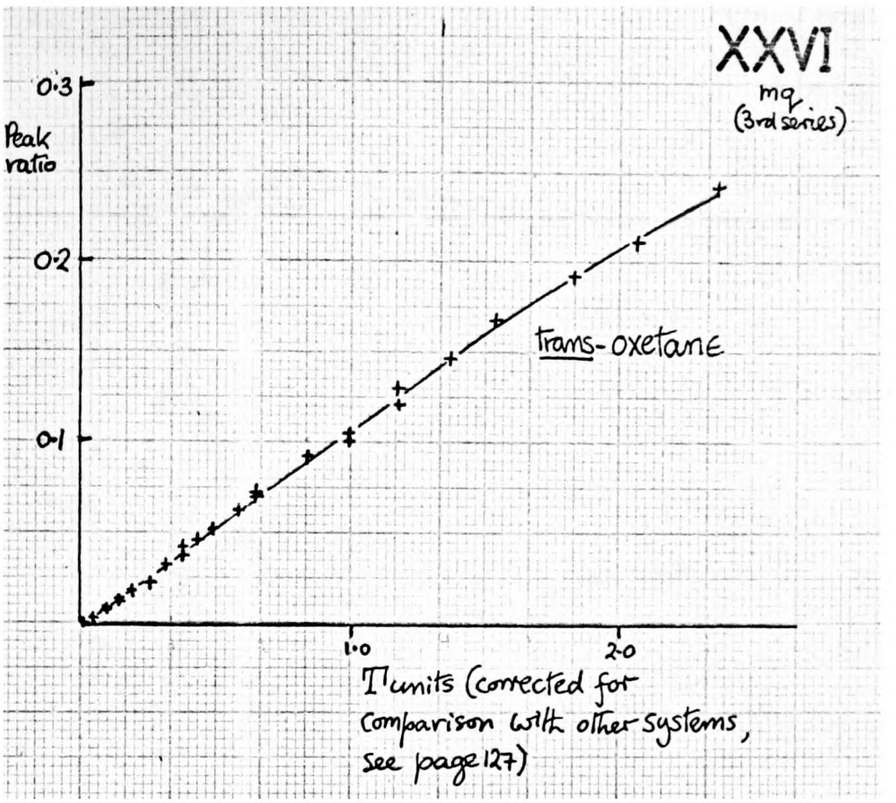
(3rd series)

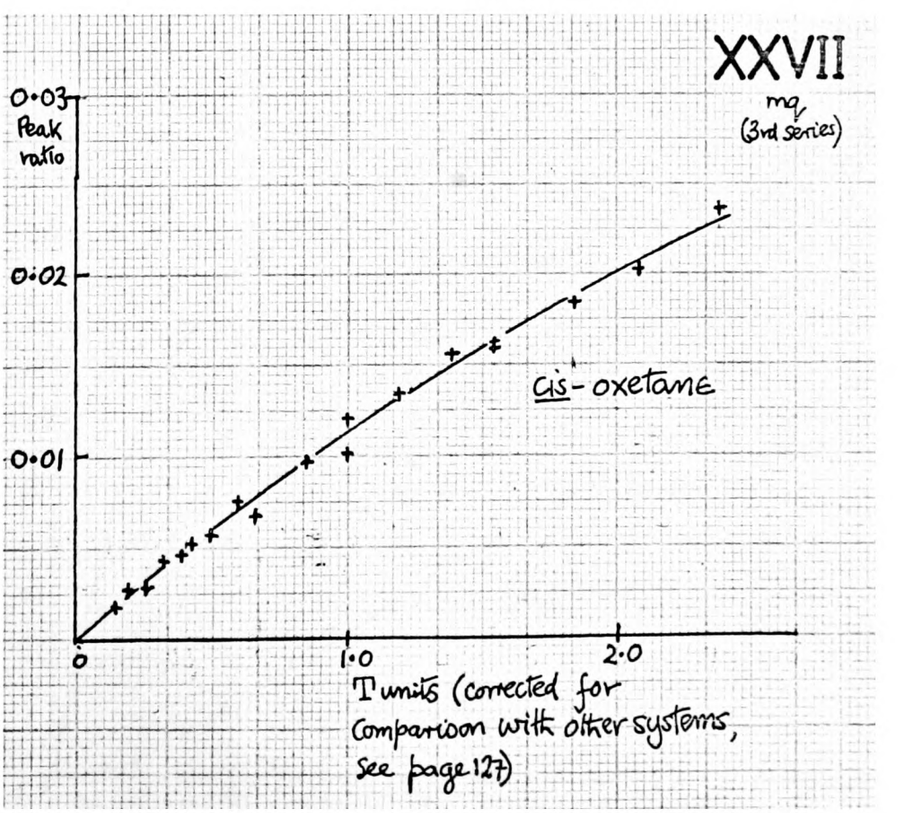

XXII
fb
(3rd series)
Peak ratio
0·2
trans-oxetane
0·1
trans-oxetane
cis-oxetane
0·002
Peak ratio
0·001
cis-oxetane
0
1
2
3
4
5
6
7
T units

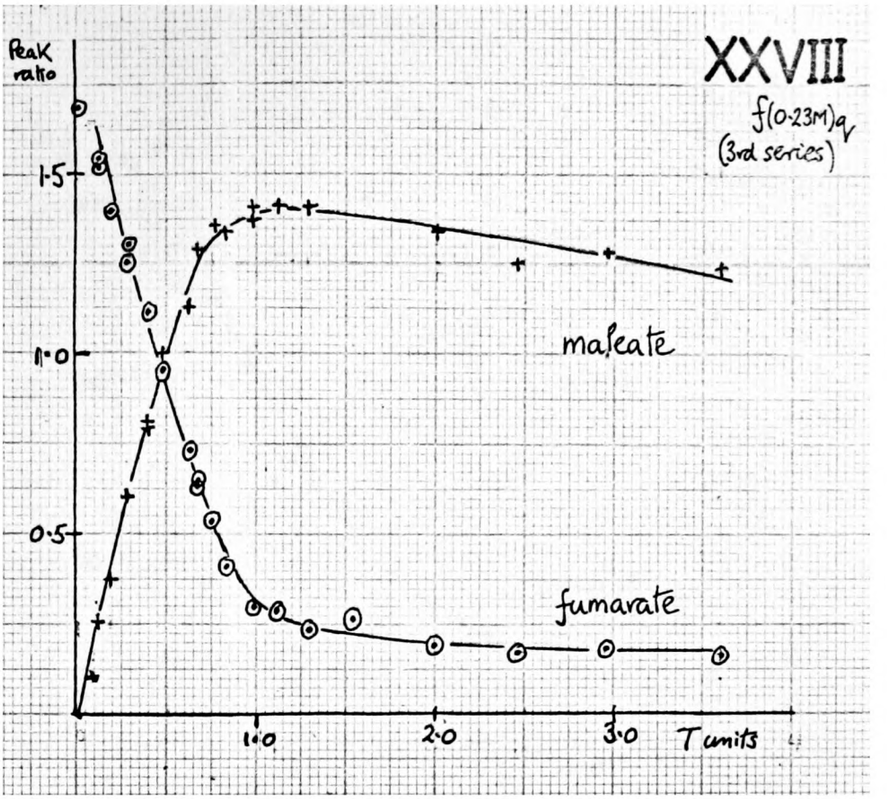

XXIII
mb
(3rd series)
0·14
Peak ratio
0·12
0·10
0·08
0·06
0·04
0·02
fumarate
0
0·4
0·8
1·2
T units

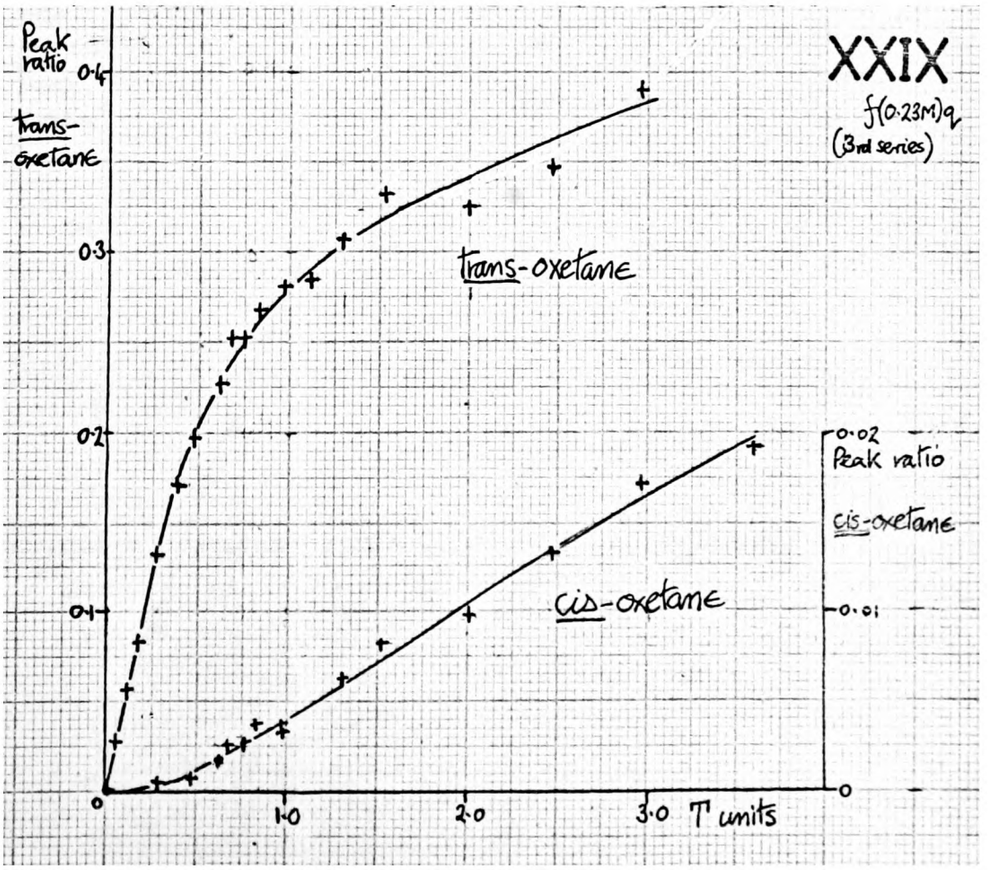

XXIV
mb
(3rd series)
Peak ratio
0·008
0·006
0·004
0·002
←concentrations→ not measureable
trans-oxetane.
Gradient of this line ≡ 0·0003 gm.mol. (trans-oxetane)/li/Tunit.
Gradient of this line ≡ 0·0002 gm.mol (cis-oxetane)/li/Tunit
see pg. 76
cis-oxetane.
0
0·2
0·4
0·6
0·8
1·0
1·2
Tunits
1·6

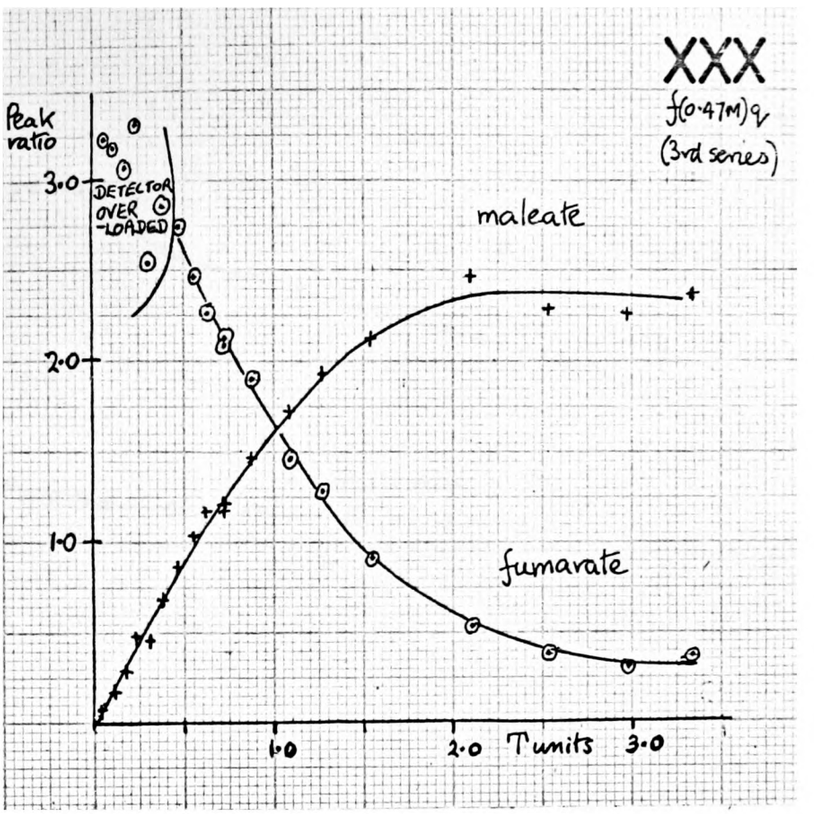

XXV
mq
(3rd series)
Peak ratio
0·3
0·2
0·1
fumarate
0
1·0
2·0
Tunits (corrected for comparison with other systems, See page 127)

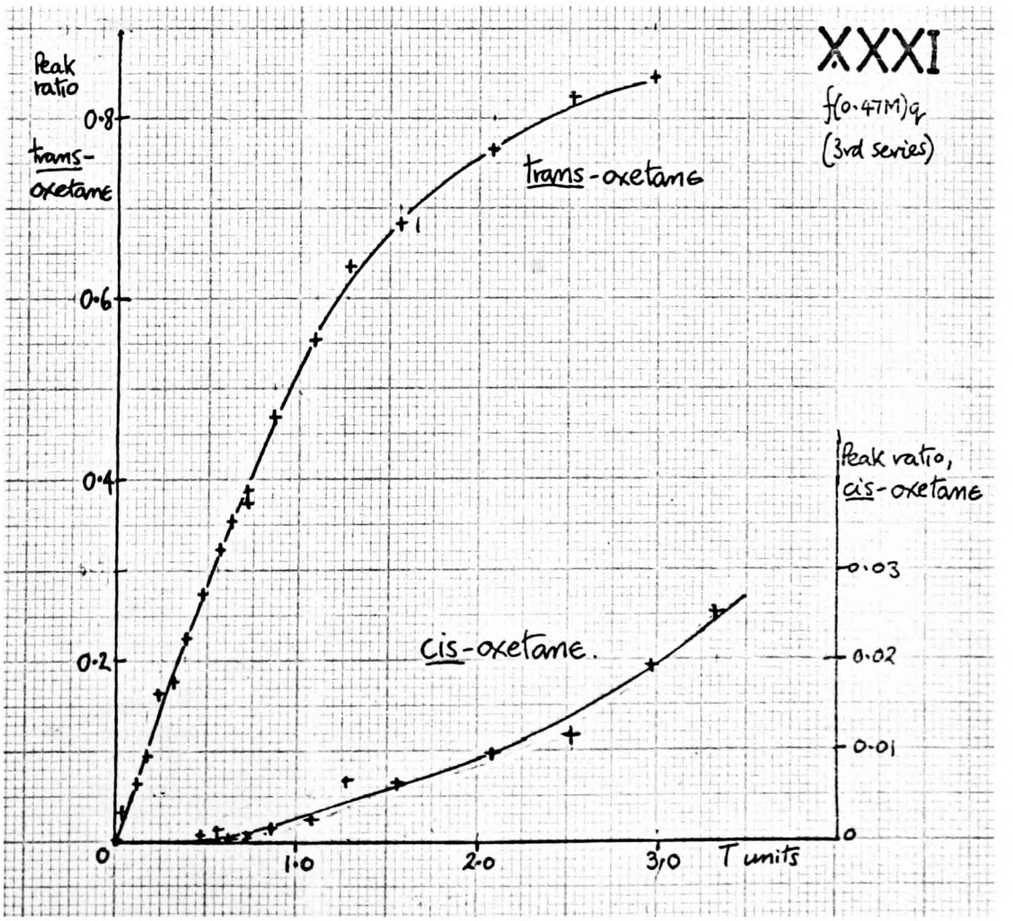

XXVI
mq
(3rd series)
0·3
Peak ratio
0·2
0·1
trans-oxetane
1·0
2·0
T units (corrected for comparison with other systems, see page 127)

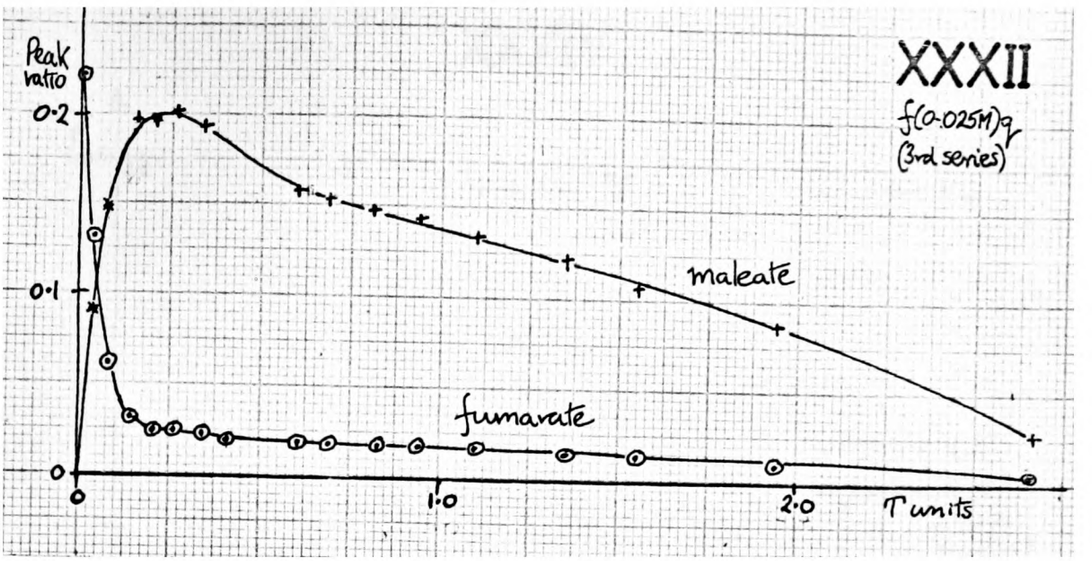

XXVII
mq
(3rd series)
0·03
Peak ratio
0·02
0·01
cis-oxetane
0
1·0
2·0
T units (corrected for comparison with other systems, see page 127)


XXVIII
f(0·23M)q
(3rd series)
Peak ratio
1·5
1·0
0·5
maleate
fumarate
1·0
2·0
3·0
T units


XXIX
f(0·23M)q
(3rd series)
Peak ratio
trans-oxetane
0·4
0·3
0·2
0·1
0
trans-oxetane
cis-oxetane
0·02
Peak ratio
cis-oxetane
0·01
0
1·0
2·0
3·0
T units

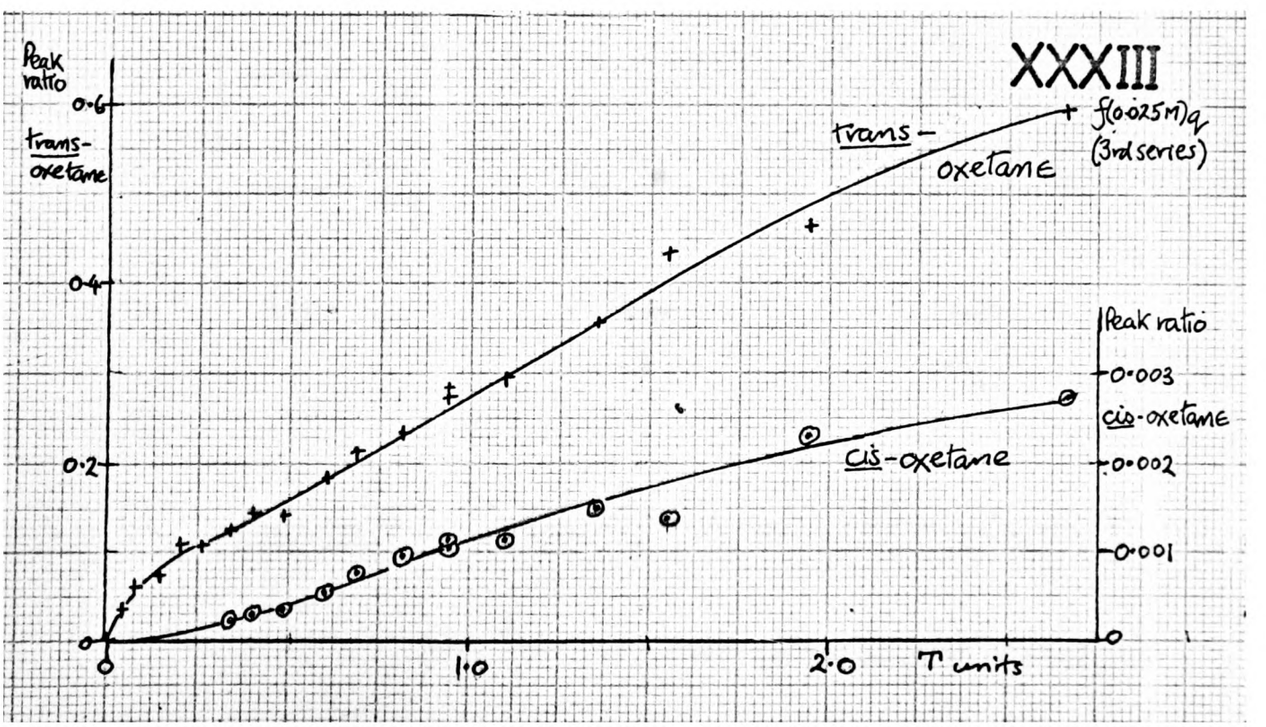

XXX
f(0·47M)q
(3rd series)
Peak ratio
3·0
2·0
1·0
DETECTOR OVER -LOADED
maleate
fumarate
1·0
2·0
T units
3·0


XXXI
f(0·47M)q
(3rd series)
Peak ratio
trans-oxetane
0·8
0·6
0·4
0·2
0
trans-oxetane
cis-oxetane.
Peak ratio, cis-oxetane
0·03
0·02
0·01
0
1·0
2·0
3·0
T units



XXXII

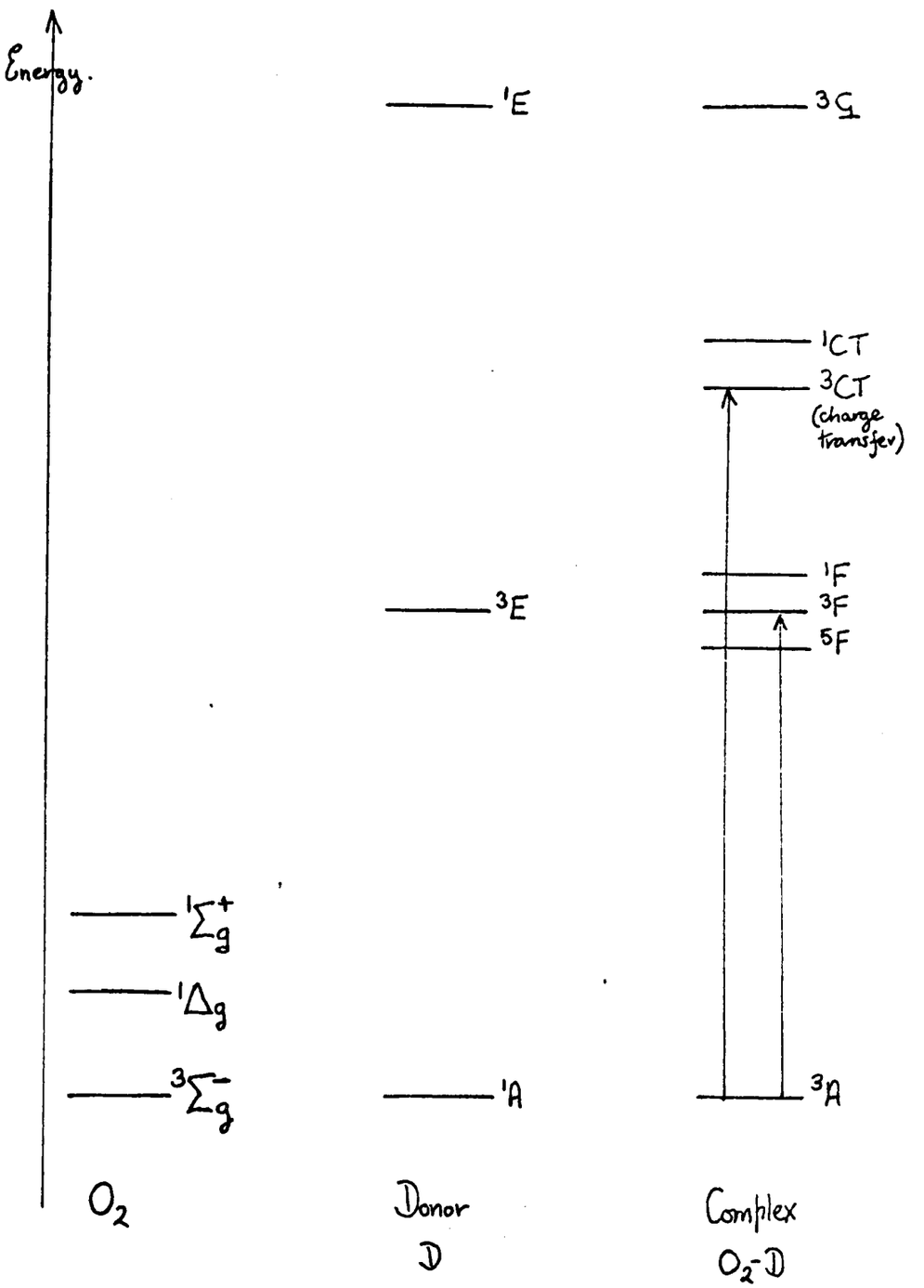
f(0·025M)q
(3rd series)



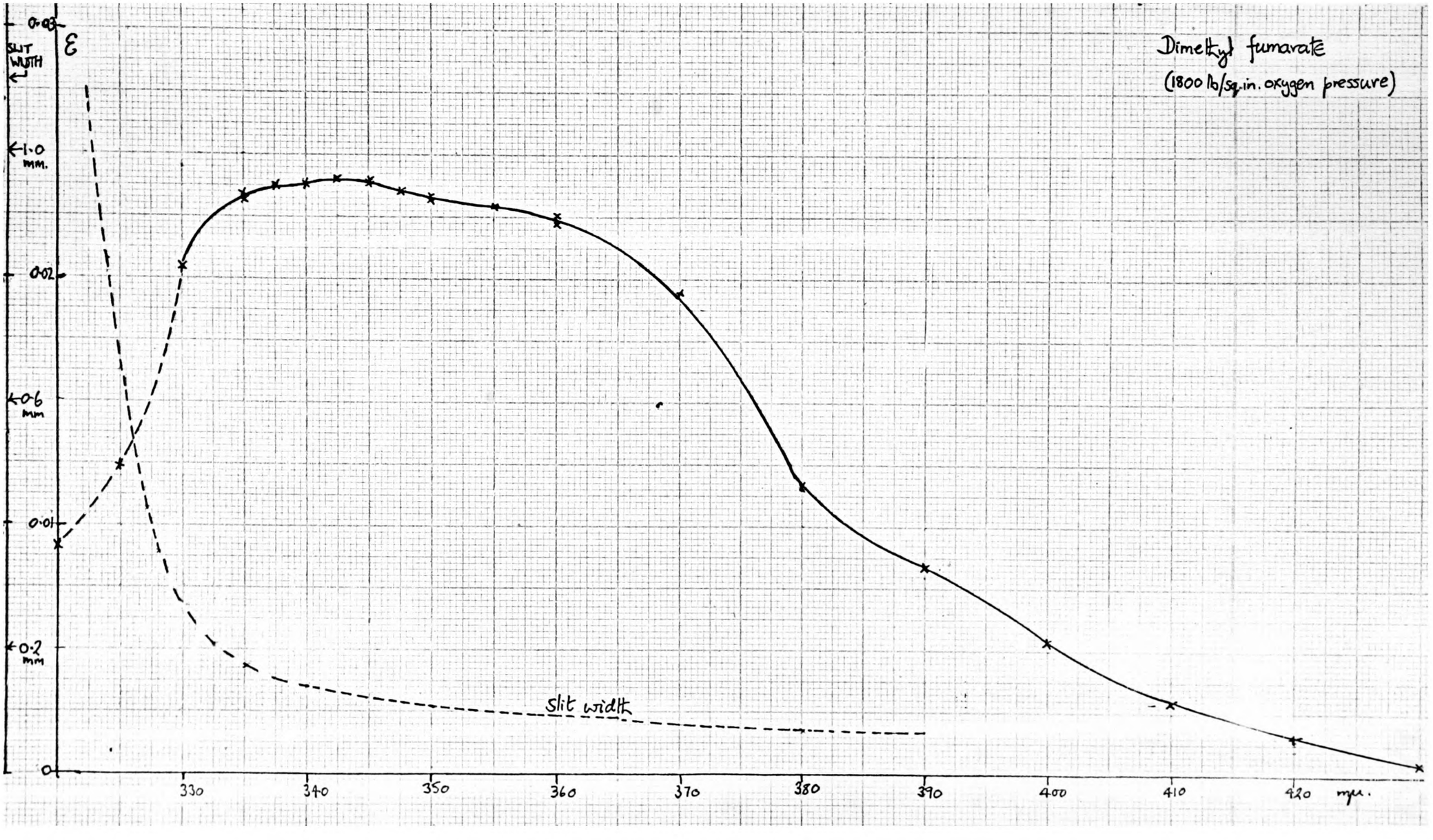
XXXIII

f(0·025M)q
(3rd series)

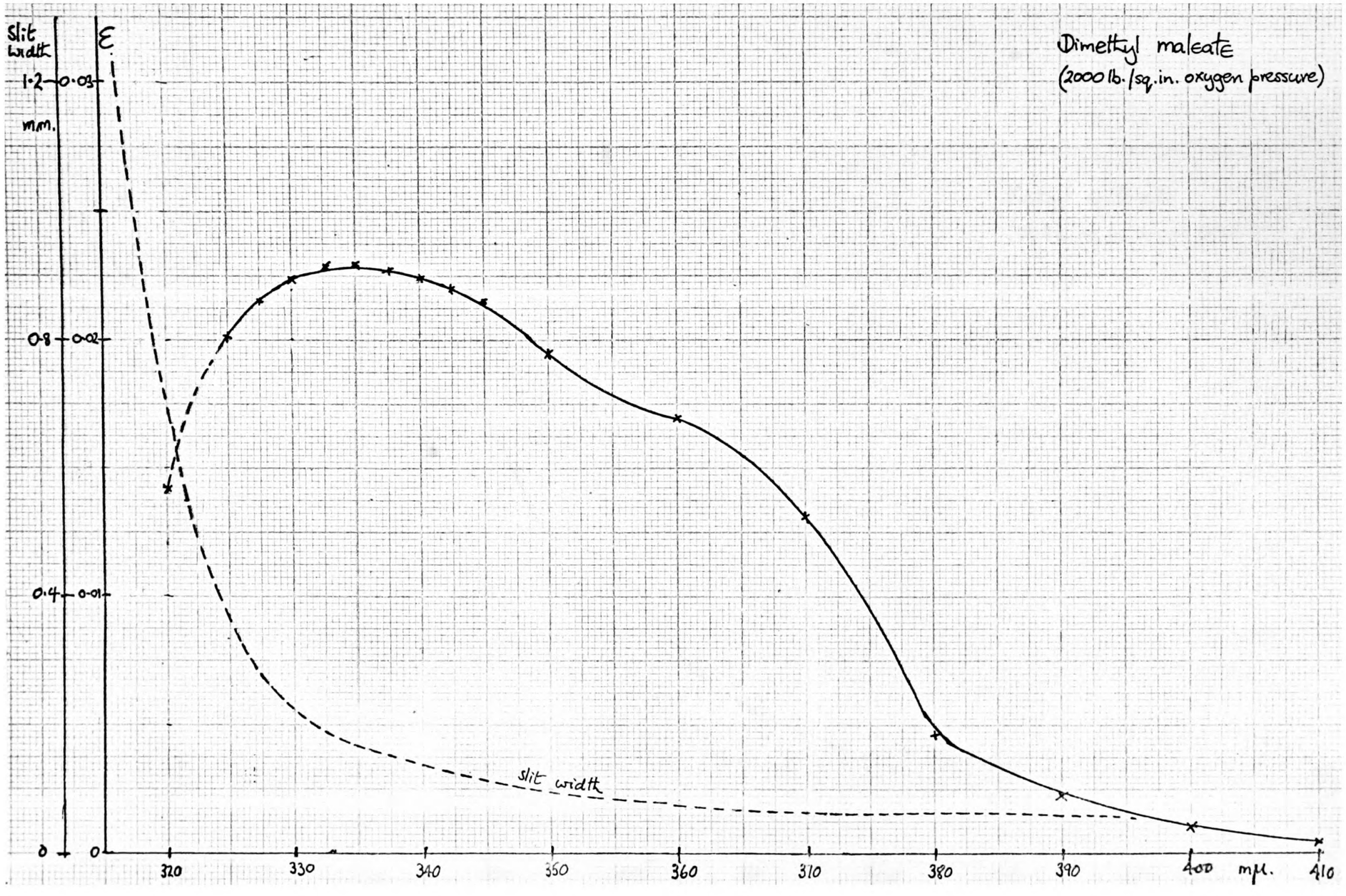
XXXIV

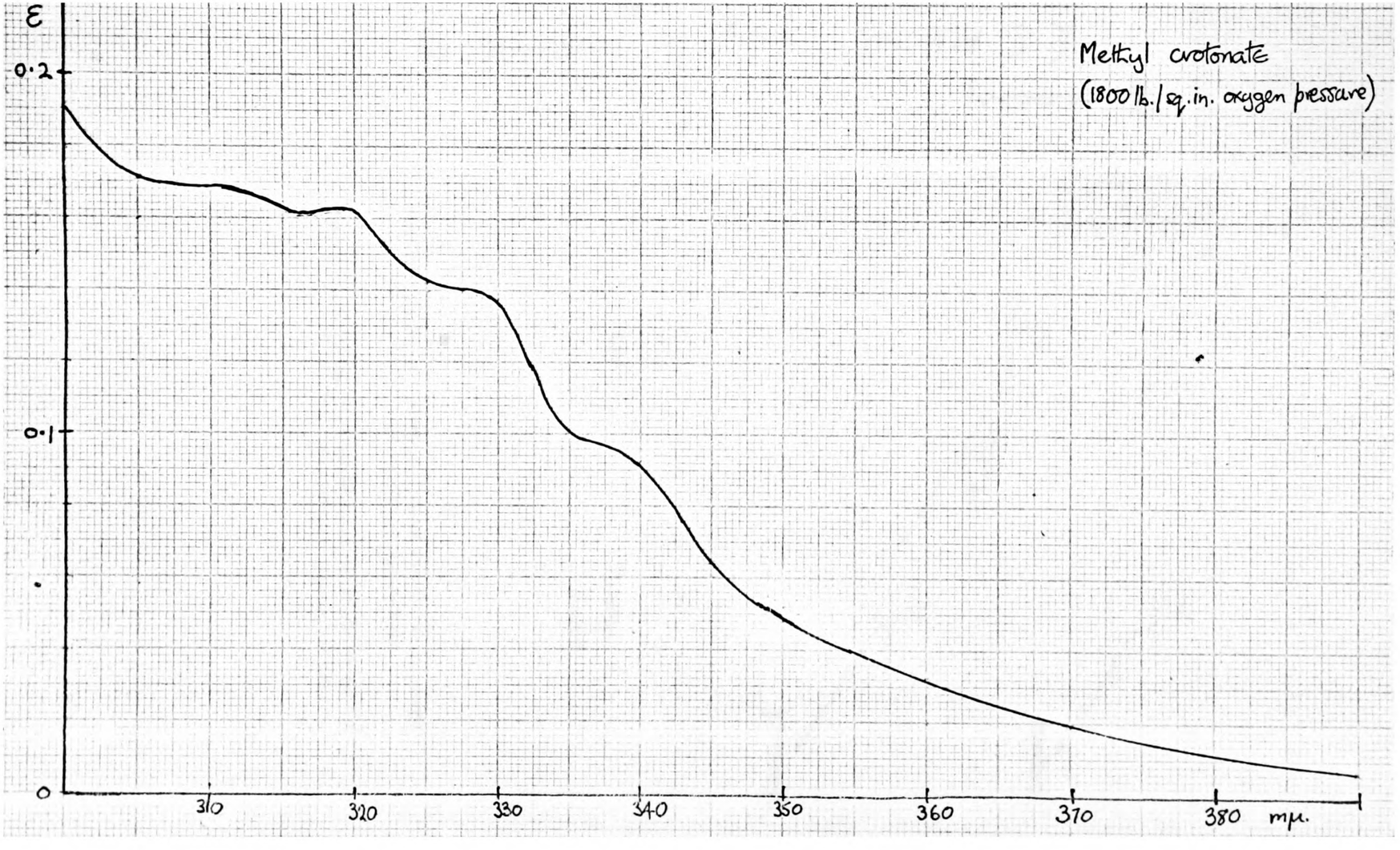


from Tsubomura & Mulliken, J. Amer. Chem. Soc., 1960, 82, 5966.

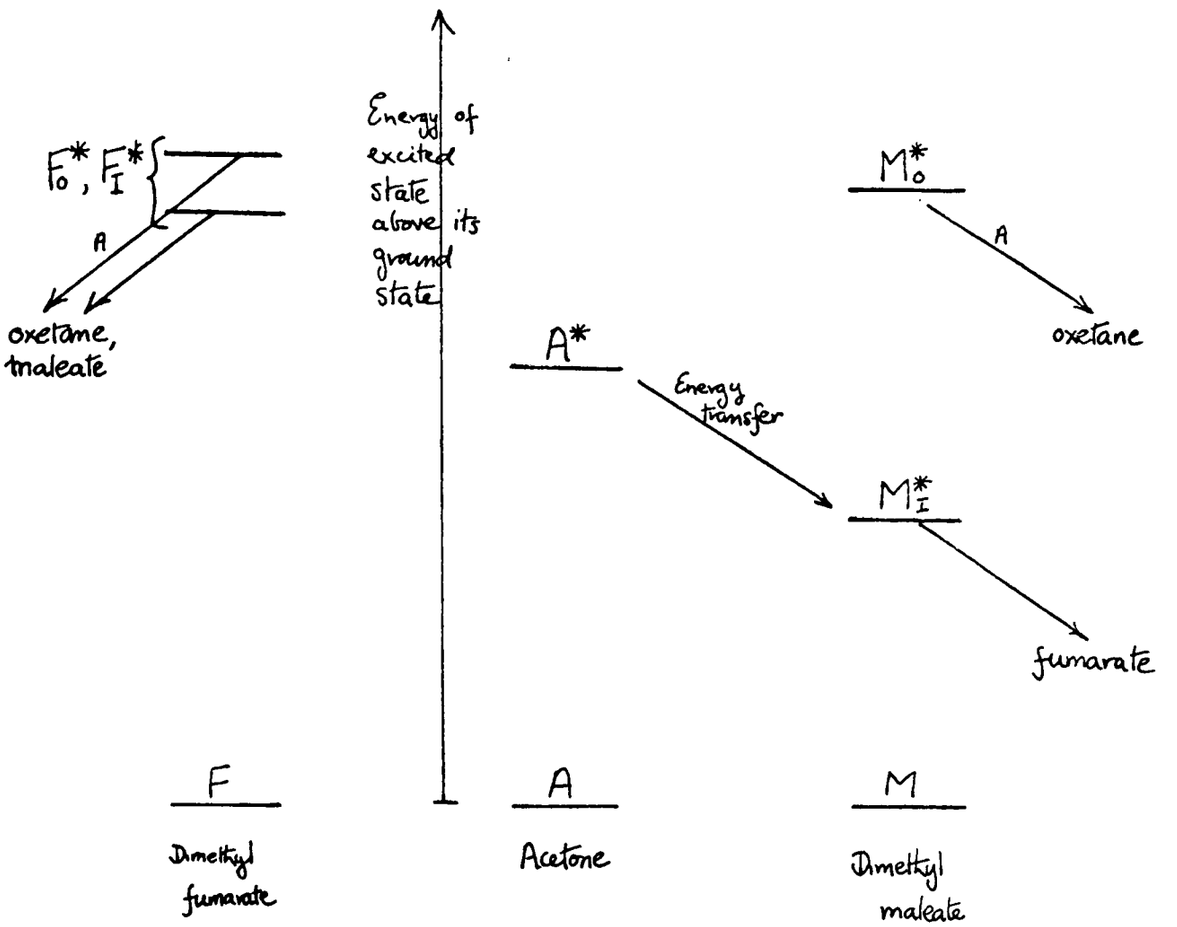

Dimethyl fumarate
(1800 lb/sq.in. oxygen pressure)
ε
SLIT WIDTH
0·03
1·0 mm.
0·02
0·6 mm
0·01
0·2 mm
0
slit width
330
340
350
360
370
380
390
400
410
420
mμ.

XXXV


Slit width
mm.
ε
1·2
0·03
0·8
0·02
0·4
0·01
0
0
Dimethyl maleate
(2000 lb./sq.in. oxygen pressure)
slit width
320
330
340
350
360
370
380
390
400
mμ.
410

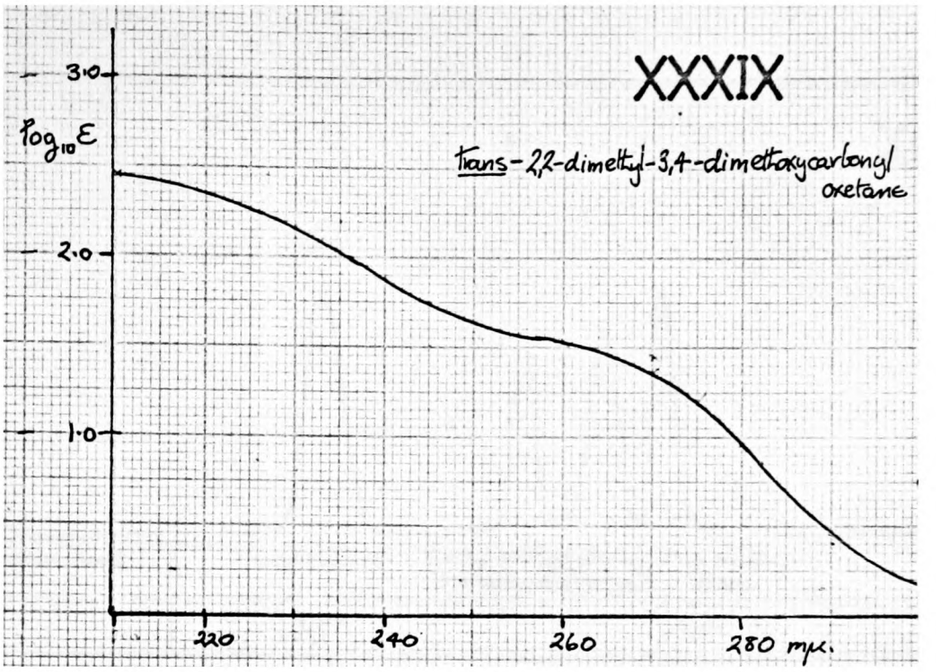

ε
0·2
0·1
0
Methyl crotonate
(1800 lb./sq. in. oxygen pressure)
310
320
330
340
350
360
370
380 mμ.

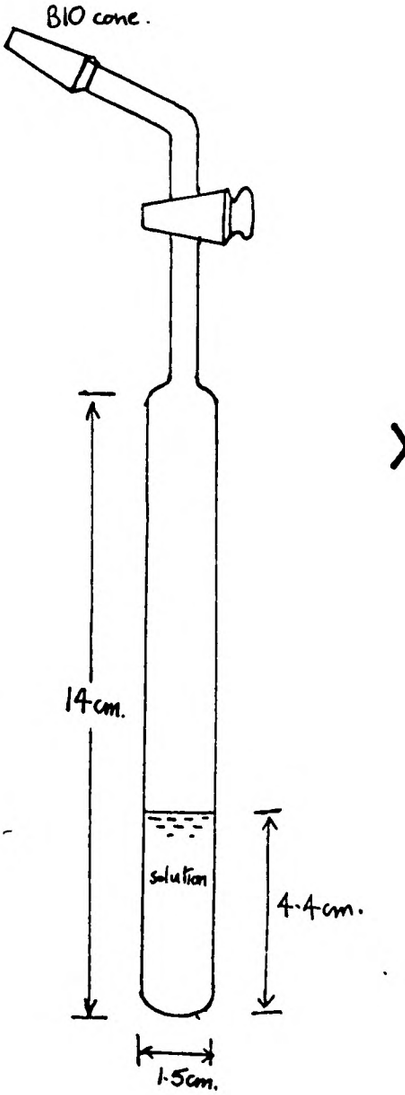
XXXVIII



F_o^*, M_o^* are excited states of fumarate and maleate involved in oxetane formation.

F_I^*, M_I^* are excited states of fumarate and maleate involved in cis↔trans isomerisation.

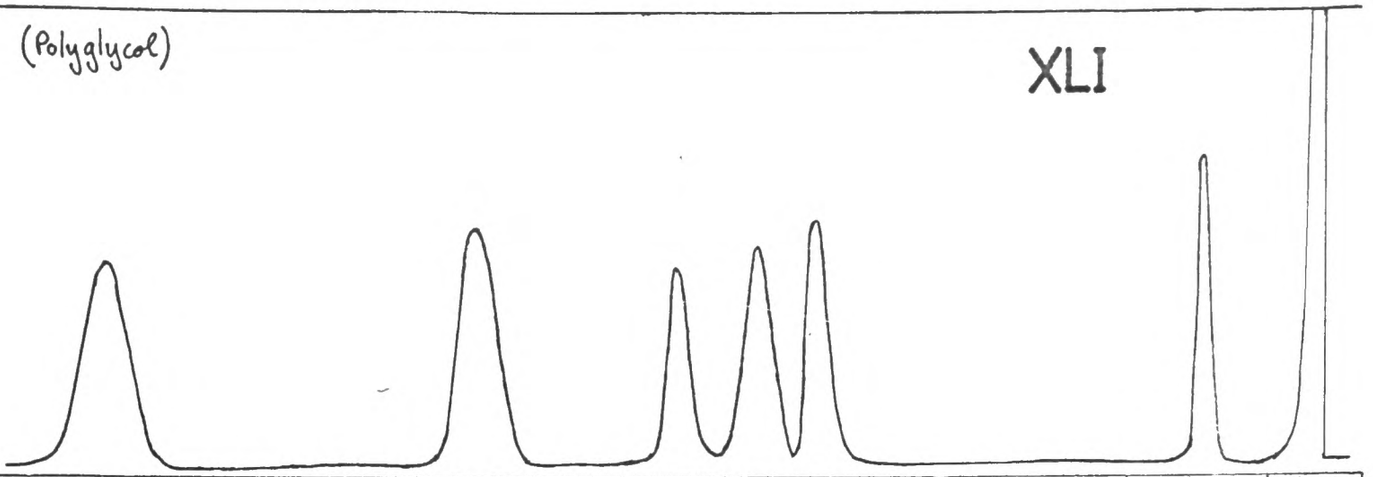

XXXIX
Trans-2,2-dimethyl-3,4-dimethoxycarbonyl oxetane
3·0
log10 E
2·0
1·0
220
240
260
280 mμ.


B10 cone.
14cm.
solution
4·4cm.
1·5cm.

XL

(Polyglycol)

XLI



COMPOUND	dimethyl propionylsuccinate	naphthalene	methyl 3-methyl-4-oxohexanoate	dimethyl maleate	ethylcyclohexyl ketone		methyl crotonate	solvents
TEMP.	150°	125°	100°				60°	
RETENTION TIME (min)	68	47	36	31	28·5		1·7	

(see page 155)

ABSTRACT

A brief review of those aspects of current photochemical research pertinent to the present study is given. The work itself is in three sections.

Section I is concerned with the photochemistry of the system dimethyl maleate/dimethyl fumarate/acetone. Irradiation of this system produced the cis- and trans-2,2-dimethyl-3,4-dimethoxycarbonyloxetanes (I and II), as well as causing cis↔trans isomerisation of dimethyl maleate/dimethyl fumarate. No tetramethoxycarbonylcyclobutane (III) was formed. A mechanistic study of the formation of oxetane was complicated by the simultaneous occurrence of the cis↔trans isomerisation of maleate/fumarate. This was overcome by examining the photochemistry of the system at irradiation time zero, before any reaction had occurred. This procedure also eliminated other difficulties inherent in any quantitative photochemical study such as the effects of polymer film formation and of the photochemical instability of the reaction products. A method was developed to evaluate the rates of formation of the irradiation products with precision. Particular emphasis was placed on assessing the errors in these quantities. The approach was to follow the light-induced reactions by means of gas chromatography and to estimate the rates at zero irradiation time by extrapolation using a polynomial least squares fit computer programme. It was found important to allow for fluctuations in lamp-output with time and a photomonitor was constructed for this purpose.

Dilute acetone solutions of pure dimethyl maleate and of pure dimethyl

fumarate were irradiated. Both quartz and borosilicate glass reactors were employed thus allowing variation in proportion of incident light absorbed by each of the two components. Irradiations of dimethyl fumarate in acetone using quartz apparatus were conducted at three different initial concentrations.

The significance of the data obtained was verified by carrying out a material balance check and by investigating the importance of any small amounts of dissolved oxygen remaining in solution after deoxygenation prior to irradiation.

From a correlation of the observed rates of formation at irradiation time zero with the light absorption properties of the solution irradiated, substantial evidence emerged that oxetanes were formed by the action of excited maleate and of excited fumarate on ground state acetone.

This is the first case reported where evidence exists that oxetanes are formed by a route other than the action of the (n,π^*) excited state of the ketone on a carbon-carbon double bond. Other workers have restricted their attention to systems involving unsaturated hydrocarbons.[1]

The data presented also indicate that another excited state of maleate (and probably also of fumarate) exists which was active in the cis↔trans isomerisation reaction but which did not form oxetane with acetone. An attempt is made to identify the oxetane-forming state with the (n,π^*) state and the state active only in cis↔trans isomerisation with the (π,π^*) state of the unsaturated ester. The further implications of the concentration dependence of these reactions is also considered.

Oxygen perturbation methods were used to obtain information concerning

the relative triplet energy levels of maleate, of fumarate and of acetone, but although singlet→triplet absorption was observed, no information concerning the chemically significant 0,0 bands was obtained. Electron impact spectroscopic studies are currently being pursued to this end.

Section II is concerned with the photochemistry of acetoxime. Irradiation of acetoxime in cyclohexene for 9 hr. yielded the adducts N-acetyl-N-methylcyclohexylamine (IV) and N-acetyl-N-methylcyclohex-2-enylamine (V) in 2% yield based on acetoxime consumed, together with bicyclohex-2-enyl (VI) and much polymer. This is the first occasion that oxime/olefin photoadducts have been recorded. Two possible mechanisms were investigated. The first involved the photoisomerisation of acetoxime to N-methylacetamide followed by the photo-addition of N-methylacetamide to cyclohexene to give the observed products. The second was the photochemical formation of a nitrone (VII) which photoisomerised to the oxazirane (VIII) and subsequently rearranged thermally to yield the observed amides. It was shown that neither mechanism was likely.

No stable products were isolated from propionaldoxime/cyclohexene irradiation mixtures.

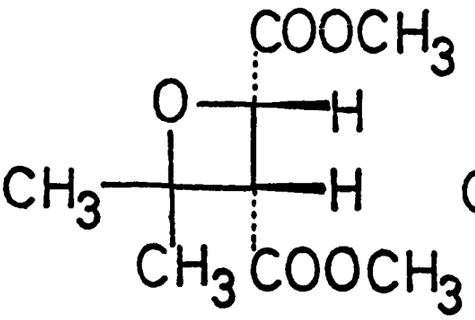
Section III is concerned with irradiations involving aldehydes. Dimethyl maleate, methyl crotonate, cyclohexene, styrene, ethyl vinyl ketone, crotonaldehyde and benzene were irradiated with propionaldehyde. One irradiation with acetaldehyde was also conducted. Adducts were observed only from dimethyl maleate, methyl crotonate and cyclohexene (IX, X and XI). The other irradiations yielded products derived from propionaldehyde alone. Competition experiments showed that the active entity

involved in these reactions was probably a nucleophilic species derived from the aldehyde. A very close correlation was found to exist between the light induced and peroxide induced reaction and this was taken as good evidence that the same acyl radical species was responsible for both reactions.

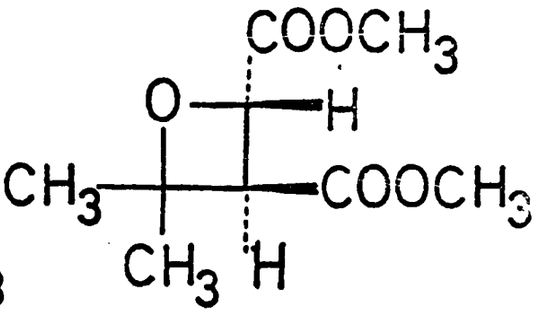
REFERENCE

1a. D.R. Arnold, R.L. Hinman and A.H. Glick, Tetrahedron Letters, 1964, 22, 1425.

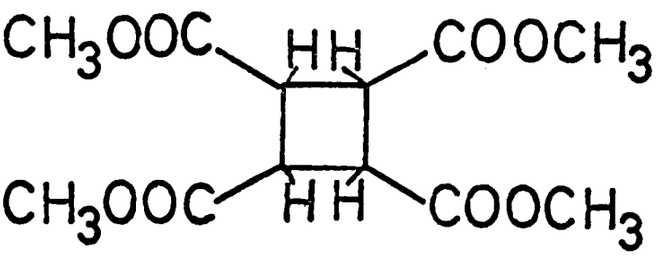
b. N.C. Yang, M. Nussim, M.J. Jorgenson and S. Murov, Tetrahedron Letters, 1964, 48, 3657.



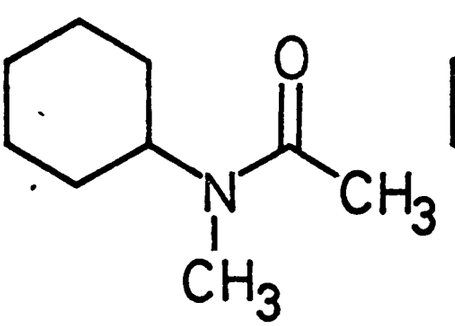
I



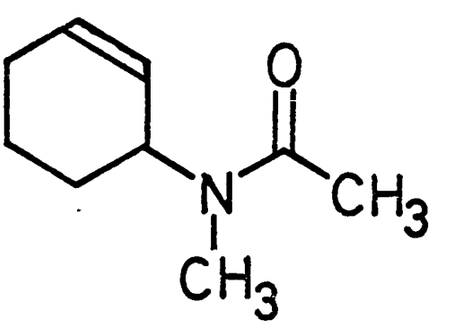
II



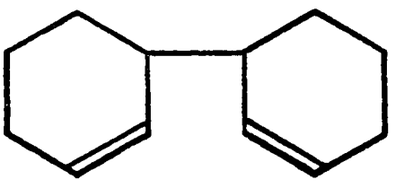
III



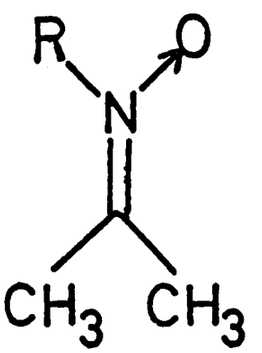
IV

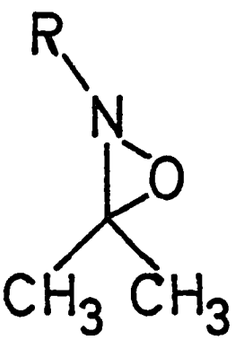


V



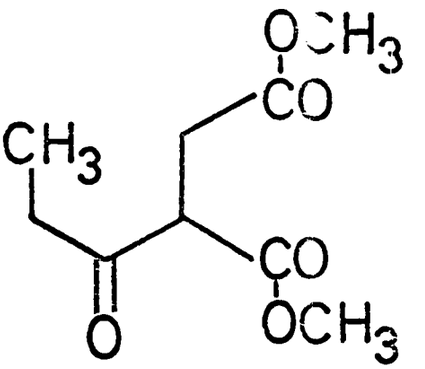
VI



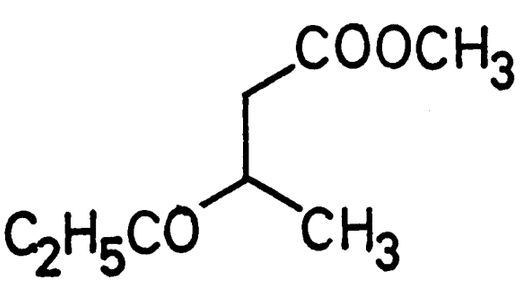


R — cyclohexyl or cyclohexenyl

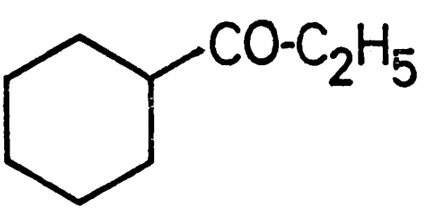
VII VIII



IX



X



XI