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Part One: Mechanistic Studies Of Cyclic Enone Photoannelation Part Two: Studies On The Excited State Properties Of Thiocarbonyl Compounds

Rafik Omar Loutfy

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PART ONE

MECHANISTIC STUDIES OF CYCLIC ENONE PHOTOANNELATION

PART TWO

STUDIES ON THE EXCITED STATE PROPERTIES OF THIOCARBONYL COMPOUNDS

by

Rafik Omar Loutfy

Department of Chemistry

Submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy

Faculty of Graduate Studies
The University of Western Ontario
London, Canada
1972

ABSTRACT

PART ONE

The thesis describes the studies undertaken to determine the nature and the energies of the reactive species in the photoannelation reaction of cyclic enones. The results indicate that the reaction proceeds via a triplet state. Dual phosphorescence from two constrained ketones was observed and evidence is presented that this occurs from a Boltzmann population of two close-lying triplet states (n,π^* and π,π^* triplets). The involvement of both excited states of cyclic enones in the photoannelation reactions is discussed.

The temperature dependence of the quantum yield of addition of cyclic enones to a variety of substrates was established. The results indicate the existence of a reversible intermediate(s) in the photoannelation reactions of cyclic enones.

Using a combination of dilution and quenching experiments it is possible to derive rate constants for reaction and decay. The data are best interpreted by involving the intermediacy of the exciplexes which are quenchable by dienes.

The structural assignments for several cyclopentenone halo-olefins adducts were made. Examination of the product distribution indicates that attack at both α and β positions to the carbonyl of cyclopentenone are occurring.

PART TWO

The emission from the lowest excited triplet state of some thiobenzophenones, xanthione and thiocholestenone was shown to be $^3(n,\pi^*)$ in character. A low intensity absorption at long wave-length of thiobenzophenone, p,p'-bis(dimethylamino)thiobenzophenone, Xanthione, and thiocholestenone was observed and assigned to singlet-triplet transition.

The photochemical reactions of Michler's thione were compared with those of the corresponding ketone.

ACKNOWLEDGEMENT

The author wishes to express his sincere gratitude and appreciation to Dr. P. de Mayo not only for the suggestion of the project but also for the intellectual guidance which was given throughout the course of this work. Thanks are due to many other members of the Department and especially to those of the Photochemistry Unit and to Dr. M.C. Woods for establishing the structure of the cycloadducts.

The author thanks most sincerely his colleagues for intellectually stimulating discussions, particularly: A.A. Nicholson, M.C. Usselman, Dr. M.F. Tchir and Dr. D.R. Kemp.

The author is deeply grateful to his wife, Rafia, for immeasurable patience, encouragement, and help.

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PART ONE

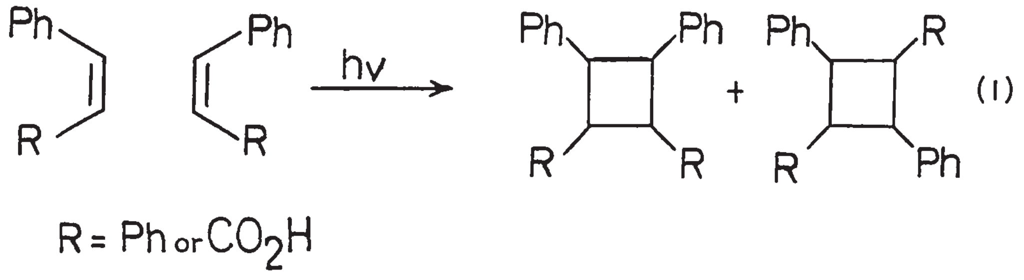
MECHANISTIC STUDIES OF CYCLIC ENONES PHOTOANNELATION

PART I. MECHANISTIC STUDIES OF CYCLIC ENONE PHOTOANNELATION.

CHAPTER I

INTRODUCTION

The subject of this thesis is the photocycloaddition reactions of α,β-unsaturated ketones, specifically 2-cyclopentenone and 2-cyclohexenone. The photoaddition reaction, which involves the addition of a photochemically excited molecule to a ground state molecule forming a cyclobutane derivative, is one of the oldest known processes in organic photochemistry; authentic cases have been reported as early as 1902 by G. Ciamician and P. Silber (1) in an investigation of the photochemistry of stilbene and styrene derivatives. The specific reaction is illustrated in reaction I. The general reaction is much too broad in scope to be discussed here, a leading reference is given by Warrener and Bremmer (2).



α,β-Unsaturated ketones are widely used in this reaction, or, more specifically cyclic α,β-unsaturated ketones, because *cis-trans* isomerization in the latter is apparently not an effective path for deactivation of the excited state, whereas the excited states of acyclic α,β-unsaturated ketones are deactivated by cis-trans isomerization with a quantum yield of near unity (3).

Cyclic α,β-unsaturated ketones exhibit two characteristic electronic transitions in the ultraviolet spectrum: a weak band ($\varepsilon \cong 100$) in the region of 325 nm which is assigned to the $n \rightarrow \pi^*$ transition (4), and an intense band ($\varepsilon \cong 15{,}000$) in the region 225 nm which is assigned to the $\pi \rightarrow \pi^*$ transition. Excitation in the n,π^* band is most frequently used in synthetic photochemistry of cyclic α,β-unsaturated ketones, particularly when medium or high pressure mercury arc lamps are employed as light sources. These have poor energy output below 290 nm (5). This is not to say that the reactions cannot be induced by light of lower wave-length (higher energy), but only that excitation of the $n \rightarrow \pi^*$ transition of enones is of sufficient energy (~85 kcal/mole) to bring about reaction. Following $n \rightarrow \pi^*$ excitation, several reaction pathways are available to the excited ketone. The most important reactions of cyclic enones which have been observed are:

I Cycloaddition reactions either at the carbonyl group or the double bond to yield 1:1 adducts.

II Addition of solvent molecules to the excited ketone molecule.

III Skeletal rearrangement to an isomer.

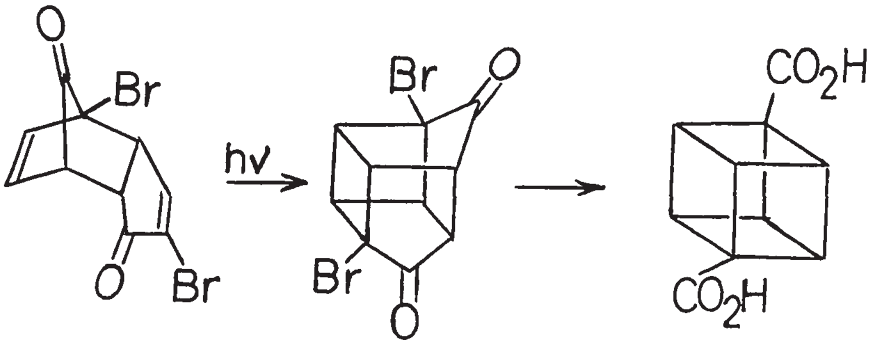
IV Cleavage of the molecule with elimination of a neutral fragment.

The photocycloaddition reactions of cyclic enones to cyclic and acyclic olefins, alkynes, alkenes and to themselves has proved to be of great synthetic value both for the synthesis of cyclobutane rings and for cyclobutane rings capable of further manipulation and ring modification (6).

A desire to extend the application of this useful reaction initiated the work presented in this thesis. The solvents generally used were ether and cyclohexane which are inert with respect to addition to photochemically excited α,β-unsaturated ketones. Excessive dimerization was precluded in this study by irradiation in dilute solution and the presence of excess substrate. The photochemical skeletal rearrangement of cyclic enones is known to proceed at a much slower rate ($\sim 10^5 sec^{-1}$) and with a much slower quantum efficiency ($\phi \sim 0.006$) as compared to the photoaddition reaction. Consequently, it was anticipated that skeletal rearrangement would not interfere with cycloaddition and the experimental conditions were selected to ensure that photochemical cycloaddition would be the major mode of deactivation of the excited state.

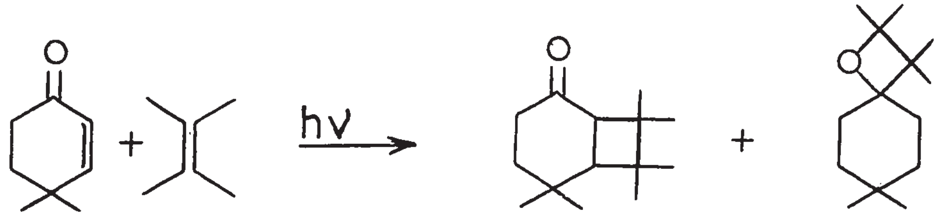
Cycloaddition reactions can be subdivided into the following categories:

a) Intramolecular cycloaddition. This occurs when double bonds are in the same molecule. An elegant example of the intramolecular cycloaddition of a cyclic enone is found (reaction II) in the key reaction in Eaton's synthesis of cubane (7).



(II)

b) Intermolecular cycloaddition. The addition of tetramethylethylene to 4,4'-dimethyl-2-cyclohexenone (reaction III) (8) and of cyclohexenone to isobutylene (reaction IV) (9).



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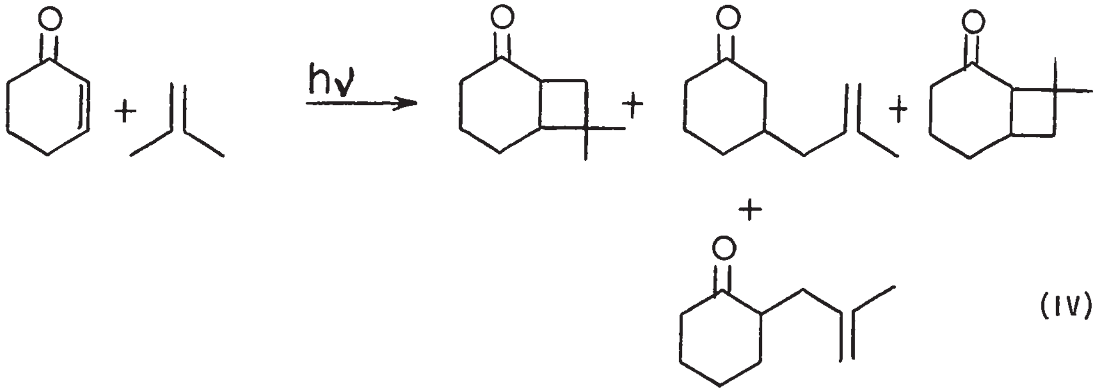
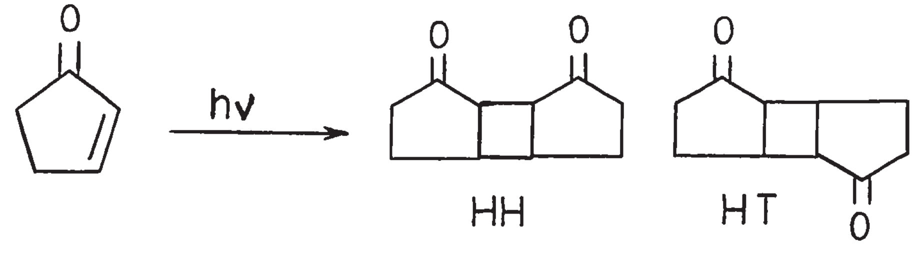


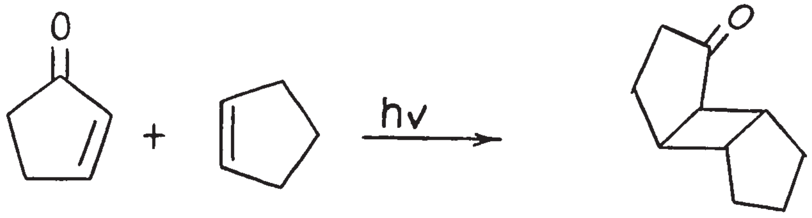
(IV)

Dimerization is a special case of the general reaction in which the unsaturated ketone also serves as the second olefin moiety. The reaction



(V)

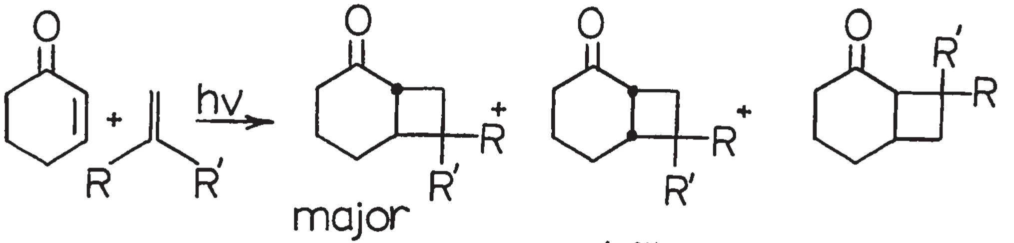
of 2-cyclopenten-1-one (reaction V) (4) is an example of this.



(VI)

Mechanism.

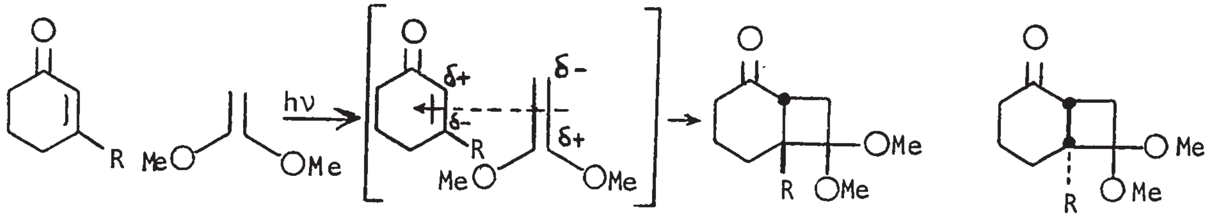
Although the photocycloaddition reaction is used in synthetic work, very little evidence was available concerning the mechanism at the time the work presented in this thesis was initiated. The data available in the literature up to 1967 were reviewed by Eaton (10) and Chapman (11). Most of the mechanistic speculation up to this time rested on the experiments of Eaton (10), Corey and co-workers (7) and later by Mayo and co-workers (12) in this laboratory. Eaton had shown that cyclopentenone added to cyclopentene on irradiation to give only one product (reaction VI). He suggested that the reaction proceeded via the triplet state since the ketone was shown to behave as a sensitizer much like acetophenone (10).



(VII)

R=R'=Me ; R=R'=OMe; R=H, R'=OMe

Corey (9) has studied the photocycloaddition of 2-cyclohexenone to various olefins. Irradiation of 2-cyclohexenone in the presence of isobutylene; 1,1-dimethoxy ethylene or methoxy ethylene gave predominantly the 7-substituted isomer rather than the 8-substituted isomer, (reaction VII) and the trans-6-4 ring juncture predominated over the cis-juncture. In contrast, with acrylonitrile the 8-substituted isomer was obtained as the major product and no trans-isomer was found. This rather high degree of orientational preference for the 7-substituted product with electron-rich olefins, and 8-substituted products with electron-deficient substrates led to the proposal of an "oriented π-complex" as the initial intermediate. The same orientation phenomenon was observed recently in the photochemical cycloaddition of a variety of 3-substituted 2-cyclohexenones with various olefins (reaction VIII represents a specific case) (13).



	yield %	
R = H	49	21
CH_3	26	38
ph	-	71
OAC	-	44
CN	-	48
OMe	-	37

(VIII)

Curiously, 2-methyl-2-cyclohexenone does not cycloadd to isobutylene whereas 3-methyl-2-cyclohexenone adds to give the cis-7-substituted adduct (14%). This indicates that steric factors can outweigh mild electronic demands in a substrate.

The formation of a trans 6-4 ring juncture, unsaturated products, and identical mixtures of products from cis- or trans-2-butene*, lead

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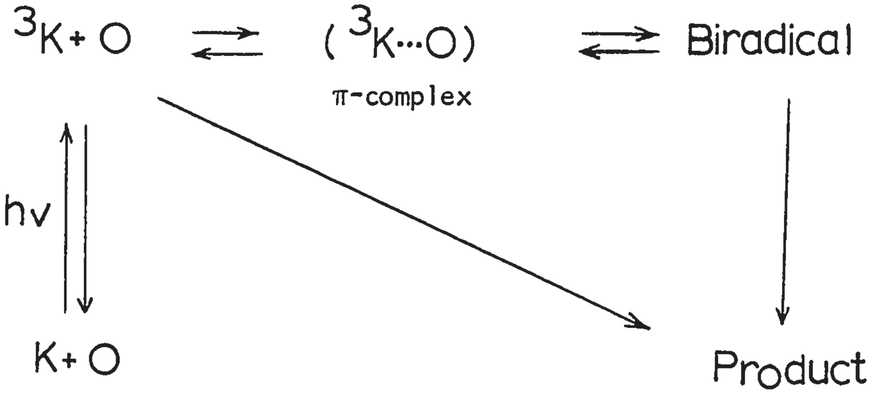
* This author has reexamined this reaction and found (contrary to Corey (9)) that 4-adducts are formed and from these an isomer which has trans 6-4 ring juncture was isolated in 10% yield. An attempt to determine the stereochemistry was made (see appendix).

Corey to the inclusion of another intermediate, a 1,4 biradical. Therefore it was believed that orientation is determined by the electronic factors when the π-complex (exciplex) is formed, and stereochemistry is determined in the biradical stage.

The relatively strained <u>trans</u>-ring junction isomers are often the major products of the cycloaddition (e.g. see reaction III), and it is hard to believe that any 1,4 biradical would close exclusively to the strained <u>trans</u>-adduct. With almost no evidence Corey (9) suggested that the <u>trans</u>-adduct could arise from a metastable <u>trans-enone</u>.

Mayo and co-workers (12a) had studied the photochemical cycloaddition of cyclopentenone in more detail. They found that the addition of cyclopentenone to cyclohexene was quenched by triplet quencher (acenaphthene E_T 59 kcal/mole or piperylene E_T 56 kcal/mole) and sensitized by sensitizers having triplet energies above 73 kcal/mole. These facts led them to the conclusion that the reactive intermediate involved in cycloaddition reactions was a triplet. Similar conclusions were reached about the same time for the dimerization of cyclopentenone by Eaton and Hurt (14) and by Ruhlen and Leermaker (15) based on piperylene quenching experiments and partly on a sensitization experiment using xanthone. Triplet-counting experiments (12b), which involved measuring the extent of sensitized isomerization of <u>trans</u> to <u>cis</u>-piperylene, indicate that the yield of triplet ketone is unity. They also reported that although benzophenone (E_T 69 kcal/mole) did not sensitize the cycloaddition of cyclopentenone (E_T ~74 kcal/mole, from sensitization) to cyclohexene, this enone quenched the photoreduction of benzophenone in isopropanol, a fact which led Mayo to the inclusion of a second lower triplet which is inactive toward cycloaddition. The mechanism can be summarized by scheme IX where K represents the enone and O represents the olefin.



(IX)

It can be seen that further spectroscopic and mechanistic studies were needed. It was hoped that a detailed mechanistic study would aid in the understanding of this photochemical process.

RESULTS AND DISCUSSION

CHAPTER II

THE REACTIVE SPECIES IN THE PHOTOCHEMISTRY OF SOME CYCLIC ENONES.

The nature and multiplicity of the reactive species in the photocycloaddition of cyclic enones to carbon-carbon multiple bonds has been the subject of many recent investigations (10-12). The main reason for this interest is that the two lowest triplets - one mostly n,π^* and the other mostly π,π^* - lie very close together, and their relative energies are quite susceptible to changes in substituent and solvent. The results reported here indicate that the two triplet states are in thermal equilibrium and reactions and emission from both states are occurring.

2.1 The Question of the Higher Triplet State of Cyclopentenone.

It has been suggested earlier that in photocycloaddition of cyclopentenone, a higher triplet was involved (12a). The triplet sensitizers having energies close to 73 kcal/mole could induce photoannelation, while the triplet energy of cyclopentenone, measured by equilibration methods, was found to be 60 kcal/mole (16). It was also found that cyclopentenone quenched the photoreduction of benzophenone in *iso*-propanol at an apparent near diffusion controlled rate. Involvement of an upper triplet in the cycloaddition reactions of cyclopentenone has since been questioned, since it has been shown that the effective triplet energy of the enone available for transfer, as measured by the photoequilibration method using stilbene (17), is about 10-15 kcal/mole below the 0-0 energy determined spectroscopically.

With the observation of the phosphorescence of benzophenone at room temperature in a variety of solvents (18-20), a direct test of the validity of the above hypothesis was possible.

The phosphorescence of benzophenone (8×10^{-2}M) in carbon tetrachloride solution was quenched by cyclopentenone (0.0-0.6M). The exciting beam was at 380 nm (cyclopentenone does not interfere at this wavelength) and the relative intensity of the emission may be represented by the following equations:

$$\begin{array}{rcl}
B & \xrightarrow{h\nu, I} & {}^3B \\
{}^3B & \xrightarrow{k_p} & B + h\nu \\
{}^3B & \xrightarrow{k_t} & B \\
K + {}^3B & \xrightarrow{k_2} & {}^3K + B \\
{}^3K + B & \xrightarrow{k_{-2}} & K + {}^3B \\
{}^3K & \xrightarrow{k_3} & K
\end{array}$$

where B is benzophenone and K represents cyclopentenone, and assuming a steady-state condition for the concentration of ^{3}B and ^{3}K, the Stern-Volmer expression

$$\phi_0/\phi = 1 + \frac{k_2 k_3 [K]}{(k_p + k_t)(k_{-2}[B] + k_3)}$$

may be derived. The constant k_p (rate constant for phosphorescence) and k_t (rate constant for radiationless decay) for benzophenone, $1.36 \times 10^2 \text{sec}^{-1}$ and $9.1 \times 10^3 \text{sec}^{-1}$ respectively, are available from room temperature measurements (20). The first-order decay of cyclopentenone is near 10^8sec^{-1} (12), and k_{-2} (bimolecular rate constant for back transfer) is taken as the diffusion rate, $10^{10}M^{-1}sec^{-1}$. From a plot of quenching of benzophenone emission with cyclopentenone (Fig. 1) a slope of 7.3 is obtained. From this, with the above values, the rate of energy transfer, k_2, is $6.1 \times 10^5 M^{-1}sec^{-1}$. This value clearly excludes the existence of a cyclopentenone triplet near or below that of benzophenone.

Assuming that the rate of energy transfer is controlled only by the endothermicity, then from the Boltzmann population distribution, the observed decrease in rate below that controlled by diffusion requires an endothermicity of about 6 kcal/mole. Since the triplet energy of benzophenone is 67.6 kcal/mole (20), a value of the cyclopentenone triplet of near 73.6 kcal/mole results, in agreement with the sensitization experiments (12).

2.2 The Reactive Species in Cyclic Enone Photocycloaddition Reactions.

It has been demonstrated by Wagner (21) that the reactive species of cyclopentenone and cyclohexenone have a very short lifetime as determined by quenching studies using dienes and di-tert-butyl nitroxide. The unimolecular decay constant (k_d) is of the order of $10^8 s^{-1}$, with the more flexible of the excited enones having shorter lifetimes. The five-membered ring cannot twist significantly in the ground state, the six-membered ring can twist but probably cannot achieve a trans double bond. In the case of cycloheptenone and cyclooctenone the rings can be twisted, and *cis-trans* isomerization represents the major deactivation mode of their excited states (22). Therefore one might expect that this difference in flexibility of cyclopentenones and cyclohexenones would lead to significant differences in their photochemical behaviour.

Table 1. Results of quenching benzophenone emission by Cyclopentenone.

[Cyclopentenone]	Intensity[a]	Φ_0/Φ
0.000	13.55	1.000
0.070	7.75	1.748
0.122	6.90	1.964
0.203	4.56	2.970
0.395	3.80	3.600
0.417	3.70	3.660
0.619	2.28	5.790

Slope[b] = 7.32 Intercept[b] = 1.13

Linear correlation coefficient[b] = 0.990

[a] Intensity of the emission measured at 453 nm.

[b] From a least squares calculation.

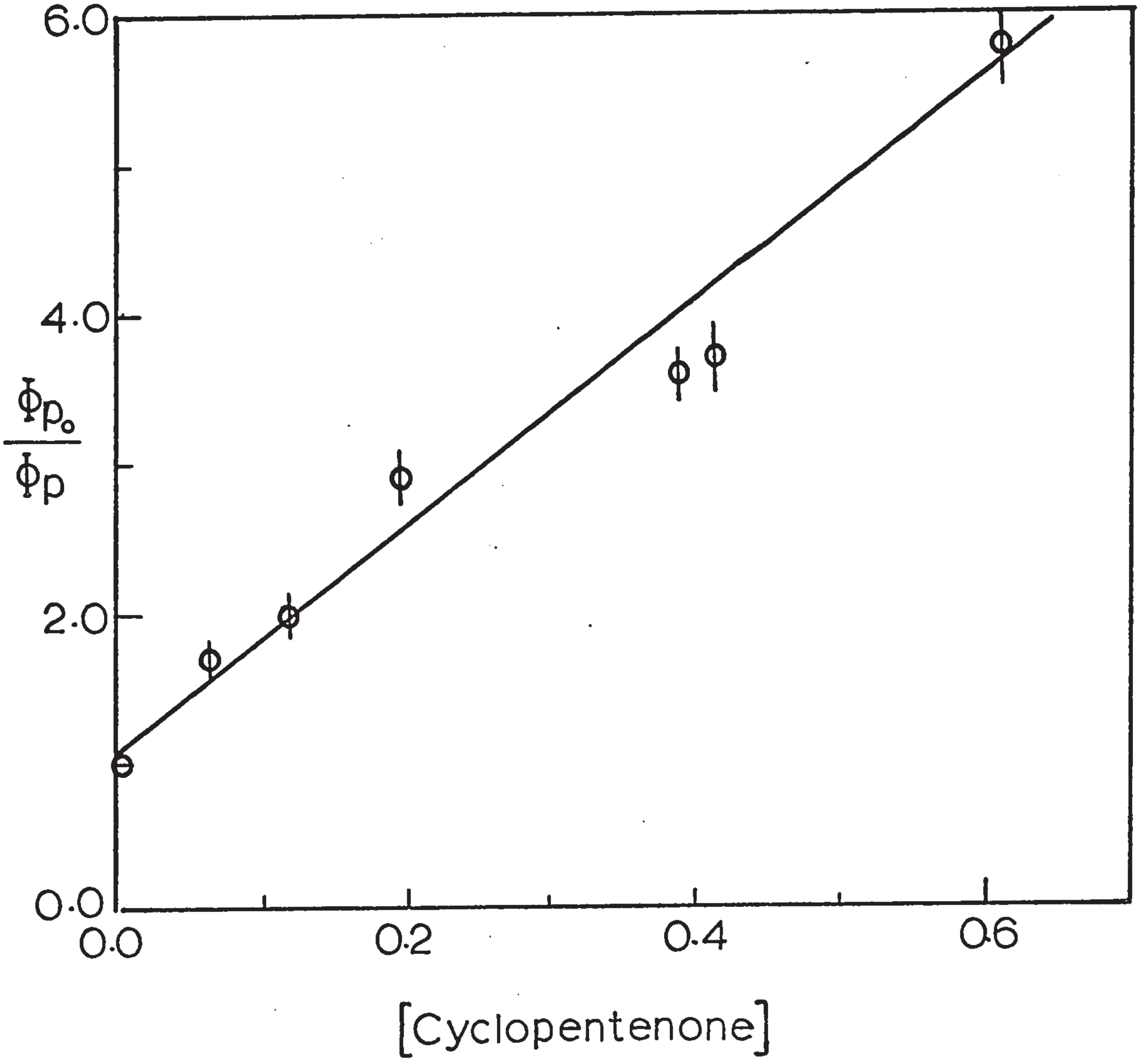
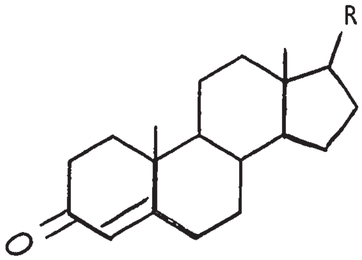


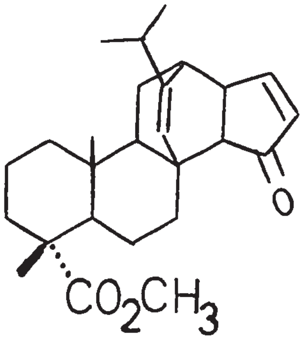
Fig. 1 Stern-Volmer plot - Quenching of benzophenone Emission by cyclopentenone in CCl_4 solution at room temperature.

Very few cyclic α,β-unsaturated ketones show luminescence; in fact only phosphorescence has been reported. In the case of steroidal enones (of the general formula 1), it has been shown that they undergo photocycloaddition reactions with a variety of olefins (23). Kearns and Shaffner (24) demonstrated that the low-lying emitting states of 19 steroidal enones in a rigid matrix, were $^3(\pi,\pi^*)$ states, and that the observed lifetimes (30-60 msec) were rather short for $^3(\pi,\pi^*)$ states and long for $^3(n,\pi^*)$ states. The observation of the $S \rightarrow T\ (n,\pi^*)$ excitation spectra for these steroids, and the existence of a gap of about 3000 cm^{-1} between this absorption and the phosphorescence, provided strong evidence that the emitting triplet states must be $^3(\pi,\pi^*)$ and that the $^3(n,\pi^*)$ states are of higher energies. Because of the proximity of the $^3(n,\pi^*)$ and $^3(\pi,\pi^*)$ states, the authors (21) invoked vibronic mixing between these states, i.e. the low-lying $^3(\pi,\pi^*)$ contains some n,π^* character. This rationalized the fact that the phosphorescence was positively polarized with respect to the $S - S\ (\pi,\pi^*)$ transition. This also explained the relatively short lifetimes observed. Alkyl substitution at the 4-position has been shown to increase the energy gap between the $^3(n,\pi^*)$ and $^3(\pi,\pi^*)$ by lowering the relative energy of the $^3(\pi,\pi^*)$ level substantially (~6 kcal/mole), while raising somewhat the energy of the $^3(n,\pi^*)$ level (~1 kcal/mole) (25). This separation should affect the magnitude of the vibronic coupling between these states and consequently the photochemical behaviour. The effect of substituents on the triplet energy levels might well account for the differences in behaviour of cyclohexenone and isophorone or 4,4'-dimethylcyclohexenone, a point which will be discussed later.

It has been reported by Harz and Nair (26) that the levopimaric acid-p-benzoquinone adduct 2 phosphoresces in EPA at 77°K giving a structured short lived emission $\tau \leq 10$ msec which was assigned to the lowest $^3(n,\pi^*)$ triplet state $E_T = 74.5$ kcal/mole. This ketone undergoes intramolecular cycloaddition reactions and it has the same substitution pattern as cyclopentenone itself.



1



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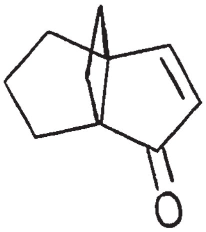

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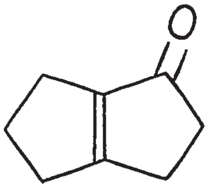

4

Emission from the constrained enones, tricyclo[3.3.2.0^{1,5}]dec-3-en-2-one, (TK) 3 and bicyclo[3.3.0]oct-1(5)-en-2-one (BK) 4 have been observed (27). The former exhibited structured emission, in EPA and MCH at 77°K in rigid media, which was assigned to the lowest $^3(n,\pi^*)$ state ($\tau < 10^{-3}$s) with triplet energy $E_T = 71.6$ kcal/mole in EPA and 70.8 kcal/mole in MCIP, while the latter in a rigid medium at 77°K exhibited long-lived non-structured emission from a state which is considered to be $^3(\pi,\pi^*)$ in character (τ = 10 msec) with a triplet energy of ~75 kcal/mole.

Both ketones ($\underset{\sim}{3}$ and $\underset{\sim}{4}$), when irradiated through Pyrex in the presence of cyclohexene gave cycloadducts. Accordingly it has been suggested that both $^3(n,\pi^*)$ and $^3(\pi,\pi^*)$ states are reactive towards cycloaddition. On the other hand, great caution is required in relating low temperature spectroscopic observations, which are measured in a glassy matrix at 77°K, to the room temperature solution photochemistry of more flexible compounds.

We decided to re-examine the emission from tricyclo[3.3.2.0^{1,5}]dec-3-en-2-one (TK) $\underset{\sim}{3}$ under conditions similar to those of the photochemical reactions. This compound was prepared following the procedure given in reference (27), chromatographed on silicic acid and purified by glc (using 3 different types of liquid phase consecutively), the purity being > 99.9% as judged from glc. The ketone was distilled (bulb-to-bulb) prior to use. The TK $\underset{\sim}{3}$ (4×10^{-2} M) emits in a rigid glass matrix (MCH) at 77°K, E_T = 70.5 kcal/mole as mentioned earlier. The phosphorescence lifetime was found to be of the order of 1.0 msec. On using the rotating can, with small inlet and very fast rotating speed (~8000 rps) the emission obtained, following excitation at 350 nm, was a non-structured and much less intense than the ordinary n,π^* phosphorescence, and appeared at slightly higher energy. The lifetime measured under these conditions was 1.6 msec which is slightly longer than the above value. These results indicate that two excited triplet states are emitting from the same molecule (lifetimes and position of emission exclude fluorescence).

The intense structured and shorter-lived emission was assigned by other authors (27) to a $^3(n,\pi^*)$ state. The weak, non-structured and slightly longer-lived emission can be attributed to a $^3(\pi,\pi^*)$ state which can only be seen after the shorter-lived $^3(n,\pi^*)$ emission has decayed. Plural emissions from triplet states have been observed by Griffin (28) for aromatic ketones by studying the time-delayed emission spectra. Double emissions from aryl alkyl ketones and 1-indanone have been reported (29, 30).

Lim (30b) recently reported that the phenomena of "dual" phosphorescence from aromatic ketones in condensed media have various origins: (1) interaction of the carbonyl compound in its gound state with solvent matrices, leading to the formation of two different solute-solvent cage configurations, e.g. emissions from benzaldehyde is believed to belong to that class; (2) existence in the excited state of two different conformations of the solute molecules, in which the equilibration to the energetically more favourable conformation is hindered or prohibited owing to steric effects of the solvent cage, e.g. phosphorescence of propiophenone and butyriophenone; (3) photochemical generation of new chemical species, e.g. 1-indanone exhibit emission from the enolate form; (4) presence of two nearly degenerate triplet states of an isolated molecule.

There can be no question of the intervention of an enol, as proposed by previous workers (29, 31) or solute-solvent cage (30b) in the present instance. These results appear to demand either a) that T_2 be a species which undergoes internal conversion at a rate comparable to, or less than phosphorescence, and b) population of the higher state from the lower state by thermal equilibration. It appears to be accepted that near-lying n,π^* and $\pi\ \pi^*$ states mix and that internal conversion between them is rapid (32). If that be so then we must attribute the emission from the upper state to thermal population and therefore, energy separation of not more than 0.3 kcal/mole is needed to obtain finite concentration of the upper state at 77°K. Change in the reactivity of aryl alkyl ketones towards type II photoelimination with substituents was attributed by Wagner (33) to equilibration of the lower $^3(\pi,\pi^*)$ with the upper $^3(n,\pi^*)$ states when the two states are very close together and vibronic mixing to take over when the two states are far apart.

We decided to study the effect of temperature on the emission spectrum of (TK) $\underset{\sim}{3}$ to test the validity of our hypothesis as well as to get a clearer picture of which state is of lower energy at room temperature. Figs. 2 and 3 show the emission from TK $\underset{\sim}{3}$ at various temperatures. Temperature variation was achieved by passing a stream of cold nitrogen through a glass tube which reached to the bottom of the dewar. The temperature was held constant within ±0.5°C over the period needed to record the spectra and was measured using an Iron-Constantan thermocouple which was placed beside the sample. On raising the temperature from 77 to 150°K the intensity of the emission decreased (Fig. 2), and the emission fine structure started to fade. Although the intensity of the emission in general was decreased, the band with a maximum at 450 nm was not diminished to the same extent. The emission from (TK) $\underset{\sim}{3}$ in PFMCH at room temperature exhibited a non-structured emission with λ_{max}(455 nm). The lifetime was too short to be measured with the apparatus available at that time (less than 10^{-3}sec).

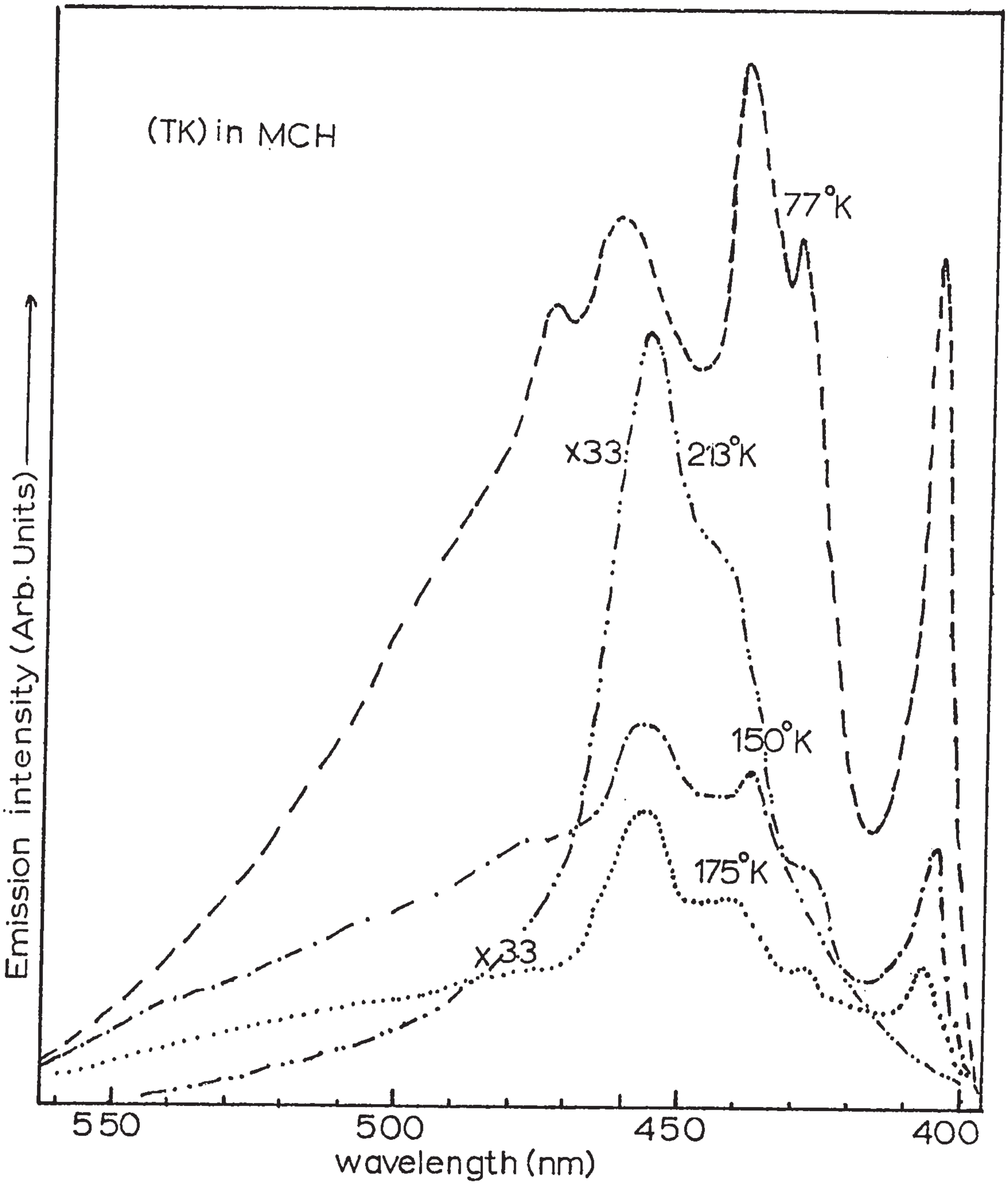

Fig. 2. Emission spectra of (TK) 3 in MCH at various temperature

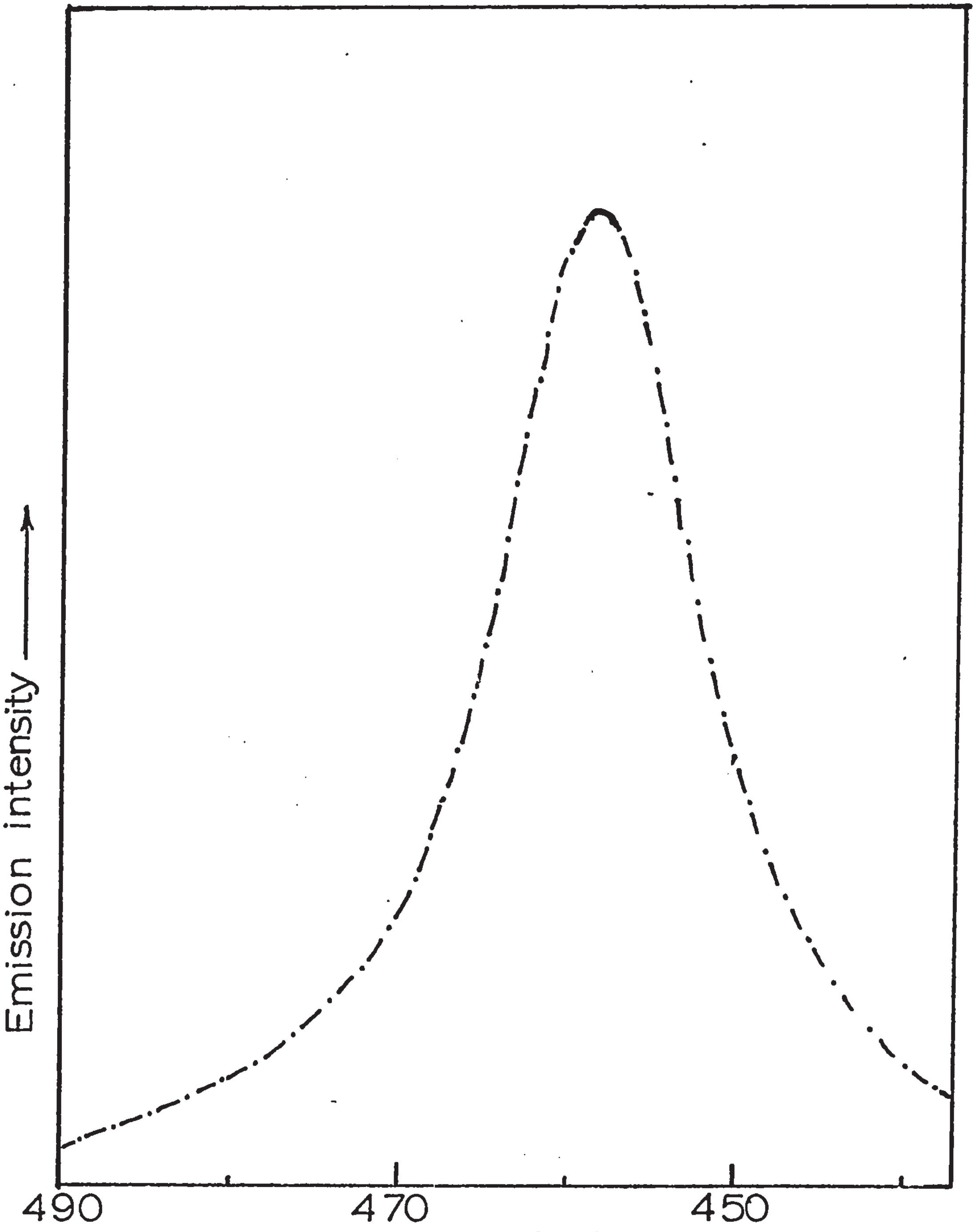

Fig. 3 Emission spectrum of TK in PFMCH at 298°K.

Theoretical calculations on acrolein triplet states indicate that the π,π^* state is stabilized by an out-of-plane distortion involving rotation about the C=C band (34), and this relaxation could cause the $^3(\pi,\pi^*)$, originally above the $^3(n,\pi^*)$ in energy, to cross below it.

In rigid matrix rotational relaxation of the $^3(\pi,\pi^*)$ state is less likely (see 30b). Increasing the temperature will increase the ratio of the upper state $^3(\pi,\pi^*)$ in the equilibrium mixture and also the resulting decrease in the rigidity of the media will allow the $^3(\pi,\pi^*)$ state to rotationally relax. The degree of twisting probably is not great since the geometry of the molecule does not allow much flexibility. Therefore it is possible that the emission observed at room temperature is from the relaxed (non-Franck Condon) $^3(\pi,\pi^*)$ state, with E_T 67 kcal/mole[†] (see Fig. 4) which is near the value of 62 kcal/mole determined by the cis-trans equilibration technique (17).

This conclusion is consistent with Wagner's proposal (21) that the $^3(\pi,\pi^*)$ states are responsible for the photocycloaddition reaction of cyclic enones to the double bond.

As mentioned before (p. 16) irradiation of the TK 3 in the presence of cyclohexene at room temperature gave twelve different products. The major component (60% of the total) was identified as cycloadduct (27). When the irradiation was performed at -75°C only seven products were obtained, and in this case the major product represented 80% of the total

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[†] The π,π^* triplet energy was taken from the onset of emission. No emission from the solvent or the supracil cell used was observed.

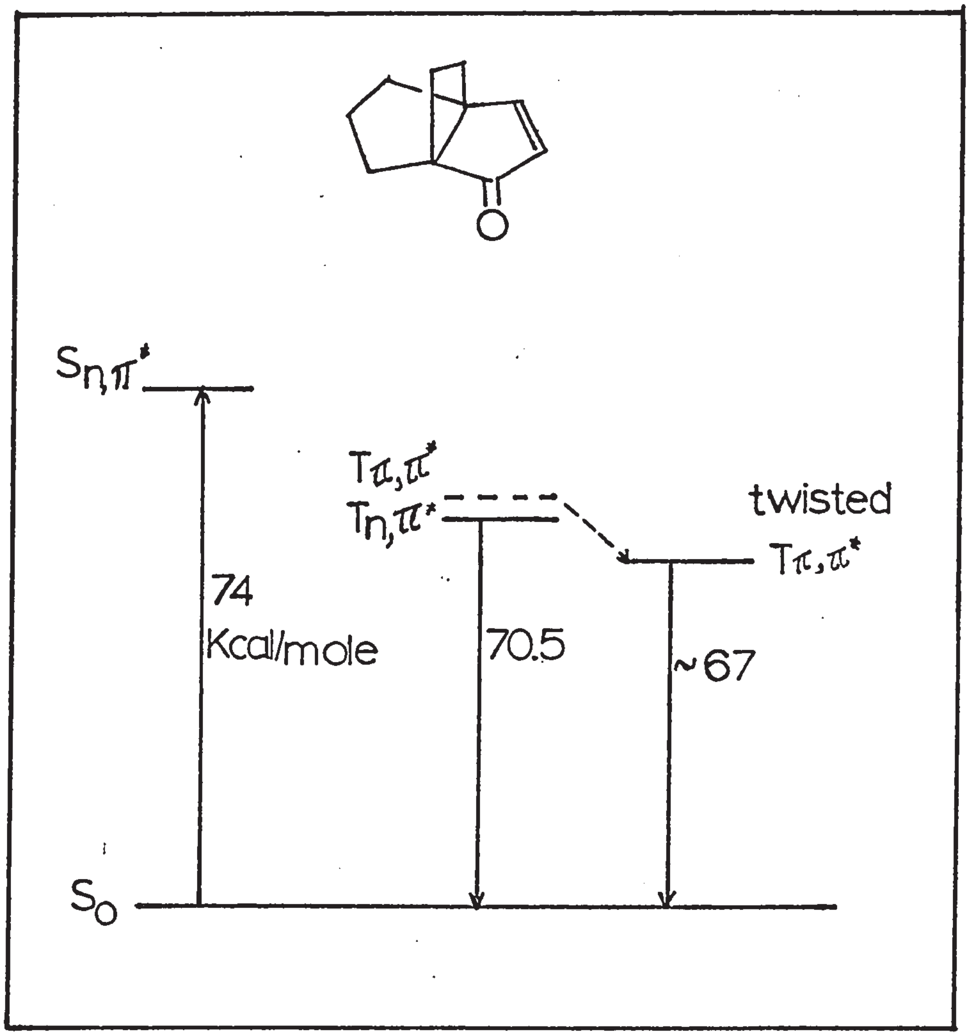


Fig.4 STATE DIAGRAM of (TK)

yield. This was accompanied by an increase in the quantum yield of the cycloaddition from $\phi_{27} = 0.19 \pm 0.01$; to $\phi_{-75} = 0.25 \pm 0.01$[†]. In view of the near degeneracy of the two excited triplet states, thermal equilibration is expected and lowering the temperature will affect the equilibrium ratio and will favour products obtained from the lower excited state. This might explain the change in the number of products.

The bicyclic enone 5, 6, 7, 7a-tetrahydro-7a-methyl-2-indenone[‡] which represents β-substituted cyclopentenones, emits in a rigid matrix of MCH at 77°K (Fig. 5). In general the emission exhibits no structure with a λ_{max} at 435 nm, and the phosphorescence lifetime is of the order of 38 msec which is much longer than that of (TK) $\underset{\sim}{3}$ and is comparable to that of A-nortestosterone acetate $\underset{\sim}{6}$ (22). The relatively long-lived structureless emission obtained from $\underset{\sim}{5}$ could be assigned to lowest $^3(\pi,\pi^*)$ state by analogy with $\underset{\sim}{6}$. The $^3(\pi,\pi^*)$ energy taken from the onset of the emission is 75.6 kcal/mole compared to 76.2 kcal/mole for $\underset{\sim}{6}$. Interestingly, on the high energy side of the emission, two bands at 377 and 403 nm with a band spacing of 1711 cm^{-1} were observed, which is compatible with the carbonyl stretching vibration. These bands were proved not to be a part of the bulk of the emission, since by varying the speed of the chopper, it was shown that these bands disappeared at high chopper speed (see Fig. 5).

[†] Determination was based on the major product and, each measurement was an average of 3 runs.

[‡] The author is indebted to Dr. D. Becker (Technion, Israel) for a sample of the indenone.

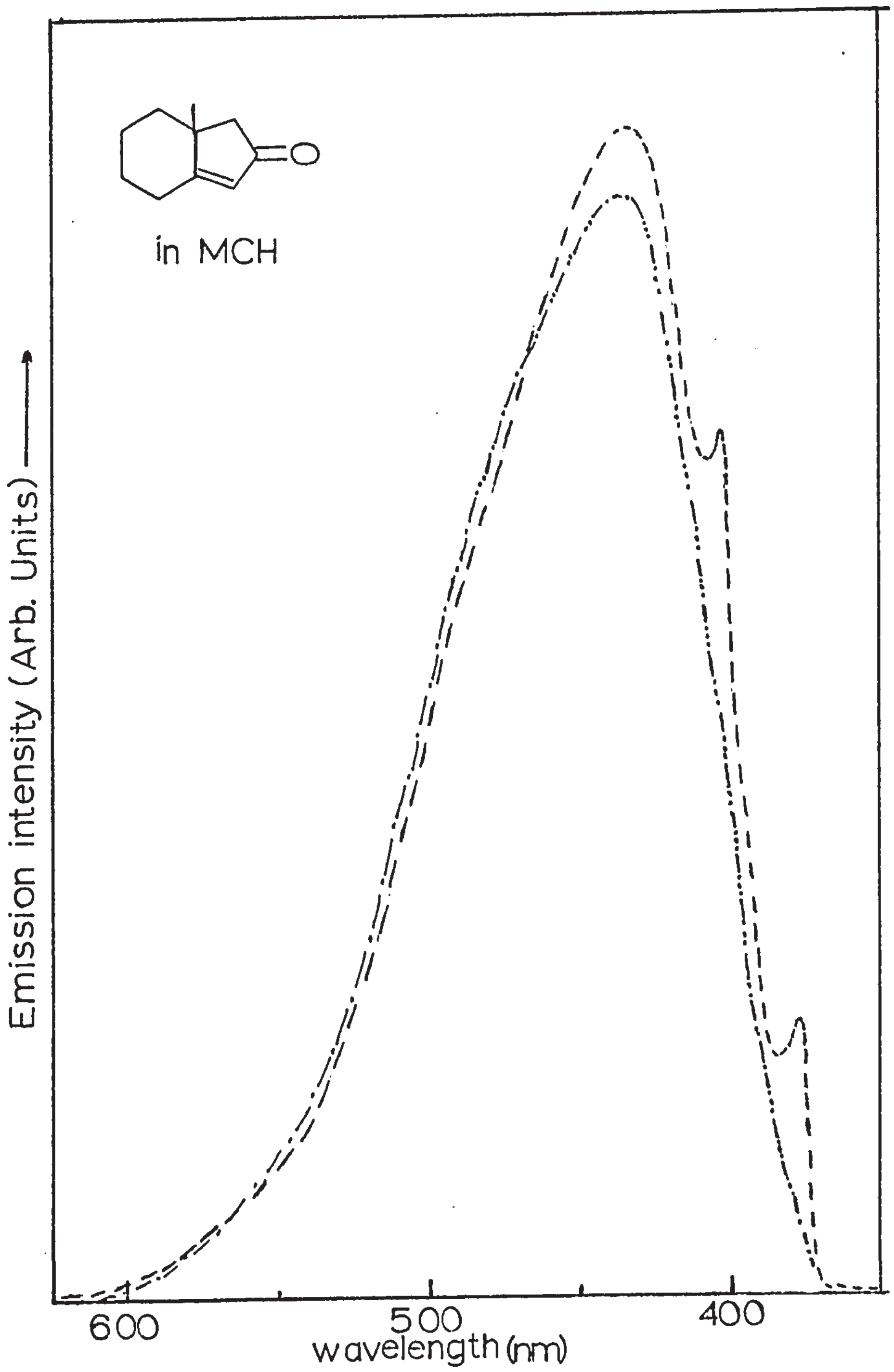
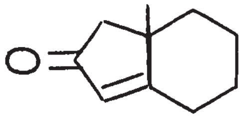
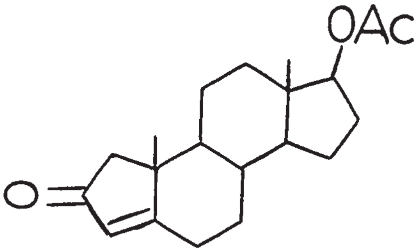


Fig. 5. Emission spectra of 5,6,7,7a-tetrahydro-7a-methyl-2-indenone, in MCH at 77°K with fast chopper speed (•—•); and slow chopper speed (-•-•-).



Tetrahydro-methyl-indenone

5



A-Nortestosterone Acetate

6

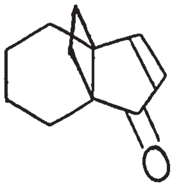
$E_{T\pi,\pi^*}$= 75.6 kcal/mole; τ = 38 msec $E_{T\pi,\pi^*}$= 76.2 kcal/mole; τ = 22 msec

E_{Tn,π^*}= 75.8 kcal/mole; τ = 3.6 msec

The lifetime measured by monitoring the emission at 377 nm was 3.6 msec. The short-lived, structured and slightly higher energy emission can be assigned to $^3(n,\pi^*)$ state. It is obvious that β-substitution in cyclopentenone lowers the energy of the $^3(\pi,\pi^*)$ state below the $^3(n,\pi^*)$.

These observations, together with the $S_0 \rightarrow S_1$ absorption spectrum, suggest very close energetic content of the three lowest excited states, $^1(n,\pi^*)$, $^3(n,\pi^*)$ and $^3(\pi,\pi^*)$, of rigid cyclopentenones.

A year later, Cargill et al (35) reported the phosphorescence spectra of a series of rigid cyclopentenones at 77°K in EPA, MCH and MCH-silica gel. They divided these into two groups; the first group exhibited structured, short-lived emissions (1-3 msec) and was assigned to lowest $^3(n,\pi^*)$ states. Alkyl substitution at the α and β carbon atoms leads to structureless long-lived emissions which are assigned to lowest $^3(\pi,\pi^*)$ states which represent the second group. The phosphorescence spectrum of tricyclo(4.3.2.$0^{1,6}$)10-methyl-undec-9-en-7-one 7 was broad and structureless with a hint of structure which was ascribed to significant (n,π^*) character mixed in the lowest $^3(\pi,\pi^*)$ state. These results are in agreement with those reported here.



7

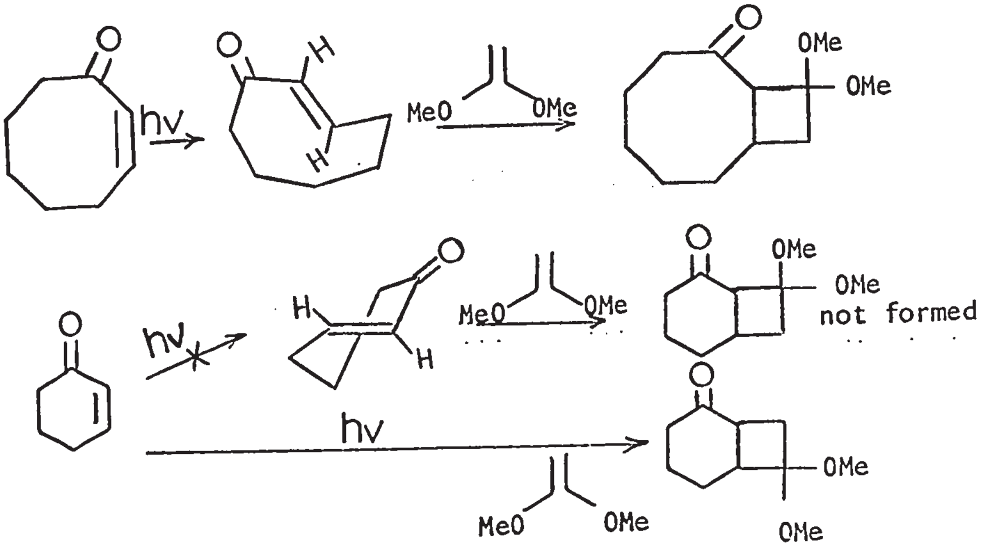
There is accumulating evidence in the literature that two triplets (or two rapidly equilibrating triplets) are involved in the photochemical reactions of cyclic enones. These two excited triplet states have been tentatively assigned $^3(n,\pi^*)$ and $^3(\pi,\pi^*)$ configurations. In the photochemistry of testosterone acetate and similar enones the photorearrangement has been ascribed to the (π,π^*) triplet state (33), while double bond migration has been related to (n,π^*) triplet states. The product distribution changes significantly in going from polar to non-polar solvents (36) (in accord with these proposals).

Similarly, Dauben (37) showed that irradiation of 4-methyl-4-phenyl-2-cyclohexenone in a non-polar solvent (benzene) gave products which are thought to result from the (n,π^*) excited triplet state. On the other hand, irradiation in polar solvent (which could lower the energy of the $^3(\pi,\pi^*)$ state) gave in addition to the above products a set of skeletal rearrangement products. The formation of the latter have been attributed to the $^3(\pi,\pi^*)$ state. Differential quenching of products was an indication of the involvement of the two excited triplet states of different lifetimes. From the slopes of the Stern-Volmer (SV) plot, Dauben demonstrated that the $^3(n,\pi^*)$ state was involved in the phenyl migration and the $^3(\pi,\pi^*)$ state was involved in skeletal rearrangement. This is an indication that the difference in electronic distribution of cyclic enones, n,π^* and π,π^* excited triplet states, plays an important role in the photochemical processes.

The photocycloaddition of 4,4'-dimethyl-2-cyclohexenone, isophorone or 2-cyclohexenone to 1,1-dimethoxy ethylene was quenched by di-t-butyl nitroxide (38). The products (cis and trans fused cycloadducts and oxetanes) were differentially quenched and the product ratios were strongly solvent dependent. This leads to the dramatic conclusion that cis and trans adducts are derived from different triplet excited states. Oxetanes may be derived from the same triplet that directly or indirectly gives the trans adduct. From the solvent effect and the slope of the Stern-Volmer plots, one can conclude that the triplet state leading to cis-adducts is $\pi\ \pi^*$ in character and that leading to trans-adducts and oxetanes is n,π^* in character.

The photodimerizations of cyclohexenones and isophorone are also differentially quenched by di-t-butyl nitroxide (39), and different excimers were postulated to explain these results. However, this paramagnetic quencher is known to deactivate both singlets and triplets.

From the previous discussion, it can be concluded that the n,π^* and π,π^* excited triplet states of cyclic enones are almost degenerate with the former lower in energy. Substitution in the α- or β-position affects the energy levels and brings the $^3(\pi,\pi^*)$ state below the $^3(n,\pi^*)$ state energy. Solvent polarity could play an important role, particularly when the two states are very close in energy and crossing of the energy levels could take place. It seems that both triplet states are capable of cycloaddition to double bonds, but due to the significant differences in the electronic distribution of both states, they lead to different products. Irradiation of cyclohexenone with various olefins afforded the *trans*-6-4 fused cycloadduct as the major product in some cases, while β-substituted cyclohexenone (π,π^* is lowered in energy) did not afford any *trans*-adduct. The possibility is that formation of *trans*- adduct could result from reaction of the $^3(n,\pi^*)$ state. Involving a metastable *trans*-enone, as has been suggested by many authors (9, 13a), could be excluded on the basis that cyclooctenone on irradiation gives the *trans*-enone which in the dark adds to 1,1-dimethoxyethylene to give the HH adduct (9), while cyclohexenone 1,1-dimethoxyethylene gives exclusively the HT adduct (9). No justification for such drastic orientation change seems likely if the same type of intermediate is involved.



CHAPTER III

EFFECT OF TEMPERATURE ON THE QUANTUM YIELD OF CYCLIC ENONE PHOTOANNELATION

A photochemical reaction requires activation by light. The quantitative relationship between the number of molecules of product formed and the number of photons absorbed by starting material in a unit time is given by the quantum yield Φ (40). The quantum yield is one of the most important single parameters describing the photochemical reaction because crucial information concerning the reaction mechanism i.e. the path by which the electronically excited molecule disposes of its energy, can be derived from its value. At the outset of the investigation the quantum yields at room temperature for photoannelation of few cyclic enones with a number of olefins were known (12). On the other hand the effect of temperature on the quantum yields of photochemical reactions had not been reported. In order to gain further information about the mechanism of cyclic enone photoannelation reactions, we thought it was necessary to study the effect of temperature on the quantum yield of these reactions.

The results are given for cyclopentenone, cyclohexenone and a tricyclic ketone (TK) with a number of olefins at various temperatures in Table 2.

It can be seen that Φ for the photoannelation of the studied cyclic enones are temperature dependent to an extent and direction dependent on the olefin used. For example, the reaction of <u>cyclopentenone</u> with <u>trans-</u>

Table 2. Quantum yields for Cycloaddition[a]

Ketone	Olefin[b]	Φ_{27}	Φ_{-5}	Φ_{-10}	Φ_{-41}	Φ_{-71}	Φ_{-90}	Φ_{-102}
Cyclopentenone	Cyclohexene[c]	0.46(.48)[d]		0.51	0.55	0.62(.72)[d]	0.684	0.72
	Cyclopentene	0.23[e]		0.31		0.61		
	trans-3-Hexene	0.22				0.19		
	cis-Dichloroethylene	0.345[f]				0.49		
	Bicyclooctene	0.23	0.25					
	3-Hexyne	0.49[g]				0.31		
Cyclohexenone	Cyclohexene	0.48				0.43	0.41	
	Cyclopentene	0.36	0.385			0.45		
	trans-3-Hexene	0.063	0.060			0.052		
Tricyclo(3.3.2.0)dec-3-en-2-one	Cyclohexene	0.19				0.21		

a. All irradiations were performed on an optical bench using 313 nm light.

b. Olefins were used as solvent (neat).

c. 3.66M in ether, the Φ was 0.52 in diglyme.

d. The values in parenthesis are for neat olefin.

e. The values reported earlier were 0.32 and 0.27. Indeed the later value was obtained if impure cyclopentene (from exposure to air) was used, and another peak appeared under that of the adduct on changing the glc condition.

f. The values reported previously was 0.24 based on the observation of 3-adducts only. The value given here was based on all 4 adducts.

g. Determined by Mr. M.C. Usselman.

3-hexene, lowering the temperature slightly decreases Φ, whilst with cyclopentene the quantum yield is more than doubled. In the addition to bicyclo[4.2.0]oct-7-ene, Φ increased slightly on lowering the temperature (strain does not apparently inhibit photoannelation), and with 3-hexyne a remarkable decrease in Φ was observed over the same temperature range (Fig. 6). The reaction of cyclohexenone with cyclohexene or trans-3-hexene, a small decrease in Φ on lowering the temperature was observed, while with cyclopentene a moderate increase was observed over the same temperature range.

The observed changes in the quantum yield might be attributed to one of several courses: 1) increased yield of reactive triplet, 2) increased rate of addition (kr) or 3) decreased rate of triplet decay (kd). The first possibility can be dismissed since it has been found that the quantum yield of triplet formation is near unity both at 20 and -71°C (see Chapter IV). The rate of addition and decay were found to decrease on lowering the temperature, but cannot account for the large change in quantum yield (see Chapter V).

This striking observation necessitates the existence of one (or more) reversible intermediate(s) in these photoannelation reactions. The same conclusion was reached independently in this laboratory (41) from a kinetic analysis of the dependence of the rate of decay (which is a property of the enone) on olefin concentration. Thus, the results presented here would indicate that the formation of cyclobutane products from an intermediate has lower activation energy than for dissociation.

The nature of the intermediate(s) could not be derived from the above results, but several possibilities can be considered:

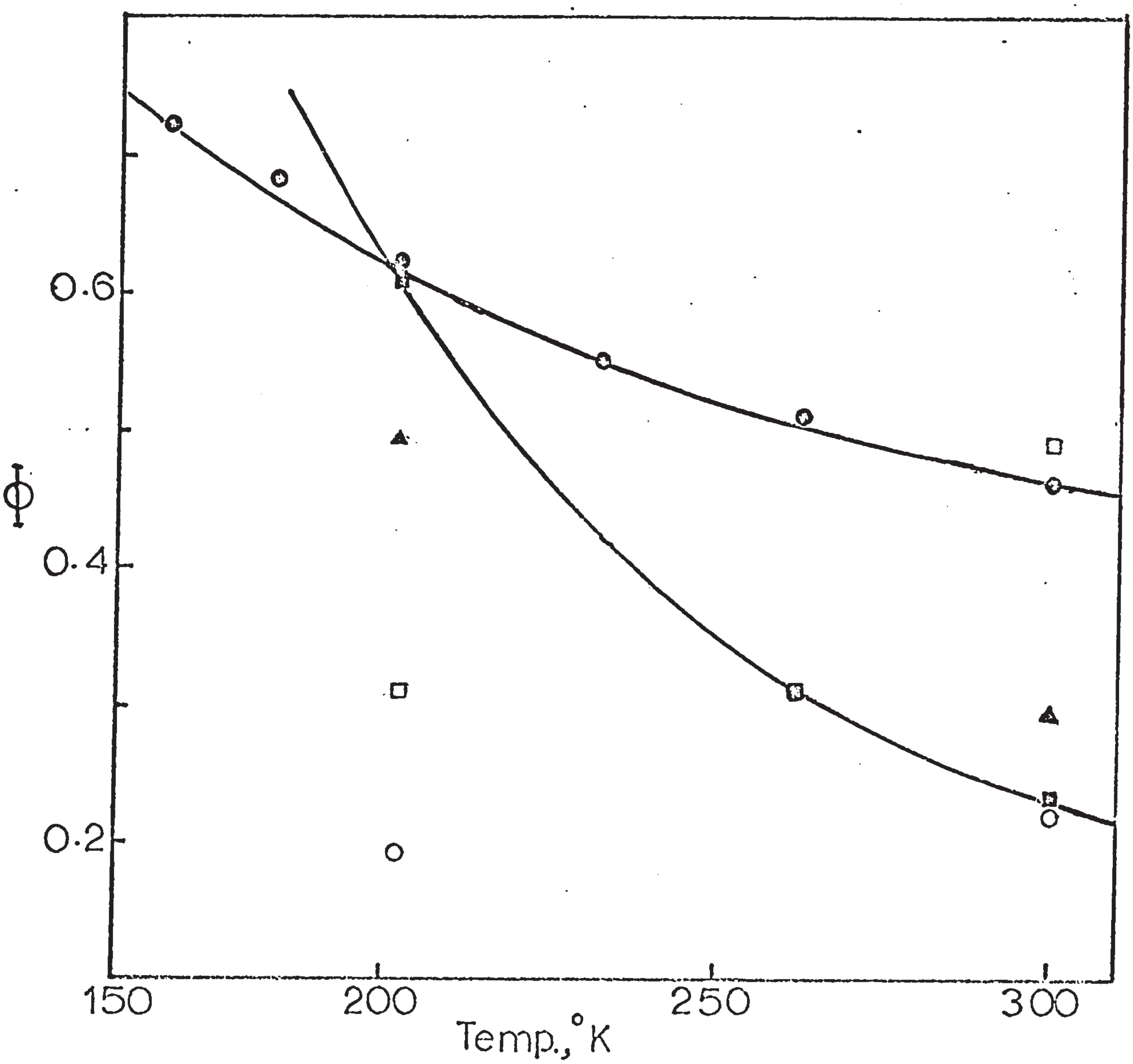
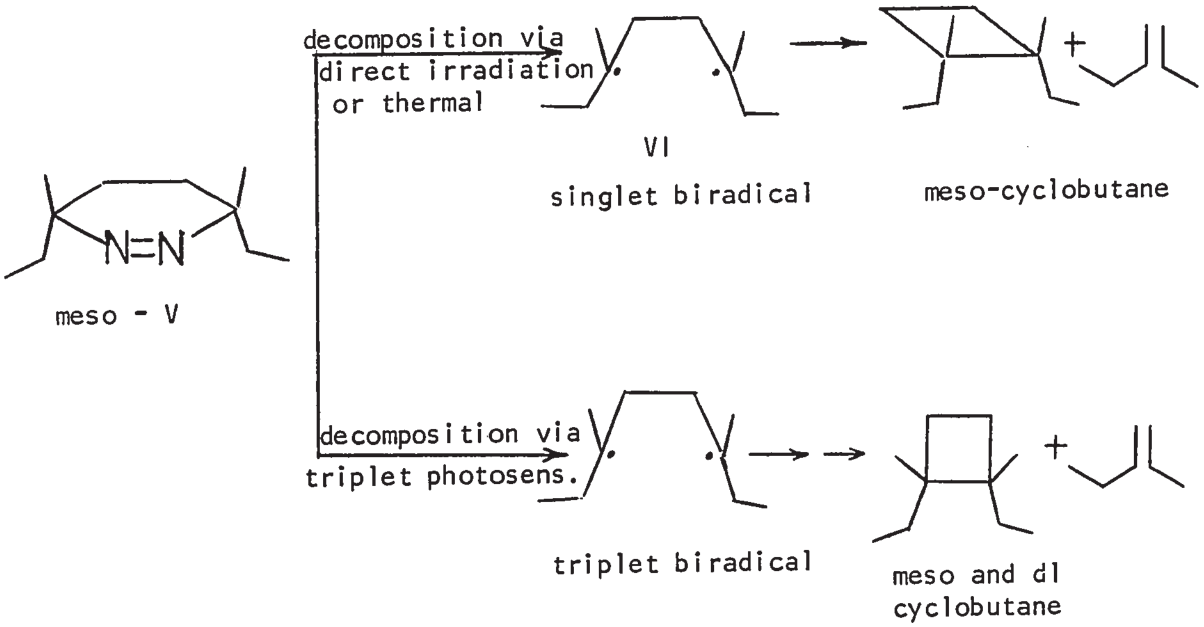


Fig. 6. Effect of temperature on the Φ of cyclopentenone photoaddition to alkene and alkyne ; o Cyclohexene, □ Cyclopentene, △ cis-Dichloroethylene, o trans-3-Hexene, □ 3-Hexyne.

A. The intermediacy of a tetramethylene(1,4-biradical) (TM), which was first suggested by Corey (9). Since it has been established that substituted tetramethylene such as VI generated by photochemical and thermal decomposition of meso-V, give both products of ring closure and fission (42) (reaction X) and since higher temperature would be expected to favour fission, it is tempting to identify the intermediate as a tetramethylene.



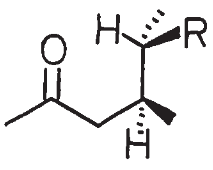
Biradicals have also been postulated as intermediates in many photochemical and thermal reactions. For example, the intermediacy of 1,4-biradical is invoked in the Norrish type II process (33). Quenching data indicated that the quenchable (triplet quencher, isoprene or naphthalene) portion of this reaction was due to reactions of the lowest triplet state of the ketone. The balance, which shows only slight or no sensitivity to added quencher, is assigned to reactions from the lowest excited singlet state of the ketone. It has recently been demonstrated that irradiation of erythro-ketone VII and threo-ketone VIII leads to the lowest excited singlet state which may decay to the ground state, intersystem-cross to the triplet manifold, or produce a singlet 1,4-biradical via γ-hydrogen abstraction. The bond forming or cleavage of the species was found to be very rapid relative to β,γ bond rotation as high stereospecificity was maintained (43). In a similar manner the ketone excited triplet state may decay to ground state or form a triplet tetramethylene. This species is long-lived, and extensive loss of configuration due to bond rotation occurs, leading to a mixture of olefins (reaction XI). These results are in accord with those of Yang and Elliot (44), and Bartlett and Porter (43).

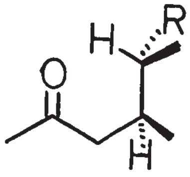
In the photocycloaddition of cyclic enones, where the initial reaction involves a triplet ketone, one would expect the formation of triplet 1,4-biradical. If indeed ^{3}(TM) is an intermediate in the enone photocycloaddition, the reaction would be expected to be non-stereospecific, which was found to be the case (see Chapter VI).

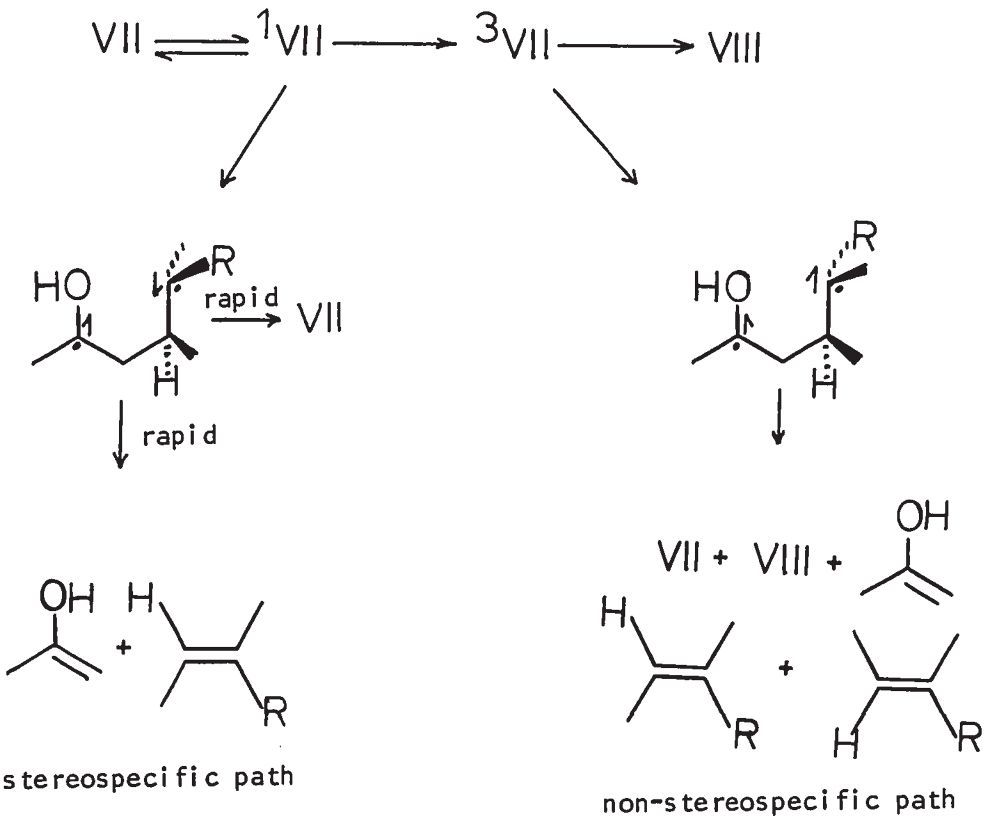
B. The other alternative is the formation of a complex (possibly charge transfer), which was a clever postulate put forward by Corey (9) based at that time on very little experimental evidence.

A simple mechanism, which includes both intermediates in sequence is given in Fig. 7, where K,0, ^{3}K...0, and TM represent ketone, olefin exciplex and tetramethylene. Taking into account the existence of this intermediate, and with the usual steady-state assumptions, it is possible to derive the expression

$$\Phi = \phi_{isc}\, K\left(\frac{k_r\,[0]}{k_r[0] + k_d}\right) \qquad (1)$$


erythro-VII


threo-VIII



(XI)

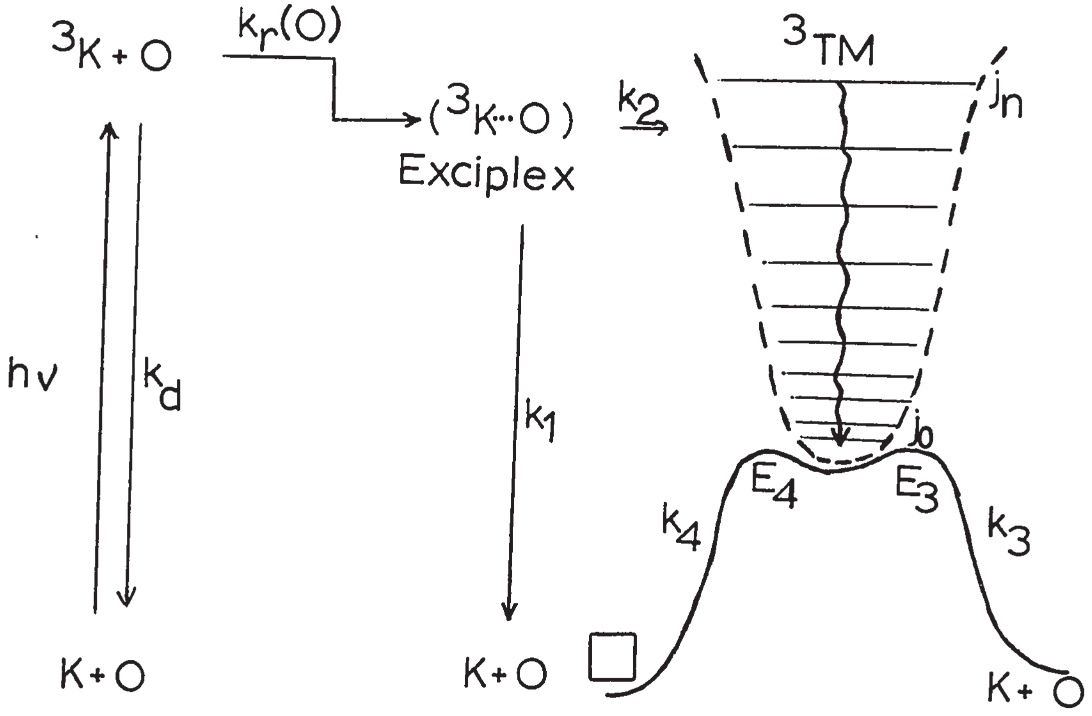


Fig.7

for the quantum yield of product formation, where ϕ_{isc} is the intersystem crossing efficiency (which is unity), k_r is the rate constant for (first) intermediate formation, k_d is the unimolecular decay constant, and K is the fraction of the intermediate that gives product and is given by the expression

$$K = \left(\frac{k_2}{k_1 + k_2} \right) \left(\frac{k_4}{k_3 + k_4} \right) \qquad (2)$$

Thus the observed change in quantum yield might be due to a change in either K or the term in brackets in equation (1) or to a change in both. However, it is evident that the last bracketed term in equation (1) is, at the concentration of olefin used, near 0.9 for cyclopentenone systems at various temperatures; this point will be discussed in more detail later. The conclusion follows that the large change in quantum yields results from changes in the partition function K. Since the nature and number of the intermediate(s) is not known, it is impossible to assign values to the rate constant which make up K. However, two possible extremes can be treated: $k_2 >> k_1$ or $k_4 >> k_3$. If the bracketed term in equation (1) is assumed to be temperature independent, then an Arrhenius type expression can be derived

$$\text{Log} \left(\frac{1}{\Phi} - 1 \right) = \log A + \frac{\Delta \text{ Ea}}{2.303 \text{ RT}} \qquad (3)$$

where A is a ratio of pre-exponential factors and Δ Ea is a difference in activation energies. In Figures 8 and 9 are shown the plots of equation (3) for cyclopentenone- and cyclohexenone olefin systems respectively. The difference between the activation energies for the competing processes is in the range 0.65 to -2.0 kcal/mole (Table 3). Calculations performed by O'Neal and Richardson (45) have indicated that the cyclization of a tetramethylene to a cyclobutane is approximately iso-energetic (Ea ~6.6 kcal/mole) with its opening to form two ethylenes, therefore, any change in the structure of either enone or substrate could greatly affect the partition function and consequently the quantum yield.

The decrease in quantum yield in the cycloaddition of trans-3-hexene and 3-hexyne to cyclopentenone observed on lowering the temperature, might be due to either a decrease in the term in brackets in equation (1), which out-weighed the increase in K, or a decrease in both which might be the case with the latter.

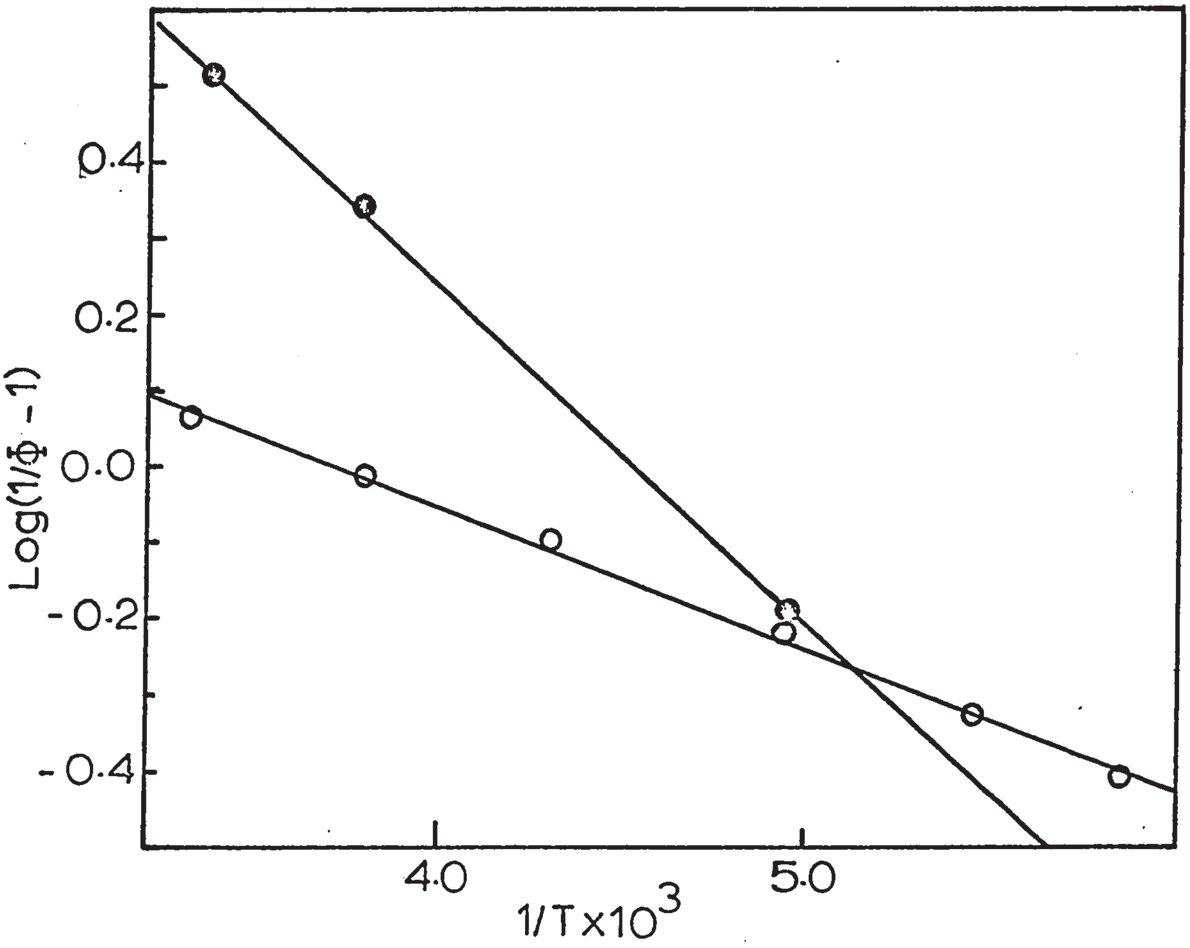


Fig. 8 Arrhenius plots for photocycloaddition of Cyclopentenone to ● Cyclopentene & ○ Cyclohexene.

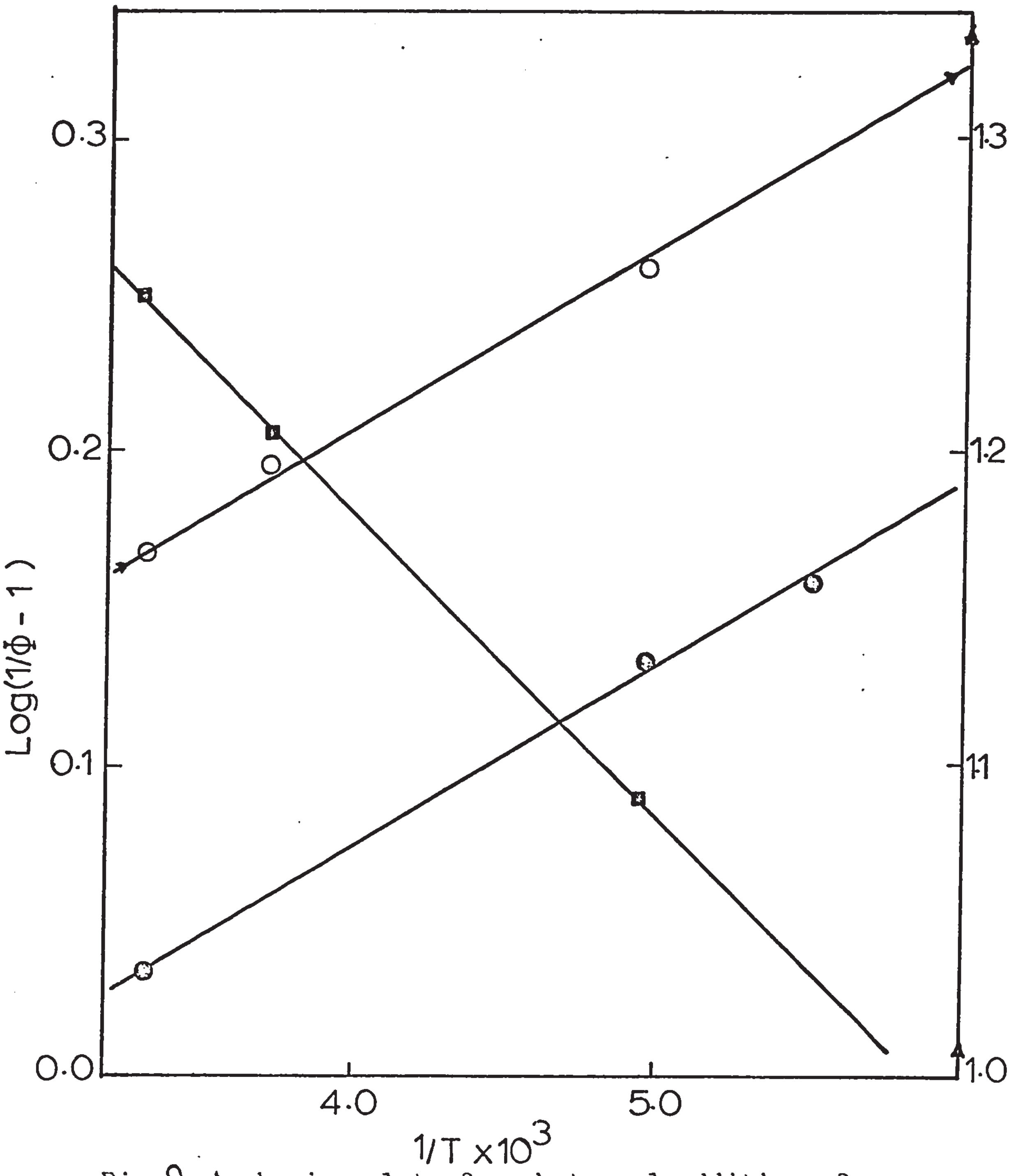


Fig.9 Arrhenius plots for photocycloaddition of 2-cyclohexenone to ⊠ cyclopentene, ⊙ cyclohexene, and ○ trans-3-hexene.

Table 3. Difference in activation energies of ring closure and fission of the intermediate tetramethylene.

Ketone	Olefin	ΔE / kcal/mole
Cyclopentenone	Cyclohexene	-0.90
	Cyclopentene	-2.10
	cis-Dichloroethylene	-0.45
	trans-3-Hexene	+0.23
	3-Hexyne	+0.65
Cyclohexenone	Cyclopentene	-0.46
	Cyclohexene	+0.27
	trans-3-Hexene	+0.25

On the other hand, it has been found that K for cyclohexenone-cyclohexene addition approach unity at 20 and -71°C (see Chapter VI) which indicates either that products are directly formed from interaction of the excited ketone and olefin or that there is one or more intermediates which do not partition but lead to product with 100% efficiency. Consequently, any change in the quantum yield must arise from the effect of temperature on the term $(k_r[O]/k_d + k_r[O])$, and in this case Δ Ea in equation (3) must represent the difference in activation energy for reaction and decay of the triplet enone. It must be noted that K for the cyclohexenone system is not always unity e.g. for cyclohexenone-3-hexyne addition is 0.13 (36) and for isophorone dimerization is 0.33 (37).

CHAPTER IV

QUANTUM YIELD OF CYCLOPENTENONE AND CYCLOHEXENONE TRIPLET FORMATION

The observed change in quantum yield for the photocycloaddition of cyclic enone on lowering the temperature might be attributed to increase in the yield of the reactive triplet. Although it has been shown that the quantum yield of intersystem crossing is near unity at room temperature for both cyclopentenone and cyclohexenone (12b), it was still necessary to determine this value at lower temperature. A recent report of Lamola and Hammond (46) gives an elegant method for determining the intersystem crossing efficiencies of triplet sensitizer. The method involved determination of the quantum yield of cis to trans isomerization of dienes (in this case 1,3-pentadiene), it was assumed that the intersystem crossing efficiency of benzophenone was unity. The decay ratio of 51% trans in methyl acetate at -71°C was determined by measuring the photostationary state with benzophenone as sensitizer. It is approximately the same as in methyl acetate at room temperature ($\phi_{c\rightarrow t}$ 0.53) and the latter is the same as in benzene (46). The intersystem crossing yields of cyclopentenone and cyclohexenone were obtained by measuring the efficiency with which the two ketones (0.2M) sensitize the cis to trans isomerization of 1,3-pentadiene.

The sensitization of the isomerization may be represented by an equation of the form

$$\frac{C}{\phi_{c\rightarrow t}} = \frac{1}{\phi_{isc}} \left(1 + \frac{1}{k_q \tau [Q]}\right)$$

where τ is the cyclic enone triplet lifetime, [Q] is the piperylene concentration, k_q is the rate constant for energy transfer, C is the quantum yield for the formation of trans-piperylene from piperylene triplet (known to be 0.51), and ϕ_{isc} is the intersystem crossing triplet yield for the sensitizer (in this case cyclic enone). A plot of $C/\phi_{c\rightarrow t}$ against the reciprocal piperylene concentration (Fig. 10) gave intercepts $(1/\phi_{isc})$ close to unity for both ketones. From the slope, k_d may be derived, which was found to be $\sim 5 \times 10^8$ sec^{-1} for cyclopentenone at -71°C, based on the assumption that the quenching rate k_q can be approximated by the diffusion rate constant k_{diff} and that this rate constant can be calculated by means of the Debye equation given below (47)

$$k_q = k_{diff} = \frac{8RT}{3 \times 10^3 \eta} \tag{4}$$

where η is the viscosity in poise units, $R = 8.31 \times 10^7$ erg/mole -deg K, k_q was found to be $0.4 \times 10^{10} M^{-1} sec^{-1}$ for such mixture at -71°C. The validity of this approximation was shown to be reasonable. Thus, the rate of energy transfer from biacetyl (E_T = 56 kcal/mole) to quenchers of E_T less than 50 kcal/mole proceeds at a rate of $8 \times 10^9 M^{-1} sec^{-1}$ (48). The calculated rate constant, using the viscosity of benzene at 20°C, is $1.0 \times 10^{10} M^{-1} sec^{-1}$ so that the agreement is good. However, recently it has been shown that the rate of triplet energy transfer from ketone to diene in solvents where $\eta > 3$ cP is very nearly equal to the rate of diffusion, but in less viscous solvents rates of energy transfer are

Table 4. Quantum yield for cyclopentenone photosensitized isomerization of cis-piperylene at -71°C.

[cis-piperylene]*	1/[cis]	$\Phi_{c-t}/0.51$	$0.51/\Phi_{c-t}$
0.2009	4.977	0.62	1.613
0.3155	3.169	0.70	1.423
0.4654	2.149	0.77	1.300
0.6038	1.656	0.82	1.220

Slope = 0.116 Intercept = 1.04

Linear correlation coefficient = 0.996

Table 5. Quantum yield for cyclohexenone photosensitized isomerization of cis-piperylene at -71°C.

[cis-piperylene]*	1/[cis]	$\Phi_{c-t}/0.51$	$0.51/\Phi_{c-t}$
0.2145	4.662	0.50	2.000
0.3813	2.623	0.61	1.642
0.4840	2.066	0.67	1.484
0.6640	1.506	0.784	1.275

Slope = 0.219 Intercept = 1.004

Linear correlation coefficient = 0.985

*The concentration was corrected for the change in volume on cooling.

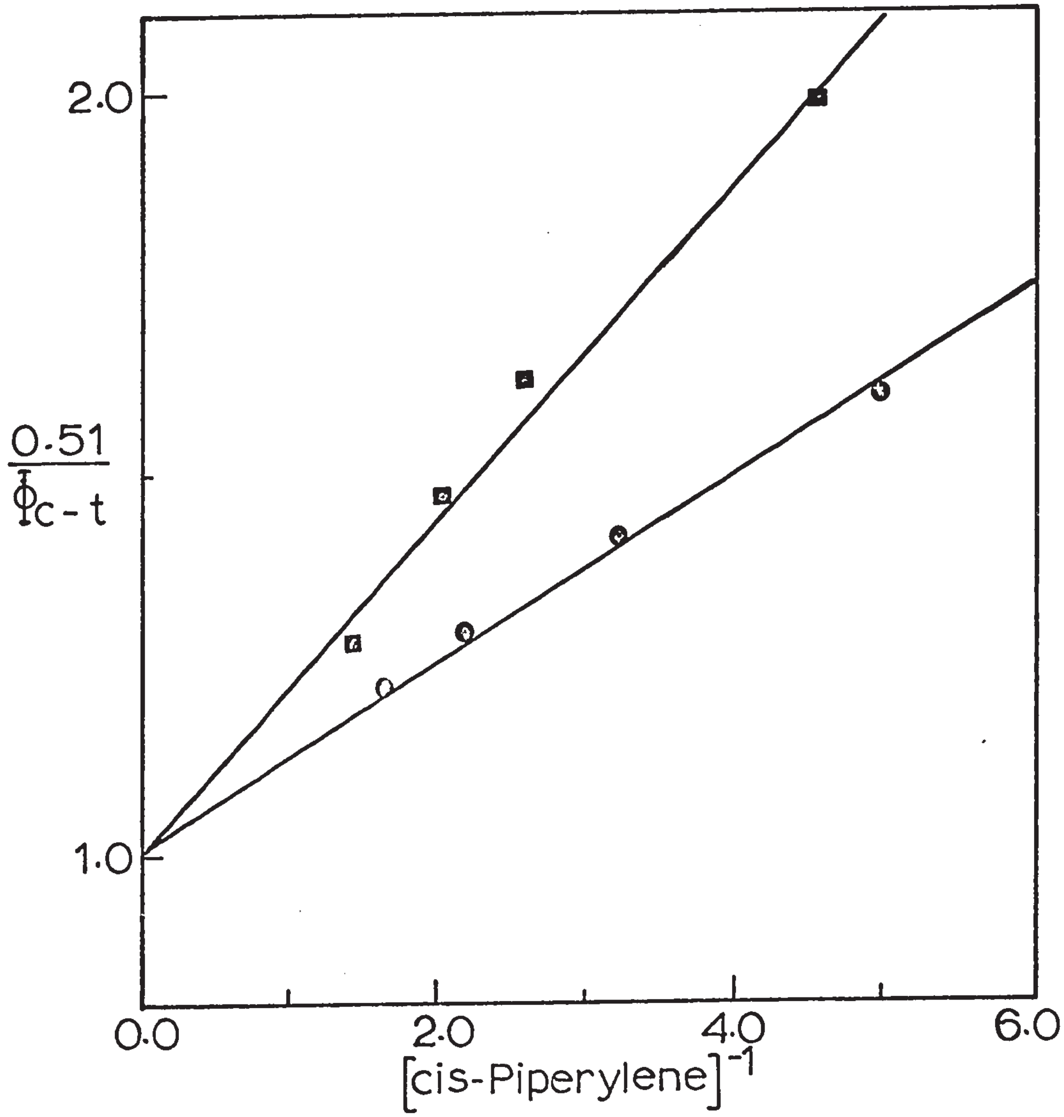


Fig.10 Variation in quantum yield of sensitized cis-trans isomerization of piperylene as a function of pentadiene concentration. Sensitizer : 0.2M Cyclopentenone ○ ; 0.2M Cyclohexenone ▣ .

slower than the rate of diffusion (49). The decay rate constant (k_d) derived from the triplet counting experiment at room temperature as measured by Dr. M.F. Tchir was found to be 7.3×10^8 sec^{-1} compared to the value of 5.0×10^8 sec^{-1} at -71°C. From these values it is concluded that there is no energy barrier for deactivation since k_d is approximately temperature independent. This conclusion is in agreement with the results obtained for cyclopentenone photoannelation reactions at various temperatures (see Chapter V). A similar conclusion has been reached for cyclohexenone.

CHAPTER V

DECAY AND REACTION RATE CONSTANTS

5.1 Introduction

It has been reported (9, 12b, 13a) that the quantum yield (or the quantum yield ratio) of cyclic enone photoannelation reactions reflect in a simple manner changes in reactivity of the substrate. Because of the occurrence of at least one energy-wasting process (reversibility of the intermediate) which includes the substrate the quantum yield does not, as has been assumed (9, 12b, 13a), reflect changes in rate of reaction. Actual measurements of the rates of cyclic enone photoannelation have been made in very few cases (41). Therefore, further kinetic studies were required to gain knowledge of the probable effects of substituents on the substrate. In addition, the external effects such as solvents or temperature on the decay and reaction rate constants of cyclic enone photoannelation were lacking in the literature. The following data are an attempt to rectify these difficiencies.

5.2 Derivation of the Kinetic Equations

A simple scheme for cycloaddition from the triplet state, can be written as follows, the inclusion of intermediate(s) which can dissociate to give starting materials was explained in the previous discussion (Chapter III):

K	$\xrightarrow{h\nu}$	^1K	I	1
^1K	$\xrightarrow{^1k_d}$	K + heat	^1k_d	2
^1K	$\xrightarrow{k_{isc}}$	^3K	k_{isc}	3
^3K	$\xrightarrow{k_d}$	K + heat	k_d	4
$^3K + 0$	$\xrightarrow{k_r}$	$[^3K...0]$	$k_r[0]$	5
$[^3K...0]$	$\xrightarrow{k_1}$	$K + 0$	k_1	6
$[^3K...0]$	$\xrightarrow{k_2}$	TM	k_2	7
TM	$\xrightarrow{k_3}$	Product	k_3	8
TM	$\xrightarrow{k_4}$	$K + 0$	k_4	9
$^3K + Q$	$\xrightarrow{k_q}$	$K + {}^3Q$	$k_q[Q]$	10

The symbols K, 0, Q, $[^3K...0]$ and TM refer to ketone, olefin, quencher, π-complex (exciplex) and tetramethylene (biradical), respectively. If it is assumed that $[^3K]$ achieves a steady state concentration, then an expression for the quantum yield of product (Φ), in the absence of quencher, can be derived

$$\Phi_0 = \left(\frac{k_{isc}}{^1k_d + k_{isc}}\right)\left(\frac{k_2}{k_2 + k_1}\right)\left(\frac{k_3}{k_3 + k_4}\right)\left(\frac{k_r[0]}{k_r[0] + k_d}\right) \quad \cdots\cdots \quad (5)$$

The term in the first parentheses is composed only of constants and corresponds to the quantum yield of intersystem crossing, Φ_{isc} which was determined (see Chapter IV) and found to be unity. Equation 5 can therefore be reduced to:

$$\Phi_0 = K\left(\frac{k_r[0]}{k_d + k_r[0]}\right) \quad \cdots\cdots \quad (6)$$

where $K = \left[\left(\frac{k_2}{k_1 + k_2}\right)\left(\frac{k_3}{k_3 + k_4}\right)\right]$, and represents that fraction of the intermediate(s) which gives the observed products, and the terms in parentheses represent the quantum efficiency of intermediate(s) formation from the triplet ketone. Inversion of this equation results in the more useful form:

$$\frac{1}{\Phi} = \frac{1}{K}\left(1 + \frac{k_d}{k_r}\frac{1}{[O]}\right) \qquad (7)$$

A linear relationship should be observed between $\frac{1}{\Phi}$ and $\frac{1}{[O]}$; the intercept would then represent K^{-1} and the slope would correspond to $\frac{k_d}{Kk_r}$. If the quenching step 10 is added to the reaction scheme, the quantum yield is given by equation 8.

$$\Phi = K\frac{k_r[O]}{k_d + k_r[O] + k_q[Q]} \qquad (8)$$

Division of equation 6 by equation 8 leads to the normal Stern-Volmer expression:

$$\frac{\Phi_0}{\Phi} = 1 + \frac{k_q[Q]}{k_d + k_r[O]} \qquad (9)$$

The slope of the Stern-Volmer plot is equal to $\frac{k_q}{k_d + k_r[O]}$.

Examination of the above reveals that we have three unknowns (k_r, k_d and k_q) but only two equations, 7 and 9. Consequently one of the rate constants must be evaluated independently in order to obtain values for the other two. Since k_r is a property of the system its value could not be determined outside of the system. The decay rate k_d should be a function of the ketone only (i.e. independent of the olefin), and as such might possibly have been determined. The triplet yield studies (see Chapter IV), however, indicated that the lifetime was too short to be measured by conventional microsecond flash apparatus. Since a nanosecond flash apparatus has become available, attempts to observe a transient absorption from cyclopentenone have been made, but have proved unsuccessful in agreement with our previously mentioned results (Chapter IV) and those of Wagner (21), that is, the triplet lifetime must be less than 10^{-8} sec. The only possibility that remained for the solution of 7 and 9 was the determination of k_q and this was the method used to obtain the results described in this thesis. The quenching rate constant k_q was assumed to be approximately equal to the diffusion rate constant k_{diff}. This can be calculated by means of the Debye equation (equation 4, Chapter IV). Some experimental justification for this approximation exists; i.e. the rate of quenching of 1-cyanonaphthalene fluorescence with 2,5-dimethyl-2,4-hexadiene (DMHD) in n-hexane at 20°C was found to be $1.5 \times 10^{10} M^{-1} S^{-1}$ (50), while the calculated rate constant, using the Debye equation is 1.8×10^{10}, so that the agreement is very good.

5.3 Variation of quantum yield of annelation with substrate concentration

As mentioned before, from equation 7 a linear relationship should be observed between the reciprocal of the quantum yield of addition and reciprocal of substrate concentration. The dilution experiments using different concentration of olefins were carried out. In Fig. 11 and 12 are given the plots of $\frac{1}{\Phi}$ vs. $\frac{1}{[0]}$ for cyclopentenone with cyclohexene and cis-dichloroethylene and cyclohexenone with cyclohexene in various solvent systems. The slope of the plot, corresponds to (k_d/Kk_r), and the intercept, represent $(\frac{1}{K})$, are given in Tables 6 and 7 for the studied systems.

Examination of the results reveals that K (which represents the fraction of the intermediate(s) leading to products) is, firstly dependent on the olefin used and, secondly, for the same substrate, is larger at lower temperatures. A similar result was obtained in this laboratory (41) where different intercepts ($\frac{1}{K}$) for dilution of the cyclopentenone-trans-3-hexene and cyclopentenone-cyclopentene systems were found.

An increase of K on lowering the temperature implies that proportionally more of the intermediate(s) go on to product rather than reversing to starting material. This results in an increase in the quantum yield as is found with cyclopentenone. In the reaction of cyclohexenone with cyclohexene in ether the value of K is unity at both 20 and -71°C, consequently the observed change in the quantum yield of this reaction must arise from changes in k_r and k_d (this point will be discussed later). Surprisingly, the value of K for the addition of cyclohexenone to cyclohexene was found to be solvent dependent (Table 7). This solvent effect cannot be rationalized either in terms of changes of the polarity or of the viscosity of the medium alone. Since in two solvents of widely different polarity (ether and cyclohexane) the value of K in both solvents is almost unity, while in two solvents of almost the same viscosity (ether and n-hexane) K was found to be different. Perhaps combination of both effects has an effect on the difference in the activation energies between decay and product formation from the intermediate.

5.4 Quenching studies (Stern-Volmer Plots).

The cycloaddition reactions of cyclic enones have been demonstrated to proceed through a triplet state (E_T 66-74 kcal/mole) (51). Therefore

Table 6. Dilution of the cyclopentenone-olefin reaction.

Olefin[a]	Temp., °C	Intercept[b]	Slope[b]	K	k_d/k_r
Cyclohexene	27	2.07	0.32	0.487	0.156
Cyclohexene	-71	1.41	0.57	0.714	0.407
cis-Dichloroethylene	27	2.79	1.37	0.360	0.490

[a] Diethyl ether was used as solvent.

[b] From a least squares calculation.

Table 7. Dilution of the cyclohexenone-cyclohexene reaction.

Solvent	Temp., °C	Intercept[a]	Slope[a]	K	k_d/k_r
Ether	20	0.984	10.67	1.019	0.88
Ether	-71	0.960	19.87	1.040	20.66
n-Hexane	20	1.280	7.73	0.781	6.03

[a] From a least squares calculation.

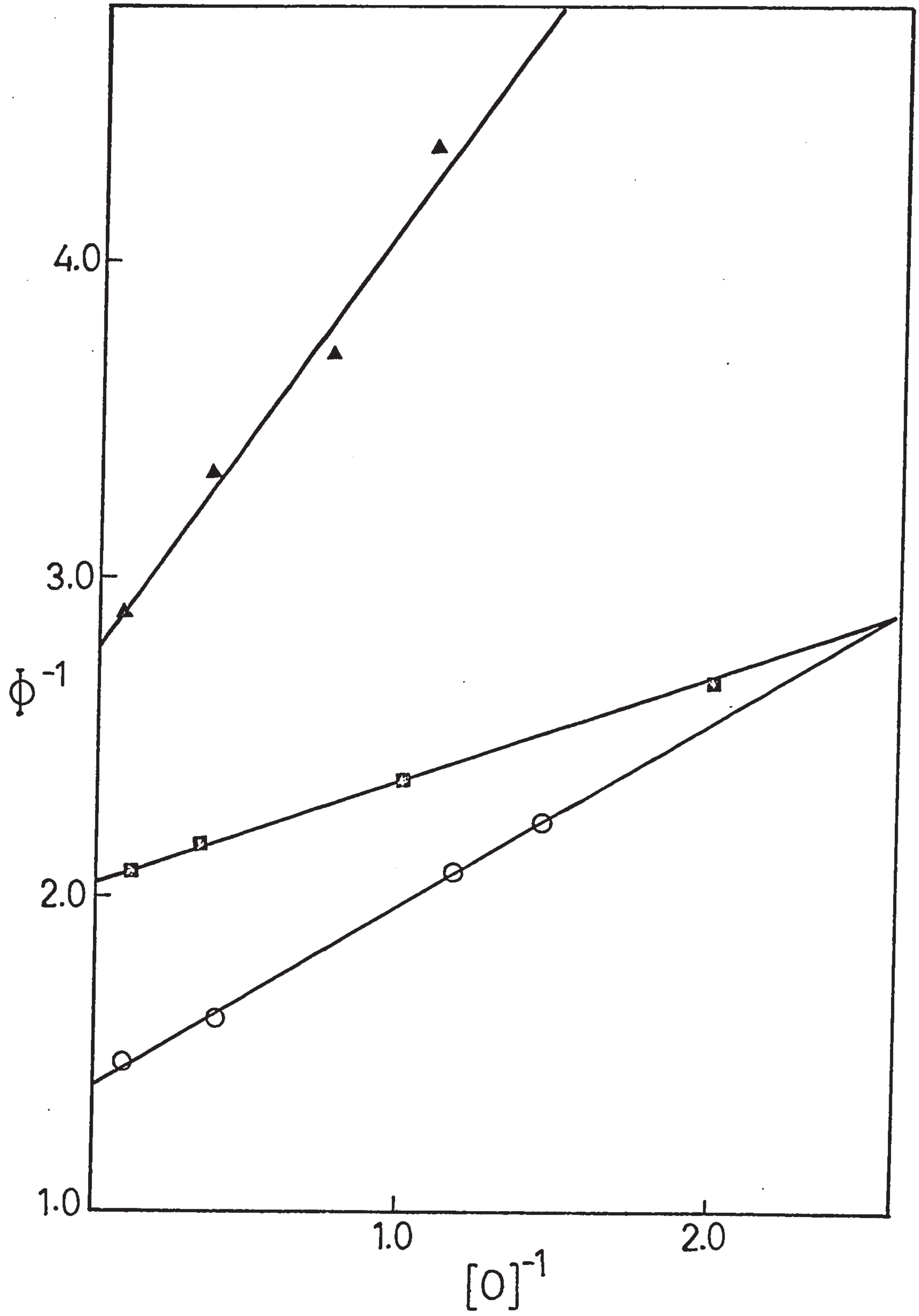


Fig.11 Dilution of Cyclopentenone-Olefin Reaction,
○ Cyclohexene in ether at 25°C.
▣ Cyclohexene in ether at -71°C.
▲ cis-Dichloroethylene in ether at 25°C.

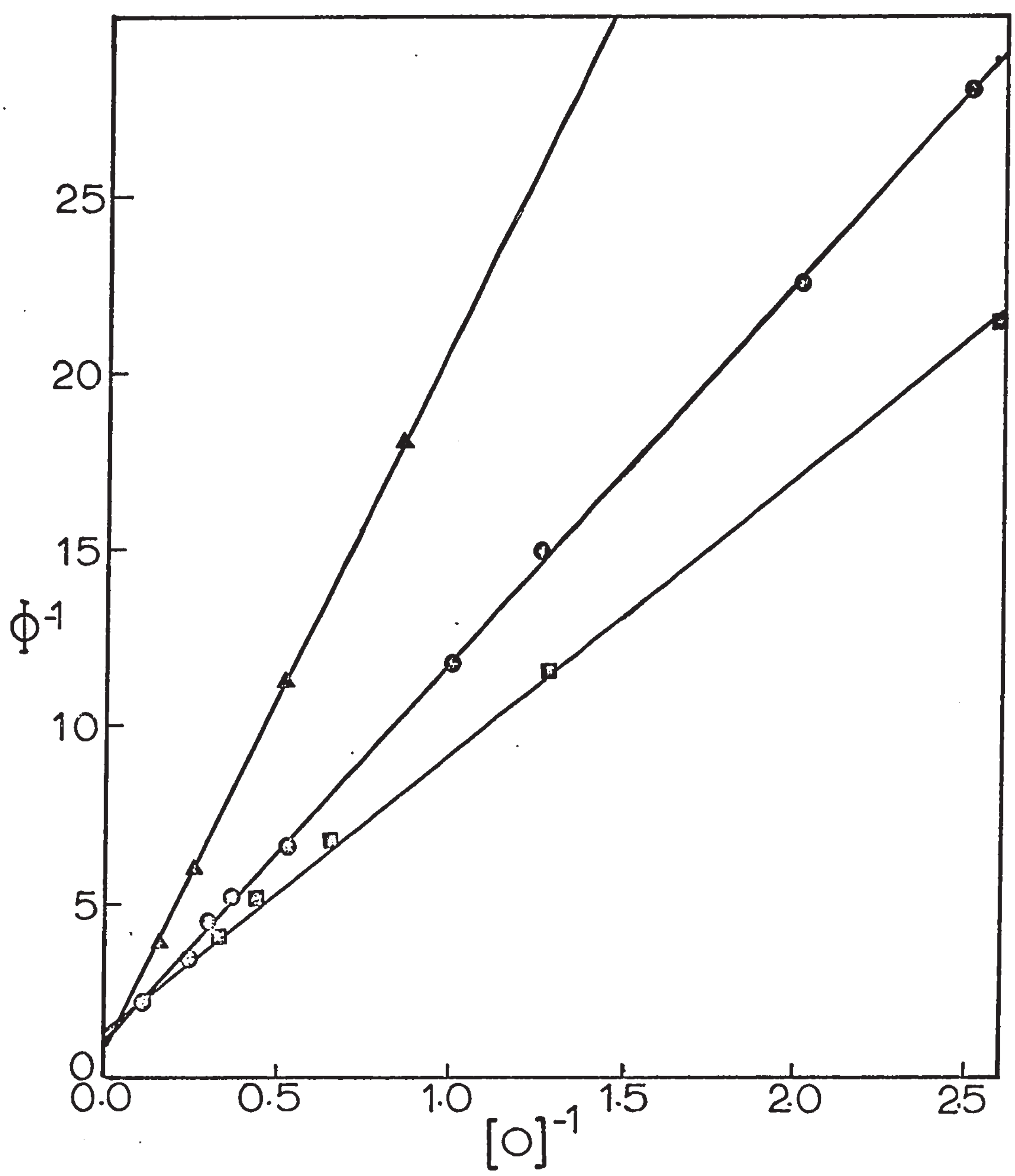


Fig.12 Dilution of Cyclohexenone-Olefin Reaction,
■ Cyclohexene in ether at 20°C.
○ Cyclohexene in ether at -71°C.
▲ Cyclohexene in n-hexane at 20°C.

dienes (E_T ~53-60 kcal/mole) should be efficient quenchers. Indeed, a powerful tool in mechanistic photochemistry, especially that of enones, has been the use of dienes such as 1,3-pentadiene and 1,3-cyclohexadiene as quantitative quenchers of the excited ketones of E_T > 60 kcal/mole. However, the use of dienes might be somewhat questionable since it has been found that cyclopentenone and cyclohexenone gave adducts with some dienes (52) as did 4,4-dimethyl-2-cyclohexenone (53) and, as recently reported, benzophenone (54) (E_T = 69 kcal/mole). In the latter case, it has been demonstrated that the photocycloaddition of benzophenone to dienes occurs by a mechanism involving attack of triplet excited benzophenone on ground state diene, with a rate constant of $1.5 \times 10^6 M^{-1} sec^{-1}$ and a quantum yield of the order of 3×10^{-4} at 0.5 M diene concentration, and that this process is in competition with the diffusion controlled quenching of triplet benzophenone by the conjugated diene. It has been noted recently (49) that dienes do not give reliable results in quantitative studies at high concentration as shown by curvature of the Stern-Volmer plots.

The plots in Figs. 13 and 14 show no deviation from linearity and therefore this problem seems to be a minor one in enone cycloaddition. 2,5-Dimethyl-2,4-hexadiene (DMHD) was chosen as the quencher in the rate determinations for several reasons; ease of quantitative handling, a more efficient quencher in enone rearrangement (55), and a lower probability of chemical interaction.

As mentioned before, the slope of the Stern-Volmer plot represents ($k_q/k_d + k_r[0]$) (equation 9). The value of k_q was determined from the Debye equation (equation 4, Chapter IV) using the measured viscosity of the Stern-Volmer solution.

Using the values of the dilution slopes and intercepts (Tables 6 and 7), the slope of the S-V plots (Tables 8 and 9) and the calculated quenching rates, it is possible to obtain k_r and k_d under a variety of experimental conditions for cyclopentenone and cyclohexenone with various olefins (see Table 10).

The rate constants obtained may be compared with that of $k_r = 6.6 \times 10^8 M^{-1}S^{-1}$; $k_d = 7.0 \times 10^7 S^{-1}$ for cyclopentenone dimerization and $k_r = 1.1 \times 10^8 M^{-1}S^{-1}$; $k_d = 3.5 \times 10^8 S^{-1}$ for cyclohexenone dimerization obtained by P.J. Wagner (21), $k_r = 4.3 \times 10^7 M^{-1}S^{-1}$; $k_d = 1.3 \times 10^8 S^{-1}$ obtained by O.L. Chapman (56) for isophorone dimerization. These values agree qualitatively with those in Table 10.

5.5 Interpretation of the Kinetic Results.

5.5.1 The effect of temperature on the quantum yield.

a. Cyclopentenone systems.

With the rate constants available, it is possible to determine the value of the term:

$$(k_r[0]/k_d + k_r[0])$$

in equation 6, which represents the quantum efficiency of intermediate formation from the triplet excited enone. It is evident that this term in equation 5 is, at the concentration of olefin and temperature used, greater than 0.9 for all cyclopentenone reactions. In fact it approaches unity when the olefin is used as solvent. It is obvious that the quantum yield of product formation depends entirely on K, and more specifically, on the relative rates of decay and product formation from the intermediate. The large changes in quantum yield on lowering the

Table 8. Results of the Stern-Volmer plots for cyclopentenone.

[Olefin]	Temp., °C	Slope[a]	Intercept[a]	$k_q \times 10^{-10}$[b] $M^{-1}S^{-1}$
Cyclohexene[c]				
1.66	27	8.72	1.03	2.00
2.88	-71	3.63	1.18	0.36
cis-dichloroethylene 2.656	20	18.8	1.02	1.89

a From least squares calculation.

b Calculated from Debye equation using measured viscosities.

c Diethyl ether was used as solvent.

Table 9. Results of the Stern-Volmer plots for cyclobexenone-cyclohexene system.

[Olefin]	Solvent	Temp., °C	Slope[a]	Intercept[a]	$k_q \times 10^{-10}$[b] $M^{-1}S^{-1}$
1.865	Ether	20	23.66	0.979	2.20
2.090	Ether	-71	13.94	0.999	0.45
1.825	n-Hexane	20	25.75	1.006	1.80

a From a least squares calculation.

b Calculated from the Debye equation using measured viscosities.

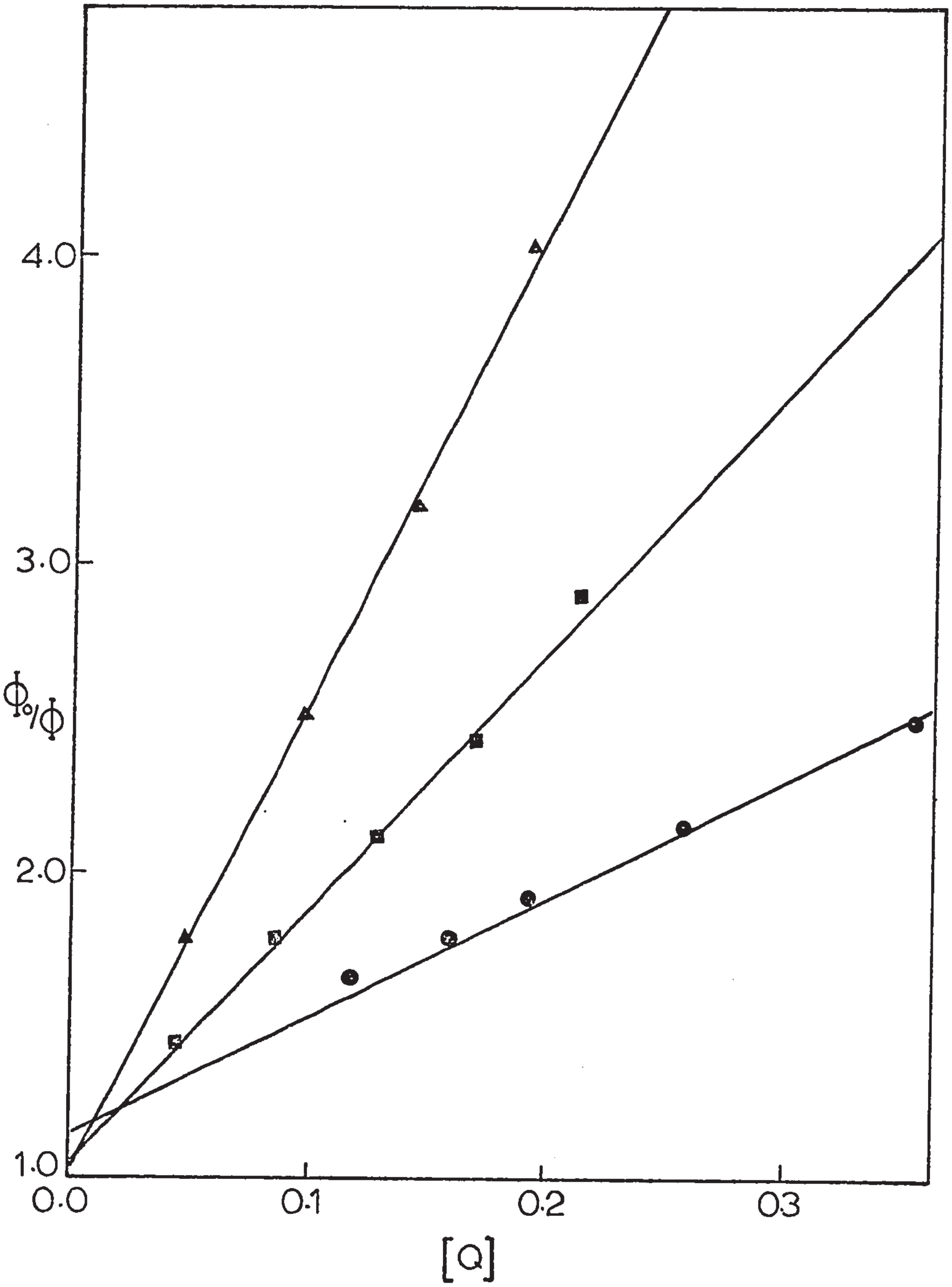


Fig.13 Quenching of Cyclopentenone-Olefin Reaction with (DMHD) in ether,
● Cyclohexene (2.88M), at -71°C,
■ Cyclohexene (1.66M), at 27°C,
▲ cis-Dichloroethylene (2.656M), at 20°C.

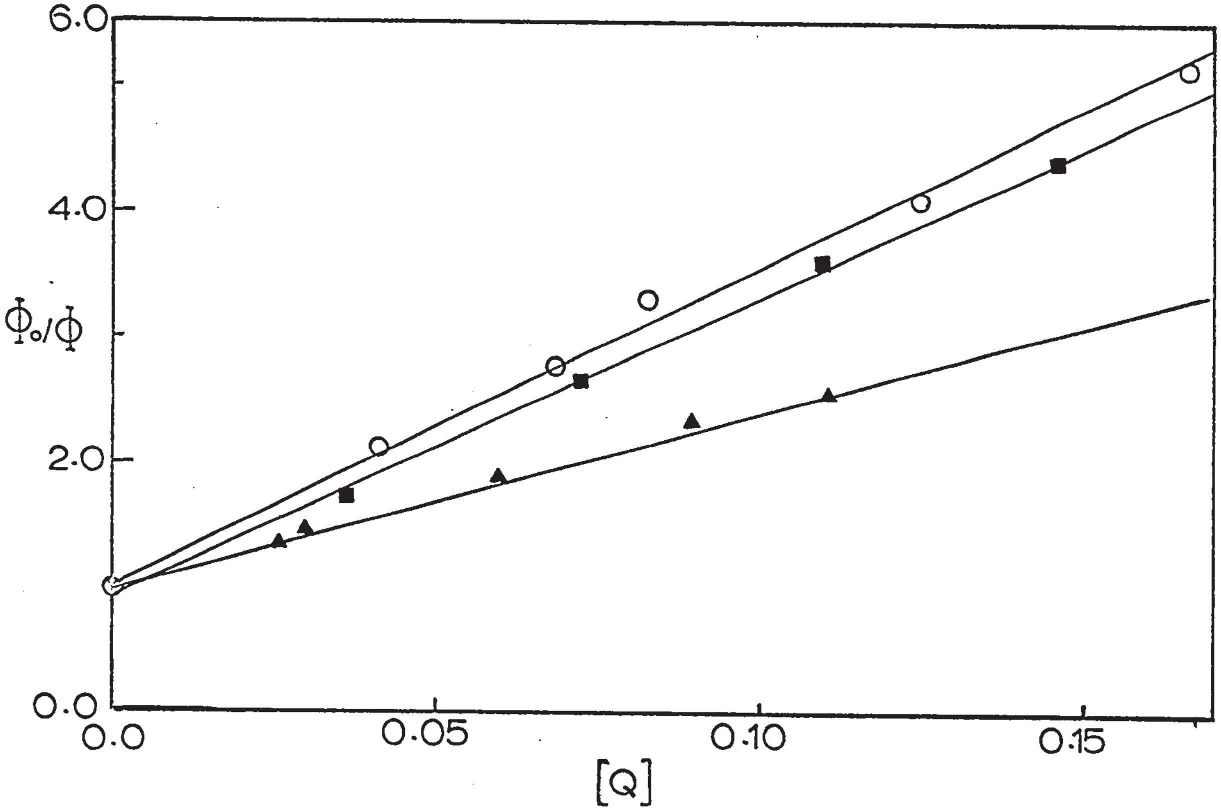


Fig.14 Quenching of Cyclohexenone-Cyclohexene Reaction with (DMHD), ▲ Cyclohexene (2.09 M) at -71° in ether ■ Cyclohexene (1.86 M) at 20° in ether, ○ Cyclohexen (1.82 M) at 20° in n-hexane.

Table 10. Rate Constants.

Ketone	Olefin	Solvent (temp., °C)	$k_q \times 10^{-10}$ $M^{-1}S^{-1}$	$k_d \times 10^{-7}$ S^{-1}	$k_r \times 10^{-8}$ $M^{-1}S^{-1}$
Cyclopentenone	Cyclohexene	Ether (27)	1.98	19.0	12.0
	Cyclohexene	Ether (-71)	0.36	13.0	3.2
	Cyclohexene[a]	Cyclohexane (20	0.66	8.0	5.2
	Cyclopentene[b]	Hexane (20)	1.90	22.0	19.0
	trans-3-Hexene[b]	Pentane (20)	2.60	8.0	3.9
	cis-Dichloro-ethylene	Ether (20)	1.89	19.5	4.0
	3-Hexyne[c]	Hexane (20)	1.97	2. 3	1.76
	3-Hexyne[c]	Ether (20)	2.20	6.9	8.5
				$k_d \times 10^{-8}$ S^{-1}	$k_r \times 10^{-7}$ $M^{-1}S^{-1}$
Cyclohexenone	Cyclohexene	Ether (20)	2.20	7.9	7.6
	Cyclohexene	n-Hexane (20)	1.80	5.4	8.9
	Cyclohexene[b]	Cyclohexane (20)	0.80	1.4	2.5
	Cyclohexene	Ether (-71)	0.46	2.95	1.48
	3-Hexyne[c]	Heptane (20)	1.66	3.20	2.30

[a] Determined in conjunction with Dr. M.F. Tchir.

[b] Determined by Mr. A.A. Nicholson.

[c] Determined by Mr. M.C. Usselman.

temperature, must result from a change in the partition function K and the product (slope × 2.303) of the plots given in (Fig. 8 page 38) would represent the difference in the activation energies between product formation and reversal to starting material. If it is assumed that the intermediate is a 1,4-biradical and as mentioned before (p. 33) calculation by O'Neal and Richardson has indicated that the cyclization of a tetramethylene to cyclobutane is approximately isoenergetic with opening to two ethylenes (~6.6 kcal/mole). Thus, for the same enone, very small changes in the structure of substrate greatly affect the partition function, which will depend on the stability of the biradicals (steric effect or conformational preferences) and the ease of formation of the second bond.

b. Cyclohexenone system.

For the reaction of cyclohexenone with cyclohexene it has been mentioned that the partition function K is unity at both 20 and -71°C. It is obvious that the changes in the quantum yield in this case must arise from change of the term:

$$k_r[O] / k_d + k_r[O]$$

of equation 6. This term decreases by 25% which is comparable to the observed decrease in quantum yield. The difference in activation energies obtained (see page 40) would represent that between the decay and reaction of the excited triplet state of cyclohexenone. It must be noted that the value of K for cyclohexenone systems is not always unity, for example, in the addition to 3-hexyne K = 0.13 and in the dimerization of isophorone K = 0.33 (56).

A slight decrease in k_d was observed as the temperature was lowered from 27 to -71°C for both cyclopentenone and cyclohexenone addition to cyclohexene in ether. These results agree with those obtained from triplet counting experiments (page 46) and are similar to those reported by Zimmerman for cyclohexenone derivatives(57). The energy of activation for decay of the triplet enone is extremely small (~0.5 kcal/mole).

5.5.2 Electrophilicity of cyclic enone reactive species.

It has been reported that the cyclic enone reactive species is moderately electrophilic. This conclusion was based on competition experiments. It has been found by Corey and co-workers (9) that the relative rate of addition of cyclohexenone to 1,1-dimethoxyethylene is slightly more than four times that to cyclopentene and much more than that to acrylonitrile. However, because of the occurrence of an energy-wasting process which includes the substrate, the quantum yield ratio obtained in competition experiments does not, as has been assumed (9), reflect the rate of a reaction. The data in (Table 10) show that the rate of cyclopentenone addition to cyclohexene or cyclopentene is about 4 to 5 times that to _cis_-dichloroethylene. It must also be noted that the rate of cyclopentenone addition to 1,1-dimethoxyethylene was found to be $6 \times 10^9 M^{-1} S^{-1}$ (58) supporting the early suggestion that the reactive species is moderately electrophilic. On the other hand, the rate of cyclopentenone addition to _trans_-3-hexene is of the same order of magnitude as that with _cis_-dichloroethylene, but in this particular case, the comparison might not be valid since steric factors might be important with _trans_-3-hexene.

CHAPTER VI

STEREOCHEMISTRY

Addition of a cyclic enone to an olefin is known (9) to afford a number of stereoisomers. For example, the addition of cyclopentenone to 1,1-disubstituted olefins (the two substituents are the same) should give two stereoisomers with the substituents at either the 6 or 7-position (reaction 1). The addition of cyclopentenone to mono-, or vic-di- or tri-substituted olefins (reactions 2, 3 and 4; the substituents on each olefin being the same), however, should afford 4 stereoisomers, while with cyclic olefins mainly two types of stereoisomers (syn- and anti-configurations) would be obtained (reaction 5). If the cyclic olefin ring is larger than five carbons, a <u>trans</u>-ring junction is also possible to give a total of 4 isomers (reaction 6). It is to be noted that so far <u>no</u> cyclopentenone photo adduct having a <u>trans</u>-5/4 ring jucntion has been isolated. On the other hand, in the case of cyclohexenone addition to olefins where a <u>trans</u> 6,4-fusion is possible (see introduction page 6) the number of <u>expected</u> isomers would be double that obtained with cyclopentenone[*]. It has also been found that base treatment of the <u>trans</u> 6,4 fused isomer induced isomerization to the corresponding <u>cis</u> 6,4 fused

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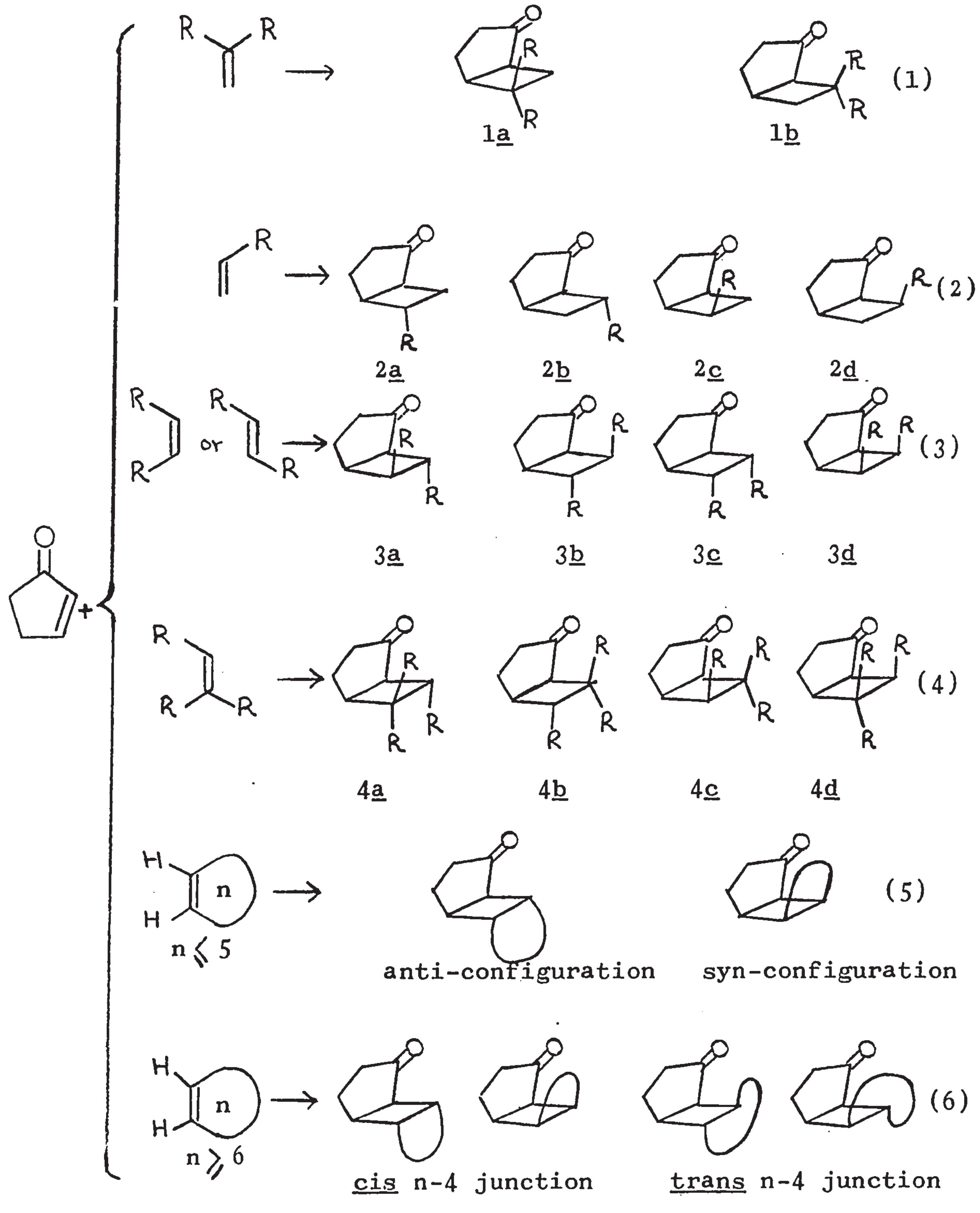
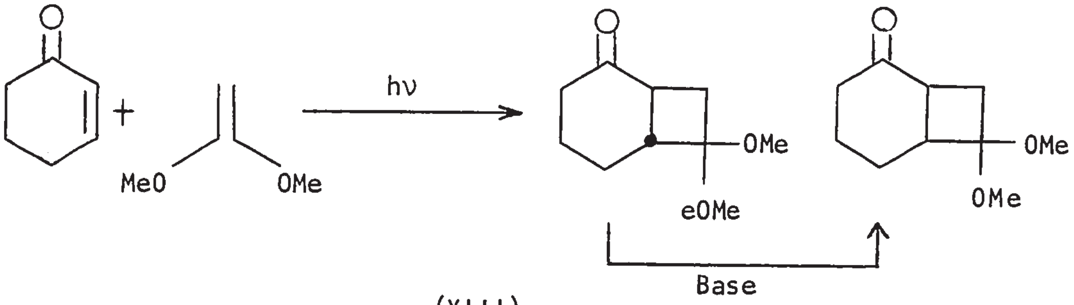
[*] Experimentally, in the case of cyclohexenone the number of obtained isomers never reaches that expected, in contrast to the cyclopentenone system where normally all the expected isomers are obtained.


R
R
1a
1b
(1)
2a
2b
2c
2d
(2)
or
3a
3b
3c
3d
(3)
4a
4b
4c
4d
(4)
H
H
n
n ⩽ 5
anti-configuration
syn-configuration
(5)
H
H
n
n ⩾ 6
cis n-4 junction
trans n-4 junction
(6)

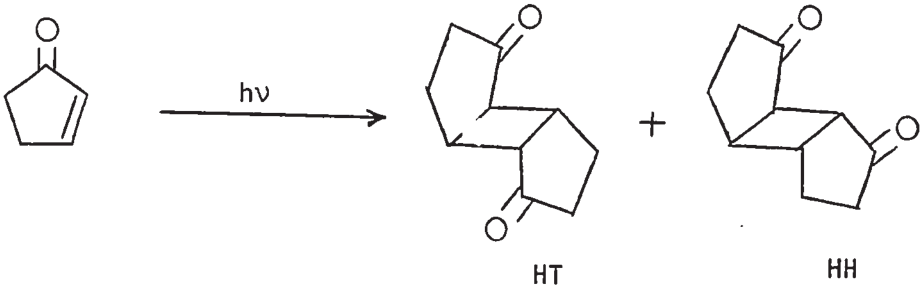
(XII)

isomer (reaction XIII) (9).



(XIII)

Eaton has shown that in the adduct of cyclopentenone with cyclopentene the two five membered rings are in the anti-configuration (4), which is also true for the HT and HH cyclopentenone dimers (4) (reaction XIV. In fact these were the first attempts to determine the stereochemistry of photo adducts.



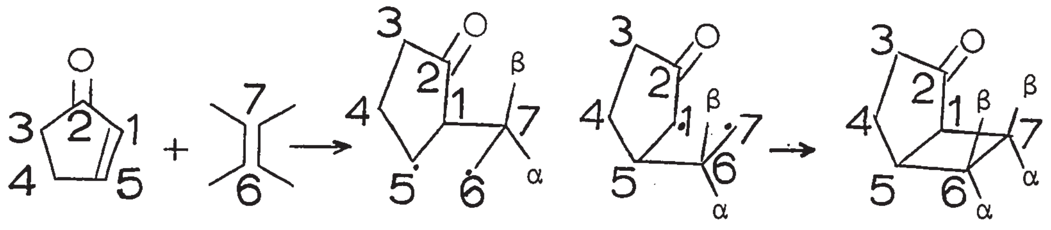
(XIV)

It was decided that initial studies would concentrate on either cyclopentenone or cyclohexenone. Of the two, cyclopentenone seemed the more desirable since it had been shown to yield fewer isomeric products, and, more importantly, the n.m.r. spectra of the cyclopentenone adducts would be easier to interpret than those of the cyclohexenone adducts where the six-membered ring is conformationally labile.

We have examined the product distributions and the effect of solvent and temperature on the cycloaddition of cyclopentenone and a variety of chlorinated olefins. The structure and stereochemistry of the products were determined in an attempt to establish which bond in the cyclobutane ring is formed initially and whether complete equilibration of the 1,4-biradical (tetramethylene) is attained before the formation of the second bond.

The structural assignments are discussed separately in section 6.1.

In the following discussion, it is helpful to use the numbering system given in scheme below, in which the precursor molecules (i.e. olefin and enone) and intermediates are numbered in the same manner as the products.



B C D

The simultaneous formation of both cyclobutane bonds (C_1-C_7 and C_5-C_6 bonds) could occur with storage of the triplet excitation energy in the ketone part of the molecule (see D). This would lead to photo adducts D where the stereochemistry at the olefin part is preserved. However, as pointed out earlier (see Chapter III), there is good evidence that a biradical precursor is involved in the cycloaddition. Nevertheless, one cannot exclude the possibility that part of the reaction is proceeding via a concerted mechanism. On the other hand, if we assume the intermediacy of a 1,4 biradical, the approach of the excited enone to the alkene could lead to bond formation at C_1-C_7 (so called α-attack) or at C_5-C_6 (β-attack) and, therefore the configuration at C_7 for the biradical B, or at C_6 for the biradical C, will be fixed for that portion of the tetramethylene which goes to products. The configuration at the second-point of union will depend on the relative rates of ring closure and C_6-C_7 bond rotation. Stephenson (43) has argued that if the triplet tetramethylene (1,4-biradical) is presumed as an intermediate, the rate of bond rotation will be faster than the rate of spin inversion and subsequent ring closure. Therefore, a slow ring closure would allow for conformational equilibration.

The product distributions obtained for the addition of cyclopentenone to a variety of chlorinated olefins under various experimental conditions are given in Tables 11, 12, 13 and 14.

Dilling (59) reported the formation of only three of the possible stereoisomeric adducts from the reaction of cyclopentenone and cis- and trans-dichloroethylene. We find, however, that a fourth isomer is also present in the reaction mixture and is the last to be eluted on the glc columns used. Its structure was determined and shown to be that of the missing isomer **3d**.

It should be noted that the product distributions from both cis- and trans-dichloroethylene reported by Dilling (59) are in excellent agreement with those expected for initial C_5-C_6 bond formation (β-attack) and complete conformational equilibration in the biradical precursor, only if the yield of the fourth isomer is zero or negligible. As can be seen from our results (Chart I), the agreement is not very good,

Table 11. Product distribution, and structures of cyclopentenone vic-dichloroethylene adducts.

Olefin	Solvent	Temp., °C	Product distribution, %*			
			3a	**3b**	**3c**	**3d**
cis-Dichloroethylene	neat (13.2M)	25	49.30	11.70	19.44	19.56
	ether	25	50.20	11.17	19.56	19.07
	ether	-75	55.97	8.03	13.26	22.73
trans-Dichloroethylene	neat (13.2M)	25	17.71	22.10	54.68	5.50
	ether	25	18.35	23.04	52.62	6.00
	ether	-75	14.85	10.83	69.94	4.28

*Each measurement was the average of three runs.

[Cyclopentenone] = 0.3M [vic-dichloroethylene] = 6.1M.

Table 12. Product distribution, and structures of cyclopentenone vinyl chloride adducts.

Solvent	**2a**	**2b**	**2c**	**2d** %
Ether (-75°C)	30.80	32.80	30.70	5.67

[Cyclopentenone] = 0.3M [vinyl ethylene] = 6M

Table 13. Product distribution, and structures of cyclopentenone gem-dichloroethylene adducts.

Ketone(M)	Olefin(M)	Solvent	Temp., °C	Prod.	Distr., %
				1a	**1b**
0.30	5	Cyclohexene	25	84.55	15.44
0.25	5	Ether	25	84.19	15.81
0.25	5	CH_3CN	25	70.65	29.35
0.25	10	Neat	25	80.51	19.49
0.25	10	Neat	-75	85.38	14.61

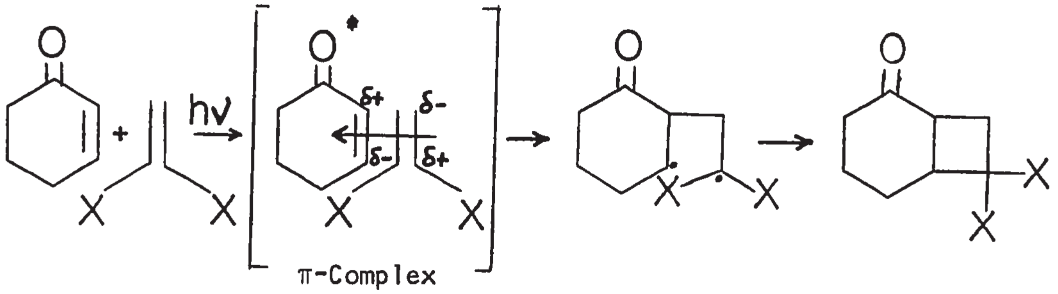
Table 14. Product distribution, and Structures of Cyclopentenone trichloroethylene adducts.

Solvent	Solvent Dielectric Constant	**4a**	**4b**	**4c**	**4d** %
Cyclohexene	2.22	28.00	23.13	32.56	16.31
Ether	4.33	25.92	22.13	35.81	16.12
Acetonitrile	37.5	23.71	21.42	41.15	13.71
Acetic acid	6.5	28.54	16.42	34.58	20.45
Ether (-75°C)		39.32	13.13	36.94	10.56

[cyclopentenone] = 0.25M [trichloroethylene] = 5M and for the reaction at -78° becomes even worse when the yield of the fourth isomer is taken into account. The deviation from equal partition of biradicals 7 and 9 and from biradicals 8 and 10 can not be interpreted in term of restricted rotation, since partition of biradical 7 would be expected to afford more of isomer 3c than that obtained from partition of biradical 9, which is not the case. By assuming that some α-attack occurs as will be discussed later, it was found that the results could be interpreted.

The current views of the orientation effect observed in the addition of excited cyclic enones to olefins are as follows:

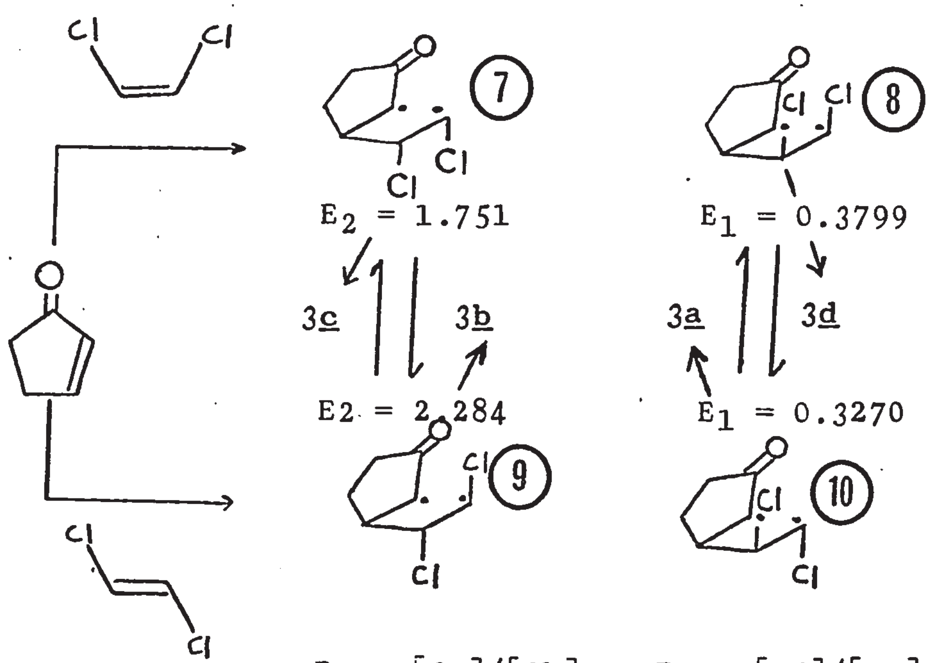
a. Corey in (1964) suggested (9) that an initial complex is formed between an excited state of the ketone and the olefin. The orientation of the enone and substrate in the complex, and subsequently in the adduct, is governed mainly by the electronic distribution in the substrate, with the more electron-rich carbon of the substrate being adjacent to the α-carbon of the enone (reaction XV). The orientation observed in the major photo-adduct of cyclohexenone with isobutylene, 1,1-dimethoxyethylene and many other olefins could be adequately explained by this picture. The orientation effect, however, was rather less marked when cyclopentenone was added to propylene (10) (see reaction XVI).



(XV)

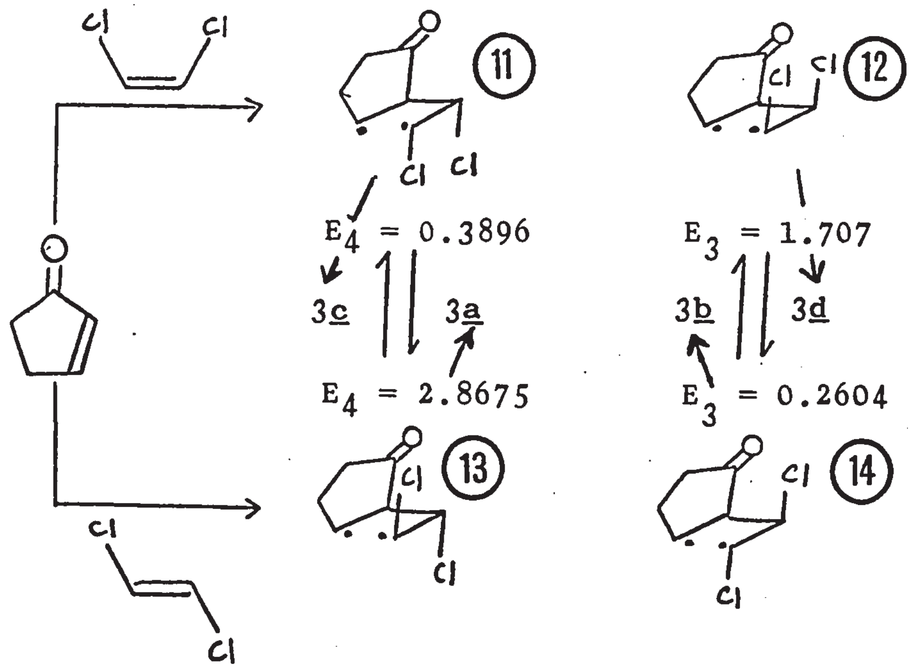
Chart I (at RT, in ether)

β-Attack:



E_2 = [3c]/[3b] ; E_1 = [3d]/[3a]

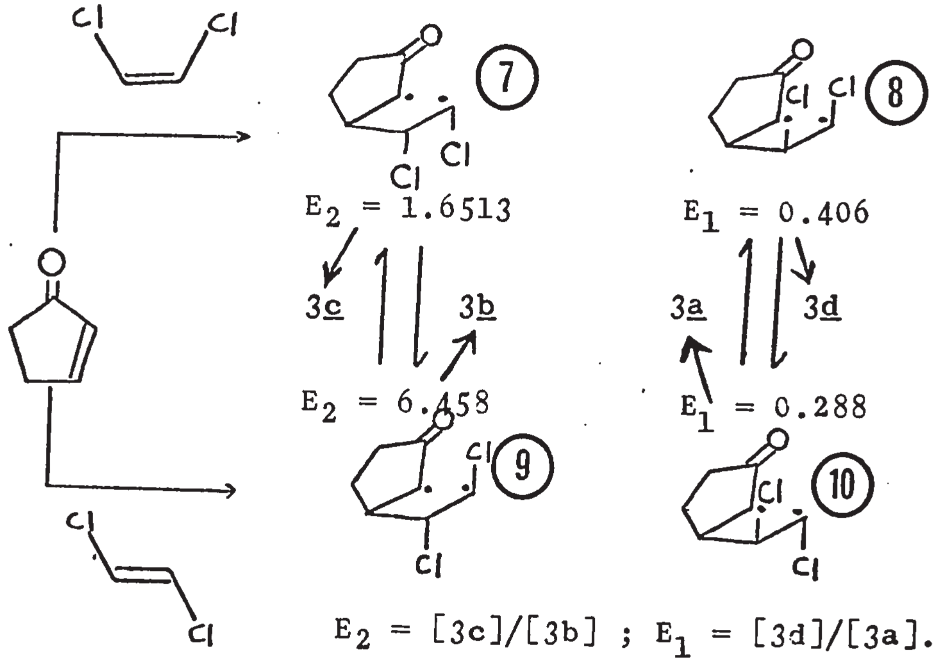
α-Attack:



E_4 = [3c]/[3a] ; E_3 = [3d]/[3b]

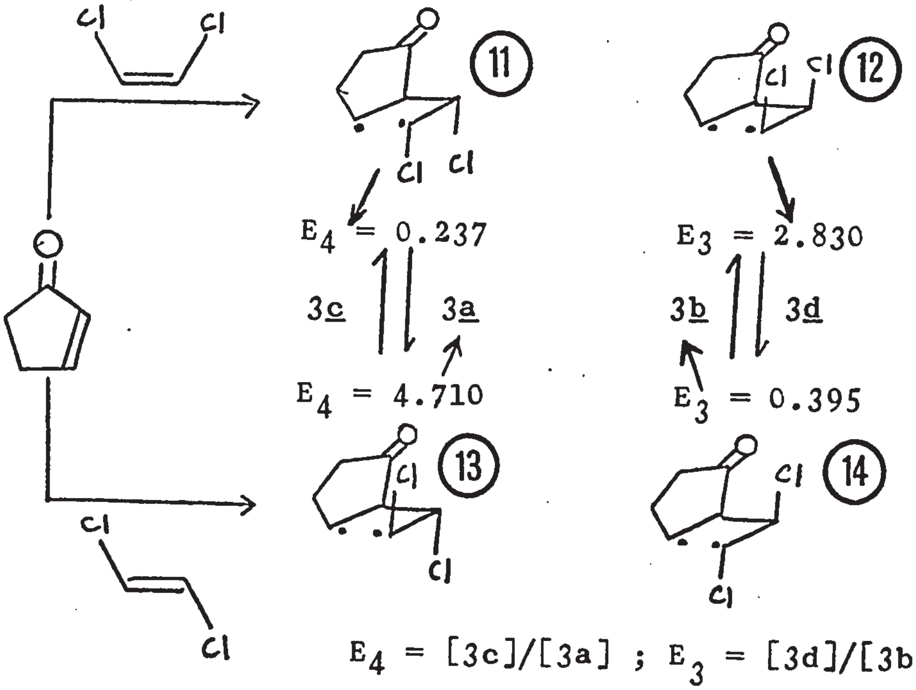
Chart II (at -75°C, in ether)

β-Attack:

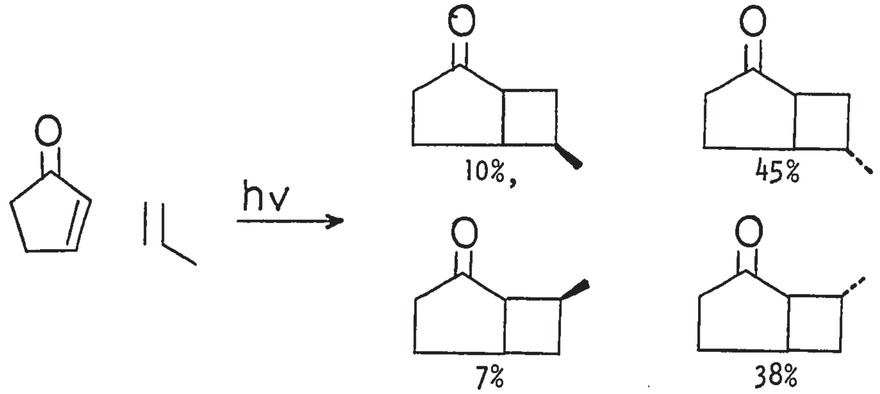


$E_2 = [3c]/[3b]$; $E_1 = [3d]/[3a]$.

α-Attack:



$E_4 = [3c]/[3a]$; $E_3 = [3d]/[3b]$.



(XVI)

The photocycloaddition of cyclopentenone to the various halogenated olefins gave orientational preferences which are not explicable in terms of the Corey hypothesis e.g. in the addition of vinyl chloride the HT/HH ratio is 1.5 and that for trichloroethylene is 0.7, which indicates that the orientational preference is not determined in the π-complexes and subsequently in the adducts. This, however, requires an α-attack, and, as we will see later the formed biradical in this case will tend to revert to the starting material.

b. Mayo and Challand (60) demonstrated that another orientation-controlling factor exists; they suggested that the solvent-dependent ratio of HT/HH adducts (15/16) (see reaction XVII) was due to an interaction of the overall dipoles of the reacting molecules. The proportion of 16 increases with the dielectric constant of the solvent, thereby showing the insulating effect of the solvent on the dipole interactions. This might be one factor which operates in the case of chlorinated olefins but certainly is not the major one. The reactive species of excited cyclopentenone is believed to be the π,π^* triplet state (21 and 35), the dipole moment of which is not known. MO calculations obtained for relaxed and bent $^3\pi,\pi^*$ acrolein indicate that the dipole moment is expected to be small and in the same general direction as in the ground state.† Therefore,

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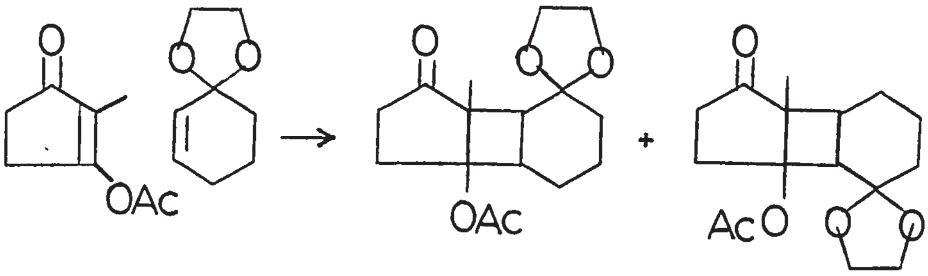
†See page 75.



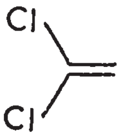
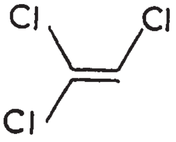
	HT 15	HH 16	Ratio HT/HH
Cyclohexane	98	2	49.0
30% w/w olefin in Cyclohexane	60	40	1.5
Acetonitrile	50	50	1.0

(XVII)

a large solvent effect on product distribution are not expected. Our results with 1,1-dichloroethylene and trichloroethylene show a decrease in the ratio of HT/HH as the solvent polarity increases. It must be noted that it was an experimental necessity to use the olefins in large excess, and they themselves have large dielectric constants which will affect the polarity of the media. However, the size of the change observed is not as large as that observed by Mayo and co-workers (67) and by Eaton (10) for cyclopentenone dimerization (see Table 16).

c. The Bauslaugh hypothesis (6): which states that the more stable intermediate biradicals return at a faster rate to the ground state starting materials. Consequently the less stable biradicals give a greater

Table 15. Ratios of HT/HH adducts of cyclopentenone and 1,1-dichloroethylene or trichloroethylene.

[Cyclopentenone]		[Olefin]	Solvents, (°C)	HT	HH %	Ratio
0.25		5	Ether, (-75)	85.40	14.60	5.85
0.30		5	Cyclohexane (RT)	84.55	15.44	5.48
0.25		5	Ether (RT)	84.19	15.80	5.33
0.25		10	neat (RT)	80.50	19.50	4.13
0.25		5	CH_3CN (RT)	70.65	38.50	2.41
0.25		5	Ether (-75)	50.00	50.00	1.00
0.25		5	Cyclohexane (RT)	44.30	55.70	0.80
0.25		5	Ether (RT)	42.00	57.90	0.72
			CH_3CN (RT)	37.40	62.60	0.60

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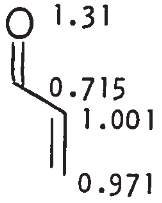
*Calculations of the electron distribution in the triplet excited state of acrolein have been done by Mr. R. West at the University of Western Ontario which show that $^3\pi,\pi^*$ should have a very small dipole moment compared to $^3n,\pi^*$.



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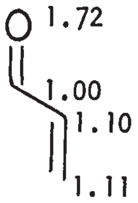
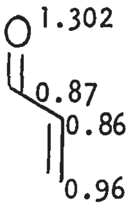
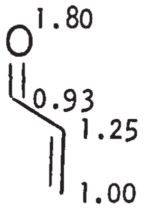


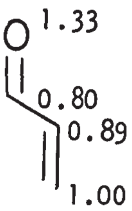
$^3n,\pi^*$



$^3\pi,\pi^*$



$^3n,\pi^*$



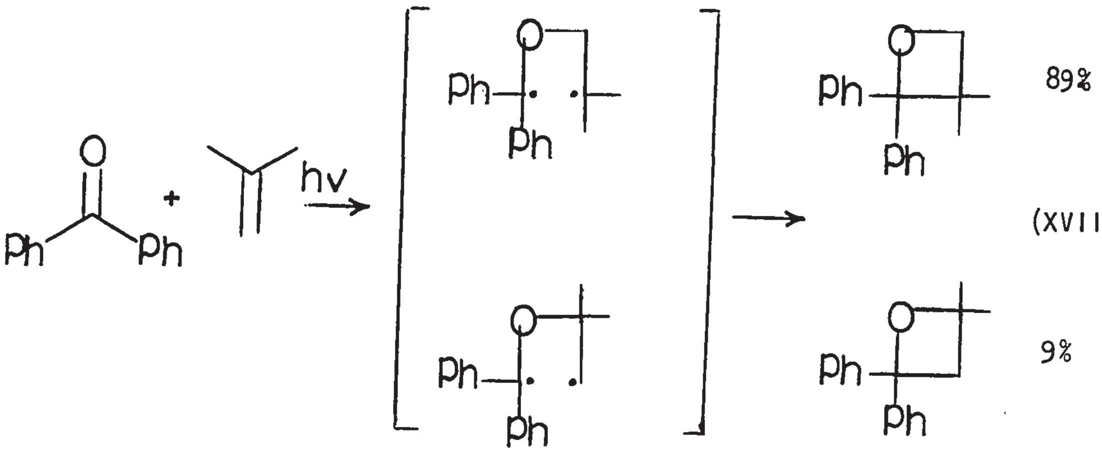
$^3\pi,\pi^*$

90° bent around C=C

Table 16. Effect of solvent in the photodimerization products of cyclopentenone (1.0 M).

Solvent	HT	HH%	Ratio
Benzene	77	23	3.35
Ethylacetate	70	30	2.33
Methanol	59	41	1.44
Neat (12 M)	57	43	1.32

amount of product. His hypothesis was based on the fact that, in the reaction of halogenated olefins with dienes, a greater degree of isomerization of the diene is obtained the stabler the intermediate biradicals formed from it and this he attributed to biradical reversion. Bauslaugh's hypothesis does not operate in the case of oxetane formation, where the orientation of the substituent appears to be governed by the relative stabilities of the intermediate biradicals. Arnold (61) has shown that photoaddition of benzophenone to isobutylene leads to both isomers and that the isomer which is formed from the more stable biradical precursor predominates (see reaction XVIII).



(XVIII)

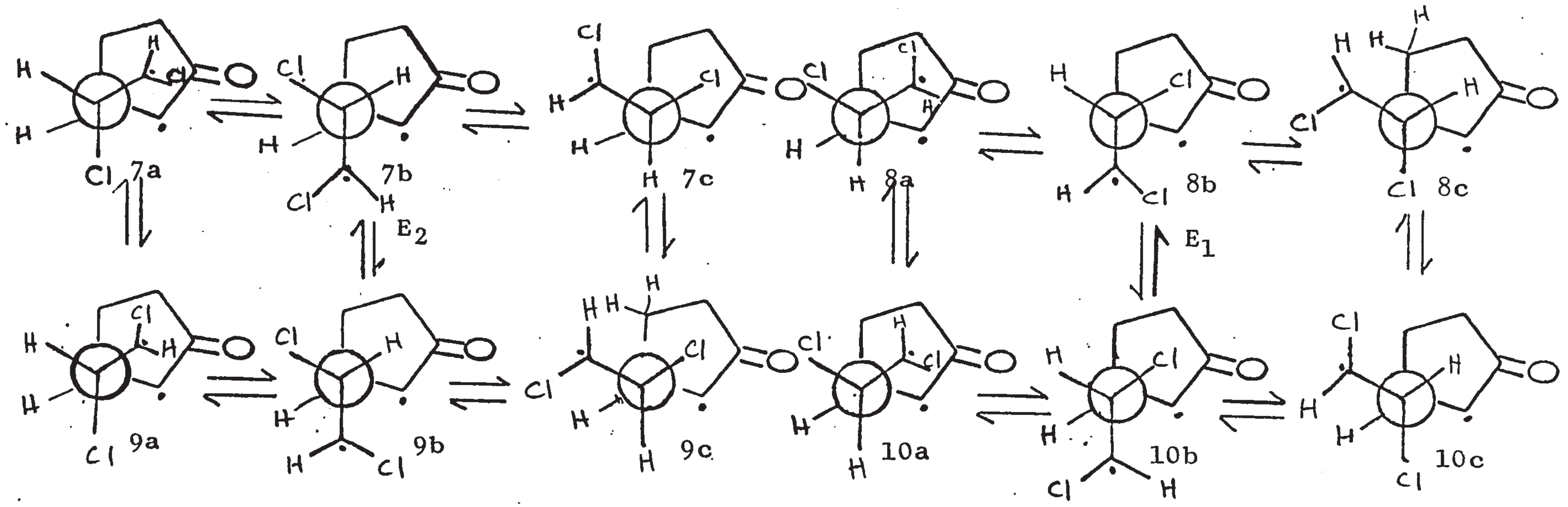
Bauslaugh applied his hypothesis to rationalize the orientational preference in cyclohexenone addition to olefin. This hypothesis, however, fails to explain the orientational preference obtained on addition of cyclopentenone to halogenated olefins e.g. in the addition to *cis*- or *trans*-dichloroethylene there would be no difference in the biradical stabilities (assuming all are formed by β-attack or all by α-attack).

Thus it appears that the orientation effects observed in the addition of cyclopentenone to halogenated olefins cannot be rationalized fully in terms of any of the above hypotheses.

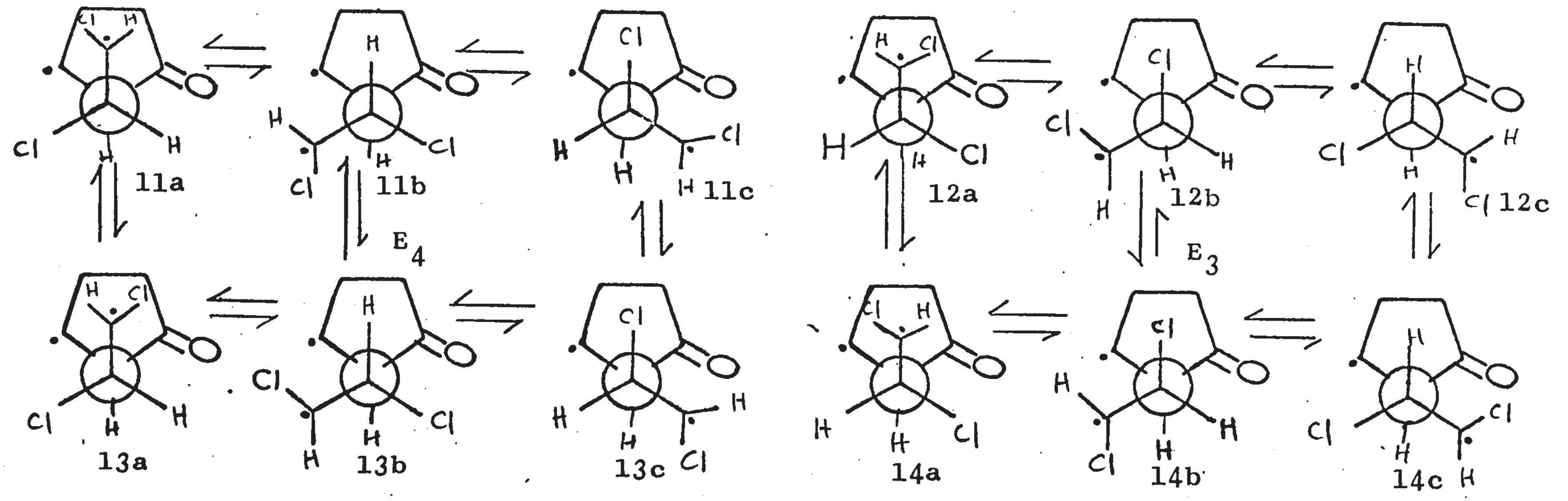
One way to interpret the results is to examine conformational preferences among the formed biradicals. Chart III represents all possible staggered conformations for the biradicals formed by an α or β-attack of *cis*- or *trans*-dichloroethylene (DCE) to cyclopentenone (CP) (assuming sp^2 hybridization of the carbon carrying the radical). *It is explicitly assumed that complete equilibration of the biradicals takes place, so as to attain the most stable conformation before closure*. According to the Curtin-Hammett principle (62) (A), the ratio of the products formed from one starting material which may exist in different conformations in no way reflects the relative population of the ground-state conformations, provided that the activation energy for reaction is large compared with the barrier to rotation. The ratio of the products will depend only on the difference in the free-energy levels of the available transition states. (B), for the other extreme, namely, that the activation energy of the reaction is small compared with the barrier for rotation, the conclusion would follow that the ratio of products is equal to the ratio of the population of the starting conformation.

Chart III (cyclopentenone/cis or trans-DCE)

β-attack :



α-attack :

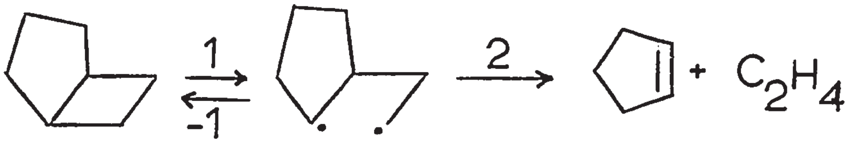


If, now, it is assumed, as one extreme, that the activation energy of the reaction is small then the ratio of isomers obtained by closure will reflect the conformation population ratios.

At the other extreme, as expressed in the Curtin-Hammett principle, if the activation energy for closure is large compared with the barrier to rotation then the ratio of the products will depend on the relative energies of the available transition states. Both of these extremes are expression of the requirement that reaction pathways follow the easiest route.

Not very many relative rates for biradical pathways are available in the literature, despite the fact that there are a number of reactions which may proceed partially or exclusively through such intermediates. The reason for this is probably the fact that beside being able to undergo rotation and cyclization, many biradicals often have at least one more pathway available to them, producing significant amount of side products. Tetramethylene species might produce olefin by 5,6 bond cleavage.

The lack of stereospecificity in cyclic enones photocycloaddition reactions demands that bond rotation rates compete with overall closure and cleavage rates. Internal rotation activation energies in the 1,4-biradical are normally equated to the barrier to rotation, which in turn seem to be reasonably approximated by the values assigned to the corresponding rotational barriers in substituted n-pentane (4-8 kcal/mole) (63). Evidence for this kind of assignment for rotational barriers in biradicals is not extensive, also Arrhenius parameters are dependent on the nature of the biradical intermediate and the nature of the substituents. The activation energy for closure of 1,4 biradical arises mainly from the strain in the cyclization step, and was predicted by O'Neal and Beanson to be equal to the activation energy of cleavage or 6.6 kcal/mole for the bicyclo(3.2.0)heptane biradical (64) (see reaction XIX). Thus, in the present case one has competition between two low energy pathways: an instance which may lie between the two extremes discussed. The results



(XIX)

$k_2 = k_{-1}$ $\qquad$ $E_2 \simeq E_{-1} = 6.6$ kcal/mole

can be rationalized on the basis of either one of the two extremes. In this case, that argument based on conformational preferences must necessarily involve some α-attack*.

It must be noted that the large difference in the dielectric constant of cis-dichloroethylene 9.20 and trans-dichloroethulene 2.25 (65), should affect the conformational equilibration and consequently product ratios obtained from these reactions. It has been reported that, in compounds having two adjacent chlorine atoms, the gauche conformation becomes more important in polar than in non-polar solvents (66). This is because of the fact that the gauche form has considerable dipole moment whereas the anti form has nearly none. Solvation is known to reduce the potential

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*Detailed discussion is not justified in view of the dubious conclusions.

energy of a dipole and therefore stabilize the gauche form relative to the anti. These facts imply that the gauche conformers (2 chlorine gauche), will be more important in the reaction of cis-DCE compared to that with trans-DCE. Evidence presented indicates that equilibrium (product ratios) attained on reaction of the cis-DCE or trans-DCE with CP would not be the same. This fact renders Dilling's analysis unacceptable (59).

The most common feature of the reaction of cyclopentenone with halo-olefins, is that the products having C_7-αCl are formed preferentially over those having C_7-βCl (see Table 17). This could be either a reflection of the energy difference of the transition states leading to these products or the difference between the ground-state conformational energies. The transition state or the conformer which has the C_7-Cl in β-configuration will be relatively higher in energy than that where the C_7-Cl is in α-configuration due to what is called the cis-effect.

From these studies, it is possible to conclude that complete equilibration of the intermediate biradicals is attained. The conformational equilibration is very sensitive to medium polarity particularly in halo-compounds and the postulate of Dilling (59) that the photocycloaddition of cyclopentenone to halo-olefin proceed through β-attack exclusively is not valid. On the other hand, α-attack cannot be excluded.

Table 17. Orientation preference around C_7 in cyclopentenone halo-olefin adducts.

Olefin[a]	Temp., °C	$C_7\alpha Cl/C_7\beta Cl$
vinyl chloride	-75	5.78
cis-Dichloroethylene	25	2.63[b]; 1.66[c]
	-75	2.46 ; 1.65
trans-Dichloroethylene	25	3.06[b]; 2.38[c]
	-75	3.47 ; 6.46
trichloroethylene	25	1.62
	-75	3.74

[a] Ether was used as solvent

[b] Represent the ratio of **3a**/**3d**.

[c] Represent the ratio of **3c**/**3b**

6.1 Assignment of structures and stereochemistry of the photo adducts.

The structures of all the adducts from the photoaddition of cyclopentenone to monochloro-, cis- and trans-dichloro-, 1,1-dichloro-, trichloro-, and tetrachloro-ethylene, respectively were deduced unequivocally from the 100 MHz n.m.r. spectra (in $CDCl_3$) of the adducts and/or their 2β-hydroxy-derivatives. By successive addition of the shift reagent, $Eu(fod)_3$ [tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione)-europium(III); for details of its use, see R.E. Rondeau and R.E. Sievers, J. Amer. Chem. Soc. 93, 1525 (1971)], in small amounts to the adduct, or its 2β-hydroxy derivative, in $CDCl_3$ solution, these complex n.m.r. spectra were simplified to such an extent that an approximate first order analysis could be made in each case. With the aid of double resonance decoupling experiments, it was thus possible to determine the coupling constants and multiplicities of each important proton signal - in particular those of H_1, H_5, $H_{6\alpha}$, $H_{6\beta}$, $H_{7\alpha}$, $H_{7\beta}$, and, in the case of the 2β-hydroxy derivative, of $H_{2\alpha}$ - which in turn enabled one to unequivocally deduce the position of the chlorine substituent(s) in each adduct.

The configuration(s) of the chlorine(s) at C_6 and/or C_7 were determined for each adduct by making use of the fact, that in the 2β-hydroxy derivatives, the 6β-hydrogen signal was shifted by about 1.5 times the extent of that for a 6α-hydrogen, and the 7β-hydrogen signal was shifted by about twice the extent of a 7α-hydrogen.

Our assignments agree essentially with those of Dilling (59) who had previously recorded the n.m.r. of the adducts from trichloro-ethylene and three of the adducts from cis- and trans-dichloroethylene. The fourth dichloro adduct (3d in XII; R=Cl) showed $\delta_{6\alpha} = 5.08$, $\delta_{7\beta} = 4.96$ ppm,

$J_{15} = 8$, $J_{17} = 8$, $J_{56} = 8$, $J_{67} = 8$ Hz.

The four monochloro adducts (2a-2d in XII, R=Cl) had $\delta_{6\beta} = 4.23$ (in 2a), $\delta_{6\alpha} = 4.74$ (in 2c), $\delta_{7\alpha} = 4.58$ (in 2d), and $\delta_{7\beta} = 4.26$ ppm (in 2b).

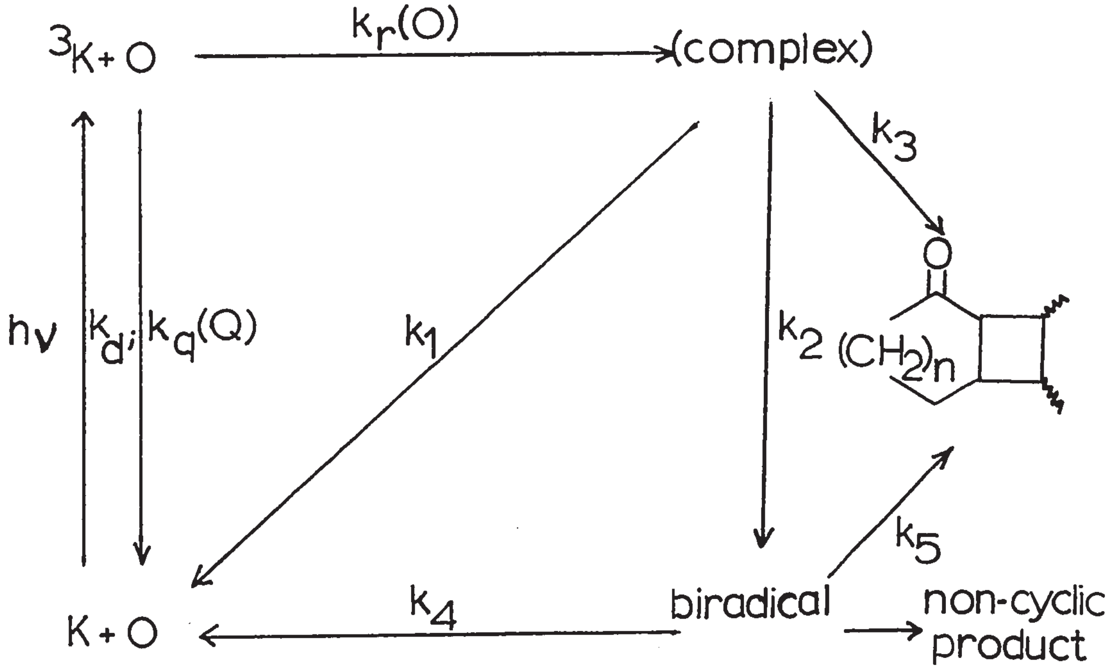
The n.m.r. of the 1,1-dichloro adducts (1a, 1b in XII, R = Cl) could only be interpreted after addition of shift reagent. Isomer 1a, for example, had $J_{1,7\beta} \simeq 6$ Hz and $J_{1,7\alpha} \simeq 10$ Hz.

CHAPTER VII

THE MECHANISM OF CYCLIC ENONE PHOTOANNELATION

In the last few years, the mechanism of cyclic enone photoannelation has received much attention and several speculations have been made. An attempt will be made to try and resolve some of the confusion in the light of the results presented in the previous chapters.

It has been found by Mayo and co-workers (12), as it had by Eaton and co-workers (4, 14) and subsequently by Ruhlen and Leermaker (15) that the cyclic enone photoannelation reactions proceed through a triplet. We also found that the yield of this triplet, that is the intersystem crossing efficiency from the singlet to the triplet of cyclopentenone and cyclohexenone (at both R.T. and -71°C) was 100% (see Chapter IV). We also found as had Mayo, Nicholson and Tchir (41) that the reaction involves an intermediate(s), a fraction of which continued to give products. The remainder collapsed to form molecules in the ground state (see Chapter III). The partition of this intermediate was the most important factor in determining the quantum yield of photoannelation. With these facts, it is possible to construct the following scheme.



It is possible that the olefin can act as a quencher as well as be involved in product formation since the triplet energy of cyclopentenone is in the region of 75 kcal/mole and that of cyclohexenone is about 67 kcal/mole (51) which is close to the triplet energy of the olefins. Deactivation of the excited ketone could take place by energy transfer to the olefin or by a Schenck-type mechanism. This would account for the dependence of the intercept of the dilution curves (see Chapter 5.3) and k_d (see Table 10) on the substrate. However, if energy transfer from the excited enone to the olefin does take place, some reaction products characteristic of the triplet olefins (e.g. dimerization or cis-trans isomerization) would be expected. It has been shown by Dr. M.F. Tchir that cyclopentenone is a very inefficient sensitizer both for cis-trans isomerization of 3-hexene and for the dimerization of cyclopentene or or cyclohexene. These results exclude energy transfer to the olefin as a major mode of deactivation of the excited enone.

As mentioned before, the existence of an intermediate(s), which act as a source for wasting the energy was proved, but the nature of this intermediate, whether π-complex or biradical, was conjectural. Examination of the data in Table 10, reveals that the rate constant (k_r) appears to be exceedingly high, perhaps four orders of magnitude higher than the usual rates of addition of radicals to olefins or acetylenes (67). This would tend to argue against the initial intermediate being formed by a radical-like attack.

This rapid rate of reaction can be interpreted in two ways, both of which involve complex formation (exciplex). If the triplet enone is quenched, the observed k_r (which then represents the rate constant for formation of the succeeding species) is more consistent with complex formation (exciplex), than with radical addition. Alternatively if an exciplex is formed, and it alone is quenched, then k_r represents the rate of tetramethylene formation from the exciplex. It cannot be excluded that both unassociated triplet enone and complex may be quenched, and in this case the interpretation of k_r becomes complex, but the values obtained must represent some weighted average of the two processes.

This exciplex, if it exists, must have a triplet energy somewhat lower than that of the unassociated triplet and hence should still be quenchable by dienes, as is the enone triplet, at a diffusion controlled rate. Tetramethylene formation from the complex, therefore, must occur at a competitive rate $>10^7 S^{-1}$. Since this is much faster than typical rates of radical olefin addition (67), the complex must act either to decrease *the activation energy or increase the pre-exponential factor in the Arrhenius rate expression*. Confirmation or rejection of this postulate was possible, since the rates of addition of cyclopentenone and cyclohexenone at different temperatures were available (see Table 10). From these data the energy of activation and pre-exponential factors were found to be (E_a = 1.7 kcal/mole, log A = 10.34 for cyclopentenone; E_a = 1.98 kcal/mole, log A = 9.30 for cyclohexenone*). These values can be compared to those for the addition of ethyl radical to 1-hexene for which typical values are E_a = 6.8 kcal/mole and log A = 7.8 (67). It is obvious that the activation energy for the cyclic enone photoannelation reactions are lower than those for radical addition to olefins, while the pre-exponential factors are higher. From these results it can be concluded that *complex between the excited enone and substrate (exciplex) is required as initial step in the reaction*.

The value of k_d, the unimolecular decay constant, should by definition be a property of the enone alone and be essentially unaffected by the substrate molecule if the enone alone is quenched. However, the decay rate is actually not constant and the variation in various cyclopentenone photoannelations is greater than can be attributed to experimental error. On the other hand, if the complex is assumed to be quenchable, k_d will depend on the substrate, and a variation in k_d with substrate

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*It must be noted that these values are computed from the rate constants determined at only two different temperatures, but since no other products, apart from cycloadducts, and no drastic change in the product ratio were observed, it is safe to assume that the Arrhenius plot will be linear and no change in mechanism is anticipated on changing the temperature.

is to be expected (the same results will be obtained if complex and enone are quenched).

Another point which might be significant is the following. For cyclopentenone addition to cyclohexene in three different solvents k_d decreases with an increase in the viscosity of the medium (see Table 10, Fig. 15). No change in quantum yield was observed in these three solvents. No correlation with solvent polarity was observed either. The same observation has been made for the addition of cyclopentenone to cyclohexene (Table 10) or 3-hexyne (68). It is hard to understand why a unimolecular process should depend on the medium viscosity, provided it remains fluid, but the phenomenon is more comprehensible if both enone and substrate are involved. If the exciplex is held together by weak electrostatic forces, then viscosity might become an important factor. The deviation from diffusion-controlled quenching in solvents of low viscosity has been explained by suggesting that the molecules could move apart before energy transfer could occur (49).

From the scheme, it was assumed that the complex or exciplex either collapses to starting material with loss of the excitation energy (probably through vibrational deactivation) or gives the tetramethylene (1,4 biradical). A third possibility, which cannot be excluded, is the direct formation of products (k_3). In general, singlet exciplexes have found more general acceptance than triplet exciplexes, but kinetic evidence for the latter is steadily mounting (67).

Some of the exciplexes will collapse to give the tetramethylene (TM). Such 1,4 biradicals have been postulated in the thermal dimerization of olefins (70) and in many photochemical reactions (71-73, see Chapter III).

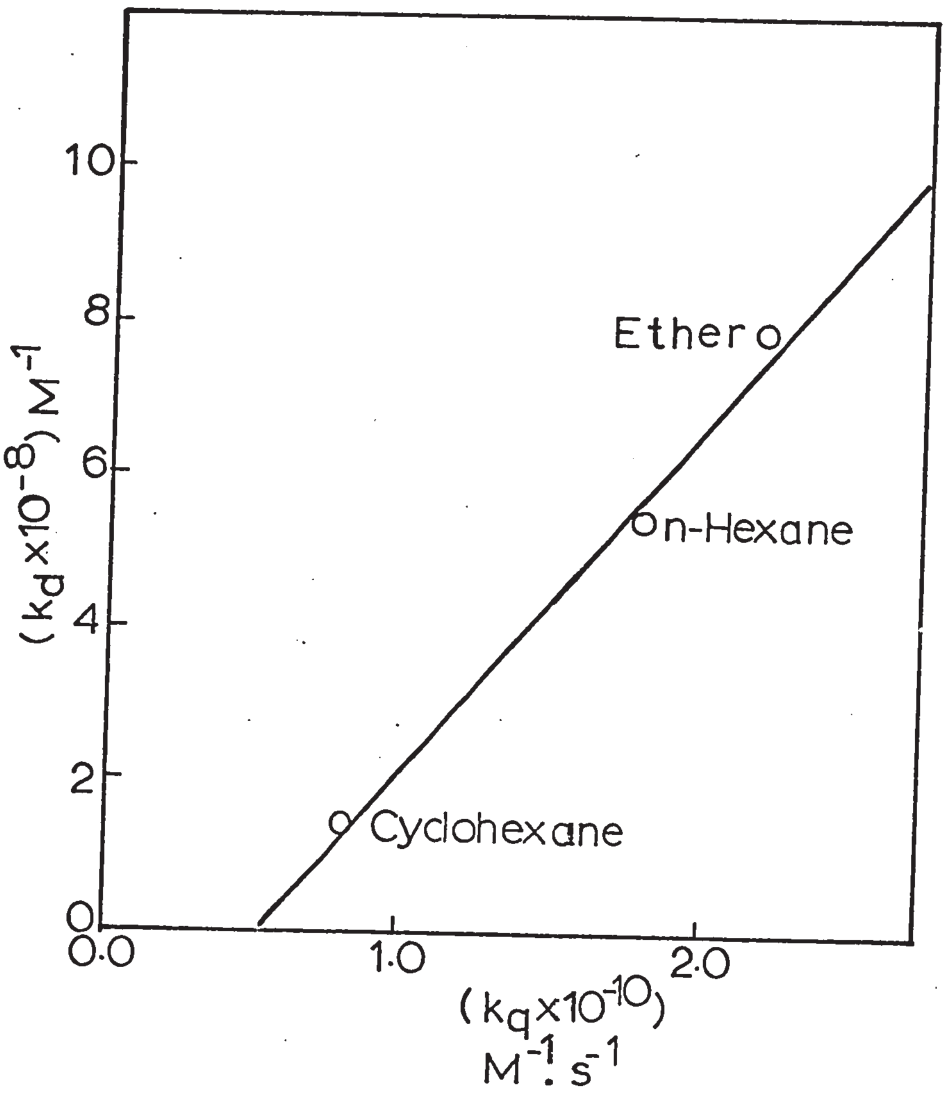
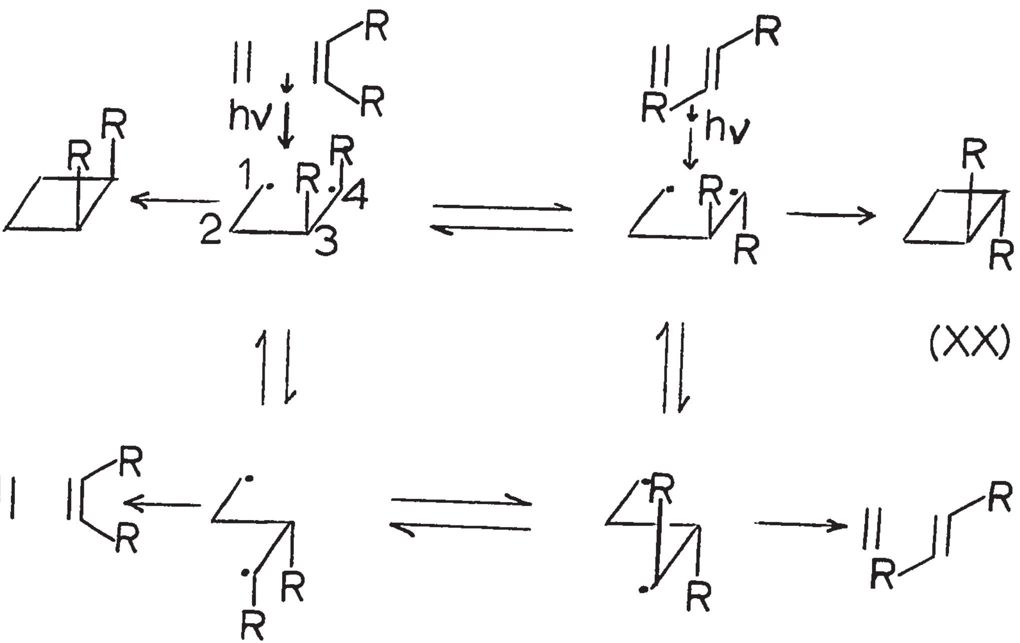


Fig.15 Correlation between Rate of decay and viscosity of the medium for Cyclo--hexenone-Cyclohexene system, k_q calculated from Debye equation α $1/\eta$.

Product formation from the biradical requires the formation of a sigma bond while dissociation requires the cleavage of a sigma bond with the formation of two pi bonds. The actual activation energies for the two processes could vary with olefins as observed from the studies of effect of temperature on the quantum yield (see Chapter III). The rate of C_3-C_4 bond rotation (see reaction XX) may be faster than the rate of closure. If so, the stereochemical integrity of cis and trans olefins will not be



(XX)

retained in the products (cyclobutanes) and some isomerization in the recovered olefins would be observed. The stereochemistry of the product will depend on the conformational preferences, if complete equilibration of the biradicals is allowed (see Chapter VI). It is possible that products could arise from a cisoid species, while cleavage would result from a transoid geometry (see reaction XX) i.e. the transoid species dissociates preferentially.

It could be concluded that the cyclic enone photoannelation reactions proceed through a triplet state. Initial formation of exciplexes between the excited enone and the substrate was concluded from the extremely rapid rate of reaction and the low activation energy and high pre-exponential factor of this reaction compared with radical addition to olefin. The exciplexes either revert back to starting molecules (energy waste process) or give product directly or collapse to tetramethylene. The energy of the exciplexes is expected to be close to that of the excited enone, consequently both are quenchable, this explains the dependence of k_d on substrate. The tetramethylene was involved to explain the loss of stereochemical integrity of the olefin in the product obtained. The tetramethylene either collapses to starting molecules or gives products.

EXPERIMENTAL

All melting points are uncorrected and were measured on a Thomas Hoover capillary melting point apparatus. Absorption spectra were measured on a Cary-14 recording spectrophotometer. All infrared spectra were recorded on a Beckman IR-10 spectrophotometer. The nuclear magnetic resonance spectra were measured on Varian Model T-60 or HA-100 at room temperature with tetramethyl silane as internal standard. Mass spectra were recorded on a Varian M-66 instrument. Details of the measurement of the emission spectra will be described in Part II.

Elemental analyses were performed by the Gygli Microanalytical Laboratory, Toronto, Canada.

Part A. Enone Photochemistry

A.1 Materials

Cyclopentenone (Aldrich), cyclohexene (Phyllips), cis-dichloroethylene (Eastman), trans-dichloroethylene (Eastman) and cyclopentene (Aldrich) were purified as described by M.F. Tchir (74). Cyclohexenone, trans-3-hexene and 2,5-dimethyl-2,4-hexadiene (Aldrich) were prepared and purified as described by A.A. Nicholson (75). Bicyclo(4.2.0)oct-7-ene was prepared by photolysis of cis-1,3-cyclooctadiene (Aldrich) following the procedure described by Liu (76). The olefin was purified by distillation through a Vigreux column (b.p. 132°C, nitrogen) and was greater than 99% pure as judged by glc on a 10% FFAP, chromosorb, P, 8' × $\frac{1}{4}$", at 110°C. *cis*-Piperylene (K & K laboratories) and *trans*-piperylene (Aldrich) were purified by distillation from sodium wire (nitrogen) and then passed over neutral alumina. The *cis*-piperylene contained 0.17% *trans*-isomer, and *trans*-piperylene contained 0.5% *cis*-isomer (glc on a column of 15% β,βoxydipropionitrile on diatoporate S, 20' × $\frac{1}{8}$", column A, at 20°C). Trichloroethylene "Baker Analyzed Reagent" was distilled (nitrogen) on a medium spinning bond column (2') and the fraction which boiled at 87.1°C was collected. Methylacetate (AR,BDH) was refluxed with acetic anhydride for six hours, followed by distillation, the fraction boiling at 56-56.5°C was collected and refractionated. Diglyme (Aldrich) was distilled from sodium under reduced pressure b.p. 124°C/126mm Hg. 1,1-Dichloroethylene (K & K laboratories) was distilled using a short Vigreux column (b.p. 32°C).

A.2 Preparation of Adducts.

The light source was a 450 W medium pressure mercury lamp (Hanovia, 679A36) which was connected to an Engelhard Hanovia power supply and housed in a water-jacketed quartz probe. The probe was immersed in a constant temperature bath.

The samples were placed in pyrex tubes and deoxygenated by nitrogen purge through a fine capillary (30 min.). The nitrogen was purified by passage through a heated BTS catalyst R3-11 (BASF) at 100°C. The catalyst turns green on use but was easily regenerated when flushed with hydrogen gas at 120°C.

The irradiations were followed by glc and infrared spectroscopy (cyclopentenone carbonyl stretching frequency is at 1710 cm^{-1} that of cyclohexenone is at 1680 cm^{-1} while the corresponding adduct had $\nu c=0$

at 1720-1750 cm^{-1}).

After irradiation the solvent was removed by distillation at low pressure (the distillate was tested by glc for any volatile adducts). The residues were chromatographed on silica gel to remove unreacted enones. The individual components were then separated by preparative glc (F & M Scientific Model 776 or Varian Areograph Model 1700). Components which had been separated were distilled (bulb-to-bulb) prior to analysis. The best separation of adducts was achieved on a FFAP column.

A.2.1 Cyclopentenone-Cyclohexene

The preparation yielded 4 adducts as reported by M.F. Tchir (74) in the ratio of 1.0 : 6.0 : 1.54 (the central peak consisted of two components which were only partially resolved. The ratio of adducts changed with temperature (see Table 18). The areas were measured using an ott-Planimeter type 31 in arbitrary units.

Table 18. Cyclopentenone-cyclohexene product distribution at different temperatures.

Temp., °C	Adducts Ratio		
	1	2	3
27	1.0	6.00	1.54
-71	1.0	5.10	1.46
-90	1.0	4.55	1.30
-102	1.0	3.40	0.90

A.2.2 Cyclopentenone-Cyclopentene

The irradiation produced only one adduct as reported by Eaton (4) and was compared (IR, NMR, mass spectrum) to that reported by M.F. Tchir (74).

A.2.3 Cyclopentenone-*trans*-3-Hexene

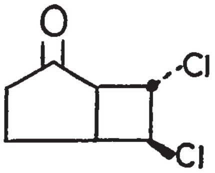
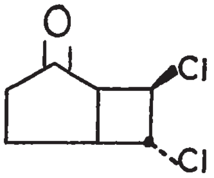
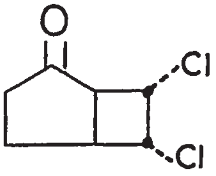
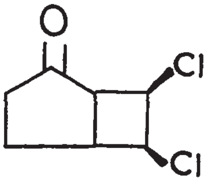
The irradiation of cyclpentenone and *trans*-3-hexene led to the formation of 4 compounds, as mentioned by Dr. J.-P. Pete, in the ratio of 5.3 : 4.9 : 4.7 : 1.00.

A.2.4 Cyclopentenone- *cis* and *trans*-Dichloroethylene

Irradiation of 120 mg (0.3M) of cyclopentenone and 5 ml (13.2M) *cis*-dichloroethylene (contains 0.2% *trans*-isomer, glc, on 20% carbowax 20M, 6' × $\frac{1}{4}$", at 50°C) or *trans*-dichloroethylene (contains less than 0.1% *cis*-isomer) in a pyrex tube (nitrogen) next to 450 watt medium pressure mercury lamp for 2 hours, followed by glc analysis (Hi-Fi-600-A hydrogen flame detector, on 5% FFAP on diatoporate S, 9' × $\frac{1}{8}$" (column B) at 130°C showed the formation of 4 compounds. The fourth compound had been missed before in this laboratory and had not been reported by W.L. Dilling (59). The four compounds had different retention times on glc (12, 16, 20 and 48 min.). The ratio of the products has been measured under different experimental conditions (see Table 11). The analysis was done using the above mentioned glc column B. The areas integrated using a Digital Readout System Model CRS-100-Infrotronics and the results corrected for the differences in hydrogen flame detector responses.

The physical constants of the isolated cycloproducts are shown in Table 19.

Table 19. Melting points, IR and structure of cyclopentenone-vic-dichloroethylene adducts.

Compound	Structure	m.p., °C	IR, cm^{-1} $\nu_{CO}^{CCl_4}$
3a		83 - 4	1746
3b		waxy	1746
3c		53 - 53.5	1740
3d		76 - 7	1747

The structures of the adducts were elucidated from the nmr analysis* (see discussion page 83).

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*The author is indebted to Dr. M.C. Woods for carrying out the n.m.r. analysis.

A.2.5 Preparation of bicyclo(3.2.0)heptane-2-ol-6,7-dichloride.

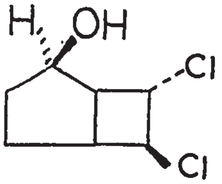
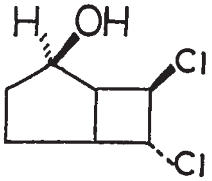
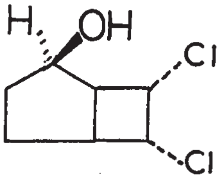
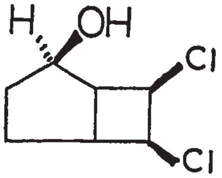
The adducts described in A.2.4 (0.1 mole) were dissolved in 10 ml methanol (Fischer), and 1 ml of a 15% solution of $NaBH_4$ in methanol was added slowly to the solution. The reaction was followed by tlc. The R_f values (silica gel, eluted with 25% ether in benzene) were 0.8 and 0.6 for the ketone and the corresponding alcohol, respectively. After the reaction was completed (30 min.), the reaction mixture was diluted with water and the product extracted with ether. The ethereal layer was dried with anhydrous $MgSO_4$ and the solvent evaporated to give a solid material (except isomer #3b which gave a liquid product). Only one isomeric alcohol was obtained in all cases (glc, 25% FFAP on chromosorb W, 6' × $\frac{1}{4}$" at 180°C). In each case the infrared spectra showed no carbonyl band and exhibited strong band at ~3600 cm^{-1}.

The physical constants and elemental analysis of the alcohols are given in Table 20. All solid alcohols were crystallized from pet. ether b.p. 60-80°C.

A.2.6 Cyclopentenone-trichloroethylene

A solution of cyclopentenone (0.25 gm) and trichloroethylene (13.2 gm) in ether (10 ml) was irradiated for 5 hours with a 450 watt mercury lamp. The reaction was followed by tlc (silica gel, eluted with 25% ether in benzene), the R_f values 0.82 and 0.63 for adducts and cyclopentenone, respectively. The distribution of the 4 adducts in different solvent systems were measured by glc (on 2.5% FFAP, diatoporate S, 6' × $\frac{1}{8}$" (column C) at 125°C) see Table 14. The product isolation was achieved using a F & M glc, as mentioned before.

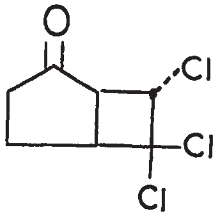
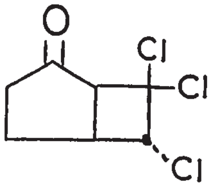
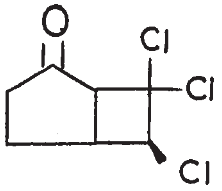
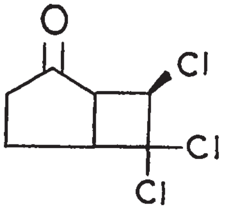
Table 20. Melting points, elemental analysis and structure of the alcohols of cyclopentenone-vic-dichloroethylene adducts.

Compound	% Yield	m.p. °C		Analysis %		
				C	H	Cl
3a'	89	62-3		46.75	5.55	39.01
3b'	90	liq.		46.70	5.75	39.10
3c'	96	69-70		46.54	5.78	39.17
3d'	95	122-4		46.55	5.67	39.01
Analysis Calc. for $C_7H_{10}Cl_2$				46.44	5.57	39.16

The configuration of the hydroxy group was established from the n.m.r. analysis of the alcohols and using a chemical shift reagent (see discussion).

The structure and other physical properties of the cyclo adducts are given in Table 21.

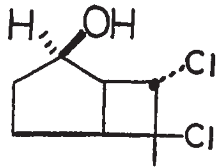
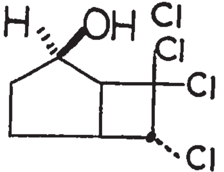
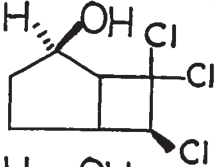
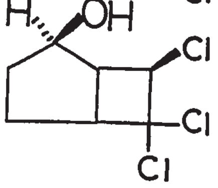
Table 21. Structure, melting point and IR of cyclopentenone-trichloroethylene adducts.

Compound	Structure	m.p., °C	IR, cm^{-1} $\nu_{CO}^{CCl_4}$
4a		69 - 70	1747
4b		waxy	1749
4c		waxy	1750
4d		waxy	1752

A.2.7 Preparation of bicyclo(3.2.0)hepten-2-ol-trichloride.

The sodium borohydride reduction of the ketones were carried out as previously described on page 98, and the β-alcohols were crystallized from light-petroleum (b.p. 60-80°C).

Table 22. Structure, melting points, yields and elemental analysis of the alcohols of cyclopentenone-trichloroethylene adducts.

Compound	Structure	m.p., °C	Yield %	Analysis, % C	H	Cl
4a'		103-4	95	39.01	4.12	49.49
4b'		liq.	89	38.84	4.28	48.60
4c'		88-9	90	39.32	4.09	48.99
4d'		72-3	85	39.15	4.10	49.60
Analysis Calc. for $C_7H_9Cl_3$				39.01	4.21	49.35

The configuration of the hydroxy group determined from n.m.r. analysis (see discussion).

A.2.8 Cyclopentenone-vinyl chloride.

A solution of cyclopentenone (1 gm) and vinyl chloride (20 ml) in ether (20 ml) was placed in a pyrex tube fitted with dry ice/acetone condenser. The solution was cooled with dry ice/methanol slurry to -75°C and irradiated for 3 hours using a 450 watt medium pressure mercury lamp. After the reaction was completed (followed by IR), the solvent was evaporated and the residue was bulb-to-bulb distilled under reduced pressure (b.p. 70°/0.05 mm). Two of the four isomeric products were easily separated from the mixture on glc (F & M) 2.5%, FFAP on chromosorb P, 7' × $\frac{1}{2}$" at 100°C. The other two isomers were reduced to the alcohols using $NaBH_4$ method. Only two alcohols were obtained and easily separated on thick tlc plate, (silica gel, 25% ether benzene mixture was used for elution), the R_f values 0.37 and 0.49.
The separated alcohols were reoxidized by Jones' reagent (see p.106) to the ketones.

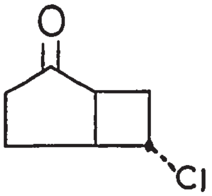
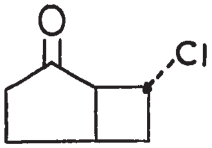
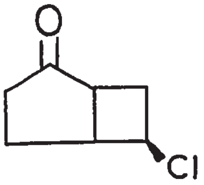
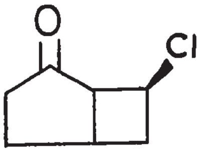
The product distribution was determined on glc (Hi-Fi, 10% SE-30, on diatoporate S, 6' × $\frac{1}{8}$" at 90°C) and the areas were integrated using the Infrotronic digital integrator, see Table 12.

The physical properties and elemental analysis of cyclopentenone-vinyl chloride adducts are given in Table 23.

A.2.9 Cyclopentenone-1,1-dichloroethylene.

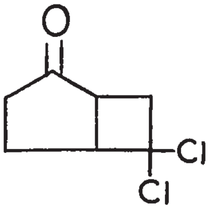
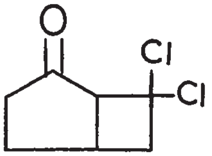
Irradiation of cyclopentenone (0.3 gm) and 1,1-dichloroethylene (15 ml) for 6 hours gave two isomeric cycloadducts which were separated by glc (6% FFAP on chromosorb W, 7' × $\frac{1}{2}$" at 110°C). The product distribution following irradiation under different experimental conditions, (see Table 13) was measured using glc (Hi-Fi, 5% FFAP on diatoporate S, 6' × $\frac{1}{8}$'' at 96°C).

Table 23. Structure, boiling points, IR, and elemental analysis of cyclopentenone-vinyl chloride adducts.

Compound		B.p., °C	IR, cm^{-1} $\nu_{CO}^{CCl_4}$	Analysis, % C	H	Cl
2a		70/0.6mm	1740	58.30	6.14	24.81
2b		50/0.2	1738.5	58.12	6.16	24.77
2c		70/0.05	1738	57.99	6.15	24.76
2d		65/0.05	1741	58.07	6.16	24.52
Analysis Calc. for C_7H_9ClO				58.13	6.22	24.56

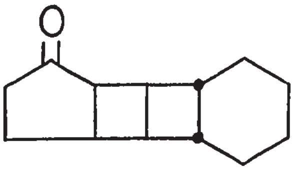
The IR, structure, and elemental analysis of cyclopentenone-gem-dichloroethylene adducts are given in Table 24.

Table 24. Structures, boiling points, IR, and elemental analysis of cyclopentenone-gem-dichloroethylene adducts.

Compound	Structure	b.p., °C	IR, cm^{-1} $\nu_{CO}^{CCl_4}$	Analysis, %		
				C	H	Cl
1a		70/0.1mm	1744	46.79	4.68	39.60
1b		75/0.1mm	1744	46.87	4.42	39.49
Analysis calc. $C_7H_8Cl_2O$				46.96	4.50	39.60

A.2.10 Cyclopentenone-bicyclo(4.2.0)oct-7-ene.

Irradiation of cyclopentenone (0.5 gm) and bicyclooctene (3 ml) in cyclohexane (10 ml) in a pyrex tube with a 450 Watt mercury lamp at 25°C for 2 hours, resulted in the formation of only one adduct, glc (column A, at 150°C). Crystals were formed during the irradiation, filtered, and identified as cyclopentenone dimer (tlc, m.p. and IR). This was followed by removal of solvent, to give an oily residue. This was chromatographed on silica gel (B.D.H., 60-120 mesh) using ethyl acetate-hexane mixed solvent. Early fractions gave the starting olefin while later fractions gave pure tetracyclo(6.5.0.$0^{2.7}$.$0^{9.13}$)tridecan-10-one I, glc (on column B at 150°C) as an oily material



(1)

$\nu_{max}^{CCl_4}$ 2935, 2855, 1735, 1450, 1410, and 1165 cm^{-1}.

NMR (CCl_4): A narrow multiplet at δ 2.9 (1H), broad doublet at 2.55 (2H), broad singlet at 2.2 (5H), multiplet from 1.8-2.15 (3H) and broad multiplet from 1.2-1.7 (8H).

Mass spectrum: M^+ at M/e 190; $(M+1)^+$ 14% of M^+ peak.

Analysis: Calc. for $C_{13}H_{18}O$: C, 82.06; H, 9.54%

Found: C, 81.75; H, 9.88%.

Baeyer-Villiger oxidation of Tetracyclic ketone 1.

To 108 mg (0.2 mole) of the ketone 1 in 1 ml of glacial acetic acid 52 mg of sodium acetate was added followed by dropwise addition of 0.8 ml (0.36 mole) of peracetic acid. The slurry was allowed to stand at 27°C overnight. The reaction was followed to completion by tlc (silica gel, 25% ether/benzene) Rp 0.86 and 0.72 for ketone and δ-lactone respectively. Dilution with water was followed by ether extraction. The ethereal layer was washed with $NaHCO_3$ solution, acidic $FeSO_4$, $NaHCO_3$ solution and water. Removal of the ether in vacuo afforded 86 mg of the δ-lactone 11 (75% yield).

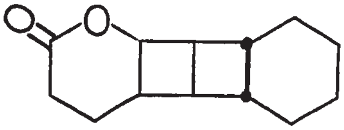
IR: $\nu_{max}^{CCl_4}$ 2930, 2850, 1745, 1450, 1235, 1140 and 1090 cm^{-1}

NMR (CCl_4): 4.85 (d.d; J = 6.0, 2.0 Hz; 1H), 1.2-2.9 (m., 17H).

Mass spectrum: M^+ at M/e = 206.12; $(M+1)^+$ 14.0% of M^+ peak.

Analysis: Calc. for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80%'

Found: C, 75.79; H, 8.95%



(II)

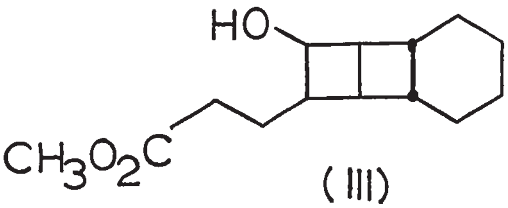
Hydrolysis and esterification of δ-lactone II

The crude δ-lactone (224 mg) was treated with alcoholic potassium hydroxide (10 ml. 0.5N). The solution was refluxed for 1½ hours, diluted with water (50 ml), acidified with diluted hydrochloric acid to pH 7, and extracted with ether. After drying, diazomethane in ether was added until a permanent pale yellow solution was obtained. Evaporation of the solvent gave triacyclohydroxyester III as a colourless oily material (220 mg, 85% yield). The purity was checked by tlc (silica gel, 25% ether/benzene) $R_f = 0.44$.

IR $\nu_{max}^{CCl_4}$: 3610, 3470, 2930, 2860, 1740, 1440, 1700, 1170, 1090, and 740 cm^{-1}.

NMR (CCl_4): 4.4 (d, J = 5.2, 1H), 3.7 (s, 3H), 3.05 (bs, 1H), 2.7-2.85 (nm, 1H), 2.2-2.6 (bm, 5H), 1.2-2.0 (bm, 11H).

Mass spectrum: $(M - 18)^+$ 220.



(III)

Oxidation of the Tricyclohydroxy Ester III

The tricyclohydroxy ester III (50 mg) was dissolved in 3 ml of dry acetone. This solution (mechanically stirred) was titrated with Jones' reagent (0.7 gm chromium trioxide in 5 ml of water and 0.6 ml of concentrated H_2SO_4). The greenish red solution was diluted with water, and extracted with ether. The ethereal layer was washed with water several times and dried with anhydrous $MgSO_4$. Evaporation of the solvent gave 35 mg (75% yield) of tricycloketoester IV as an oily material (tlc, silica gel, 25% ether/benzene, $R_f = 0.57$).

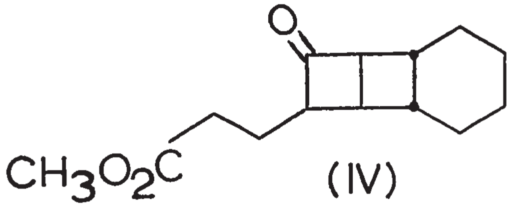
IR $\nu_{max}^{CCl_4}$: 2930, 2870, 1790 (C=0 in four membered ring), 1745 (ester) 1440, 1170 and 1120 cm^{-1}.

NMR (CCl_4): δ 3.60 (s, 1H), 1.9-2.5 (m, 8H), 1.0-1.9 (m, 9H).

Mass spectrum: M^+ at M/e 236.

Analysis: Calc. for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53%

Found : C, 71.71; H, 8.83%



(IV)

The adducts of cyclohexenone with cyclohexene and trans-3-hexene were prepared by Mr. A.A. Nicholson (75).

A.2.11 Cyclohexenone-cyclopentene.

A solution of cyclohexenone (0.5 gm) and cyclopentene (5 ml) in 10 ml cyclohexane was irradiated for 45 min at 25°C using a 450 Watt mercury lamp. Glc (on column B at 140°C), showed the formation of three bicyclo(4.2.0)octan-2-one adducts in the ratio 14.7 : 1.0 : 5.6. During isolation of the adducts by glc (25% FFAP, chromosorb P, 8' × $\frac{1}{4}$' at 145°C) the second product isomerized.

Peak 1.

IR $\nu_{max}^{CCl_4}$: 2930, 2850, 1700, 1440, 1320 and 1135 cm^{-1}

NMR (CCL_4): δ 2.35-2.8 (bm), 2.1-2.3 (nm), and 1.4-2.0 (bm).

Mass spectrum: M^+ at M/e = 164, $(M+1)^+$ is 12.2% of M^+.

Peak 3.

IR $\nu_{max}^{CCl_4}$: 2940, 2850, 1700, 1440, 1320 and 1135 cm^{-1}.

NMR (CCl_4): δ 2.6-2.8 (nm, 2.1-2.5 (bm), and 1.4-2.0 (bm).

Mass spectrum: M^+ at M/e 164, $(M+1)^+$ is 12.30% of M^+.

On reinjection of adduct 3 on glc (column A at 160°C), two peaks were observed (the new peak had a different retention time from the other three adducts). These results indicate that adduce #3 (<u>trans</u>-fused 6-4 ring) isomerizes at high temperature to adduct #4 (<u>cis</u>-fused 6-4 ring).

<u>Treatment of cyclohexenone-cyclopentene adducts with neutral alumina.</u>

A mixture of cycloadducts (3 isomers; 0.2 gm) in 2 ml ether was passed through a short column of alumina (Woelm neutral, activity 1). The adducts were eluted with ether, and evaporation of the solvent afforded the cycloadducts without any loss in weight. Analysis of the mixture on glc showed the existence of only two peaks, the first corresponding to adduct #1 (<u>cis</u>-fused 6-4 ring), and the second to the isomerized product from adduct #3. Analysis of the same mixture by glc using the same column as that of Corey (9) (column D, at 120°C) showed only one peak. This indicates that adduct #3 was mistakenly believed to be the <u>trans</u>-isomer of the cis adduct #1.

A.2.12 Tricyclo(3.3.2.$0^{1.5}$)deca-3-en-2-one(TK)-cyclohexene.

TK was prepared following the procedure described by P. de Mayo and co-workers (27). The ketone was chromatographed on silicic acid (BDH; 40 gm : 1 gm ketone) using a 5% ether/benzene mixture as solvent, and further purified by glc (10% DEGS on chromosorb P, 5' × $\frac{1}{4}$" at 150°C).

A mixture of products (eight) was obtained on irradiation of degassed solutions of TK and cyclohexene. The main product (represent 60% of the total) was isolated using glc (5% FFAP on chromosorb P, 6' × $\frac{1}{4}$" at 170°C) and identified as cycloadduct (1).

A.3 Low temperature quantum yields measurements.

Quantum yields were determined on an optical bench. The apparatus has been described in detail by M.F. Tchir (74, p. 102). The sample was placed in a specially designed quartz apparatus which allowed liquid at low temperature to be circulated around a (2 × 3 cm) oval sample cell (1 cm path length and 5 ml capacity). The sample cell was situated in a quartz envelope, equipped with two windows parallel to that of the cell. This was evacuated to prevent condensation forming on the surface of the cell (Fig. 16). The cell was attached to a pyrex degassing bulb by means of a graded seal. The apparatus was then attached to an all glass vacuum system by means of greaseless O-rings stopcocks (8194, ACE GLASS Inc.). An oil diffusion pump, separated from the manifold by a liquid nitrogen trap, was used to degas the solutions by repeated freeze-pump-thaw cycles to a residual pressure of less than 10^{-4} mm. The apparatus was then detached, the sample tipped into the cell and placed in the transmittance position on the optical bench. The sample was cooled by

Fig. 16

Fig. 16

circulating an acetone/ether mixture, which was held at the required temperature by means of a thermostatted bath (Lunda constant temperature bath and circulator Model M2, connected to a solid carbon dioxide heat exchanger Model KS). Temperatures below -60°C were obtained by circulating acetone/ether through a copper coil placed in a suitable slurry (see Table 25).

Table 25. Different Coolant Slurry

Temp., °C	Slurry
-70	Dry ice/acetone
-90	Methylene chloride/liq. N_2
-102	Carbon disulfide/liq. N_2

The sample temperature was measured using Iron-Constantan thermocouple connected to 5 mv Sergent-Welch recorder. The sample was then irradiated for 1 hour, at constant temperature (5-7% conversion). The total amount of light absorbed was determined by use of the ferrioxalate actinometer developed by Parker and Hatchard (77). The transmittance to reflectance ratio (T/R) was predetermined for the apparatus by placing actinometer solutions in both sides and irradiating for about 7 min. The amount of ferrous ion produced was determined colorimitrically at 510 mm using a Hitachi-Perkin Elmer spectrophotometer (Model 139) and a calibrating curve obtained using ferrous sulfate. Knowing T/R and the total light flux falling on the actinometer in the reflectance position, permitted the calculation of the number of einsteins absorbed by the sample. An actinometer was always placed behind the sample during irradiation to correct for incomplete absorbance by the sample.

The sample was then allowed to warm to room temperature, and the products analysed quantitatively by glc, (Aerograph 600-D Hi-Fi equipped with a hydrogen flame detector). The carrier gas used was helium (Matheson), the hydrogen and air used in the detector were supplied by an Aerograph Model 650 Hydrogen-Generator. Traces were recorded on a Honewell recorder equipped with disc integrator. Peak areas were integrated using either a disc integrator, Ott-planimeter or Digital Readout system, Model CRS-100 Infrotronic, depending on the nature of the base line obtained.

Calibration was achieved by measuring the area ratio (A_{add}/A_{cal}) of known weight ratio (W_{add}/W_{cal}) of adduct and calibrating compound. Several weight ratio were used, and a linear plot of A_{add}/A_{cal} vs. W_{add}/W_{cal} was obtained which passed through the origin. An unknown weight of adduct could then be calculated following the addition of a known weight of calibrating compound and measurement of the area ratio.

All measurements were an average of three runs.

A.4 Quantum yield of additon of cyclopentenone and cyclohexene to olefins at various temperatures.

Using the above mentioned procedure, and after irradiation at the desired temperature, the sample was allowed to warm to room temperature. Air was admitted to the cell and the contents transferred by ether extraction to a 25 ml Erlenmayer conical flask containing a known weight

Table 26. Cyclopentenone and cyclohexenone addition to olefins. Irradiation temperatures and glc conditions.

Ketone	Olefin	Irrad. temp., °C	glc Column	Column Temp.	Calibrating compound	No. of adducts
Cyclopentenone[a]	Cyclohexene	27, -10, -40, -71, -90, and -102	E	130	Acenaphthene	4
	Cyclopentene	27, -10 and -71	B or F	110	Naphthalene	1
	trans-3-Hexene	27 and -71	E	85	2-Methyl-naphthalene	4
	cis-Dichloro-ethylene	27 and -71	B	130	2-Methyl-naphthalene	4
	Bicyclooctene	27 and -5	B	145	Acenaphthalene	1
Cyclohexenone[b]	Cyclohexene	27, -71 and -90	B	146	2-Methyl-naphthalene	4
	Cyclopentene	27, -5 and -71	E	145	Acenaphthalene	3
	trans-3-Hexene	27, -5 and -71	B	116	Biphenyl	8
Tricyclo(3.3.2.0^{1,5})dec-3-en-2-one	Cyclohexene	27 and -71	E	155	—	1

of calibrating compound. The area ratio was determined using the appropriate glc column. In all cases olefin was used as solvent (see Table 26).

a. Irradiation wave-length 313 mm, Kasha filter C' (78) $NiSO_4 \cdot 6H_2O$ (200 gm/l,5 cm), K_2CrO_4(0.2 gm/l, 1 cm) and corning glass CS 7-54.

b. Irradiation wave-length 366, corning glass filter CS 0-52 and CS 7-60.

Column B (5% FFAP on diatoporate S, 9' × $\frac{1}{8}$'').

E (5% FFAP on diatoporate S, 5' × $\frac{1}{8}$'').

F (5% Carbowax 20M, on diatoporate S, 5' × $\frac{1}{8}$'').

A.5 Quantum yield of cyclopentenone-cyclohexene in viscous solvent.

A solution of cyclopentenone (0.11 M) and cyclohexene (3.66 M) in diglyme (η^{25} = 1.01 cP) was degassed to residual pressure of 10^{-4} mm, and irradiated on an optical bench (313 mm light) at room temperature for 75 min. The quantum yield was measured as described previously and found to be $\Phi = 0.52$ (average of three measurements). This value is to be compared with the corresponding value in non-viscous solvent of 0.46.

A.6 Quantum yield of cyclopentenone and cyclohexenone triplet formation at -71°C.

A.6.1 Quantum yield of sensitized isomerization of piperylene with benzophenone in methyl acetate.

Benzophenone 91 mg (0.05 M) and 320 mg of cis- or trans-piperylene were dissolved in 10 ml methyl acetate, 5 ml of this mixture transferred to the irradiation cell, degassed and irradiated at 366 nm on an optical bench. The irradiated solution was distilled to remove benzophenone (no isomerization occurred during distillation). The isomerization was carried out to about 4% conversion. The amount of *cis*-isomer formed starting from *trans*-piperylene, or the *trans* starting from *cis*-piperylene (corrected for the amount of that isomer initially present), was determined using glc (on column A, at 20°C) from which the $\Phi_{c\to t} = 0.53$ and $\Phi_{t\to c} = 0.47$ were calculated. The experiment was repeated, but the solution was irradiated at -71°C. The $\Phi_{c\to t}$ was changed slightly to 0.51.

A.6.2 Measurement of cyclopentenone triplet formation at -71°C.

Cyclopentenone (190 mg) and the appropriate weight of *cis*-piperylene were dissolved in 10 ml methyl acetate. Five ml of this solution was degassed and irradiated on an optical bench using 313 nm light at -71°C. The amount of *trans*-isomer was determined on glc (column A, at 20°C) and corrected for the amount of *trans* initially present. The quantum yield was determined using the expression:

$$= \frac{\text{moles of } \underline{\text{trans}} \text{ formed}}{0.51 \times \text{flux}} \qquad \frac{\% \text{ of } \underline{\text{trans}} \times \text{moles of } \underline{\text{trans}} \times 1.04}{0.49 \times \text{flux}}$$

The experiment was repeated for cyclohexenone also at -71°C. A plot of Φ^{-1} vs. (*cis*-piperylene)$^{-1}$ (the concentration was corrected for contraction of the solution on cooling, $d^{25} = 0.921$ gm/cm^3 that at $-71 = 1.046$ gm/cm^3, details of these measurements will be described later) was done. A linear plot was obtained yielding an intercept of 1.042 and 1.0038 for cyclopentenone and cyclohexenone, respectively (least squares fit, computer programmed), (see Fig. 10, Tables 4 and 5).

A.7 Determination of rates.

A.7.1 Dilution curves.

A.7.1a Dilution of cyclopentenone-cyclohexene system in ether.

Cyclopentenone (50 mg, 0.1 M) and different concentration of cyclohexene (0.5 to 10 M) were dissolved in diethyl ether (distilled from sodium prior to use) (total volume of solution was 5 ml) degassed and irradiated at 313 nm on the optical bench at 27°C (air was circulated around the cell). The actual quantum yield for four different olefin concentrations was determined on column E at 130°C with acenaphthalene as calibrating compound. A linear plot of Φ^{-1} vs. [cyclohexene]$^{-1}$ was obtained, and the slope and intercept determined from least squares fit of the data (see Table 6; Fig. 11).

The experiments were repeated at -71°C for olefin concentrations (0.68, 0.86, 2.58 and 9.9 M) in ether, and in these cases the total volume of the solution was 5.8 ml which contracted to 5.2 ml after cooling to -71°C (the details of this will be discussed later).

A.7.1b Dilution of the cyclopentenone-cis-dichloroethylene system.

Solutions of cyclopentenone (50 mg) containing different weights of cis-dichloroethylene (0.9 to 12.95 M) in ether (total volume 5 ml) were degassed and irradiated on the optical bench at 313 nm. The quantum yields were determined using glc Aerograph Hi-Fi equipped with a column of (10% SE-30 on diatoporate S, 6' × $\frac{1}{8}$'' at 125°C), dibenzyl being used as the calibrating compound (see Table 6, Fig. 11).

A.7.1c Dilution curve for the cyclohexenone-cyclohexene system at 20°C.

Cyclohexenone (71.0 mg) and different weight of cyclohexene were weighted into a 5 ml volumetric flask. Ether was added to make the volume up to the mark. From the mixture 3 ml was pipetted into six identical pyrex tubes (12 cm height, 12 mm O.D.) and sealed to 9 mm (F.P.J.) Fischer Porter Joint.

The samples were degassed by the freeze-pump-thaw technique and irradiated at 313 nm on a merry-go-round apparatus, as described by F.G. Moses and R.S.H. Liu (79) at 20 ± 1°C.

A control experiment to determine the uniformity and the matching of the tubes was done by Mr. M.C. Usselman using the benzophenone, iso-propanol system.

After irradiation, 1 ml of a 2-methylnaphthalene solution (8 mg/10 ml) was added to each tube. The amount of adduct was determined using column B at 130°C. The slope and intercept of dilution curve were determined and fitted to one point done on an optical bench (the quantum yield was measured for that concentration, 10 M olefin) by a least squares computer programmed technique. The result was an average of two sets of runs. (See Table 7, Fig. 12).

The experiment was repeated using n-hexane as solvent.

A.7.1d Dilution curve for the cyclohexenone-cyclohexene system at -71°C.

Cyclohexenone (72 mg) and different weights of cyclohexene (1.1 to 10.7 M) were dissolved in diethyl ether (AR), the total volume being 5.9 ml. The samples were degassed and irradiated (313 nm) at -71°C using the specially designed cell (see Fig. 16) on the optical bench. The actual quantum yield was determined for each of the five points using column B at 130°C, and the data computed to obtain the slope and intercept (see Table 7 and Fig. 12).

A.7.2 Stern-Volmer plot.

A.7.2a Quenching of cyclopentenone-cyclohexene reaction with 2,5-dimethyl-2,4-hexadiene (DMHD).

The following solutions were prepared: (1) cyclopentenone 0.3 gm/10 ml; (2) cyclohexene 4.086 gm/10 ml and (3) DMHD 0.3473 gm/5 ml. The solvent was diethyl ether in each case.

For the quenching experiments, 1.0 ml cyclopentenone solution, 1.0 ml cyclohexene solution (1.66 M), and quencher (0, 0.2, 0.4, 0.6, 0.8, and 1.0 ml) were pipetted into each of six MGR tubes. Ether was added to make the volume in each tube 3.0 ml. The solutions were degassed and irradiated at 313 nm in an MGR apparatus at 20 ± 1°C for a period of 5 hours. After irradiation, 1 ml of calibrating solution (7 mg/10 ml acenaphthalene) was added to each tube. The amount of adduct was determined using glc (column E, at 130°C). The quantum yield for a solution containing that concentration of cyclopentenone and cyclohexene as in tube #1 was measured on the optical bench, and this point assigned as Φ_0 point. A linear plot of Φ_0/Φ vs. the concentration of quencher [Q] was obtained (see Table 8 and Fig. 13).

A.7.2b Quenching of cyclopentenone-cyclohexene reaction with DMHD in ether at -71°C.

The actual quantum yield of solutions containing cyclopentenone (50 mg), cyclohexene (1.23 gm, 2.88 M) and different concentrations of

DMHD (0.0, 0.53, 0.356, 0.257, 0.192, 0.162 and 0.116 M) in diethyl ether (total volume at room temperature 5.9 ml) were measured point by point. The solutions were degassed, irradiated (313 nm) on the optical bench at -71°C, and the products analysed on glc column E at 130°C using acenaphthalene as calibrating compound (see Table 8 and Fig. 13).

A.7.2c Quenching of cyclopentenone-cis-dichloroethylene reaction with DMHD.

The concentration of cyclopentenone in each tube was 0.2 M; *cis*-dichloroethylene was 2.66 M; the quencher ranged from zero to 0.2377 M in ether. All solutions were degassed, and irradiated (313 nm) on a MGR apparatus at 20 ± 1°C (see Table 8, Fig. 13).

A.7.2d Quenching of cyclohexenone-cyclohexene reaction with DMHD at 20°C.

The concentration of cyclohexenone in each tube was 0.14 M; cyclohexene 1.865 M; quencher concentration ranged from zero to 0.171 M. The solvent was *ether* for one run and *n-hexane* for the other (see Table 9, Fig. 14).

A.7.2e Quenching of cyclohexenone-cyclohexene reaction with DMHD in ether at -71°C.

Solutions, each containing cyclohexenone (0.14 M); cyclohexene (2.089 M), and different concentrations of DMHD ranging from (0.0 to 0.112 M), was prepared in diethyl ether (the total volume at room temperature was 5.8 ml). These solutions were degassed, and irradiated on the optical bench (313 nm) at -71°C. The quantum yield for each point was determined by glc using column B (at 130°C) and 2-methylnaphthalene as the calibrating compound. (See Table 9, Fig. 14).

A.8 The determination of the densities of solutions.

The Pycnometer (Fig. 17) was calibrated with double distilled water at 20.5°C (d = 0.9981 gm/cm^3), by determining the volume at each mark. The density of diethyl ether and n-hexane was determined and the obtained values were compared with those in the literature, the accuracy being within ± 0.2%. The density of the solutions were measured by filling the Pycnometer with a known volume and weighing.

For density measurements at -71°C, the Pycnometer was filled with solution, weighed and immersed in a dry ice/acetone mixture with the top covered to prevent moisture from condensing. After the Pycnometer had reached the required temperature, the volume was measured, this volume was corrected for contraction of the pyrex glass as follows: the volume of the Pycnometer immersed in each use was 35 ml, the decrease in temperature was 95°C, and taking the value of the expansion coefficient to be 0.000025 ml/deg (80), the correction was estimated to 0.08313 cm^3. Knowing the weight and the volume, the density of the solution could be calculated. For all experiments carried out at -71°C, the concentration of reactants were corrected for the change in the volume of the solution on cooling.

cyclopentenone-cyclohexene solution in ether,

$d^{20} = 0.744$ gm/cm^3 $d^{-75} = 0.840$ gm/cm^3

cyclohexenone-cyclohexene solution in ether,

$d^{20} = 0.740$ gm/cm^3 $d^{-75} = 0.832$ gm/cm^3

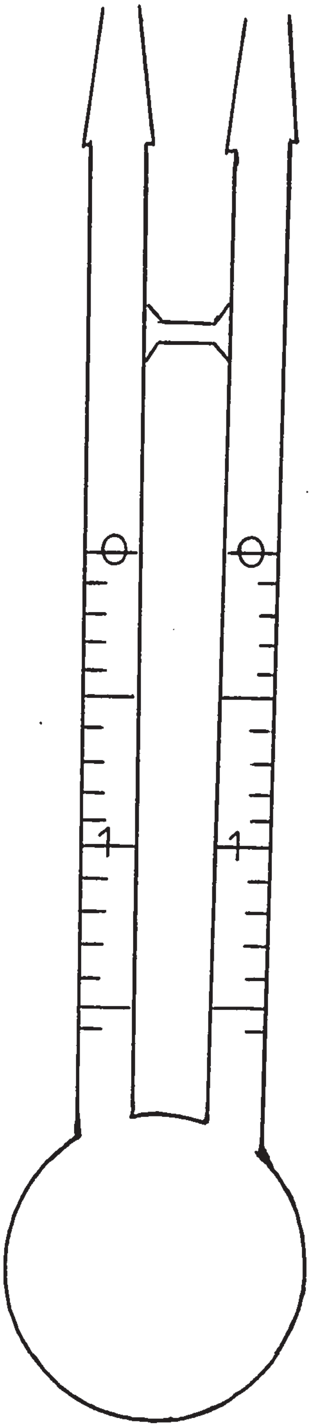


Fig.17 Pycnometer

each determination was an average of three measurements.

A.9 Viscosity of samples.

The Oswald viscometer was calibrated using water, cyclohexane, and n-pentane at 20°C. The amount of liquid used was 3.0 ml. The viscosity at -75°C was determined by using the weight which will give 3 ml at -75°C, and the viscometer was immersed in dry ice/acetone solution. The viscosity of all quencher samples were taken to be represented by a sample of about median quencher concentration.

The viscosity in (centipoise) was given by the expression

$$\eta = 1.23 \times 10^{-2} \times t \times d$$

where d is the density in gm/cm^3, and t is the time in seconds.

cyclopentenone-cyclohexene-DMHD solution in ether

$$\eta_{-75} = 1.259 \text{ cp}$$

cyclohexenone-cyclohexene-DMHD solution in ether

$$\eta_{-75} = 0.9835 \text{ cp}$$

A.10 Luminescence from cyclic enones.

The apparatus used for the measurement of luminescence from cyclic enones has been previously described by M.F. Tchir (74 p. 111).

The light source was a Hanovian 150 watt D.C. Xe compact arc.

The light was passed through a Bausch and Lomb grating monochromater 0.25 m. (Model 33-88-07).

The sample was contained in cylindrical supracil quartz tube, 8 mm O.D. (Amersil Inc.). This glass showed no detectable emission under ultraviolet or visible irradiation. The tube was sealed to a pyrex degassing bulb through a graded seal. This tube was fitted in a specially designed double wall dewar which had the lower section made of quartz. The incident and emitted light passed through about 1 cm of coolant.

The monochromatic light was focused using a quartz lens, reflected at 90° by means of an aluminized mirror and focused on to the sample. The emitted light was monitored at 90° to define this using a Jarrel-Ash spectrometer (Model #82-029) equipped with EMI 7256 photomultiplier. A photometer (Eldorado Electronic Model 201) was used to amplify the signal and to provide the high voltage to the phototube (1.2 V). The signal was recorded on a Leeds and Northup recorder.

The apparatus was also used for lifetime determination. In this case, the photometer was eliminated and the power to the photo-tube was supplied by a NJE Model S-325 variable voltage D.C. power supply. The signal was recorded on an oscilloscope (Tektronix type RM503).

For phosphorescence measurements a high speed rotating slit was used to eliminate the incident light and also as a triggering device for the lifetime studies. All solutions were degassed by the freeze-pump-thaw technique to residual pressure 5×10^{-5} mm.

A.10.1 Emission spectrum of 5,6,7,7a-tetrahydro-7a-methyl-2-indenone (THMI) 5*.

The emission spectrum of THMI (3×10^{-2} M) in MCH (American Instrument Co.) was recorded at 77°K using excitation wave-length of

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*The author is indebted to Dr. D. Becker for supplying a sample of this compound. The sample was distilled (bulb-to-bulb) before use b.p. 80°C/0.2 mm Hg.

313 nm. A 0-52 Corning filter was placed in front of the Jarrel-Ash entrance slit to remove scattered exciting light (this filter shows no detectable emission in the ultraviolet region).

The emission exhibited some structure (two bands at 377 and 403 nm) but the main portion of the emission could be described as non-structured emission with a maximum at 435 nm. The spacing between the first two bands was 1711 cm^{-1}. These two bands disappeared when a smaller rotating slit was used at lower speed, while the rest of the emission was unchanged (see Fig. 5).

The lifetime measured at 435 nm was 3.8×10^{-2} S while at 377 nm it was 3.6×10^{-3} S.

THMI 5 (3×10^{-2} M) was found to emit at room temperature in MCH, the emission consisting of a non-structured band with maximum at 410 nm. The lifetime was too short ($< 10^{-4}$ seconds) to be measured with our instrument.

A.10.2 Emission spectra of tricyclo(3.3.2.0)deca-3-en-2-one (TK) 3.

The emission spectrum of TK (4×10^{-2} M) in MCH was measured at different temperatures (-196 to 25°C) using a Xe arc lamp,350 nm light being used to excite the ketone. The emission at 77°K (medium rotating slit) exhibited fine structure with the 0-0 band located at 405 nm (E_T = 70.6 kcal/mole) and other maxima at 426.3, 435, 443, 455 and 470 nm. Using the small rotating slit, a structureless emission was obtained (1000 times less intense than the structured emission) (see Fig. 2.)

The lifetime measured at 435 nm at 77° K was 1×10^{-3} S (medium rotating slit), and at 455 nm was 1.55×10^{-3} S (small rotating slit).

On raising the temperature the intensity of the emission decreased, the fine structure slowly disappeared until at room temperature only a structureless emission with maximum at 455 nm was observed, see Fig. 3.

The TK, also emitted at room temperature in perfluoromethyl cyclohexane (Peninsular Chemresearch Inc.) or carbon tetrachloride (Fischer, spectral grade), and the emission was structureless with maxima at 459 and 425 nm respectively.

A.10.3 The emission spectrum of the levopimeric acid-p-benzoquinone adduct (HK) 1.

The emission spectrum of HK at 77°K in MCH has been observed previously by Herz (26). This compound was found to emit at room temperature in PFMCH (10^{-4}M) and exhibited a structureless emission with a maximum at 422.5 nm.

A.10.4 Quenching of the emission of benzophenone with cyclopentenone in carbon tetrachloride.

A solution of benzophenone (crystallized twice from 95% ethanol) (8×10^{-2} M) and different concentrations of cyclopentenone (0.0 to 0.62 M) in carbon tetrachloride were prepared. The solutions were degassed by the freeze-pump-thaw technique to a residual pressure of 5×10^{-5} mm, and the emission spectra recorded (each sample was measured under exactly the same circumstances). The exciting radiation was 380 nm light (where cyclopentenone does not absorb). The areas under the emission spectra were integrated using a Ott-planimeter (three runs for each sample the accuracy being within ± 10%). Since the areas are proportional to the quantum yield of phosphorescence, a plot of A_o/A vs. the concentration of cyclopentenone afforded a straight line (see Fig. 1), where, A_o and A are the integrated areas in the absence and presence of cyclopentenone, respectively.

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APPENDICES

Appendix A.

Cyclopentenone-tetrachloroethylene cycloadducts.

Irradiation of a mixture of cyclopentenone (1 gm) and tetrachloroethylene (Barker Analytical Reagent) (50 ml) for 6 hours, using 450 Watt medium pressure mercury lamp at room temperature, afforded the desired cycloadduct. Evaporation of the solvent gave an oily residue, which was chromatographed on silica gel (benzene/ether mixture was used as solvent), the early fractions containing the cycloadduct (R_f = 0.65 on silica gel plates; 25% ether in benzene). The product was crystallized from pet. ether 30-60° to give colourless needles, m.p. 44-5°C.

IR $\nu_{C=0}^{CCl_4}$: 1752 cm^{-1}.

Analysis Calc. for $C_7H_6Cl_4O$: C, 33.87; H, 2.42; Cl, 57.26%

Found : C, 34.11; H, 2.61; Cl, 57.32%

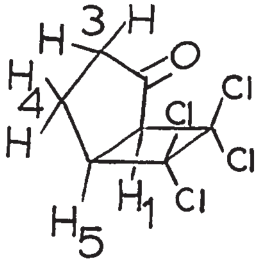
Sodium Borohydride Reduction.

To a mixture 52 mg of the ketone in methanol, 25 mg of sodium borohydride were added and the mixture stirred at room temperature for 15 min. The reaction was worked up as usual (see p. 98). A colourless solid was obtained which was crystallized from pet. ether 60-80° to give colourless needles, m.p. 92-3°C.

Analysis Calc. for $C_7H_8Cl_4O$: C, 33.60; H, 3.20; Cl, 56.80%

Found : C, 33.28; H, 3.06; Cl, 56.13%

The ketone and the corresponding alcohol were prepared to assign the chemical shifts and coupling constants J_{15}, J_{45} and $J_{4'5}$, which assisted



in the determination of the stereochemistry of other halogenated cycloadducts (see Chapter VI).

PART TWO

"STUDIES ON THE EXCITED STATE PROPERTIES OF THIOCARBONYL COMPOUNDS"

PART II. STUDIES ON THE EXCITED STATE PROPERTIES OF THIOCARBONYL COMPOUNDS

Introduction

The spectroscopy and photochemistry of carbonyl compounds have received much attention over the past decade, primarily because of the ease of manipulation. In contrast, thioketone compounds have been almost entirely neglected. This is probably due to their high ground state reactivity. However, there are now some of these substances available which are sufficiently stable in the ground state to enable their excited state properties to be investigated.

The absorption spectra of a considerable number of thioketones have been reported recently (1). In general, thioketones exhibit a low-intensity absorption band in the region of ($\bar{\nu}$ = 17000-20000 cm^{-1}) for the aliphatic-alicyclic and ($\bar{\nu}$ = 15000-20000 cm^{-1}) for the aromatic thioketones, which was first postulated (2) to be an $n \rightarrow \pi^*$ transition. The absorption shows a blue shift on transferring to a more-polar solvent (1) which is characteristic of an $n \rightarrow \pi^*$ singlet transition (3).

During the last few years the field of thioketone photochemistry has become active, particularly with regard to thiobenzophenone (4, 5, 6). It has been found that thiobenzophenone cycloadds to a large variety of carbon-carbon multiple bonds on excitation in either the n,π^* or π,π^* singlet absorption bands (5, 6) and a number of new reactions were observed. For a detailed discussion see references (6, 7). For the understanding of the reaction mechanisms involved, it was necessary to establish the nature and energy of the low-lying excited states, therefore the work presented in the first section of this part was initiated. The spectroscopic properties of thiobenzophenones 1a, b, c, xanthione 1d and thiocholestenone 2 were examined. There was little in the literature to guide us. The earliest record of an emission from a thioketone was that reported by Lewis and Kasha (8) from thiobenzophenone. They designated it phosphorescence ($\bar{\nu}_{max}$ 13900 cm^{-1}) on the basis of an approximate mirror-image relationship to the absorption spectrum which at that time was believed to be singlet-triplet absorption. (It is now known that they were using an impure sample of thiobenzophenone, as a result the absorption at 600 nm had an extremely low absorption intensity ε ca = 3). More recently the luminescence from thiobenzophenone and xanthione have been designated fluorescence (9). It is obvious that not only was the data in the literature slight, but was also conflicting.

It was concluded from our studies that the low-lying excited state of p,p'bis(dimethylamino)thiobenzophenone is a triplet with n,π^* character which is contrary to that found for the oxygen analog p,p'-bis(dimethylamino)benzophenone (Michler's ketone) where the low-lying triplet state is π,π^* with charge-transfer (CT) character† (10). Therefore, considerably different photochemical behaviour was anticipated. This led to the examination of a few photochemical reactions, mainly photoreduction and photocycloadditions of Michler's thione which is reported in the second section of this part.

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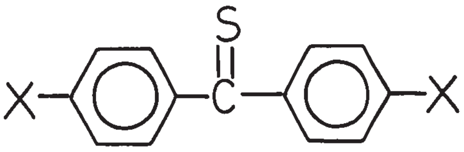
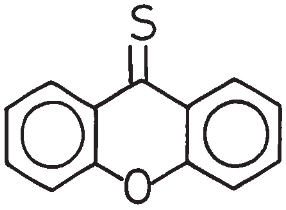
†A transition can be considered to have charge-transfer (CT) character if the change of the dipole moment associated with the electronic transition is large ($\Delta\mu \geq 5D$). The excited state dipole moments can be determined by indirect methods based on solvent effect on absorption and emission spectra (11).



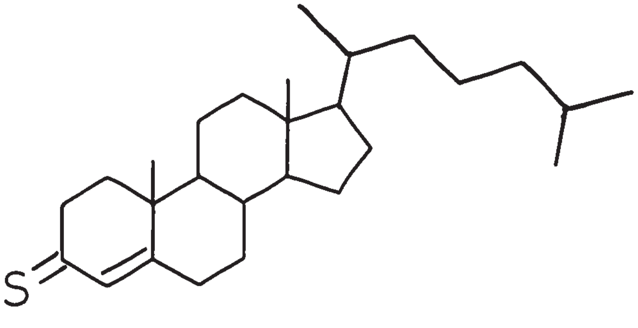
1a X = H

b = OCH_3

c = $N(CH_3)_2$



1d



2

RESULTS AND DISCUSSION

1. Low Temperature Absorption Spectra.

The five thioketones studied were thiobenzophenone **1a**, the p,p'-dimethoxythiobenzophenone **1b**, the p,p'-Bis (dimethylamino)-derivative **1c**, xanthione **1d**,and thiocholestenone **2**. Thiobenzophenone which had been prepared by the method of Gofton and Brande (12) was obtained from Mr. A.A. Nicholson. p,p'-Dimethoxythiobenzophenone and p,p'-Bis-(dimethylamino) thiobenzophenone (crystallized from ethanol and chloroform respectively) were obtained from K. & K. laboratories. Xanthione was obtained according to Schoenberg, Schultz and Nickel (13). Thiocholestenone, prepared by Bourdon's method (14) and chromatographed on silica gel at 0°C (pet. ether used as eluent) was obtained from Mr. D. Blackwell.

All five compounds exhibit low intensity absorption bands at long wave length, which, as mentioned before, (p.135) were attributed to an $n\rightarrow\pi^*$ (singlet) transition. The absorption spectra at room temperature show no fine structure, and consequently, accurate assignments of the singlet energy of these compounds was not possible. However, at liquid nitrogen temperature structure appears for all the compounds (Figs. 1-5). On the assumption that the first resolved band is the 0-0 band, the singlet energies are presented in Table 1. The energy difference between the 0-0 band and the next vibronic band was found to be ~1030 cm^{-1}, which is compatible with the symmetric C=S stretching mode. The absorption spectrum of thiobenzophenone in a crystal lattice at 77°K has

Table 1. Spectroscopic data for some thioketones, and the n,π^* energy levels.

Compound	Solvent	Temp., °K	F. C.[a] $^1n,\pi^*$	Logε	0-0,n,π^* [a] Band	Logε	E_s, Kcal/mole	$S_0 \rightarrow T$ [a]	Logε	Progression cm^{-1}
Thiobenzophenone	Benzene	298	604	2.30						
	EPA	77			626	2.4	45.67	685	$\bar{1}.95$	1000
p,p'-Dimethoxythiobenzophenone	Benzene	298	590	2.48						
	EPA	77			607	2.6	47.2	-	-	1039
p,p'-Bis(dimethylamino)thiobenzophenone	Benzene	298	580	3.02						
	E.E.	77			582	3.36	49.0	640	1.74	1033
Thiocholestenone	EPA	298	555	1.45						
	EPA	77			585	1.43	48.96	620	0.92	1187
Xanthione	MCH	298			632	1.42	45.24	665	1.00	1126

[a] all wave-length in nm.

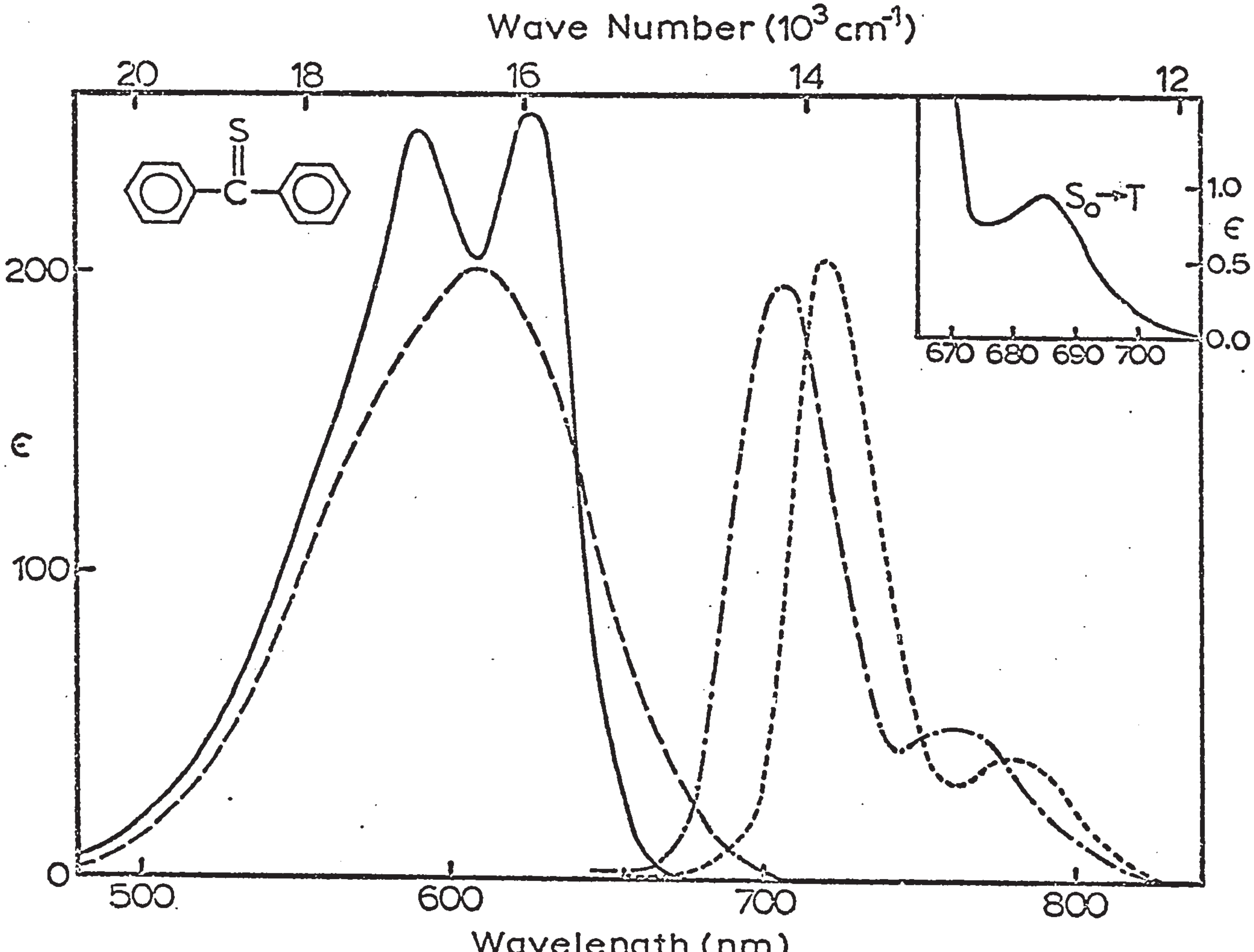


Fig.1 Absorption spectra(——) at 77°K in EPA, (---) at R.T. in benzene; Luminescence at 77°K (-.-) in EPA, (...) in MCH,n-P, of thiobenzophenone.

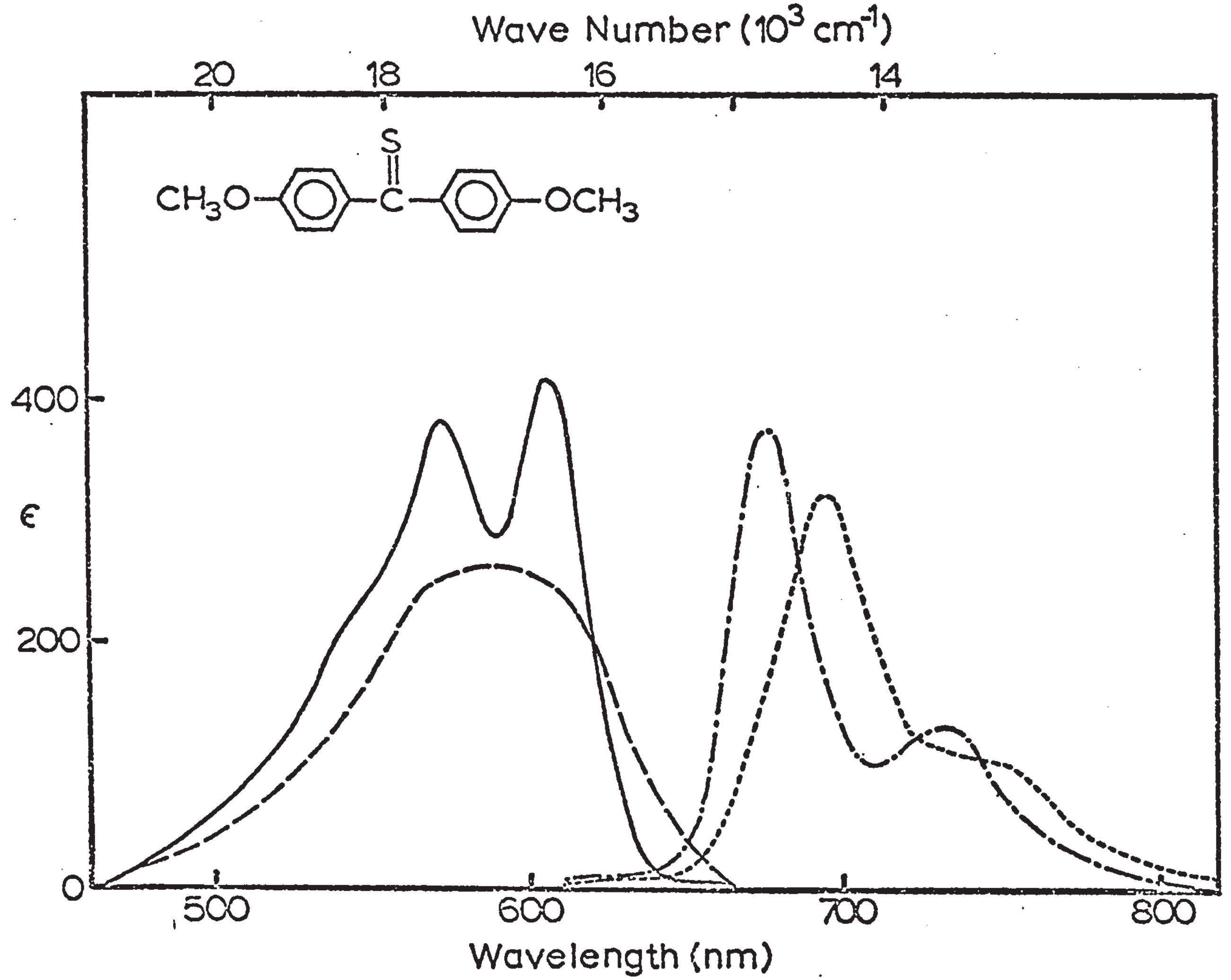


Fig.2 Absorption spectra(——) at 77°K in EPA, (--) in benzene at RT; Luminescence at 77°K, (-.-) in EPA,(...) in MCH, of p,p'-dimethoxythiobenzophenone.

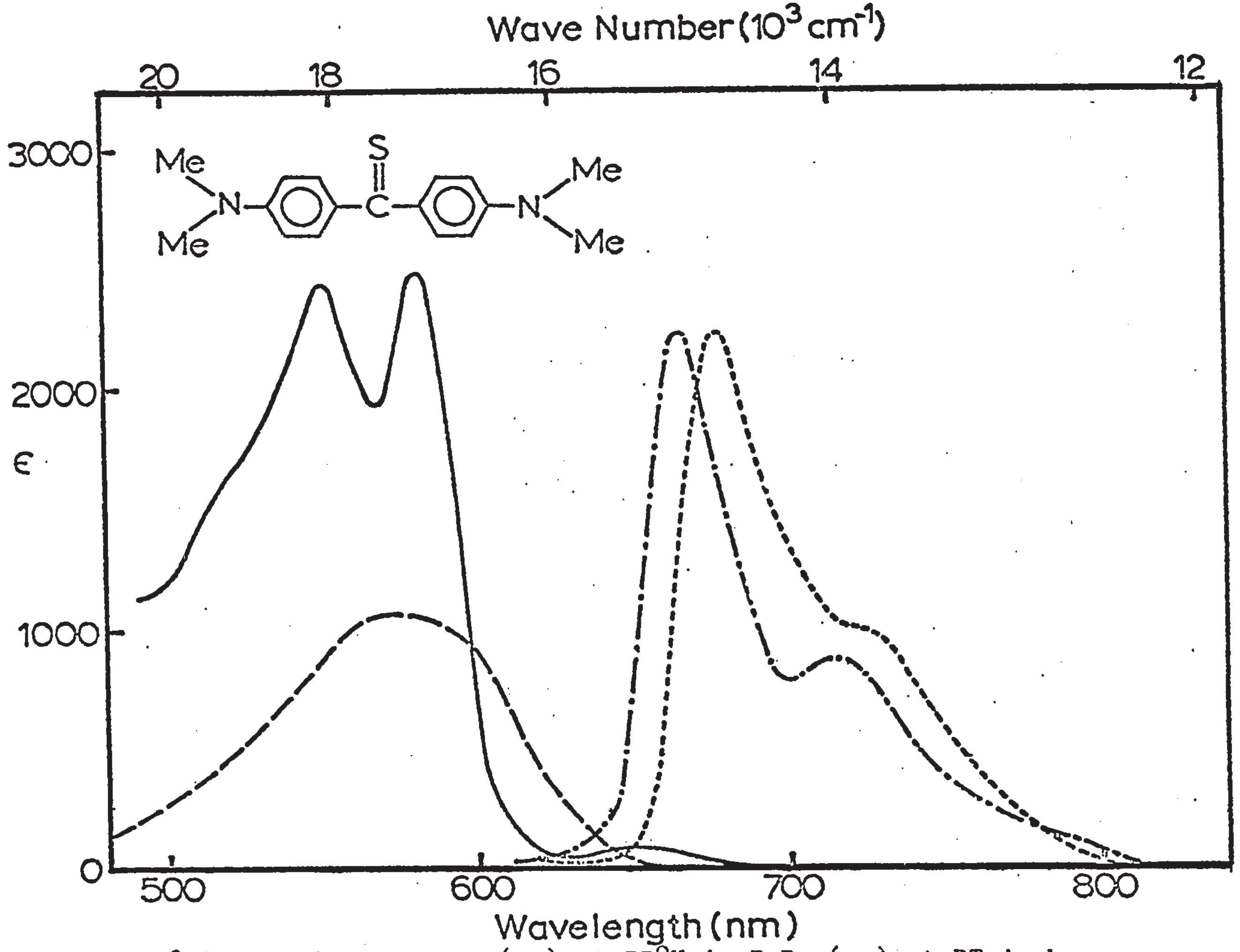


Fig.3 Absorption spectra (—) at 77°K in E.E, (--) at RT in benzene; Luminescence at 77 K (-.-) in E.E, (..) in MCH,n-P of Michler's thione.

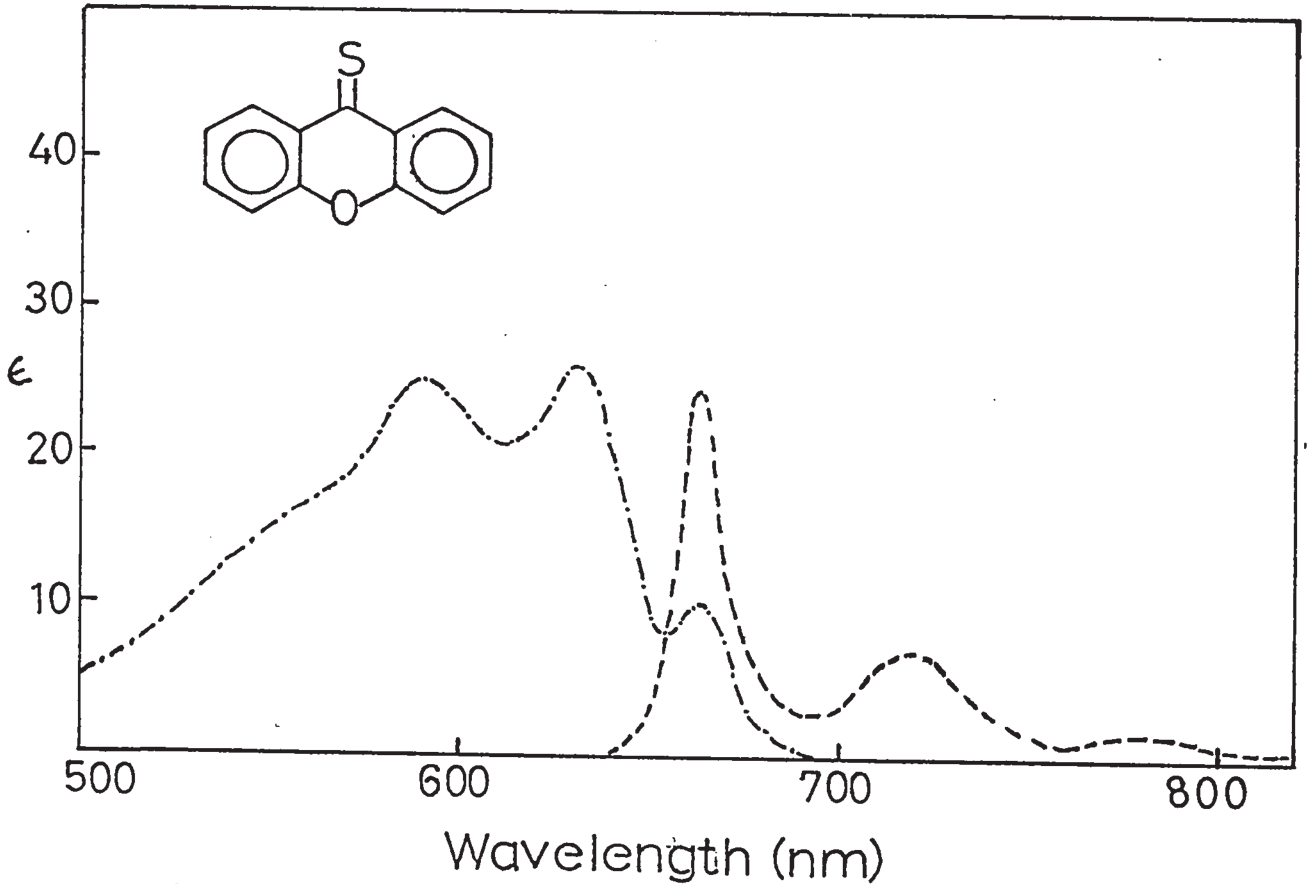


Fig.4 Absorption spectrum at RT in MCH,n-P (-.-); Luminescence at 77°K in MCH,n-P of Xanthione.

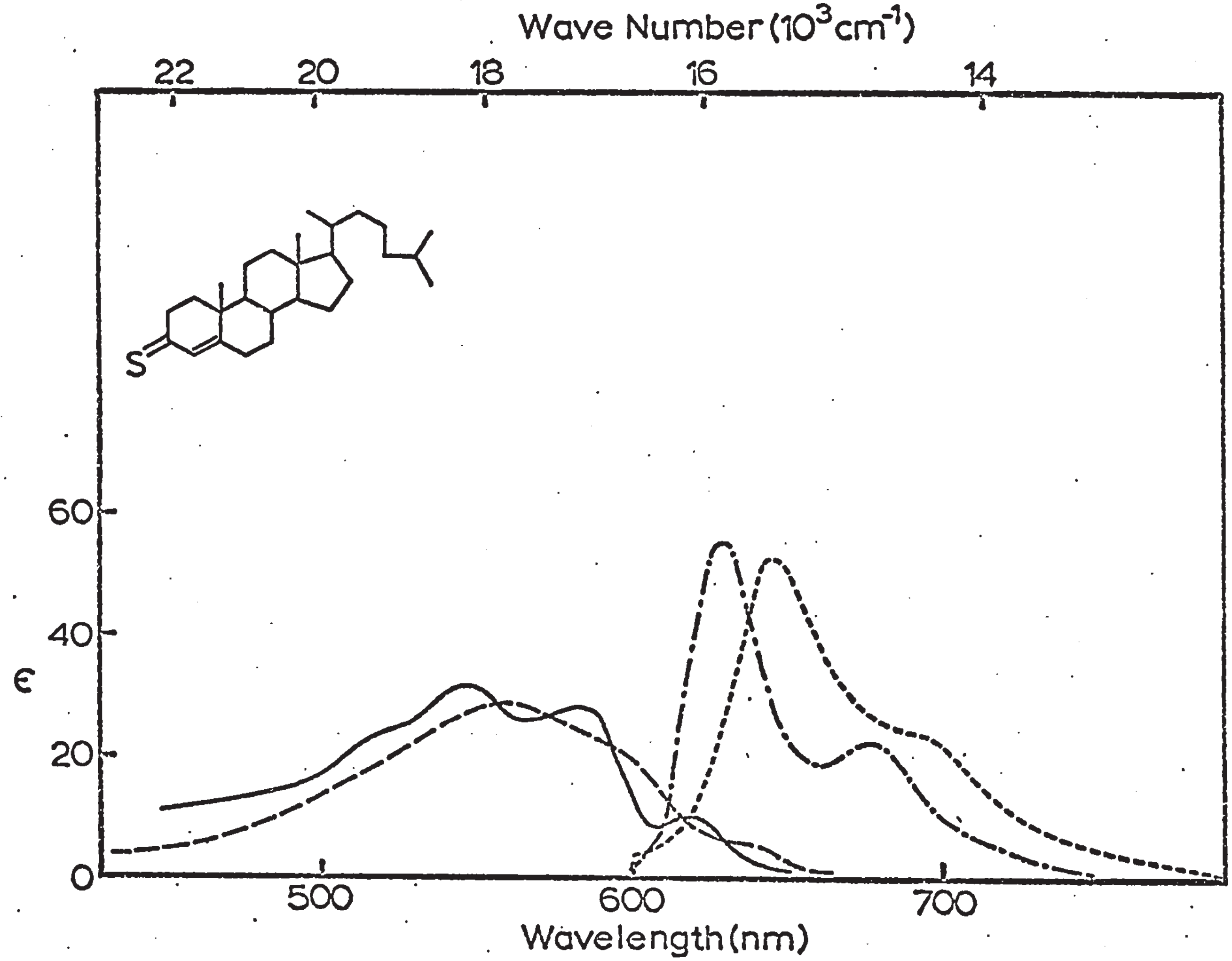


Fig.5 Absorption spectra of thiocholestenone, in EPA, (—) at 77°K, (--) at RT; Luminescence at 77°K, (-.-) in EPA, (...) in MCH.

been reported recently (15), with ($S_0 \rightarrow S_1$) 0-0 band observed at 650 nm, which is considerably displaced towards the red compared to our measurement. This seems to be a common phenomenon from crystal absorption spectra (16 footnote 2).

In the case of (1a, 1c, 1d and 2) a low intensity band at lower energy than the (n,π^*) was observed. This absorption was not visible at room temperature for either 1a or 1c, but was observable in case of 1d and 2. There is no band corresponding to this in the absorption spectrum of the corresponding ketone under similar conditions. We believe that the band is due to the $S \rightarrow T_{n,\pi^*}$ transition for three reasons: first if this band is assumed to be the 0-0 band of the $S_0 \rightarrow S_1$ transition, it does not appear to fit into the vibrational progression. Secondly, the rigidity of xanthione system does not allow for geometrical changes in the excited state and the 0-0 band of the emission coincide with that absorption band (Fig. 4). Since we have reason (see latter discussion) to conclude that the emission is phosphorescence, then it would follow that it is a singlet-triplet absorption that is observed. Thirdly a similar conclusion has been reached in the case of thiocamphor (17) and trans-β-thiohydrindanone (18), (the former on the basis of circular dichroism and the latter from circular dichroism and ORD studies).

The short wave length absorption band was attributed to a $\pi \rightarrow \pi^*$ transition because it exhibits a bathochromic shift going from non-polar to polar solvents. Also, a bathochromic shift is exhibited as the electron donating strength of the substituent increases, which indicates an increase in the charge-transfer character in this transition.

These bands show no structure, even at 77°K.

The absorption spectrum of Michler's thione obeyed Beer's Law over a concentration range of four powers of ten (in ether:methyl acetate; 3:2). This suggests that no association was occurring.

A change in color of the solution (green to red) was, however observed on cooling. This change was more pronounced the more concentrated the solution, and was due to a shift of 20 nm to longer wave-length of the charge-transfer band on cooling to 77°K. This led us to test the validity of Beer's Law at low temperature, but unfortunately the concentration limits were set because only one path length cell was available to fit the low temperature apparatus (Fig. 15). The absorption spectra were measured at room temperature and at 77°K over the wave-length range (470-700 nm) for two solutions (S_1 6×10^{-4}M; S_2 3×10^{-4}M) and the 77°K spectra were compared to the room temperature absorption and also the two 77°K spectra were compared with one another (Table 2). It is obvious, that on cooling, the optical density will increase due to contraction of the solution and consequently there will be an apparent increase in the concentration. However, this increase in the optical density was not consistent over the whole spectrum. A large increase in the absorption may be observed at wave-lengths below 520 nm, and this increase reaches a maximum at 480 nm for both solutions. This increase in absorption was also more pronounced, by about 50%, in the more concentrated solution, which is a clear indication that the phenomenon is concentration dependent. This observation explains the observed shift of the charge-transfer transition on cooling, since it is due to the formation of, and increase absorption by, a complex species which absorbs in the region 520-450 nm. This absorption added

Table 2

Variation of the O.D. of Michler's thione with concentration and temperature.

	25°C		77°K		Increase (%)	
λ(nm)	S_1^a	S_2^b	S_1	S_2	S_1	S_2
580	0.43	0.21	0.77	0.37	79	76
560	0.425	0.21	0.75	0.37	75	76
540	0.34	0.17	0.76	0.32	123	88
520	0.23	0.12	0.57	0.24	148	100
510	0.19	0.10	0.49	0.20	165	100
500	0.15	0.075	0.435	0.17	190	120
490	0.14	0.07	0.44	0.17	214	140
485	0.17	0.085	0.60	0.215	253	150
480	0.22	0.115	1.2	0.40	440	248

a 6×10^{-4}M   b 3×10^{-4}M to the charge-transfer absorption, result in the observed net shift of the band. A similar shift of CT band on cooling was observed by O'Connell (19) in the case of 4-aminobenzophenone and it was interpreted in terms of aggregate formation.

These results reveal that Michler's thione has a high tendency to form a ground state complex (the nature and stoichiometry of which is not known) which might affect its photochemical behaviour. Excitation in the band (520-460 nm) might be expected to show considerably different spectroscopic behaviour.

It is obvious that replacing the C=O by C=S reduces the energies of both π,π^* and n,π^* singlet states (Table 3). It was noticed that the n,π^* singlet energies are reduced by a constant value of ~31 kcal (10600 cm^{-1}). This value is of interest since it represents the difference in C=O and C=S bond strength.

A linear correlation was obtained between the (n,π^*) energies of the thiones and the corresponding ketones* (Fig. 6). The equation for the best fit of the line is:

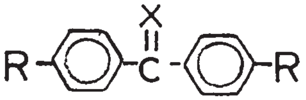
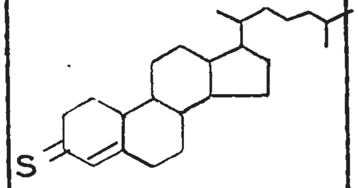
$$E_{(S_1,C=S)} = 1.544\ E_{(S_1,C=O)} - 73.56 \text{ kcal}$$

Since it has been known for a long time that the lowest-excited singlet state of Michler's ketone is CT in character (10) it was not possible to obtain the energy of the n,π^* singlet state. From (Fig. 6), knowing the n,π^* singlet energy of Michler's thione, that of the ketone can be predicted to be ~79.5 kcal. The CT singlet energy of Michler's

---

* The values represent the energies calculated from the 0-0 band, as obtained from the absorption at 77°K for the thiones and that of the ketones from refs. (20 a and b). Lack of reliable data which give the 0-0 band energies for substituted benzophenones limited the plot to 3-points.

Table 3. A comparison between the singlet electronic transitions of some thioketones and the corresponding ketones.

Compound	X = S					X = 0				
	$S_2(\pi,\pi^*)^b$		$\Delta\nu$ S_2-S_1 cm^{-1}	$S_1(n,\pi^*)^c$		$S_2(\pi,\pi^*)^b$		$\Delta\nu$ S_2-S_1 cm^{-1}	$S_1(n,\pi^*)^c$	
	ν cm^{-1}	E_{S_2} [a]		ν cm^{-1}	E_{S_1} [a]	ν cm^{-1}	E_{S_2} [a]		ν cm^{-1}	E_{S_1} [a]
R = H	31746	90.3	15720	16026	45.82	40322	115	13295	27027	77.27
R = OCH_3	28571	81.69	12097	16474	47.10	37037	106	9640	27397	78.33
R = $N(CH_3)_2$	23256	66.49	5974	17182	49.12	29940	85.6	[2163] [d]	[27777] [d]	[79.5] [d]
	33113	94.67	16019	17094	48.87	43196	124	15496	27700	79.2

a in Kcal/mole. b measured in non-polar solvent, and the values represent the Franck-Condon maximum.

c these values represent the 0-0 band as obtained from ref. 20. d predicted values.

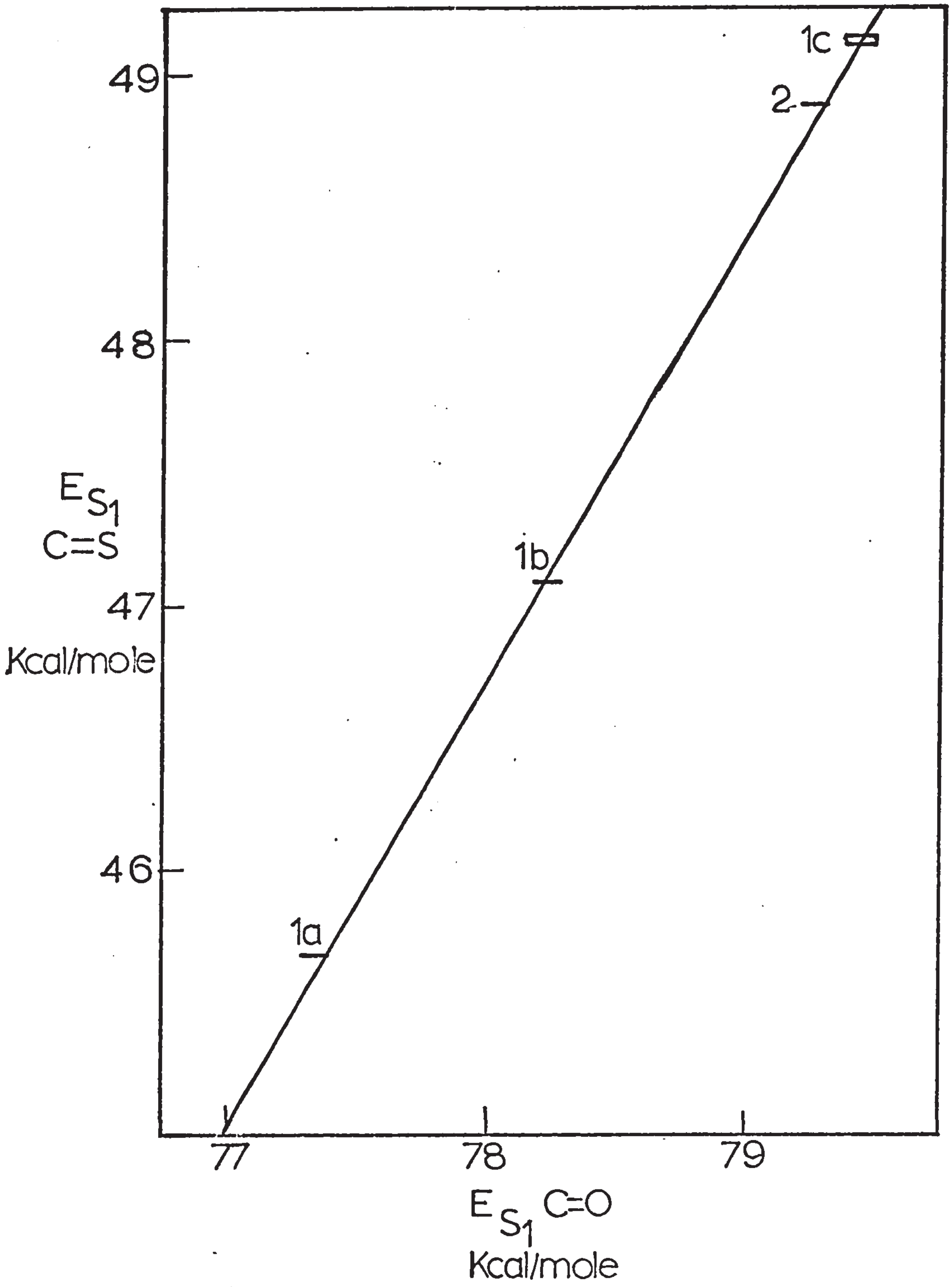


Fig. 6 Correlations between the n,π* singlet energies of carbonyl and thiocarbonyl compounds.

ketone is about 85 kcal/mole. This value represents the Franck-Condon maximum and it is therefore conceivable that both n,π^* and CT singlet states are almost degenerate, with the weak n,π^* absorption hidden beneath the strong CT absorption.

This correlation enables us to predict the energy of the n,π^* singlet states which cannot be obtained spectroscopically.

Similarly, a linear correlation of the π,π^* singlet energies of thioketones and the corresponding ketones (Table 4, Fig. 7) was obtained in non-polar solvents, taking the Franck-Condon maximum as basis for the measurement, which fit the equation:

$$E_{(S_2,C=S)} = 0.859\ E_{(S_2,C=O)} - 7.998\ \text{kcal}$$

These results can be rationalized as follows:

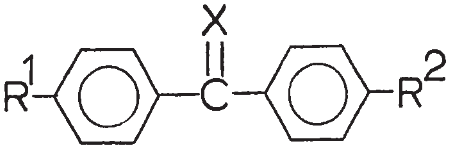
On substitution of a group with a lone pair of electrons, such as NR_2, OR or X, into the aromatic system of benzophenone or thiobenzophenone, the resonance interaction will perturb both the π and π^* levels raising the energy but the π level will be raised more. The n- level is largely unaffected by such interaction, since the n-electrons are oriented in a plane perpendicular to the π-system. <u>If the π^*-level is perturbed by a substituent to the same extent in thiobenzophenones as it is in benzophenones</u>, a correlation between $E_{(S_1,C=S)}$ and $E_{(S_1,C=O)}$ is expected.

2. <u>Luminescence from Thioketones.</u>

The path of molecular deactivation following light absorption has been of interest to chemists for many years. It is known that, in molecules like aldehydes and ketones, light absorption, which in general

Table 4.

Comparison between the π,π^* singlet energies of some thioketones and the corresponding ketones.



R^1	R^2	X=S $E_{S_2}(\pi,\pi^*)^a$	X=0 $E_{S_2}(\pi,\pi^*)^a$
H	H	90.3	115.0
MeO	MeO	81.69	105.9
$N(Me)_2$	$N(Me)_2$	66.49	85.6
Me	Me	88.1	110.8
OH	H	77.7	99.61
Me	H	89.62	113.23
$N(Me)_2$	H	65.47	86.64

a in Kcal/mole.

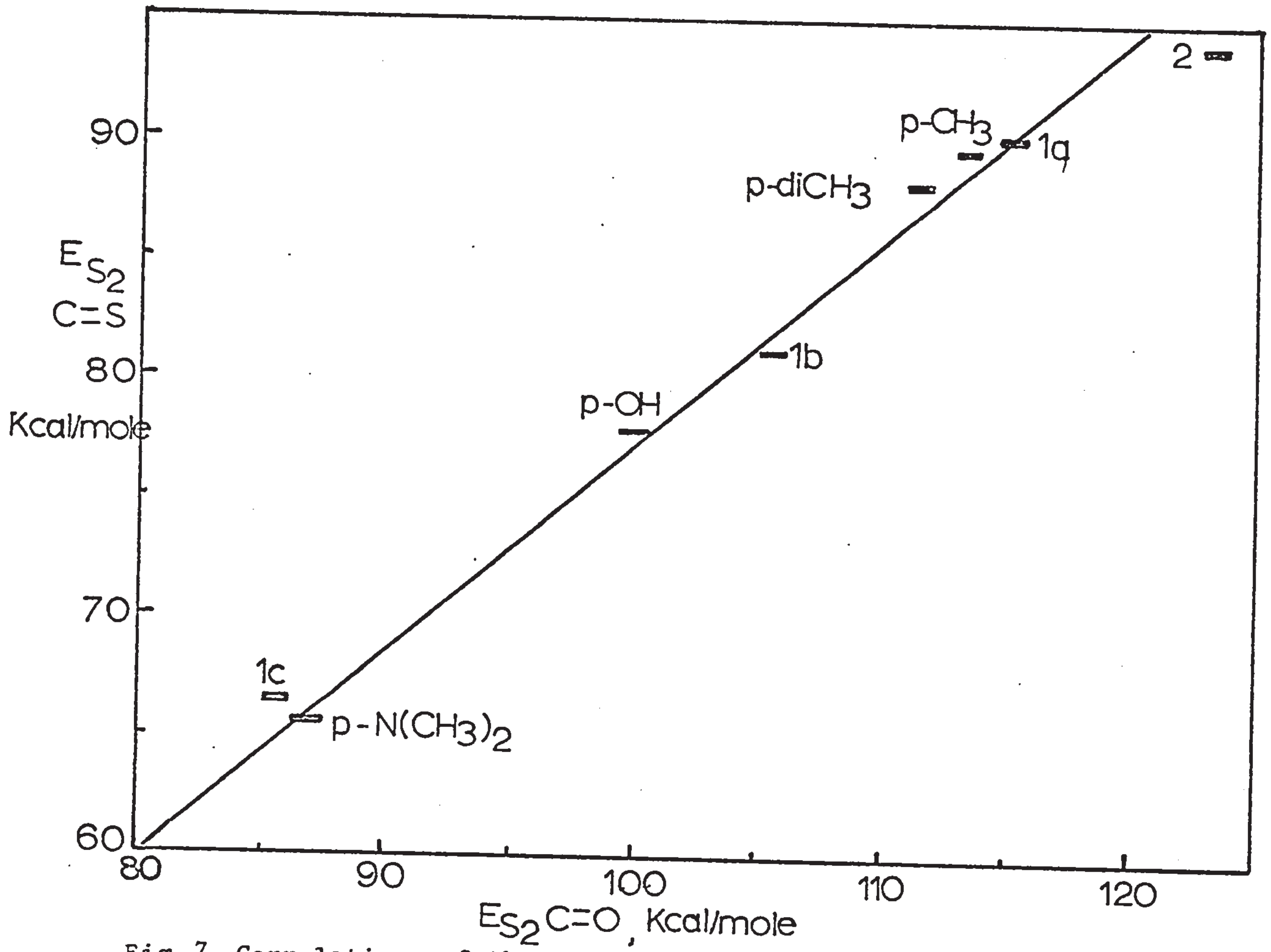


Fig. 7 Correlations of the π,π^* singlet energies of carbonyl and the analogous thiocarbonyl compounds

excites the ground singlet electronic state (S_0) to higher electronic singlet states, is followed by electronic non-radiative relaxation to the lowest excited singlet state S_1 with a rate of $10^{11}sec^{-1}$. This process is followed either by the radiative process giving rise to fluorescence ($S_1 \rightarrow S_0$ transition) or non-radiative processes: e.g. $S_1 \rightsquigarrow S_0$, $S_1 \rightsquigarrow T_1$, or bimolecular quenching processes of S_1. However, fluorescence commonly does not occur in aromatic molecules containing a carbonyl group that have n,π^* singlet as the lowest excited singlet state: examples are benzophenone, and many of its derivatives, and acetophenone. The reason for this is that almost complete intersystem crossing takes place from the lowest n,π^* singlet state to the triplet ($S_1 \rightsquigarrow T_1$, rate $\sim 10^8$-$10^{11}sec^{-1}$ manifold.

The molecules that successfully reach the lowest triplet state T_1, lose their excitation energy either by the radiative process, phosphorescence, ($T_1 \rightarrow S_0$) or by the non-radiative $T_1 \rightsquigarrow S_0$ process, or by bimolecular quenching processes.

As mentioned before thioketones characteristically have the $^1(n,\pi^*)$ excited state energy much lower than their oxygen-containing analogs. By analogy with the carbonyl compounds, thioketones are expected to exhibit no fluorescence. In addition, replacing an oxygen by a sulfur atom (the latter being a heavy atom), it is expected that this will cause: enhancement in intersystem crossing rate (change in the mechanism of spin-orbit coupling), a high phosphorescence quantum yield and a short phosphorescence lifetime.

Thiobenzophenone (10^{-3}-10^{-4}M) luminesces in a rigid glassy matrix at 77°K in EPA (Ether, <u>iso</u>-pentane, ethanol in 5:5:2 ratio) or methyl cyclohexane (MCH)-n-pentane (n-P) (4:1) mixture (Fig. 1). The emission shows resolved vibronic bands (660-800 nm). The 0-0 transition occurs at 704 nm ($\bar{\nu}$ = 14200 cm^{-1}; E_T = 40.6 kcal/mole) in EPA and 720 nm ($\bar{\nu}$, 13890 cm^{-1}; E_T = 39.7 kcal/mole) in MCH, n-P. These values are in good agreement with those reported by Lewis and Kasha (16) of ($\bar{\nu}_P$ = 14100 cm^{-1}) in EPA at 90°K and by the Russian (9) of ($\bar{\nu}_F$ = 13900 cm^{-1}) in n-hexane at 77°K.

It is very common that in the emission spectra from the n,π^* state of aromatic carbonyl molecules that the C=O stretching may be observed as the dominating structural feature. Similarly, emission from the n,π^* state of aromatic thiocarbonyl molecules is expected to contain C=S stretching (~ 1100 cm^{-1}). The energy difference between the 0-0 band transition and the next vibronic band is 1077 cm^{-1} (compatible with the C=S stretching mode) which is slightly larger than those found in the low temperature absorption spectra (1000 cm^{-1}). This indicates that the vibrational levels are farther apart in the ground singlet state than in the n,π^* singlet state.

There is a wide separation (1775 cm^{-1}) between the emission $\bar{\nu}_{0-0}$ = 14200 cm^{-1} and the absorption $\bar{\nu}_{0-0}$ = 15975 cm^{-1} which indicates that the emission is not fluorescence.

The phosphorescence lifetime is 44 μ sec. in EPA and 30 μ sec in a MCH, n-P matrix. This is in accord with a short lived triplet rather than a singlet (Table 5).

The emission was quenched with cyclooctatetraene (COT) at 77°K (Fig. 8), giving a linear plot (slope 4.84 M^{-1}) from which an apparent kq may be derived from the usual Stern-Volmer expression as $1.1 \times 10^5 M^{-1} S^{-1}$.

Table 5. Emission spectroscopy, data for the studied thioketones measured in glassy matrix at 77°K.

Compound	Solvent	λexcit. nm	λmax, nm	E_T, Kcal/mole	$(\tau\times10^{5}$, sec^{-1}	Progression cm^{-1}
			704	40.6	4.4	1077
Thiobenzophenone	EPA	550	762			
	MCH,n-p (4:1)	or 313	720	39.7	3.0	
			778			
p,p'Dimethoxythiobenzophenone	EPA	520	673	42.1	12.3	1170
		or 395	730			
	MCH	520	694	41.2	13.0	
		or 395	746			
Michler's Thioketone	E.E (1:1)	550	664	43.4	17.0	1074
			715			
		480	623	45.89	1.73	
			664			
			715			
	MCH,n-p (4:1)	550	678	42.17	8.0	
		or 410				
Thiocholestenone	EPA	550	627	45.6	4.8	1097
		or 350	673			
	MCH	550	644	44.39	2.7	
		or 350	686			
Xanthione	EPA	520	635	45.02	6.56	1149
		or 400	685			1175
			745			
	MCH,n-p (4:1)	400	662	43.19	3.50	1168
			717.5			1165
			783			

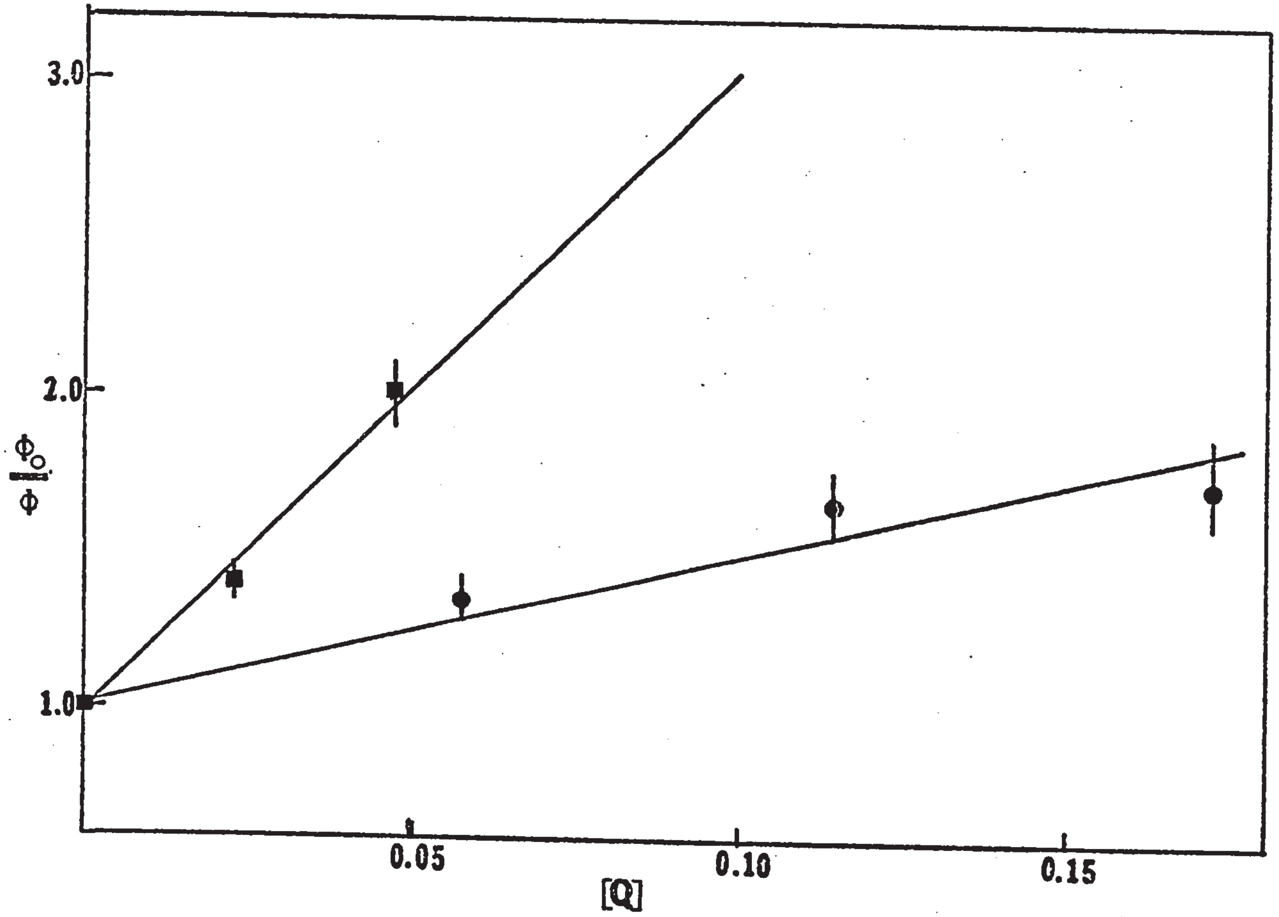


Fig.8 Quenching of thiobenzophenone emission ● with COT, and Michler's thione with ■ 9-methylanthracene at 77°K.

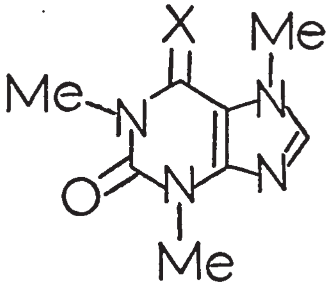
Cyclooctatetraene is known to quench benzophenone photoreduction with a diffusion controlled rate kq = $4 \times 10^9 M^{-1}S^{-1}$ (21) presumably by triplet-triplet energy transfer process. COT also quenches triplet reactions which anthracene (E_T 40 kcal/mole) fails to quench (22). Accordingly Schenk suggested that COT triplet energy must be < 40 kcal/mole. Since, despite its long tail in the ultraviolet absorption, it is very unlikely that the singlet of COT has lower energy than the thioketone. Therefore, we believe that the observed quenching at 77°K is genuine triplet-triplet quenching, unless either exciplex or chemical product formation occurs. It was noted that there was very little change in the phosphorescence lifetime under these conditions (see Table 6) i.e. the normal diffusion-controlled quenching is not being observed. As a first approximation the lifetime should be unaffected since nearest neighbour molecules quench instantaneously and

Table 6. Quenching of thiobenzophenone emission with COT.

COT.,(M)	$\tau/10^{-5}$S	% $\Delta\tau$	Rel. Inten.	% quenching
0.00	4.7	0.0	1.00	0.0
0.058	4.6	2.1	0.73	27
0.173	4.47	4.9	0.57	43

others outside the quenching sphere have no effect. However, the slight change in decay rate (4.9%) with 43% quenching of phosphorescence is probably due to the slower quenching by acceptor molecules at the periphery of the quenching sphere. This is compatible with the theory developed by Inokuti and Hirayama for energy transfer by exchange interaction (23) as has been shown in the case of the benzophenone-naphthalene, benzophenone-1-naphthal and benzaldehyde-naphthalene systems (24). 9-Methyl anthracene (E_T = 41.9 kcal/mole (25); 40.6 kcal/mole (26)) did not quench thiobenzophenone emission.

It can be seen that the emission of thiobenzophenone is red-shifted in hydrocarbon solvent with respect to EPA. This observation parallels others made with respect to aromatic ketone emission from the $^3(n,\pi^*)$ state under similar condition (27, 28). This is an added support to our view that the thiobenzophenone emitting state is $^3(n,\pi^*)$ in character, along with the chemical behaviour of that state $^3(n,\pi^*)$, the pronounced progression due to C=S stretch; the small singlet-triplet splitting (1800 cm^{-1}); and the short lifetime. It must be noted that the phosphorescence lifetime of thiobenzophenone is two powers of ten shorter than benzophenone triplet (n,π^*) 4m sec (20). It has been reported very recently that caffeine $\underset{\sim}{3}$ possesses low-lying π,π^* singlet and triplet. This compound fluoresces as well as phosphoresces and τ_P = 1.9 sec typical of phosphorescence from π,π^* triplet state. The same author reported that thiocaffeine $\underset{\sim}{4}$ also possesses π,π^* low-lying excited singlet and triplet states, and that this compound shows no fluorescence. It has τ_P = 24 m sec which is two powers of ten shorter than the corresponding carbonyl compound (29). Thus, replacing an oxygen



3 X = O

4 X = S

by a sulfur atom reduces the triplet lifetime by approximately the same extent for both n,π^* and π,π^* excited states based on the above analogy, and as can be seen the lifetime of $^3(\pi,\pi^*)$ of thioketone is expected to be 1000 times longer than $^3(n,\pi^*)$ states which is reminiscent of the behaviour of the carbonyl analog.

The emission from p,p'-dimethoxythiobenzophenone was recorded, and was broadly similar to that of thiobenzophenone (Fig. 2). The 0-0 band in a matrix at 77°K occurs at 673 nm (E_T = 42.1 kcal/mole) in EPA and at 694 nm (E_T = 41.2 kcal/mole) in MCH. The energy difference between the 0-0 band and the next vibronic band is 1170 cm^{-1}, which was also found for thiobenzophenone, compatible with the C=S stretching mode.

The phosphorescence lifetime of **1b** was 130 μ sec in MCH and 123 μ sec in EPA, and the emission was quenched with COT with an apparent kq of $3.2 \times 10^4 M^{-1}S^{-1}$. Again no change in the lifetime was observed when quencher was added.

The p,p'-Bis(dimethylamino)thiobenzophenone presented a number of new features. It exhibits strong absorption at 433 nm (benzene) which was solvent dependent and appeared to show behaviour similar to the equivalent band of Michler's ketone. The latter has been classified as charge-transfer (11). The $S_0 \rightarrow S_1$ transition resembles that of $\underset{\sim\sim}{1a}$ and $\underset{\sim\sim}{1b}$ and at longer wave-lengths the singlet-triplet absorption band is visible. The area under this absorption curve of the latter represents $\int \varepsilon \, d\bar{\nu}$, and assuming that the visible band represents most of the absorption band, the natural lifetime ($\tau°$) can be calculated very approximately from equation 1.

$$\tau° = \frac{3.47 \times 10^8}{\int \varepsilon \, d\bar{\nu} \; \bar{\nu}_A^2} \frac{g_u}{g_i} \qquad (1)$$

where $\bar{\nu}_A$ is the wave number at maximum absorption and $g_u/g_i = 3$ for triplet and one for singlet. We find $\tau° = 97$ μ sec for the triplet. Using the same treatment for the singlet we find $\tau° = 0.29$ μ sec in ether:methylacetate (3:2) (using the 0-0 band only since the whole band is not visible and we are primarily interested in order of magnitude). The measured phosphorescence lifetime observed with excitation by irradiation into the (n,π^*) singlet absorption band was 80 μ sec (hydrocarbon matrix, MCH, n-P) and 170 μ sec in EPA matrix at 77°K. This is considerably longer than the calculated singlet lifetime, and therefore reinforces the conclusion that the emission observed is phosphorescence. The vibrational progression again shows the C=S stretching mode (1075 cm^{-1}) as the dominant feature (Fig. 3).

Excitation by irradiation in the observed ground state (see page 146) complex absorption band (in the wave-length region 460-520 nm) induced an

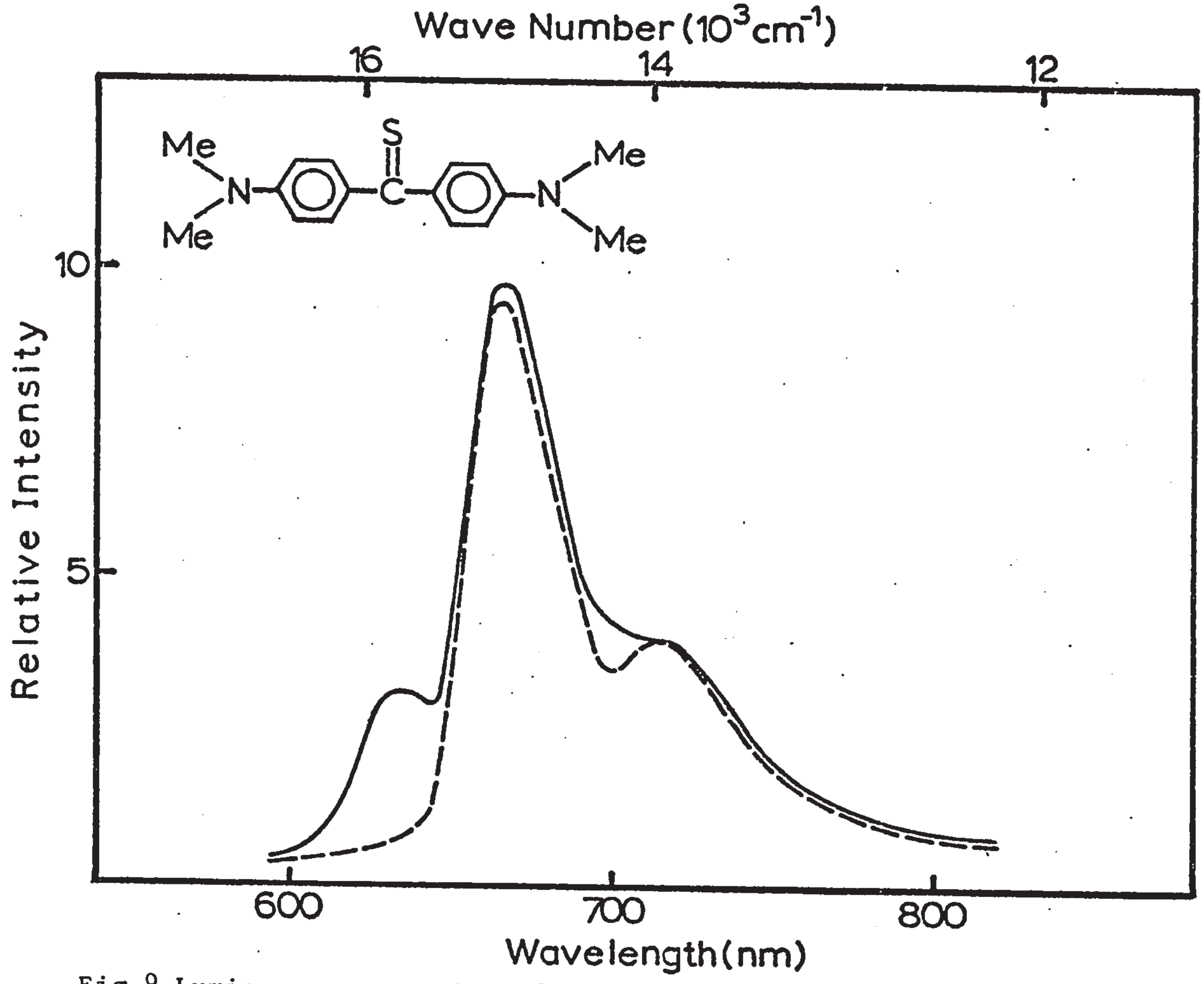


Fig.9 Luminescence spectra of Michler's thione at 77°K in E.E, (—) λexcit. 480nm, (---) λexcit. 520nm.

additional emission which was observed on the high energy side of the normal emission (Fig. 9). This new emission varied in intensity with exciting wave-length and reaches a maximum on exciting at 480 nm. No such emission was observed on exciting below 460 nm although irradiation into the CT band is still taking place. The lifetime determined for the emitting species was 17 μ sec although this figure is probably not reliable, being at the limits of the present instrumentation.

It was also found that the ratio of this emission to the $^3(n,\pi^*)$ emission was concentration dependent, decreasing with decreasing concentration (Table 7, Fig. 10). The relative intensity of this emission varies exponentially with concentration (Fig. 11). The nature of the species responsible for this emission appears most likely to be that of an excimer. Excimer phosphorescence has been observed for several halogenated aromatic hydrocarbons (30). A perhaps more relevant observation, is that the photoreaction of Michler's ketone with benzophenone was proposed to proceed through a triplet "exciplex". Michler's thione appears to be the first instance of a carbonyl or thiocarbonyl derivative reported to exhibit excimer emission. The excimer emission is not simply one band on the high-energy side of the n,π^* phosphorescence; rather it extends under the normal phosphorescence spectrum. This is most clearly demonstrated in (Fig. 9), by the growth of emission in between the fine structure of the normal phosphorescence.

Both emissions were quenched with COT, anthracene and 9-methylanthracene, and with the latter an apparent bimolecular quenching rate constant of $1.23 \times 10^5 M^{-1}S^{-1}$ was obtained. Again very slight change in the phosphorescence lifetime was observed in presence of quencher. A

Table 7. Effect of concentration on the ratio of excimer emission to the n,π^* phosphorescence emission of Michler's thione measured at 77°K in rigid matrix (λ excit. 485).

No.	$A_D/A_{n,\pi^*}$ ±	Conc./10^{-5}M
1	0.21	70
2	0.20	35
3	0.187	23
4	0.180	17.6
5	0.166	8.9
6	0.158	4.75
7	0.12	0.89
8	0.10	0.57

± Where A_D and A_{n,π^*} are the integrated areas of excimer and n,π^* emission respectively.

Fig.10 Change in the relative intensity of Michler's thione Excimer emission with concentration.

Fig.11 Change in the relative intensity of Michler's thione Excimer emission with the log[C].

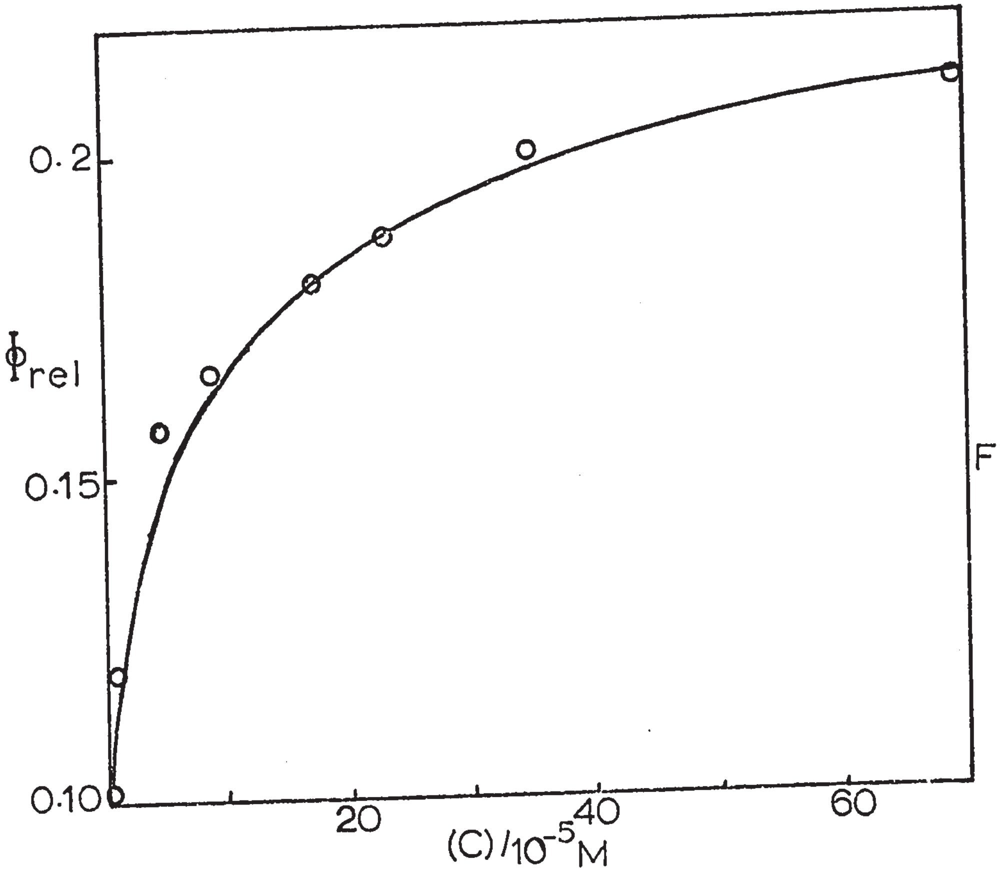

0.2
0.15
0.10
Φ_{rel}
20
40
60
(C)/10^{-5}M

Fig.10

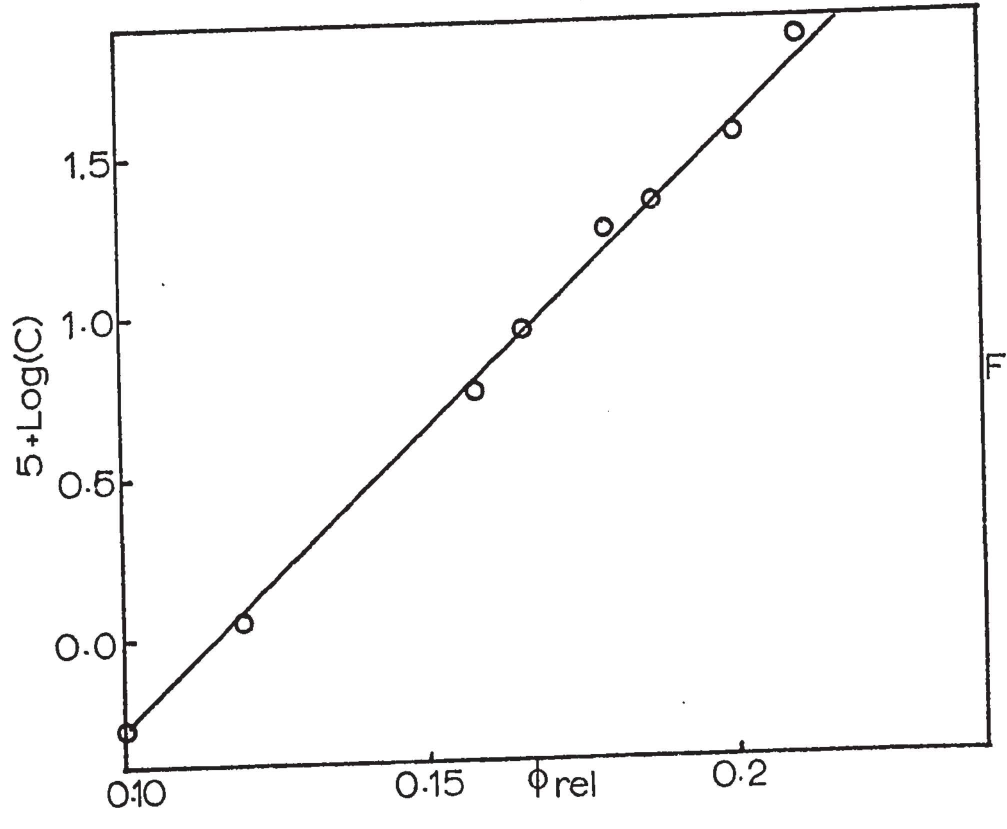

1.5
1.0
0.5
0.0
5+Log(C)
0.10
0.15
0.2
ϕ_{rel}

Fig.11

change of 3.6% with 50% quenching of phosphorescence is detected.

After our work was completed, similar observations with Michler's ketone was reported by Klöpffer (31). He reported that Michler's ketone shows phosphorescence from two levels which are populated by intersystem crossing from two connected singlet levels. This is indicated by the dependence of phosphorescence spectra, decay time, and fluorescence-phosphorescence intensity ratio on the wave-length of the exciting light. The electronic nature of these states was not discussed.

Xanthione exhibited structured emission in a rigid matrix at 77°K, with a band progression of 1165 cm^{-1}. The 0-0 band occurs at 662 nm (E_T = 43.2 kcal/mole) in MCH, n-P, and at 635 nm (E_T = 45.02 kcal/mole) in EPA. The emission showed a large red shift in changing from polar to non-polar solvent.

The phosphorescence lifetime of 1d was 35μ sec in MCH, n-P and 65.6 μ sec in EPA. By analogy the emission is phosphorescence from $^3(n,\pi^*)$ state.

As an example of α,β-unsaturated thioketones we chose thiocholestenone 2. This possesses, unlike the corresponding ketone (20b), a low-lying $^3(n,\pi^*)$ state (Fig. 4) which shows structured emission. The 0-0 band occurs at 627 nm (E_T = 45.6 kcal/mole) in EPA and at 644 nm (E_T = 44.39 kcal/mole) in MCH in rigid matrix at 77°K. The band progression was 1097 cm^{-1}. The phosphorescence lifetime was 48 μ sec in EPA, 27 μ sec in MCH at 77°K, and the triplet was quenched by cyclooctatetraene with an apparent bimolecular rate constant of $1.1 \times 10^5 M^{-1} S^{-1}$ at 77°K. As with the aromatic thioketone there was a red shift in changing from polar to non-polar solvent.

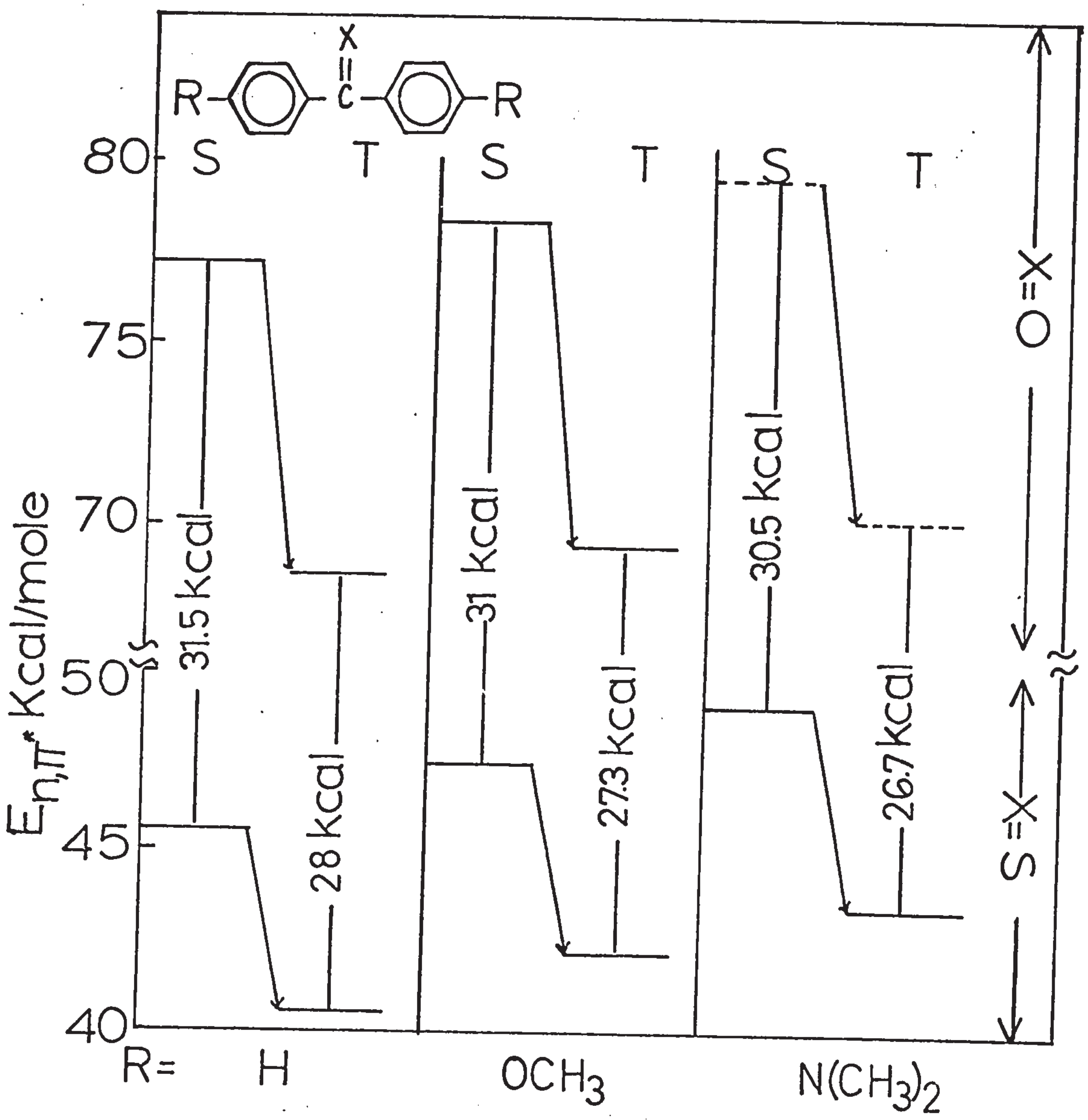
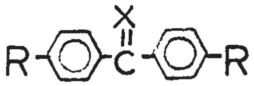
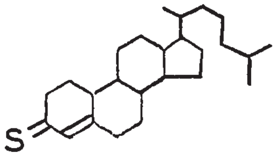


Fig.12 Correlation diagram of the n,π* singlet and triplet levels of benzophenones and their corresponding thiobenzophenones.

Table 8. Correlation of the n,π^* triplet energies of thioketones and the corresponding ketones.

Compound	X = S	ΔE	X = O	
	$E_T(n,\pi^*)$		$E_T(n,\pi^*)$	E_T S-T
				
R = H	40.6	28	68.6[a]	70.6[c]
R = MeO	42.1	27.3	69.4[a]	71.5[c]
R = $N(Me)_2$	43.4	26.7	70.1[b]	
	45.6			74.2[d]

All values are in kcal/mole. a D.R. Arnold, "Advances in Photochemistry", Vol. 6, 328 (1968), John Wiley and Sons, New York. b R.O. Loutfy and R.O. Loutfy, J. Phys. Chem., in press. c ref. 20a d ref. 20b.

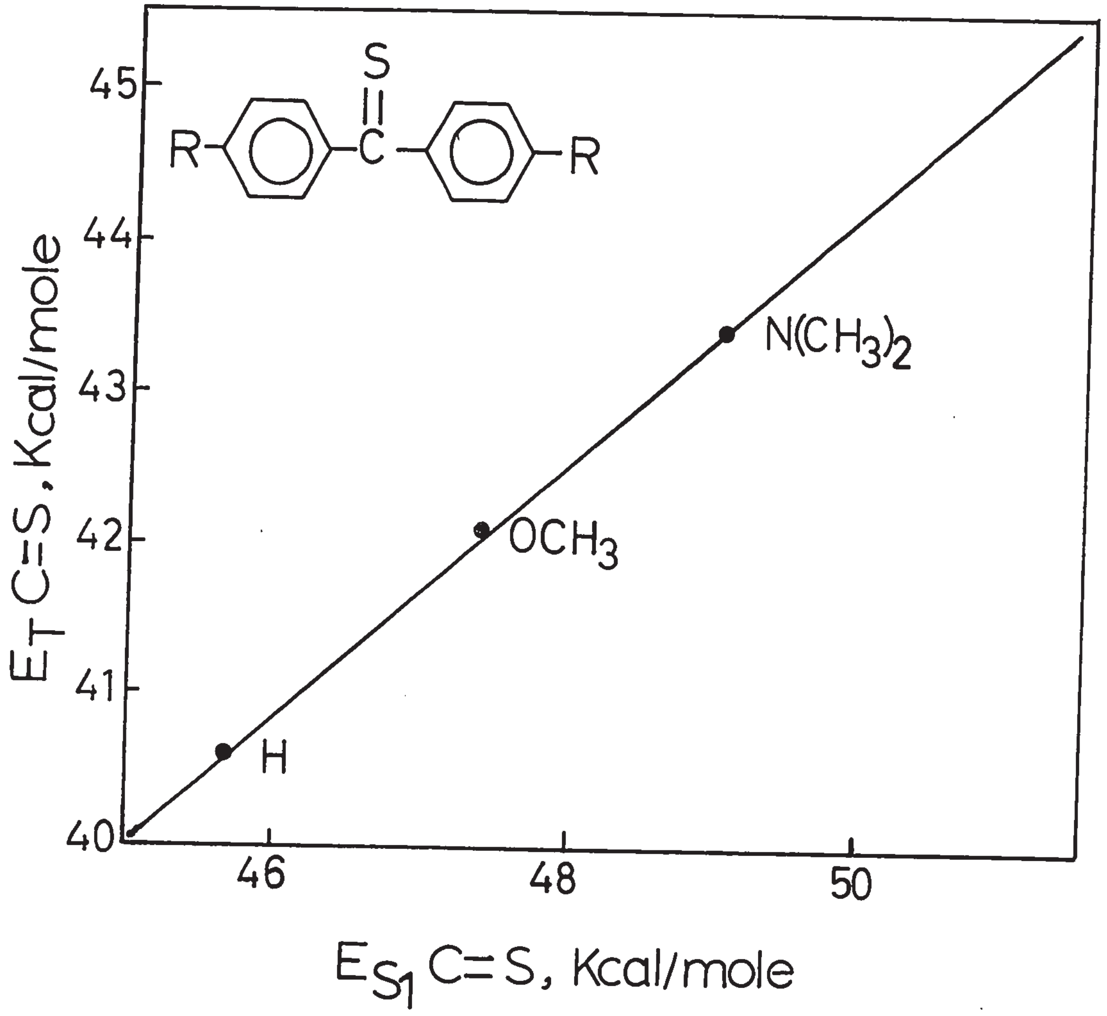


Fig.13 Correlation between the singlet and triplet n,π* levels of thiobenzophenones.

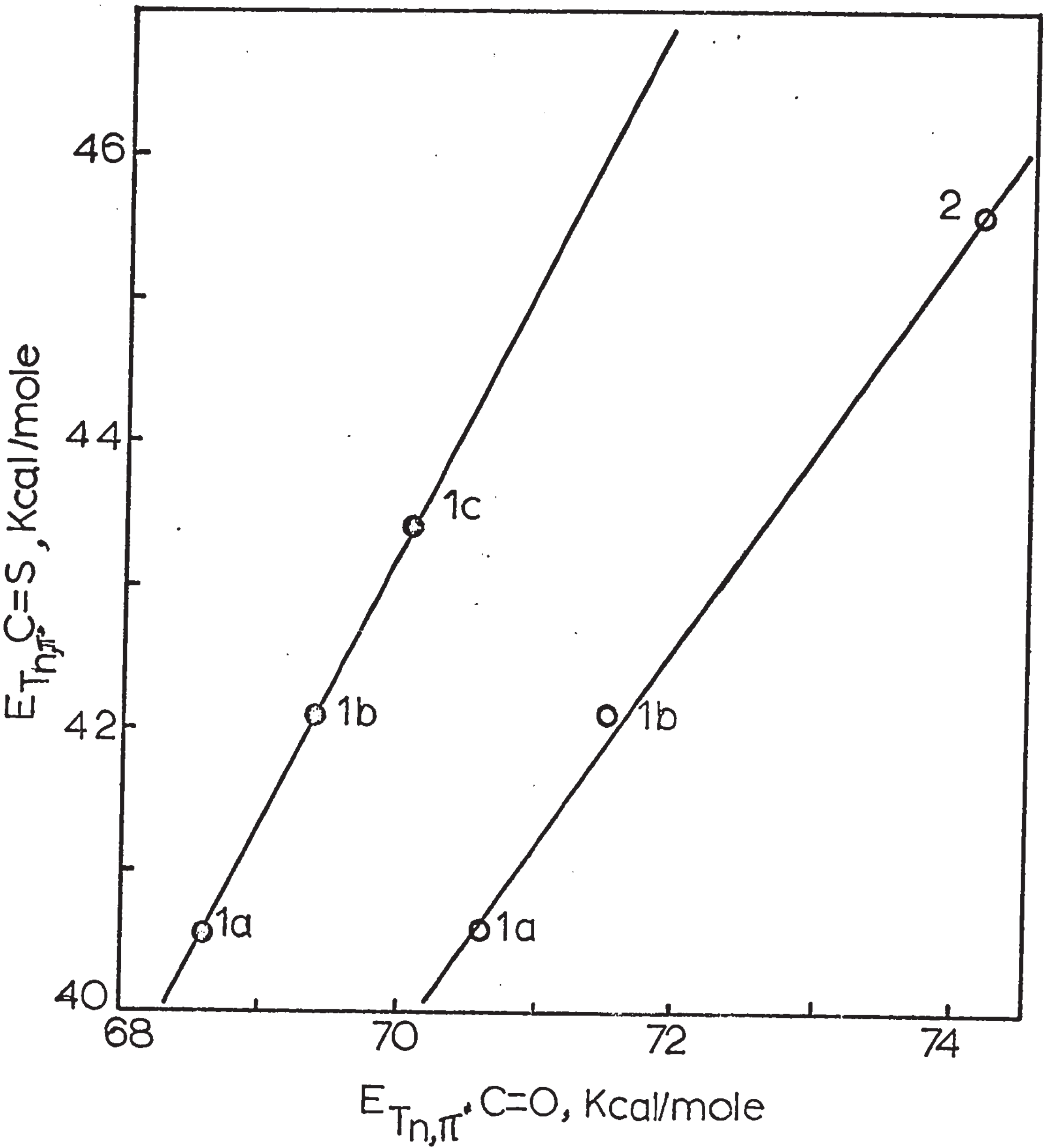


Fig. 14 Correlations of the n,π^* triplet energies of thioketones and ketones ; o from phosph. O-O band; o from S-T excitation absorption.

The singlet-triplet splitting can be given by the equation

$$E_{(S)} - E_{(T)} = 2\ K_i$$

where K_i is called exchange integral, which becomes large as the space to which the electrons are confined become smaller (32).

The singlet-triplet splitting of some benzophenones and thiobenzophenones are shown in (Fig. 12). The constancy of the S-T splitting is remarkable, this necessitates that K_i is constant for each series. A linear correlation between $E_{(S_1,C=S)}$ and $E_{(T_1,C=S)}$ was obtained (Fig. 13) from which the following equation was derived.

$$E_{(T_1,C=S)} = 0.85\ E_{(S_1,C=0)} + 1.76\ \text{kcal}$$

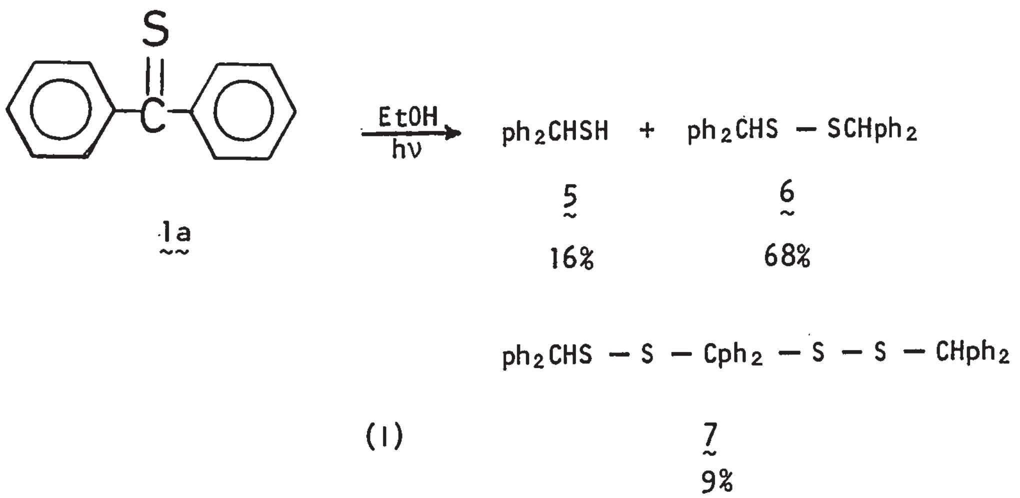
From (Fig. 12) it is obvious that the energy differences between the singlets and triplets of benzophenones and the corresponding thioketones are almost constant and as mentioned before this is a reflection of the equal effect of a substituent on the energy of the π^* level in the ketone and thione series. Again a linear correlation between $E_{(T,C=S)}$ and $E_{(T,C=0)}$ was found (Table 8, Fig. 14) which fits the equation

$$E_{(T_1,C=S)} = 1.867\ E_{(T_1,C=0)} - 87.47\ \text{kcal}$$

The triplet energy of cholestenone was obtained by a different technique from the other values, which explains the deviation of this compound.

3. Photochemistry of p,p'-Bis(dimethylamino)thiobenzophenone (Michler's thione).

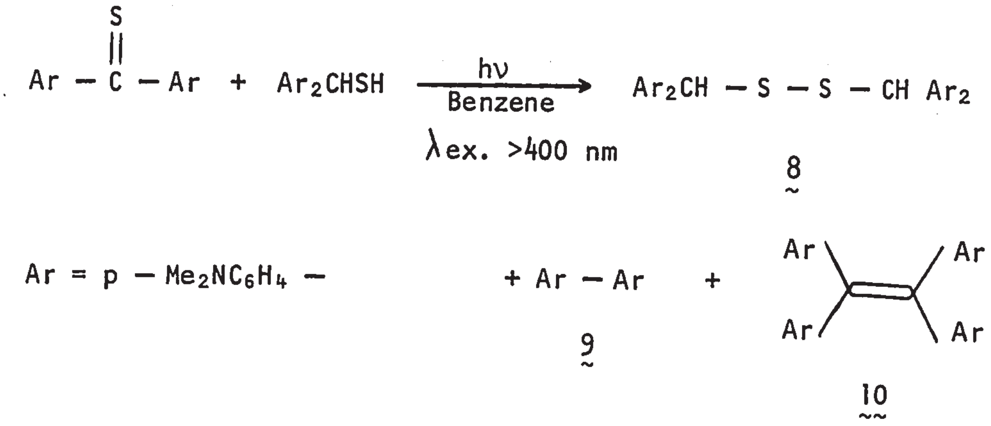
In recent years the relationship between the nature of the lowest excited states and the photochemical reactivity of ketones has received a great deal of attention. In general, it has been shown that the excited states in question can be classified broadly as $n-\pi^*$ or $\pi-\pi^*$ on the basis of their photochemistry. Ketones with a lower n,π^* triplet are known to be reactive with regards hydrogen abstraction and photocycloaddition reactions, while those with a lower $\pi-\pi^*$ triplet show little, if any reactivity toward hydrogen abstraction. Thioketone photochemistry has been studied only recently (6, 33) and whether the above criteria can be extended to the thioketone or not, needs extensive investigations. Thiobenzophenone has been shown to add to carbon-carbon multiple bonds to give thietanes (6, 33), and it is photoreduced in ethanol to give thiol 5, disulfide 6 and tetrasulfide 7 (see Reaction I) (5). These results indicate that thiobenzophenone behaviour is similar to that of benzophenone, the triplet state being reactive toward cycloaddition and hydrogen abstraction.



(I)

The quantum yield of disappearance of Michler's ketone in ethanol was found to be $< 10^{-4}$ while that in cyclohexane was 0.4. This observation with the large change in the phosphorescence lifetime in different solvent led Suppan (34) to the conclusion that a crossing of an $^3n,\pi^*$

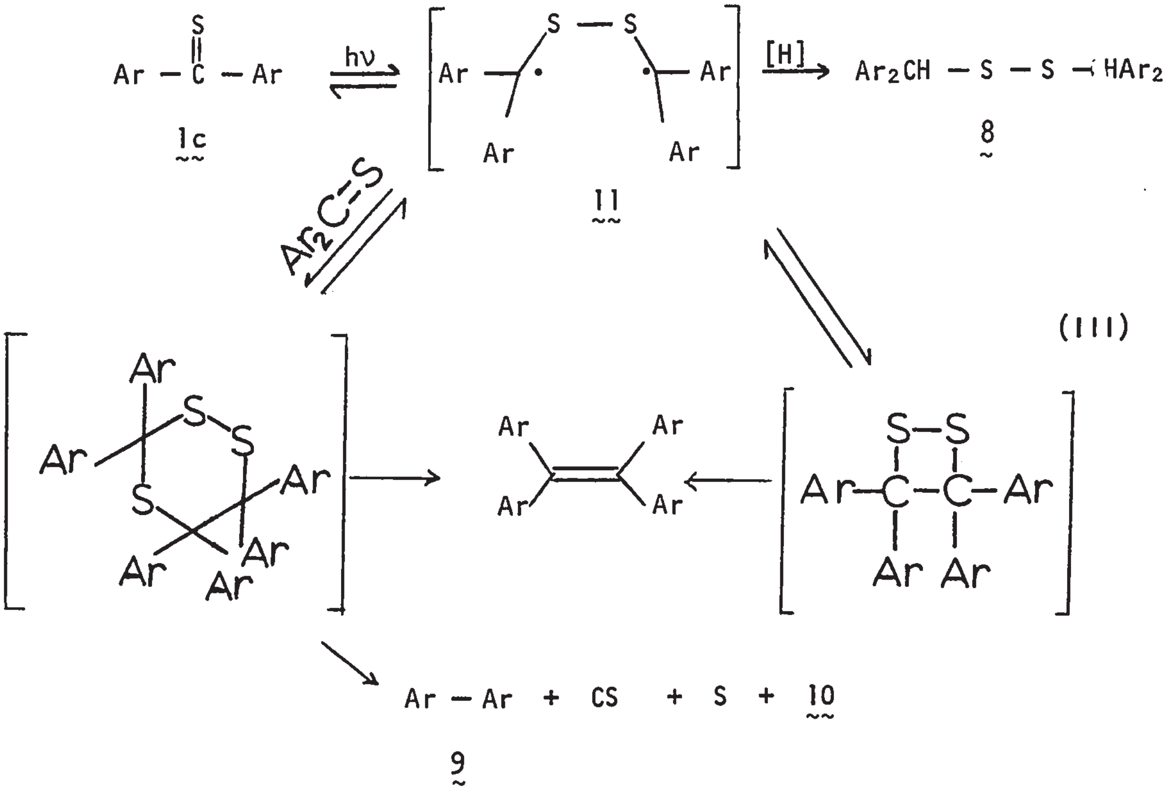
and a ^{3}CT state had taken place. It has been mentioned earlier, that in contrast with Michler's ketone, the lowest triplet excited state of Michler's thioketone was n,π^*. This was supported by, aside from the spectroscopic data, the fact that the transient (triplet) in flash photolysis decays faster in the presence of isopropanol (with first order decay rate constant of $1.7 \times 10^7 S^{-1}$) than in benzene (kd $7.0 \times 10^6 S^{-1}$) (7), i.e. it was being reduced. Such reduction is usually accepted as a characteristic of such n,π^* states. This led us to study the photoreduction of Michler's thione, and to simplify the system, we used the corresponding thiol as a hydrogen donor. The main product obtained was the disulfide 8 (in 55-60% yield). At the same time two other substances were isolated and found to be p,p'Bis(dimethylamino)biphenyl 9 and the olefin 10 based on physical and spectroscopic evidences (see Reaction II).



(II)

It was also found that product 9 and 10 were formed when Michler's thione was irradiated in benzene solution in the absence of thiol. No disulfide 8 formed under these conditions.

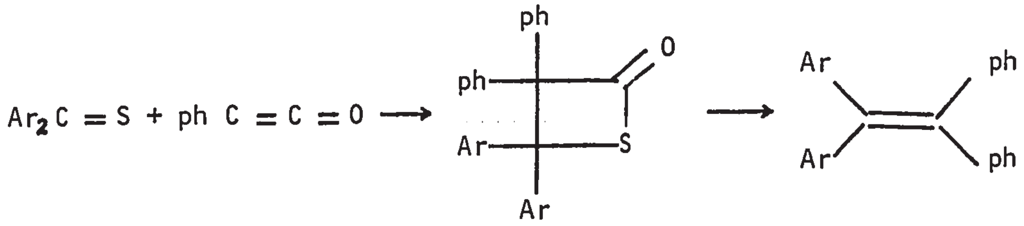
Evidence for the mechanism is not available. Bearing in mind the relative stability of the thioketyl radical, the observed emission from the excimer and the presence of a self-quenching mechanism as indicated by flash-technique (7) ($k_{sq} = 4 \times 10^9 M^{-1}S^{-1}$) it cannot be excluded that the olefin 10 derives from attack on the thioketone by the triplet, a process so far unobserved in ketone photochemistry. The resultant dithiotetramethylene 11 could be reduced to the disulfide, although other mechanisms can be invoked, or could cyclize to the diathia analogue of the now known 1,2-dioxetanes. The latter may eliminate diatomic sulfur. Alternatively, further addition of thioketone could give trimer from which 10 may also be derived.



(III)

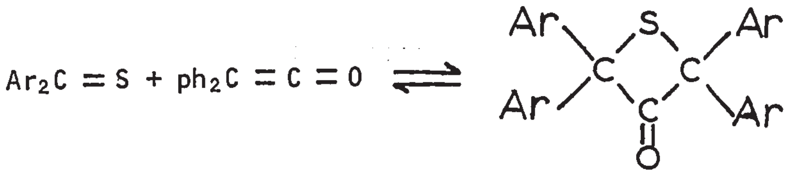
In the absence of the thiol the reaction is 12 times slower. This indicates that dithia tetramethylene 11 is reversibly decomposing to starting material, the reaction lying far to the left (see scheme), but in the presence of thiol there is a reaction occurring with 11 shifting the equilibrium to the right.

Michler's thioketone is known to undergo dipolar addition reactions (see reaction IV) while thiobenzophenone and its p,p'-dimethoxy derivative react differently (see reaction V). This presents major difference



12

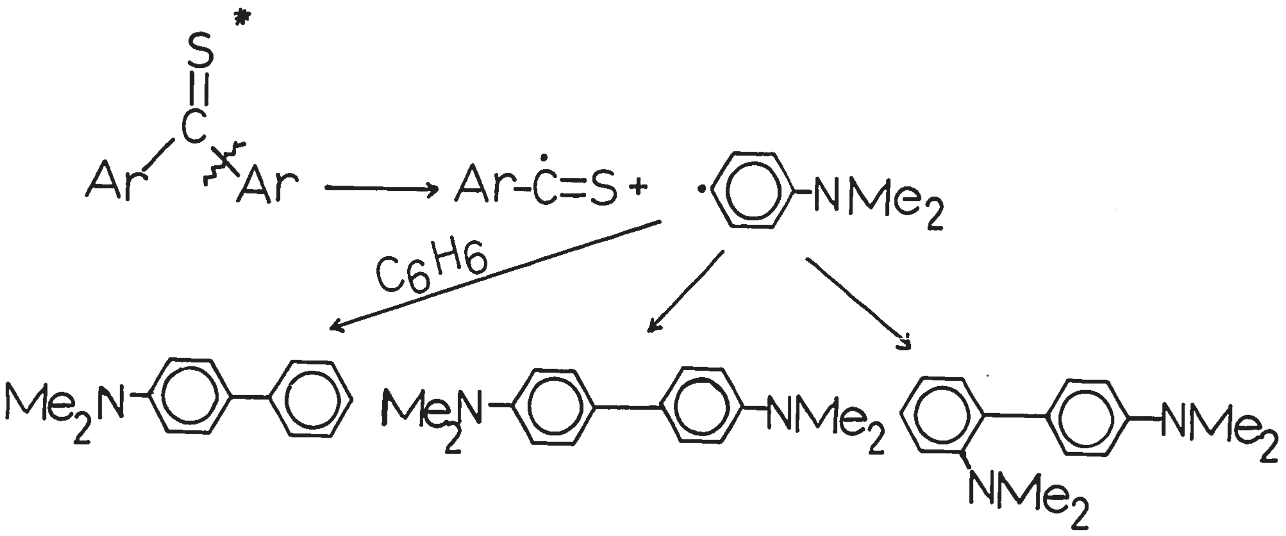
Ar = p, $Me_2NC_6H_4$ − (IV)

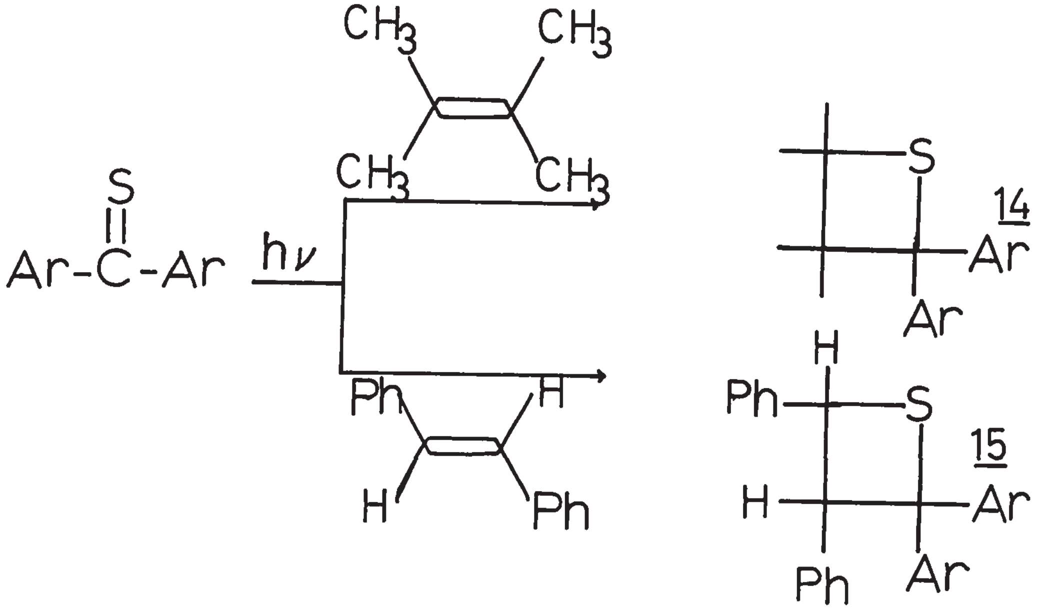


Ar = ph or p, $MeOC_6H_4$− (V)

in behaviour. The formation of intermediate **12** is quite analogous to the proposed formation of diathiaoxetanes as the intermediate in the formation of **10**.

The formation of **9** represents a problem, since it must be formed intramolecularly. This is based on the fact that if Norrish type I photodissociation, which has never been observed with aromatic carbonyl compounds, were to take place, then a dimethylaminophenyl radical and thiyl radical would be obtained in the benzene solution. We would then expect the formation of mixed diphenyl derivatives (see below). However, since the only isolated diphenyl was the p,p'-disubstituted one this excludes Norrish type I cleavage. Product **9** could be obtained from the





14

15

Ar = p, $Me_2N-C_6H_4-$

trimer with loss of CS_2, S and a thione. On the other hand the intermediacy of a "zwitter ion" cannot be totally excluded.

Similarly we have found that Michler's thione adds rapidly to tetramethylethylene ($\lambda > 420$; 80%) and to stilbene to give thietane 14 and 15 respectively (see experimental section for assignment of structure).

The large difference in the reactivity of Michler's thione and ketones reflects the difference in the nature of the lowest triplet state.

Conclusion.

Sulfur-containing compounds have red-shifted absorption bands as compared to their oxygen-containing analogs. The higher intensity of the singlet-triplet absorption of the thioketones as compared with ketones indicates a new mechanism of spin-orbit coupling which results from the higher nuclear charge of sulfur. The same factor together with the smaller singlet-triplet splitting will enhance crossing from the $^1(n,\pi^*)$ to the $^3(n,\pi^*)$ state. This may account for the absence of fluorescence at room temperature. The phosphorescence lifetime of the thioketone is much shorter than that of the corresponding ketones which again is a result of very efficient spin-orbit coupling and high intersystem probability for the thioketones.

The observed correlations between the energy levels of thioketones and the corresponding ketones could be a useful tool for prediction of the nature and position of an energy level which cannot be obtained elsewhere.

The photochemical behaviour of the thioketones seems quite similar to those of the ketones.

EXPERIMENTAL

Part B - Photochemistry of Sulfur Compounds.

B.1. Materials.

Thiobenzophenone was obtained from Mr. A.A. Nicholson, and had been crystallized from ethanol and sublimed before use. p,p'-Dimethoxylthiobenzophenone and p,p'-Bis-(dimethylamino)thiobenzophenone (K & K laboratories) were crystallized from ethanol and chloroform, respectively. Thiocholestenone was kindly prepared by Mr. D.S. Blackwell, and chromatographed on an alumina column prior to use (eluted with 20% benzene/pet. ether 60-80°, at 0°C). Cyclooctatetraene (BASF) was distilled under nitrogen (b.p. 43°/17 mm). 9-Methylanthracene (Aldrich) was chromatographed over alumina (pet. ether 60-80° was used as solvent), and crystallized twice from ethanol.

B.2. Low Temperature Absorption Spectra.

General Procedure.

The thiones were dissolved in EPA and the solution placed in a pyrex cell (2 cm O.D., 0.8 mm path length and 3 ml capacity), and the sample sealed. The cell was placed in a brass holder and inserted in a specially designed dewar (Jencons Scientific Limited), which had quartz windows facing the cell (Fig. 15). The dewar was evacuated (10^{-3} mm Hg) and filled with liquid nitrogen, the sample being cooled by conduction through the brass jacket. A clear glassy matrix was obtained at 77°K

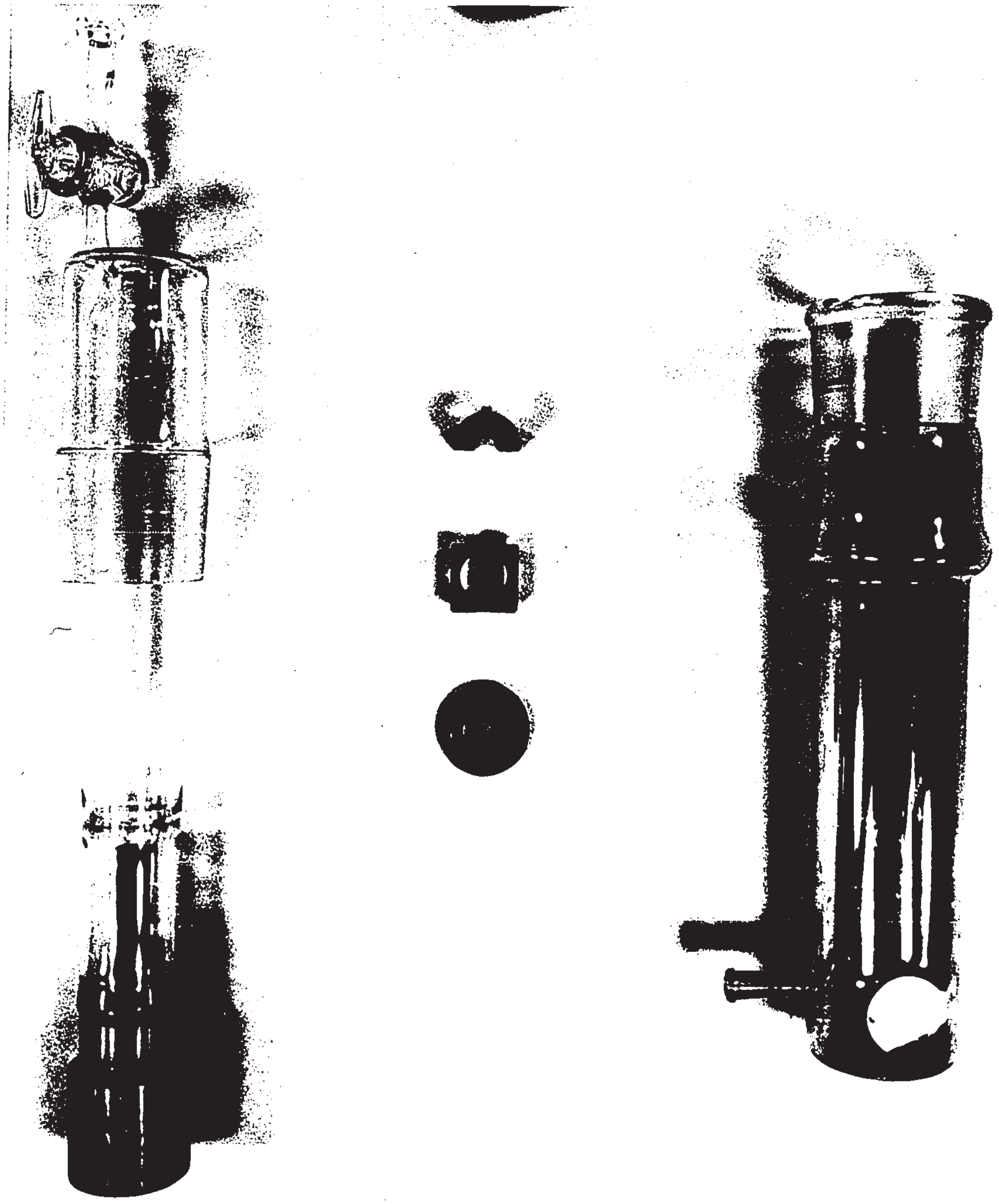


Fig.15

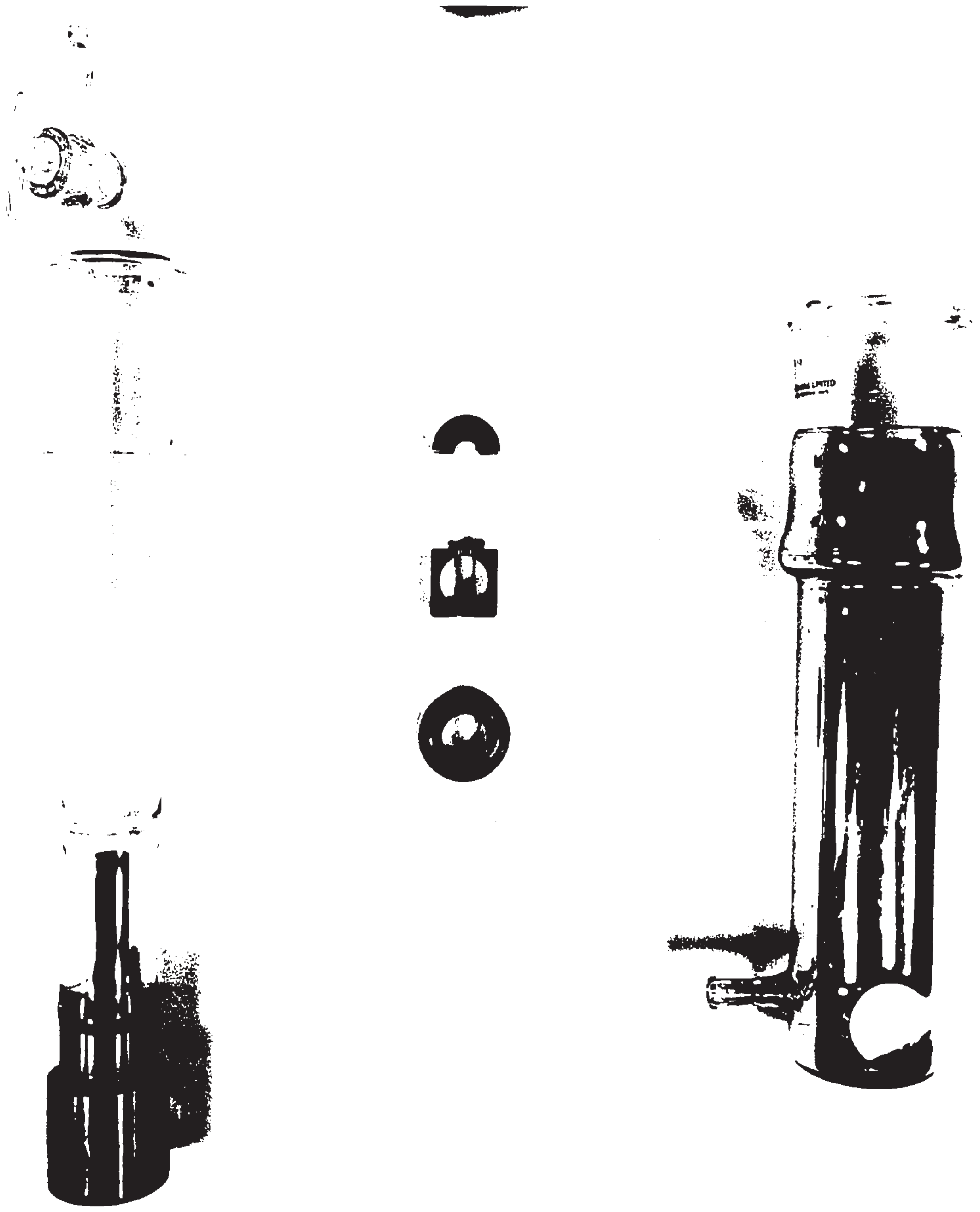


Fig.15

and the absorption spectrum was measured on a Carey 14 spectrophotometer.

All four thioketones showed low intensity absorption at long wavelength with vibrational structure in a glassy matrix at 77°K. The spacing between the bands was ~1100 cm^{-1}.

In thiobenzophenone, p,p'-Bis(dimethylamino) thiobenzophenone and thiocholestenone a low intensity band at lower energy has been observed.

B.3. Luminescence.

The apparatus used for emission spectroscopy was a modification of that described before (p.122). The light from a Hanovian 150 Watt Xe lamp passed through a Bausch and Lomb 0.25 m monochromater, and focussed directly on the sample by means of a quartz lens (the aluminized mirror having been eliminated). The emitted radiation from the sample was scanned using the Jarrel-Ash spectrophotometer which was equipped with an EMI 9558QD photomultiplier (S-20 response), since it had a greater wave-length range more sensitivity and stability than S-11 photomultiplier. The phototube was cooled with solid carbon dioxide, and was supplied by an NJE Model S-325 variable voltage D.C. power supply (1.25 KV). The photomultiplier was connected to a timing Filter Amplifier (Ortec Model 454) which amplified the signal (amplitude ranges from 1 to 100 mv) 200 times. It was also equipped with variable filter, but it has been found that passing the amplified signal without filtering to a Fast Discriminator (Ortec Model 417) gave better spectra.

The FD was adjusted to a 5V threshold, so that only a signal having an amplitude of 5V or more was measured as a count. This operation standardized the signal height which was fed to a multi-channel analyzer

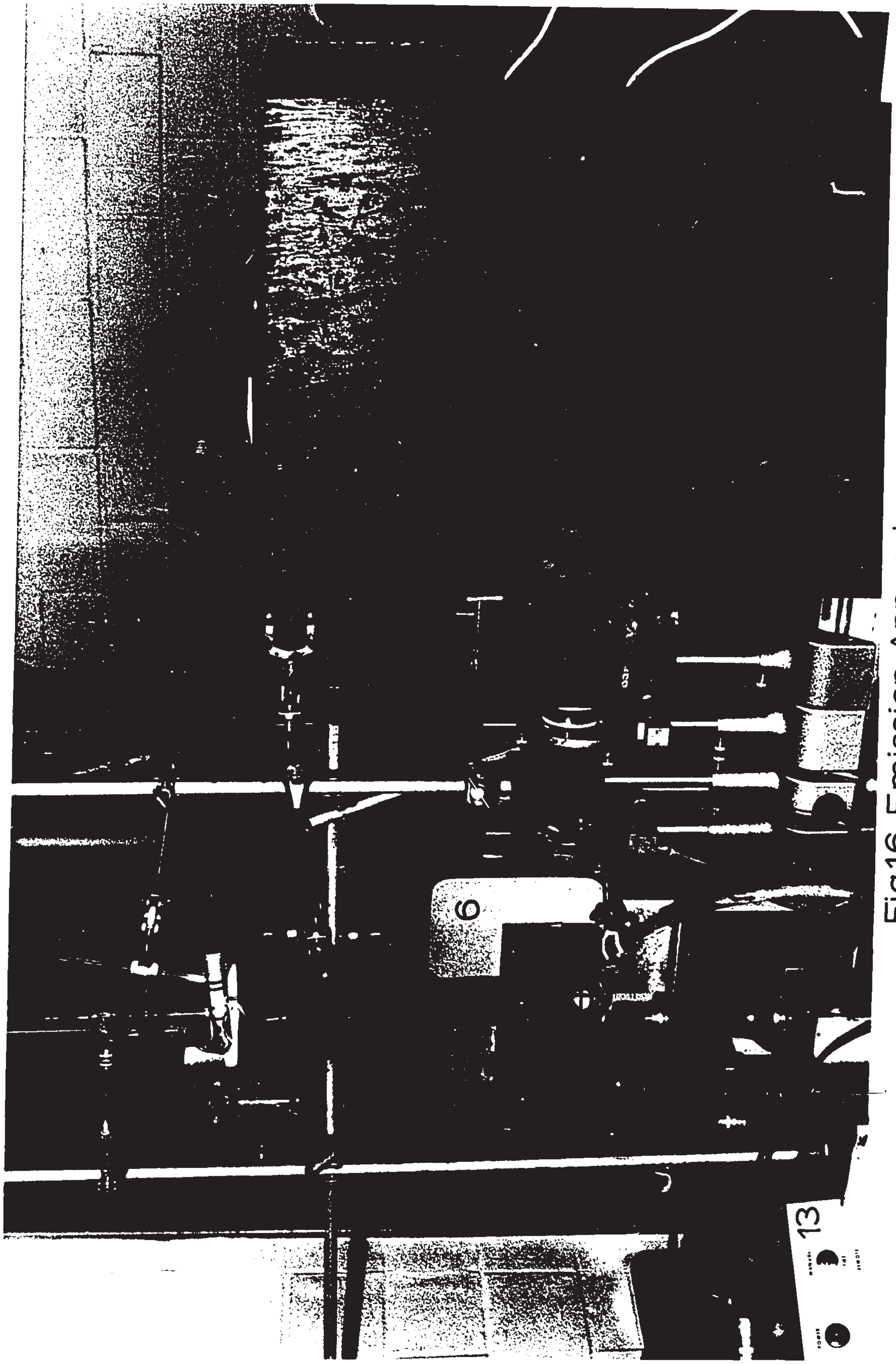
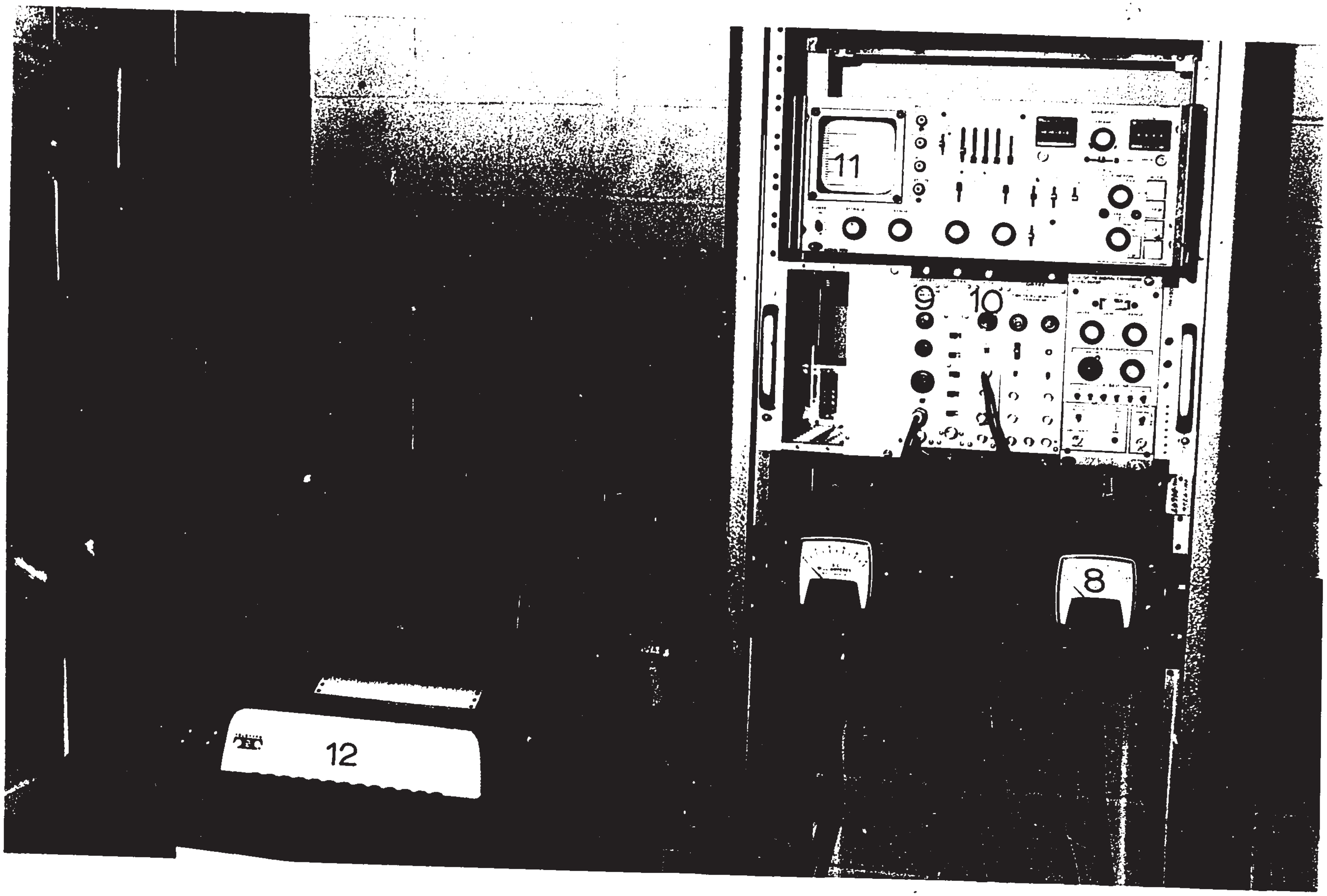


Fig.16 Emission Apparatus

Fig.16 Emission Apparatus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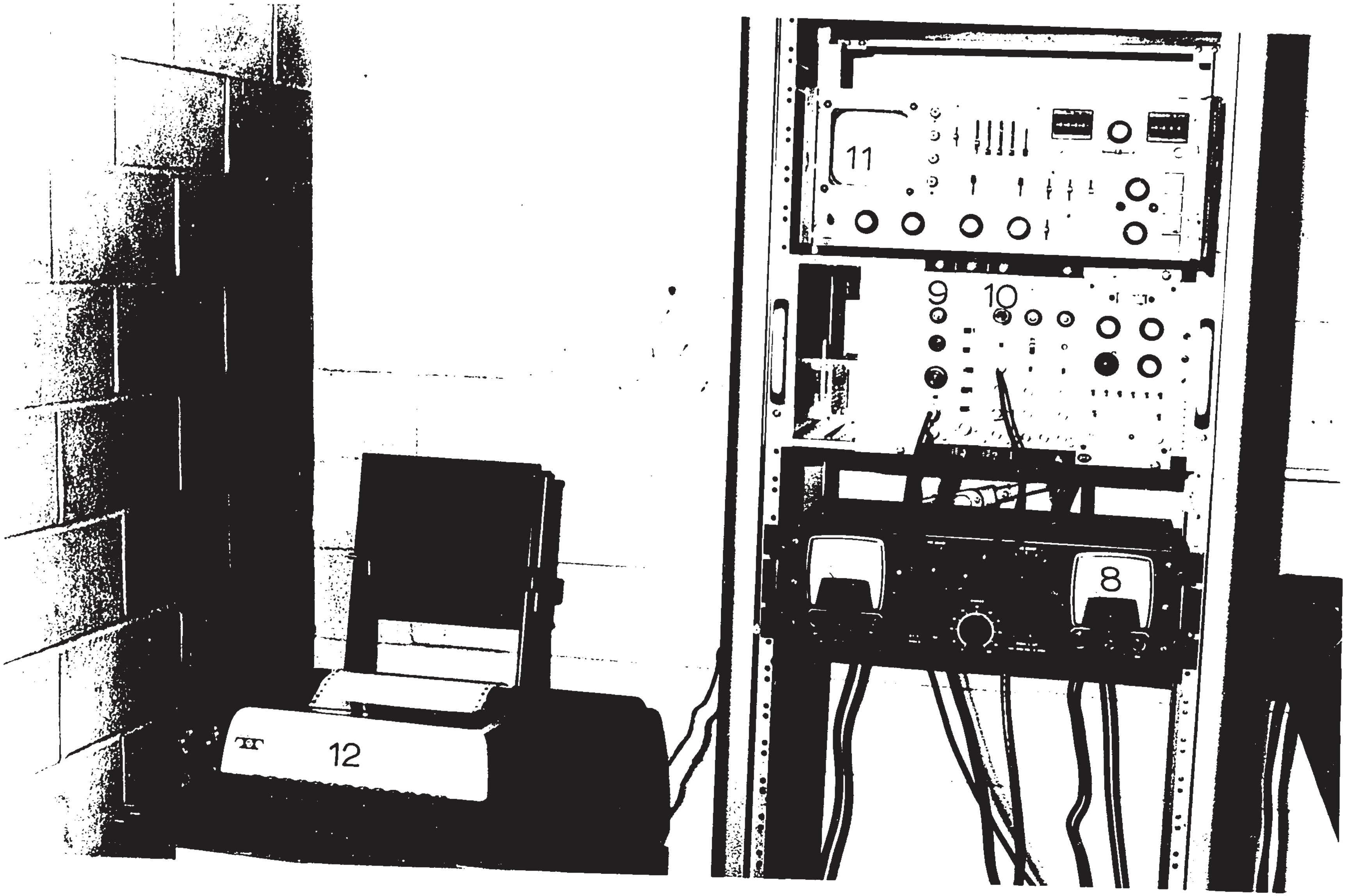
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1. Light source, 150 Watt Xe arc lamp
2. Monochromater Baush and Lomb 0.25 m.
3. Lens
4. Supra cell quartz double wall dewar
5. Sample tube
6. Jarrel Ash spectrometer
7. Photomultiplier, (in the Fig. is IP 28), normally EMI 9558 QD (S20 response).
8. High voltage power supply
9. Timing filter amplifier Ortec Model 454
10. Fast discriminator Ortec Model 417
11. Multichannel analyzer Geos Model 7010
12. Teletype terminal
13. Nanopulser power supply

(Geos Model 7010) possessing 1024 channels operated in the signal averaging mode. For phosphorescence, the emission over the desired wavelength range was accumulated on 256 channels, where the scanning time was one second per channel and the scanning speed was 500 Å/min. The emission was displayed on an oscilloscope or recorded on an Infrotronic steping recorder.

For lifetime measurements, a nanopulser light source was used (Xenon Corp. Model 437), which had a rise time of 2-3 nsec. and a pulse width of 30-50 nsec.

The change of intensity of the radiation from the sample with time was displayed on 256 channels of the digital processor, where the time base per channel was 10^{-5} sec. The data was recorded on the Infrotronic recorder or Teletyped.

All samples were degassed by the usual Freeze-pump-thaw technique cycles and all determinations done at 77°K (liquid nitrogen was used as coolant).

B.3.1. Emission Spectra of Thiobenzophenone.

The emission spectra of thiobenzophenone (10^{-3}-10^{-4}M) were obtained in EPA or MCH-n-pentane (4:1 mixture) at 77°K. The exciting wave-length was 520 nm. A Corning glass filter 3-68 was placed in front of the entrance slit of the Jarrel-Ash monochromater to prevent scattered light. The emission exhibited structure with maxima at 704 and 762 nm in EPA and 720 and 780 nm in hydrocarbon matrix, with band spacings of 1040 cm^{-1}.

The phosphorescence lifetime was 4.4×10^{-5} seconds in EPA, and 3.0×10^{-5} seconds in MCH-n-P at 77°K. In these determinations, a nanopulser was used as the light source, and the change of intensity of emitted radiation with time, was monitored at different wave-lengths throughout the emission spectrum to insure that emission occurred from one species. The signal was fed to the multichannel analyzer which was triggered externally and had a base time of 10^{-5} second per channel. The decay curve was displayed on the oscilloscope after (3000-6000 pulses) and was measured over 2-4 decades. The relative intensities of each point in the decay curve were teletyped. A linear first order curve was obtained from a plot of log Io/I vs time, and from the slope. The rate constant of decay was calculated using a least squares computer program.

The excitation spectrum (a reproduction of the absorption spectrum) was obtained by monitoring the change in emission intensity at 704 nm due to change in the wave-length of excitation. It has been found that no correction is needed since the output of the Xe lamp is steady in the region concerned (320-600 nm).

B.3.2. Quenching of the Emission of Thiobenzophenone in Rigid Media.

Solutions containing thiobenzophenone (4×10^{-4}M) and different concentrations of cyclooctatetraene (0.0, 0.058, 0.115 and 0.173 M) in EPA were degassed and the emission spectra recorded as described above. The areas were integrated using a Ott-Planimeter. A linear Stern-Volmer plot was obtained from a plot of Ao/A vs (Q).

The phosphorescence lifetime was measured in each case and only a very slight change was observed from that where no quencher was present.

When 9-methylanthracene was used instead of cyclooctatetraene, no change in the emission intensity was observed for solutions containing up to 0.15 M 9-methylanthracene.

B.3.3. Emission Spectra of p,p'-Dimethoxythiobenzophenone, Xanthione and Thiocholestenone.

Following the same procedure described for thiobenzophenone, the emission spectra of p,p'-dimethoxythiobenzophenone, xanthione and thiocholestenone were obtained in EPA and MCH at 77°K. The emission exhibited fine structure with maxima at 673, 730 nm; 635, 685, 745 nm; 627, 673 nm in EPA and 694, 750 nm; 662, 717, 783; 645, 684 nm in MCH respectively. The phosphorescence lifetimes were 1.23; 6.56; 48 × 10^{-5} seconds in EPA and 1.30; 3.3; 27 × 10^{-5} seconds in MCH for p,p'-dimethoxythiobenzophenone, xanthione and thiocholestenone, respectively.

The emissions were quenched with cyclooctatetraene at 77°K in EPA, yielding a linear Stern-Volmer plot. Excitation spectra were obtained for these compounds, as previously described.

B.3.4. Emission Spectra of p,p'-Bis(dimethylamino)thiobenzophenone (MT)

The emission spectra of M.T. (1.5×10^{-4}M) in ether ethanol (1:1 mixture) and in MCH-n-pentane (4:1 mixture) were obtained at 77°K by exciting in the n,π^* singlet absorption band. The emission showed fine structure with maxima at 664, 715 nm ($\tau = 17 \times 10^{-5}$ seconds) in E.E. and 678, 724 nm ($\tau = 8 \times 10^{-5}$ seconds) in the above two mentioned solvents respectively.

Excitation into the wave-length region 520-460 nm in E.E. at 77°K lead to an additional emission band observed on the high energy side of the normal emission max 623 nm. It was found that the intensity of this band was wave-length dependent. The intensity decreases as we move out of the CT band. The phosphorescence lifetime was 1.7 × 10^{-5} seconds.

Both emissions were quenched with cyclooctatetraene and 9-methylanthracene. A linear Stern-Volmer plot was obtained with the latter over a quencher concentration range (0.0, 0.023 and 0.047).

An excitation spectrum was obtained in the usual manner by monitoring at 650 nm.

B.4. Photochemistry of p,p'-Bis(dimethylamino) thiobenzophenone.

B.4.1. Synthesis of Michler's Thiobenzhydrol.

The method previously described by R. Mohlau (35) was found to give low yields, and therefore modified as follows.

Michler hydrol (K & K laboratories, 6 gm)was dissolved in 5 ml of glacial acetic acid, and to the dark blue solution, 20 ml of ethanol was added. Hydrogen disulfide gas was bubbled into the solution until the color changed to green (about 10 min.). The solution was diluted with water, and extracted with n-hexane several times. The n-hexane layer was dried with anhydrous $MgSO_4$ and filtered. The filtrate, on cooling, gave a colourless precipitate mp. 75°C.

NMR ($CDCl_3$): δ 2.17 (d, $1H_A$), 2.9 (s, 12H), 5.35 (d, $1H_B$), 6.6 (d, 4H) and 7.25 (d, 4H). J_{AB} = 5 Hz.

B.4.2. Photoreduction of p,p'-Bis(dimethylamino) thiobenzophenone.

Michler's thione (84 mg) and Michler thiol (0.4 gm) were dissolved in 20 ml benzene (Fischer spectral grade benzene was irradiated for 7 days in presence of chloranil using a 450 W medium pressure mercury lamp, then distilled under a nitrogen atmosphere using a Vigreux column).

The solution was placed in a degassing bulb which was sealed to a 5 cm (O.D.) quartz cell (1 cm path length) by means of a graded seal, and deoxygenated by the freeze-pump-thaw technique. The solution was irradiated for 20 hrs by placing the cell beside a 450 W medium pressure mercury lamp in a water bath, the light being filtered (3-69 Corning filter) to allow light only above 520 nm to pass. After the irradiation was complete (decolorization of the solution indicated 100% conversion), the solvent was evaporated under reduced pressure. The n.m.r. spectrum (100 Hz) of the residue in $CDCl_3$ was measured and the integration of the singlet at 4.65 ppm (corresponds to H-C-S-S- of tetramethyldiaminodiphenylmethyl disulfide, this compound was prepared independently by the method of R. Mohlau) was compared to that of the aldehydic proton of o-nitrobenzaldehyde (10.4 mg) and indicated that 90 mg of disulfide were formed (55-60% yield).

The reaction products were examined by tlc (35% methyl acetate/pet. ether 60-80° was used as solvent) and showed at least 6 spots, of these spots, the thiol; Rf = 0.51, thione; Rf = 0.36, tetramethyldiaminodiphenylmethyl sulfide; Rf = 0.25 (this compound has been prepared independently following the procedure described by R. Mohlau (35)), the disulfide; Rf = 0.21. It was found that the thiol partially transferred to the sulfide on the tlc plate, or on heating in benzene thus accounting for the observation of a spot on tlc corresponding to the sulfide.

The reaction products were chromatographed on silica gel (60-200 mesh), ethyl acetate/pet. ether 60-80° mixture being used as solvent. The following fractions were obtained:

Fraction 1.

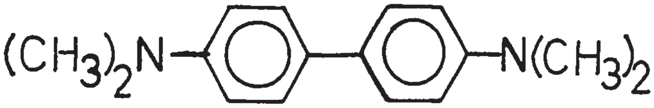
It had an Rf value similar to the thiol (during elution on the column all the thiol was converted to sulfide, so that the thiol does not interfere with this fraction). Evaporation of the solvent gave a colorless crystalline solid mp. 195-6°C which increased to 198-8.5°C following crystallization from ethanol.

NMR ($CDCl_3$): at δ 2.96 (s, 3H), and pair of doublets at 6.8-7.45 (2H).

Mass spectrum: M^+ at 240.2, (M+1) 18.5% of M^+, and (M+2) 15.6% of M^+ which corresponds to $C_{16}H_{32}N_2$.

IR: $\nu_{max}^{CHCl_3}$, 1610, 1500, 1440, 1340, 1220, 1190, 1160, 945, 735 and 665 cm^{-1}.

The data are consistent with 4,4'-bis-dimethylaminodiphenyl 9.



9

The following two fractions were found to contain thiol (which did not convert to sulfide) and thione, respectively. These identified by n.m.r., mp. and tlc retention.

Fraction 4

Evaporation of the solvent afforded a yellowish green solid mp. 330°C.

NMR ($CDCl_3$): shows singlet at 2.9 ppm for the NCH_3 group and phenyl protons signal (pair of doublets) in ratio 3:2.

Mass spectrum: M^+ at m/e 504.2 corresponds to $C_{34}H_{40}N_2$.

The data are consistent with tetra(p-dimethylaminophenyl)ethylene 10.

This fraction was followed by two fractions which contained the sulfide and disulfide, the mp's 174 and 210°C respectively.

Fraction 7.

The amount separated was too small to be properly identified. It had an Rf value similar to that of Michler's hydrol. By comparing the intensity of that spot (developed by I_2) for non-irradiated solution to that of the reaction mixture after irradiation, it was found that the latter was more intense. On irradiation of the Michler thione with the hydrol in benzene (as described before), the tlc of the reaction products showed an intense spot having the same Rf value as that of fraction 7. This indicates that the fraction 7 might be a pinacol type compound.

B.4.3. Irradiation of Michler's Thione in Benzene.

A solution of Michler's thione (50 mg) in 20 ml benzene was degassed and irradiated as mentioned before. After the irradiation was complete (100% conversion), the solvent was evaporated and the reaction products chromatographed on silica gel (60-200 mesh), using the methyl acetate/pet. ether 60-80° mixture as solvent. The 4,4'-bis(dimethylamino)diphenyl and tetra(p-dimethylaminophenyl)ethylene were obtained. A yellow solid, had an Rf value of 0.2, was insoluble in ether, has mp. 130°C (dec.) and has not been identified.

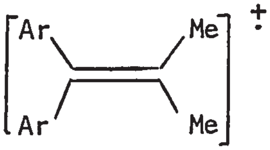
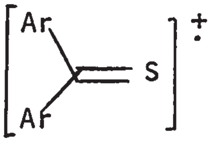
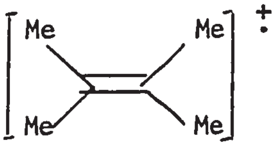
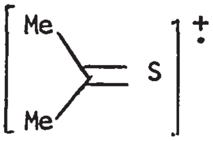
Irradiating two solutions contains the same amount of Michler thione (50 mg) in 20 ml benzene and to one of them (0.5 gm) thiol was added, under similar condition, and following the rate of Michler thione disappearing by monitoring the absorption at 650 nm, indicates that the rate of reaction in presence of thiol is 12.7 times faster.

B.5. Photocycloaddition of Michler's thione to Olefins.

B.5.1. Tetramethyl ethylene (TME)

A mixture of Michler's thione (36 mg) and 10 ml TME in 10 ml benzene was degassed and irradiated as described for the photoreduction. After 15 min. the reaction was complete, as judged from the discharge of Michler's thione color. The reaction mixture showed only one major spot on tlc (silica gel pH 7, 35% ethyl acetate in pet. ether 60-80°). Evaporation of the solvent gave thiatane as a brown solid in 80% yield, and was crystallized to colorless needles from ethyl acetate mp. 210°C. NMR ($CDCl_3$) - 100 MHz: δ at 1.25 (s, 3H), 2.86 (s, 3H), 6.60 (d, 1H) and 7.40 (d, 1H).

The mass spectrum showed no molecular ion peak. The following fragments were obtained:

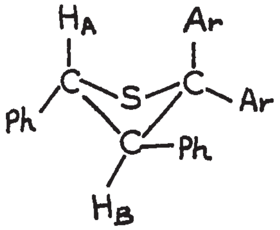
m/e	Fragment
294	
284	
84	
74	

Analysis calc. for $C_{23}H_{32}N_2S$: C 74.9, H 8.75, N 7.60 and S 8.70%

Found: C 74.23, H 8.63, N 7.59 and S 8.55%

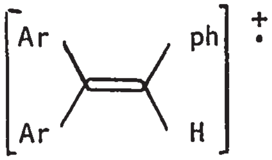
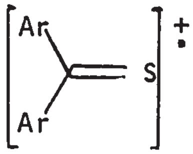
B.5.2. trans-Stilbene.

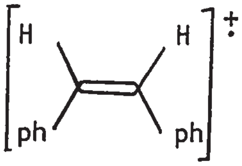
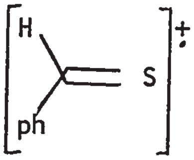
Irradiation of a deoxygenated solution of Michler's thione (47 mg) and trans-stilbene (0.24 gm/in 20 ml benzene (3-72 filter) for 30 min. gave only one product as judged by tlc). The reaction mixture was chromatographed on silica gel (60-200 mesh), using benzene/pet. ether as solvent. Evaporation of the solvent gave the thiatane as a yellowish brown solid (45 mg), which was crystallized from ethyl acetate mp. 108-9°C (dec.). NMR ($CDCl_3$) - 100 MHz: δ 2.87 (s, 3H), 2.9 (s, 3H), 5.02, 5.32 (d,d, J_{AB} = 10.5 cps, 1H), and 6.5-7.5 (m, 9H).



Ar = p, $(CH_3)_2N - C_6H_4$

The high value of J_{AB} indicates a trans geometry. Mass spectrum: the compound decomposed at high temperature, no molecular ion peak was observed. The following fractions were obtained:

m/e	Fragment
342	
284	

m/e	Fragment
180	
122	

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