

I. PHOTODIMERIZATION OF CYCLOHEXENONE
II. RADIATION CHEMISTRY OF BENZOPHENONE IN
CYCLOHEXENE SOLUTION

Thesis by

Ernest Yee Yeung Lam

In Partial Fulfilment of the Requirements
for the Degree of
Doctor of Philosophy

California Institute of Technology

Pasadena, California

1968

(Submitted September 20, 1967)

ACKNOWLEDGEMENT

To my wife, Sau Ling, I express my warm admiration of her understanding and patience.

I am deeply indebted to my research advisor, Professor G. S. Hammond for his guidance throughout my years at Cal Tech. Without his encouragement, patience, and kind concern over things both academic and personal, the work described in this thesis would have been impossible.

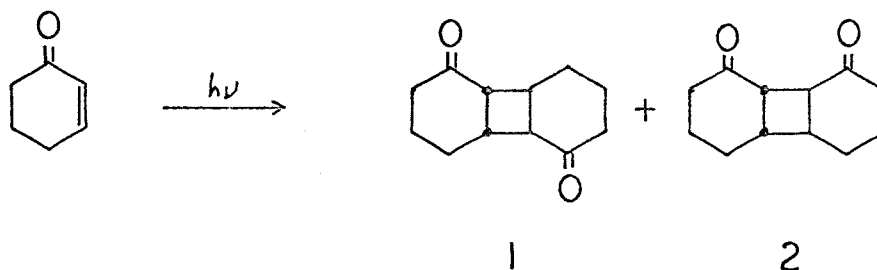
The privilege of working in the Hammond group will be remembered in the years to come. Stimulating and helpful discussions with Drs. John King, D. Whitten, D. H. Valentine, L. M. Stephenson and G. F. Vesley are gratefully acknowledged.

Financial aid in the form of Teaching and Research Assistantships from the California Institute of Technology is gratefully acknowledged. It has been a privilege to work under Professor Jurg Waser as a teaching assistant.

I express my appreciation to Misses Mei Lin Leung and Margaret Chu for taking much of their time in typing this thesis.

ABSTRACTS

PART I: The photodimerization of cyclohexenone has been studied in the neat liquid and in solvents. Although four products can be detected, 1 and 2 predominate under all conditions. The reaction can be sensitized by benzophenone, thioxanthone, acetophenone, and naphthalene. The enone was used as a sensitizer for the cis- trans isomerization of three pairs of isomeric olefins and the response was used to estimate the triplet excitation energy of the enone as 61 ± 1 kcal per mole. Dimerization can be quenched by addition of piperylene. Most evidence points to a triplet mechanism for the reaction. However, the ratio of 1 to 2 varies with reaction conditions and the quantum yield does not show the expected variation with enone concentration. These phenomena are attributed to solvent effects, rather than to a change of mechanism.



PART II. Gamma-irradiation of benzophenone in cyclohexene solution produced 3,3'-dicyclohexenyl and cyclohexenyldiphenylcarbinol as main products. The reaction was quenched by phenyl disulfide and to a less extent by chloroform. It was not significantly affected by 2-propanol. Naphthalene also acted as a quencher. The reaction probably involved the cleavage of the allylic C-H bond of cyclohexene to a cyclohexenyl radical and a hydrogen atom. Benzophenone effectively took up the hydrogen atom to give a ketyl radical. The main cross product, cyclohexenyldiphenylcarbinol, resulted from a combination of the ketyl radical with the cyclohexenyl radical.

Quenching by naphthalene was taken to be an indication that excited states of cyclohexene played an important role, probably as a precursor of cyclohexenyl radical. This was supported by the fact that gamma-irradiation or cis- or trans-2,3-diphenylpropenes in cyclohexene solution resulted in isomerization. That benzophenone did not act as an energy sink in cyclohexene was probably due to inefficient energy transfer from an excited cyclohexene triplet to benzophenone.

ABSTRACTS OF PROPOSITIONS

Proposition I

A proposal to study the charge transfer bands of n,π nature in polar solvents to see if they are blue shifted.

Proposition II

It is proposed to study the effect of carbon tetrachloride, an electron scavenger, on the gamma-irradiation of pyridine. The production of pyridine radical cation is expected to increase in its presence.

Proposition III

A series of 1-hydroxyphenyl-2-arylcyclopentanes are proposed to be used as model compounds to study intramolecular π -H bonding. $-\Delta F$ measurements using I. R. technique can be obtained and compared with those for intermolecular complexes studied by Yoshida and Osawa. A test in their postulate that the intermolecular complexes are of a labile nature can then be made.

Proposition IV

Photolysis of 9,10-phenanthrenequinones is proposed to study the competition between 9-10 bond fission and hydrogen abstraction by the carbonyl groups.

Proposition V

Photosensitized generation of a triplet ω -alkenylcarbene is proposed to study the correlation between spin state and the competition between intramolecular addition and insertion reactions of the carbene.

TABLE OF CONTENTS

	Page
<u>Part I</u>	
Introduction	2
Results and Discussion	
Products from Cyclohexenone Dimerization	9
Triplet Energy of Cyclohexenone	11
Attempt to Detect a Higher Triplet	13
Dimer Ratio Variation with Concentration	14
Quantum Yield Variation with Concentration	16
Sensitized Dimerization	17
Effect of Piperylene as Quencher	21
Dimer Ratio Variation in the Presence of Sensitizer and Quencher and in Different Solvents	22
Intersystem Crossing Efficiency Variation with Concentration	27
Apparent Extinction Coefficient Variation with Concentration	30
Experimental	35
References	41
<u>Part II</u>	
Introduction	44
Results and Discussion	
Identification of Gamma-products	50
Scavenging by Phenyl Disulfide	56
Quenching by Naphthalene	62
Isomerization of 1,2-Diphenylpropenes in cyclohexene	65

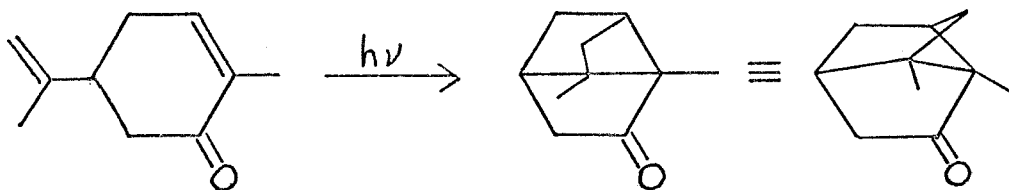
TABLE OF CONTENTS (continued)	Page
Scavenging by Chloroform	67
Scavenging by 2-Propanol	70
Proposed Mechanism	73
Variation of G with Irradiation Time	78
Variation of Alcohol/Oxetane Ratio with Benzophenone Concentration	81
Experimental	87
References	92
<u>Propositions</u>	94

PART I

PHOTODIMERIZATION OF CYCLOHEXENONE

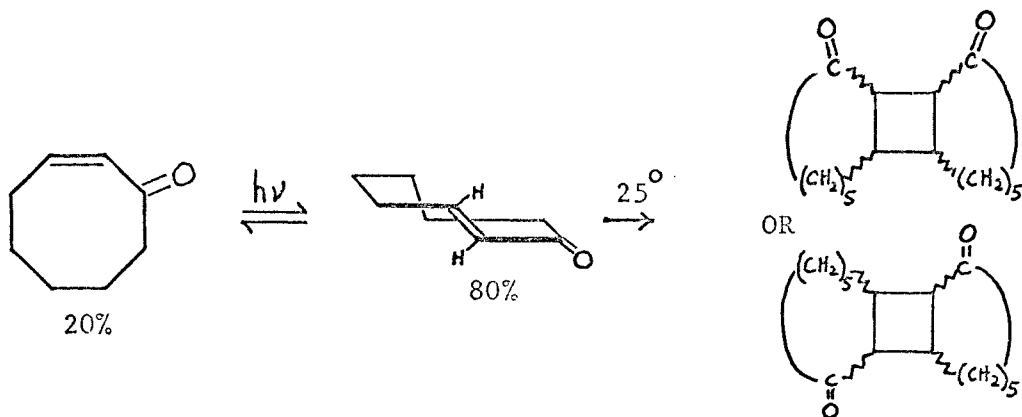
INTRODUCTION

The different modes of photoreactions undergone by α, β - unsaturated cyclic ketones are very intriguing. As early as 1908, Ciamician and Silber¹ exposed carvone to sunlight for several months and obtained carvonecamphor. This provided a convenient means of synthesizing tricyclic small-ring molecules, and became the first example of a photo-intramolecular cycloaddition of the enone moiety



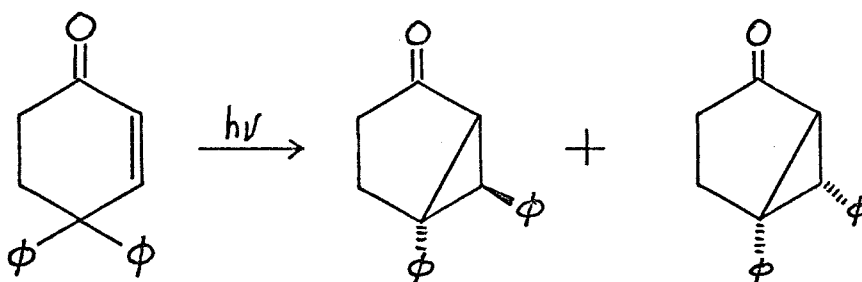
to a double bond. This, however, was by no means the only mode of photoreactions of the enone moiety. Since then, other interesting enone reactions came into existence.

Irradiation of cis-2-cyclooctenone² leads to the unstable



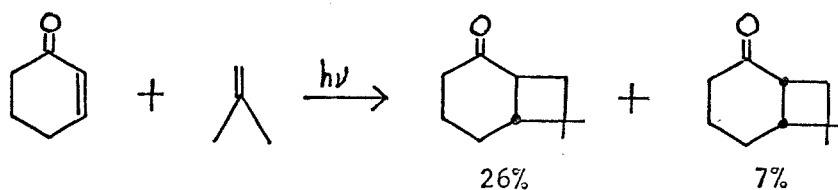
trans isomer which spontaneously undergoes dimerization in the dark at room temperature. Here we have isomerization instead of cycloaddition as the primary process. Another more recently reported example was the photo-isomerization of trans-2-ethylidene cyclohexanone to the cis isomer.³

α,β -unsaturated cyclic ketones, with suitable substituents, undergo rearrangement reactions which are typical of dienones. These reactions have been a subject of very intense studies notably by Zimmerman and his group.⁴



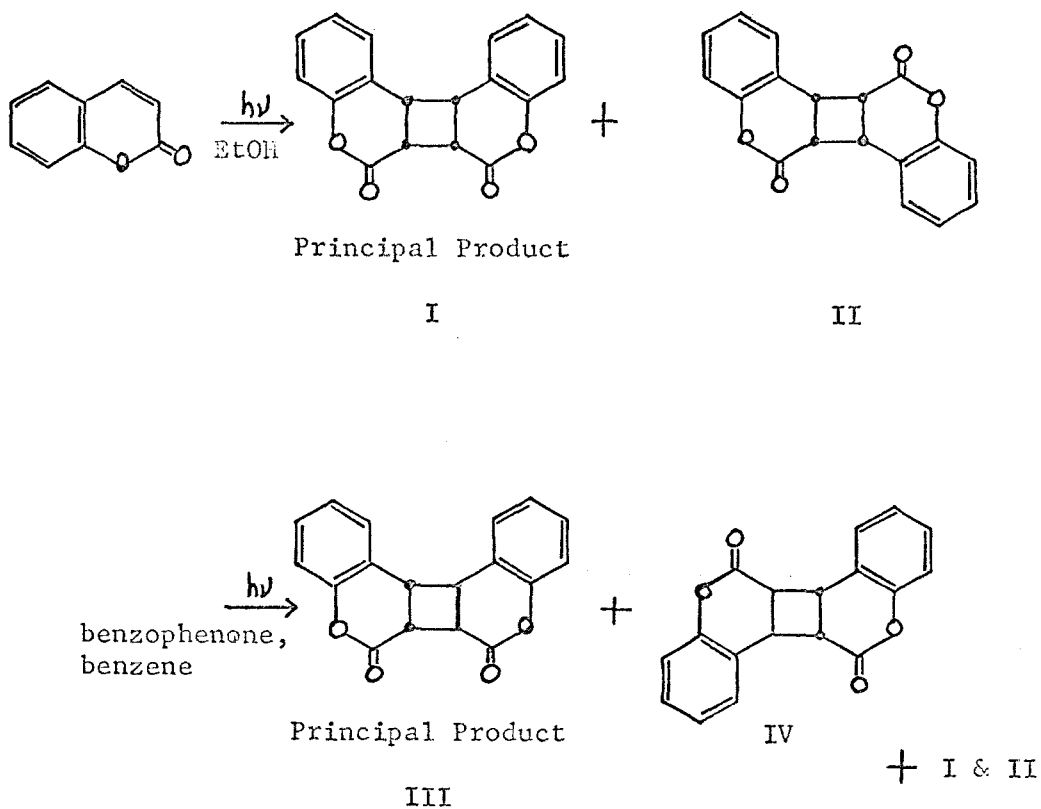
4,4-diphenylcyclohex-2-en-1-one

Corey,⁵ in his elegant synthesis of caryophyllene, made use of the cycloadditive property of cyclohexenone to olefins, and achieved the production of compounds with a six:four trans ring juncture.



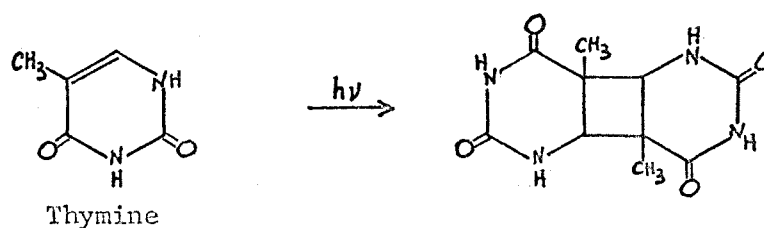
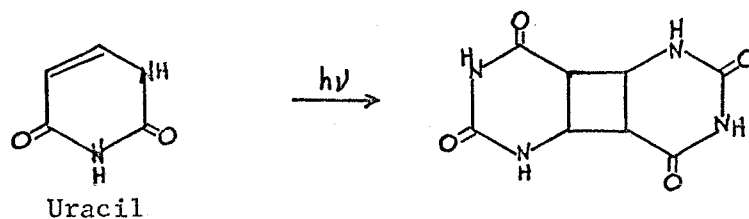
Dimerization of α, β -unsaturated ketones is a common phenomenon. In fact, the same workers, Ciamician and Silber, who photolysed carvone, also discovered in 1902 that coumarin, when exposed to light, gave dimers.⁶

This reaction has since then been studied in detail by workers such as Anet,⁷ Schenck,⁸ Hammond, Stout and Lamola,⁹ and most recently by Cole.¹⁰

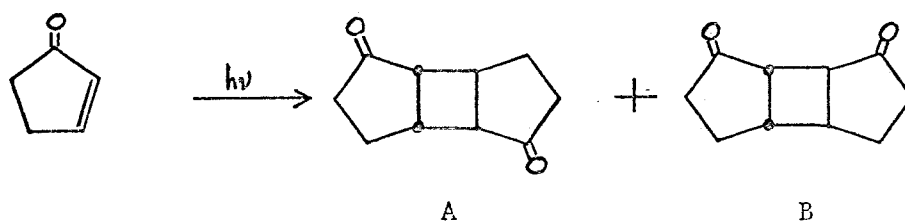


This type of dimerization has aroused great interest among photobiochemists and photophysicists since Wacker¹¹ and later Setlow¹² demonstrated the formation of thymine dimers in bacteria irradiated with ultraviolet light. Similarly, Uracil also formed

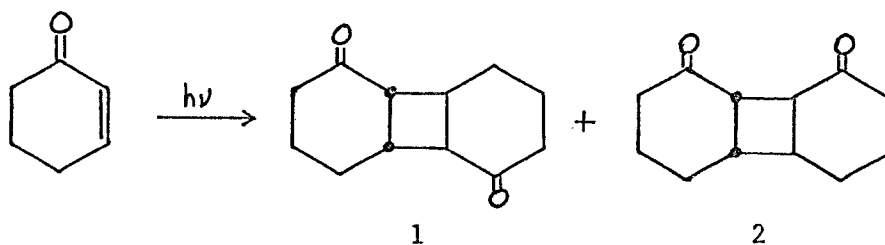
dimers.



Such photodimerizations have also been reported for less complicated enones. Irradiation of cyclopentenone gave two dimers A and B in the ratio of one to one.¹³ Under similar conditions,



Eaton found that cyclohexenone gave dimers 1 and 2 in a one to one ratio plus a small amount of unidentified product.¹⁴ Turro,¹⁵ however, reported that the reaction led to not less than 4 dimers.



In all of the examples cited above, one interesting feature apparent is that the photochemistry of α,β -unsaturated cyclic ketones is quite distinct from that of the saturated ketones in spite of the fact that n,π^* excitation of the carbonyl group is responsible for the reaction. In every case, the excitation at the carbonyl group is delocalized and the reaction takes place at the ethylenic double bond leaving the carbonyl group intact.

The reactions briefly described above by no means represent a comprehensive survey of the photochemistry of α,β -unsaturated cyclic ketones. Numerous other examples can be found in the literature. Although such reactions have found a wide-spread application in synthetic chemistry as well as in the investigation of biological systems, the reaction mechanism has remained to be an obscure subject of speculation and controversy.

Although coumarin dimerization is now fairly well understood mechanistically, the findings, however, cannot be generalized to cases like cyclopentenone or cyclohexenone. In several recently published monographs, different authors have expressed different opinions concerning the mechanism of the cyclohexenone dimerization. Turro¹⁵ and Calvert and Pitts,¹⁶ feel that the nonselectivity of

the reaction is an indication that it involves at least partially the singlet state of the enone. Saltiel¹⁷, however, feels that the intermediacy of a triplet state is more likely since irradiation of cyclohexenone in the presence of cyclopentadiene yields the diene dimers as major products. Eaton¹³ also supported a triplet mechanism for cyclopentenone.

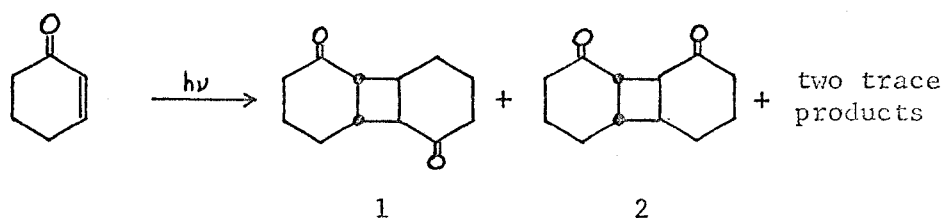
In view of the lack of a clear understanding of these reactions, it became apparent that a systematic definitive study should be undertaken to probe the mechanistic details of such reactions.

Cyclohexenone was chosen as a candidate for the study because of its simplicity in the structure thus avoiding complication due to substituents or other structural effects. Its choice over cyclopentenone is based on the fact that most α,β -unsaturated ketones undergoing dimerization and cycloadditions are six-membered ring compounds. Cyclohexenone would serve as a better model for these compounds than cyclopentenone. Upon excitation of the enone, the ethylenic portion of the triplet state will undergo a torsional distortion in much the same way as an unconjugated olefin as pointed out by Mullikan¹⁸. A Drieding model of the triplet cyclopentenone shows a maximum twist of 20° in the α,β -dihedral angle, whereas in cyclohexenone, a twist of 60° is possible. This shows that the difference in having the enone chromophore as part of a six-membered ring or of a five-membered ring can therefore be significant. The decision was also made to study the dimerization reaction instead of cycloadditions with olefins in the anticipation of a simpler analysis of the kinetics.

Before the completion of this project, independent findings by Eaton^{13, 19} and Leermakers²⁰ on cyclopentenone dimerization have provided a fairly definitive mechanistic picture. Two isomeric products A and B are formed in variable ratio but the variation has been attributed to solvent effects on the reactivity of a single species, the lowest triplet state of the ketone. The alternative possibility that both excited singlets and triplets are involved in the product formation was rejected on the basis of sensitization and quenching experiments.¹⁹ We have reached similar conclusions in a study of cyclohexenone dimerization.

RESULTS AND DISCUSSION

As mentioned in the introduction, irradiation of cyclohexenone with ultraviolet light gives two compounds 1 and 2 as the principal products, and two other materials of unknown structures are formed in trace amounts. Because of their retention times in vapor chromatograms, the minor products are also believed to be dimers.



Pure cyclohexenone is a colorless liquid. Preparative dimerization was carried out by irradiation of a carefully degassed sample of purified neat cyclohexenone using a uranium glass filter which transmits mainly 3660 Å light. The resulting mixture after irradiation contains unreacted ketone and dimers. This mixture was analysed by vapor phase chromatography with the results shown in Table I. The column used was a twelve-foot column of fluorosilicone (Dow Corning FS 1265) (10 per cent) on Diatoport S, which was reported by Corey⁵ to have the special property that it does not effect the isomerization of an unstable trans- ring juncture to a more stable cis- ring juncture.

Table I. Products from Dimerization of Cyclohexenone

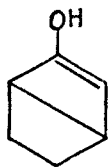
Conditions	Percentage of Various Products			
	1	2	3	4
Neat ketone	47	44	2	7
0.5 M ketone in benzene	60	25	5	10

The dimers were separated from the unreacted ketone by fractional distillation. Further separation of the two main dimers were effected by chromatography on alumina. It was found that if the irradiation was done on a solution of the ketone, the same dimers were formed, but the relative amounts became different. This is illustrated by Table I.

The distribution of the products were determined by measuring the areas of the peaks in the chromatograms assuming equal detector sensitivity response. The two minor products have shorter retention times and they were followed by dimers 1 and 2. The separation of the peaks were fairly good but the base line was not perfect. This makes it difficult to carry out a precise measurement of the minor products. No significance is therefore attached to the apparent variation of the minor products. The main peaks due to 1 and 2, however, were broad and quite well defined and hence good accuracy was achieved in determining the ratio of 1 to 2. This ratio has been chosen to be a key variable in our investigation. Specifically, we set out to determine whether or not the variability of the product distribution could be attributed to the involvement of more than one

electronically excited state of the ketone.

One of our preliminary objectives in this project was the characterization of the triplet state of cyclohexenone. Earlier results on this matter have been discouraging. Lamola²¹ observed weak phosphorescence from the compound corresponding to an excitation energy of 62.4 kcal per mole from a glass containing the enone at liquid nitrogen temperature, but this result unfortunately has not been reproducible. Lock of Harvard⁵ failed to observe fluorescence from the n, π^* state of the ketone in dilute hydrocarbon solution. Arnold⁵ of Union Carbide Research Laboratory also found that phosphorescence from n, π^* excited cyclohexenone was absent. Corey⁵ reported that there does not appear to be phosphorescence in the region expected for the lowest π, π^* triplet. He postulated that the absence of phosphorescence for the n, π^* triplet and for the π, π^* triplet of cyclohexenone could be attributed to rearrangement to form energetic, unstable but ground state species such as I and II.



I



II

These structures could be envisaged to revert to cyclohexenone by non-radiative processes. Another possible explanation advanced by Corey was that the triplet state could be stabilized by the twisting of the α, β -dihedral angle. This would prevent efficient radiative

decay to the ground state by virtue of the Franck-Condon Principle. We have made no attempts to test these postulates.

We decided to determine the triplet energy of cyclohexenone by using a different approach. Since Hammond et al²² in their study of the photoisomerization of olefins have developed the so-called Saltiel plots which are plots of the cis/trans ratio of the olefin at photostationary state versus the triplet energies of a number of sensitizers, we decided to make use of such plots to evaluate the triplet energy of cyclohexenone. This was done by using the ketone as a sensitizer to sensitize the isomerization of stilbene, 1,2-diphenylpropene and 2,3-diphenyl-2-butene. From the photostationary state cis/trans ratio of the olefin, the triplet energy of the ketone was estimated on the Saltiel plots of the three olefins. The results are shown in Table II and a value of 61 ± 1 kcal per mole was found in the three cases.

A study of the U.V. absorption spectrum of cyclohexenone reveals that it has an n, π^* maximum at $337 \text{ m}\mu$. This corresponds to a vertical excitation energy of 85 kcal per mole. The onset of the absorption occurs at about $379 \text{ m}\mu$ which corresponds to a measure of the separation between the ground state and the lowest excited state without excess vibrational excitation in either. This excitation energy is 75.5 kcal per mole. Since the splitting between n, π^* singlet and triplet energy levels is usually small, whereas we have a splitting of some 14.5 kcal per mole for cyclohexenone, this probably is an indication that the triplet is of a π, π^* configuration. This presents a new challenge that the

Table II. Use of Cyclohexenone as a Sensitizer

Cyclohexenone Concentration	Olefin	Total Olefin Concentration	<u>cis</u> / <u>trans</u> ^a	Estimated E _T kcal/mole
0.025	2, 3-Diphenyl- 2-butene	0.1 M	0.115	61 ± 0.5
0.1 M	1, 2-Diphenyl- propene	0.05 M	1.8	61 ± 1
0.1 M	Stilbene	0.05 M	1.9	61 ± 1

^aRatio of isomers at the photostationary state.

reaction might involve the participation of two triplets. The initial excitation to the lowest n, π^* singlet state could result in its intersystem crossing to the n, π^* triplet state with a high efficiency because the splitting should be small, but this triplet could undergo an internal conversion to the lower π, π^* triplet state -- the one detected to have 61 kcal per mole responsible for the sensitization of the isomerization of the olefins. The n, π^* triplet, in its transient appearance, is a potential chemically active species. An attempt was made to intercept such a higher triplet by using a very high concentration of 2, 3-diphenyl-2-butene (1.5 M/L, limited by its solubility in benzene) in sensitized isomerization experiments. This olefin was chosen because the slope of a plot of the stationary state ratio against excitation energy for the substrate is very steep in the region of 61 kcal. Consequently, one could expect the cis/trans ratio at photostationary

state to be a very sensitive function of the triplet energy of the sensitizing molecule if energy transfer from a high energy triplet were to occur with any appreciable efficiency. The cis/trans ratio at the stationary state under such conditions was 0.117, essentially identical with the value of 0.115 obtained in the presence of 0.1 M olefin. We therefore infer that such a high triplet, if present, must be very short-lived and will not play a significant role in a bimolecular reaction involving making and breaking of bonds.

Having eliminated the possibility of a double-triplet mechanism, we turned to the hypothesis that an excited singlet state might be involved in addition to the lowest triplet. This was tested by two approaches: (1) by observing the change in behaviour of the reaction as the concentration of the cyclohexenone is varied, (2) attempts to isolate a triplet mechanism using sensitizers and quenchers.

Using the first approach, we took the ratio of the dimers 1 to 2 as a parameter and measured its variation as a function of cyclohexenone concentration in benzene solution. Figure 1 is a plot of this variation and shows that the ratio changes continuously from 5.15 at 0.05 M/L to 0.95 at 10.0 M/L. The lower value apparently is a high concentration limit. The plot at the lower concentration region, however, does not approach to a limiting value for the ratio. Although superficial consideration might lead to the conclusion that a singlet mechanism is dominant at high concentrations, a closer examination at these results shows that they actually do not support this view. Since the ratio levels off as the

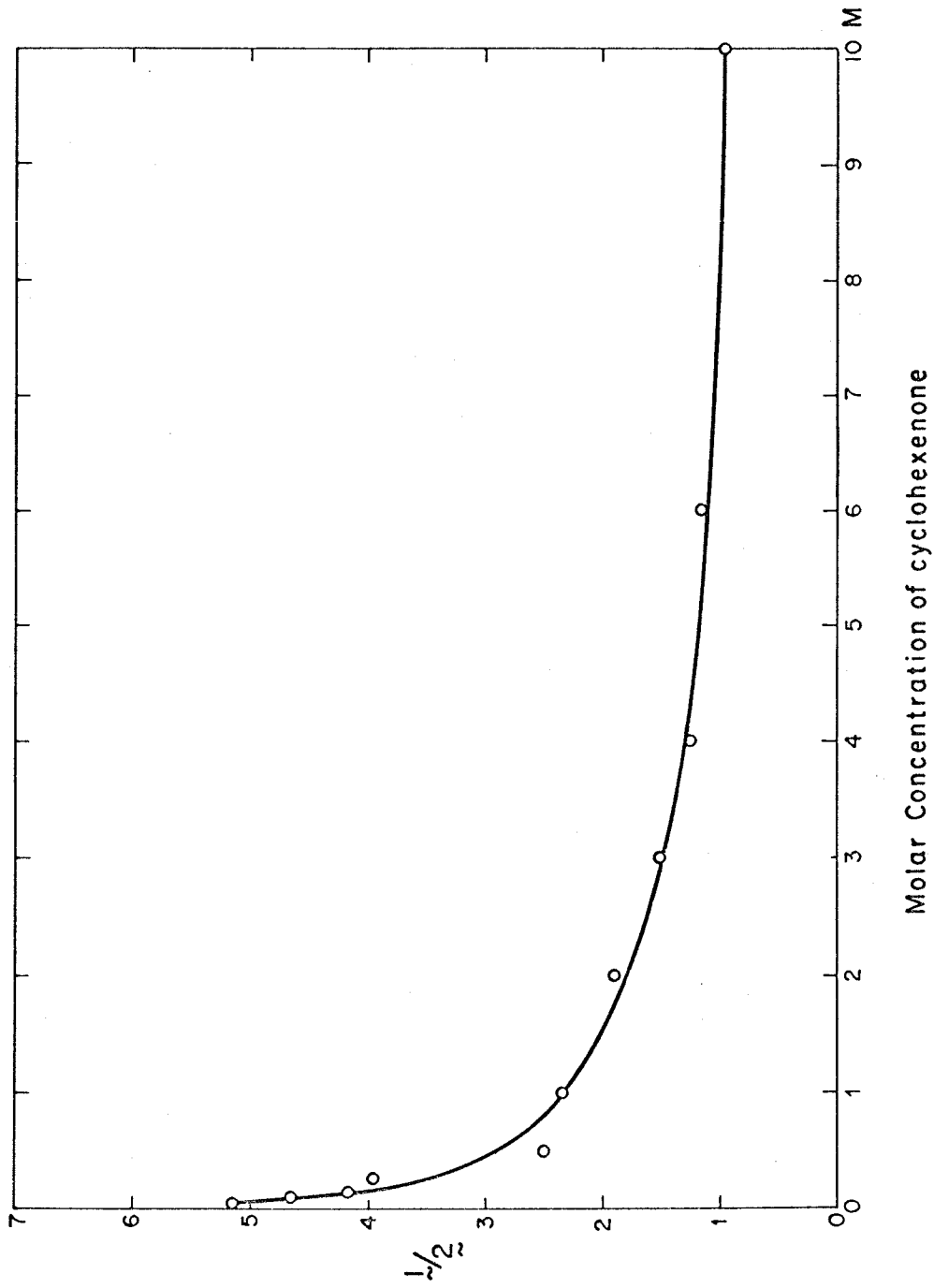


Figure 1. Yield ratio, $1/2$, as a function of cyclohexenone concentration in benzene.

concentration is increased, one would have to posit that dimers are formed virtually exclusively from excited singlets at higher concentrations and since in the lower concentration region, the dimer ratio does not approach a limit, it would mean that the singlet mechanism is still significant at 0.05 M. The highest rate constant that can be given to a diffusion-controlled dimerization is of the order of 10^{10} l mole⁻¹ sec⁻¹. At a concentration of 0.05 M/L, the rate would be 5×10^8 sec⁻¹. This rate is certainly much too low to compete with intersystem crossing. Although the intersystem crossing efficiency in this case is not known, judging from the absence of fluorescence, the argument should be a sound one.

The next parameter measured to observe the effect of concentration was the quantum yield of the reaction. The reaction was monitored by vapor phase chromatography both for the appearance of dimers and for the disappearance of the ketone. Figure 2 shows a Stern-Volmer plot of the reciprocal of the quantum yield versus the reciprocal of the ketone concentration. Both the quantum yields for the disappearance of the ketone and for the appearance for the dimers are shown on the same plot in terms of quantum yield for the latter process Φ' . If dimerization is the only means of consumption of the ketone, the two plots should coincide. The actual data however, show that the rate of disappearance of the ketone is about ten per cent greater that would be indicated by the rate of dimer formation. It is difficult to ascertain if any significance should be attached to this discrepancy because of experimental uncertainty. Following the disappearance of the monomeric ketone is inherently more

difficult than monitoring the appearance of the products. The former determination must involve substantial conversion (about 15-20 per cent), and measured results require correction to take account of the change in the concentration of the reactant during a run. A 1.5 per cent error would lead to the resulting 10 per cent discrepancy. This could very well be a systematic error. If such a discrepancy were real, it must be attributed to the occurrence of some minor side reactions to account for the additional consumption of the ketone. No additional peaks from the monomeric region to the dimeric region in the vapor phase chromatogram can be detected. No further investigation was therefore pursued.

One striking feature of the Stern-Volmer plot is immediately apparent and that is its significant deviation from the commonly observed linear relationship. A non-linearity in this type of a plot usually indicates an involvement of more than one excited state. Such a hasty conclusion, however, cannot survive further scrutiny. If the reaction were dominated by a singlet mechanism at higher concentrations and the triplet mechanism is phased in as the concentration is lowered, the quantum yield at lower concentration should be higher than would be expected by extrapolation from the concentrated solution. The results show that the quantum yields are actually lower than expected at lower concentration.

There seems to be no doubt at this stage that the triplet must play an important role. The second approach to ascertain this was to employ sensitizers and quenchers. As would be expected of a triplet mechanism, the dimerization was found to be sensitized by

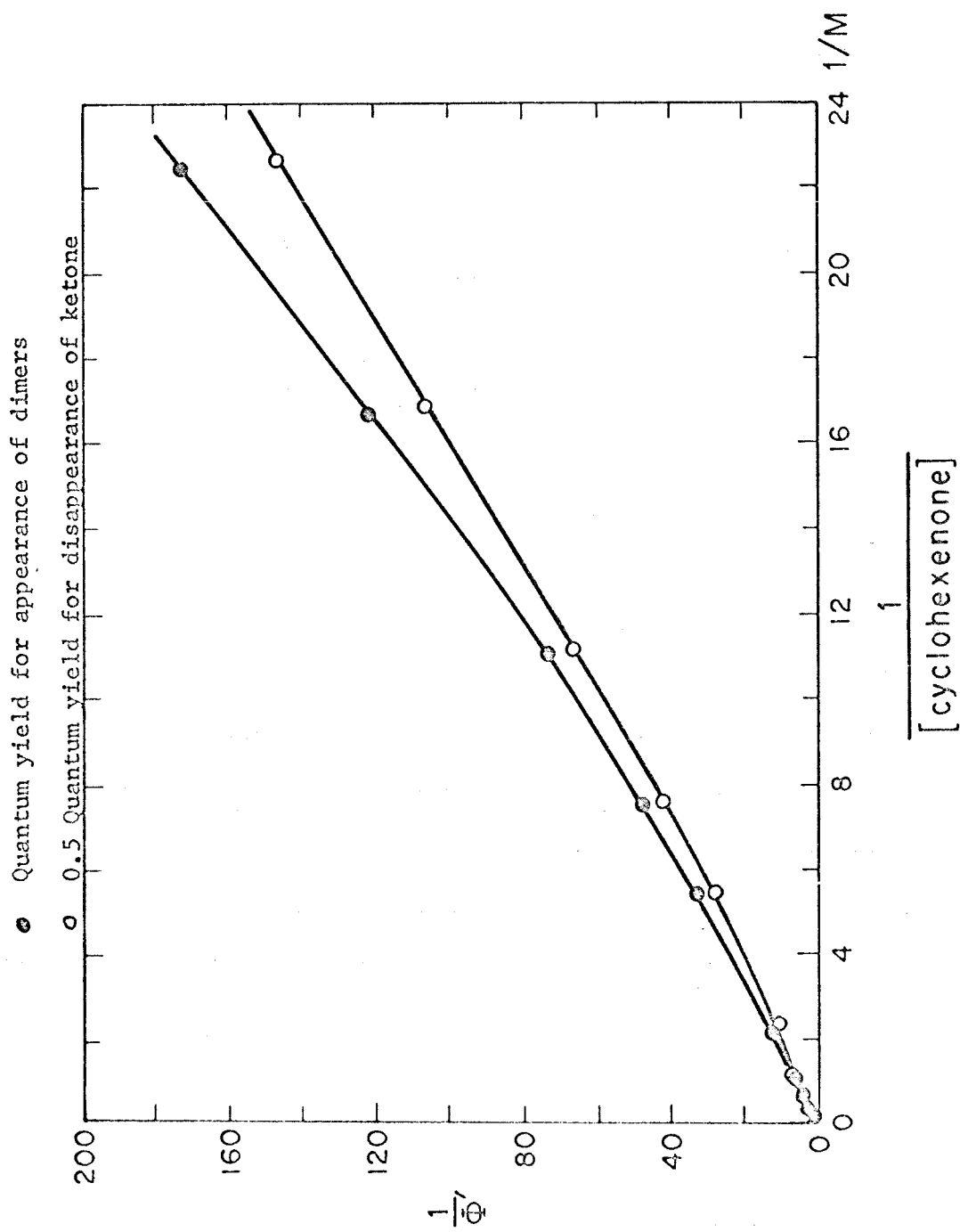


Figure 2. Quantum yield for photoreaction of cyclohexenone.

Table III. Quantum Yields for Disappearance of Cyclohexenone

Initial ketone concn. M	Per cent Conversion	Φ'	$\frac{1}{\Phi'}$
0.048	16.5	0.0134*	74.6*
0.065	17.9	0.0186*	53.7*
0.099	19.6	0.0295	33.91
0.146	20.9	0.0467	21.43
0.202	21.1	0.0648	15.43
0.506	19.2	0.1480	6.77
1.017	18.1	0.28000	3.57
1.523	19.1	0.4470	2.24
2.549	17.1	0.6640	1.51
3.059	16.2	0.5750	1.32

* Corrected to 99 per cent absorption of light.

Φ' - 0.5 Quantum yield for disappearance of ketone

Table IV. Quantum Yields for Appearance of Dimers

Initial ketone concentration M	Per cent Conversion	Φ'	$\frac{1}{\Phi'}$
0.048	13.7	0.0115*	86.9*
0.065	15.1	0.0163*	61.4*
0.099	17.0	0.0266	37.6
0.146	18.0	0.0416	24.0
0.202	18.4	0.0587	17.0
0.506	18.1	0.1450	6.90
1.017	17.4	0.2800	3.57
1.523	16.7	0.4000	2.50
2.549	15.9	0.6400	1.56
3.059	14.3	0.6900	1.45

* Corrected to 99 per cent absorption of light.

Φ' -Quantum yield for appearance of dimers

acetophenone (triplet energy $E_T = 73$ kcal/mole), benzophenone ($E_T = 68.5$ kcal/mole), thioxanthone ($E_T = 65.5$ kcal/mole) and naphthalene ($E_T = 61$ kcal/mole). These experiments also provided another means of checking on the cause for the variation of dimer 1/2 ratio with ketone concentration. If the decrease in the ratio at high concentration of the ketone were due to incursion of a singlet mechanism, the sensitized reaction should not show a similar trend. The data in Table V show that at a given concentration, the 1/2 ratio of the sensitized reaction was found to be the same as in the case of direct excitation of the ketone. This was found to be true for several concentrations and for different sensitizers. This leaves no room for further suspicion that the variation of dimer composition is an indication of a mixed singlet-triplet mechanism.

Quenching experiments lead to the same conclusion. In the presence of piperylene, in direct excitation experiments, strong quenching of the dimerization was observed. Under these conditions, cross products of the diene and the enone were found, but they have not been characterized. The effect of the quencher on the 1/2 ratio again confirms our previous conclusion. 1/2 ratio remains essentially constant with varying amounts of the quencher up to 2 M piperylene (experiments 2 to 6 in Table V). This indicates that the formation of the different dimers are quenched to the same extent and hence a common triplet precursor must be responsible for their formation. The reaction was monitored by following the appearance of the dimers and the reciprocal of the relative quantum yields for dimerization plotted against the quencher concentration

Table V. Variation in Product Ratio

Run No.	Reaction Mixture	1/2 Ratio ^b
1	1 M cyclohexenone in benzene	2.31
2	1 M cyclohexenone - 0.01 M piperylene in benzene	2.31
3	1 M cyclohexenone - 0.05 piperylene in benzene	2.35
4	1 M cyclohexenone - 0.50 piperylene in benzene	2.36
5	1 M cyclohexenone - 1.00 M piperylene in benzene	2.35
6	1 M cyclohexenone - 2.00 M piperylene in benzene	2.24
7	3 M cyclohexenone in benzene	1.52
8	3 M cyclohexenone - 0.07 thioxanthone in benzene	1.48
9	3 M cyclohexenone - 1.17 M naphthalene in benzene	1.56
10	0.5 M cyclohexenone in benzene	2.50
11	0.5 M cyclohexenone in n-hexane	5.21
12	0.5 M cyclohexenone in water	
	a. aqueous layer ^a	0.98
	b. organic layer ^a	0.54
13	3 M cyclohexenone in water	
	a. aqueous layer ^a	0.74
	b. organic layer ^a	0.64
14	1 M cyclohexenone in methanol	0.65

^aReaction mixture became heterogeneous during irradiation and the two liquid layers were sampled separately. Most of the dimers were in the organic layer. ^bError is ± 0.05 .

as shown in Figure 3. The linearity of this plot confirms our view that the non-linearity of the former Stern-Volmer plots in Figure 2 cannot be attributed to a mixed singlet-triplet mechanism. Eaton and Hurt,¹⁹ in their study on cyclopentenone dimerization came up with the same findings when piperylene was used as the quencher and these workers gave the same interpretation.

The variation of the $1/2$ dimer ratio with concentration of the ketone is not difficult to understand if one considers the change in the medium in going from a dilute solution of the ketone in benzene to the neat ketone. This presents a very good opportunity for medium-dependent variations in the specific rate constants for the reactions of the excited state. Coumarin^{7,8,9,10} is a good precedent example of such a medium dependence. This hypothesis was tested by looking at the $1/2$ ratio in other solvents of different polarities such as n-hexane, water and methanol. Results listed in Table V show that in experiments 10, 11 and 12, for a given concentration of 0.5 M/L cyclohexenone in benzene, n-hexane and water, $1/2$ ratio varies drastically. The ratio decreases by almost a factor of four for a one molar solution when the solvent is changed from benzene in experiment 1 to methanol in experiment 14. The change in going from 1 M/L to 3 M/L in water is small. The trend is therefore clear that $1/2$ ratio decreases as the polarity of the medium is increased.

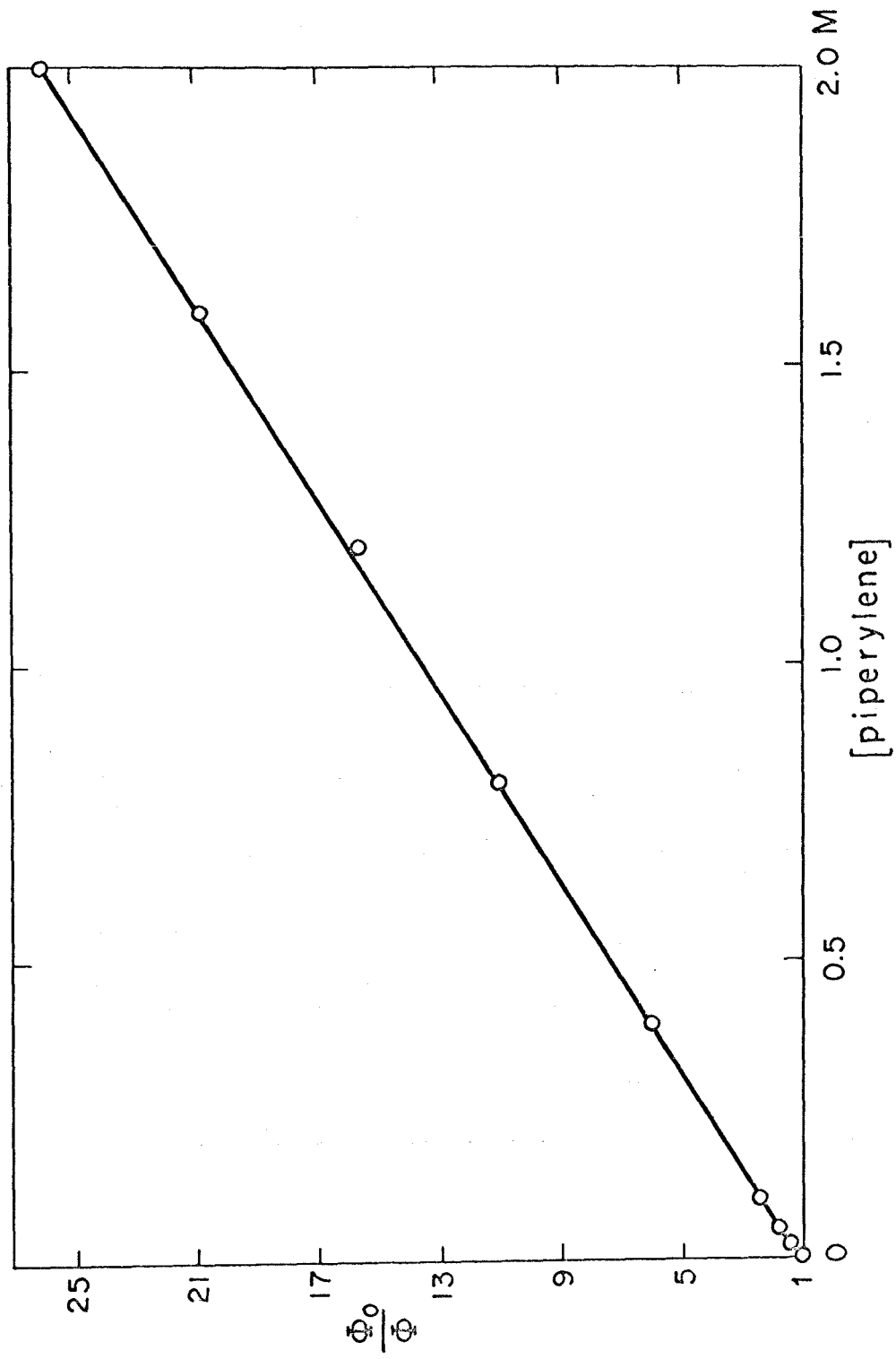


Figure 3. Quenching of dimerization by piperylene; $[\text{cyclohexenone}]_0 = 1.02 \text{ M}$; $k_0 = 0.28$.

Table VI. Quenching of Dimerization by Piperylene

Piperylene concentration M	Per cent Conversion	$\frac{\Phi_0}{\Phi}$
0.000	14.60	1.00
0.020	11.40	1.29
0.050	9.90	1.48
0.100	6.34	2.31
0.400	2.40	6.12
0.800	1.37	11.03
1.200	0.95	15.42
1.600	0.74	19.91
2.000	0.56	26.29

Initial cyclohexenone concentration - 1.02 M

Φ_0 - Quantum yield in the absence of piperylene

Φ - Quantum yield in the presence of piperylene

The following mechanism seems to be demanded by many of the data:



K = cyclohexenone

Q = quencher

S = sensitizer

$$\frac{\bar{\Phi}}{\bar{\Phi}'} = \frac{1}{\bar{\Phi}'_{ic}} = \frac{1}{\bar{\Phi}'_{ic}} \left\{ 1 + \frac{k_2}{k_4 [K]} + \frac{k_5 [Q]}{k_4 [K]} \right\} \quad (8)$$

$\bar{\Phi}$ = quantum yield for disappearance of enone

$\bar{\Phi}'$ = quantum yield for appearance of dimers

$$\bar{\Phi}'_{ic} = \frac{k_1}{k_1 + k_3} = \text{quantum yield for intersystem crossing}$$

In the absence of complications, equation (8) predicts a linear plot of the reciprocal of the quantum yield versus the reciprocal of the ketone concentration for the direct excitation experiment without the presence of a sensitizer or a quencher. The actual plots obtained both for the disappearance of the ketone

and for the appearance of dimers show the same kind of deviation from this prediction. Nevertheless, we have information on the medium dependence of the rate constants as a clue to a better explanation to this non-linearity. We therefore adopt the view that the mechanism is probably fundamentally correct and the failure of equation (8) indicates that either the intersystem crossing efficiency Φ_{ic} or k_2/k_4 or both must be variable.

Our next step was to employ the elegant triplet counting method developed by Hammond and Lamola²³ to measure Φ_{ic} of cyclohexenone at different concentrations. This was done by using the ketone to sensitize the isomerization of 1,2-diphenyl-propenes. The values of Φ_{ic} were computed from the known decay ratio. Carefully filtered 3660 Å light was used to avoid competitive absorption by the isomerizable substrate. Due to the low extinction coefficient of cyclohexenone, not all of the incident light was absorbed by the solutions containing the lowest concentrations of the ketone. Correction was necessary for incomplete absorption. This however, could not be done accurately because of the optics of the system. The tubes containing the solutions were ordinary pyrex culture tubes (internal diameter about 11 mm) and the average width of the solution traversed by the light was taken approximately to be one centimeter. The results of this experiment are given in Table VI. Because of this difficulty in the correction, the indication that Φ_{ic} increases in dilute solutions may well be an illusion. Even if the results are valid, they do not account for the curvature in the plots of Figure 2. The latter would have suggested that the Φ_{ic} decreases

Table VII. Quantum Yields for Isomerization of 1,2-Diphenylpropenes Sensitized by Cyclohexenone

Concentration of cyclohexenone	Initial diphenylpropene, isomer, and concentration	Per cent Conversion	Φ^c	Φ_{ic}	$\frac{\Phi_{t \rightarrow c}}{\Phi_{c \rightarrow t}}$
0.052 ^a	<u>cis</u> 0.0526	2.70	0.17		
0.053 ^a	<u>trans</u> 0.0528	4.09	0.26	0.43	1.5
0.102 ^b	<u>cis</u> 0.0526	3.00	0.13		
0.104 ^b	<u>trans</u> 0.0528	5.37	0.24	0.37	1.9
0.202	<u>cis</u> 0.0526	2.91	0.11		
0.205	<u>trans</u> 0.0528	5.62	0.22	0.33	2.1
0.409	<u>cis</u> 0.0526	2.90	0.11		
0.406	<u>trans</u> 0.0528	5.60	0.21	0.32	2.0
0.513	<u>cis</u> 0.0542	2.91	0.11		
0.515	<u>trans</u> 0.0539	5.37	0.21	0.31	2.0

^aThe ketone absorbs about 62 per cent of the incident light.

^bThe ketone absorbs about 87 per cent of the incident light.

^cCorrected for back reaction.

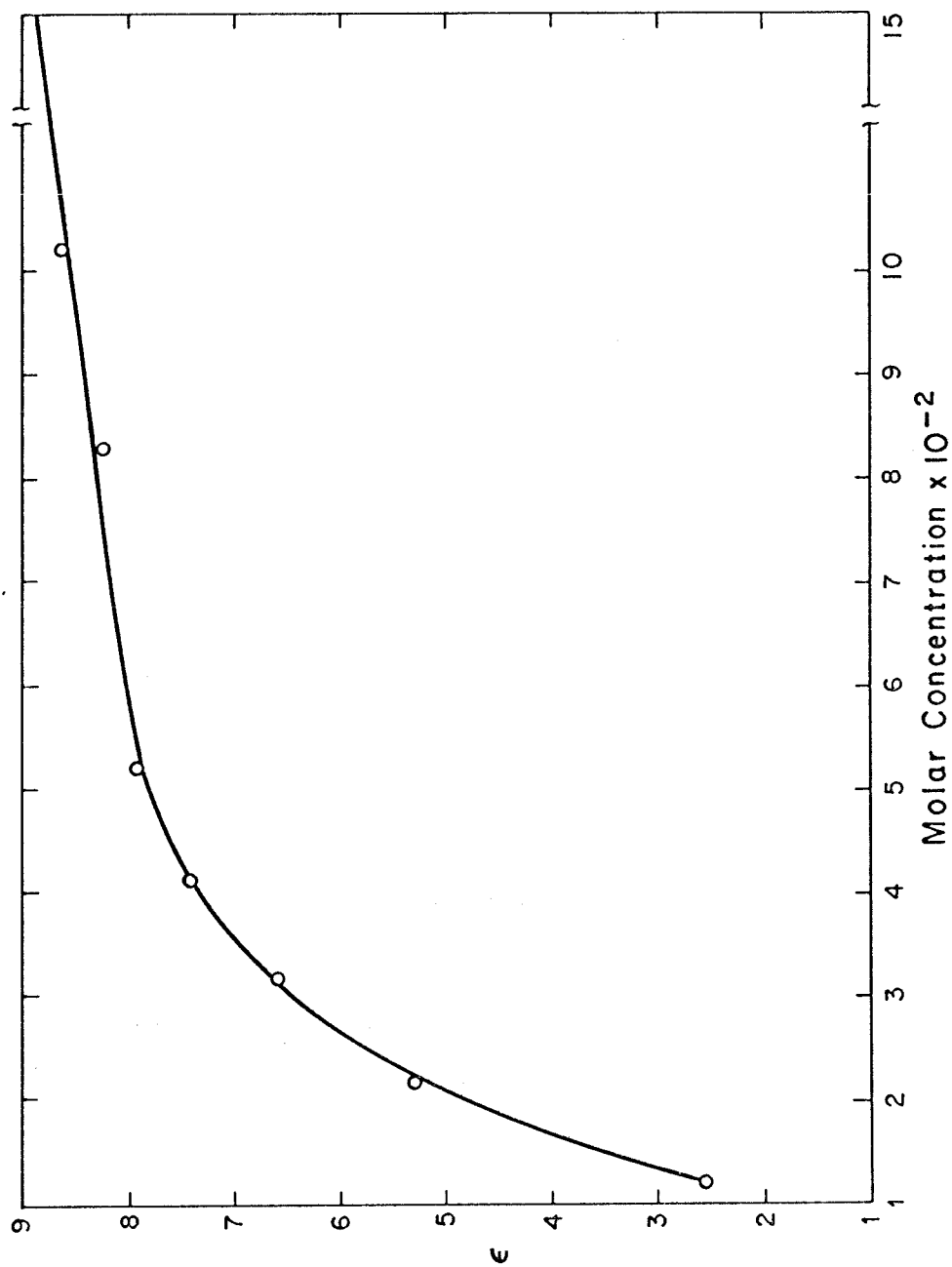


Figure 4. Molar extinction coefficient for concentrated solutions of cyclohexenone at 3660 Å

at low concentrations of the enone.

A further investigation of the interaction of light with cyclohexenone molecules in benzene solution was made by studying the absorbancies of such solutions at different concentrations using 3660 Å light. This reveals a startling fact. The apparent molar extinction coefficients are plotted as a function of concentration in Figure 4. Clearly, Beer's law is not obeyed on the tail of the absorption band. This indicates that at this wavelength of the incident light, the absorption is due to aggregates of two or more molecules and not by single isolated molecules. This could very well lead to the formation of excimers which would produce a major perturbation in the chemical quantum yields. Actual measurements of quantum yields with 3130 Å and 3660 Å wavelength excitation show that they are the same. Since the relative amounts of excimers and excited monomers formed by absorption at the two wavelengths are expected to be different, a possible explanation to the common quantum yield is that the monomeric excited species and the excimers must become equilibrated at a rate that is rapid in comparison with the rate of dimerization. This view can be supported by looking at Figure 3 which gives the ratio of k_5/k_4 equal to 90. k_5 is the quenching rate constant and k_4 is the dimerization rate constant. Since k_5 is unlikely to exceed the diffusion controlled limit, this ratio means that the dimerization reaction occurs at a maximum of only about one out of ninety encounters when the enone concentration is one molar. The principle of microscopic reversibility requires that there be no significant "cage effect"

on the dissociation of an excimer having the same multiplicity as the chemically active excited state. Consequently, the failure to observe high quantum yields when 3660 Å light is absorbed by aggregates only confirms once more that no significant amount of the reaction occurs by way of excited singlets.

According to the triplet mechanism set up for the dimerization, an independent check on the Φ_{ic} value should be available from the plot in Figure 2. The extrapolation of the quantum yield to infinitely high concentration should be equal to Φ_{ic} . Figure 5 is an expanded plot of the data of Figure 2 for the high concentration region. It can be seen that even in this expanded plot, the curvature of the plot is present and is continued up to the neat state of the ketone. Due to scatter in the data and the curvature of the plot, extrapolation to $1/\text{enone} = 0$ cannot be obtained with confidence. It is, however, clear from the plot that the extrapolated value should lie somewhere between 0.5 and 0.8. A single determination of 0.72 was made in neat cyclohexenone. This clearly is higher than the value of Φ_{ic} measured with the highest concentration of enone in Table VII. It can be envisaged that the latter values may be slightly low because of competition of the dimerization reaction with energy transfer to piperylene²¹ so that rate of dimer formation may be more than 10 per cent of the rate of energy transfer in solutions in which the ratio of the enone concentration to the olefin concentration is 10 based on the value of $k_5/k_4 = 90$. Note however, that even if the transfer ratios are identical, k_5/k_4 at one molar enone cannot be used as an exact value for other enone

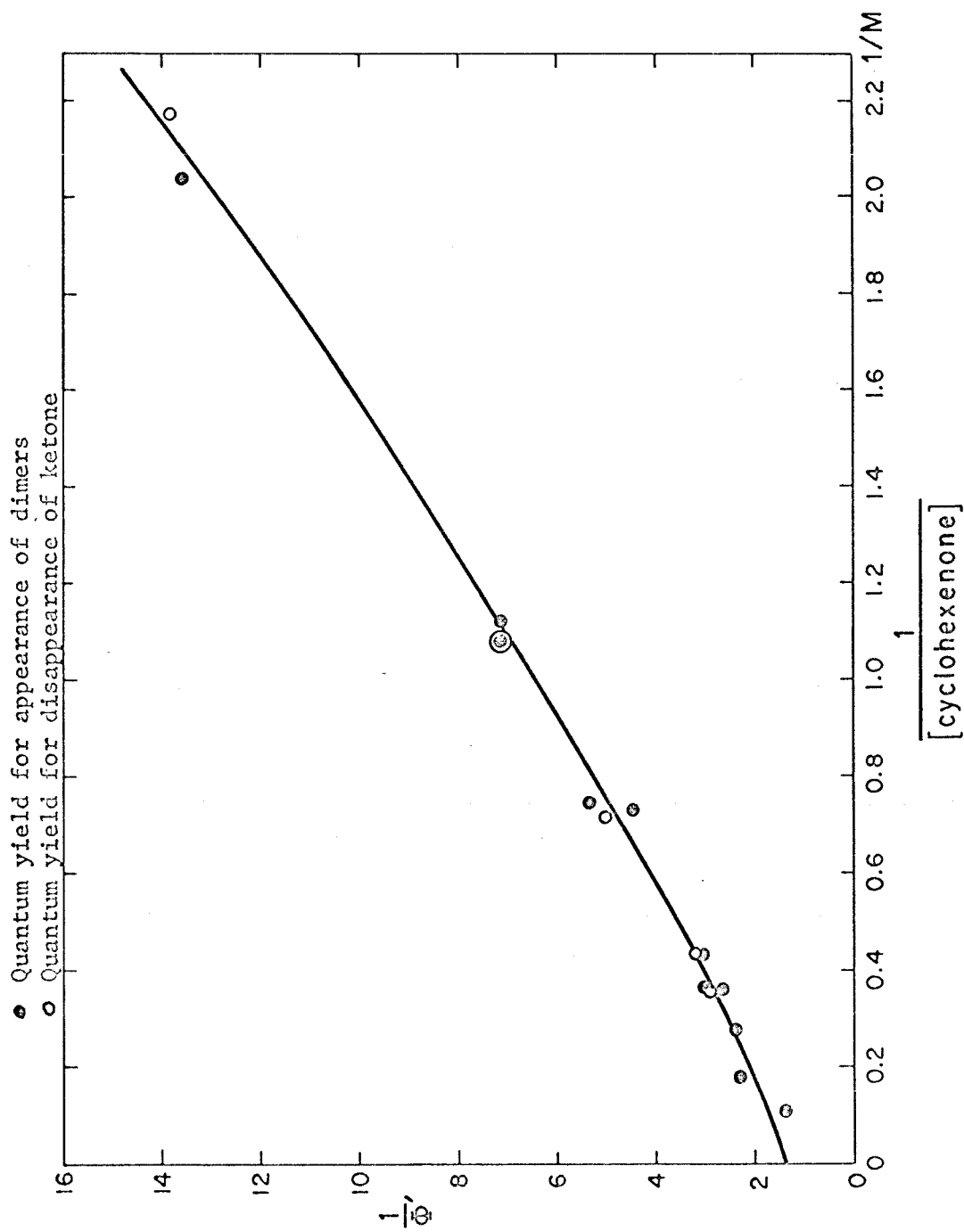


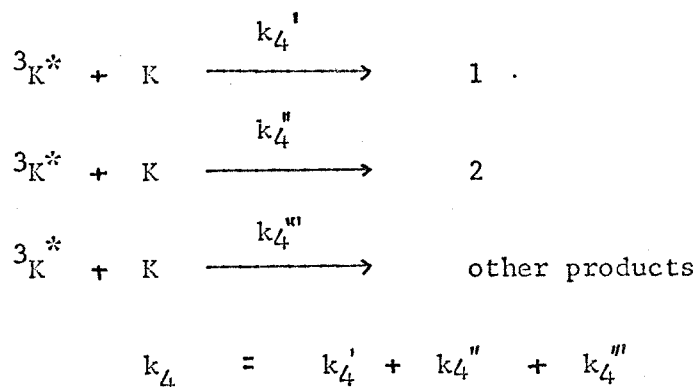
Figure 5. Quantum yields for dimerization and disappearance of monomer in concentrated solutions of cyclohexenone.

concentrations since we maintain that k_5 is concentration dependent. In any case, this will not serve as an adequate explanation for the discrepancy.

Literal interpretation of the discrepancy would infer that dimerization is twice as efficient as the energy transfer from the enone to the diphenylpropenes. This could mean that some dimers are derived from an intermediate that is incapable of transferring energy to the olefins. In fact, one can recall that in the case of *cis*-cyclooctenone, the dimers are formed in the secondary dark reaction from the *trans*- isomer, an intermediate formed from the excited *cis*- isomer. This explanation, though attractive, is not consistent with the quenching and the sensitizing experiments and so its validity cannot be accepted.

Since we have tentatively accepted the conclusion that the dimerization involves only the lowest lying triplet state and that the Φ_{isc} variation with concentration, if real, does not account for the non-linearity of the Stern-Volmer plot in Figure 2, we have two variations to deal with. These are the composition of the dimeric mixture and the ratio k_2/k_4 . They both vary as the concentration of the enone is changed. It is not difficult to see that the two observations are not independent. Step (5) in our triplet reaction mechanism is an oversimplified presentation. Since more than one dimer is formed, k_4 in reality is a composite rate constant equal to the sum of the rate constants for the reactions leading to the different dimers. If the reactions proceed in two or more steps, the number of rate constants may be smaller than the number of

products. However, the usual kind of stepwise mechanism would require different initial steps in the formation of dimers 1 and 2. Hence, we really ought to expand step (5) into the following:



As the concentration is changed, the medium changes and thus affecting each of the k_4' , k_4'' , and k_4''' . These rate constants vary relative to each other and on no basis can one expect their sum to remain constant. k_2 , the rate constant for non-radiative decay of the triplet may also vary, but pertinent information is lacking to enable us to discuss on it.

Our findings are parallel to those of Eaton and Hurt for their study of the photodimerization of cyclopentenone, and these authors have also attributed the variation in the products to the influence of solvent polarity on the relative values of rate constants analogous to k_4' and k_4'' . In both studies, the same phenomenon is found that the product having a large permanent dipole is favored in polar solvents, indicating dipole-dipole interaction between reactants play an important role in determining the rates of the dimerization.

EXPERIMENTAL

Materials. Benzene, Baker and Adamson reagent grade, was washed with concentrated sulfuric acid until the acid no longer developed color and then washed three times with distilled water, dried over sodium hydroxide pellets, and then over anhydrous magnesium sulfate, and finally distilled over phosphorus pentoxide. One ml of α -naphthyl isocyanate was added to 20 g of 2-cyclohexen-1-one (Aldrich) and the mixture was heated on a steam bath for 30 to 45 minutes to remove any cyclohexenol. The precipitates formed were removed by filtration and the filtrate was allowed to stand over anhydrous magnesium sulfate and sodium bicarbonate. This was followed by filtration and distillation under reduced pressure to give a colorless oil. Further purification was done by preparative gas chromatography either using a Beckman Megachrome equipped with a 12-ft Apiezon J Column or a Wilkins Autoprep equipped with a 9-ft column of 20 per cent Ucon polar on Chromosorb G. The column temperatures were in the vicinity of 140°C. The purified ketone was distilled under reduced pressure. A v.p.c. analysis on the fluorosilicone column showed that it contained less than 1.5 per cent impurities, which remained inert in all the experiments conducted. The ultraviolet absorption spectrum of cyclohexenone was taken with the Beckman DU and showed maxima at 290, 313, 325, 337, 366, 370 m with molar extinction coefficients 9.8, 19.7, 25.8, 27.5, 6.6, 5.3 (concentration = 3.18×10^{-2} M in benzene). Reagent grade

Benzophenone was recrystallized twice from n-hexane. Twenty-five g of cyclohexadiene (Aldrich) was washed three times with 10 ml portions of 5 per cent sodium bisulfite and then three times with 10 ml portions of water and dried over anhydrous magnesium sulfate. After Filtration, the diene was distilled through a spinning band column (b.p. 79.5°C) under atmospheric pressure, degassed in a manifold using three freeze-thaw cycles and sealed under vacuum. When not in use, the manifold was stored at temperatures below 0°C. The manifold was designed in such a way that bulb-to-bulb distillation could be done from a main bulb to small ampules. These ampules could be sealed and detached from the manifold. The diene was used immediately when the ampule was opened. Thirty ml of hexadecane obtained from the stockroom was washed with 10 ml portions of concentrated sulfuric acid until the acid did not turn yellow (three times) and then twice with 10 ml portions of 5 per cent sodium bicarbonate and several times with distilled water. It was then dried over anhydrous magnesium sulfate. After filtration, it was distilled under reduced pressure (b.p. 85-91°C at about 1 mm). The product was shown to be pure by v.p.c. Carefully purified thioxanthone stored under nitrogen was obtained from Dr. H. Furrer and used without further purification. Acetophenone purified by Dr. L. M. Stephenson was used without further purification. Zone-refined naphthalene was obtained from Mr. G. F. Vesley and used without further purification. Cis- and trans-Stilbenes were obtained from Dr. D. H. Valentine and were used without further purification. cis-and trans-1,2-Diphenylpropenes were obtained

from Dr. L. Coyne and were used without further purification. cis- and trans-2,3-Diphenyl-2-butenes were obtained from Dr. L. M.

Stephenson and were used without further purification.

Actinometry. Photosensitized dimerization of 1,3-cyclohexadiene by benzophenone has been investigated by Dr. G. F. Vesley in our laboratory and the quantum yield is given by the expression,

$$\frac{1}{\Phi} = 1 + \frac{0.028}{[D]_{av}}$$

where Φ is the quantum yield for the sensitized formation of the diene dimers and $[D]_{av}$ is the mean concentration of the diene.

A reaction mixture containing benzophenone (0.06 M), cyclohexadiene (1.05M) and hexadecane (0.3M) as internal standard, in benzene solution was used as actinometer in all the quantum yield determinations. Aliquots (3 ml) of the actinometer solution were pipetted into pyrex culture tubes (13 x 100 mm) which had a constriction to facilitate sealing. These were then degassed using three freeze-thaw cycles and sealed under pressures of the order of 3×10^{-4} torr. These tubes were stored at below 0° prior to use.

Quantum yield experiments were performed using the "quantum yield merry-go-round" equipped with a 450 watt Hanovia medium pressure mercury arc. The filter systems described by Hammond et al.²⁴ were used to allow transmission of light of wavelengths centered at 3650 \AA , and at 3130 \AA . The dimerization of cyclohexadiene has the same quantum yield with light of these two wavelengths. The actinometers were run to 5 per cent conversion of the diene and v.p.c.

analysis was used to follow the appearance of the diene dimers using the 12-ft fluorosilicone column (vide supra). Following the enone dimerization by v.p.c., the 12-ft fluorosilicone column was used to follow: (a) the disappearance of cyclohexenone using hexadecane as the internal standard, and (b) the appearance of the dimers by using benzophenone as an internal standard added after the reaction. For concentrations lower than 1 M, hexadecane was added before the reaction, and for higher concentrations, hexadecane was added after the reaction. It was checked that the quantum yield was not affected by the presence of hexadecane.

Cyclohexenone as a Sensitizer. The reaction mixtures containing the olefin (cis- or trans-isomer) and cyclohexenone were prepared in a benzene solution and 0.5 ml aliquots were transferred with a hypodermic syringe into pyrex tubes (4 mm internal diameter, 15 cm long). These solutions were degassed using three freeze-thaw cycles and sealed under a pressure of about 3×10^{-4} torr. These tubes were then wrapped around a pyrex immersion well and irradiated with a 450 watt Hanovia medium-pressure mercury arc through a uranium glass filter that is opaque to light of wavelengths shorter than 3340 Å. Virtually all the absorbed light was in the 3660 Å group of lines. Isomerization was followed by v.p.c. until the same cis/trans ratio was reached from both starting states. A 9-ft column of 10 per cent Apiezon L on Chromosorb W was used to analyze the mixtures.

Quantum Yields of Dimerization of Cyclohexenone. Solutions of cyclohexenone at different concentrations with or without hexadecane

were prepared in benzene. Aliquots (3 ml) were degassed using three freeze-thaw cycles and sealed under a pressure of about 3×10^{-4} torr in 13 x 100 mm pyrex culture tubes. Irradiation was done in "quantum yield merry-go-round" using light of 3130 Å. Vapor chromatographic analysis on 12-ft fluorosilicone column was used to follow both the disappearance of the ketone and the appearance of the dimers. The relative rates of reaction were determined and in the case of low concentration where under 99 per cent of the light was absorbed by the enone, the rates were corrected for incomplete absorption before calculation of quantum yields. A correlation of the relative quantum yield with the absolute quantum yield was made by irradiation of a solution 1.016 M in cyclohexenone to 20 per cent conversion with cyclohexadiene actinometers. The quantum yield for the disappearance of the ketone was found to be 0.286.

Product Distribution. The cyclohexenone dimers were analyzed on the 12-ft fluorosilicone column and the relative areas under the peaks were taken as the relative amounts of the dimers formed. The column temperature was 250°.

Quenching by Piperylene. Solutions containing the same concentration of cyclohexenone (1.024M) but containing different concentrations of piperylene (from none to 2 M) were prepared, degassed in the usual manner and irradiated in the "quantum yield merry-go-round" with the 3660 Å filter system until a conversion of 15 per cent was obtained in the sample containing no piperylene. The tubes were opened and analyzed for the appearance of dimers by vapor phase

chromatography using the fluorosilicone column.

Intersystem Crossing Efficiencies. One set of solutions containing 0.05 M, 0.10 M, 0.2 M, and 0.4 M cyclohexenone and 0.526 M cis-1,2-diphenylpropene and another set containing the same concentrations of cyclohexenone along with 0.0525 trans-1,2-diphenylpropene were prepared as usual and irradiated using the 3660 Å filter system. Actinometric solutions containing 0.06 M benzophenone and 0.0526 M cis-1,2-diphenylpropene or 0.0528 M trans-1,2-diphenylpropene were irradiated in parallel with the test solution. The tubes were opened and analyzed using the fluorosilicone column described above. Conversions were 6 per cent or less. The values of Φ_{ic} were calculated using the published method assuming that Φ_{ic} for benzophenone is unity and that decay of diphenylpropene triplets gives 44.5 per cent of the trans isomer.

REFERENCES

1. G. Ciamician and P. Silber, Chem. Ber., 41, 1928 (1908).
2. P. E. Eaton and K. Lin, J. Amer. Chem Soc., 86, 2088 (1964).
3. R. A. Schneider and J. Meinwald, ibid, 89, 2023 (1967).
4. H. E. Zimmerman, R. D. Ricke and J. R. Scheffer, J. Amer. Chem. Soc., 89, 2033 (1967).
5. E. J. Corey et al., J. Amer. Chem. Soc., 86, 5570 (1964).
6. G. Ciamician and G. Silber, Ber., 35, 4129 (1902).
7. R. Anet, Can. J. Chem., 40, 1249 (1962).
8. G. O. Schenck, et al., Chem. Ber., 95, 1409 (1962), Ber., 99, 625 (1966).
9. G. S. Hammond, C. A. Stout and A. A. Lamola, J. Amer. Chem. Soc., 86, 3103 (1964).
10. R. Cole, Ph. D. Thesis, California Institute of Technology, 1967.
11. A. Wacker, H. Dellweg, and D. Weinblum, Naturwissenschaftler, 47, 477 (1960).
12. R. B. Setlow, Biochem. Biophys. Acta., 49, 237 (1961).
13. P. E. Eaton, J. Amer. Chem. Soc., 84, 2344 (1962); ibid, 84, 2454 (1962).
14. P. E. Eaton, unpublished results.
15. N. J. Turro, Molecular Photochemistry, W. H. Benjamin, inc., New York, 1965, p.203.
16. J. G. Calvert, and J. N. Pitts, Jr., Photochemistry, John Wiley & Sons, Inc., New York, 1966, p.537.

17. J. Saltiel, Survey of Progress in Chemistry, Vol. 2, (1964), p. 304. Chapter on The Mechanisms of Some Photochemical Reactions of Organic Molecules.
18. R. S. Mullikan and C. C. J. Rootham, Chem. Rev., 41, 219 (1947).
19. P. E. Eaton and W. S. Hurt, J. Amer. Chem. Soc., 88, 5038 (1966).
20. J. L. Ruhlen and P. A. Leermakers, Ibid. 88, 5672 (1966).
21. A. A. Lamola, unpublished results.
22. G.S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsel, V. Vogt, and C. Dalton, J. Amer. Chem. Soc., 86, 3197 (1964).
23. A. A. Lamola and G. S. Hammond, J. Chem. Phys., 43, 2129 (1965).
24. R. S. H. Liu, N. J. Turro. and G. S. Hammond, J. Amer. Chem. Soc., 87, 3406 (1965).

PART II

RADIATION CHEMISTRY OF BENZOPHENONE

IN

CYCLOHEXENE SOLUTION

INTRODUCTION

The discovery of x-rays by Roentgen in 1892 and of radioactivity by Becquerel opened the field of radiation chemistry, which can be defined as "a study of the chemical effects produced in a system by the absorption of ionizing radiation."¹ This includes both high energy electromagnetic photons such as x-rays and gamma-rays as well as high speed material particles such as α -particles, electrons, neutrons, protons, etc. These ionizing radiations when applied to matter, lead essentially to the production of ions, electronically excited molecules, electrons, and radicals. In general, the state of affair is much more complicated than that initiated by ultraviolet light. In this study, we confine ourselves to the use of gamma-rays emitted from a Co^{60} source on a liquid system of a dilute solution of benzophenone in cyclohexene.

It is appropriate at this point to emphasize a few significant differences between gamma-irradiation and ultraviolet irradiation. Both of these are electromagnetic in nature but the former is very much more energetic than the latter. Photochemistry is confined to interaction between matter and quanta of several electron volts in energy; radiation chemistry, in the case of hard x-rays and gamma-rays, involves quanta of several kilovolts to several million electron volts in energy. It is therefore not surprising that we see differences both quantitatively and qualitatively. Using U.V. light, the primary process is generally

the production of electronically excited state, and with a suitable choice of monochromatic light, it is often possible to bring the absorbing molecule to a single well-defined excited state. This process is governed by selection rules and the extent of the absorption is controlled by the probability of the electronic transition. The excited molecules are distributed uniformly in the plane at a right angle to the direction of the incident beam of light.

In gamma-irradiation, the photon is not selective and its high energy becomes a more important controlling factor than its wavelength. The cross section for interaction depends on the number of electrons in a molecule, and not on its structure, and therefore the energy of such an irradiation is absorbed almost entirely by the solvent molecules of a dilute solution because of this statistical control. A gamma photon tends to lose a large fraction of its energy through a single interaction with matter. This quick release of a large amount of energy, which is higher than the ionizing potential of organic molecules, causes the molecules to become ionized. Photoelectric effect, Compton effect and pair-production are responsible for this kind of ejection of electrons from the molecules. In our study, no attempt is made to investigate the nature of this primary interaction.

This primary interaction is only the beginning of a series of many possibilities. The ionized molecule may undergo bond breaking leading to fragmentation, or it may form a radical which in turn lead to whatever chemistry it is supposed to have under such circumstances. The molecular ion may accept an electron to produce

an electronically excited species or it may undergo chemical reactions of its own. One can elaborate on this and go on to describe many other plausible processes.

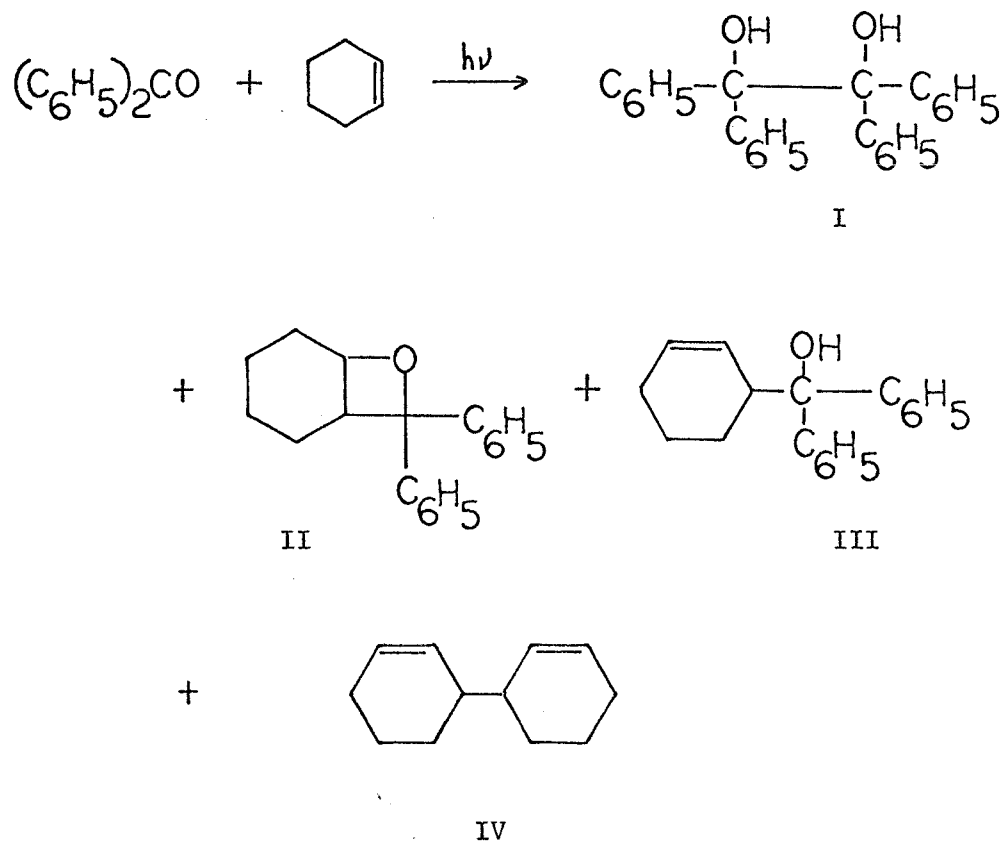
The situation becomes even more complicated when we take into the consideration that the ejected electrons are themselves energetic enough to cause further excitation and ionization. The energy of these electrons (about 100 e.v.) however, is much lower than the primary gamma-photon and they have a much shorter range. The overall result is a production of a cluster or spurs of reactive species. Samuel and Magee² have calculated that for these secondary electrons produced by high energy gamma-irradiation of water or organic liquids, the spurs are separated by an average interval of about 10^4 \AA , and they have an initial diameter of about 20 \AA .

As contrast^{ed} with U.V. irradiation, the absorption of gamma-photons does not obey Beer's law. A small fraction of the incident photons are completely absorbed but most of them emerges from the sample with essentially no change in energy.

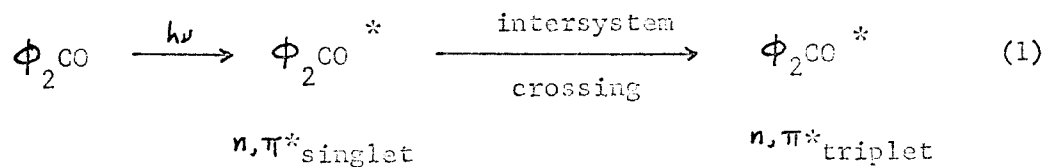
Having described the major differences between photochemistry and radiation chemistry, we narrow our discussion to our specific system of interest viz. a dilute solution of benzophenone in cyclohexene. The photochemistry of this system has been fairly well studied but its radiation chemistry has yet to be explored.

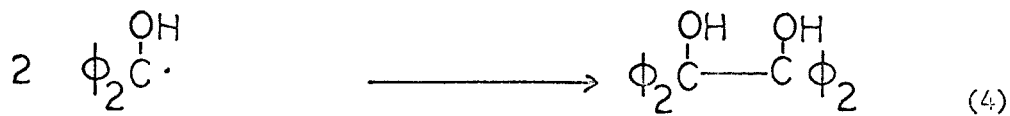
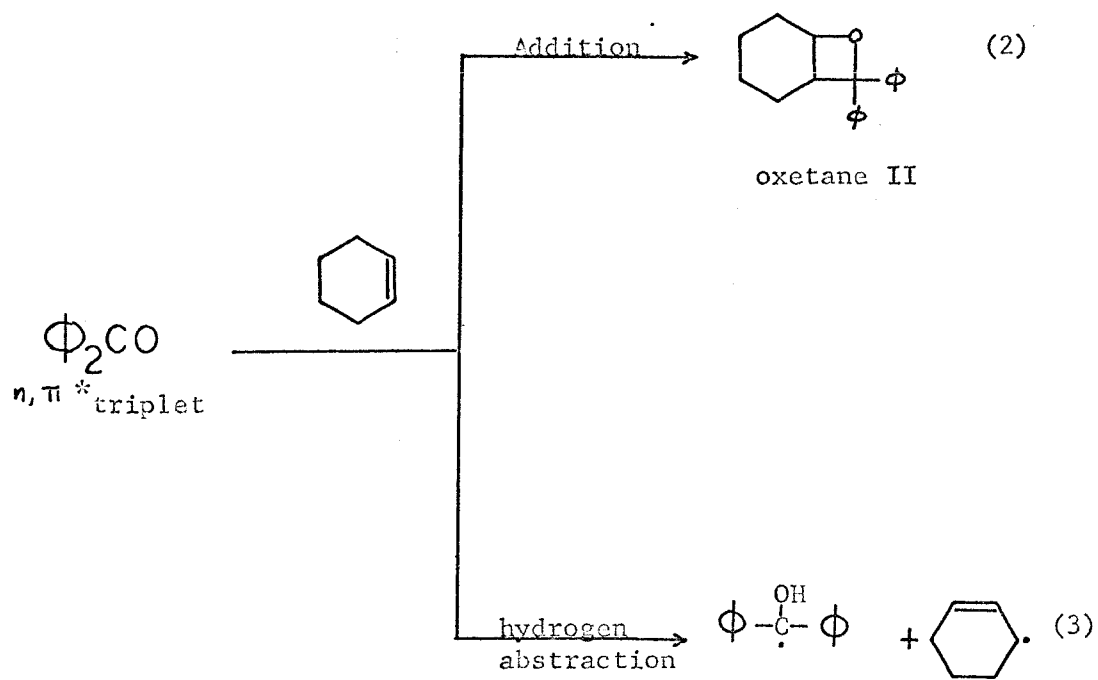
Bradshaw³ carried out a U.V. irradiation of a 0.137 M solution of benzophenone in cyclohexene to near complete consumption of the ketone. The light was filtered by a pyrex sleeve which filtered all light below 2900 \AA . He was able to isolate four products: benzo-

pinacol I, oxetane II, alcohol III and 3,3' -dicyclohexenyl IV.

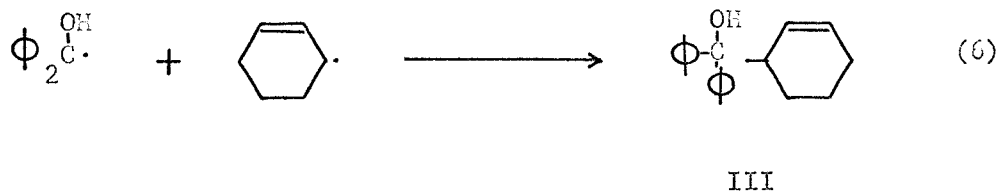
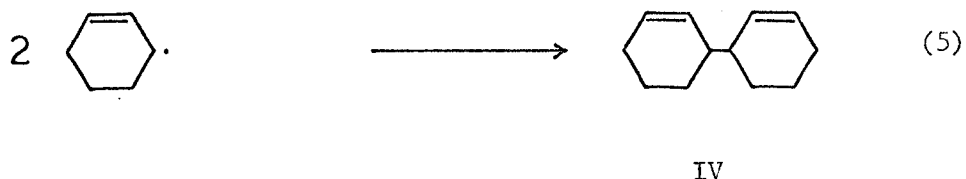


Since the irradiation creates n, π^* excited benzophenone^{4,5} and this ketone is known to have an intersystem crossing efficiency of 1, there is little doubt that the n, π^* triplet state of benzophenone is responsible for this reaction. The mechanism given by Bradshaw is as follows:





I



The yields of I, II, III, and IV are 47 per cent, 13 per cent, 27 per cent and 6 per cent respectively.

In the hope of getting a better correlation between this photoreaction and the radiation study of the same system, we attempted to do a mechanistic study of the photoreaction by taking quantum measurements with or without a triplet quencher. The interpretation of results obtained was unfortunately rendered uncertain by the reformation during irradiation of a transient species which also absorbs light in the n, π^* region of the ketone. In the absence of better documentation of the above mechanism written for the photoreaction, we give it a tentative acceptance.

RESULTS AND DISCUSSION

Since gamma-irradiation of a dilute solution of benzophenone in cyclohexene has never been reported, we were interested to find out what products this irradiation would lead to. Degassed solutions ranging from 0.05 M to 0.5 M benzophenone in cyclohexene were subjected to gamma-irradiation to not more than 20 per cent consumption of the ketone and then analysed by v.p.c. using a 12 foot $\frac{1}{4}$ in. diameter column of fluorosilicone (Dow Corning FS 1265) (10 per cent) on Diatoport S. At a column temperature of 215^o C, peaks with retention times A (3.5 min.), C (11.7 min.), D (23.6 min.), and E (37.7 min.) were observed with D having a poor base line indicative of its decomposition on the column. The same peaks were observed for all the concentrations used. C was identified to be the unreacted benzophenone by comparison of retention time with an authentic sample.

We were interested in identifying the other peaks. Since the products of the photoreaction are known, a comparison was made by irradiating a 0.12 M benzophenone solution in cyclohexene with 3660 Å light to 20 per cent conversion and analysing the solution on the same v.p.c. column under the same conditions. Peaks having same retention times as A, C, D, and E plus an additional one B which comes off in 8.8 min. were observed. A more careful repetition of the chromatographic study reveals that B is also formed in the gamma-irradiation. It is present in a trace amount and it is almost hidden among the peaks of the cyclohexene products.

Separation of the photoproducts was carried out using the procedure of Bradshaw. Isolation of benzopinacol and dicyclohexenyl presented no problem, but it was difficult to get a clean separation of the alcohol from the oxetane. Ultimately, an analytical v.p.c. with a thermal ionization detector was employed to obtain small samples of the alcohol D.

Comparison of the retention time revealed that peak A was due to 3,3'-dicyclohexenyl and peak C was due to benzophenone. Benzopinacol at the column temperature used gave peak B and the benzophenone peak. This is expected because benzopinacol is known to decompose into benzophenone and benzohydrol at 185° C, and so peak B must be benzohydrol. D was shown to be the alcohol and again this was in accord with the observation that D was the one which showed sign of decomposition on the column. Since D is a tertiary alcohol, it should dehydrate easily at elevated temperatures. An authentic sample of the oxetane E was obtained from Mr. Jim Taylor and shown to have the same retention time as peak E. The oxetane E is stable at the column temperature of 215° C.

Although the gamma-reaction and the photoreaction give the same products, the analogy seems to stop here. Even an approximate estimate of the product distribution in the two cases shows that they are quite different. This means that the mechanism of the photoreaction is not followed when the reaction is initiated by gamma rays. The photoreaction gives a ratio of the areas of peaks A:B:D:E: of about 5:2:8:2 whereas the gamma-reaction gives A:B:D:E: of 31:1:16:1. With reference to the size of the peak of the unreacted benzophenone as an

internal standard, the amount of 3,3'-dicyclohexenyl produced in the gamma-reaction is about four times as much as that produced in the photoreaction. In both cases, the reactions were carried to about 20 per cent completion.

In the process of gamma-irradiation, the energy is absorbed mainly by the cyclohexene solvent, it is therefore necessary to distinguish between those products derived from the solvent itself from those products produced as a result of the presence of the solute. The radiolysis of cyclohexene in its neat liquid state was studied by Wakeford and Freeman.⁶ They found that 3,3'-dicyclohexenyl was the main dimeric product with the G value of its production equal to 1.9. Other products included hydrogen (G = 1.28), cyclohexane (G = 0.95), 3-cyclohexylcyclohexene (G = 0.6), dicyclohexyl (G = 0.23), unidentified dimer (G = 0.22) and polymer (G = 2.3).

Since these workers have reported a good discussion of the radiolysis of cyclohexene, we turn our interest to the investigation to the reactivities of cyclohexene towards benzophenone under gamma-irradiation conditions. In our general comparison of radiation chemistry and photochemistry in the introduction, one might expect that high energy radiation could lead to many products. Indeed in many cases, the number of products are so bewilderingly large as to discourage many workers from venturing any further than a preliminary attempt.* Our results on the present system are therefore received

* Unpublished results of this author show that gamma-irradiation of stilbene epoxide in cis-2-butene leads to no less than eighteen products.

with some degree of relief and thankfulness because we got only one main cross product, the alcohol III. It was decided that further evidence be gathered to ascertain its structure.

A small sample of III was collected on an analytical v.p.c. unit as described before and was used to obtain its n.m.r. spectrum. Due to the small size of the sample, the spectrum was taken with a Varian A56/60-A spectrometer with the aid of a Varian C-1024 time averaging computer (132 scans). The spectrum agrees with that reported by Bradshaw.³

The calculated molecular weight of the alcohol is 264, but the largest molecular ion determined by mass spectrometry at a sample temperature of 200° C was found to have $m/e = 246$, which was in agreement with the finding of Bradshaw,³ and this was attributed to dehydration of the alcohol under the experimental conditions. Bradshaw used a 210° C inlet system. The I.R. -OH stretching was found to be 3590 cm^{-1} , in fairly good agreement with the value of 3540 cm^{-1} reported by Bradshaw.

Knowing the main products of the reaction, we decided to conduct a more definitive study of the reactive precursors of these products by using scavengers and quenchers. By introducing an additive (e.g. a triplet quencher) to prohibit the reaction due to a certain reactive entity, and seeing how this affects the reaction, inference can often be obtained from the results on the reaction mechanism. This technique has become a useful tool in mechanistic studies of radiation chemistry as well as photochemistry. We must hasten to point out the limitation that the scavenger concentration

must stay low so that the energy will still be absorbed by the solvent to avoid complications due to the scavenger. In our studies, the scavenger concentration is of the order of 10^{-3} to 10^{-2} M/L. At these concentrations, we can only hope to see scavenging of species that get diffused out of the spurs.

Taking the system under investigation, a priori, one could expect benzophenone to act as an energy sink. The energy of the triplet state of cyclohexene is not known. Ethylene has been measured to have a spectroscopic triplet energy of 83 kcals/mole by Evans.⁷ Adding substituents and incorporating ethylene to make it into a cyclohexene molecule probably lower its energy by a few kcals to about 80 kcals/mole. The planar Franck-Condon triplet can relax into a non-planar triplet with a lower energy. Since the double bond is now somewhat restricted in the cyclic system, the relaxation is not as free as in an acyclic olefin, and the drop of energy in the relaxation may be of the order of five kcals. This brings the relaxed triplet to a level of about 75 kcals/mole. In order for a diffusion control energy transfer to take place, the process must be exothermic by about 3 kcal/mole, and the de-excitation of the donor molecule will be a Franck-Condon process. This means that the energy given up by the non-planar cyclohexene triplet will be about 70 kcals/mole, which makes the energy transfer to be exothermic by only about 1.5 kcals/mole since benzophenone has a triplet energy of 68.5 kcals/mole.⁸ Of course the energies for the Franck-Condon and the relaxed triplets of cyclohexene are only estimated values, and we end up with a number of 1.5 kcals/mole that is on the borderline on the requirement for

diffusion control energy transfer. If the irradiation results in the production of electronically excited cyclohexene molecules, energy transfer could be an important feature leading to benzophenone triplets. It is a well known fact that aromatic compounds are stable towards gamma-irradiation and they can share their stability towards an aliphatic solvent. This phenomenon is called "protection" of the solvent and is often attributed to the fact that the aromatic is acting as an energy sink. If this should be the case, the chemistry that follows from the benzophenone triplets should resemble the photo-reaction. Looking at the actual experiment results, this is clearly not a significant process and at best can only account for the production of the trace amounts of oxetane and benzopinacol. Obviously it cannot account for the preferential production of cyclohexenyl-diphenylcarbinol D. This is an indication that either the triplet yield of cyclohexene was low or the energy transfer process from cyclohexene triplet to ground state benzophenone was not efficient, or a combination of both factors.

The high production of 3,3'-dicyclohexenyl agrees with the findings of Wakeford and Freeman.⁹ In the study of these workers on the radiolysis of cyclohexene in its neat liquid state, 3,3'-dicyclohexenyl was also found to have a high yield compared with other dimeric products. The G value for its production is 1.94. They inferred from this and from the nature of other products formed that radical formation and combination is important in the system. This hypothesis was supported by Ohnishi and Nitta¹⁰ who detected by e.s.r. spectroscopy the allylic type 3-cyclohexenyl radical in

irradiated cyclohexene. Farmer and Moore¹¹ also found that 3,3'-dicyclohexenyl was the main dimeric product of the free radical initiated reaction of cyclohexene.

Phenyl disulfide was chosen as a radical scavenger. This compound has been found by Cohen and his co-workers^{12, 13} to be very effective in transferring hydrogen atoms to and from free radicals. In a system where radical R· combination to give dimer R:R is important, the presence of the disulfide causes the radical R· to form RH instead, and dimerization is suppressed. The rate constants of transfer of hydrogen atoms by phenyldisulfide in some cases reach a value above $7 \times 10^5 \text{ mole}^{-1} \text{ sec}^{-1}$.

Samples of 0.16 M benzophenone solution in cyclohexene containing varying amounts of phenyl disulfide were degassed and gamma-irradiated. The G value for the disappearance of the ketone was measured by monitoring its disappearance spectrophotometrically using the wavelength 3660 Å. Strong quenching of the reaction was observed, but even up to nearly 0.1 M of the disulfide, no levelling off of the quenching was observed and the reaction was not completely prohibited. The G value for the disappearance of benzophenone drops to 0.46 compared with 1.37 in the absence of the disulfide. This represents a quenching of about two thirds of the reaction. A plot of G versus phenyl disulfide concentration is found in Figure I.

It appeared at first to be surprising that the quenching of the reaction was not close to completion even at about 0.02 M phenyl disulfide, but a plot of 1/G for the disappearance of benzophenone versus the scavenger concentration (see Figure II) showed that up to

0.012 M scavenger, the plot was a straight line, but the last point at 0.02 M of the disulfide gave a value of more scavenging than expected. This perhaps means that at least up to 0.012 M disulfide, we are scavenging the radicals outside the spurs, and when the disulfide concentration is further increased, we begin to scavenge some radicals in the spurs.

One experiment was performed using a solution of phenyl disulfide (0.018 M) in cyclohexene. The solution was degassed and irradiated. The production of 3,3'-dicyclohexenyl was compared with that of a sample of neat cyclohexene having been given the same treatment. The dimer was detected by vapor phase chromatography using a fluorosilicone column. The data, however, can only be taken as semi-quantitative due to the presence of a shoulder of the dimer peak. It was found that in the presence of the disulfide, the production of the dimer was cut down to about 57 per cent.

In our G value studies of the system, we monitor spectrophotometrically the disappearance of benzophenone using the wavelength 3660 Å. This method was found to be useful by Sherman and Cohen¹³ in their study of radiolysis of benzophenone in 2-propanol. In our study of the photochemistry of benzophenone in cyclohexene, however, we have found that this method could not be used. When a sample of a 1.78×10^{-2} M benzophenone in cyclohexene is degassed and sealed under vacuum into an ampule and irradiated with 3660 Å light in a quantum yield "merry-go-round", absorption of the solution at the same wavelength is followed without opening the tube. It is found that the absorbance increased instead of decreased with time. This

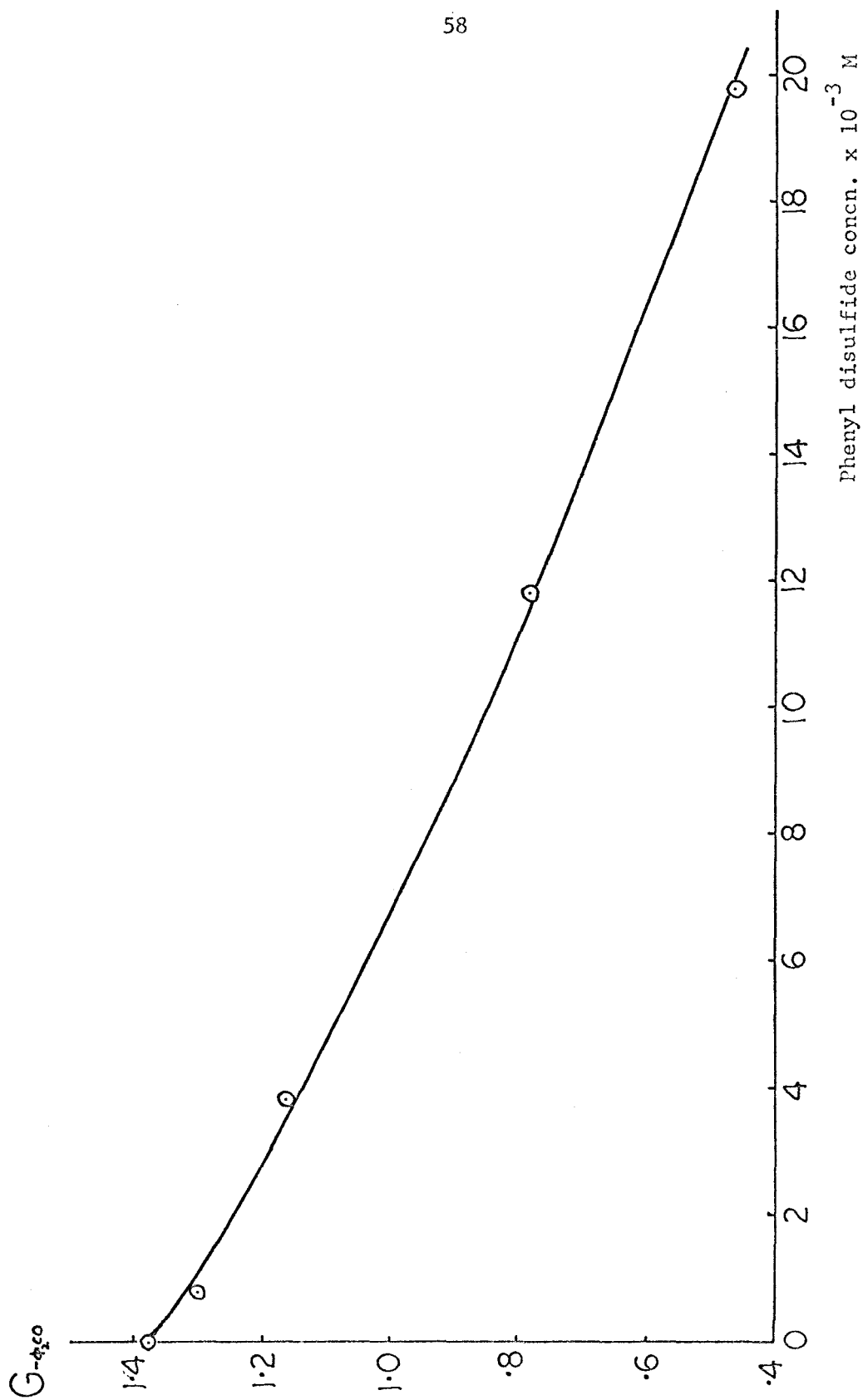


Figure 1. Scavenging by Phenyl Disulfide

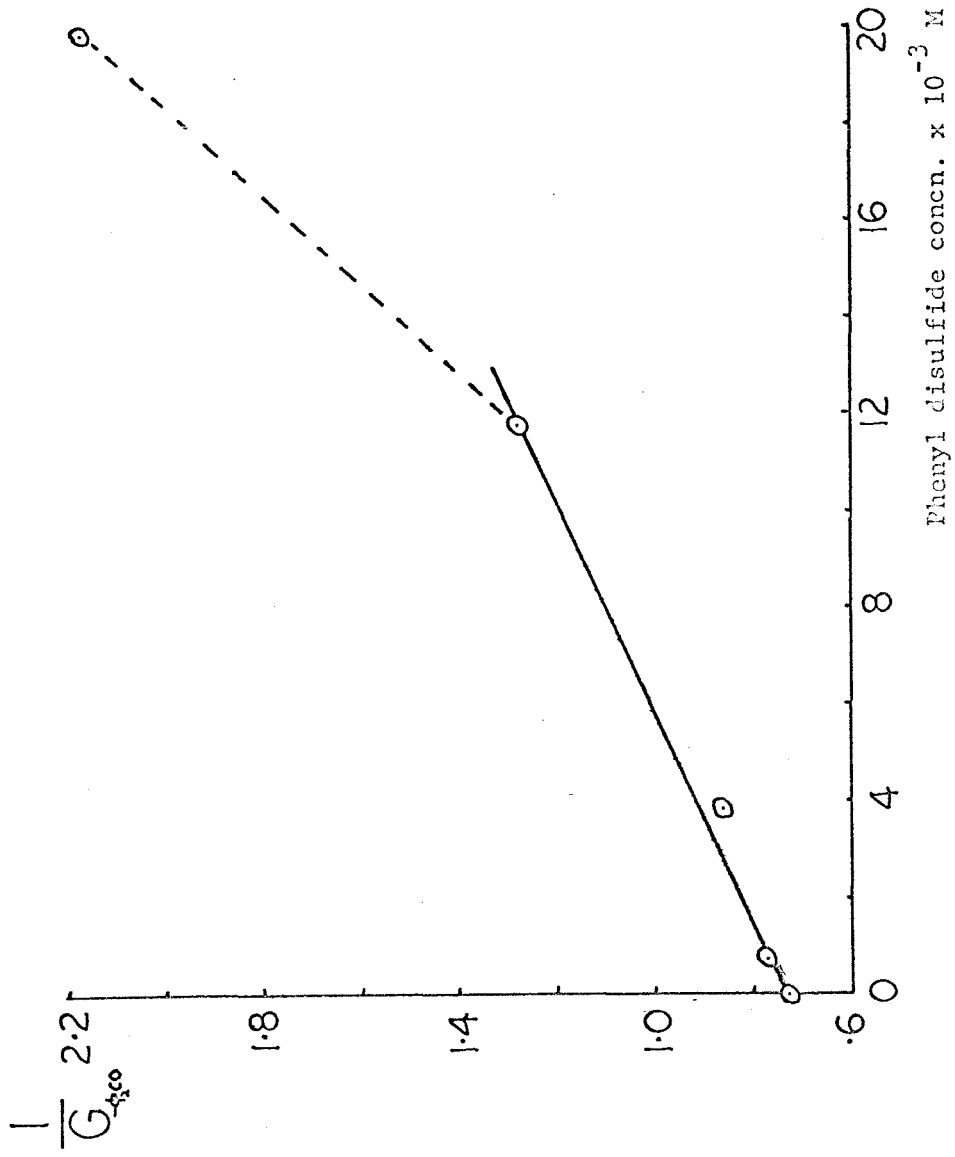


Figure II. Scavenging by Phenyl Disulfide

Data for Figure I and II. Scavenging by Phenyl Disulfide

Phenyl disulfide concn. X 10^{-3} M	Per cent Conversion	G	1/G
0.0000	18.5	1.37	0.73
0.7557	17.6	1.30	0.77
3.800	15.6	1.16	0.86
11.770	10.4	0.78	1.28
19.740	6.2	0.46	2.17

G - for the disappearance of benzophenone

Initial concentration of benzophenone - 0.1612 M

Time of gamma-irradiation - 23.5 hrs.

went on for an irradiation of up to 51 hours. The solution was kept in dark for 18 hours after the irradiation and the absorbance checked again. It was found to be the same as that taken immediately after the 51 hours of irradiation.

In another experiment, a 3 ml sample of degassed and U.V. irradiated 0.184 M benzophenone solution in cyclohexene was opened and the content diluted with benzene to 50 ml and the absorbance at 3660 Å taken immediately. This was found to decrease from 0.65 to 0.59 in ten minutes.

In view of this transient species absorbing at 3660 Å, in the photochemical case, we wanted to make sure that the gamma-radiolysis was free from this complication before we could be safe in monitoring the disappearance of benzophenone by following its absorbance at 3660 Å.

A degassed and gamma-irradiated 0.184 M benzophenone solution in cyclohexene was opened and diluted with benzene and the absorbance at 3660 Å was found to remain at 0.605 after 4.9, 6.7, 8.7, 16.7 and 46.8 minutes. This proved that no transient species was produced and our analytical method was reliable.

From our disulfide experiments, there is no doubt that because of a high concentration of cyclohexenyl radicals produced in the spurs, radical recombination is an important process in the spurs, but the results also suggest that a large fraction of these radicals do diffuse out of the spurs to become scavengeable by the disulfide molecules, and these radicals probably react with benzophenone accounting for part of the consumption of the ketone. This reaction is also quenchable by the disulfide.

We next turned to an attempt to evaluate the importance of electronically excited molecules, especially triplets, as precursors of the products. Naphthalene, a radiation-resistant aromatic hydrocarbon commonly used for radiation "protection" was chosen to be a triplet quencher.* It has a low triplet energy of 61 kcal/mole⁸ so that quenching of both benzophenone triplets and cyclohexene triplets should be highly efficient.

Samples of benzophenone solution (0.162 M) in cyclohexene containing varying amounts of naphthalene up to 0.093 M were degassed and irradiated. G values for the disappearance of the ketone were determined spectrophotometrically. The plot of G versus quencher concentration is shown in Figure III.

The quenching effect seemed to level off at a quencher concentration of 0.06 M, and about half of the reaction due to the ketone was quenched. This substantial quenching can only be interpreted as quenching of the olefin triplets as the major process instead of a significant quenching of benzophenone triplets. As we have seen from the product distribution, benzophenone triplet cannot be an important precursor.

Our results seem to be in discrepancy with those of Cundall and Griffiths¹⁴ who observed no isomerization of trans-2-butene in cyclohexene after gamma-irradiation. They concluded that cyclohexene

* Cyclohexadiene, a popular singlet and triplet quencher, in this case would be a bad choice because it has been shown to be a radical scavenger when present as an additive in the radiolysis of cyclohexene.

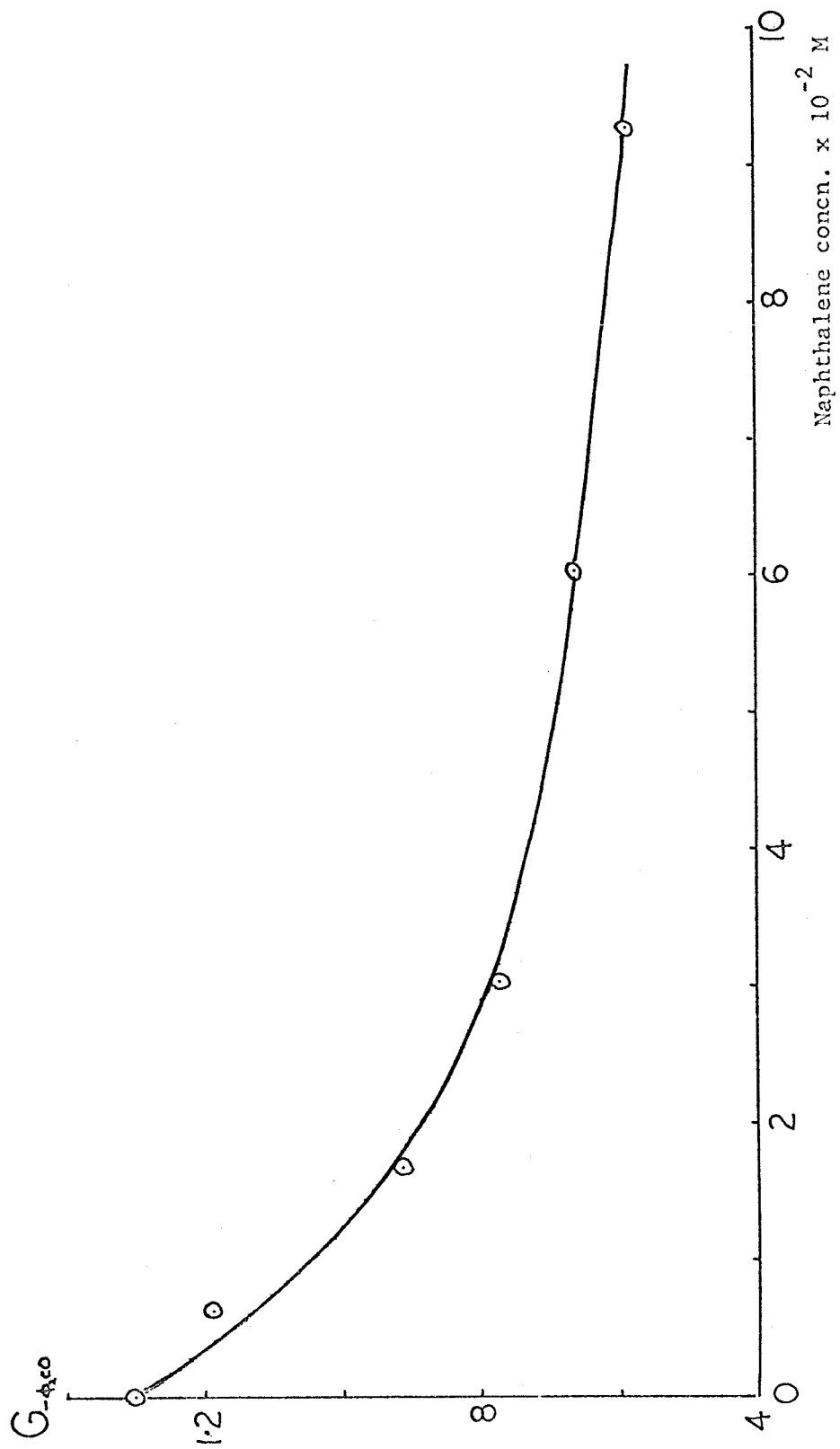


Figure III. Quenching by Naphthalene

Data for Figure III. Quenching by Naphthalene

Naphthalene concn. X 10 ⁻³ M	Per cent Conversion	G
0.0	18.5	1.30
6.5	17.3	1.19
16.9	12.9	0.91
30.4	11.0	0.77
60.3	9.3	0.66
92.6	8.2	0.58

G - for the disappearance of benzophenone

Initial concentration of benzophenone - 0.1623 M

Time of gamma-irradiation - 23.87 hrs.

triplets were not produced. In view of the fact that the triplet energies of trans-2-butene and of cyclohexene are not known, it is quite possible that the failure to induce isomerization of trans-2-butene could be due to the endothermicity of the reaction. Relaxation of cyclohexene triplets may be an important cause of this endothermicity. We decided to repeat Cundall's approach using cis- and trans-1,2-diphenylpropenes which have triplet energies below 60 kcal/mole.

A 0.1 M solution of cis-1,2-diphenylpropene and a 0.1 M solution of the trans isomer in cyclohexene were irradiated for five hours and eight minutes. Vapor phase chromatographic analysis showed that in both cases, the isomerization occurred to about six per cent. The results are tabulated in Table I.

Table I. Radiation Induced Isomerization of 1,2-diphenylpropenes in Cyclohexene

Olefin	Per cent Conversion	G
<u>trans</u> -1,2-diphenylpropene	6.19	} av. 5.89 0.62 (trans → cis)
	5.75	
	5.72	
<u>cis</u> -1,2-diphenylpropene	6.08	} av. 5.84 0.61 (cis → trans)
	5.94	
	5.50	

If the sum of the G values for the trans → cis and cis → trans reactions is taken as the G value for the formation of cyclohexene triplets,¹⁵ this gives the value of 1.23. This, however, does not

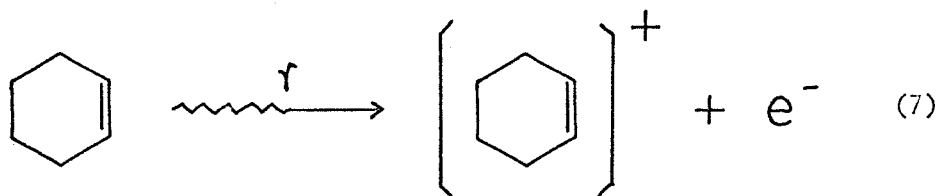
necessarily mean that all the triplets formed take part in reacting with benzophenone in our system of interest because Hammond et al¹⁵ have obtained evidence that in the case of radiation induced cis-trans isomerization of the 1,2-diphenylpropenes in benzene, the olefin solutes act as reactive energy acceptors which can compete effectively with other reactions in regions of high excitation density within spurs.

Even with this explanation, it is still doubtful if it can account for the high G value for apparent triplet formation. This G value is about equal to the total G value for all the reactions leading to the consumption of benzophenone. From the naphthalene quenching experiment, it is apparent that the G value for cyclohexene triplet is probably about 0.7. We therefore prefer to interpret the high G value of isomerization of the stilbenes by saying that the contribution due to singlet energy transfer from cyclohexene to the stilbenes is probably significant in the isomerization process.

With these scavenging results, we can go back to reexamine the two possibilities we discussed regarding the inefficient energy transfer from cyclohexene triplet to ground state benzophenone. It is now clear that we do get a substantial amount of cyclohexene triplets, and these are quite efficiently quenched by naphthalene. They are, however, not significantly affected by benzophenone acting as an energy acceptor. The difference seems to involve a criterion based on consideration of the energetics. We mentioned that the deactivation of the relaxed triplet could be so low as to make its energy transfer to ground state benzophenone inefficient, but since naph-

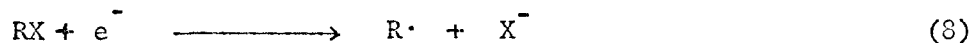
thalene has a triplet energy of only 61 kcal/mole, some 7.5 kcal/mole lower than benzophenone, the energy transfer from the relaxed cyclohexene triplet to naphthalene must have become an efficient one.

To evaluate the importance of ionic species such as the radical cation III produced by electron ejection, we prepared two experiments



using chloroform as electron scavenger and isopropanol as radical cation scavenger.

It is well known that aliphatic halides, with the exception of fluorides, are very susceptible to gamma-irradiation. The carbon-halogen bond is more easily cleaved than the carbon-carbon bond or the carbon-hydrogen bond and the high electron affinity of the halogen causes an easy attachment of electrons giving the general reaction:



Chloroform was therefore used as an electron scavenger.

As in previous scavenging experiments, samples of benzophenone solution (0.164 M) in cyclohexene containing varying amounts of chloroform up to 0.126 M were irradiated and the G value for the disappearance of the ketone, determined in the usual way, was plotted against scavenger concentration in Figure IV. The results show

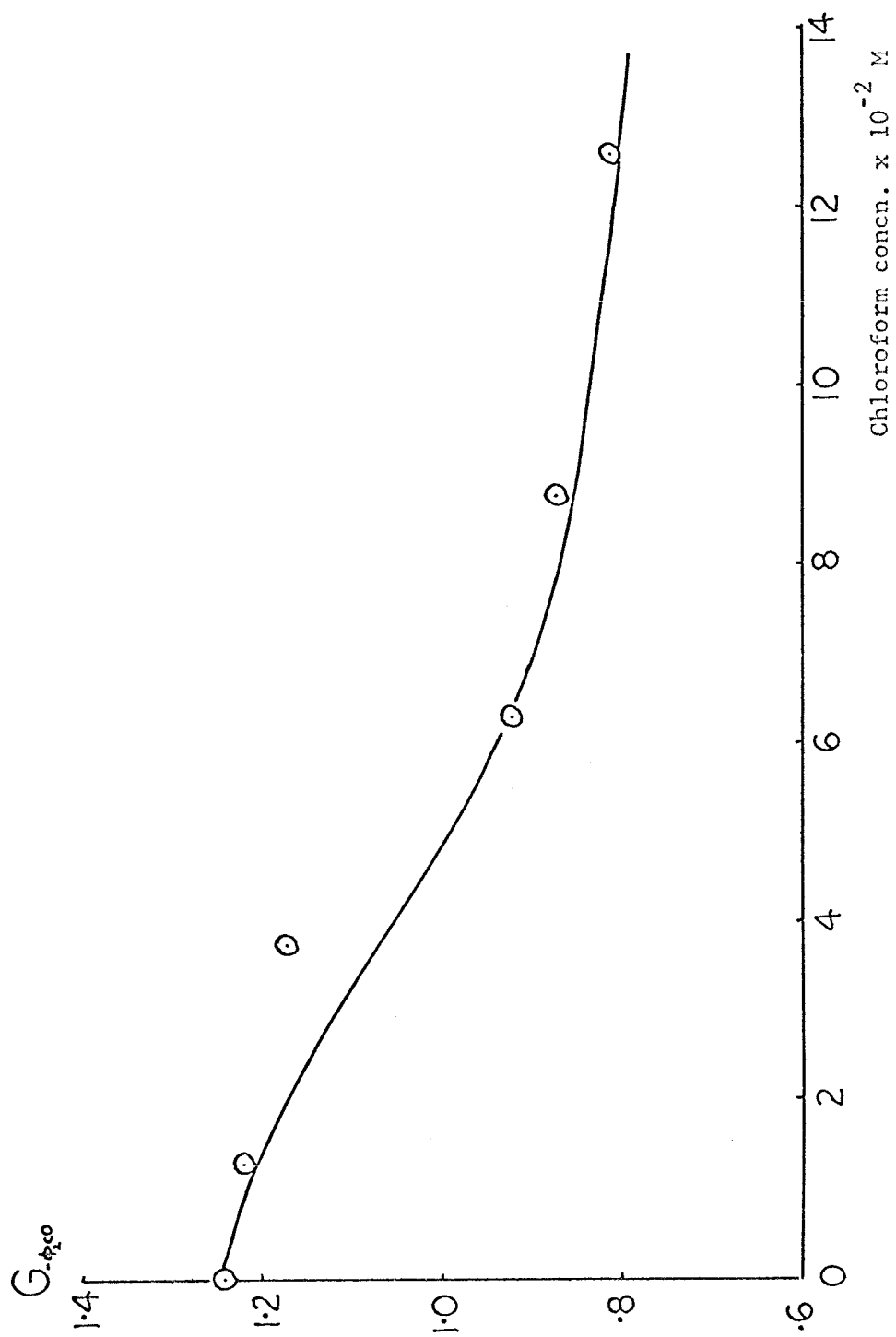


Figure IV. Scavenging by Chloroform

Data for Figure IV. Scavenging by Chloroform

Chloroform concn. $\times 10^{-2}$ M	Per cent Conversion	G
0.00	17.5	1.24
1.26	17.3	1.22
3.76	16.6	1.17
6.28	13.0	0.92
8.79	12.3	0.87
12.57	11.4	0.81

G - for the disappearance of benzophenone

Initial concentration of benzophenone - 0.1643 M

Time of gamma-irradiation - 23.87 hrs.

some quenching of the reaction.

To ascertain the importance of the electron ejection process to give a radical cation (equation 1) and an electron, an experiment was undertaken using 2-propanol to scavenge radical cations. The method is the same as described for other scavenging experiments with 0.021 M as the highest concentration of the scavenger. No quenching was observed, and the reaction was actually slightly enhanced, as shown in Figure V. This shows that no scavengeable radical cations are present in the solution. The slight enhancement is probably due to interference of isopropanol with benzophenone triplets. The latter is known to abstract hydrogen from the alcohol with a quantum yield of 2. In view of the high efficiency of the reaction, it is conceivable that it accounts for the extra consumption of benzophenone leading to a high apparent G values.

The isopropanol results and the chloroform results are not necessarily conflicting because of uncertainty in the role played by chloroform. van Duren and Hamill¹⁶ in their study of the radiolysis of benzene also used chloroform as an electron scavenger, but came up with the postulate that energy transfer could be an important process in the quenching process. We have established earlier the substantial production of cyclohexene triplets and therefore the chloroform in this case could be scavenging both triplets and electrons.

All the data presented above indicate that the reaction mechanism is probably as shown below:

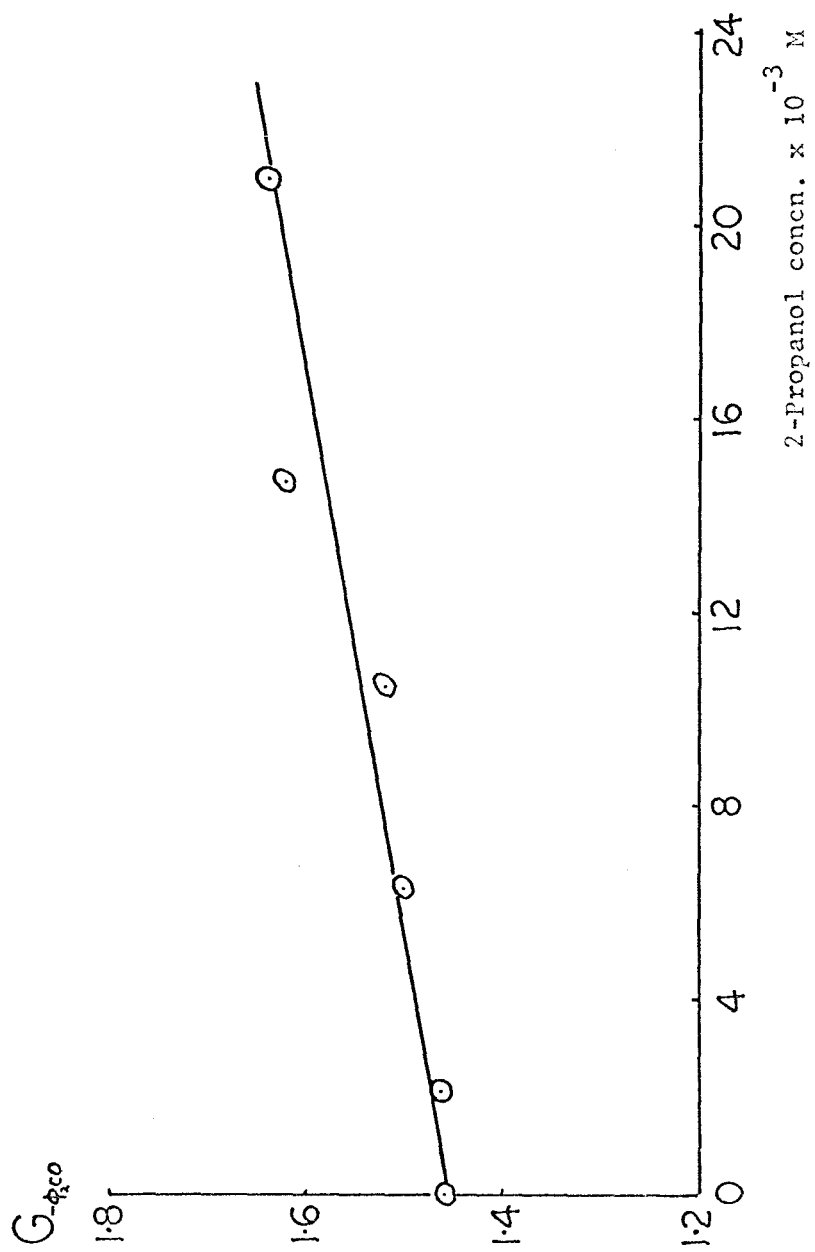


Figure V. Scavenging by 2-Propanol

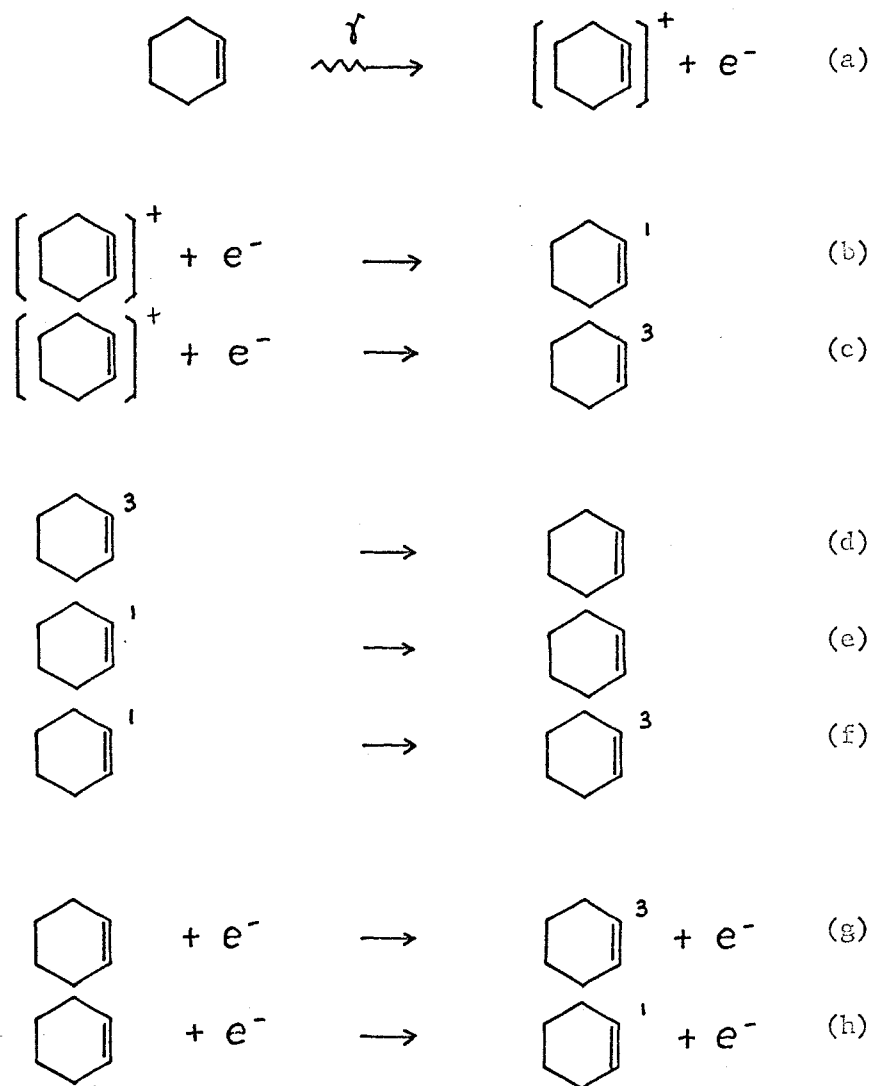
Data for Figure V. Scavenging by 2-propanol

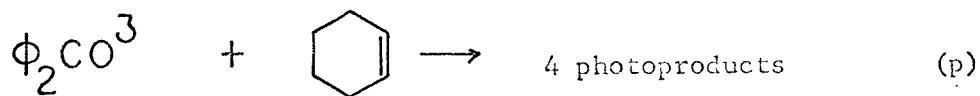
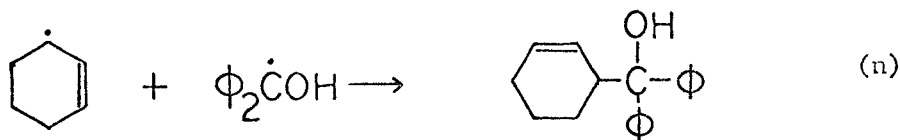
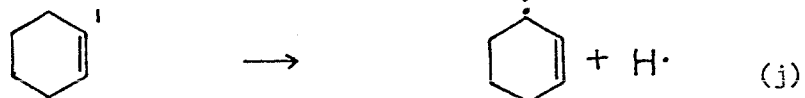
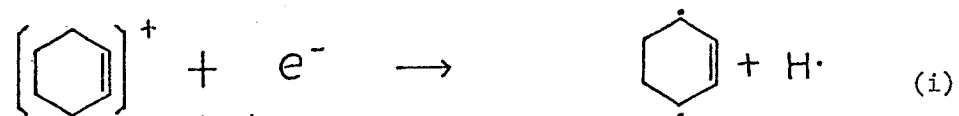
2-Propanol concn. x 10 ⁻³ M	Per cent Conversion	G
0.00	19.3	1.46
2.10	19.3	1.46
6.30	19.9	1.50
10.50	20.2	1.52
14.70	21.4	1.62
21.00	21.6	1.64

G - for the disappearance of benzophenone

Initial concentration of benzophenone - 0.1836 M

Time of gamma-irradiation - 25.5 hrs.





Multiplicity of excited state indicated by superscripts.

Other important primary processes can also be included to account for products such as hydrogen, cyclohexane, bicyclohexyl and polymers from cyclohexene, but since this aspect of the subject has been well studied,⁶ they will be deleted here. We limit ourselves only to those processes giving rise to dicyclohexenyl and cross products between cyclohexene and benzophenone.

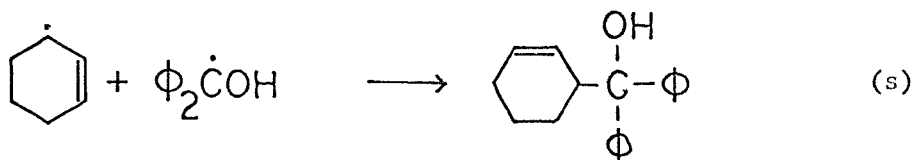
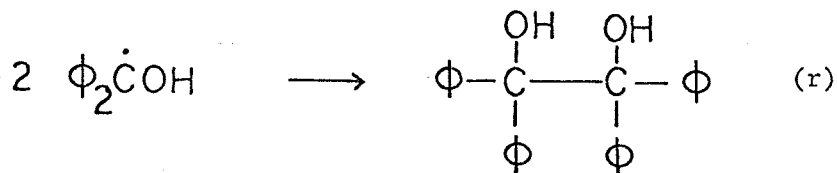
Although scavenging experiments with chloroform and isopropanol failed to intercept the ionic species produced in (a) to give unequivocal quenching, the importance of (a) as a primary process cannot be ruled out. It is reasonable to expect rapid recombination of the radical cations and the ejected thermal electrons to give singlets and triplet states as well as cyclohexenyl radicals as presented in (b), (c), and (i). These processes probably take place within the spurs so that the ionic species are not easily accessible to scavengers present in dilute concentrations.

Electron recapture to give both triplets (b) and singlets (c) is probable since the process is not restricted by quantum mechanical selection rules. The singlets, however, are not expected to be long-lived and either decay to the ground state or undergo intersystem crossing into the triplet state. The involvement of the singlets in the chemical reactions are probably of minor importance. It is also known that slow moving secondary electrons can excite a molecule to its excited states. This process includes optically forbidden transitions so that direct production of triplets without going through the singlet manifold is possible. This is particularly true when the electron does not have quite enough energy to excite a molecule to

its singlet state but possess/sufficient energy to raise it to its triplet state. These processes are written as (g) and (h). For completeness, (d) and (e) are included. They are simply the trivial decays of the excited states to the ground state.

The net important consequence of steps (b), (c), (d), (e), (f), (g), and (h) is therefore the production of excited states with the triplets as the more important species.

When these excited states are produced by recapture of energetic thermal electrons, the energy involved is often large enough to bring the molecule to high vibronic levels of the electronic state and bond breaking becomes quite probable. That this should lead to the cyclohexenyl radical is not surprising since the unpaired electron is stabilized as a part of the allylic system. It is necessary to put down (k) because triplet quenching by naphthalene and radical scavenging by phenyl disulfide total to more than 100 per cent of the reaction. We prefer to explain this by putting down the triplet state as a precursor of the radical because it would be difficult to envision the production of a triplet state from the radical. This also fits the stoichiometry of the reaction—the observation of cyclohexenyl-diphenylcarbinol as the main product and the photo-products are present only in trace amounts. (m), (n) are suggested steps towards the production of cyclohexenyldiphenylcarbinol. We recall that in the photoreaction, the ketyl radical $\phi_2\dot{\text{C}}\text{OH}$ is also formed, and combination of two ketyl radicals gives benzopinacol. In the radiolysis, our rough estimate showed that we were getting about four times as much cyclohexenyl radicals produced as in the photoreaction. It is



therefore reasonable to see that reaction (s) predominates at the expense of reaction (r).

Steps (p) and (q), judging from the stoichiometry of the reaction must be of minor importance only, and we have explained this by saying that the energy transfer from the cyclohexene triplet to ground state benzophenone is an inefficient step. The importance of cyclohexene triplet yield is maintained.

Figure IV shows that the G values for the disappearance of benzophenone rises rapidly with its concentration up to about 0.25 M, and then the increase is slowed down somewhat. This is probably an indication that in the first section of the curve up to 0.25 M, the ketone is scavenging hydrogen atoms leading to the formation of cyclohexenyldiphenylcarbinol. In the absence of other processes, this process should lead to a levelling off of the curve beyond the

point where scavenging is complete. The continuing rise of the G value probably is a result of the phasing in of the triplet mechanism and possibly some singlet mechanism. That the solute is beginning to absorb appreciable amounts of energy must also be taken into consideration.

Quantitative analysis of this plot is not made because the G value for a given concentration decreases somewhat with increase in dose and the values used in plotting Figure VI are not corrected for this. One run was made using a 0.15 M solution of benzophenone in cyclohexene, and the G value obtained after different time of irradiation are tabulated in Table II.

Table II. Variation of G with Time of Irradiation

Benzophenone Concentration	Time of Irradiation	Per cent Conversion	G
0.15 M	7 hr. 20 min.	6	1.21
0.15 M	16 hr. 9 min.	15	1.18
0.15 M	24 hr. 3 min.	19	1.09

This kind of phenomenon is not uncommon in radiolysis because of build up of side reaction products as scavengers. In all of our scavenging studies that we have described, in view of this slight decrease of G with dose, the benzophenone concentration used was always in the

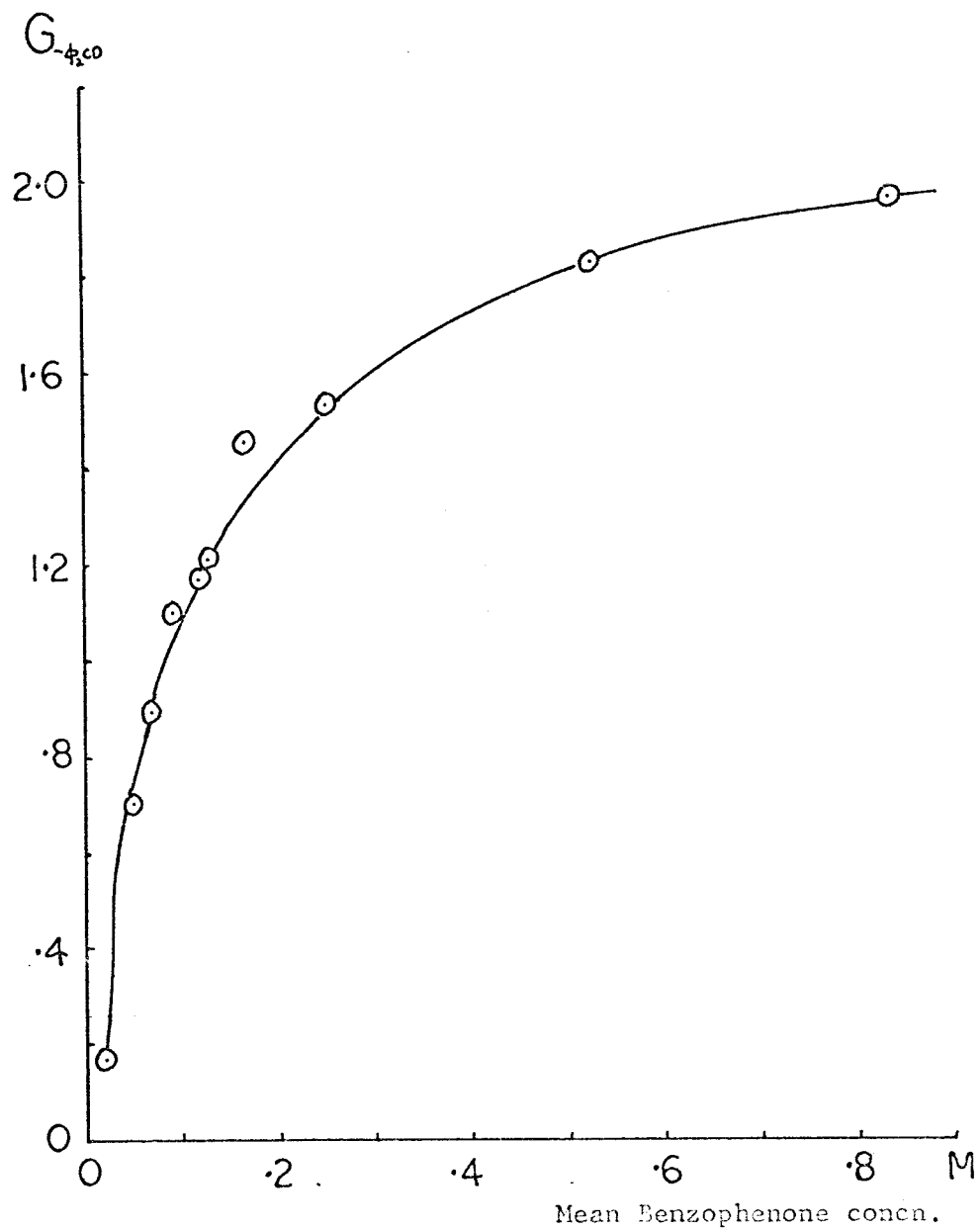


Figure VI. Variation of G with Concentration

Data for Figure VI. Variation of G with concentration

Initial ($\phi_2\text{CO}$) M	Final ($\phi_2\text{CO}$) M	Irrad. time hrs.	per cent conv.	G
0.021	0.018	7.33	12.45	0.37
0.053	0.048	7.33	9.63	0.70
0.071	0.065	7.33	9.13	0.89
0.099	0.091	7.33	8.08	1.09
0.123	0.115	7.33	6.97	1.17
0.150	0.141	7.33	6.00	1.21
0.184	0.148	25.50	19.20	1.46
0.271	0.234	24.00	13.60	1.53*
0.546	0.503	24.00	8.00	1.83*
0.859	0.803	25.40	6.50	1.96

*

determined by v.p.c. analysis of benzophenone using
hexadecane as internal standard on 10 per cent
fluorosilicone column.

vicinity of 0.16 M and the irradiation time was controlled to be about 24 hours so that the different sets of results can be used for a comparative study.

Our hypothesis regarding the roles played by cyclohexenyl radicals and the cyclohexene triplets at different concentrations seems to be confirmed by the observation that we do see an increase in the relative yield of the oxetane with the concentration of benzophenone. In Figure VII the ratio of alcohol/oxetane in terms of relative areas of their peaks on the vapor phase chromatograms is plotted against the benzophenone concentration and clearly it shows that the oxetane is becoming higher in yield as the concentration of benzophenone is raised. At 0.55 M benzophenone, its production, however, is still only about ten per cent of the yield of the alcohol. This interpretation, however, is not unambiguous. If we take the data of Figure VII and plot the oxetane-alcohol ratio versus the electron fraction of benzophenone, we get a linear plot (see Figure VIII) showing that the increase in oxetane formation could simply be due to increase in the direct excitation of benzophenone. At 0.55 M, benzophenone has an appreciable electron fraction of 11 per cent. Quantitative information in this case again cannot be obtained with much confidence because of the alcohol decomposition on the analytical column. The ratio is found also to vary with dose.

In an experiment with a solution of 0.16 M benzophenone, the alcohol/oxetane ratio drops from 8.3 to 7.1 when 3.8×10^{-3} M of phenyl disulfide is present as a radical scavenger. The ratio moves up to 11.6 when 0.147 M naphthalene is present as a triplet quencher.

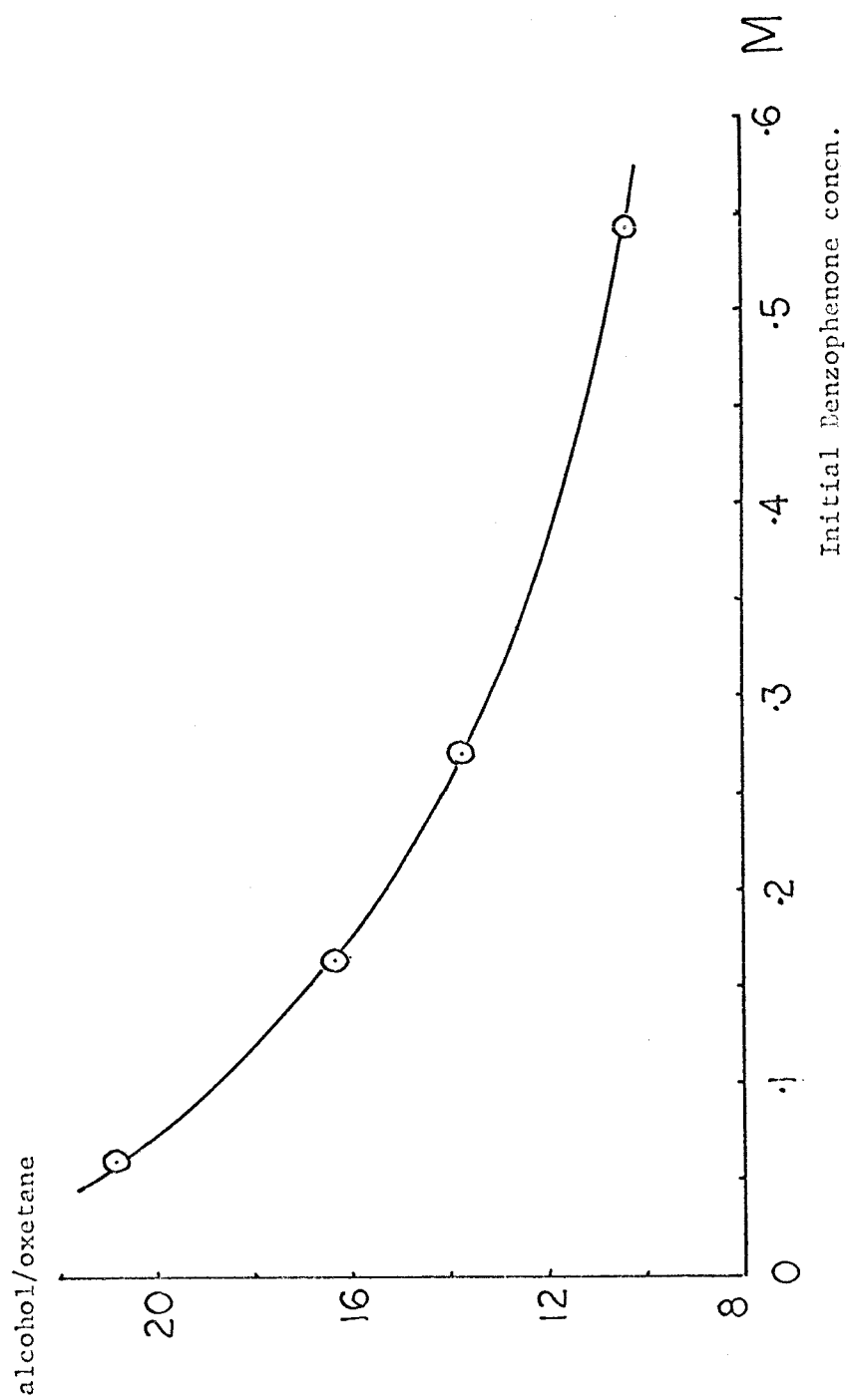


Figure VII. Variation of Alcohol/Oxetane Ratio with Benzophenone Concentration

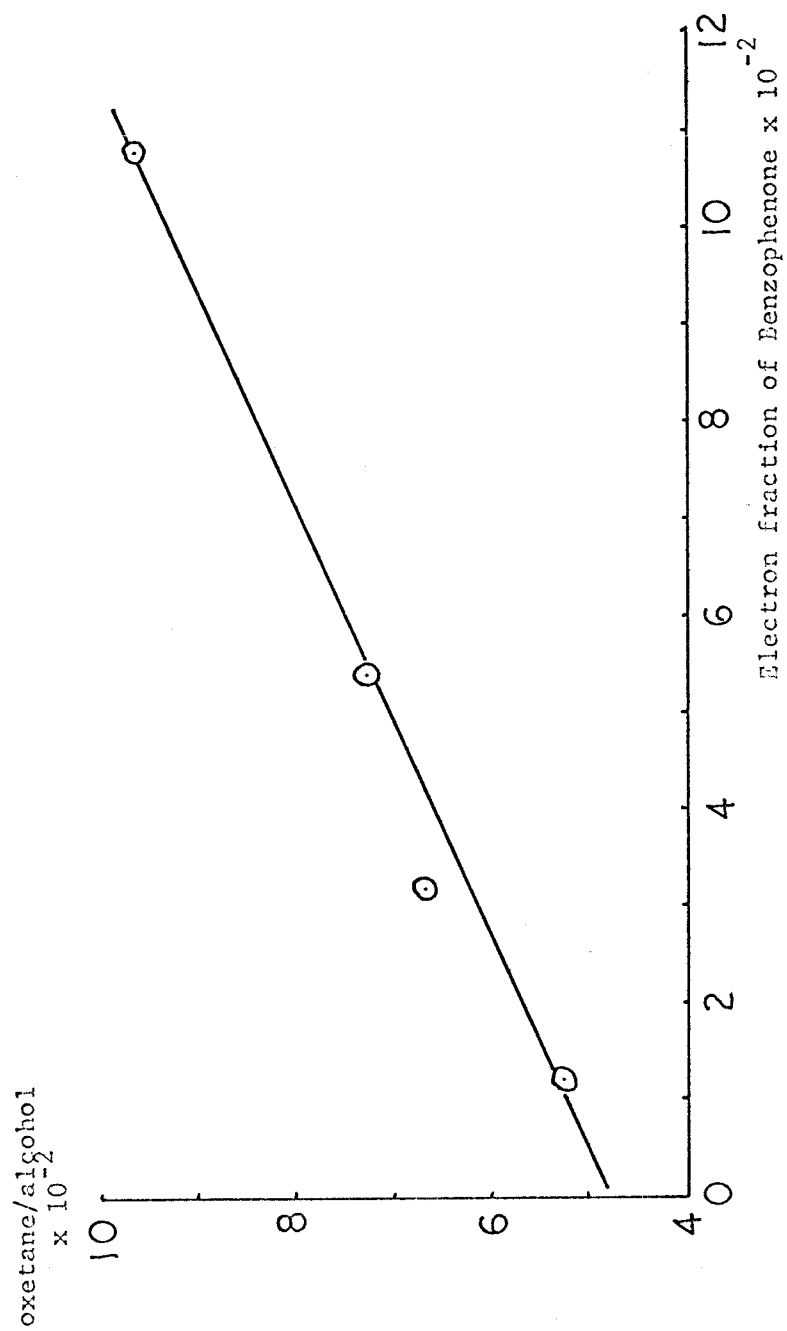
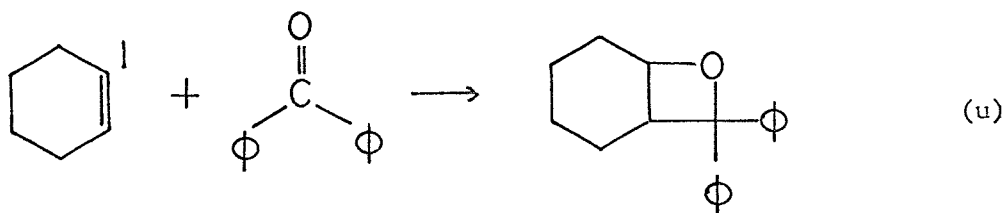
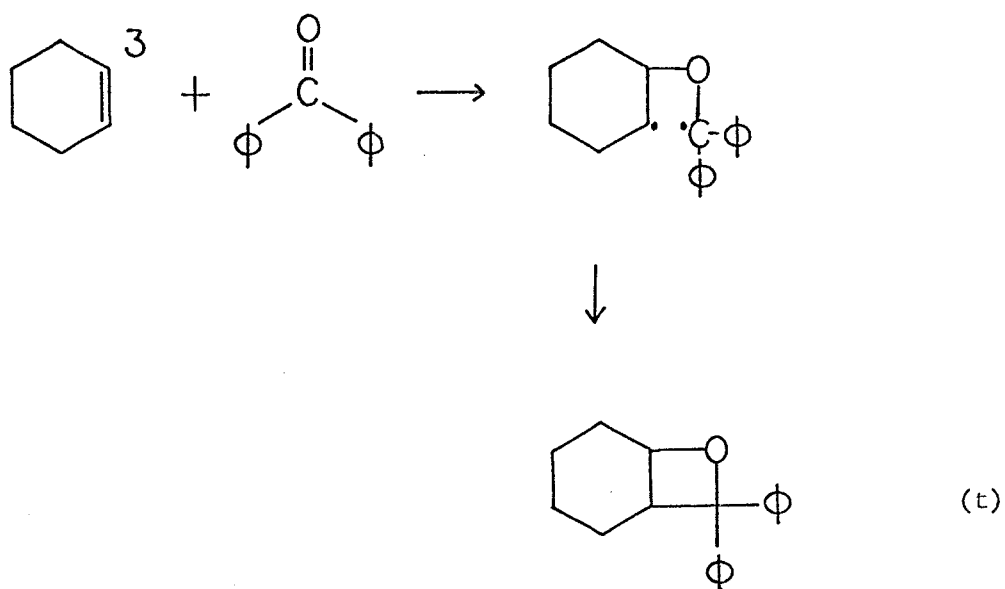


Figure VIII. Variation of Oxetane/Alcohol Ratio with Benzophenone Electron Fraction

Data for Figures VII and VIII. Variation of alcohol/oxetane ratio
with benzophenone concentration

Initial (O_2CO) M	per cent conv.	alcohol/oxetane	oxetane/alcohol	electron fraction
0.060	33.8	20.8	5.27×10^{-2}	1.2×10^{-2}
0.162	17.2	16.4	6.70 "	3.2 "
0.271	13.6	13.8	7.25 "	5.4 "
0.546	8.0	10.4	9.61 "	10.8 "

With this concentration of naphthalene, complete quenching of all triplets is expected. The fact that oxetane formation still persists perhaps indicates that it involves cyclohexene singlets. There is also nothing in our data to rule out the possibility that cyclohexene triplets could also form oxetane.



The singlet mechanism is depicted as concerted, and the triplet mechanism as stepwise because of spin inversion involved.

One of the main reasons why the application of radiation chemistry has not been as fully exploited as photochemistry is the randomness of the primary interaction of the gamma photon with the substrate. The reaction in many cases seem to be under no more control than a statistical one, leading to a great diversity of products. Our present study reveals a significant encouragement that the reaction does possess a remarkably high degree of specificity. The energy absorbed by the system is channelled to perform a rather specific task of breaking a carbon-hydrogen bond of the solvent molecule. This is followed by a rather clean reaction to give one main product.

EXPERIMENTAL

Materials. Chromatoquality cyclohexene (Matheson Coleman and Bell) kept under an atmosphere of nitrogen was shown to be pure by vapor phase chromatographic analysis using a silver nitrate column which separates cyclohexene from cyclohexadiene. It was used without further purification. Benzophenone (Matheson Coleman and Bell) was recrystallized from ligroin. Spectroquality 2-propanol (Matheson Coleman and Bell) was used as received. Cis- and trans-1,2-diphenyl-propenes prepared and purified by Dr. L. J. Altman was used without further purification. Naphthalene, recrystallized from methanol and twice sublimed was obtained from Mr. Shui Pong Van. Spectroquality chloroform (Matheson Coleman and Bell) and phenyl disulfide (Eastman Organic Chemical) were used without further purification.

Preparation of Samples. Solutions in all radiolysis studies were made up in volumetric flasks and 3.0 ml aliquots transferred using pipettes to constricted 13 mm. o.d. pyrex culture tubes. These samples were degassed using three freeze-thaw cycles on the vacuum line and sealed off in the last cycle under a vacuum of 5×10^{-4} mm or better.

Analysis of Samples. The disappearance of benzophenone was monitored by following its absorbance at 3660 \AA using a Beckman DU spectrophotometer.

Radiolysis. Degassed solutions for radiolysis in sealed pyrex

ampules were irradiated in a Co^{60} cavity source * equipped with a water cooling system to maintain the temperature at 30-35°C. The dose rate was measured by Fricke dosimetry ¹⁷ ($G_{\text{Fe}^{+3}} = 15.5$) to be 8.19^{19} ev c.c.⁻¹ hr⁻¹ by Dr. D. G. Whitten on December 2, 1965 and the dose absorbed by each run was corrected for source decay by using the expression:

$$\frac{A_T}{A_{T_0}} = e^{-.131 T}$$

where A_T = dose rate of source in ev c.c.⁻¹ hr⁻¹ at time=T

A_{T_0} = dose rate of source in ev c.c.⁻¹ hr⁻¹ at time=0

T = time in years

Half-life of $\text{Co}^{60} = 5.25$ yr.

Since the G value decreases somewhat with increasing dose, the irradiation time for all the scavenging runs was kept to be about twenty four hours, and the concentration of benzophenone used was about 0.16 M in these experiments. This choice of time and concentration results in a convenient twenty per cent conversion of the ketone. Each ampule containing three ml. of the solution was opened after irradiation and the content transferred quantitatively into a 50 ml. volumetric flask and diluted to the 50 ml mark with Mallinkrodt A.R. grade benzene. The absorbance of this diluted solution at 3660 Å was

* Thanks are due to Dr. James King, Jr. and the National Aeronautics and Space Administration for the use of the Co^{60} cavity source at the Jet Propulsion Laboratory, Pasadena, California.

taken. The extinction coefficient of benzophenone at 3660 Å was found to be 68.36 by a Beer's law plot. This value remains the same when the solvent was either benzene or a mixture of benzene and cyclohexene.

Preparation and identification of photolysis and radiolysis products

A solution of 12.5 g. of benzophenone in 87 ml of cyclohexene (about 0.8 M) was placed in a reaction vessel and a quartz immersion well was fitted into the reaction vessel. A Hanovia 450-w medium pressure mercury arc was used with a pyrex sleeve filter (to cut out light below 2900 Å). Nitrogen was allowed to bubble through the solution for five minutes and then the solution was maintained under an atmosphere of nitrogen before the arc was turned on. The irradiation was continued for four days to about 80 per cent completion of the reaction. Solid crystals of benzopinacol were deposited and removed by filtration. Recrystallization of benzopinacol was done in benzene. The filtrate was concentrated by using a rotatory evaporator evacuated by a water pump. This gave a viscous yellow liquid. Vapor phase analysis using a 12' column of 10 per cent fluorosilicone on Diatoport S at a column temperature of 215^o on a Loenco model 70 dual flame gas chromatograph gave five peaks:

A (3.5 min), B (8.8 min.), C (11.7 min.), D (23.6 min.), and E (37.7 min.). 4.5 g. of this liquid was absorbed on 150 g. of acid washed alumina (Merck). The column was eluted with 250 ml portions of (1) pentane (2) pentane and ether 1:1 (3) ether (4) ether and methanol 1:1 and (5) methanol. Fractions (50 ml) were collected. C was identified to be the unreacted benzophenone by comparison with an

authentic sample which gave the same retention time. Benzopinacol gave peaks B and C. Since it was known to decompose at 185°C to give benzohydrol and benzophenone, peak B was taken to be benzohydrol.

Fractions 1-5 have been reported³ to contain dicyclohexenyl. These fractions were found to give predominantly peak A and hence A was taken to be the olefin dimer. That peak A was the dimer was also in agreement with the fact that it was also observed as the main dimeric peak in a gamma irradiated sample of cyclohexene.

Fraction 10-15 contained mainly E and comparison with Bradshaw's results showed that this must be the oxetane. Confirmation was obtained by checking the retention time of an authentic sample obtained from Mr. Jim Taylor. The oxetane was found to be stable at the column temperature of 215°C used.

Subsequent fractions contained mainly peak D and this must be cyclohexenyldiphenylcarbinol. Peak D showed sign of decomposition on the column into a new peak with a shorter retention time. This was probably due to dehydration of the tertiary alcohol.

Solutions of 0.04 M, 0.10 M, 0.13 M, 0.22 M, 0.41 M and 0.50 M of benzophenone in cyclohexene were gamma-irradiated and analysed by vapor phase chromatography using the same conditions as above and were found to give the same peaks A,B,C,D and E. A and D were the main product peaks. The chromatogram was complicated by minor peaks which appeared between the solvent peak and B. These are presumably products from cyclohexene as compared with a gamma irradiated sample of neat cyclohexene. B, which was present in trace amounts, appeared among the cyclohexene product peaks. This made its measurement difficult.

A gamma-irradiated sample was injected into a Loenco Model 70 gas chromatograph with a thermal ionization detector and fitted with a fluorosilicone column. By this means, a small amount of D was collected. An I.R. spectrum of it was taken on the Beckman IR-7 spectrophotometer and showed the -OH stretching at 3490 cm^{-1} . The solvent used was chloroform. An n.m.r. spectrum was taken by Mr. Frank Weigert with a Varian A 56/60-A spectrometer with the aid of a Varian C-1024 time averaging computer (132 scans). It showed 10 protons at $\delta = 7.4$, 2 protons at $\delta = 5.7$, one proton at $\delta = 3.4$, and 7 protons at $\delta = 1.3-2.1$. This agrees well with that reported by Bradshaw³. Mass spectrometric analysis was kindly done by Mr. Ron Kiefbeck using a C.E.C. Model 21-103 C mass spectrometer in connection with a Model 2-084 A heated inlet system. The inlet temperature used was 200°C and the electron beam energy was 70 ev. The parent molecular ion observed had a m/e value of 246, the same value reported by Bradshaw³. The loss of 18 mass units from the calculated molecular mass was attributed to dehydration at the high temperature used.

REFERENCES

1. J. W. T. Spinks and R. J. Woods, "An Introduction to Radiation Chemistry," John Wiley & Sons, Inc., New York, 1964, p.1.
2. A. H. Samuel and J. L. Magee, J. Chem. Phys., 21, 1080 (1953).
3. J. S. Bradshaw, J. Org. Chem., 31, 237 (1966).
4. G. S. Hammond, W. D. Baker, and W. M. Moore, J. Amer. Chem. Soc., 83, 2795 (1961).
5. M. W. Moore, G. S. Hammond and R. P. Foss, J. Amer. Chem. Soc., 83, 2789 (1961).
6. B. R. Wakeford and G. R. Freeman, J. Phy. Chem., 68(9), 2635 (1964).
7. D. F. Evans, J. Chem.Soc., 1735 (1960).
8. W. G. Herkstroeter, A. A. Lamola and G. J. Hammond, J. Amer. Chem. Soc., 86, 4537 (1964).
9. B. R. Wakeford and G. R. Freeman, J. Phy. Chem., 68 (10), 2992 (1964).
10. S. Ohnishi and I. Nitta, J. Chem. Phys., 39, 2147 (1963).
11. E. H. Farmer and C. G. Moore, J. Chem. Soc., 131 (1951).
12. Saul G. Cohen, U. S. Atom. Energy Comm., NYO-2479-16. (Chem. Abstr. 64: 5987 g).
13. U. V. Sherman and S. G. Cohen, J. Phy. Chem., 70 (1), 178 (1966).
14. R. B. Cundall and P. A. Griffiths, J. Amer. Chem. Soc., 85, 1211 (1963).

15. R. A. Caldwell, D. G. Whitten and G. S. Hammond, J. Amer. Chem. Soc., 88, 2659 (1966).
16. W. van Duren, Jr., and W. H. Hamill, J. Amer. Chem. Soc., 84, 3648 (1962).
17. J. W. T. Spinks and G. J. Woods, " An Introduction to Radiation Chemistry," John Wiley & Sons, Inc., New York, 1964, pp. 106-112.

PROPOSITIONS

PROPOSITION I

The two most commonly encountered electronic transitions in U.V. spectroscopy are the n, π^* and the π, π^* transitions. It is often desirable to distinguish one from the other in assignment of absorption bands of a molecule, in particular, one that allows both kinds of transitions. Sidman¹ in 1958 compiled some general features of n, π^* transitions and compared them to the π, π^* transitions. It began to be apparent that the two kinds of transitions seemed to be subjected to different solvent effects. Kasha² was the first to suggest that these solvent effects might be of value in distinguishing between the two kinds of transitions. The wavelengths of n, π^* transitions are generally found to decrease (blue shift) with increase in polarity of the solvent and sometimes the vibrational structures of such bands are completely blurred in more polar solvents. On the other hand, polar solvents generally shift (but not always) π, π^* transitions to lower wavelength (red shift).

McDonnell³ examined the n, π^* spectra of some thirty compounds and found that all of them were consistently blue shifted in polar solvents and concluded that probably all n, π^* transitions had the same kind of behavior.

The qualitative theoretical explanation given for this empirical method was given by McDonnell³. In the ground state

the molecule is surrounded by solvent molecules in such a way as to effect the strongest binding between them and the ground state charge distribution of the solute molecule. This pattern of orientation is more pronounced when the solvent molecules are more polar. When the solute molecule is excited, the charge distribution will be changed significantly, and by Franck-Condon Principle, it is reasonable to suppose that the polar solvent molecules will not have the proper orientation to bind most strongly with the excited charge distribution. In the extreme cases, the original binding forces may very well become repulsive. This gives rise to the blue-shift because the solvation energy of the solute molecule in the excited state may be less than that in the ground state. No explanation, however, was given for the red-shift of π, π^* transitions in polar solvents.

Turning to the spectroscopic properties of charge transfer complexes, it is immediately apparent that such solvent effects are largely unknown. Most charge transfer complexes of organic molecules involve the use of aromatic hydrocarbons which function only as π electron donors. There are few studies on donors such as amines, ethers, or alcohols which function as n donors. ^{4,5}

The difficulty arises in identifying the nature of the complex when the donor molecule can potentially act either as an n donor or a π donor. The azaaromatics are an example of such donors. The subject of electron-donating properties of azines has been a controversial one for some time. ⁶⁻¹⁰

Recently, Kearns et al.¹¹ studied the spectroscopic properties of complexes formed between eight azaaromatic donors and π electron acceptors trinitrobenzene, p-benzoquinone, and tetrachloro-1,4-benzoquinone at 77°K. They used such criteria as donor ionization potentials, energy of charge transfer bands, and substituent effects on the energy of the charge-transfer absorption bands, and concluded that quinoline, 6-bromo-, 8-bromo-, 1,2,3,4-tetrahydro- and 2-methylquinoline and isoquinoline function as n electron donors.

It is proposed to take these donor-acceptor pairs which have been characterized as n, π complexes and study if they also exhibit the blue shift effect in polar solvents.

Different theories for charge transfer complexation have been advanced by workers in the field such as Weiss^{12,13}, Woodward¹⁴, Briegleb^{15,16} and Brackman¹⁷ but they all have their shortcomings. The most satisfactory theory seems to be that due to Mulliken.¹⁸⁻²⁵

In this theory, the complex is depicted to exist in two energy state, and the difference in energy between the two is equal to the energy of a quantum at the maximum of the absorption band. In the ground state, the donor and the acceptor are held together by such weak forces as that due to van der Waals interaction, dipole orientation, induced dipole, London dispersion, and other effects. The contribution arising from charge transfer from the donor to the acceptor ($D^+ A^-$) in the ground state giving rise to electrostatic, polarization and possibly covalent interactions is thought to be small. In the excited state, the predominant structure is that due

to (D^+A^-) in which the charge transfer from D to A is essentially complete.

Several characteristics of the absorption bands of charge-transfer complexes give strong indication that in the ground state, the donor and acceptor molecules are very loosely bound. The λ_{\max} is several thousand Å greater than the λ_{\max} of absorptions by the donor or acceptor components. This indicates a decrease of some 20 kcal-mole for the most loosely bound electron in the complex. The heats of formation are in general very low (about 1-5 kcal/mole). This also means that the binding in the ground state must be very loose. The absorption band usually extends over a range of wavelength continuously and this also suggests the loose nature of the binding in the ground state of the complex. There is no rigid configuration of the donor and the acceptor in the ground state.

In view of this loose configuration, it is reasonable to expect that the n electron involved in the transfer process is not significantly shielded by the acceptor and should be quite accessible to interact with solvent molecules. The perturbation due to these solvent molecules should be quite similar to that of a single molecule.

If this blue shift is established as a general phenomenon among n, π complexes, the convenient empirical rule can be extended to identifying n, π charge transfer complexes.

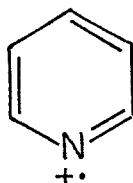
REFERENCES

1. J. W. Sidman, Chem. Rev., 58, 689 (1958).
2. M. Kasha, Discussions Faradays Soc., 9, 14 (1950).
3. H. McDonnell, J. Chem. Phys., 20, 700 (1952).
4. M. Tawres and M. Brandon, J. Amer. Chem. Soc., 82, 2134 (1960).
5. G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer Verlag, Berlin, 1961.
6. C. Reid and R. S. Mulliken, J. Amer. Chem. Soc., 81, 823 (1959).
7. M. Chowdhury, J. Phys. Chem., 65, 1899 (1961).
8. R. E. Miller and W. F. K. Wynne-Jones, J. Chem. Soc., 2372 (1959).
9. R.E. Miller and W. F. K. Wynne-Jones, ibid., 4886 (1961).
10. D. C. Mukherjee and A. K. Chandra, Spectrochim. Acta, 19, 731 (1963).
11. D. R. Kearns, P. Gardner and J. Carmody, J. Phy. Chem., 71, 931 (1967).
12. J. Weiss, J. Chem. Soc., 245 (1942).
13. J. Weiss, ibid., 462 (1943).
14. R. B. Woodward, J. Amer. Chem. Soc., 64, 3058 (1942).
15. G. Briegleb, Z. Physik. Chem., B 31, 58 (1936).
16. G. Briegleb and J. Kambeitz, ibid., B 32, 305 (1936).
17. W.Brackman, Rec. trav, chim., 68, 147 (1949).
18. R. S. Mulliken, J. Amer. Chem. Soc., 72, 600 (1960).
19. R. S. Mulliken, J. Chem. Phys., 19, 514 (1951).
20. R. S. Mulliken, J. Amer. Chem. Soc., 74, 811 (1952).

21. R. S. Mulliken, J. Chem. Phys., 56, 801 (1952).
22. R. S. Mulliken, Symposium on Molecular Physics, Nikko, Japan p.45 (1953).
23. R. S. Mulliken, J. Chem. Phys., 51, 341, (1954).
24. R. S. Mulliken, J. Chem. Phys., 23, 397 (1955).
25. R. S. Mulliken, Rec. trav. chim., 75, 845 (1956).

PROPOSITION II

Tsuji et al ¹, in their study of the gamma-irradiation of pyridine, found that the main free radical produced at -196°C was the radical cation (A) formed by ionization of an electron of the



A

nonbonding orbital of nitrogen. The G value for the radical cation formation was 1.0. The evidence for the radical cation was based on the observation of a triplet ESR spectrum.

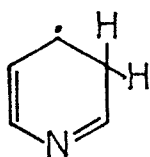
The work was extended to investigate the effect of iodine as an additive. ² It was found that the G value for the formation of free radicals increased rapidly with the iodine content. At 2 mole per cent of I_2 , $G=10$; at 5 mole per cent, $G=17$, and at 50 mole per cent, G became 28. With 1.7 mole per cent of I_2 , the concentration of the radical cation was about 45 per cent of the total concentration of all free radicals.

Good evidence was obtained showing that with I_2 as an additive, the radical cation A was formed through the excited state of the charge transfer complex of pyridine and iodine. This was done by irradiating the pyridine- I_2 system at -196°C with ultraviolet light near 2350 \AA from a xenon lamp. The same triplet ESR spectrum

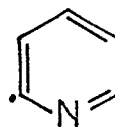
of A was obtained. The wavelength of the charge transfer band of the complex is 2351 Å. (5.3 eV).

There is little doubt that the enhancement in the G value for the production of A is due to the charge transfer complex formation of pyridine with iodine. One possible mechanism depicts the excited state of the complex dissociating into A and I_2^- (or $I\cdot + I^-$). Here, the electron transfer is probably complete at the excited state and so it is not appropriate to label iodine in this case as an electron scavenger.

In view of the importance of radical cation production in gamma irradiation of organic compounds, it is desirable to investigate the behavior of such species. For example, if radical cations are generated when a compound is subjected to gamma-irradiation, they may undergo chemical reactions to form products. In order to ascertain the radical cations as precursors of these products, iodine can perhaps be added to see if the G value for the formation of these products is enhanced. This is based on the assumption that iodine will bring about a higher yield of radical cations as in the case of pyridine. This method will be of value only if we know that the compound forms a charge transfer complex with iodine. This presents one limitation. The second disadvantage of using iodine is that it also acts as a radical scavenger. In the case of pyridine, its concentration effect on the production of A cannot be resolved easily because iodine scavenges the free radicals B and C which are also formed under the experimental conditions.



B



C

Whitten³ in his studies of gamma-irradiation of cyclohexadiene, obtained indications that the radical cation of the diene was the precursor of the "thermal" dimers, i.e. dimers formed by pyrolysis of the diene. Penner⁴, in an attempt to use Tsuji's method to assess the importance of the diene radical cation in gamma-irradiation, found that the method did not work. Although iodine forms a charge transfer complex with cyclohexadiene, on gamma-irradiation, iodination complicates the dimerization reaction of the diene.

With the hope of eliminating the above limitations due to iodine, it is proposed to extend Tsuji's experiment to use carbon tetrachloride, a well-established electron scavenger, instead of iodine as an additive in the gamma-irradiation of pyridine. Since electron ejection does occur when neat pyridine is gamma-irradiated to give A, with $G=1.0$, there is a good chance that electron capture by carbon tetrachloride will enhance the formation of A. Penner⁴ found that adding carbon tetrachloride to cyclohexadiene enhanced the production of the "thermal" dimers in gamma irradiation. In this case, however, there is no good direct evidence that the production of the diene radical cation is actually increased. In the pyridine system, the production of A can be monitored by its triplet ESR spectrum.

Carbon tetrachloride does not form a charge transfer complex with pyridine, and so if the production of A is increased as result of its presence, complexation is not a necessary condition. The method will therefore gain a wider application. It has other advantages over iodine in that it does not scavenge radicals like B and C. In most systems, halogenation as in the case of iodine and cyclohexadiene will probably be minimized if carbon tetrachloride is used instead of iodine.

REFERENCES

1. K. Tsuji, H. Yoshida and K. Hayashi, J. Chem. Phys., 45, 2894 (1966).
2. K. Tsuji, H. Yoshida and K. Hayashi, ibid., 46, 2808 (1967).
3. D. Whitten, unpublished results.
4. T. Penner, unpublished results.

PROPOSITION III

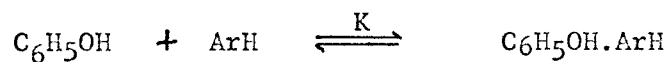
It is well established that π electron systems can serve as bases in forming a hydrogen bond with proton donating compounds. Such a bond is known as a π -hydrogen bond.^{1,2,3} Such an interaction can be envisaged to play an important role in macromolecules in biological systems. Its importance in the dye industry has been realized in what is known as the "cellulose substantivity hypothesis" which postulates that O-H... π electron type bond between cellulose OH and delocalized π -electron clouds of the dye molecules is partly responsible for the affinity of dye for cellulose materials.^{4,5}

Different kinds of means have been employed in exploiting the nature of π -H bond, but the most popular method is by infra-red spectroscopy. The most convenient donor compounds are the phenols. The advantages of the phenols lie in their high acidities, high absorbancy in the I.R. and their slight tendency to self-dissociate. Other methods include U.V. spectroscopy, refractometry, and nuclear magnetic resonance. In the I.R. studies, the detection of a π -H bond is based on a red shift $\Delta\nu$ in the wave number and the increase in the intensity of the OH stretching in the region 3000 to 3800 cm^{-1} .

Compared with research on other types of hydrogen bondings, investigation into π -H bonding may be said to be only at its infancy. Little is known about the nature of this bonding, and only scanty data have been collected on thermodynamic measurements.

Yoshida and Osawa⁶ recently studied the interaction of phenol and various π -bases using the I.R. method, and measured the

$-\Delta F$ values for the complexations:-



They found a linear correlation between $\Delta\nu$ and the number of methyl groups on the base as shown in Fig. 1.

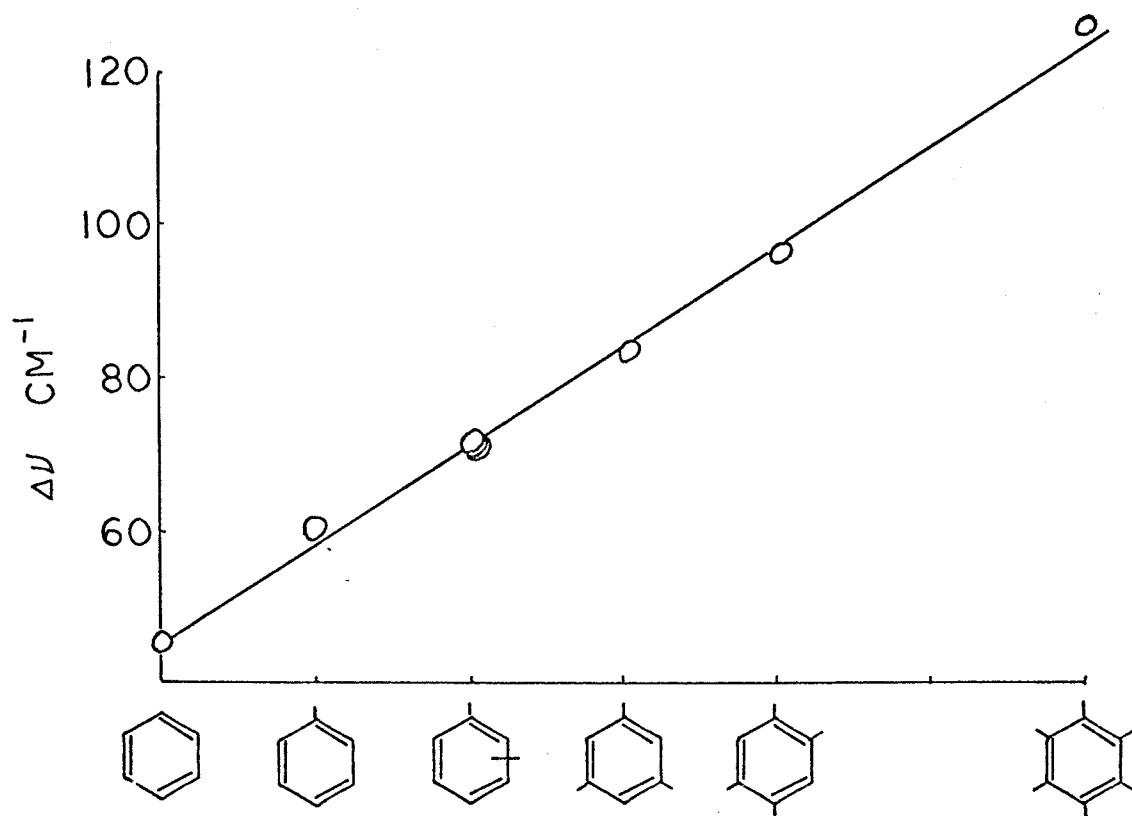


Fig. 1

This is reasonable since $\Delta\nu$ is considered to be proportional to the energy of X-H...Y interaction when X is fixed and Y substituents are changed within closely related structures. ^{3,7}

Another of their finding on the same series of π -bases was unexpected by them in that $-\Delta F$ also increased with the number of substituents as indicated in Fig. 2. They then said that,

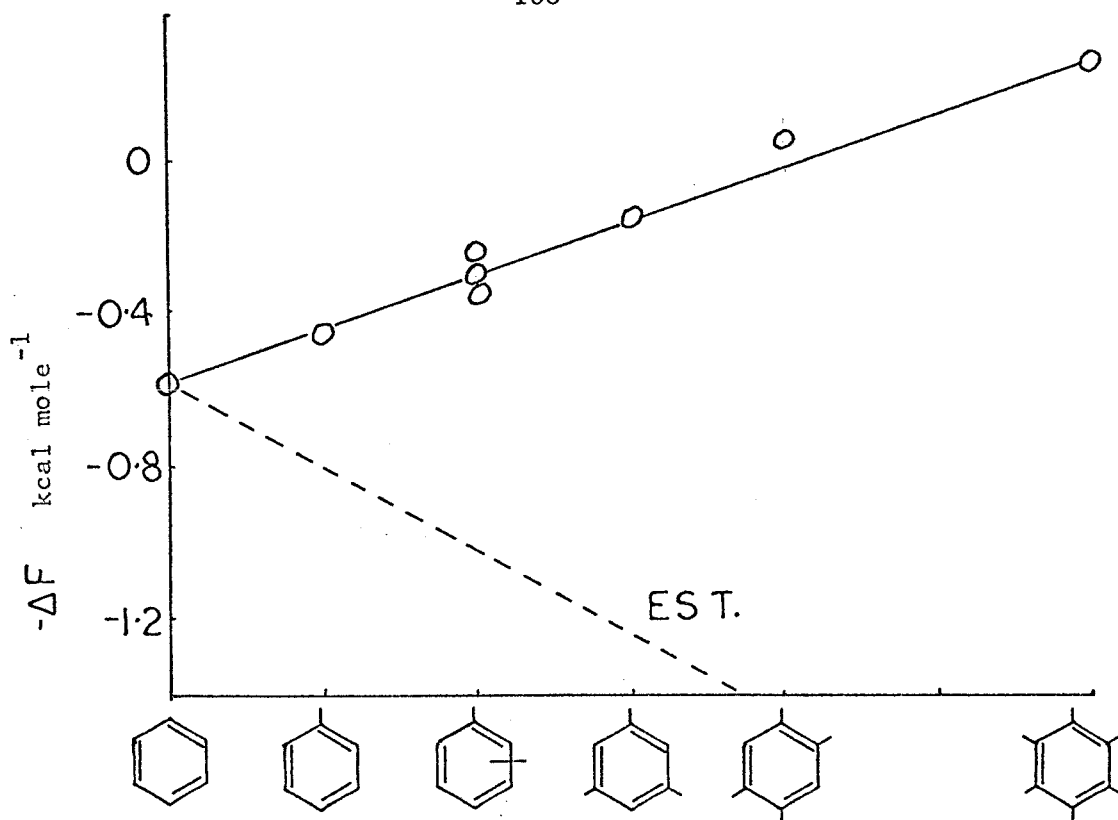


Fig. 2

"... this is strange in the present case because, by the approach of a large molecule such as phenol near methylbenzene, a large entropy loss is expected to occur and to compensate for the enthalpy gain... it would be possible to evaluate the change in free energy of π -hydrogen bond formation with the change of the number of methyl groups on benzene by the use of (a) ΔH and ΔS values for phenol-benzene complex formation and (b) the relation between ΔF and the number of methyl groups (fig.1). The relation estimated is shown in Fig. 2 as a dotted line. Observed $-\Delta F$ values are much higher than what has been estimated. This suggests that the $-\Delta S$ value of O-H... π - bonding is small compared to that of O-H...O bonding." They used the reported values of $-\Delta H = 1.7 \pm 0.2$ kcal/mole, $-\Delta S = 8.3 \pm 0.3$ cal/deg. mole and $-\Delta F = 0.66 \pm 0.2$ kcal/mole (20°). Clearly, $-\Delta F$ should be

-0.66 \pm 0.2 kcal/mole, which is the value used in Fig. 2.

The conclusion was then drawn that the O-H ... π bond was not the σ -type but the more labile π -type in which the phenol molecule might possess some degree of freedom of movement over an isopotential plane within the framework of the diffused π -electrons.

This argument clearly is based on the assumption that the enthalpy change arises exclusively from the interaction of the hydroxyl group and the π -base. While so little is known about the nature of the π -hydrogen bond, it is perhaps too early to say that we can really ignore other kinds of forces binding the molecules together, or the importance of steric effects. After all, we possess no knowledge on the configuration of such a complex. Intuitively, it is difficult to accept the idea that the hydroxyl group together with the rest of the phenol molecule should move around in the π electron cloud and that this freedom of movement should increase in going from benzene to higher and higher substituted benzenes.

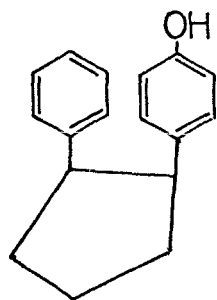
This question can of course easily be settled by a direct determination of ΔH and ΔS . From the magnitude of the uncertainty in the ΔF values reported, however, it can be inferred that such an experiment will be very difficult if not impossible.

Another type of so-called unexpected phenomenon was observed by R. West² in connection with a rule proposed by Huggins and Pimentel⁸. Huggins and Pimentel showed that the intensity change of the -OH band from the non-bonded state to the bonded state is proportionally related to the free energy change and is ordinarily proportional to the basicity of the base. West found that whereas

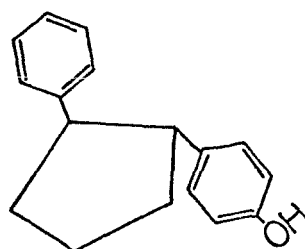
olefins are stronger hydrogen bonding bases than simple aromatic compound the least basic olefins, the 1-alkenes, are about as basic as p-xylene. The intensity change of a 0.02 M phenol solution which is also 1 M in p-xylene, is greater than even that of one with 0.02 phenol and 1 M 2-methyl-2butene. West also speculated on this and suggested the idea of a labile π -hydrogen bonding. In this case, however, West also said that it might be just a steric effect.

To throw light on the problems afore-mentioned, it is proposed that the infra-red spectroscopic studies be extended to the following compounds in carbon tetrachloride solution to study their intramolecular π -hydrogen bonding.

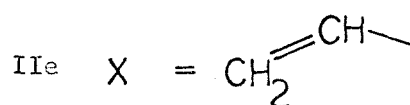
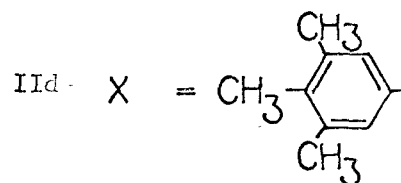
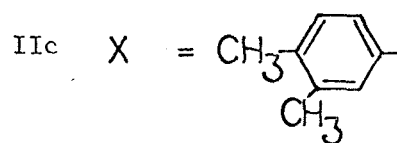
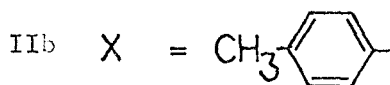
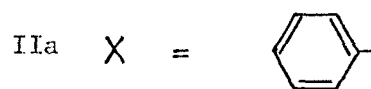
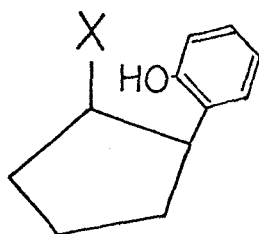
By virtue of the geometry of the compound Ia, no π -hydrogen bonding is possible. This is however, quite possible in IIa. A comparison of the spectra of Ia and IIa should show a red shift $\Delta\nu$ and an intensity change from which $-\Delta F$ may be calculated using the same method employed by Yoshida and Osawa.⁶ The same can also be measured for IIb, IIc and IId. In these molecules, the movement of the hydroxyl group is much more restricted and also the trend of having more freedom of movement in going from lower to higher substituted π -bases should not be permissible any more. This series of compounds therefore should serve as a very good test on the validity of Yoshida and Osawa's postulate. If ΔS effect could indeed be held responsible for the dramatic change in $-\Delta F$ values in Yoshida and Osawa's series, then in the present series, we should definitely see also a dramatic difference in the behavior of $-\Delta F$ in the absence of the ΔS effect.



Ia



Ib



Since p-methylphenyl group should have about the same basicity as the vinyl group, a comparison of the spectra of IIb and IIc should serve as a good test of the Huggins-Pimentel rule under these circumstances.

It might be added here that these intra-molecular studies have another important advantage that a 1:1 interaction is much more certain than in the intermolecular case.

As mentioned before, the role played by π - π interaction in π -hydrogen bonding is not known. The comparison of the spectra of Ia and Ib should lead to an answer of this question. π - π interaction has been detected in cis- and trans-1,2-diphenylcyclopentanes⁹ by U.V. studies. If π - π interaction contributes to the π -hydrogen bonding, then a comparison of the spectra of Ia and Ib should show a change in the -OH bond.

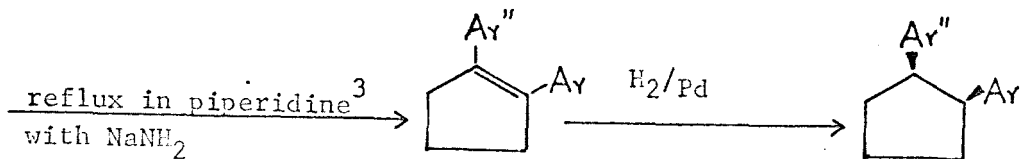
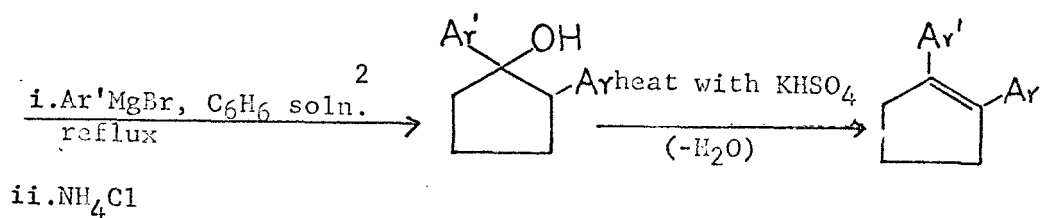
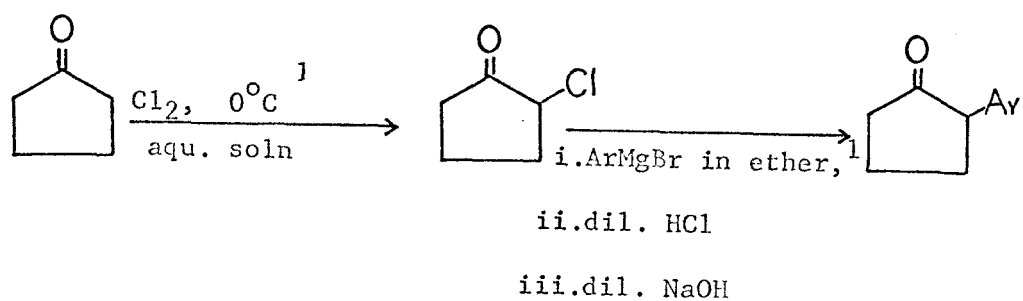
REFERENCES

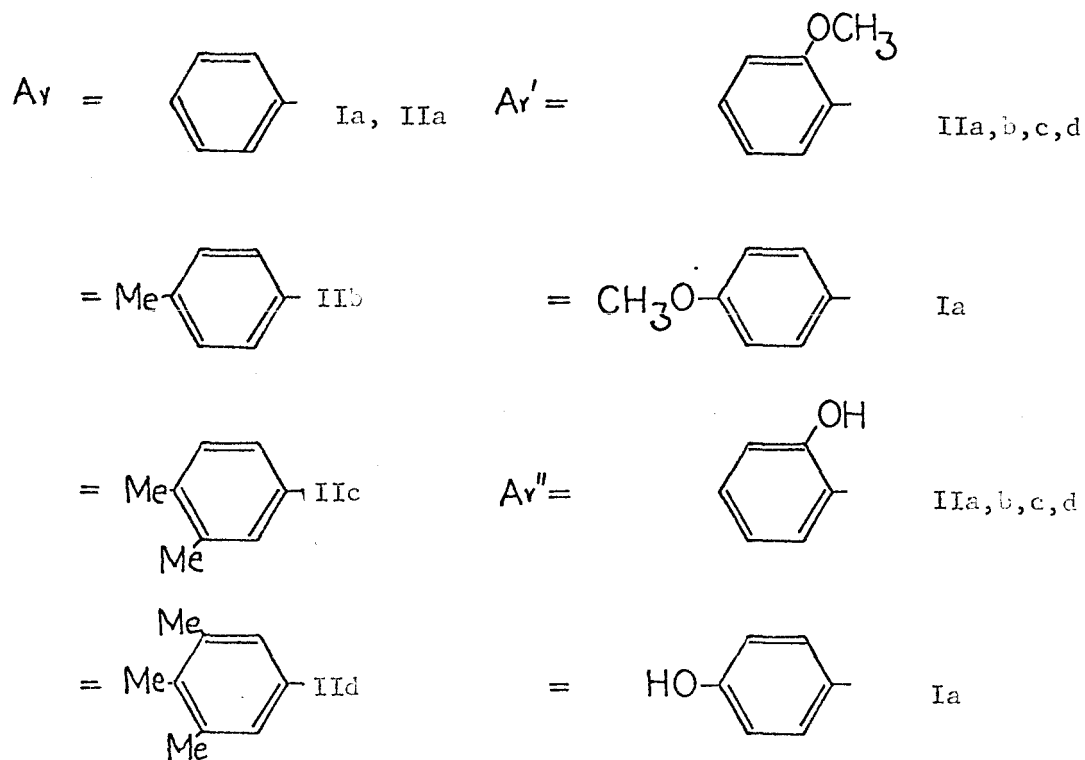
1. G. C. Pimentel, A. L. McClellan, "The Hydrogen Bond" (1960)
p.202
2. R. West, J. Am. Chem. Soc., 81, 1614 (1959).
3. P. von R. Schleyer, D. S. Trifan, R. Bacskai, J. Am. Chem. Soc.,
80, 6691 (1958).
4. C. H. Bamford, Dis. Faraday Soc., 16, 229 (1954).
5. W. L. Lead, J. Soc. Dyers Colorists, 73, 464(1957),
ibid, 75, 195 (1959).
6. Z. Yoshida, E. Osawa, J. Am. Chem. Soc., 87, 1467 (1965).
7. R. West et al. J. Am. Chem Soc., 86, 3227 (1964).
8. M. L. Huggins, G. C. Pimentel, J. Phy. Chem., 60, 1615 (1956).
9. L. J. Andrews, R. M. Keefer, "Molecular Complexes in
Organic Chemistry" p.70.

ADDENDUM TO PROPOSITION III

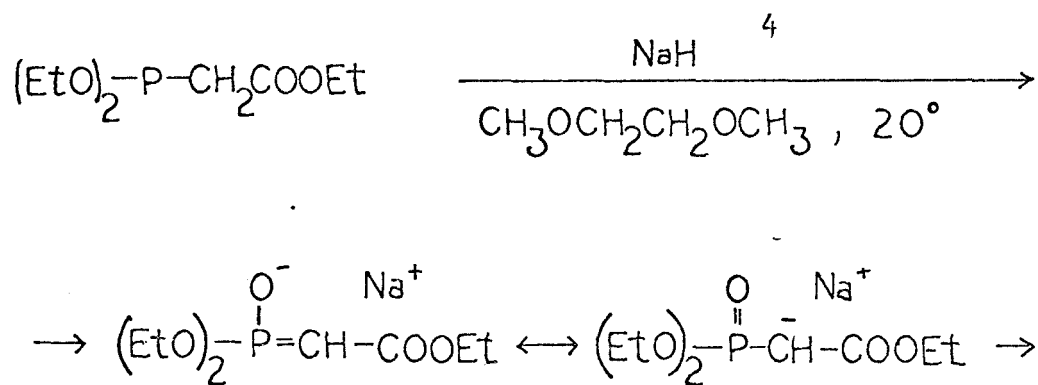
Suggested general methods for the synthesis of compounds Ia, Ib, IIa,b,c,d and e.

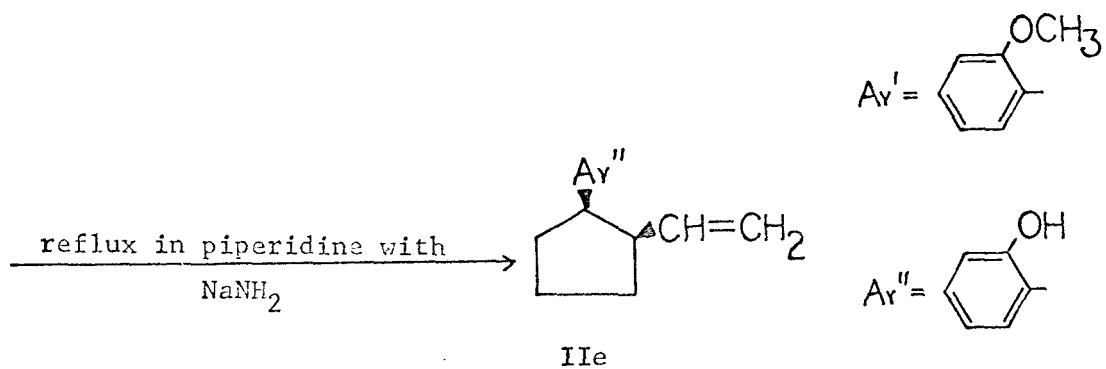
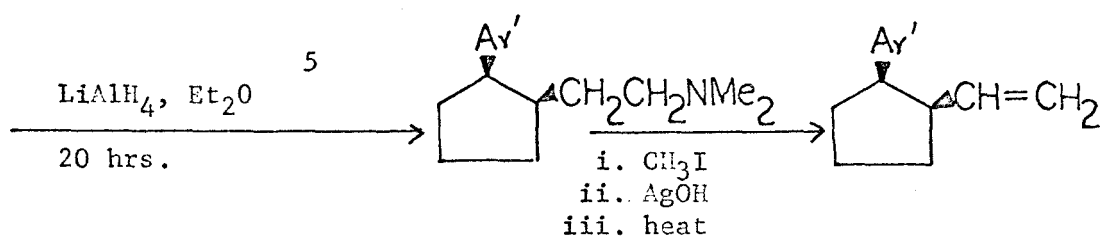
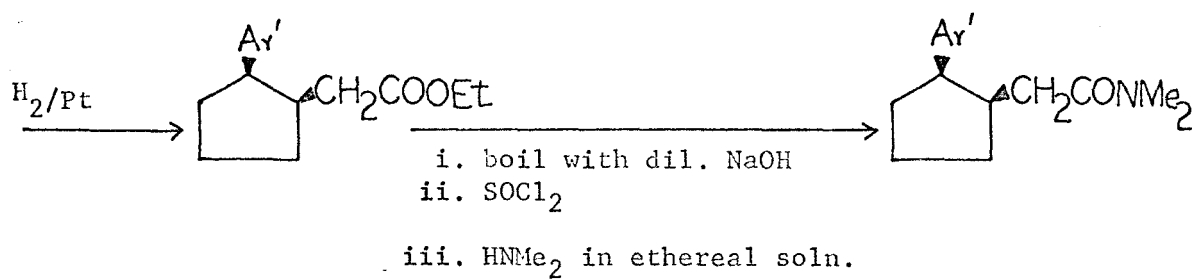
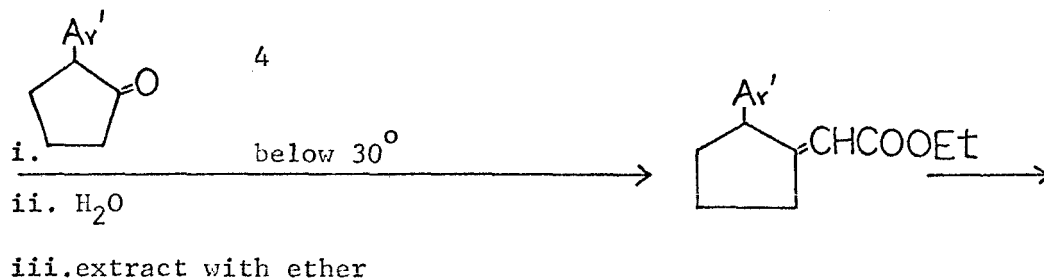
A. Synthesis of Ia, IIa,b,c, and d.

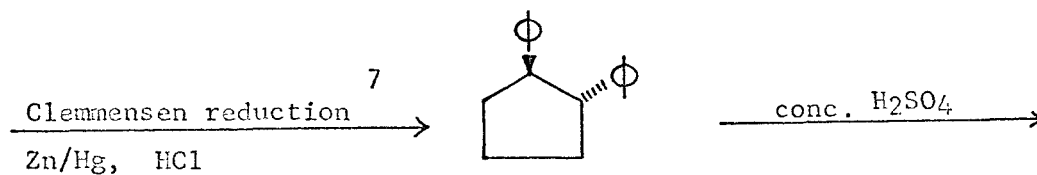
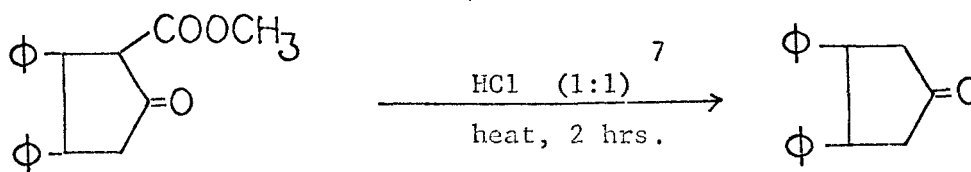
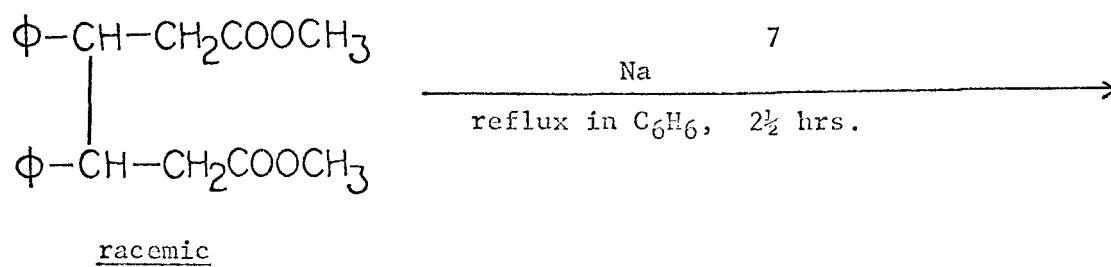
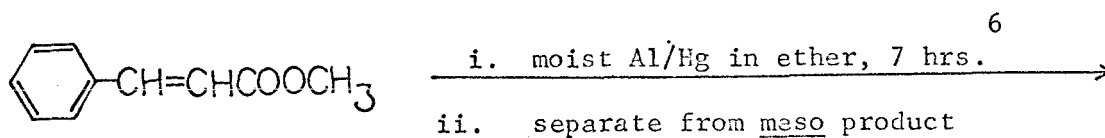


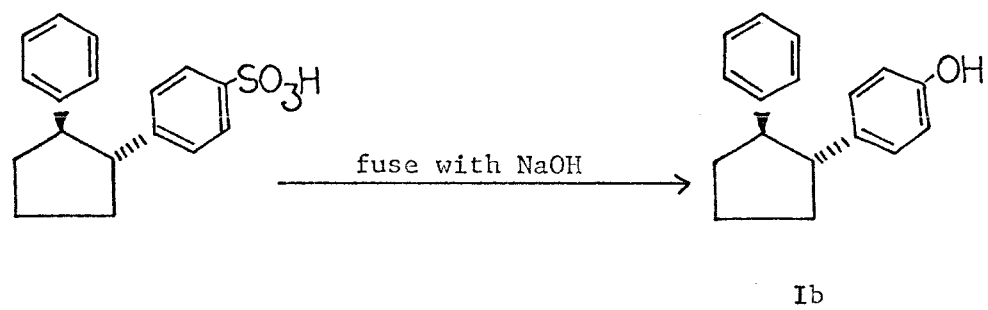


B. Synthesis of IIe.





C. Synthesis of Ib.

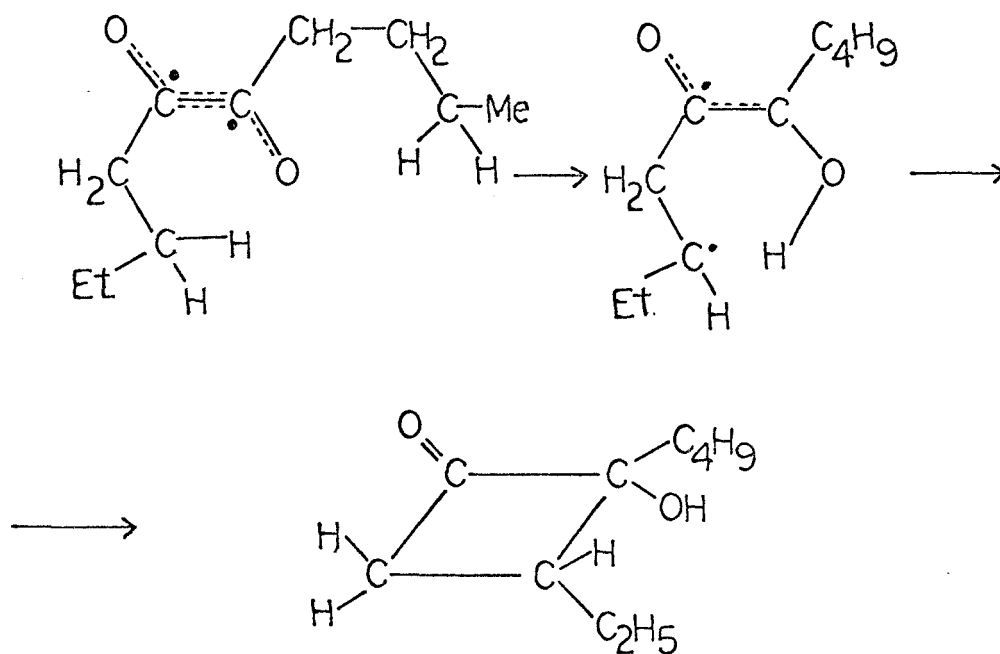


REFERENCES TO ADDENDUM

1. K. Mislow, C. L. Hamermesh, J. Amer. Chem. Soc., 77, 1590 (1955).
2. R. C. Fuson, R. L. Pedrotti, J. C. Hill, J. Org. Chem., 27, 1578 (1962).
3. T. K. Brotherton, J. F. Bunnett, Chem & Ind., 1957, 80.
4. W. S. Wadsworth, Jr., W. D. Emmons, J. Am. Chem. Soc., 83, 1733 (1961).
5. von A. Uffer, E. Schlittler, Helv. Chem. Acta, 31, 1397 (1948).
6. M.P. Oomen, A. I. Vogel, J. Chem. Soc., 1930, 2150.
7. Hans A. Weidlick, Ber., 71B, 1601 (1938).

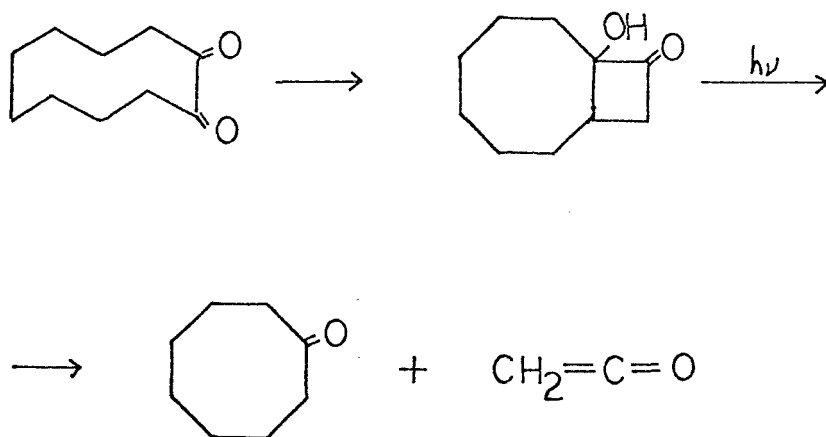
PROPOSITION IV

Urry and Trecker, in their studies on the photochemistry of α -diketones^{1,2} found that when 5,6-decanedione in cyclohexane solution was subjected to photolysis under sunlight, the reaction was strikingly selective and gave an exclusive product of 2-butyl-3-ethyl-2-hydroxycyclobutanone with a yield of 89%. The intramolecular reaction dominated even in solvents highly reactive toward radical attack. The reaction was envisaged to take place via a six-membered, cyclic transition state for the hydrogen atom transfer.



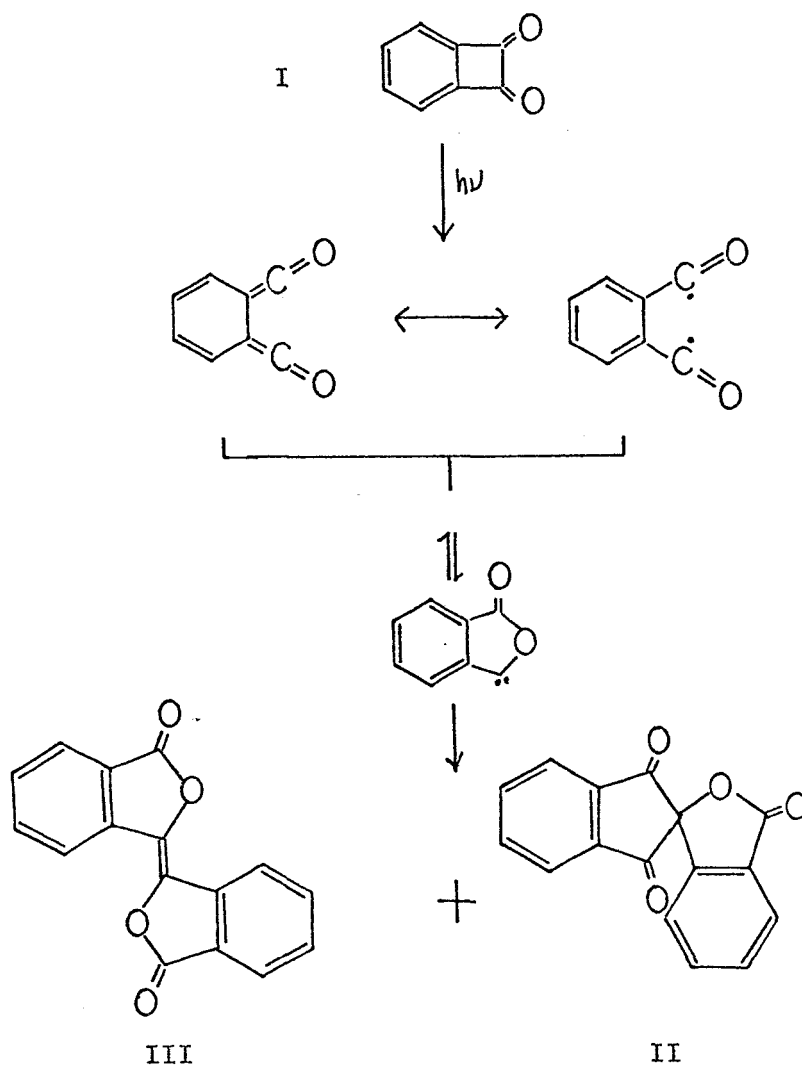
By means of triplet quenchers and benzophenone as sensitizer, the reaction was shown to proceed in the triplet state. Other experiments also indicated that abstraction of secondary hydrogen was much easier than primary hydrogen.

The same mechanism was found to apply in the case of cyclic diketones. 1,2-cyclodecanedione gave an 83% conversion into 1-hydroxybicyclo-6.2.0-decan-10-one that further underwent slow photochemical cleavage to give cyclooctanone and ketene.



The spin state of the reaction was not studied in this case.

Brown and Solly³ recently made the discovery that a dilute solution of benzocyclobutanedione I in cyclohexane irradiated under sunlight, underwent a novel reaction leading to the spiro lactone II as the major product (38%) and biphthalyl III as the minor product (5.5%). The reaction presumably involved a carbene intermediate, but this was not rigorously proved.

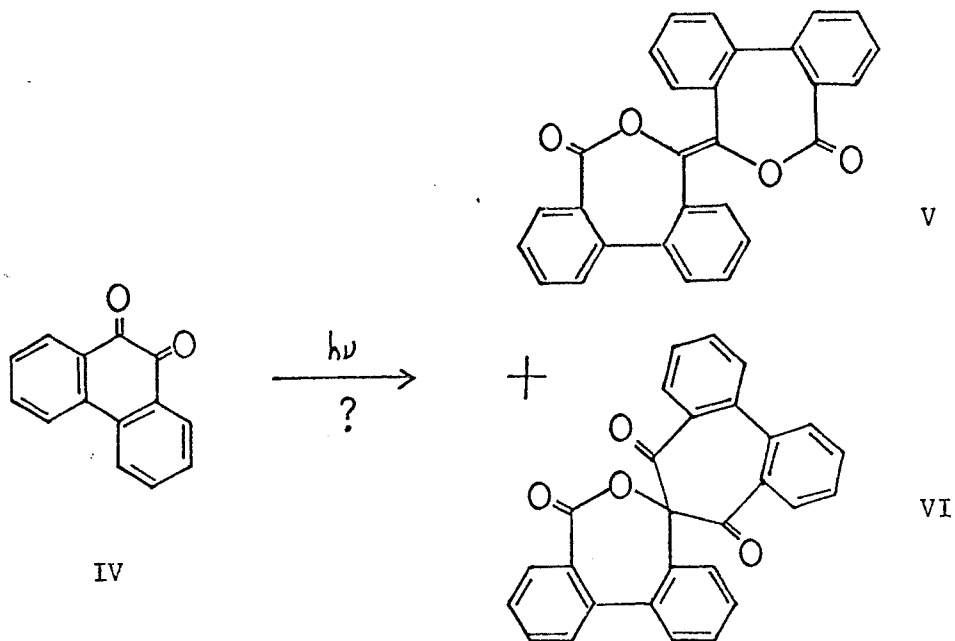


Since in this case, hydrogen abstraction was no longer possible, fission of the -CO-CO- bond became the primary process. The spin multiplicity of the reaction has not been identified.

It is proposed that the relative importance of hydrogen abstraction and CO-CO bond fission as a primary process and their relationship with the spin multiplicity of the excited state be investigated using 9,10-phenanthraquinone and its derivatives.

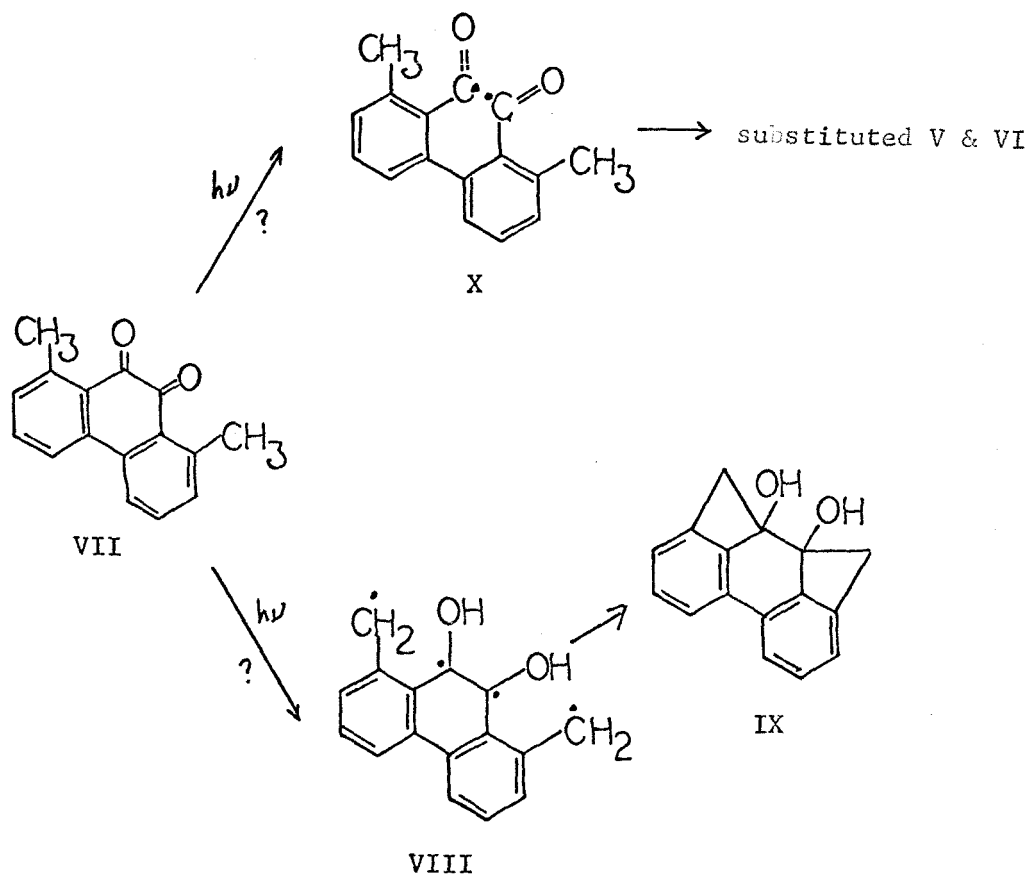
Part I

Photolysis of 9,10-phenanthraquinone will establish if the same reaction route as benzocyclobutanedione is followed.



Part II

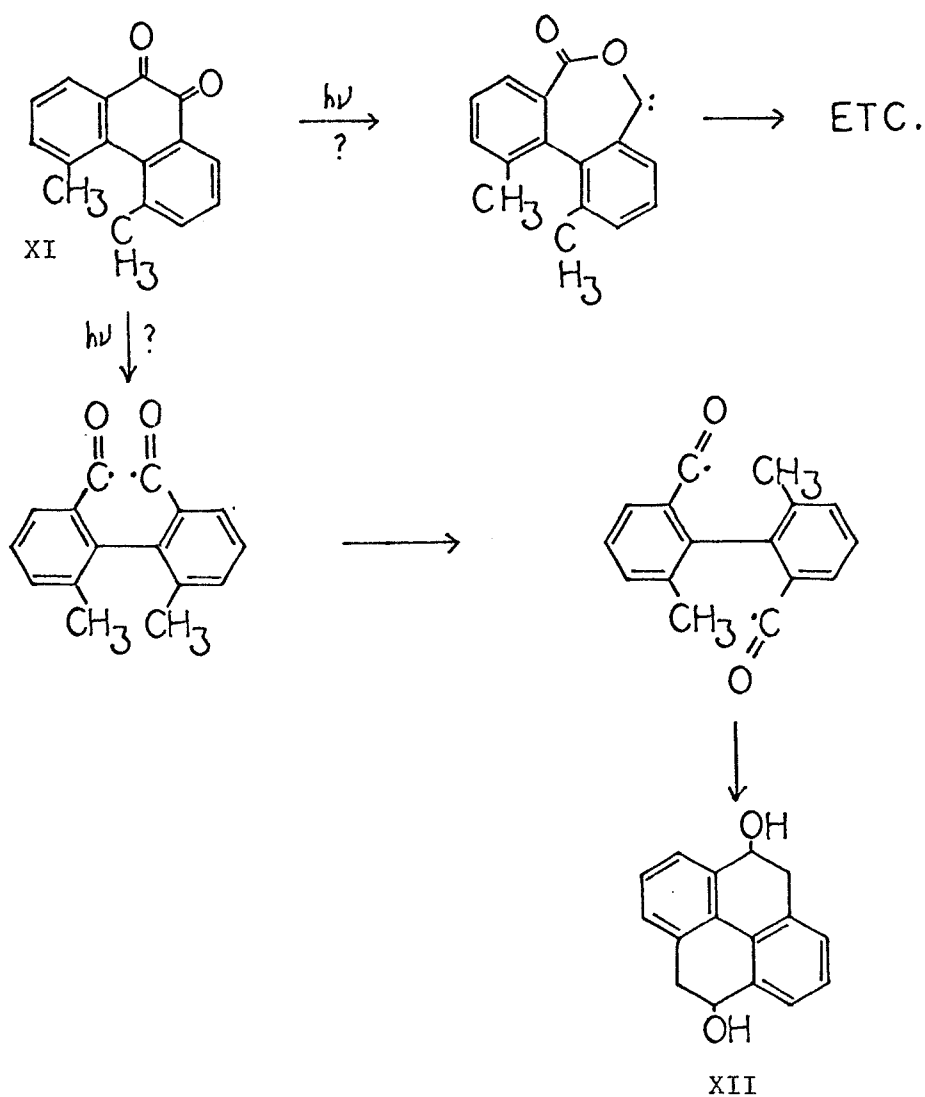
In the presence of methyl groups on the 1 and 8 positions, several possibilities may be surmised.



This experiment, however, does not settle the question whether hydrogen abstraction occurs before or after the bond fission, or whether the two processes are concerted if only substituted V and VI are obtained.

Part III

If methyl groups are placed on the 4 and 5 positions, then clearly hydrogen abstraction cannot be a primary process. The formation of product XII will however establish the fact that hydrogen abstraction is possible after bond fission.



The use of appropriate sensitizers and quenchers will answer questions such as whether multiplicity of the excited state is the controlling factor in determining the course of the reaction or whether there is a true competition between hydrogen abstraction and bond fission resulting from the same excited state.

REFERENCES

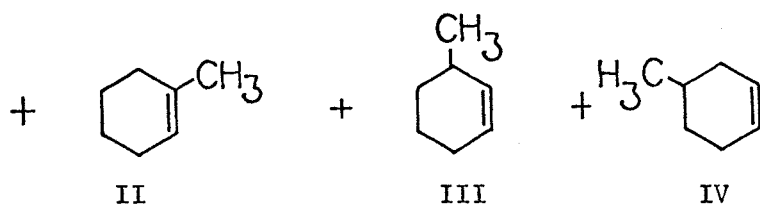
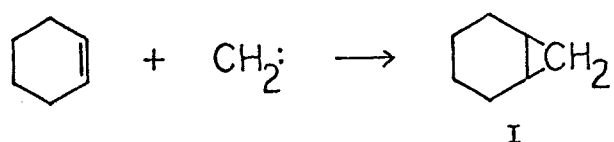
1. W. H. Urry, D. J. Trecker and D. A. Wirrey, Tetrahedron Letters, 14, 609 (1962).
2. W. H. Urry, D. J. Trecker, J. Amer. Chem. Soc., 84, 118 (1962).
3. R. F. C. Brown, R. K. Solly, Tetrahedron Letters, 2, 169-174 (1966).

PROPOSITION V

The reactions of carbenes fall into two main categories, namely, insertions and addition reactions. Insertion into a saturated C-H bond is a common phenomenon. In general, a singlet carbene has less selectivity towards the nature of the C-H bond, but for a triplet carbene, the selectivity follows the order of tert > sec > p C-H bond.¹ Addition of a carbene to an olefinic bond to form a cyclopropane derivative occurs most readily and provides the synthetic chemist with an invaluable means of synthesizing small-ring compounds.

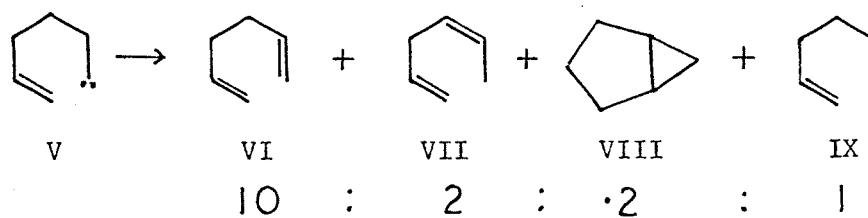
The competition between insertion reaction and addition is a rather complicated problem. It depends on the structural nature of the carbene, its spin state as well as considerations of the substrate such as its stereochemistry. In general, irrespective of spin state, the addition reaction is usually favored over insertion probably because the former is less energetic than the latter^{2,3}.

It is now quite well established that a singlet carbene adds with much higher stereospecificity than a triplet carbene⁴. The spin state of a carbene is an important factor governing the competition between insertion and addition. Normal direct photolysis of diazomethane in cyclohexene leads to C-H insertion, and C=C addition products. The carbene in this case is probably a singlet⁵. However, when Kopecky, Hammond and Leermakers⁶ photolyzed the diazomethane

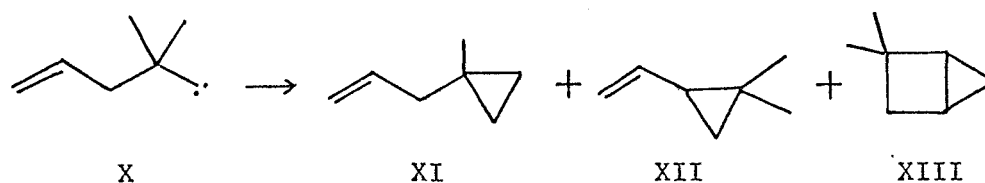


in cyclohexene using benzophenone as sensitizer, the main product was norcarane I. 3130 Å light was used to avoid direct photolysis of diazomethane. This shows that a triplet does not undergo C-H insertion readily.

A few interesting, and perhaps rather surprising, intramolecular carbene reactions have recently been reported. Kirmse and Grassmann⁷ showed that ω -alkenylcarbenes such as V yielded as main products the α,ω -dienes. Intramolecular addition to form dicycloalkanes occurred only to a very slight extent.



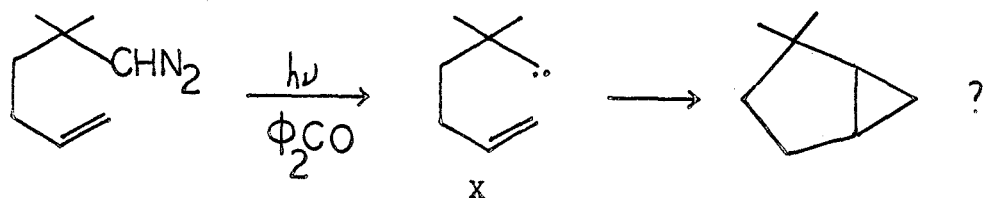
The results, though perhaps unexpected, were not too disturbing since elimination in this case is a common and efficient process when β -hydrogens are available. Kirmse and Grassmann⁷, however, also reported that the carbene X also failed to add to the ω -double bond. The reaction gave a 95% yield of XI and XII but XIII was not formed. In this case, elimination was not possible since there was no β -hydrogen.



The spin state of the carbene X was not specified. In other studies, it has been shown that when a singlet carbene is responsible in a gas phase reaction, triplet contribution will become appreciable when the reaction is carried out in the liquid phase¹. The above results of Kirmse and Grassmann can be rationalized by the hypothesis that the carbene X generated is a singlet and the reactivity of this energetic singlet is so high that it inserts efficiently to the C-H bonds in its proximity so that addition to a double bond is completely suppressed. We recall the case of methylene and cyclohexene

where insertion became important when the methylene was a singlet. In this intermolecular case, cross over of the singlet into the triplet aided by collisions with solvent molecules must be given an important consideration. Addition was therefore observed. In the intramolecular case, however, the singlet probably reacts before it has a chance to cross over to the triplet. The addition is therefore totally suppressed.

This hypothesis can be tested by using benzophenone to photosensitize the generation of the carbene X. In doing so, we can be sure that its spin state is a triplet. It is quite conceivable that such a carbene will undergo intramolecular addition to form product XIII, and provide the first example of such a triplet carbene reaction.



+ cyclopropanes XI and XII ?

REFERENCES

1. B. M. Herzog and R. W. Carr, Jr., J. Phy. Chem., 71, 2688 (1967).
2. P. S. Skell and R. C. Woodworth, J. Amer. Chem. Soc., 78, 4496 (1956).
3. W. V. E. Doering and P. La Flamme, J. Amer. Chem. Soc., 78, 5447 (1956).
4. P.P. Gaspar and G. S. Hammond, "Carbene Chemistry" by W. Kirmse, Chap. 12 Academic Press, London. (1964).
5. W. v. E. Doering, R. G. Buttery, R. G. Laughlin, and N. Chaudhuri, J. Amer. Chem. Soc., 78, 3324 (1956).
6. K. R. Kopecky, G. S. Hammond and P.A. Leermakers, J. Amer. Chem. Soc., 84, 1015 (1962), 83, 2397 (1961).
7. W. Kirmse and D. Grassmann, Chem. Ber., 99, 1746-63 (1966).