Mechanisms of Photochemical Reactions in Solution. XLIV.[1] Photodimerization of Cyclohexenone

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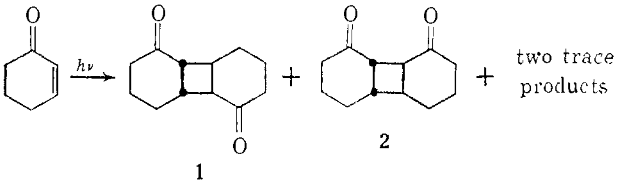
Abstract: The photodimerization of cyclohexenone has been studied in the neat liquid and in solvents. Although four products can be detected, **1** and **2** predominate under all conditions. The reaction can be sensitized by benzophenone, thioxanthone, acetophenone, and naphthalene. The enone was used 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/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.

There have been several reports of the photodimerization of cyclic, α,β-unsaturated ketones.[3–8] Work by Eaton[5,6] and Leermakers[8] with cyclopentenone has provided a fairly definitive mechanistic picture. Two isomeric products 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 product formation was rejected on the basis of sensitization and quenching experiments.[6] We have reached similar conclusions in a study of cyclohexenone.

Results and Discussion

Irradiation of cyclohexenone gives two compounds, **1** and **2**, as the principal products and two other materials of unknown structure are formed in trace amounts.[7,9] Because of their retention times in vapor chromatograms, the minor products are also believed to be dimers.



Preparative dimerization was carried out by irradiation of neat cyclohexenone using 3660-A light.[8] The mixture of dimers was analyzed by vapor chromatography with the results shown in Table I. The mixture was vacuum distilled, and the major products were separated by chromatography on alumina. Dimerization carried out under other conditions gave the same products but in different relative amounts, as is illustrated by Table I.

Table I. Products from Dimerization of Cyclohexenone

Conditions	Various products, %			
	1	**2**	**3**	**4**
Neat ketone	47	44	2	7
0.5 *M* ketone in benzene	60	25	5	10

The precision of determination of the minor products is not high, but the ratio of the yields of products **1** and **2** can be made with good accuracy. Consequently, variation in this has been chosen as 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 involvement of more than one electronically excited state of the ketone.

A first objective of our study was characterization of the triplet state of cyclohexenone. Weak phosphorescence corresponding to an excitation energy of 62.4 kcal/mole was observed from a glass containing the enone but has not been reproducible.[10] Apparently, other workers have also failed to obtain useful emission spectra.[11] Therefore, we studied the behavior of the enone as a sensitizer in standard photoisomerization reactions. The compound is effective as a sensitizer for isomerization of the stilbenes,[12] 1,2-diphenylpropenes,[12] and 2,3-diphenyl-2-butenes.[13] With each of the three pairs of olefins, stationary states untypical of high-energy sensitizers are established. If Saltiel plots[12] are used to estimate the sensitizer excitation energy, a value of 61 ± 1 kcal/mole is found with each of the pairs. The results are shown in Table II.

If the assignment is correct, the lowest triplet of the enone probably has a π–π^* configuration. The maximum in the π–π^* absorption band (337 mμ) corre-

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(1) Part XLIII: W. M. Hardham and G. S. Hammond, *J. Am. Chem. Soc.*, **89**, 3200 (1967).

(2) Lecturer on study leave from United College, Chinese University of Hong Kong.

(3) A. Butenandt, L. Karlson-Poschmann, G. Failer, U. Schiedt, and E. Biekert, *Ann. Chem.*, **575**, 123 (1951).

(4) H. P. Throndsen, G. Cainelli, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, **45**, 2342 (1962).

(5) P. E. Eaton, *J. Am. Chem. Soc.*, **84**, 2344, 2454 (1962).

(6) P. E. Eaton and W. S. Hurt, *ibid.*, **88**, 5038 (1966).

(7) D. Valentine, N. J. Turro, Jr., and G. S. Hammond, *ibid.*, **86**, 5202 (1964).

(8) J. L. Ruhlen and P. A. Leermakers, *ibid.*, **88**, 5672 (1966).

(9) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York N. Y., 1965, p 203.

(10) A. A. Lamola, unpublished results.

(11) E. J. Corey, J. D. Bass, R. Le Mahieu, and R. B. Mitra, *J. Am. Chem. Soc.*, **86**, 5570 (1964).

(12) G. S. Hammond, *et al.*, *ibid.*, **86**, 3197 (1964); W. G. Herkstroeter and G. S. Hammond, *ibid.*, **88**, 4769 (1966).

(13) L. M. Coyne, unpublished results.

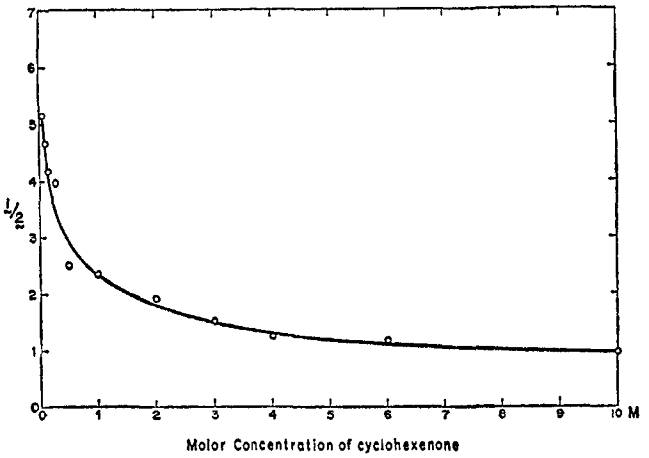

Figure 1. Yield ratio, **1**:**2**, as a function of cyclohexenone concentration in benzene.

sponds to a vertical excitation energy of 85 kcal/mole,[11] and the onset of absorption occurs at about 379 mμ, corresponding to an excitation energy of 75.5 kcal. The splitting between n–π^* singlets and triplets is usually very small so there should be an n–π^* triplet lying above the 61-kcal triplet. An attempt was made to intercept such a higher triplet by using very high concentrations of 2,3-diphenyl-2-butene 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 would expect an easily measurable change in the result if energy transfer from a high-energy triplet were to occur with any appreciable efficiency. The [*cis*]/[*trans*] ratio at the stationary state in the presence of 1.5 *M* olefin was 0.117, essentially identical with the value of 0.115 obtained in the presence of 0.1 *M* olefin. We infer that any high-energy triplet must be very short-lived and an unlikely candidate for participation in a bimolecular reaction involving making and breaking of bonds.

Table II. Use of Cyclohexenone as a Sensitizer

Cyclohexenone concn, *M*	Olefin	Total olefin concn, *M*	[*cis*]/[*trans*][a]	Estimated E_T, kcal/mole
0.025	2,3-Diphenyl-2-butene	0.1	0.115	61 ± 0.5
0.1	1,2-Diphenylpropene	0.05	1.8	61 ± 1
0.1	Stilbene	0.05	1.9	61 ± 1

[a] Ratio of isomers at the photostationary state.

Having obtained evidence against the involvement of a second triplet, we turned to the hypothesis that an excited singlet state might be involved in addition to the lowest triplet. The two approaches used were: (1) variation in the concentration of cyclohexenone, and (2) attempts to isolate a triplet mechanism using sensitizers and quenchers.

Figure 1 shows the way in which the ratio **1**:**2** varies as a function of the concentration of cyclohexenone in benzene. The ratio is observed to change from 5.15 to 0.95 with the lower value apparently being essentially a high concentration limit; over the concentration range studied (0.05–10.0 *M*) there is no indication of an approach to a low concentration limit. Although superficial consideration might lead to the conclusion that a singlet mechanism is dominant at high concentration, the results actually do not support this view. One would have to posit that dimers are formed virtually exclusively from excited singlets at higher concentrations and that the singlet mechanism is still quite important at 0.05 *M*.[14] The largest value that one can imagine for the rate constant for diffusion-controlled dimerization is about 10^{10} l. mole^{-1} sec.$^{-1}$. This would produce a dimerization rate of 5×10^8 sec^{-1} when the diene concentration is 0.05 *M*. It is almost inconceivable that such a rate could be competitive with intersystem crossing; and, if it were, fluorescence from the ketone should be observed.

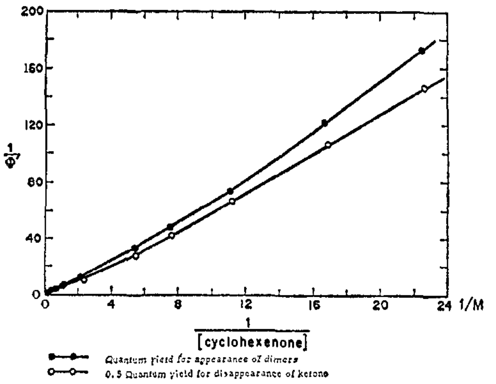

Figure 2. Quantum yield for photoreaction of cyclohexenone.

The total quantum yield for formation of dimers was also measured and the results are presented as a reciprocal plot in Figure 2. The figure also shows the data for quantum yields for enone disappearance. The latter should be twice the quantum yields for appearance of dimers if dimerization is the only reaction of the ketone. The rate of disappearance of the ketone is actually about 10% greater than would be indicated by the rate of dimer formation. There can be little doubt that the data deviate significantly from the commonly observed linear relationship. The Stern–Volmer plot would be nonlinear if two excited states were involved in the reaction. However, the direction of the deviation should be opposite to that observed. If the reaction were dominated by a singlet mechanism at high concentration, the phasing-in of a triplet mechanism at lower concentrations should make quantum yields at low concentration *higher* than would be expected by extrapolation from concentrated solutions; in actual fact, the quantum yields in dilute solutions are *lower* than would be expected.

As would be expected of a triplet mechanism, the reaction can be sensitized by acetophenone (E_T = 73 kcal/mole), benzophenone (E_T = 69 kcal/mole), thioxanthone (E_T = 65.5 kcal/mole), and naphthalene (E_T = 61 kcal/mole). If the decrease in the **1**:**2** ratio at high concentration of the enone were due to incursion of a singlet mechanism, the sensitized reaction should not show a similar trend. The data in Table III show that the same variations in the product ratio are observed in both the sensitized and unsensitized reactions. The results show clearly that the course of the triplet

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(14) Because of the absence of a low concentration limiting ratio.

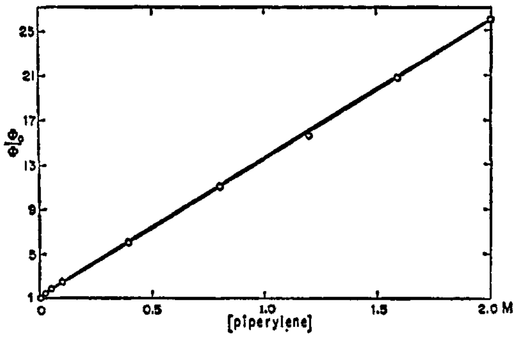

Figure 3. Quenching of dimerization by piperylene; [cyclohexenone]$_0$ = 1.02 *M*; $\Phi_0 = 0.28$.

reaction can be strongly influenced by variation in the reaction medium.

Quenching experiments lead to the same conclusion. Addition of piperylene in direct excitation experiments leads to strong quenching of dimerization and to the formation of crossed products of as yet unknown structure. However, experiments 2–6 in Table III show that quenching is not accompanied by any change in the **1**:**2** ratio. Figure 3 shows a plot of the reciprocal of the relative quantum yield for dimerization against piperylene concentration. The linearity of this plot confirms our view that the nonlinearity of Figure 2 cannot be attributed to a mixture of singlet and triplet mechanisms. Eaton and Hurt[6] observed the same behavior when piperylene was used as a quencher with cyclopentenone and gave the same interpretation.

Table III. 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 *M* piperylene in benzene	2.35
4	1 *M* cyclohexenone + 0.50 *M* 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 *M* 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

[a] Reaction mixture became heterogeneous during irradiation, and the two liquid layers were sampled separately. Most of the dimers were in the organic layer. [b] Error is ±0.05.

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

$$\mathrm{K} \xrightarrow{h\nu} {}^1\mathrm{K}^* \tag{1}$$

$${}^1\mathrm{K}^* \xrightarrow{k_1} {}^3\mathrm{K}^* \tag{2}$$

$${}^3\mathrm{K}^* \xrightarrow{k_2} \mathrm{K} \tag{3}$$

$${}^1\mathrm{K}^* \xrightarrow{k_3} \mathrm{K} \tag{4}$$

$${}^3\mathrm{K}^* + \mathrm{K} \xrightarrow{k_4} \mathrm{KK}\,(\text{dimers}) \tag{5}$$

$${}^3\mathrm{K}^* + \mathrm{Q} \xrightarrow{k_5} \mathrm{K} + {}^3\mathrm{Q}^* \tag{6}$$

$$\mathrm{K} + {}^3\mathrm{S}^* \xrightarrow{k_6} {}^3\mathrm{K}^* + \mathrm{S} \tag{7}$$

K = cyclohexenone, Q = quencher, S = sensitizer

The quantum yield for the unsensitized reaction is given by

$$\frac{2}{\phi} = \frac{1}{\phi'} = \frac{1}{\phi_{\mathrm{ic}}}\left\{1 + \frac{k_2}{k_4[\mathrm{K}]} + \frac{k_5[\mathrm{Q}]}{k_4[\mathrm{K}]}\right\} \tag{8}$$

where ϕ = quantum yield for disappearance of enone, ϕ' = quantum yield for appearance of dimers, and $\phi_{\mathrm{ic}} = k_1/(k_1 + k_3)$ = quantum yield for intersystem crossing.

As is shown by comparison of Figures 2 and 3, the quantum yields for disappearance of monomeric ketone are about 10% greater than twice the quantum yields for formation of dimers. The discrepancy is probably significant although accurate measurement of the rate of disappearance of starting material is inherently more difficult than monitoring formation of a product. The former determination *must* involve substantial conversion, and measured results require correction to take account of the change in the concentration of the reactant during a run. The small difference, if real, must be attributed to the occurrence of some minor side reaction of the ketone in addition to dimerization. Deviation of the results from the prediction of eq 8 is shown by both sets of measurements. If we adopt the view that the mechanism is probably fundamentally correct, the failure of eq 8 indicates that either ϕ_{ic} or k_2/k_4 or both must be variable. The study involved changing the medium from neat cyclohexenone to essentially pure benzene so there is ample opportunity to see medium-dependent variations in the specific rate constants for reactions of excited states.

We were interested in trying to allocate the variables somewhat more precisely and returned to the use of cyclohexenone as a sensitizer in order to obtain a separate measurement of ϕ_{ic}. Table IV shows initial quantum yields for sensitized isomerization of the 1,2-diphenylpropenes and the values of ϕ_{ic} calculated using the known decay ratio. Details of the triplet counting method have been discussed earlier.[15] In order to avoid competitive absorption by the isomerizable substrate we used a 3660-A filter system. In the solutions containing the lowest concentrations of cyclohexenone not all of the incident light was absorbed. Correction for incomplete absorption was made, but correction is not very accurate because of the optics of the system. Consequently, the indication that ϕ_{ic} increases in dilute solutions may well be an illusion. Even if the result is accurate, it does not account for the

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(15) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

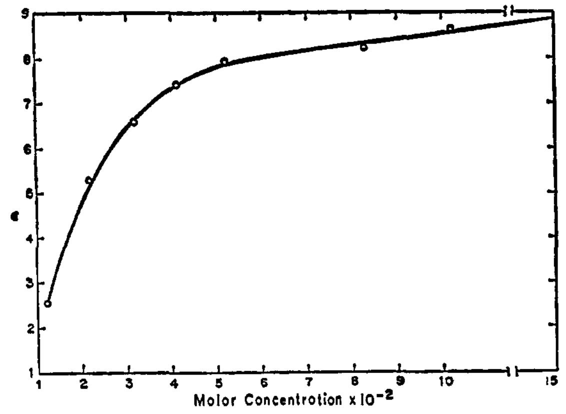

Figure 4. Molar extinction coefficient for concentrated solutions of cyclohexenone at 3660 A.

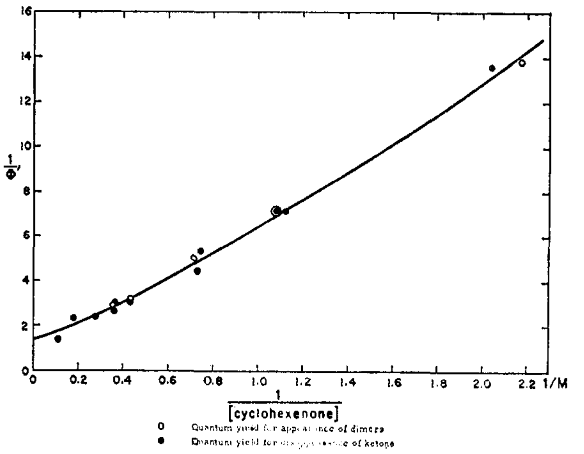

Figure 5. Quantum yields for dimerization and disappearance of monomer in concentrated solutions of cyclohexenone.

curvature of the plots in Figures 2 and 3. The latter would have suggested that the ϕ_{ic} decreases at low concentrations of the enone.

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

Cyclohexenone concn, *M*	Initial diphenylpropene isomer and concn, *M*	Conversion, %	ϕ^c	ϕ_{ic}	$\phi_{t\to c}/\phi_{c\to t}$
0.052[a]	*cis* 0.0526	2.70	0.17	0.43	1.5
0.053[a]	*trans* 0.0528	4.09	0.26		
0.102[b]	*cis* 0.0526	3.00	0.13	0.37	1.9
0.104[b]	*trans* 0.0528	5.37	0.24		
0.202	*cis* 0.0526	2.91	0.11	0.33	2.1
0.205	*trans* 0.0528	5.62	0.22		
0.409	*cis* 0.0526	2.90	0.11	0.32	2.0
0.406	*trans* 0.0528	5.60	0.21		
0.513	*cis* 0.0542	2.91	0.11	0.31	2.0
0.515	*trans* 0.0539	5.37	0.21		

[a] The ketone absorbs about 62% of the incident light. [b] The ketone absorbs about 87% of the incident light. [c] Corrected for back reaction.

Measurement of the absorbancies of concentrated solutions of cyclohexenone at 3660 A reveals a startling fact. The apparent molar extinction coefficients are plotted as a function of concentration in Figure 4. Obviously, Beer's law does not hold at all on the tail of the absorption band. Probably all of the absorption at 3660 A is due to aggregates of two or more molecules. The first species produced is an excimer so one might expect that this would produce a major perturbation in the chemical quantum yields. However, direct comparison shows that quantum yields for dimerization are the same with 3130- and 3660-A excitation. Since the relative amounts of excimer and excited monomer formed by absorption at the two wavelengths must be different, the common result shows that monomeric and aggregated excited species must become equilibrated at a rate that is rapid in comparison with the rate of dimerization. The result is not unexpected. The slope of the plot in Figure 4 indicates that k_5/k_4 is about 90. The rate constant for quenching is unlikely to be greater than the diffusion-controlled limit so the dimerization reaction occurs at a maximum of only about one out of ninety encounters. 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-A light is absorbed by aggregates only tells us once again that no significant amount of reaction occurs by way of excited singlets.

According to the basic mechanism the quantum yield for dimer formation at infinitely high enone concentration should be equal to ϕ_{ic}. Figure 5 shows an expanded plot of the data of Figure 2 for the more concentrated solutions. The curvature noted before is continued up to the highest concentrations studied. However, there is enough scatter in the data to render extrapolation to $1/[\text{enone}] = 0$ rather uncertain. The extrapolated value would certainly be finite and probably lies between 0.5 and 0.8. A single measurement of 0.72 was made in neat cyclohexenone. This is higher than the values of ϕ_{ic} measured with the highest concentrations of enone. The latter may be slightly low because of competition of the dimerization reaction with energy transfer. The rate constant for transfer to the diphenylpropenes is probably about the same as for transfer to piperylene[10] so the rate of dimer formation may be more than 10% of the rate of energy transfer in solutions in which the [enone]/[olefin] ratio is 10.[16] Literal interpretation of discrepancy would lead to the conclusion that some dimer must arise from an intermediate that is incapable of transferring energy to the diphenylpropenes. This is contradictory to other indications, such as the quenching and sensitization experiments; consequently we point out the problem but will temporarily ignore it in discussion.

Once there has been tentative acceptance of the conclusion that only the lowest triplet state is involved in dimerization, there are two highly informative features of the data. The composition of the dimeric mixture and the ratio k_2/k_4 both change as the concentration of enone is changed. The two observations are not independent. The rate constant for dimeriza-

(16) Note that even if the transfer rates are identical, the value of k_5/k_4 measured with 1 *M* enone cannot be used as an exact value at other concentrations since we are maintaining that k_5 is concentration dependent.

tion, k_4, is in reality the sum of the rate constants for reactions leading to the different products.[17]

$$^3\mathrm{K}^* + \mathrm{K} \xrightarrow{k_4'} \mathbf{1}$$

$$^3\mathrm{K}^* + \mathrm{K} \xrightarrow{k_4''} \mathbf{2}$$

$$^3\mathrm{K}^* + \mathrm{K} \xrightarrow{k_4'''} \text{other products}$$

$$k_4 = k_4' + k_4'' + k_4'''$$

We know that the ratio, k_2/k_4, varies with enone concentration. This is consistent with the view that k_4 is a variable, as would be normally expected since it is the sum of constants (k_4' and k_4'') which vary relative to each other. The rate constant for nonradiative decay of the triplet, k_2, may also vary but we have no information to bear on the question.

Eaton and Hurt[6] have attributed variation in the products of dimerization of cyclopentenone to the influence of solvent polarity on the relative values of rate constants analogous to k_4' and k_4''. We agree and find that the ratio **1**:**2** can be changed by varying the polarity of the solvent at constant concentration of the enone (see Table III). In both studies the product having a large permanent dipole is favored in polar solvents, indicating that dipole–dipole interactions between the reactants are of some significance in determining the rates of the dimerization reactions.

Conclusions

We have reached the following, tentative conclusions. (1) Dimerization of cyclohexenone proceeds exclusively by a triplet mechanism. (2) The rate constants for the reactions of ketone triplets with ground-state molecules are subject to polar solvent effects.

Acceptance of the above conclusions must be subject to reservation because of the puzzling discrepancy between the quantum yields of dimerization and those in reactions in which the enone serves as a sensitizer.

Experimental Section

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. α-Naphthyl isocyanate (1 ml) was added to 20 g of 2-cyclohexen-1-one (Aldrich), and the mixture was heated on a steam bath for 30–45 min 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% Ucon Polar on Chromosorb G. The column temperatures were in the vicinity of 140°. The purified ketone was distilled under reduced pressure. A vpc analysis on the fluorosilicone column showed that it contained less than 1.5% 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 mμ 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. Cyclohexadiene, 25 g (Aldrich), was washed three times with 10-ml portions of 5% 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 (bp 79.5°) 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°. The manifold was designed in such a way that bulb-to-bulb distillation could be done from a main bulb to small ampoules. These ampoules could be sealed and detached from the manifold. The diene was used immediately when the ampoule was opened. Hexadecane (30 ml) 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% sodium bicarbonate and several times with distilled water. It was then dried over anhydrous magnesium sulfate. After filtration, it was distilled under reduced pressure [bp 85–91° (1 mm)]. The product was shown to be pure by vpc. Carefully purified thioxanthone stored under nitrogen was obtained from Dr. H. Furrer and used without further purification. Acetophenone purified by Mr. 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 Mr. L. M. Stephenson and were used without further purification.

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

$$1/\phi = 1 + 0.028/[\mathrm{D}]_{\mathrm{av}}$$

where ϕ is the quantum yield for the sensitized formation of the diene dimers and $[\mathrm{D}]_{\mathrm{av}}$ is the mean concentration of the diene. A reaction mixture containing benzophenone (0.06 M), cyclohexadiene (1.05 M), and hexadecane (0.3 M) 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 × 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-w Hanovia medium-pressure mercury arc. The filter systems described by Hammond, *et al.*,[15,18] were used to allow transmission of light of wavelength centered at 3650 A and at 3130 A. The dimerization of cyclohexadiene has the same quantum yield with light of these two wavelengths. The actinometers were run to 5% conversion of the diene and vpc analysis was used to follow the appearance of the diene dimers using the 12-ft fluorosilicone column (*vide supra*). Following the enone dimerization by vpc, 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-w Hanovia medium-pressure mercury arc through a uranium glass filter that is opaque to light of wavelengths shorter than 3340 A. Virtually all the absorbed light was in the 3660-A group of lines. Isomerization was followed by vpc until the same *cis*/*trans* ratio was reached from both starting states. A 9-ft column of 10% 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

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[17] If the reaction proceeds 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 mechanisms leading to **1** and **2**.

[18] R. S. H. Liu, N. J. Turro, Jr., and G. S. Hammond, *J. Am. Chem. Soc.*, **87**, 3406 (1965).

using three freeze–thaw cycles and sealed under a pressure of about 3×10^{-4} torr in 13 × 100 mm Pyrex culture tubes. Irradiation was done in a "quantum yield merry-go-round" using light of 3130 A. Vapor chromatographic analysis on a 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 concentrations where under 99% 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% 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 (1.024 *M*) 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-A filter system until a conversion of 15% was obtained in the sample containing no piperylene. The tubes were opened and analyzed for the appearance of dimers by vapor chromatography using the fluorosilicone column.

Intersystem Crossing Efficiencies. One set of solutions containing 0.05, 0.10, 0.2, and 0.4 *M* cyclohexenone and 0.0526 *M* *cis*-1,2-diphenylpropene and another set containing the same concentrations of cyclohexenone along with 0.0525 *M* *trans*-1,2-diphenylpropene were prepared as usual and irradiated using the 3660-A 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% 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% of the *trans* isomer.

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The Photochemistry of Thiophenes. IV. Observations on the Scope of Arylthiophene Rearrangements

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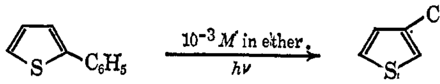
Abstract: Upon irradiation with ultraviolet light in benzene or ether solution 2-phenylthiophene rearranges smoothly and irreversibly to 3-phenylthiophene. The phenyl group remains attached to the same carbon atom during rearrangement as shown by a ^{14}C labeling experiment. A series of previously unreported arylthiophenes have been synthesized to help establish the scope and mechanism of the reaction. Experiments with 2-*p*-tolyl- and mesitylthiophenes show that rearrangement is confined to the thiophene ring and does not occur in the phenyl ring. Photolysis of 2-(α-naphthyl)thiophene leads to 3-(α-naphthyl)thiophene and similarly 2-(β-naphthyl)-thiophene affords 3-(β-naphthyl)thiophene upon photolysis. 2,3-Diphenylthiophene undergoes a cyclohexatriene-type ring closure to form the previously unreported phenanthro[9,10-*b*]thiophene. 3,4-Diphenylthiophene rearranges to 2,3-diphenylthiophene (isolated as phenanthro[9,10-*b*]thiophene) plus a small amount of 2,4-diphenylthiophene. Photolysis of 2,4-diphenylthiophene gives 3,4-diphenylthiophene as the primary photolysis product. 2,5-Diphenylthiophene is virtually unreactive even upon extended photolysis.

The photoinduced rearrangement of 2-phenyl- to 3-phenylthiophene (eq 1) and variations of this reaction have been briefly described by us.[2-5] Attempts have been made to investigate both the scope and mechanism of this rearrangement and to correlate some of our findings with new results in the rapidly growing field of photolysis of aromatic systems. The possible connection between this photorearrangement and those reported in some benzenoid systems was pointed out earlier,[2,3] and investigations on this reaction have been designed to shed some light on this hypothesis. This paper reports studies of the reaction scope from which certain mechanistic conclusions can be drawn. Following papers[6,7] report labeling experiments carried out to elucidate the mechanism in more detail and conclusions are contained in the last paper of this series.[8]



1 2 (1)

Results

Irradiation of 2-phenylthiophene in dilute ether solution leads to 3-phenylthiophene as the exclusive rearrangement product (eq 1). No rearrangement occurs in the absence of ultraviolet irradiation. Careful gas chromatographic analysis of reaction mixtures failed to give any evidence of the presence of other products even in trace amounts. Solutions became light yellow on extended irradiation and a solid, intractable precipitate formed on the lamp. The progress of the reaction with time is shown in Figure 1. The

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(1) Royal Dutch Shell Fellow, 1963–1966.

(2) H. Wynberg and H. van Driel, *J. Am. Chem. Soc.*, **87**, 3998 (1965).

(3) H. Wynberg and H. van Driel, *Chem. Commun.*, **204** (1966).

(4) H. Wynberg and R. M. Kellogg, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

(5) H. Wynberg, R. M. Kellogg, H. van Driel, and G. E. Beekhuis, *J. Am. Chem. Soc.*, **88**, 5047 (1966).

(6) R. M. Kellogg and H. Wynberg, *ibid.*, **89**, 3495 (1967).

(7) H. Wynberg, G. E. Beekhuis, H. van Driel, and R. M. Kellogg, *ibid.*, **89**, 3498 (1967).

(8) H. Wynberg, R. M. Kellogg, H. van Driel, and G. E. Beekhuis, *ibid.*, **89**, 3501 (1967).