evaporation with nitrogen (isobutylene) or with an aspirator (2-methyl-2-butene), leaving white solid products whose spectra (Tables II and III) indicate they are oxetanes **27** and **28**. The solids are stable at low temperatures, but undergo decomposition at room temperature to give triene **29**.

4-Isopropylidene-1-methyl-1-trichloromethyl-2,5-cyclohexadiene (29). The best method for effecting the decomposition of oxetanes **27** and **28** to triene **29** was as follows. The oxetane was put onto a neutral alumina column of large diameter which was eluted as rapidly as possible with hexane. The first fractions were concentrated at aspirator pressure, and a solid precipitated on cooling. Residual liquid was removed with a pipet, and the solid was dissolved in hexane and allowed to crystallize slowly on cooling in a freezer. Repetition of this process gave pure triene, mp 73–75°, some of whose spectral data are given in the text. The complete mass spectrum showed peaks at *m*/*e* 250, 223, 215, 187, 153, 133, 128, 115, 105, 93, and 91. The ir spectrum had prominent bands at 3015, 1675, 1620, 920, 720, and 700 cm^{-1}.

Irradiation of triene 29 in ethyl ether (1.5 g in 640 ml) resulted in disappearance of the triene (uv spectroscopy). The crude photolysate was analyzed by glpc and spectroscopy and chromatographed on neutral alumina. No *p*-cymene could be found in the product by any of these methods.

Rearrangement of 29 to 2-*p*-Tolyl-2-trichloromethylpropane (30). This rearrangement was detected in a carbon tetrachloride solution of triene **29** kept for an extended time in an nmr tube, and was much slower than the formation of **29** from the oxetanes. The rearrangement could be carried out more efficiently by reflux in toluene at 100°. The product **30** could be isolated by rapid chromatography, as in isolation of **29**, followed by recrystallization at freezer temperatures from hexane. The nmr and ir spectra are given in the text. The uv spectrum in cyclohexane showed maxima at 256, 262, and 268 mμ typical of a benzenoid aromatic compound.

Photolysis in Aqueous Dioxane.[31,32] This irradiation was carried out in 1:1 water–dioxane through Pyrex by a procedure modeled on that of King and Leaver.[31] The solid product was recrystallized from chloroform–hexane, mp 91.8–92.3°. The spectra of the compound are given in Tables II and III. *Anal.* Calcd for $C_8H_8Cl_2O_2$: C, 46.39; H, 3.89; Cl, 34.24. Found: C, 46.34; H, 4.24; Cl, 34.44.

The product **22**, R = H, gave a positive periodate test. An inconclusive result was obtained on attempts to characterize the hydroxyl group as primary, secondary, or tertiary using the nmr method of Chapman and King.[42] Hydrogenation of the photoproduct over 5% Pd–C resulted in rapid uptake of 1 equiv of hydrogen, while exhaustive hydrogenation over 10% Pd–C in ethanol containing potassium hydroxide (in an attempt to hydrogenolyze the chlorine atoms) resulted in uptake of 4 equiv of hydrogen. Analysis of the crude reaction product in both instances by glpc and by nmr spectroscopy showed that complex product mixtures were formed. Attempts to isolate pure compounds by column chromatography were unsccessful.

Acknowledgment. We are indebted to the U. S. Army Research Office for generous grants in support of this research under Project 4019-C.

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[42] O. L. Chapman and R. W. King, *J. Amer. Chem. Soc.*, **86**, 1256 (1964).

The Photochemistry of 4-Methyl-4-trichloromethyl-2,5-cyclohexadienone. II. Mechanistic Studies and Characterization of the Excited State[1,2]

David I. Schuster[3] and Dinshaw J. Patel

Contribution from the Department of Chemistry, New York University, New York, New York 10453. *Received February 21, 1968*

Abstract: Sensitization, quenching, and emission data are presented which require that the excited state responsible for the various photochemical transformations of 4-methyl-4-trichloromethyl-2,5-cyclohexadienone is the n,π^* triplet state. The various primary processes open to this triplet are hydrogen abstraction, rearrangement to lumiketone, and oxetane formation. Rate constants of 3.9×10^8 l. mol^{-1} sec^{-1} and 6.9×10^8 sec^{-1} are obtained for the first two reactions, respectively, from Stern–Volmer quenching data. Mechanisms are proposed for all of the observed reactions. The possible role of zwitterions in the lumiketone rearrangement is specifically defined, as is the sequence of appearance of the various reaction intermediates.

The previous paper[2] described the products of photolysis of 4-methyl-4-trichloromethyl-2,5-cyclohexadienone (**1**) in a variety of solvents. A radical abstraction–fragmentation reaction ensued in hydrogen donor solvents to give *p*-cresol (**2**), and this reaction was in competition with the rearrangement to give (stereospecifically) lumiketone (**3**). In a number of solvents, both of these reactions take place simultaneously. While photolysis in 2-propanol gives high yields of *p*-cresol and no lumiketone, neither of these products is formed in methanol or aqueous dioxane. Instead, an ionic fragmentation reaction takes place in neutral or basic solution to give the cyclopentenone derivative **4**, with loss of HCl and addition of ROH. In methanol acidified with gaseous HCl, the fragmentation reaction is quenched and a new product is formed, tentatively assigned structure **5**.[4] Finally, irradiation in isobutylene or 2-methyl-2-butene gives very high yields of oxetanes **6**. All of these reactions could be carried out using a high-pressure mercury lamp and Pyrex filters. Photolysis of lumiketone **3** in all solvents gives an isomeric ketone **7a**, accompanied by a trace of a stereoisomer **7b**, and polymer. The data which follow allow postulation of a complete mechanistic scheme for these reactions.

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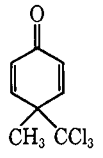
(1) Part XVII of a series on the photochemistry of unsaturated ketones in solution. Portions of this work were published in preliminary form: (a) D. I. Schuster and D. J. Patel, *J. Amer. Chem. Soc.*, **87**, 2515 (1965); (b) *ibid.*, **88**, 1825 (1966); (c) D. J. Patel and D. I. Schuster, *ibid.*, **89**, 184 (1967).

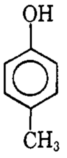
(2) Previous paper, part XVI: D. J. Patel and D. I. Schuster, *ibid.*, **90**, 5137 (1968).

(3) Fellow of the Alfred P. Sloan Foundation, 1967–1969.

(4) As described in ref 2, this product could not be isolated in a pure state and the structure is assigned solely on the basis of nmr and ir spectra of solutions rich in this product.



1



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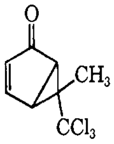

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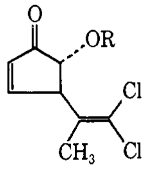
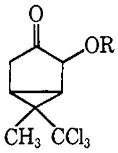
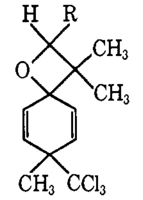


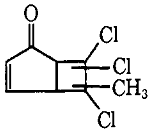
4, R = H, CH$_3$



5, R = CH$_3$



6, R = H, CH$_3$



7

Results

Sensitization and Quenching. The data, a portion of which is given in Table I, show that the photorearrangement of dienone **1** to lumiketone **2** is sensitized by benzophenone (E_{T} = 69 kcal/mol)[5] and benzene (E_{T} = 85 kcal/mol),[6b] and quenched by piperylene (E_{T} = 57–60 kcal/mol)[7] and 1,3-cyclohexadiene (E_{T} = 54 kcal/mol).[6a,7b] Dimers of 1,3-cyclohexadiene, known to be produced only on triplet sensitization,[8] were isolated by column chromatography and compared with authentic materials. Using *trans*-piperylene as quencher, *cis*-piperylene was detected among the products by glpc analysis. The *trans–cis* isomerization of the piperylenes is known to occur only on triplet sensitization.[7a,9]

Table I. Irradiation of Dienone **1**. Sensitization and Quenching Studies

Solvent	Procedure[a]	Sensitizer or quencher	Glpc analysis[b]	Irradiation time, min	Yield, %				
					1	**2**	**3**	**4**	**7a**
Benzene	A	None	A	5	77	. .	11	. .	7
Benzene	A	None	A	20	23	. .	4	. .	34
Benzene	A	Benzophenone[c]	B	5	65	. .	20	. .	6
Benzene	A	Benzophenone[c]	B	20	5	. .	6	. .	32
Benzene	A	Piperylene[d]	A	5	96	. .	<1	. .	Trace
Benzene	A	Piperylene[d]	A	20	79	. .	<1	. .	5
Benzene	B	None[e]	A	40	51	. .	27	. .	4
Benzene	B	Benzophenone[f]	B	40	47	. .	26	. .	15
Benzene	C	None	A	20	30	. .	8	. .	29
Benzene	C	1,3-Cyclohexadiene	A	20	70	. .	2	. .	2
Benzene	C	*cis*-Piperylene	A	20	81	. .	1	. .	3
Ethyl ether	A	None	B	20	11	65	. . .	. .	. . .
Ethyl ether	A	Benzophenone[c]	B	20	2	68	. . .	. .	. . .
Ethyl ether	A	Piperylene[d]	B	20	72	15	. . .	. .	. . .
Isooctane	A	None	B	20	26	13	. . .	. .	15
Isooctane	A	Piperylene[d]	B	45	86	1	. . .	. .	. . .
Benzene–ether (5.4:1)	A	None	B	20	26	24	. . .	. .	12
Benzene–ether (5.4:1)	A	Piperylene[d]	B	20	74	3	. . .	. .	3
Methanol (CaCO$_3$)[g]	A	None	A	20	11	. .	. . .	81	. . .
Methanol (CaCO$_3$)[g]	A	Benzophenone[c]	A	20	5	. .	. . .	35	. . .
Methanol (CaCO$_3$)[g]	A	Piperylene[d]	A	20	41	. .	. . .	31	. . .

[a] Irradiation conditions: A, solvent (640 ml) containing 0.01 mol of dienone **1**, 450-W high-pressure Hanovia lamp, quartz immersion well, Pyrex filter sleeve, λ >3000 Å; B, same solution as in A, Srinivasan-Griffin reactor with battery of 2537-Å lamps; C, light source as in A, merry-go-round apparatus, solution total vol 40 ml containing 8.87×10^{-4} mol of **1** and 8 ml of quencher. [b] A, $^1/_8$ in. × 4 ft 10% XF-1150 on Chromosorb P; B, $^1/_8$ in. × 4 ft Carbowax 20M on Chromosorb P. Compounds **1** and **3** not separated on column B; amounts determined by nmr. [c] Benzophenone (54.6 g) absorbs >99% of incident light. [d] Commercial mixture of *cis*- and *trans*-piperylene, 68 g. [e] Benzene absorbs 98% of incident light. [f] Light absorbed by benzophenone (84%) and benzene (16%). [g] Slurry of 20 g of CaCO$_3$ in 640 ml of methanol.

The formation of *p*-cresol (**2**) from dienone **1** in ethyl ether is also sensitized by benzophenone and quenched by piperylene (Table I). In poorer hydrogen donors in which rearrangement to lumiketone **3** competes with hydrogen abstraction, both processes are quenched by piperylene.

The photorearrangement of the lumiketone **2** to ketones **7a**, **7b** and polymer can be sensitized (in benzene using Pyrex filters) by benzophenone, but it is not quenched by *cis*-piperylene (E_{T} = 57 kcal/mol),[7] 1,3-cyclohexadiene (E_{T} = 54 kcal/mol),[6,7b] *trans*-stilbene (E_{T} = 50 kcal/mol),[7a] or biacetyl (E_{T} = 55 kcal/mol).[5] This was determined by irradiation of different solutions competitively on a merry-go-round apparatus,[9b] as well as by separate irradiations under identical conditions (with and without added quencher) with monochromatic light at 366 mμ.

Irradiations in methanol in the presence of calcium carbonate (conditions for formation of **4** but not **5**) show sensitization by benzophenone and quenching by piperylene (Table I). The quenching is not as efficient as observed in benzene and ether. However, the methanol runs are carried out in a heterogeneous system and the data may not be quantitatively significant.

Simultaneous irradiation under nitrogen or oxygen of solutions of dienone **1** in ethyl ether or benzene

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(5) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 4537 (1964).

(6) (a) D. F. Evans, *J. Chem. Soc.*, 1735 (1960); (b) G. N. Lewis and M. Kasha, *J. Amer. Chem. Soc.*, **66**, 2100 (1944).

(7) (a) G. S. Hammond, *et al.*, *ibid.*, **86**, 3197 (1964); (b) R. E. Kellogg and W. T. Simpson, *ibid.*, **87**, 4230 (1965).

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

(9) (a) G. S. Hammond, N. J. Turro, and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1144 (1962); (b) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, 43, 2129 (1965).

showed no differences within experimental error in the rates of disappearance of **1** or appearance of products. Thus, oxygen is apparently not an efficient quencher of the photochemistry of dienone **1**.

Quantum Yields. Quantum yields were determined for appearance of products (lumiketone **3** and *p*-cresol **2**, respectively) in benzene and ether using a monochromatic light source at 366 mμ (Table II). Reactions were carried to low conversions to prevent appreciable light absorption by the products (most important in benzene) and yields of products were determined by glpc using internal standards. The quantum yield for formation of ketone **7a** from lumiketone **3** is also included. Ferrioxalate actinometry was used throughout.[10]

Table II. Quantum Yield Data for Product Formation at 3660 Å[a]

Reaction	Solvent	Conversion,[b] %	Φ
1 → **3**	Benzene	2.8	0.74
			0.76
			Av 0.75
1 → **2**	Ethyl ether	6.1	0.65
			0.79
			Av 0.72
3 → **7a**	Benzene	3.9	0.35
			0.37
			Av 0.36

[a] Irradiation at 3660 Å in Pyrex cells using a Bausch and Lomb grating monochromator with a 200-W super-pressure mercury lamp. Ferrioxalate actinometry. [b] Analysis by glpc on $^1/_8$ in. × $5^1/_4$ ft. 15% cyanosilicone XF-1150 on Chromosorb P column. Acenaphthene used as internal standard was added after irradiation.

A value for the quantum yield of intersystem crossing for dienone **1** in benzene was determined using a triplet counting method,[9b] with 1,3-cyclohexadiene as the quencher. The amount of cyclohexadiene dimers formed[8] (irradiation at 366 mμ in benzene) on absorption of light by dienone **1** was compared quantitatively[11-13] (glpc) with that formed on irradiation under identical conditions of light output and irradiation time as a benzene solution of benzophenone containing 1,3-cyclohexadiene. The concentration of 1,3-cyclohexadiene used in this study was 1.16 *M*, which would quench 93% of the triplets of **1**, according to further studies from this laboratory.[13b] The experimental value for the relative amount of dimer formed was 0.73:1 for the dienone and benzophenone solutions, respectively. Since $\Phi_{ST} = 1.00$ for benzophenone,[9b,14] the quantum yield for intersystem crossing in **1** in benzene is $0.73/0.93 = 0.79$.[11,13b]

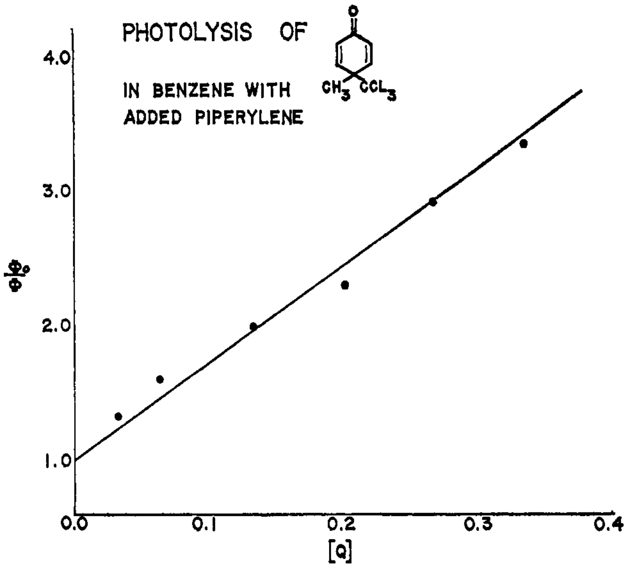

Figure 1. Effect of *trans*-piperylene on the quantum yield for formation of lumiketone **3** from dienone **1** in benzene.

Kinetic Studies. The extent of conversion of dienone **1** to lumiketone **3** in benzene was studied as a function of the concentration of *trans*-piperylene as quencher. The data are presented graphically in Figure 1 in the usual form of a plot of relative quantum yield for product appearance *vs.* quencher concentration, fitting the Stern–Volmer equation (eq 1)[15] where k_q is the specific rate constant for energy transfer, k_r is that for unimolecular rearrangement of the triplet, and k_d for

$$\Phi_0/\Phi_Q = 1 + \frac{k_Q[Q]}{k_r + k_d} = 1 + k_Q\tau_0[Q] \qquad (1)$$

decay of the triplet to ground state. Since the quantum yield Φ_0 for formation of lumiketone **3** is 0.75 and $\Phi_{ST} = 0.79$, it appears that rearrangement competes very efficiently with decay, *i.e.*, $k_d \ll k_r$. Thus the slope of the Stern–Volmer plot is equal to $k_Q/k_r = 7.2\ M^{-1}$. The value of k_Q in benzene is taken to be 5×10^9 l. mol^{-1} sec^{-1},[16] giving $k_r = 6.9 \times 10^8$ sec^{-1}.[17-20] This is the first determination of the rate constant for rearrangement of the triplet state of a 2,5-cyclohexadienone.

The extent of conversion of dienone **1** to *p*-cresol **2** in ethyl ether as a function of the concentration of *trans*-piperylene is pictured graphically in Figure 2, from a single merry-go-round run. Other data agree, but

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[10] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.* (London), **A235**, 518 (1956).

[11] (a) The yield of cyclohexadiene dimers is known to be very sensitive to the amount of oxygen in the system.[12,13] In this experiment, both solutions were purged with oxygen-free nitrogen for 1 hr prior to photolysis, as the vessels used did not permit degassing by the usual freeze–thaw technique. Traces of oxygen may have remained, but it is assumed that resultant errors would largely cancel, since the relative yield of dimers in the solutions is the quantity of interest.

[12] G. S. Hammond, Abstracts of the 20th National Organic Symposium of the American Chemical Society, Burlington, Vt., June 1967; D. Valentine, Ph.D. Dissertation, California Institute of Technology, Pasadena, Calif., 1966.

[13] (a) A. C. Fabian, Ph.D. Dissertation, New York University, New York, N. Y., 1967; (b) D. H. Sussman, unpublished results.

[14] W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Amer. Chem. Soc.*, **83**, 2789 (1961).

[15] N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965.

[16] P. J. Wagner and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 1245 (1966).

[17] This assumes that *trans*-piperylene (E_T = 59 kcal/mol)[6] is a completely efficient quencher of the triplets of dienone **1** (E_T = 67 kcal/mol). Because of the short lifetime of the triplet (1.45×10^{-9} sec), it is possible that quenching is not "diffusion controlled" in this case. It has been shown[18] that there is considerable variation in the efficiencies of piperylene and cyclohexadiene as quenchers of the triplet of α-santonin (E_T = 68 kcal/mol, lifetime 10^{-10} sec),[18,19] with the latter more efficient by a factor of 5–6. Wagner[20] has raised objections regarding the validity of data obtained with quenchers in high concentration, although efficient quenching is observed with **1** at quencher concentrations below 0.5 *M*. Additional experiments are in progress in response to these new and interesting observations. See also D. I. Schuster, A. C. Fabain, N. P. Kong, W. C. Barringer, W. V. Curran, and D. H. Sussman, *ibid.*, **90**, 5027 (1968).

[18] D. I. Schuster and A. C. Fabian, *Tetrahedron Lett.*, 1301 (1968).

[19] M. H. Fisch and J. H. Richards, *J. Amer. Chem. Soc.*, **85**, 3029 (1963).

[20] P. J. Wagner, *ibid.*, **89**, 5715 (1967).

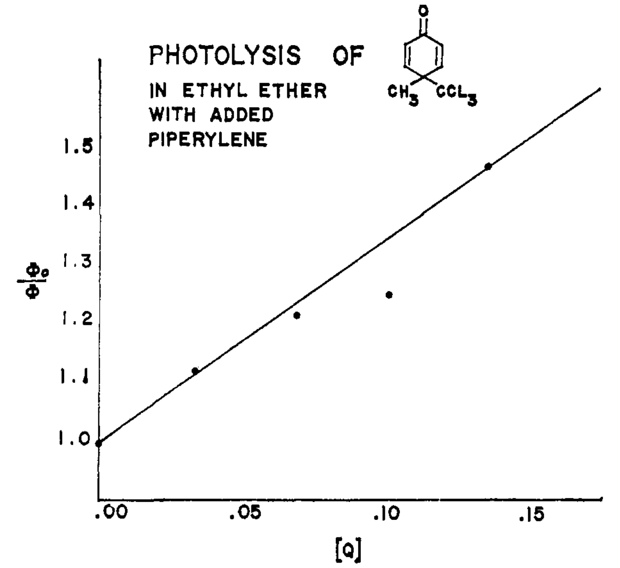


Figure 2. Effect of *trans*-piperylene on the quantum yield for formation of *p*-cresol **2** from dienone **1** in ethyl ether.

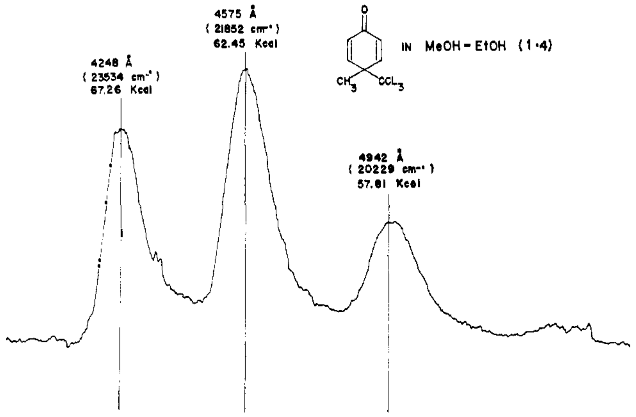


Figure 3. Phosphorescence spectrum of dienone **1** in a 4:1 ethanol–methanol glass at 77°K.

are not presented because of some experimental uncertainties in their determination. The Stern–Volmer relationship for this reaction is given in eq 2, where k_a is the rate constant for hydrogen abstraction from RH. From the quantum yield data, virtually every triplet undergoes hydrogen abstraction and not

$$\Phi_0/\Phi_Q = 1 + k_Q\tau_0[Q] = 1 + \frac{k_Q[Q]}{k_a[RH] + k_d} \qquad (2)$$

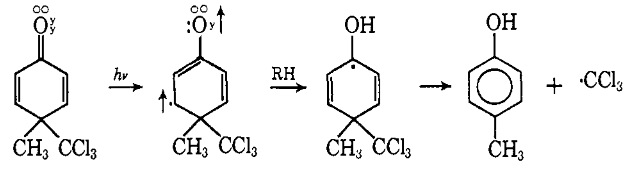
radiationless decay, *i.e.*, $k_d \ll k_a[RH]$. Thus, the slope of the straight line is equal to $k_Q/k_a[RH] = 3.5$ M^{-1}. The value for k_Q in ether is calculated to be 1.3×10^{10} l. mol^{-1} sec^{-1}, using the value of k_Q in benzene[16] of 5×10^9 l. mol^{-1} sec^{-1} and the coefficients of viscosity in ether and benzene of 0.215 and 0.564, respectively.[21] The concentration of ethyl ether is 9.65 *M*, giving $k_a = 3.9 \times 10^8$ l. mol^{-1} sec^{-1}.[17]

Phosphorescence Emission of Dienone 1. The phosphorescence spectra were kindly measured by Dr. D. Arnold and Mrs. L. Gillis of the Union Carbide Research Institute in Eastview, N. Y. The spectrum in a 4:1 ethanol–methanol glass at 77°K is shown in Figure 3. Using a fast-speed chopper, the spectrum is broadened but still well resolved. The spectrum, reported earlier,[1c] has also been reported recently by Zimmerman, *et al.*[22] The separation between the 0–0 and 0–1 bands is 1680 cm^{-1}, typical of emission from triplet n,π* states.[15,22] The location of the 0–0 band allows assignment of the triplet energy of **1** at 67.2 kcal/mol (lit.[22] 67.0 kcal/mol). No fluorescence emission from **1** was observed.

Discussion

The Reactive Excited State. It is clear from the sensitization and quenching studies together with the quantum yield and emission data that the photochemistry of 4-methyl-4-trichloromethylcyclohexa-2,5-dienone is entirely derived from the lowest triplet state, and that this state has an n,π* configuration. In the cases of other cyclohexadienones, the only primary reaction observed in nonacidic media was the lumiketone rearrangement,[23–26] aside from subsequent photoreactions of the primary products. In this study, two primary reactions of the dienone **1** have been observed in addition to formation of lumiketone **3**. These are formation of *p*-cresol (**2**) in those solvents which are good hydrogen donors, and oxetane formation.[2] Yields of *p*-cresol are high in ethyl ether, dioxane, diglyme, tetrahydrofuran, and 2-propanol, and moderate to poor in hexane, cyclohexane, toluene, and cumene.[2] No *p*-cresol is observed in photolysis of **1** in benzene or methanol.[2]

The photoreduction of benzophenone in hydrogen donor solvents involves the n,π* triplet state as the chemically active species.[14,15,27–30] Furthermore, it has been suggested that only those ketones that have lowest triplet states with an n,π* configuration undergo photoreduction efficiently,[30] although this conclusion has recently been challenged.[31] The reactivity of the triplet n,π* state is quantitatively similar to that of alkoxy radicals,[32] consistent with the observation of selectivity in hydrogen abstraction for the reactive triplet of dienone **1** which shows the behavior of a radical-like species **8**.[33,34] The formation of *p*-cresol



1 **8** **9** **2**

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[31] N. C. Yang, D. S. McClure, S. L. Murov, J. J. Houser, and R. Dusenbery, *J. Amer. Chem. Soc.*, **89**, 5466 (1967).

[32] C. Walling and M. J. Gibian, *ibid.*, **86**, 3902 (1964); **87**, 3361 (1965); A. Padwa, *Tetrahedron Lett.*, 3465 (1964).

[33] The problem of representation of excited states by valence bond structures has recently been discussed by Taylor[34a] and by Zimmerman.[34b]

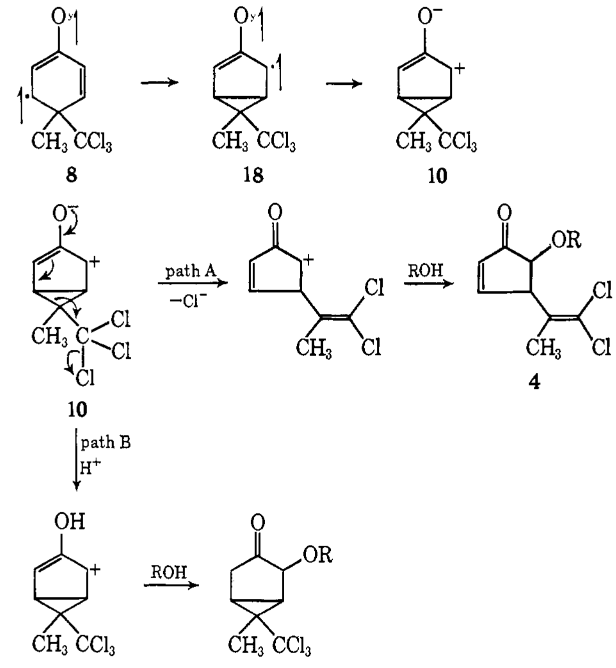
[34] (a) G. A. Taylor, *Chem. Commun.*, 896 (1967); (b) H. E. Zimmerman, *ibid.*, 174 (1968).

must involve a sequence in which hydrogen abstraction precedes cleavage to give the trichloromethyl radical.

The formation of oxetanes is also considered to be a reaction characteristic of triplet n,π* excited states.[35–38] Oxetanes were observed on photolysis of **1** in olefin solvents, a reaction not previously observed in dienone photochemistry, further supporting the assignment of an n,π* configuration to the lowest triplet of dienone **1**. Thus, all the criteria previously used for such an assignment in the case of ketones such as benzophenone (emission spectrum, hydrogen abstraction, oxetane formation) are found in the case of dienone **1**.

Sequential Formation of Diradical and Zwitterionic Intermediates. The formation of products of structure **4** on irradiation of dienone **1** in methanol or aqueous dioxane[2] is a reaction which occurs (at least in part) also from the triplet state of **1** (Table I). The reaction can be rationalized satisfactorily only by an ionic fragmentation of the zwitterion **10**, a mechanism previously suggested by King and Leaver[39] (Scheme I, path A), and supported by the observation that the course of reaction can be diverted when methanol is saturated with HCl, leading to a new product **5** rather than **4**.[2,40] Protonation of zwitterion **10** prevents the fragmentation (path A), and one might speculate that the new product arises from reaction of carbonium ion **11** with methanol (Scheme I, path B).

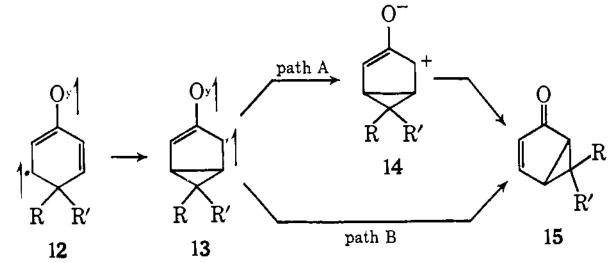
Scheme I



The formation of **4** (and **5**) provides compelling evidence for the intermediacy of zwitterionic intermedicate **10** in these reactions in methanol and aqueous dioxane. It is concluded that zwitterion **10** arises from a diradical-like precursor, as originally suggested by Zimmerman and Schuster,[23] since **4** and **5** are (at best) trace products on photolysis of **1** in isopropyl alcohol.[2] That is, isopropyl alcohol is capable of trapping by hydrogen abstraction an intermediate which otherwise proceeds to give the zwitterion **10** and products derived from it,[41] assuming a comparison of the reactions in these different alcohols is justified. Thus, the diradical-like n,π* triplet of **1** (**8**) appears to be the precursor of **10**. This is the strongest evidence which has yet been obtained on the sequential formation of radical and ionic intermediates in the photochemistry of cyclohexadienones.

The Role of Zwitterions in the Dienone–Lumiketone Rearrangement. The results show that the photochemical processes leading to *p*-cresol (**2**) (by hydrogen abstraction–fragmentation) and to lumiketone **3** are competitive, proceeding from the lowest n,π* triplet state of dienone **1**. Since both reactions proceed with high quantum yield (0.75), the possibility is small that they occur *via* different excited states.[41a] It was originally postulated[23] that the course of formation of lumiketones from dienones involved the sequence of events shown in Scheme II, path A, namely, rebonding of the triplet excited state **12** to give the bridged excited state **13**, followed by demotion to the ground-state zwitterion **14** and rearrangement of **14** to the product **15**. That the immediate precursor to the lumiketone is a zwitterion has been assumed in recent discussions and reviews of this reaction,[15,23–26,42] although supporting evidence is lacking.

Scheme II



There are two possibilities, which differ only in their chronology. Either electron demotion precedes rearrangement as in Scheme II, path A,[43] or rearrangement and electron demotion occur simultaneously without involvement of a zwitterion intermediate (path B). It

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(35) N. C. Yang, *Pure Appl. Chem.*, **9**, 591 (1964).

(36) D. R. Arnold, R. L. Hinman, and A. H. Glick, *Tetrahedron Lett.*, 1425 (1964).

(37) In certain special cases, with electron-deficient olefins such as dicyanoethylene or maleic anhydride, oxetane formation apparently can occur from the n,π* singlet state.[38] The reported results[2] do not *demand* that oxetanes **6** arise from the same triplet state responsible for lumiketone formation and hydrogen abstraction, although further studies indicate this is the case (S. M. Denver, unpublished results from this laboratory).

(38) N. J. Turro, P. Wriede, J. C. Dalton, D. Arnold, and A. Glick, *J. Amer. Chem. Soc.*, **89**, 3950 (1967).

(39) J. King and D. Leaver, *Chem. Commun.*, 539 (1965).

(40) Since compound **5** has not been isolated and its structure rigorously proven, conclusions based on this structure must be regarded somewhat tentatively.

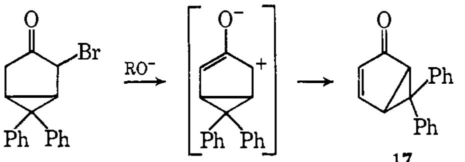
(41) There is no evidence for the formation of *p*-cresol in more than trace quantities on photolysis of **1** in methanol or ethanol. From other work [W. H. Urry, F. W. Stacey, E. S. Huyser, and O. O. Juveland, *J. Amer. Chem. Soc.*, **76**, 450 (1954); C. Walling and M. J. Mintz, *ibid.*, **89**, 1515 (1967); A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2038 (1963)], one expects a decrease in the formation of *p*-cresol on photolysis of dienone **1** in isopropyl, ethyl, and methyl alcohols, respectively. It is surprising that the falloff in hydrogen abstraction by the n,π* triplet of **1** on proceeding from isopropyl to ethyl alcohol is apparently so great.

(41a) NOTE ADDED IN PROOF. Formation of **2** and **3** concomitantly in 4:1 benzene–ether is quenched by piperylene. The identical Stern–Volmer line is obtained for each product, confirming that they each derive from the identical triplet state (S. D. Denver, unpublished results from this laboratory).

(42) H. E. Zimmerman, *Advan. Photochem.*, **1**, 183 (1963); O. L. Chapman, *ibid.*, **1**, 323 (1963).

(43) H. E. Zimmerman and J. S. Swenton, *J. Amer. Chem. Soc.*, **89**, 906 (1967).

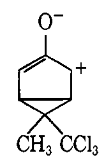
is expected that both intermediates **13** and **14** would have accessible pathways for rearrangement to **15**. Originally,[23] the rearrangement of a diradical by a 1,2-alkyl shift to give the lumiketone was not considered likely, by analogy with the well-known absence of such 1,2 shifts in the chemistry of simple free radicals.[44] However, 1,2 shifts of hydrogen, alkyl, or aryl groups in 1,3 diradicals are facile processes and are now well documented.[45] The strong driving force for such a diradical rearrangement is the pairing of spins during the reaction, *i.e.*, the product has one more bond than the diradical.[46,47] Zimmerman and his coworkers have demonstrated that a ground-state species, assumed to have structure **16**, rearranges to lumiketone **17**.[48] However, this study[48] shows that a zwitterion (if indeed such a species was formed in this reaction) *can* rearrange



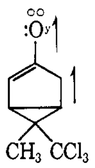
16 **17**

to the lumiketone, but this does not *prove* that such an intermediate is the precursor to the lumiketone **17** in the photochemistry of 4,4-diphenylcyclohexadienone.[23,43]

In the case of dienone **1**, different reaction pathways are open to the bridged excited-state diradical **18** and the corresponding zwitterion **10**. The chemistry of the zwitterion **10** in methanol or aqueous dioxane does not



10



18

involve rearrangement to **3** but rather ionic fragmentation to give **4**, suggesting that **10** is not the precursor to lumiketone **3**, and that the rearrangement is occurring directly from **18**. Since hydrogen abstraction is competitive with rearrangement and fragmentation, intermediates **8** and **18** must be precursors to the zwitterion **10** in the media in which **10** is formed.

Alternatively, **10** might be the precursor to the lumiketone **3** if its chemistry is solvent dependent, since ionic fragmentation may have a strong driving force in solvation of the incipient chloride ion. In addition, reaction at the electrophilic site of the zwitterion **10** may initiate the reaction, so that fragmentation would be seen only in nucleophilic media.

It may be experimentally impossible to distinguish between the alternatives above because of the very short lifetimes of the intermediates involved in these rearrangements. It should be recognized, however, that it is by no means obvious that zwitterions are involved in the dienone–lumiketone rearrangement in nonpolar media, as has been generally assumed.[17,23–26,35,36,48a]

In Scheme III, the photochemistry of 4-methyl-4-trichloromethylcyclohexa-2,5-dienone is summarized together with the proposed mechanisms for the observed transformations. Since the structure of **5** is tentative,[2,4] it is shown in brackets.

Quantitative Considerations. The rate constant k_a for hydrogen abstraction from ethyl ether by the n,π^* triplet of **1** was found to be 3.9×10^8 l. mol^{-1} sec^{-1}. Other rate constants for intermolecular hydrogen abstraction (l. mol^{-1} sec^{-1}) by n,π^* triplets are 1.3–5 $\times 10^6$ for benzophenone in benzhydrol,[14,28] isopropyl alcohol,[49,50] and methyl 2-octyl ether,[51] 3×10^3 for a tetrahydrophenanthrone in isopropyl alcohol,[52] and 5.2×10^6 for pyruvic acid in isopropyl alcohol.[53] The high reactivity of the triplet of **1** in intermolecular hydrogen abstraction is comparable to that observed for some aliphatic ketones in intramolecular γ-hydrogen abstraction, *e.g.*, 1×10^9 for 2-hexanone and 2×10^8 for 2-pentanone.[16] The unusually high reactivity toward hydrogen abstraction of the n,π^* triplet of **1** can be rationalized if carbon–carbon cleavage to give $\cdot CCl_3$ occurs simultaneously with hydrogen abstraction, as shown in **19**. If the transition state for the reaction involves (at least to some extent) aromatization in the six-membered ring and formation of the stable trichloromethyl radical, the activation energy would be less than that for intermolecular hydrogen abstraction by n,π^* triplets of molecules such as benzophenone.[54]

The rate constant for rearrangement of the n,π^* triplet of dienone **1** has been found to be 6.9×10^8 sec^{-1}.[17,55] From the lack of quenching of the n,π^*

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(44) C. Walling in "Molecular Rearrangements," Vol. 1, P. DeMayo, Ed., John Wiley and Sons, Inc., New York, N. Y., 1963, Chapter 7.

(45) H. Kristinsson and G. W. Griffin, *J. Amer. Chem. Soc.*, **88**, 378 (1966), and earlier papers cited therein; C. McKnight and F. S. Rowland, *ibid.*, **88**, 3179 (1966); D. I. Schuster and I. S. Krull, *ibid.*, **88**, 3456 (1966); H. Kristinsson and G. S. Hammond, *ibid.*, **89**, 5968 (1967); H. E. Zimmerman, B. R. Cowley, C.-Y. Tseng, and J. W. Wilson, *ibid.*, **86**, 947 (1964); H. E. Zimmerman, P. Hackett, D. F. Juers, and B. Schröder, *ibid.*, **89**, 5973 (1967).

(46) There is no difficulty if the diradical is a triplet, rather than a singlet, as change of spin state to give the singlet ground state of the product is expected to occur at least as fast as the geometric changes involved in the rearrangement.[47]

(47) (a) J. R. Fox and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 4031 (1964); (b) S. F. Nelsen and P. D. Bartlett, *ibid.*, **88**, 143 (1966), including comments on the preceding reference; (c) P. Scheiner, *ibid.*, **88**, 4759 (1966); **90**, 988 (1968).

(48) H. E. Zimmerman, D. Döpp, and P. S. Huyffer, *ibid.*, **88**, 5352 (1966).

(48a) Note Added in Proof. The recent observation of a dienone–lumiketone rearrangement in the gas phase [J. S. Swenton, E. Saurborn, R. Srinivasan, and F. I. Sonntag, *ibid.*, **90**, 2990 (1968)] was interpreted as implying that a zwitterionic intermediate was "not likely to be involved" in this reaction. This is based on the assumption that such an intermediate, in the absence of solvation, would be too high in energy to be attainable. This assumption may not be justified, however, since the extent of charge separation and interaction in a mesoionic intermediate (such as **10**) is not known, and also since this intermediate is generated from an excited state about 100 kcal/mol above the ground state. This is quite a different situation from, for example, the formation of an ion pair R^+X^- from a neutral molecule RX in the gas *vs.* the liquid phase. Furthermore, the parent oxyallyl ion $CH_2{=}C(O^-)CH_2^+$ is calculated to be more stable (in the absence of solvation) than the corresponding neutral molecules cyclopropanone and allene oxide: R. Hoffmann, *ibid.*, **90**, 1475 (1968). Thus, the interpretation of the gas-phase results must remain equivocal at this time.

(49) A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2038, 2051 (1963).

(50) S. G. Cohen and W. V. Sherman, *J. Amer. Chem. Soc.*, **85**, 1642 (1963).

(51) S. G. Cohen and S Aktipis, *ibid.*, **88**, 3587 (1966).

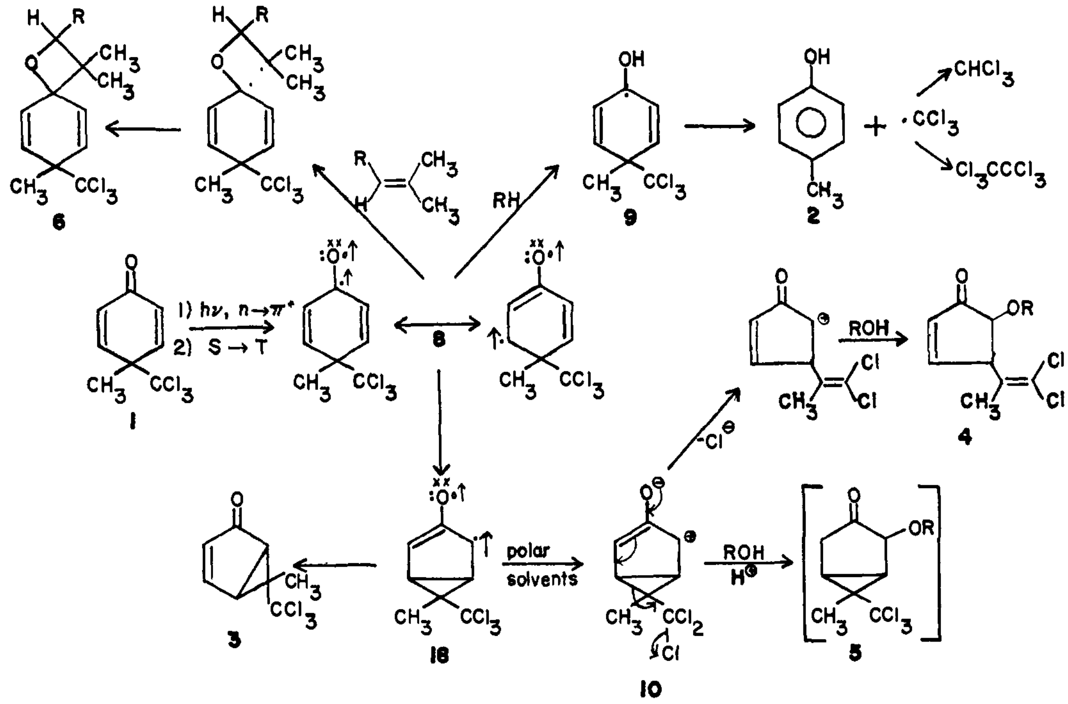
(52) H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, S. W. Staley, and M. Semmelhack, *ibid.*, **88**, 1965 (1966).

(53) D. S. Kendall and P. A. Leermakers, *ibid.*, **88**, 2766 (1966).

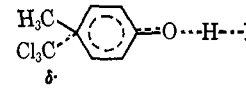
(54) This does not, of course, require that the extent of C–C bond breaking be the same as the extent of O–H bond formation in **19**.

(55) If this rate constant were also valid in ethyl ether, lumiketone ought to have been formed in ether in observable amounts, which was not the case. This implies an appreciable solvent effect on k_r, and/or that the assumption of diffusion-controlled energy transfer is incorrect.[17,18]

Scheme III



triplet of 4,4-diphenylcyclohexadienone, Zimmerman and Swenton[43] estimate the rate of rearrangement (Φ 0.86) of this triplet to be greater than 10^{10} sec^{-1}, while Schuster and Fabian[18] have determined the rate constant for rearrangement of α-santonin triplet to lumisantonin to be 8.6×10^{9} sec^{-1} (Φ 0.86[18] – 1.0[19]).



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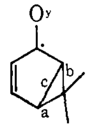
Rearrangement of Lumiketone 3 to Ketones 7a and 7b. Ketones 7a and 7b, produced from irradiation of lumiketone 3 in a variety of solvents,[2] appear to be stereoisomers of general formula 7. The "normal" reaction of bicyclo[3.1.0]hex-3-en-2-ones[23–26] is illustrated by the diphenyl derivative 20 which rearranges (Φ 0.15) to phenols 22 and 23 and the acid 24 by processes involving both singlet and triplet excited states as reactive intermediates (Scheme IV).[23,56] Lumisantonin 21 rearranges photochemically to the linearly conjugated dienone 25, which is the precursor for photosantonin and photosantonic acid.[19,57,58] These and related reactions[24–26] involve primarily opening of the endocyclic cyclopropane bond c in the excited state of the lumiketone (26), the bond which appears to be least suited for effective overlap with the p orbitals in the π system. Only product 24 results from opening of bond a in the excited state. The evidence is compelling that rearrangement of the diphenyl lumiketone 20 occurs after electron demotion, from studies of migratory aptitudes of substituted aryl groups.[56b]



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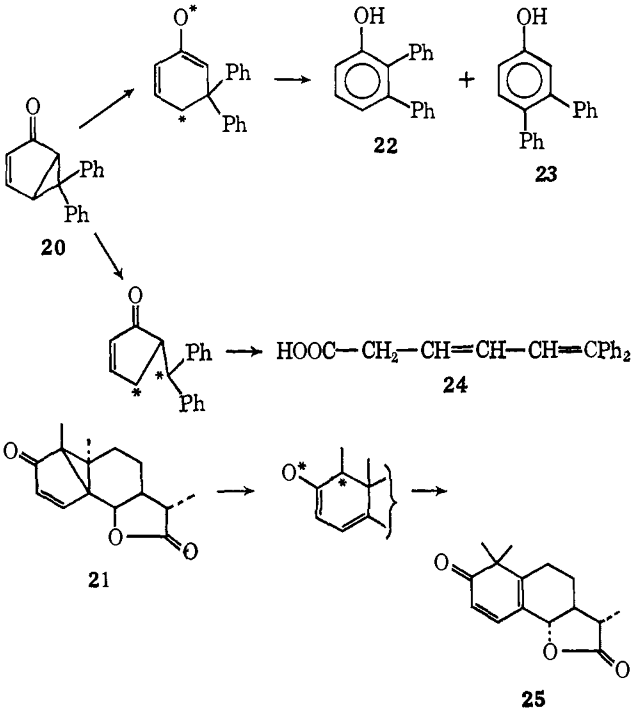
Scheme IV



In the case of lumiketone 3, the photochemical products, Φ 0.36, arise from opening of the exocyclic cyclopropane bonds a and/or b to give diradicals 27 and/or 28, which proceed to the products by 1,2-chlorine migration[44] and ring closure (Scheme V). The chlorine shift competes effectively with the alternative ring cleavage seen in the conversion of 20 to 24. No products of cleavage of bond c have been observed with ketone 3 such as *m*-cresol, which was definitely not formed in the reaction. The possibility cannot be excluded, however, that the unidentified polymeric

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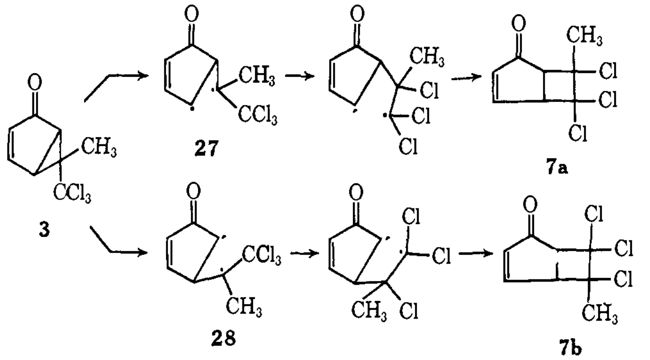
[56] (a) H. E. Zimmerman, R. Keese, J. Nasielski, and J. S. Swenton, *J. Amer. Chem. Soc.*, 88, 4895 (1966); (b) H. E. Zimmerman and J. O. Grunewald, *ibid.*, 89, 3354, 5163 (1967).

[57] O. L. Chapman and L. F. Englert, *ibid.*, 85, 3028 (1963).

[58] M. H. Fisch and J. H. Richards, *ibid.*, 90, 1547, 1553 (1968).

Scheme V



material (>50% yield) arises all or in part from cleavage of bond c. Since the photochemistry of **3** could be sensitized by benzophenone (E_T = 69 kcal/mol) but is not quenched by triplet quenchers (E_T = 50–60 kcal/mol), the multiplicity of the excited state(s) responsible for the reaction remains in doubt.[59]

Experimental Section

Details of photochemical apparatus and procedures, instrumentation, and analytical methods are given in the previous paper.[2] In all quantitative analyses by gas–liquid partition chromatography (glpc), per cent yields of products were determined using an internal standard. The ratio of products to the known amount of internal standard was determined from the average of several independent analyses of each sample. These were converted to per cent yields using response factors determined from carefully prepared solutions of reactant, products, and internal standard, whose ratio simulated that of the photolysate solutions as closely as possible. Response factors were determined before and after each set of analysis. For details on columns and analytical conditions, see ref 2 and 60.

Quantum Yield Determinations. The light source was a Bausch and Lomb Model 33-86-25 uv grating monochromator equipped with a 200-W super-pressure mercury arc and power supply. Cylindrical Pyrex vessels, which fitted into a special holder, with a capacity of 90 ml and equipped with an inlet and outlet for nitrogen, were kindly supplied for this work by Professor S. Z. Lewin. Stirring was maintained by bubbling nitrogen through the cells. The lamp output at 366 ± 10 mμ was determined before and after quantum yield measurements by ferrioxalate actinometry (4-min exposure). The amount of light transmitted through the sample solution was measured by an actinometer solution placed immediately behind the reaction vessel. The photolysate after reaction was concentrated at room temperature and aspirator pressure to approximately 15 ml. A known amount of internal standard was then added, and the mixture was well shaken and then analyzed by glpc. The results are given in Table II.

Intersystem Crossing Quantum Yield.[11] Sensitized Dimerization of 1,3-Cyclohexadiene.[8] The solutions used for this study contained 5×10^{-3} mol of either dienone **1** or benzophenone, 10 ml of 1,3-cyclohexadiene, and 80 ml of benzene. The samples were purged with nitrogen for 1 hr prior to irradiation and irradiated for the same time period at 366 mμ using the Bausch and Lomb monochromator. The concentrations of the ketones were such that all of the incident light was absorbed in each solution. Weighed amounts of naphthalene were added to each solution as internal standard for glpc analysis, and the mixtures were analyzed for the cyclohexadiene dimers on a $^1/_8$ in. × 5.25 ft 15% cyanosilicone XF-1150 on Chromosorb P column. Authentic samples of the dimers were prepared by irradiation (Pyrex filter) of benzophenone in benzene in the presence of 1,3-cyclohexadiene.[8] Column chromatography on neutral alumina of the photolysate and collection of initial hexane eluents yielded the dimers, identified by comparison of their nmr spectra with those reported.[8] Analysis of the mixture on the XF-1150 column at 80° gave two peaks, whose ratio in the photolysate of dienone **1** in benzene containing 1,3-cyclohexadiene (Pyrex filter) was the same as in the benzophenone runs. The dimers from reactions sensitized by **1** were isolated by column chromatography and had the same spectroscopic properties and glpc retention times as those formed in the benzophenone runs.

trans–cis **Isomerization of Piperylene.** A glpc column of 20% saturated silver nitrate in ethylene glycol on Chromosorb P is able to separate *trans*- and *cis*-piperylene.[9a] However, *trans*-piperylene has a retention time close to that of benzene on this column. A benzene solution of 0.2 g of dienone **1** and 10 ml (100-fold excess) of *trans*-piperylene (total volume 32 ml) was irradiated for 2 hr (Pyrex filter). Analysis of the photolysate by glpc showed a peak due to *cis*-piperylene (identified by conjection with peak enhancement) which was larger than that present before photolysis due to the small impurity of *cis* in the sample of *trans*-piperylene (J. T. Baker).

Kinetic Studies. The data for the Stern–Volmer plots were obtained from runs on a 12-tube "merry-go-round" turntable described previously.[2] The Pyrex tubes, closed with ground-glass joints, were filled with accurately weighed amounts of dienone **1**, 15 ml of predistilled solvent (benzene or ether), and the required amount of quencher measured with 50- and 100-μl syringes. Solutions were well shaken. Irradiation was carried out with a 100-W Hanovia high-pressure mercury arc for 20 min in benzene and 40 min in ether. After irradiation, the identical amount of recrystallized internal standard was added to each tube, and the solutions were well shaken and then analyzed by glpc.

Acknowledgment. We are deeply grateful to the U. S. Army Research Office (Durham) for generous support of this research under Project 4019-C.

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(59) A broad phosphorescence emission from **3** in 4:1 ethanol–methanol at 77°K was observed, as well as weak fluorescence in the absence of a chopper. It is not clear whether this spectrum is to be assigned to **3** or to some product of photolysis. Further work is in progress.

(60) D. J. Patel, Ph.D. Dissertation, New York University, 1968.