with light λ >500 nm (glass-color filter 3-69, Corning, N. Y.) for 10 min. The cell was then returned to the spectrometer as soon as possible and the absorbance at 465 nm continuously recorded by allowing the chart to move while the wavelength was set at 465 nm. This procedure could be started usually within 1 min after the irradiation had been stopped. The absorbance for the equilibrium state found after irradiation was always within 0.5% of the value, measured before irradiation.

Equilibrium Measurements. The reference temperature, T^0, chosen was 32° and X_A^0 was found to be 0.141 ± 0.006 from nmr measurements of five solutions, 0.01–0.015 *M* **16** in CH_2Cl_2. These were prepared in the dark and immediately placed in the nmr probe for equilibration. After 10–15 min a series of 6–10 integrals were run over the methyl peaks at 3.07 and 2.95 ppm. Impurities could not be detected in these solutions after this procedure. Two of these samples were irradiated at $T^1 = -60°$ with light of λ >500 nm under nitrogen until the photostationary state was reached (~15 min); the mole fraction of dithiete, determined by nmr, was found to be (X_A^1) 0.96 ± 0.1. A solution of **16** under N_2 with an optical density of $E^0_{465} = 1.49$ at 32° showed, after irradiation at −60° with light λ >500 nm, a residual absorption of $E^1_{465} = 0.24$. (The uv spectrum, obtained after irradiation for 15 min, did not change on further irradiation for 30 min and was not changed after keeping the solution for 30 min at this temperature in the spectrometer.)

The density data for CH_2Cl_2 were taken from the literature.[36] The ratio of the molar absorptivities of **16** and **22** was thus determined as $\epsilon_r = 11.5 \pm 1.3$. It was assumed that the position of the photostationary state is not concentration dependent.

The temperature dependence of the optical density of solutions of **16** was determined as follows. Through a CH_2Cl_2 solution of **16** ($\sim 3 \times 10^{-5}$ mol l.$^{-1}$), placed in the uv cell mentioned above, was passed a stream of nitrogen for 30 min. The uv cell was closed and placed into the spectrometer. The optical density E_{465} at 465 nm was measured as a function of temperature. An increase of approximately 10% in E_{465} for a 20° decrease in temperature was observed. Solutions at higher temperatures reached the equilibrium state within a few minutes, while solutions at lower temperatures were allowed to equilibrate overnight. The sequence, in which the measurements were carried out, is given in Table II, along with the equilibrium constants and equilibrium concentrations for **16**.

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[36] Landoldt-Börnstein, 2. Band, 2. Teil, Bandteil a, p 199.

Photochemistry of Ketones in Solution. XXXIX. 3,4-Dimethyl-4-trichloromethyl-2,5-cyclohexadien-1-one[1a]

David I. Schuster*[1b] and K. Vasanth Prabhu

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Received August 4, 1973

Abstract: The photochemistry of the title compound **5** in a number of solvents is described and compared with that of the parent dienone **1** originally studied by Schuster and Patel. The effects on the photochemistry produced by introduction of the additional methyl group are varied and pronounced. In *tert*-butyl alcohol, both epimeric 6-methyl-6-trichloromethylbicyclo[3.1.0]hexenones (lumiketones) **7** and **8** are formed from **5**. The stereochemistry, assigned on the basis of spectral data, hydrogenation experiments, and an X-ray crystal analysis, shows the major product has the CCl_3 group in the exo orientation. It is concluded that the sole lumiketone formed from the parent dienone **1** also has an exo CCl_3 group. These results are rationalized mechanistically on the basis of a competition of steric effects, favoring an endo orientation in the intermediate and derived lumiketone of the bulkier dienone C-4 substituent (CCl_3 in these systems), and coulombic effects favoring an exo orientation of CCl_3 and other electron-rich groups. The electronic effects clearly dominate the reaction course in these systems. Other photoproducts include 2-chloro-3,4-dimethyl-4-trichloromethylcyclohex-2-en-1-one (**10**), a bicyclo[3.2.0]hexenone (**13**), 3,4-dimethylphenol (**14**), 3,5-dimethylphenol (**15**), and hydrogen chloride. Compounds **13** and **15** are formed by secondary photolyses of the initially formed lumiketones. Mechanisms for formation of all products are suggested. Noteworthy is the novel formation of **10**, which is proposed to involve trapping of zwitterion **37**, derived from **5**, by HCl generated *in situ*, a new mode of zwitterion trapping. The surprising formation of phenol **14** in good yield in benzene, *t*-BuOH, and other poor H-donor solvents, in contrast to the lack of phenol formation from **1** in such solvents, was shown in benzene to involve H abstraction not from the solvent but from ground state dienone, presumably from the allylic methyl group. Quantum yield data are presented. The triplet yield for **5** in benzene was found to be close to unity. Sensitization and quenching experiments in several solvents confirm that all products are triplet derived. As in earlier studies, quenching by 1,3-cyclohexadiene is somewhat more efficient than by *trans*-piperylene. The Stern–Volmer quenching slopes in 2-propanol for formation of lumiketone **7** decreased as dienone concentration was increased, while the slopes for formation of phenol **14** simultaneously increased. These results require two different triplets as precursors to these products, at least in 2-propanol. The triplet leading to lumiketones is suggested to be a π,π^* triplet, showing a typical self-quenching effect. The triplet which abstracts hydrogen from the solvent, leading to phenol **14**, is suggested to be the lowest n,π^* triplet. The increased quenching slopes in the latter case are tentatively attributed to trapping by ground state dienone of radicals, produced in the reaction, which could act as triplet quenchers. The "two triplet" mechanism required by the results is compared to previously proposed mechanisms in cyclohexadienone and cyclohexenone photochemistry. The broad emission of **5** at low temperature is likewise attributed tentatively to a low π,π^* triplet stabilized by the 3-methyl relative to the n,π^* triplet, which was suggested to be the lowest triplet in the case of the parent dienone **1**.

Previous papers from this laboratory have demonstrated the variety of reactions which ensue on electronic excitation of 4-methyl-4-trichloromethyl-2,5-cyclohexadienone (**1**).[2] The unusual richness of the photochemistry of this system, which is a sensitive

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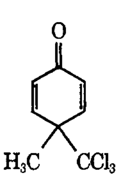
[1] (a) Part XXXVII: D. I. Schuster and T. M. Weil, *J. Amer. Chem. Soc.*, **95**, 4091 (1973). (b) Address correspondence to this author at Department of Chemistry, New York University, Washington Square, New York, N. Y. 10003.

[2] D. J. Patel and D. I. Schuster, *J. Amer. Chem. Soc.*, **90**, 5137 (1968); D. I. Schuster and D. J. Patel, *ibid.*, **90**, 5145 (1968).



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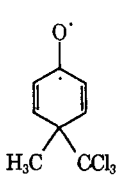

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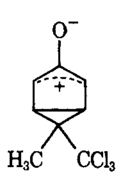

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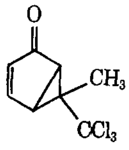
function of reaction conditions, including the choice of solvent, provides a useful probe for determination of reaction mechanism. The distribution of products and the ability to trap one or another intermediate by addition of specific reagents has permitted elucidation of the nature and sequence of intermediates involved in this photochemical system.[2] Thus, some reactions of **1** (*e.g.*, hydrogen abstraction from solvent) involve radical-like intermediates **2**, while other reactions involving interaction with nucleophilic reagents (such as alcohols and halide ions) are most readily rationalized in terms of zwitterionic intermediates (**3**).[2,3]

For the purpose of elucidating in an unequivocal manner the detailed molecular motions involved in the photochemical rearrangement of 2,5-cyclohexadienones such as **1** to bicyclo[3.1.0]hex-3-en-2-ones such as **4**, it was necessary to use a chiral dienone as the reactant. It was desirable to have a compound for which the extrapolation of mechanistic information from the studies on **1** would be as valid as possible. The present paper describes the photolyses of the racemic dienone 3,4-dimethyl-4-trichloromethyl-2,5-cyclohexadien-1-one (**5**) and focuses on the considerable effects produced by a second methyl group on the detailed photochemistry of dienone **1**. The results of photolysis of the optically active dienone **5** will be described separately.



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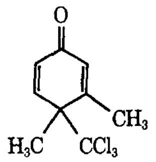

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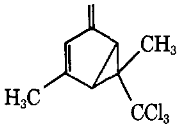
Dienone **5** was conveniently prepared by the procedure of Newman and Wood,[4] and its physical and spectroscopic properties agreed with those previously reported (see Experimental Section).

Results

Isolation and Identification of Photoproducts. Photolysis of 5 in *tert*-Butyl Alcohol. Irradiation of **5** in *tert*-butyl alcohol in a quartz vessel at 254 nm gave a number of products, isolated by column chromatography, of which nine have been identified. Details of procedures and weights of chromatographic fractions are given in the Experimental Section.

The first compound to be eluted was a solid, mp 68–70°, whose elemental analysis and mass spectrum (Table I) indicated the composition $C_9H_9Cl_3O$, isomeric with the starting material. The compound had prominent infrared bands (Table I) indicating an α,β-unsaturated ketone, corroborated by the ultraviolet spectrum. The nmr spectrum (Table I) in carbon tetrachloride showed a single vinyl hydrogen (δ 5.6 ppm), a vinyl methyl (2.12), another methyl, and a pair of doublets (2.59 and 2.89), attributed to cyclopropane protons. All of the data are very similar to those obtained for the lumiketone **4**,[2] except for the added vinyl methyl resonance in the nmr spectrum, and strongly suggest that this compound, ketone A, has the structure of the analogous lumiketone **6**. The assignment of stereochemistry as **7** or **8** depended on comparison with data for the second stereoisomer.



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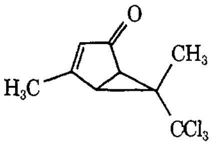

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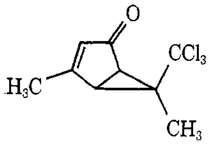

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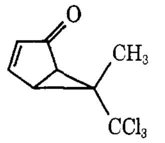

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In order of elution from the silica gel column, the next compounds isolated were unreacted dienone **5**, a new photoproduct X (whose structure was elucidated as described below), and then in small quantity another isomeric photoproduct which proved to be the isomeric lumiketone, as will now be shown. This ketone B, mp 91–93°, has infrared and ultraviolet spectra (Table I) strikingly similar to those of lumiketone A. The nmr spectrum of ketone B showed one vinyl hydrogen with the same chemical shift as in lumiketone A, a vinylic methyl group very slightly deshielded in B compared to A, a methyl on a quaternary carbon deshielded in B to a larger extent (0.08 ppm), and two hydrogens whose position and coupling constant strongly suggested they were the cyclopropane bridgehead hydrogens, significantly (0.32 ppm) shielded in B compared to A. The data left little room for doubt that this ketone B was indeed the stereoisomeric lumiketone.

With the two epimeric ketones in hand, a confident assignment of stereochemistry could be made. Shielding of *endo*- relative to *exo*-6-methyl groups in nmr spectra of bicyclo[3.1.0]hexenones has been used previously to assign stereochemistry at C-6 in such systems.[5–7] Such shielding, albeit quite small, was seen in ketone A compared with B, suggesting A had the stereochemistry shown in **7** and B that shown in **8**. More reliably, the cyclopropyl protons are extensively deshielded in A relative to B, consistent with the above assignments, since these protons are respectively syn and anti to CCl_3 in A and B. Furthermore, the C-6 methyl resonance in A is measurably broadened relative to that in B, consistent with long-range coupling in A to the proton at C-5 according to the familiar W plan,[8] which is only possible if the methyl group has the endo orientation as in the proposed structure **7**.

An X-ray crystallographic analysis on ketone A in collaboration with Professor van der Veen and Fujiwara

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[3] D. I. Schuster and K. Liu, *J. Amer. Chem. Soc.*, **93**, 6711 (1971); D. I. Schuster and V. Y. Abraitys, *Chem. Commun.*, 419 (1969).

[4] M. S. Newman and L. L. Wood, *J. Amer. Chem. Soc.*, **81**, 6450 (1959).

[5] T. Matsuura, *Bull. Chem. Soc. Jap.*, **37**, 564 (1964); K. Ogura and T. Matsuura, *ibid.*, **43**, 2891 (1970).

[6] B. Miller and H. Margulies, *J. Amer. Chem. Soc.*, **89**, 1678 (1967).

[7] D. W. Swatton and H. Hart, *J. Amer. Chem. Soc.*, **89**, 1874 (1967).

[8] L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, New York, N. Y., 1969, p 334 ff.

Table I. Spectral Data

Compd	Infrared,[a] cm^{-1}	Mass,[b] m/e	Ultraviolet,[c] λ_{max} (ϵ), nm	Nmr, ppm[d]
Dienone **5**	2990, 2950, 1680, 1620, 1450, 1404, 1380, 1340, 1295, 1240, 1040, 900	238 (3), 203 (2), 175 (2), 140 (1), 139, 121*, 105 93, 91, 77	EtOH: 238 (12,150), 337 (22) Hexane: 230 (16,100), 252 (4200), 258 (3100), 263 (2200), 330 (6), 342 (9), 356 (12), 372 (11), 384 (78)	1.68 (s, 3 H) 2.23 (d, J = 1, 3 H) 6.13 (m, 1 H) 6.25 (d, J = 10, 1 H) 7.33 (d, J = 10, 1 H)
Lumiketone **7**	2980, 2950, 1711, 1613, 1430, 1370, 1340, 1310, 1255, 1180, 1028, 950, 900, 885	203 (2)*, 175 (2), 167 (1), 140 (1), 139 (1), 125, 105, 103, 77	257 (3,720), 208 (6,170)	1.54 (s, 3 H) 2.12 (m, $J \sim 1$, 3 H) 2.59 (d, J = 5, 1 H) 2.89 (d, J = 5, 1 H) 5.67 (m, 1 H)
Lumiketone **8**	2990, 2950, 1709, 1622, 1430, 1375, 1270, 1180, 1120, 1020, 910, 870	238 (3), 203 (2)*, 175 (2), 167 (1), 140 (1), 139 (1), 125, 105, 94, 77	266 (3,630), 212 (6,170)	1.62 (s, 3 H) 2.15 (d, $J \sim 1$, 3 H) 2.31 (d, J = 5, 1 H) 2.54 (d, J = 5, 1 H) 5.67 (m, 1 H)
Ketone **10** (X)	2990, 2910, 1695, 1625, 1450, 1410, 1390, 1350, 1290, 1270, 1185, 1155, 1050, 990, 940, 928	274 (4), 239 (3), 223 (3), 203 (2), 199, 197, 175, 157*, 129, 116, 93, 77	250 (9,320), 315 (sh), 325 (sh)	1.47 (s, 3 H) 2.13 (s, 3 H) 2.88 (m, 4 H)
Ketone **13** (Y)	2990, 1720, 1620, 1435, 1375, 1305, 1270, 1180, 1080, 1040, 945, 910, 860	238 (3), 203 (2)*, 175 (2), 167 (2), 140 (1), 139, 125, 105, 94, 77	234 (9,960)	1.97 (m, 3 H) 2.27 (d, $J \sim 1$, 3 H) 3.07 (d, J = 6, 1 H) 3.77 (d, J = 6, 1 H) 6.03 (m, 1 H)
Dihydroketone **19**	2960, 1745, 1450, 1420, 1375, 1320, 1260, 1240, 1190, 1150, 1100, 1045, 1020, 960, 905, 880, 840	240 (3), 205 (2), 198 (3), 187 (2), 163 (2)*, 141 (1), 127 (1), 95, 91, 89, 87, 81, 77		1.19 (d, J = 6.5, 3 H) 1.61 (s, 3 H) 1.8–3.0 (m, 5 H)
Dihydroketone **20**	2960, 1745, 1450, 1400, 1380, 1270, 1190, 1160, 1100, 1040, 1015, 960, 900	*e*		0.94 (d, J = 7.0, 3 H) 1.78 (s, 3 H) 1.9–3.0 (m, 5 H)

[a] Spectra in CCl_4. [b] Number of chlorine atoms in ion shown in parentheses, based on relative intensities of M + 2 and M + 4 ions. Base peak designated by an asterisk. [c] Spectra in ethanol unless indicated otherwise. [d] Peaks in ppm (δ) relative to internal tetramethylsilane. CCl_4 solvent, [e] Not determined.

at Stevens Institute of Technology was initiated before B was isolated and verified our independent assignment made above on the basis of the spectral data.[9]

On the basis of this unequivocal stereochemical assignment, the stereochemistry of the lumiketone **4** formed stereospecifically from dienone **1**[2] can be assigned as **9**. The C-6 methyl resonance of **4** at δ 1.55 is the same as in ketone A (**7**), while the cyclopropane proton resonances in **4** at δ 2.65 and 3.20 are much more consistent with these found for **7** than for **8**.

Lumiketone B (**8**) was not formed on photolysis of A (**7**) in *tert*-butyl alcohol, nor was A formed on photolysis of B. Heating of xylene solutions of dienone **5** at reflux for 3 days gave neither A nor B. Furthermore, heating A (**7**) at reflux in toluene for 3 hr led to complete recovery of the material (no new products according to glpc analysis), while B (**8**) proved to be thermally labile under similar conditions, giving photoproduct Y but not any measurable amounts of A. Thus, the two lumiketones must be primary photoproducts of dienone A and are not equilibrated thermally or photochemically. The absence of photolytic interconversion of **7** and **8** is consistent with results of earlier studies of sets of epimeric lumiketones[10,11] and is in contrast to the known photoisomerization of epimeric bicyclo[3.1.0]hex-2-enes and bicyclo[3.1.0]hexanones.[12]

Photoproduct X is a white solid mp 89–90°. The elemental analysis and mass spectrum indicate a molecular formula $C_9H_{10}Cl_4O$. This photoproduct was not formed from either dienone **5** or lumiketones **7** and **8** on treatment with hydrochloric acid in *tert*-butyl alcohol in the dark or on heating the lumiketones in boiling xylene. Photoproduct X was formed on photolysis of either of the lumiketones in *tert*-butyl alcohol at 254 nm. In the presence of triethylamine, the yield of X was appreciably reduced on photolysis of **5**, **7**, or **8**, and a similar effect was seen if the photolysis solutions were continuously purged with nitrogen gas at a high flow rate in the absence of triethylamine.

This new product showed ir and uv spectra (Table I) characteristic of an α,β-unsaturated ketone. The nmr spectrum had quaternary (δ 1.47) and vinylic (δ 2.13) methyls and no vinyl hydrogens. The base peak in the mass spectrum corresponds to $M^+ - CCl_3$, prominent in all compounds studied in our laboratory containing geminal methyl and trichloromethyl groups. On the basis of these data, structure **10** is assigned to this photoproduct. Spectral data are available for a similar compound **11**[13] and compare very well with those of

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[9] D. I. Schuster, K. V. Prabhu, S. Adcock, J. van der Veen, and H. Fujiwara, *J. Amer. Chem. Soc.*, **93**, 1557 (1971).

[10] H. E. Zimmerman and J. O. Grunewald, *J. Amer. Chem. Soc.*, **89**, 5163 (1967).

[11] D. I. Schuster and W. V. Curran, *J. Org. Chem.*, **35**, 4192 (1970).

[12] D. L. Garin and K. O. Henderson, *Tetrahedron Lett.*, 2009 (1970); B. M. Resnick, unpublished results from this laboratory.

[13] M. Tomoeda, M. Inuzuka, T. Furnata, M. Shinozuka, and T. Takahashi, *Tetrahedron*, **24**, 959 (1968).

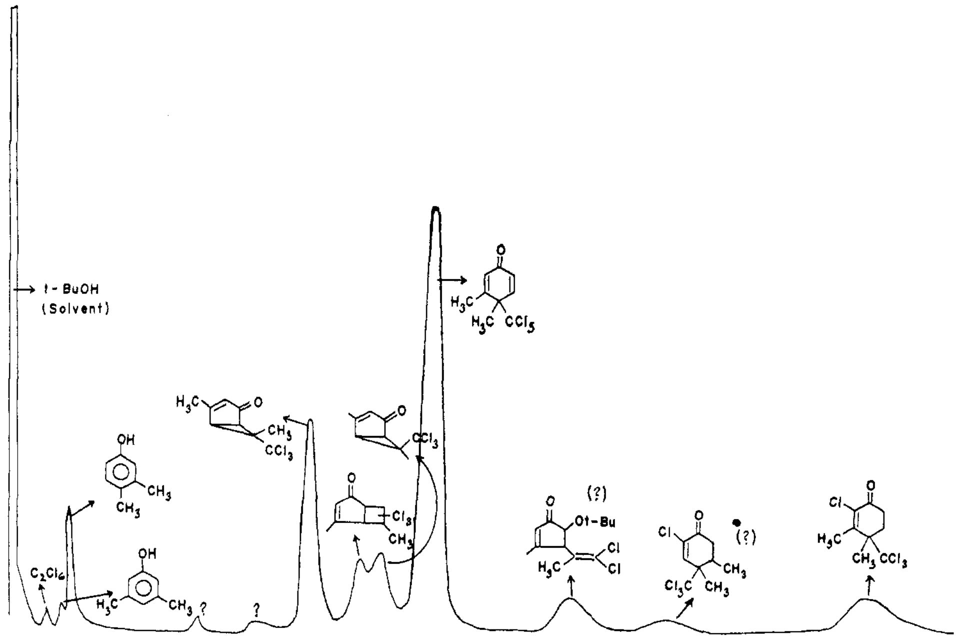
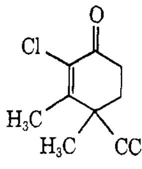


Figure 1. Typical vapor chromatogram of a *tert*-butyl alcohol solution of dienone **5** after photolysis for 1 hr at 254 nm.



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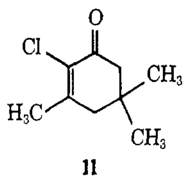

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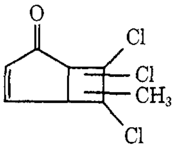
10: ir bands at 1625 and 1695 cm^{-1} for **10** and at 1618 and 1690 cm^{-1} for **11**; uv $\lambda_{\max}^{\mathrm{EtOH}}$ 250 nm (ϵ 9320) for **10** and 253 (ϵ 9900) for **11**; nmr (CCl$_4$) vinylic methyl at δ 2.13 for **10** and 2.13 for **11**.

The last compound to be isolated from the silica gel column was a white solid, mp 64–65°. Again, the ir and uv data (Table I) indicate an α,β-unsaturated ketone. The elemental analysis and mass spectrum indicate this is yet another isomer of dienone **5**. There is a peak corresponding to M$^+$ − CH$_3$ not noticed with the lumiketones, as well as the peak corresponding to M$^+$ − C$_3$H$_3$Cl$_3$. The nmr spectrum showed one vinyl proton, a vinyl methyl, a quarternary methyl at δ 1.97 (deshielded compared to **5**, **7**, and **8**), and two 1 H doublets. The compound gave an immediate white precipitate on treatment with an alcoholic silver nitrate solution, indicating a labile chlorine.

This photoproduct Y could be formed on photolysis of **7** in *tert*-butyl alcohol at 254 nm. It was also formed slowly on allowing **8** to stand at room temperature and more rapidly on heating **8** above 100°. It was observed previously[2] that photolysis of dienone **1** gave two bicyclo[3.2.0]hept-3-en-2-ones which were found to be secondary photoproducts derived from further photolysis of the first-formed lumiketone **9**. The structure of these ketones could be generally represented as in **12**, with the uncertainty as to placement of the methyls at C-6 or C-7 and exo or endo. The data for photoproduct Y (Table I) are quite comparable to the data for one of these ketones **12**: ir in CCl$_4$, carbonyl at 1740 cm^{-1}; uv $\lambda_{\max}^{\mathrm{dioxane}}$ 226 nm (ϵ 7200); nmr (CDCl$_3$) δ 1.98 (3 H), 3.20 (1 H), and 4.04 (1 H). On the basis of these data and analogy with the behavior of dienone **1** and lumiketone **9**, the generalized structure **13** is assigned to photoproduct Y. Again, the exact location of the methyl is not unequivocally provided by these data.



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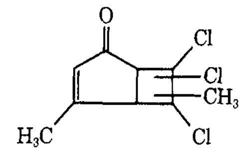

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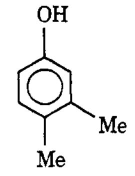
The four new ketone photoproducts plus recovered dienone accounted for 78% of the material when 10 g of dienone **5** was photolyzed in 250 ml of *tert*-butyl alcohol (see Experimental Section). Other products of fragmentation reactions[2] (see later discussion) were identified by glpc by coinjection with authentic samples, but the amounts of these products were not established. These were hexachloroethane, chloroform, 3,4-dimethylphenol (**14**) and 3,5-dimethylphenol (**15**). The glpc peaks attributed to the phenols disappeared when the photolysate was treated with dilute alkali before analysis. The rearranged phenol **15** was identified by glpc coinjection on two different columns. Phenol **15** was also formed on irradiation of *tert*-butyl alcohol solutions of lumiketones **7** and **8**, indicating that it is probably a secondary photoproduct.

Hydrogen chloride was also a product of photolysis of **5**, as established by sweeping the solution during photolysis with nitrogen into a silver nitrate solution, whereupon a white ammonia-soluble precipitate formed. Photolysis of **5** in hexane in the presence of triethylamine gave the amine hydrochloride, identified by its melting point and mixture melting point with an authentic sample.

A vapor chromatogram of a typical *tert*-butyl alcohol photolysis solution of **5** on 5% SE-30 is shown in Figure 1. There are two minor peaks at short retention time which remain unidentified and two somewhat larger peaks at longer retention times. These are tentatively suggested to be the alternate HCl addition product **16** (see later discussion) and ether **18** (R = *tert*-butyl), the



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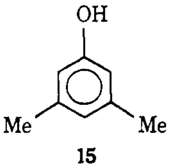

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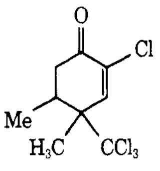

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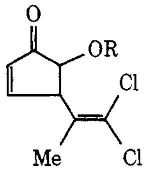

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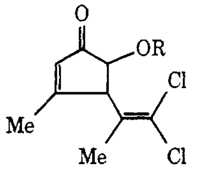

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latter analogous to ethers of type **17** formed on photolysis of dienone **1** in alcohol solution. The material balance in the *t*-BuOH photolysis is quite high, probably >90% in terms of converted dienone **5**.

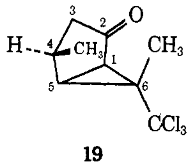
Photolysis of 5 in Other Solvents. When dienone **5** was irradiated at 254 nm in benzene, the products were lumiketones **7** and **8** (the latter seen only in trace amounts after prolonged irradiation), C_2Cl_6, 3,4-dimethylphenol **14**, and ketone **13**. Two additional products, not identified, were observed in the vapor chromatogram. Biphenyl was not detected on excitation of **5** in benzene.

In hydrogen-donor solvents (hexane, cyclohexane, dioxane, and toluene), the products of photolysis of **5** were lumiketone **7**, ketone **13**, 3,4-dimethylphenol **14**, and C_2Cl_6. None of ketone **10** could be detected. Bibenzyl was produced in the toluene runs.

In polar solvents which do not act effectively as H donors (methanol, trifluoroethanol, and acetonitrile), a wide spectrum of products is formed, including both lumiketones **7** and **8**, ketones **10** and **13**, 3,4-dimethylphenol (**14**), and C_2Cl_6. A new major product was formed in methanol, which is probably the ether **18** (R = methyl),[2] although this compound was not isolated. The amounts of lumiketone **8** in methanol photolyses were such as to be barely detectable by glpc, definitely much less than were formed in *t*-BuOH or benzene.

Photolysis of Lumiketones 7 and 8. When a *t*-BuOH solution of the major lumiketone epimer **7** was irradiated in quartz at 254 nm, the major products formed were ketones **10** and **13** and 3,5-dimethylphenol (**15**). Neither lumiketone **8**, C_2Cl_6, or 3,4-dimethylphenol (**14**) were formed in this reaction. Similarly, irradiation of lumiketone **8** gave ketone **10** and **15**, and none of lumiketone **7**, **14**, C_2Cl_6, or ketone **13**. The yield of **10** decreased in both cases when the photolysis was carried out in the presence of triethylamine. Also, **10** was not formed on adding dilute HCl to *t*-BuOH solutions of **7** or **8** in the dark.

Hydrogenation of Lumiketones 7 and 8. Catalytic hydrogenation of the lumiketone epimers with 1 equiv of hydrogen over 5% Pd/C gave the respective dihydrolumiketones **19** and **20**. Spectral data for these compounds are summarized in Table I. It was expected that hydrogen would add to the double bond from the less hindered exo (outside) face of the double bond, leading to products with the C-4 methyl endo (inside). The most apparent spectral differences in these compounds are (1) that the C-4 methyl in **20** is significantly shielded relative to the same methyl in **19** (δ 0.94 *vs.* 1.19) and (2) that the C-6 methyl in **20** is deshielded relative to the same methyl in **19** (δ 1.78 *vs.* 1.61). While the close proximity of the C-4 methyl and C-6 CCl_3 in **20** might have been expected to lead to steric compression and consequent deshielding,[14,15] the observed relative shielding in **20** must be ascribed to the effect of the nonbonding electrons in the CCl_3 group on the C-4 methyl. Shielding of the *endo*-6-methyl by the carbonyl also appears to dominate.[16] The hydrogenation product of lumiketone **4**, derived from dienone **1**, shows a resonance for the 6-methyl group at δ 1.55,[2] indicating an endo orientation of the methyl group as in **19**, consistent with the assignment of stereochemistry made above.



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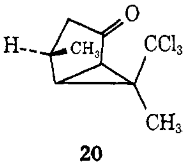

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Quantum Yields. Product Formation. Absolute quantum yields for formation of lumiketone **7** and 3,4-dimethylphenol (**14**) were measured at 366 nm in four solvents in duplicate. The results are summarized in Table II. Ferrioxalate actinometry[17] was used, and the product yields were determined by glpc with internal standards.

Table II. Quantum Yields for Product Formation at 366 nm[a]

Run	Solvent	Lumiketone **7**	Phenol **24**
1	*tert*-Butyl alcohol[b]	0.52	
2		0.53	
		Av. 0.53 ± 0.01	
3	Benzene[b]	0.35	
4		0.39	
		Av. 0.37 ± 0.02	
5	2-Propanol[b]	0.24	0.074
6		0.29	0.062
		Av. 0.27 ± 0.02	Av. 0.068 ± 0.006
7	Ethyl ether[c]	0.064	0.51
8		0.056	0.43
		Av. 0.060 ± 0.004	Av. 0.47 ± 0.04

[a] The light source was a 200-W super-pressure mercury lamp used with a Bausch and Lomb high-intensity grating monochromator. All solutions were deoxygenated by bubbling nitrogen gas through the solutions for 1 hr prior to photolysis. Glpc analysis was on a 6 ft × 1/8 in. 5% SE-30 on Chromosorb G/AW/DMCS column. A split beam technique was used, in which the light from the monochromator was split by a fused silica disk, one beam focussed on the sample solution and the other on the actinometer solution. The ratio of light intensities in the two beams was previously determined with actinometer solutions in both positions. [b] Irradiation time was 15 min. [c] Irradiation time was 20 min.

Intersystem Crossing. The quantum yield for formation of triplets was determined by a triplet counting technique[18] using 1,3-cyclohexadiene (CHD) as the

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(14) See S. Winstein, P. Carter, F. A. L. Anet, and A. J. R. Bourn, *J. Amer. Chem. Soc.*, **87**, 5257 (1965), and references cited therein.

(15) D. I. Schuster and W. V. Curran, *J. Org. Chem.*, **35**, 4192 (1970).

(16) In the absence of other substituents, there is very little difference (δ 1.09 and 1.11 ppm) between the resonances of *exo*- and *endo*-6-methyl groups in a bicyclo[3.1.0]hexan-2-one: O. L. Chapman, T. A. Rettig, A. A. Griswold, A. I. Dutton, and P. Fitton, *Tetrahedron Lett.*, 2049 (1963).

(17) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 517 (1956).

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

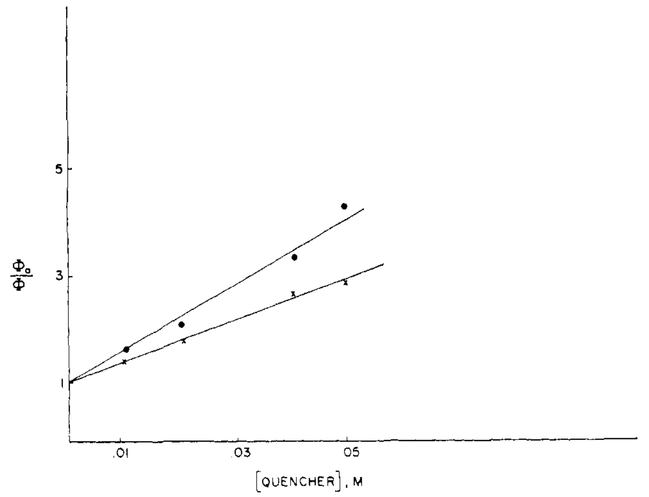

Figure 2. Stern-Volmer plots for quenching of formation of lumiketone 7 in *tert*-butyl alochol. Quenchers: *trans*-piperylene (×); 1,3-cyclohexadiene (●).

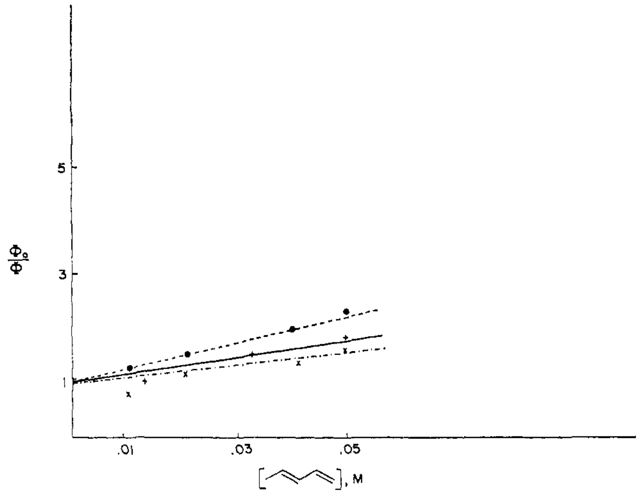

Figure 3. Stern-Volmer plots for quenching of formation of lumiketone 7 in 2-propanol by *trans*-piperylene at varying ketone concentrations: 0.018 *M* (●); 0.101 *M* (+); 0.167 *M* (–·×·–).

quencher (for kinetic quenching studies see below). The amount of CHD dimers[19] formed at 366 nm in the presence of CHD in rigorously degassed solutions on absorption of light by dienone **5** was quantitatively compared with the yield of CHD dimers produced competitively on absorption by benzophenone using a split-beam technique. After irradiation at 366 nm, yields of dimers in each solution were determined by glpc with internal standards. After correction for differences in optical densities in the solutions, and assuming the diene concentration (1.26 *M*) was sufficient to quench all ketone triplets, the ratio of CHD dimer yields is equivalent to the ratio of intersystem crossing yields (Φ_{ST}). From the value of Φ_{ST} for benzophenone of 1.00,[18–20] values of Φ_{ST} for dienone **5** of 0.95 ± 0.02 and 0.96 ± 0.02 were determined.[21]

Sensitization and Quenching Studies. Sensitization. Photolysis of benzene solutions of dienone **5** in the presence of several typical triplet sensitizers, under conditions such that >95% of the Pyrex-filtered light was absorbed by the sensitizer, led to formation of lumiketone **7**. The sensitizers used were acetophenone (E_T 74 kcal/mol), benzophenone (E_T 69), and thioxanthone (E_T 65). Comparison with a dienone solution with the same absorbance in the absence of sensitizer indicated relative sensitization yields on the order of 23–35%. Because of possibilities of sensitizer self-quenching,[22] as well as other possible sources of inefficiency on transfer of triplet excitation to dienone **5**,[23] these data have only qualitative significance.

Quenching Studies. The formation of lumiketone **7** from dienone **5** in benzene was found qualitatively to be quenched in the presence of naphthalene (E_T 61). Quantitative studies were carried out using *trans*-piperylene (E_T 59) and 1,3-cyclohexadiene (E_T 52.5) as triplet quenchers in three solvents, *viz.*, *tert*-butyl alcohol, 2-propanol, and benzene, using light (Hanovia 450-W lamp and Corning 7380 filters) with λ ≤350 nm, with solutions in Pyrex tubes in a "merry-go-round" apparatus.[24] Product yields were measured by glpc with internal standards added after photolysis. Plots of relative quantum yields for product formation *vs.* quencher concentration are shown in Figures 2–6. Runs were made at varying concentrations of dienone **5** in each solvent.

Figure 2 shows quenching plots in *t*-BuOH for both quenchers at similar, but not identical, ketone concentrations. Figure 3 shows quenching by *trans*-piperylene of formation of lumiketone **7** in 2-propanol at three different ketone concentrations and indicates that the slopes decrease as the ketone concentration increases, while a similar plot (Figure 4) for formation of 3,4-dimethylphenol in this solvent shows, in contrast, an *increase* in slope as ketone concentration is increased. Figure 5, analogous to Figure 2, shows results of quenching of formation of lumiketone **7** in benzene with both quenchers, using somewhat different dienone concentrations. Finally, Figure 6 dramatically illustrates the different efficiencies of quenching by *trans*-piperylene of formation of lumiketone **7** and phenol **14** in the same benzene solution. The values of the Stern-Volmer slopes, from a least-squares fit of the data to eq 1, are

$$\Phi_0/\Phi_q = 1 + k_q\tau_0[Q] \qquad (1)$$

summarized in Table III, where k_q is the rate constant for energy transfer, and τ_0 is the lifetime of dienone triplet in the absence of quencher under the given conditions of solvent and concentration.

Mechanistic Discussion

Stereoselectivity in the Lumiketone Rearrangement. Irradiation of dienones with different alkyl groups at C-4 invariably leads to predominant formation of lumiketone with the bulkier alkyl group in the endo orientation at C-6[6,25] as in the example of **22** shown below. Furthermore, as the steric requirement of the sub-

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[19] G. S. Hammond, N. J. Turro, and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1144 (1962).

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

[21] We are grateful to Mr. George Barile for this experiment.

[22] D. I. Schuster and T. M. Weil, *J. Amer. Chem. Soc.*, **95**, 4091 (1973); D. I. Schuster and M. D. Goldstein, *ibid.*, **95**, 986 (1973).

[23] P. S. Engel and B. M. Monroe, *Advan. Photochem.*, **8**, 245 (1971).

[24] F. G. Moses, R. S. H. Liu, and B. M. Monroe, *Mol. Photochem.*, **1**, 245 (1969).

[25] T. R. Rodgers and H. Hart, *Tetrahedron Lett.*, 4485 (1969).

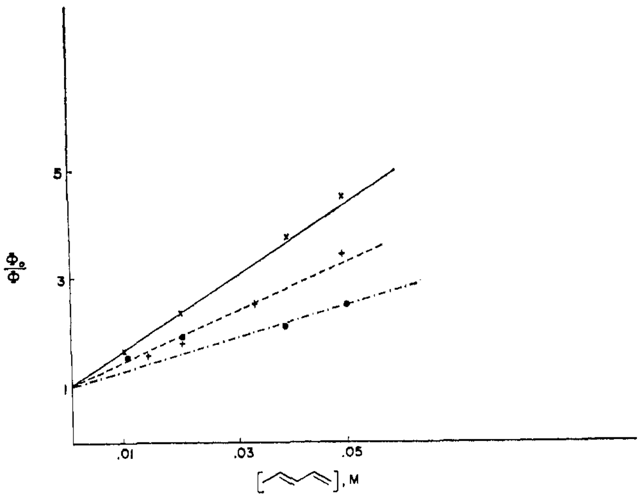


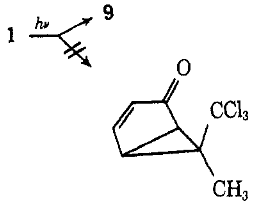
Figure 4. Stern–Volmer plots for quenching of formation of 3,4-dimethylphenol (**14**) in 2-propanol by *trans*-piperylene at varying ketone concentrations: 0.018 M (-●-); 0.101 M (-+-); 0.167 M (×).

Table III. Stern–Volmer Quenching Slopes

		Quenching slopes, $k_q\tau_0$, M^{-1}		
		Lumiketone **7**		Phenol **14**
Solvent	[Dienone **5**], M	Piperylene[a]	CHD[a]	Piperylene[a]
tert-Butyl alcohol	0.194	35.1		
	0.157		45.5	
2-Propanol	0.167	14.9		69.9
	0.101	18.3		51.4
	0.0182	26.2		26.0
Benzene	0.220	33.2		
	0.126		67.7	
	0.134	27.4		160

[a] The quencher was either *trans*-piperylene or 1,3-cyclohexadiene (CHD).

stituents at C-3 and C-5 in **22** increased, an increased proportion of the lumiketone isomer **23** with the bulkier group (n-Pr) in the endo orientation was formed.[25] However, dienone **1** leads to lumiketone **9** and not **21**,



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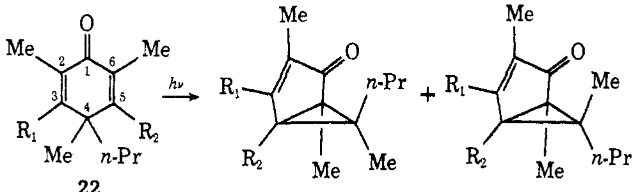


22

23
major

24
minor

while irradiation of dienone **5** gives lumiketone **7** as the major isomer and **8** as the minor isomer, in an initial ratio of about 5:1.[26] Thus, in the trichloromethyl dienones **1** and **5**, the photochemical rearrangement occurs so as to place the bulkier substituent, CCl_3, in the exo (outside) and not the endo (inside) orientation.

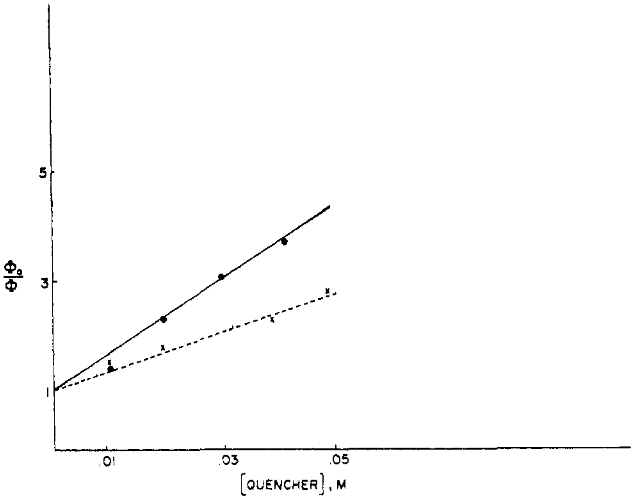


Figure 5. Stern–Volmer plots for quenching of formation of lumiketone **7** in benzene by *trans*-piperylene (×) and 1,3-cyclohexadiene (●).

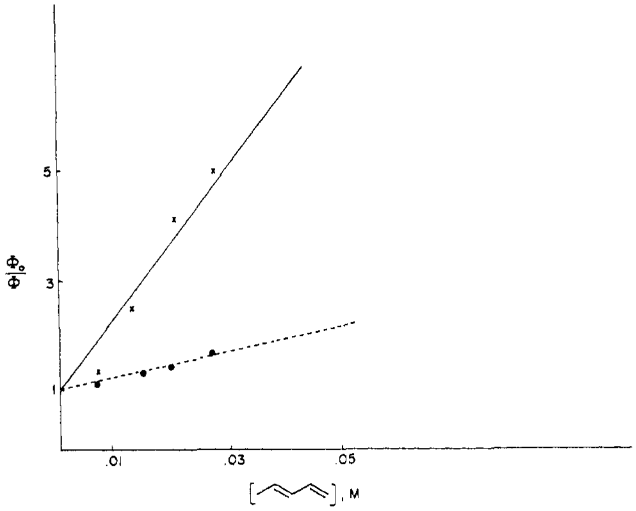
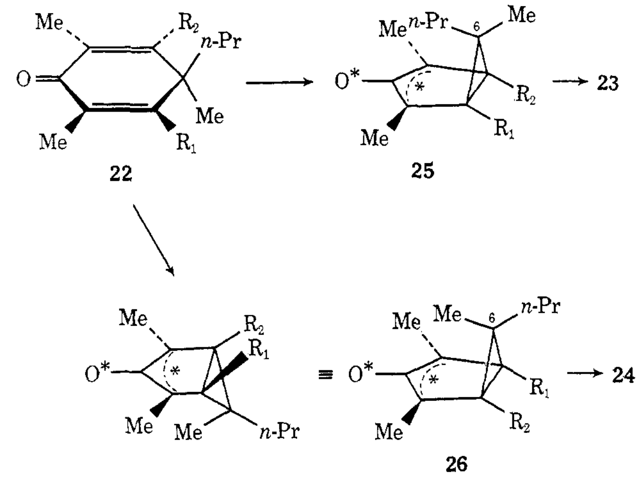


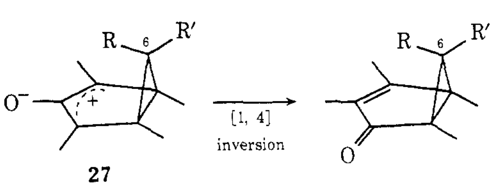
Figure 6. Stern–Volmer plots for quenching of formation of lumiketone **7** (●) and 3,4-dimethylphenol (**14**) (×) in benzene by *trans*-piperylene.

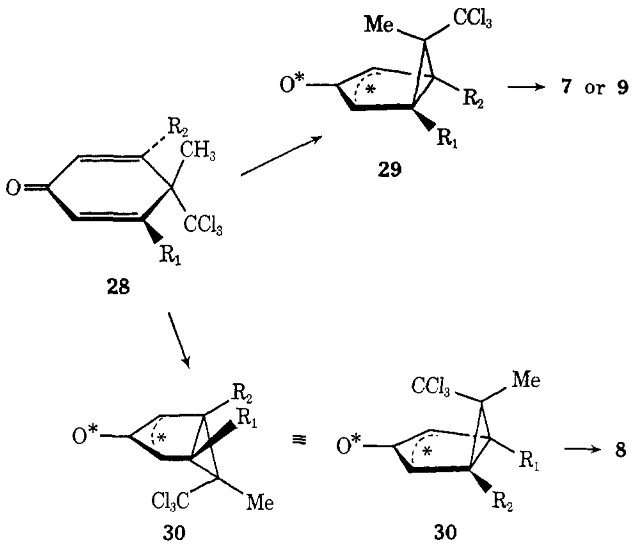
The contrasting results with these sets of dienones indicate that more than one factor controls the stereochemical course of these rearrangements. Rodgers and Hart[25] argued plausibly that increased steric requirements of substituents at C-3 and C-5 directs the bulkier C-4 substituent into the endo orientation, in the absence of other perturbations in the system. Thus, in the initial disrotatory ring closure leading to formation of a bond between C-3 and C-5, it was proposed that the intermediate of structure **25** would be formed from **22** in preference to **26**. This is because the molecular motions leading to **26** would require the larger C-4 substituent (n-propyl in this case) to pass by the substituents at C-3 and C-5, which becomes relatively more difficult as the bulk of these substituents is increased. However, this rationalization depends on the

(26) In our earlier communication,[9] a **7**/**8** ratio of 15:1 was reported based on glpc analysis. It was later found that **8** was thermally unstable under the glpc conditions, being partially converted to **13**. The ratio of 5:1 is based on the weights of the products obtained by column chromatography of short-term (<10% conversion) photolyses.



assumption that the position of substituents at C-6 (formerly C-4) in the intermediates **25** and **26** is unchanged in the subsequent 1,4-sigmatropic shift which leads to lumiketone, that is, that the product stereochemistry is determined completely in the first stage of the reaction. As a ground state rearrangement of a zwitterion **27**,[27] the 1,4-sigmatropic shift is predicted to occur with inversion of configuration at C-6,[28,29] maintaining the exo–endo orientation of substituents at C-6 on proceeding from the intermediate **27** to lumiketone. However, there is as yet no *direct* experimental evidence which proves *unequivocally* that the sigmatropic shift indeed proceeds in this manner in the photochemistry of monocyclic dienones, although there is circumstantial evidence to this effect.[30,32]





Upon excitation of the generalized trichloromethyl-substituted dienone **28**, disrotatory ring closure with formation of the 3,5 bond results in intermediate **29** (CCl_3 exo) or **30** (CCl_3 endo) by either upward or downward movement, respectively, of C-4. The steric factors would favor the downward motion to give **30** since this avoids interaction of the large CCl_3 group with the flanking substituents at C-3 and C-5. However, this same motion propels the electron-rich CCl_3 group into the heart of the dienone π system, which would induce considerable coulombic charge repulsions. In the extreme situation when **30** is fully formed, there should be extensive repulsion between the nearly parallel CCl_3 and $>C{=}O$ dipoles. Thus, the pathway leading to **30** is electronically unfavorable (*i.e.*, of higher energy), although sterically favored, compared with that leading to **29**. The experimental observations with dienone **1** (making the same assumptions regarding the stereochemistry of the 1,4-sigmatropic shift as made by Rodgers and Hart[25]) indicate that *only* one mode of disrotatory ring closure takes place, the motion which results in **29** with CCl_3 exo. Thus, the electronic effects dominate the reaction in this system, so that the barrier to formation of intermediate **30** when $R_1 = R_2 = H$ is sufficiently higher than that leading to **29** that none of **30** is formed (or, at least no products derived from **30** have been detected in any study to date). There is, however, a subtle balance of steric and electronic effects, as seen on introduction of only one methyl group. In the case of dienone **5**, the electronic effects are hardly unchanged from those in **1**, but the steric effects operating against formation of **29** when $R_1 = CH_3$ and $R_2 = H$ are enhanced, resulting in competitive formation of both intermediates, with **29** apparently still in excess. Furthermore, formation of products derived from **30** seems to occur only in polar solvents where coulombic interactions can be somewhat reduced by solvation, permitting the steric effects a more prominent role, and thus diverting at least some of the reaction along the sterically more favorable pathway leading to **30**. The present rationalization of the results leads to some obvious predictions. First of all, as the number and bulk of flanking substituents in dienones of type **28** is increased, the proportion of products derived from intermediates with CCl_3 endo should increase.[33] Secondly, the electronic effects introduced by the CCl_3 group should be shown by other electron-withdrawing groups, such as CF_3, CO_2R, CN, etc. In any event, it is obvious that both electronic and steric effects must be invoked in discussions of the stereochemical consequences of cyclohexadienone rearrangements.[33a]

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(27) H. E. Zimmerman and D. I. Schuster, *J. Amer. Chem. Soc.*, **84**, 4527 (1962); H. E. Zimmerman, *Advan. Photochem.*, **1**, 183 (1963).

(28) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, p 144 ff.

(29) C. H. Depuy and O. L. Chapman, "Molecular Reactions and Photochemistry," Prentice-Hall, Englewood Cliffs, N. J., 1972.

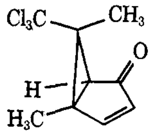
(30) In the case of a tetracyclic spirodienone derived from dehydrotestosterone acetate, it was concluded[31] that the formation of lumiketones involved exclusively inversion of configuration in the sigmatropic rearrangement. The complexity of this system, however, is such that extrapolation of behavior from it to simple systems is sufficiently indirect as to be ambiguous.

(31) F. Frei, C. Ganter, K. Kagi, K. Kocsis, M. Miljkovic, A. Siewinski, R. Wenger, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **49**, 1049 (1966).

(32) Determination of the stereochemistry of some ground state sigmatropic rearrangements formally related to the zwitterion rearrangement thoroughly supports the theoretical predictions; see R. F. Childs and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 7145 (1968); T. M. Brennan and R. K. Hill, *ibid.*, **90**, 5614 (1968); H. E. Zimmerman, D. S. Crumrine, D. Döpp, and P. S. Huyffer, *ibid.*, **91**, 434 (1969).

(33) Some preliminary studies have been made with 3,4,5-trimethyl-4-trichloromethyl-2,5-cyclohexadienone (**28**, $R_1 = R_2 = CH_3$), but difficulty was encountered in isolating the lumiketones. Phenols were the predominant products in all solvents studied.

Mechanisms for Formation of Products. Lumiketones. In addition to the formation of lumiketones **7** and **8**, it was possible *a priori* that lumiketones **31** and **32** could have been formed by sigmatropic rearrangement of intermediates **29** and **30** in the opposite direction on the five-membered ring. However, as in several cases of unsymmetrical dienones examined previously,[15,34] rearrangement occurred only in one direction, so as to place the C-3 alkyl group in the β position of the α,β-unsaturated ketone group rather than on the cyclopropane ring. An extended discussion of the sequence of intermediates involved in these rearrangements will appear elsewhere when we discuss the full results of our studies of quenching of zwitterions derived photochemically from cyclohexadienones.[3,35]



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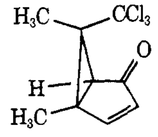

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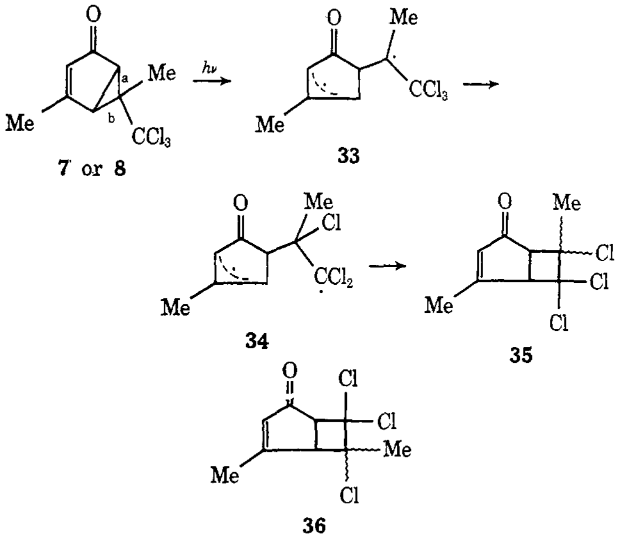
Ketone 13. The formation of this ketone photolytically from either of the epimeric lumiketones **7** and **8** is analogous to the formation of ketone **12** from lumiketone **9** in the unsubstituted series,[2] and a likely mechanism is shown in Scheme I. The more stable diradical **33**, formed preferentially by opening of bond "b" in the excited lumiketones, rearranges to **34** by a 1,2-chlorine shift[36] followed by ring closure at the allylic position (C-3). This proposed mechanism predicts the product has the constitution **35** (exo or endo orientation of the methyl group is unspecified) and not **36**, although this has not been settled on the basis of the available experimental data.

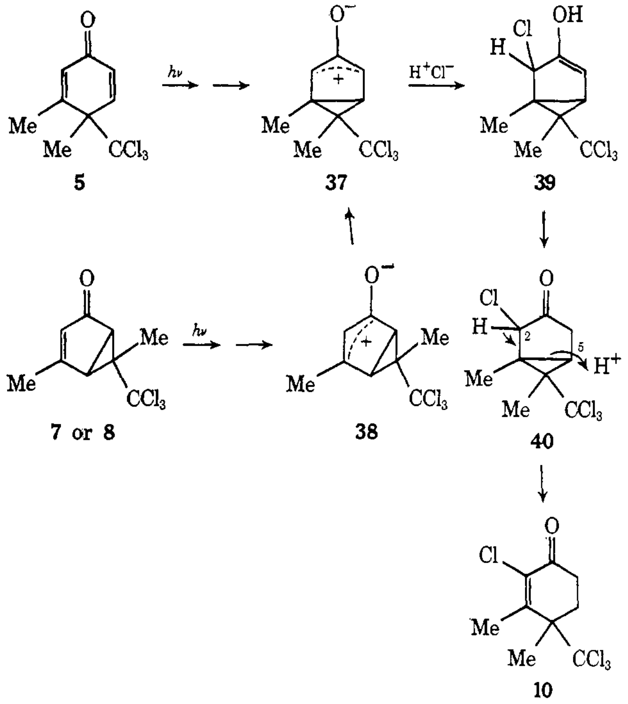
Scheme I. Mechanism for Formation of Ketone **13**

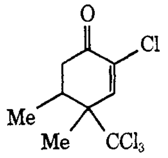


It should be noted that this same ketone **13** was formed on heating **8** but not **7**. This is consistent with the stereochemical assignments to these lumiketones, since **8** is a much more crowded molecule than **7** and thermal cleavage of bond "b" in **8** should be assisted by the relief of steric strain in the starting material.

Ketone 10. This ketone was formed when dienone **5** was irradiated in polar solvents or when lumiketones **7** and **8** were irradiated in *t*-BuOH but not on heating the lumiketones. In addition, **10** was not formed on addition of hydrogen chloride in the dark to solutions of **5**, **7**, **8**, or **13**. These observations indicate that ketone **10** arises from an excited state species or from a ground state species derived only from an electronically excited molecule. These observations are best understood on the basis of the scheme presented below (Scheme II). The zwitterion **37** (stereochemistry unassigned at this point) could arise from dienone **5** or it could be produced from excited lumiketones **7** or **8** by a reverse 1,4-sigmatropic shift, perhaps *via* **38**. From the work of Liu[3,35] it is known that zwitterions such as **37** can be intercepted by chloride ions. Accordingly, it is proposed that **37** reacts with HCl to give **39**, the tautomer of chloro ketone **40**. Ring opening upon protonation at C-5 and loss of a proton at C-2 would give **10**. The reaction to give **10** represents a new mode of trapping of photochemically generated zwitterions. Chloride addition at the opposite side of the zwitterion **27** would lead by the same mechanism to tetrachloro ketone **41**. This compound was not isolated, but it may correspond to one of the unassigned peaks in the vapor chromatogram (Figure 1).

Scheme II. Mechanism for Formation of Ketone **10**





41

(33a) Note Added in Proof. Similar effects operate in the photochemical ring closure of cyclohexadienyl cations derived from these and related dienones: J. W. Pavlik and R. J. Pasteris, abstr. ORGN 111, 167th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1–5, 1974.

(34) For recent reviews, see (a) P. J. Kropp, *Org. Photochem.*, **1**, 1 (1967); (b) K. Schaffner, *Advan. Photochem.*, **4**, 81 (1966).

(35) D. I. Schuster and K. Liu, to be submitted for publication; K. Liu, Ph.D. Dissertation, New York University, 1973.

(36) For examples of 1,2-chlorine shifts in free radical chemistry, see (a) W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966; (b) C. Walling, "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Wiley-Interscience, New York, N. Y., 1963, Chapter 7.

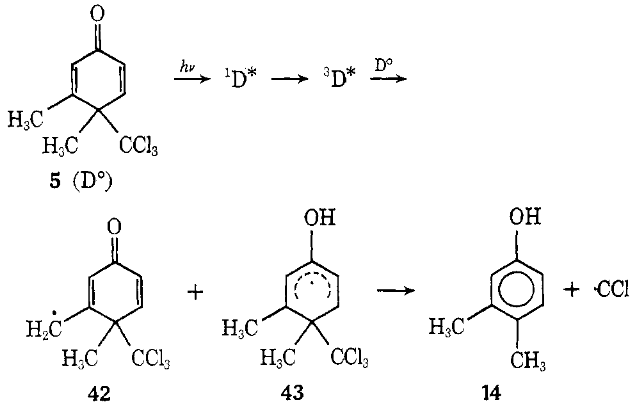
Phenols and Other Fragmentation Products. The free radical fragmentation reaction[37] in this system was found to be quite facile, giving 3,4-dimethylphenol (**14**) and either $CHCl_3$ or C_2Cl_6 in all the solvents studied. These observations differ from the case of **1**[2,37] where photochemical fragmentation of **1** to *p*-cresol was noted only in good free radical hydrogen-donor solvents. Thus, fragmentation of **1** to *p*-cresol was not observed at all in benzene, although phenol **14** is a major photoproduct of **5** in benzene. However, biphenyl was absent in the vapor chromatograms of the crude photoproduct mixture from benzene photolyses, in contrast to its formation in photochemical and free radical reactions[1,36a] involving H abstraction from benzene. Secondly, the data in Table IV show that the yields of phenol **14** and hexachloroethane were sharply dependent on the dienone concentration, indicating that the hydrogen donor in the benzene photolyses is the ketone itself. A suggested mechanism for the fragmentation reaction in benzene and other poor H-donor solvents (*e.g.*, *t*-BuOH and CF_3CH_2OH) is given in Scheme III, in which abstraction from the allylic methyl group at C-3 is proposed, leading to the allylic radical **42** and the ketyl **43**. Cleavage of the latter would give phenol **14** and the trichloromethyl radical, which (in benzene) mainly dimerizes. The fate of radical **42** is uncertain. It could regenerate starting material after H abstraction from some available donor (such as one of the ketone photoproducts) or it could dimerize to give a product not isolated by the techniques utilized. In good H-donor solvents, such as 2-propanol or toluene, the "normal" route in Scheme IV would presumably be followed.[2]

Table IV. Dependence of Product Yields in Benzene on Ketone Concentration[a]

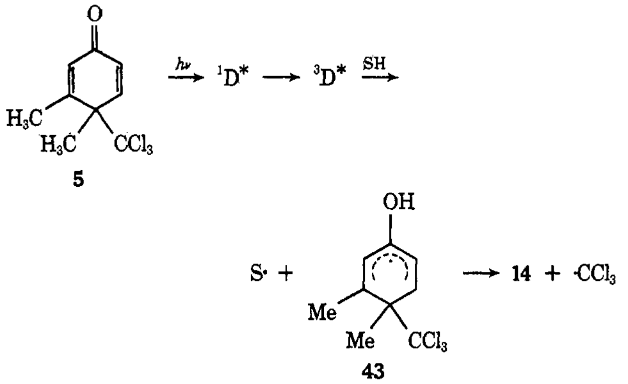
Concn of dienone **5**, *M*	Relative yields[b]	
	Phenol **14**	C_2Cl_6
0.042	1.00	1.00
0.084	3.33	3.01
0.125	6.16	4.77

[a] Photolysis in a "merry-go-round" at 254 nm for 1 hr in quartz tubes. [b] From glpc analysis on a 6 ft × 1/8 in. 5% SE-30 on Chromosorb G column. Areas were measured to those of an internal standard (biphenyl) added after photolysis. The yields given are in each case relative to the yields in the least concentrated solution taken as 1.00.

Scheme III. Mechanism for Formation of 3,4-Dimethylphenol in Benzene

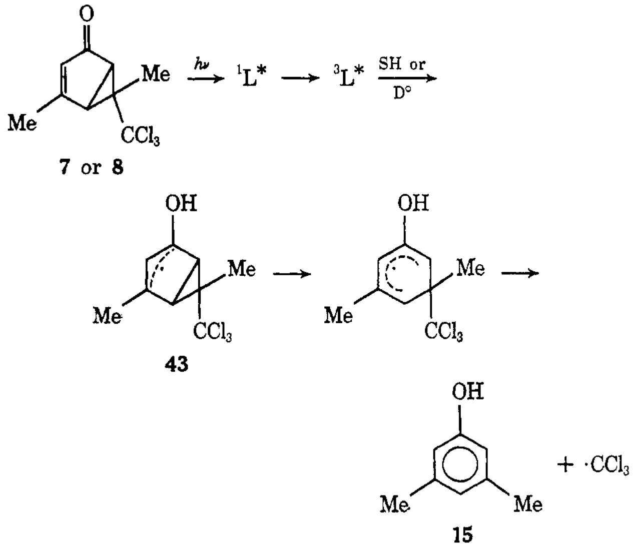


Scheme IV. Formation of 3,4-Dimethylphenol in H-Donor Solvents



There is no analogy in the photochemistry of **1**[2] for the formation of 3,5-dimethylphenol (**15**) from **5** in *t*-BuOH. Since **15** but not **14** was produced on irradiation of lumiketones **7** or **8** in *t*-BuOH, it appears that **15** is not a primary product of excitation of **5**. A reasonable mechanism for formation of **15** is given in Scheme V. The contrast with the lack of formation of *m*-cresol on excitation of **1** may have to do with the role of the ring methyl in stabilizing radical **43** and enhancing cleavage of the internal cyclopropane bond in competition with the cleavage of the external bonds in **7** and **8** which leads to **13** (see above).

Scheme V. Mechanism for Formation of 3,5-Dimethylphenol (**15**)



Hydrogen Chloride. By analogy with the well documented behavior of **1** in irradiation in alcohol solution,[2,3,35] formation of ethers of structure **18** was expected, according to Scheme VI. Additional products were indeed observed in the vapor chromatograms of methyl alcohol and *tert*-butyl alcohol photolysates of **1**, but the supposed ethers were not isolated. A by-product of this reaction is hydrogen chloride, and it is known that the alcohol solutions become increasingly acidic as reaction proceeds. In nonpolar solvents, such as benzene and hexane, the source of hydrogen chloride is less clear. Since chloroform gives HCl on irradiation at 254 nm, it is conceivable that chloroform produced initially on irradiation of **5** (see above) may undergo

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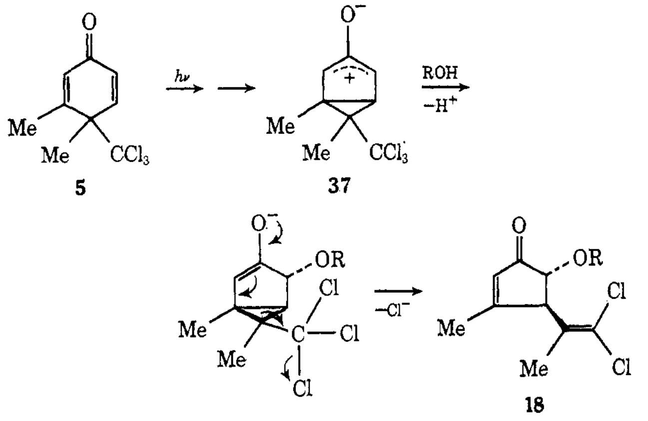
(37) D. I. Schuster and D. J. Patel, *J. Amer. Chem. Soc.*, **87**, 2515 (1965).

Scheme VI. Mechanism for Formation of Ethers **18** by Trapping of Zwitterion **37** with Alcohols



some photochemical decomposition to give HCl. Other reactions for which evidence was not otherwise obtained are conceivable as routes to HCl.[38]

Nature of Excited States. The sensitization and quenching data and the fact that the intersystem crossing efficiency on excitation of **5** is on the order of unity all support the conclusion that the photoreactions of **5** originate only from triplet excited states. The differential quenching observed for formation of lumiketone **7** and 3,4-dimethylphenol (**14**) in 2-propanol as well as benzene indicates that these products are derived from two different kinetically distinguishable triplet excited states. Furthermore, the Stern–Volmer slopes, $k_q\tau_0$, derived from the quenching data show opposite dependencies on the concentration of starting dienone. The slopes for quenching of lumiketone **7** decrease with increasing dienone concentration, while the slopes for quenching of phenol **14** show a pronounced increase. The effect is large and well outside of experimental error.

We attribute the concentration effect in the case of **7** to a decrease in triplet lifetime as ketone concentration is increased, *i.e.*, self-quenching. Thus we propose that there are at least two competitive pathways for the triplet $^3K^*$ involved in formation of **7**. One of these paths, summarized in eq 2, involves decay to a zwitterion **37** which rearranges to **7**. The other path involving self-quenching, which may or may not involve a triplet excimer intermediate,[22] is basically a pathway for energy wastage, resulting in enhanced deactivation of excited state to ground state.[23] Self-quenching is a well known mode of decay of π,π^* triplets, for ketones as well as hydrocarbons, and values of k_{sq} can be nearly diffusion controlled, on the order of 10^{8-9} M^{-1} sec^{-1}.[22,23,39] We have recently reported that self-quenching of ketone $^3n,\pi^*$ states, as in the case of benzophenone,[22] can be kinetically significant, but only in poor H-donor solvents such as benzene, water, and CCl$_4$. The pronounced self-quenching effect seen for $^3K^*$ in 2-propanol is therefore most consistent with assignment of a $^3\pi,\pi^*$ configuration to this triplet. Thus, we conclude that the lumiketone rearrangement in the case of **5** proceeds from a π,π^* triplet. This conclusion is contrary to that reached in the earlier work on **1**[2] and also to the assignments of configuration to reactive triplets in Type A rearrangements of 4,4-diarylcyclohexadienones made by Zimmerman and his coworkers.[27,40,41] On the other hand, it was previously postulated that the lumiketone rearrangement in α-santonin proceeds *via* a $^3\pi,\pi^*$ state.[42] The photorearrangement of a number of cyclohexenones to bicyclic[3.1.0]hexanones, which is in some ways analogous to the lumiketone rearrangement of cyclohexadienones, has also been ascribed to intermediate $^3\pi,\pi^*$ states in several investigations.[43]

$$^3K^* \xrightarrow{k_r} 37 \longrightarrow 7 \tag{2}$$

$$^3K^* + K^0 \xrightarrow{k_{sq}} {}^3[K\cdots K]^* \longrightarrow 2K^0 \tag{3}$$

$$^3K^* \xrightarrow{k_d} K^0 \tag{4}$$

Based on the idea that, in general, ketones undergo photoreduction efficiently only *via* $^3n,\pi^*$ excited states,[44,45] we suggest that the triplet responsible for formation of 3,4-dimethylphenol (**14**) has a $^3n,\pi^*$ configuration. The novel observation that the Stern–Volmer slopes *increase* for formation of **14** on increasing the concentration of **5** in 2-propanol is perplexing. This might arise if ground state dienone were consuming or interacting with some species which might otherwise quench the n,π^* triplet. A specific suggestion along these lines arises from studies of Liu[35] made after completion of the present investigation,[38] involving the role of CCl$_3\cdot$ produced concomitantly with phenols in the photofragmentation of trichloromethyl dienones. Using $^3D^*$ to denote the triplet responsible for phenol formation, the following series of reactions is proposed in 2-propanol solution.

$$^3D^* + Me_2CHOH \longrightarrow DH\cdot + Me_2\dot{C}OH \tag{5}$$

$$DH\cdot \longrightarrow ArOH + CCl_3\cdot \tag{6}$$

$$CCl_3\cdot + Me_2CHOH \longrightarrow CHCl_3 + Me_2\dot{C}OH \tag{7}$$

$$Me_2\dot{C}OH + D^0 \longrightarrow DH\cdot + Me_2CO \tag{8}$$

$$2\ Me_2\dot{C}OH \longrightarrow \text{pinacol} \tag{9}$$

It is known that the principal product derived from CCl$_3\cdot$ in 2-propanol photolyses is chloroform. In the case of **1** the yield of acetone was very high, suggesting

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[38] See K. V. Prabhu, Ph.D. Dissertation, New York University, 1972.

[39] O. L. Chapman and G. Wampfler, *J. Amer. Chem. Soc.*, **91**, 5390 (1969); Th. Forster, *Angew. Chem., Int. Ed. Engl.*, **8**, 333 (1969); G. Briegleb, H. Schuster, and W. Herre, *Chem. Phys. Lett.*, **4**, 53 (1969); T. H. Koch and A. H. Jones, *J. Amer. Chem. Soc.*, **92**, 7503 (1970).

[40] (a) H. E. Zimmerman and J. S. Swenton, *J. Amer. Chem. Soc.*, **89**, 906 (1967); **86**, 1436 (1964); (b) H. E. Zimmerman, R. W. Binkley, J. J. McCullough, and G. A. Zimmerman, *ibid.*, **89**, 6589 (1967).

[41] It is recognized that this represents an important change in our mechanistic view of these reactions. We have until now held to the original postulate that in dienone photochemistry zwitterions arise exclusively from $^3n,\pi^*$ states and that the molecular orbital picture of this stepwise process was not only satisfying and consistent with fundamental theory but also was sufficient to account for the available data.[27,40] We are now moving toward the view that zwitterions may arise from $^3\pi,\pi^*$ as well as $^3n,\pi^*$ states, although the exact details may differ somewhat in the two cases. It is also a possibility that zwitterion formation may in fact be characteristic of $^3\pi,\pi^*$ states and that the instances in which $^3n,\pi^*$ states are implicated (such as 4,4-diphenylcyclohexadienone[27,40] and dienone **1**[2]) may come about because of near triplet degeneracy and perhaps similar equilibrium triplet geometries in these systems. Our further studies of **1** in 2-propanol[35] suggest that at least in this solvent rearrangement to **9** and fragmentation to *p*-cresol originate from two different kinetically distinguishable triplets, as in the case of **5**. These questions will be discussed at length in later papers when more data bearing on these points have been accumulated.

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

[43] (a) D. Bellus, D. R. Kearns, and K. Schaffner, *Helv. Chim. Acta*, **52**, 971 (1969); (b) W. G. Dauben, W. A. Spitzer, and M. S. Kellogg, *J. Amer. Chem. Soc.*, **93**, 3674 (1971).

[44] A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2038 (1963).

[45] For reviews of ketone triplet reactivity, see (a) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965; (b) P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 21 (1968).

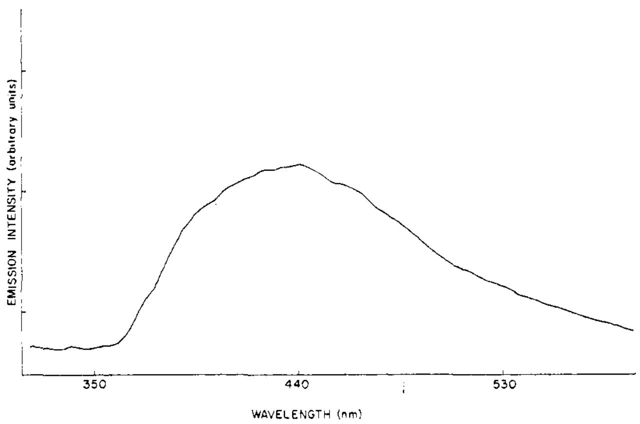

Figure 7. Phosphorescence emission spectrum of dienone **5** in an ethanol–methanol (4:1 by volume) glass at 77°K. Excitation wavelength 310 nm.

that the second H transfer to ground state dienone, reaction 8, is important, as is well documented for benzophenone photoreduction in 2-propanol.[44,45] The ketyl radical $Me_2\dot{C}OH$ may well be a quencher of ketone triplets, promoting triplet deactivation, as is suggested in some studies of Yang and coworkers[46] and by other known cases of quenching of triplets by radicals.[47] To the extent that ground state dienone D^0 consumes ketyl radicals according to reaction 8, the radical lifetime is decreased and its effectiveness as a triplet quencher is diminished. As $[D^0]$ is increased, longer triplet lifetimes would result, as measured in this study by Stern–Volmer slopes. Furthermore, the measured quantum efficiencies of 3,4-dimethylphenol formation may be considerably larger than the efficiency of H abstraction by triplets (reaction 5) because of the chain reaction represented by eq 6–8.

The data for quenching of formation of lumiketone **7** in 2-propanol can be correlated using the basic eq 10 for

$$1/\tau_{\text{obsd}} = 1/\tau_0 + k_{\text{sq}}[\text{K}^0] \qquad (10)$$

self-quenching, where τ_{obsd} is the measured triplet lifetime, τ_0 is the lifetime at infinite dilution in the absence of self-quenching, and k_{sq} is the rate constant for reaction 3. This can be modified in terms of Stern–Volmer slopes as in eq 11. A plot of the reciprocal of the slopes

$$\frac{1}{k_q\tau} = \frac{1}{k_q\tau_0} + \frac{k_{\text{sq}}[\text{K}^0]}{k_q} \qquad (11)$$

vs. ketone concentration shows the three points do fall in fact on a straight line, whose intercept, 0.035, is the reciprocal of the limiting Stern–Volmer slope (28.6) and whose slope, 0.193, is the ratio of the rate constants for self-quenching and energy transfer to *trans*-piperylene. As an order of magnitude estimate, if $k_q \sim k_{\text{dif}} \sim 3 \times 10^9\ M^{-1}\ \text{sec}^{-1}$,[44,45] the limiting triplet lifetime τ_0 would be 9.5 nsec, and k_{sq} would be $5.7 \times 10^8\ M^{-1}\ \text{sec}^{-1}$. The latter is in the range of values found for $^3\pi,\pi^*$ states of other ketones.[22,23,39] The total efficiency of disappearance of **5** was not quantitatively measured, and there are still some unidentified products. However, what residual inefficiency does remain is not necessarily due to decay of triplets to ground state, since our studies of **1**[35] indicate that decay to ground state from zwitterions is significant, contrary to expectations.

Since the two reactive triplets in this system show different kinetic properties on quenching, it can be concluded that they are not in thermal equilibrium. Most likely, their equilibrium geometries are quite different, one having a nearly flat geometry quite similar to the ground state and the other having undergone considerable twisting. It would appear that the former is more likely $^3n,\pi^*$ and the latter $^3\pi,\pi^*$.[48] The emission spectrum of **5** in 4:1 ethanol–methanol at 77°K (Figure 7) is broad and structureless with a maximum at 440 nm, suggesting but not requiring $^3\pi,\pi^*$ emission (lifetime not determined). The emission spectra of a number of steroidal enones and dienones and santonin derivatives are also generally broad and structureless and have been interpreted by Kearns, *et al.*,[49] as indicating that the lowest energy triplet in these cases is $^3\pi,\pi^*$. The broad emission of **5**, in contrast to the sharp vibronic structure seen in the emission from **1**,[2,40b] suggests that the additional ring methyl in **5** stabilizes the $^3\pi,\pi^*$ state relative to the $^3n,\pi^*$ state. Even if the latter is the lowest triplet in the case of **1**, the energies of the two triplets may be so similar that subtle structural variation may have important consequences on the relative energies of the two states in these systems.

In the case of **1** we had concluded[2] that the photochemical data are consistent with a single reactive triplet excited state or perhaps two thermally equilibrated triplets. That conclusion is contrary to the present case where we are required to invoke two different reactive triplets. In the past, we have not been kindly disposed toward "two triplet" mechanisms, despite their increasing prevalence in the photochemical literature, and we were able to show[50] that the data upon which one such mechanism was proposed was indeed erroneous. In other cases, where it was proposed that reaction occurred *via* an upper triplet,[51] other more attractive explanations have been proposed.[52] However, in the cases of the photochemistry of cyclohexenones[43,53] and now of at least some cyclohexadienones there seems no available mechanistic alternative to the proposal that these reactions involve more than one excited triplet as reactive intermediates.[54]

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(46) N. C. Yang and S. Murov, *J. Amer. Chem. Soc.*, **88**, 2852 (1966); see, however, J. Dedinas, *ibid.*, **95**, 7172 (1973).

(47) R. E. Schwerzel and R. A. Caldwell, *J. Amer. Chem. Soc.*, **95**, 1382 (1973).

(48) N. C. Baird and R. M. West, *Mol. Photochem.*, **5**, 209 (1973), and references cited therein. See also H. E. Zimmerman and G. Jones II, *J. Amer. Chem. Soc.*, **92**, 2753 (1970).

(49) G. Marsh, D. R. Kearns, and M. Fisch, *J. Amer. Chem. Soc.*, **92**, 2252 (1970); *Helv. Chim. Acta*, **51**, 1890 (1968); D. R. Kearns, G. Marsh, and K. Schaffner, *J. Chem. Phys.*, **49**, 3316 (1968).

(50) D. I. Schuster and B. M. Resnick, *J. Amer. Chem. Soc.*, **92**, 7502 (1970).

(51) P. de Mayo, J. P. Pete, and M. F. Tchir, *J. Amer. Chem. Soc.*, **89**, 5712 (1967); *Can. J. Chem.*, **46**, 2535 (1968).

(52) R. L. Cargill, P. de Mayo, A. C. Miller, K. R. Neuberger, D. M. Pond, J. Saltiel, and M. Tchir, *Mol. Photochem.*, **1**, 301 (1969); P. J. Wagner and D. J. Bucheck, *J. Amer. Chem. Soc.*, **91**, 5090 (1969).

(53) O. L. Chapman, P. J. Nelson, R. W. King, D. J. Trecker, and A. A. Griswold, *Rec. Chem. Progr.*, **28**, 167 (1967); O. L. Chapman, T. H. Koch, F. Klein, P. J. Nelson, and E. L. Brown, *J. Amer. Chem. Soc.*, **90**, 1657 (1968); G. Wampfler, Ph.D. Thesis, Iowa State University, 1970; O. L. Chapman and D. S. Weiss, *Org. Photochem.*, **3**, 197 (1973); B. M. Resnick, Ph.D. Thesis, New York University, 1974.

(54) The situation in cyclohexanone photochemistry has recently been muddied even further since it now appears that the data which formed the basis of the postulation of a dual triplet mechanism in one important study[43b] require reevaluation for experimental reasons, and the claim for such a mechanism in that case is being withdrawn. We are deeply indebted to Professor K. Schaffner, University of Geneva, for this information received in November 1973 prior to its publication; P. Margaretha and K. Schaffner, *Helv. Chim. Acta*, **56**, 2884 (1973).

Experimental Section

Nuclear magnetic resonance spectra were run on a Varian Model A-60 spectrometer using tetramethylsilane as an internal standard. A Perkin-Elmer Model 337 grating infrared spectrometer was used for measuring ir spectra. Ultraviolet spectra were recorded on a Cary-15 spectrophotometer. Mass spectra were recorded on a Varian M-66 double focusing cycloidal path mass spectrometer. Glpc analyses were made using an F and M Model 5750 research chromatograph. The areas under the peaks in chromatograms were measured using a K and E Model 4236M planimeter and in some cases using the disk integrator. Photolyses were carried out using either a "merry-go-round" apparatus or a Srinivasan–Griffin photochemical reactor. Melting points were recorded using a Mel-Temp capillary melting point apparatus and are uncorrected. All chemical analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

All the solvents and reagents used were reagent grade and used directly without further purification unless otherwise mentioned.

Synthesis of 3,4-Dimethyl-4-trichloromethyl-2,5-cyclohexadien-1-one (5). Reaction of 3,4-dimethylphenol and carbon tetrachloride in the presence of anhydrous aluminum chloride gave the dienone according to the published procedure.[4]

Anal. Calcd for $C_9H_9Cl_3O$: C, 45.09; H, 3.75; Cl, 44.42. Found: C, 45.29; H, 3.77; Cl, 44.55.

Preparative Photolysis of 3,4-Dimethyl-4-trichloromethyl-2,5-cyclohexadien-1-one. Photolysis was carried out in a 500-ml quartz vessel in the Srinivasan–Griffin apparatus using 2537-Å lamps. In a typical run 10 g of dienone was dissolved in 250 ml of *tert*-butyl alcohol in a quartz vessel. Nitrogen was bubbled through the solution for 0.5 hr and the photolysis was carried out for 5–6 hr with nitrogen gas continuously bubbling through the solution. The solution turned yellow at the end of photolysis. The solvent was removed on a Roto-vap and the residue was chromatographed on a silica gel column. The column was prepared by the slurry technique using 200 g of silica gel (Fischer 60–200 mesh) on a 1-in. column. A mixture of ether–hexane (1:3 v/v) was used to prepare the slurry. Reagent grade hexane was purified by washing with concentrated sulfuric acid. The organic layer was then washed with water, dried, and distilled. An automatic fraction collector was used to collect the fractions from the column. The column was first eluted with ether–hexane (1:3 v/v) followed by 1:2 and 1:1 mixtures of ether–hexane. The photoproducts and unreacted dienone appeared in the chromatographic fractions in the following order: (1) photoketone **10**; (2) lumiketone **7**; (3) unreacted dienone; (4) photoketone **13**, and (5) lumiketone **8**. A summary of a typical chromatographic separation of the photolysate on a silica gel column is given in Table V.

Lumiketone 7. The product from column chromatography was purified by recrystallization from hexane and then by vacuum sublimation. It was obtained as a white solid, mp 68–70°.

Anal. Calcd for $C_9H_9Cl_3O$: C, 45.09; H, 3.75; Cl, 44.42. Found: C, 45.87; H, 3.95; Cl, 45.14.

Lumiketone 8. Purification of this compound was done by recrystallization from hexane and vacuum sublimation. The pure product is a white solid, mp 91–93°.

Anal. Calcd for $C_9H_9Cl_3O$: C, 45.09; H, 3.75; Cl, 44.42. Found: C, 45.20; H, 3.69; Cl, 44.42.

Photoketone 13. Purification of the product obtained from column chromatography by recrystallization from hexane gave pure photoketone, mp 63–64°.

Anal. Calcd for $C_9H_9Cl_3O$: C, 45.09; H, 3.75; Cl, 44.42. Found: C, 45.21; H, 3.83; Cl, 44.90.

Photoketone 10. The product obtained from the column chromatography was purified by recrystallization from hexane. The pure photoketone is a white solid, mp 89–90°.

Anal. Calcd for $C_9H_{10}Cl_4O$: C, 39.13; H, 3.62; Cl, 51.45. Found: C, 39.46; H, 3.56; Cl, 51.33.

Hydrogenation of Lumiketones. Hydrogenation was carried out using 5% Pd/C as a catalyst. In a typical run, 50 mg of ketone **7** was dissolved in 15 ml of purified hexane and 2 mg of 5% Pd/C catalyst was added to the solution. Hydrogenation was then carried out at room temperature under atmospheric pressure until almost all the lumiketone disappeared, as seen by a glpc analysis on a 6 ft × 1/8 in. 5% SE-30 on Chromosorb G/AW/DMCS column (about 3 hr). The catalyst was then removed by filtration and the solvent on a Roto-vap. Further purification of the hydrogenated product was done by chromatography on silica gel and then by vacuum sublimation to get 25 mg of the dihydrolumiketone **19**, mp 68–70°.

Table V. Summary of Chromatography of Photolysate from Photolysis of Dienone **5** in *t*-BuOH[a]

Fraction	Eluent	Vol collected, ml	Wt of residue	Major product(s)
1	1:3 ether–hexane	300	Nil	None
2		300	0.5	Unidentified
3		200	0.6	Lumiketone **7**
4		120	0.14	Lumiketone **7** + dienone **5**
5	1:2 ether–hexane	600	5.42	Dienone **5**
6		120	0.6	Dienone + photoketone **10**
7	1:1 ether–hexane	100	0.2	Photoketone **10** + lumiketone **8**
8		150	0.12	Lumiketone **8**
9		150	0.22	Photoketone **13**
		Total	7.80	

[a] Experiment started with 10.0 g of dienone **5**. Other products not included above include chloroform, hydrogen chloride, unidentified photoproducts (see Results), and a small amount of (apparently) polymeric material.

A similar method gave dihydrolumiketone **20**, mp 113–115°.

Photolysis in Different Solvents. Dienone **5** (0.2 g) was dissolved in 8 ml of the solvent in quartz test tubes and the solution degassed by bubbling nitrogen gas for 15 min. Photolysis was carried out at 2537 Å in the Srinivasan–Griffin photochemical reactor using a "merry-go-round" attachment. The photolysates were concentrated and the product analyses were done by glpc and coinjection with authentic samples. The following solvents were used: *tert*-butyl alcohol, benzene, toluene, hexane, cyclohexane, dioxane, acetonitrile, and trifluoroethanol. A typical chromatogram of the *tert*-butyl alcohol photolysate is shown in Figure 1.

Photolysis in Presence of Triethylamine. To a solution of 0.2 g of dienone in 8 ml of *tert*-butyl alcohol was added 0.02 g of triethylamine. The solution was then photolyzed at 2537 Å in a "merry-go-round" using a Srinivasan–Griffin reactor. A probe containing no triethylamine was also photolyzed simultaneously. Product analysis was done by glpc using a 6 ft × 1/8 in. 5% SE-30 column.

Photolysis of Lumiketones. Solutions of 50 mg of each lumiketone in 10 ml of *tert*-butyl alcohol were photolyzed as above and glpc analysis was done using a 5% SE-30 column.

Sensitized Photolyses of Dienone 5. This experiment was carried out using benzene which was purified by photochlorination.[55] Acetophenone was distilled before use. Zone-refined benzophenone was used without further purification. Thioxanthone was recrystallized from benzene and naphthalene from ethanol. The solutions of the dienone and respective sensitizers were prepared so that (1) they each had the same absorbance at 3500 Å and (2) the sensitizers absorbed >95% of the light. After photolysis, the same amount of biphenyl was added to each photolysate, which was then concentrated and analyzed by glpc.

Quenching Experiments. *trans*-Piperylene and 1,3-cyclohexadiene were used as quenchers and were freshly distilled before use. Studies were done in *tert*-butyl alcohol, benzene, and isopropyl alcohol. A known volume of the dienone solution was placed in different Pyrex test tubes and known amounts of quenchers were added to all but one test tube, which were stoppered and photolyzed for 0.5 hr in a "merry-go-round" using a 450-W Hanovia high-pressure mercury lamp with Corning Pyrex filter 7380. A known amount of the internal standard (biphenyl or acenaphthene) was added to the photolysates in the test tubes, which were concentrated and then analyzed by glpc. Slopes and intercepts of Stern–Volmer plots were obtained with a least-squares program on a Univac 1103 data processor.

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(55) J. Saltiel and L. Metts, private communication.