J. Org. Chem. 1987, *52*, 3644-3649

Photochemistry of Ketones in Solution. 80. Irradiation of 3,4-Dimethyl-4-(trichloromethyl)-2,5-cyclohexadienone in Methanolic Solutions[1]

David I. Schuster* and Angelo C. Brisimitzakis

Department of Chemistry, New York University, New York, New York 10003

Received August 28, 1986

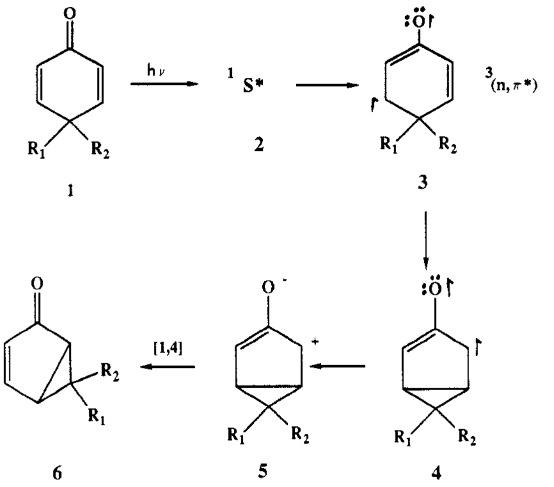
The photochemistry of the title compound in methanolic solutions has been studied as a function of acidity, temperature, and dienone concentration. A large number of products are formed under these conditions, 12 of which have been isolated and characterized spectroscopically and, in some cases, by comparison with products previously isolated from irradiations in other solvents. Relatively minor variations in the temperature and acidity of the reaction medium had a profound effect on the product distribution. The relative yield of all but one product (18) increased with temperature, and the formation of a subset of products was facilitated in more highly acidic solutions. The yields of two of the products, 11 and 16, increased as a function of starting dienone concentration, which is attributed to reaction via a triplet excimer leading to a radical ion pair, the proposed source of these products. Naphthalene quenches formation of all the products with the same efficiency, indicating a common triplet precursor for all products. Differential quenching by 1,3-cyclohexadiene is attributed to quenching of both the monomeric and excimeric triplet states, the latter having too low a triplet excitation energy to allow quenching by naphthalene. The unique temperature dependence and quenching of formation of 18 prompted a study to determine if this product was indeed a product of the n,π^* triplet state of the starting dienone. A dioxetane which would lead to this triplet was prepared by photooxygenation of an appropriate triene. This dioxetane was unstable even at −70 °C in methanol, under which conditions the rearrangement product 18 was indeed formed. Mechanisms for formation of most of the products are proposed in this and a previous paper, and an overall mechanistic scheme is presented emphasizing the points at which there is partitioning of the reaction pathway; i.e., formation of the proposed triplet excimer is directly competitive with the route leading to 3,5-bridged zwitterions, and there is an additional bifurcation with one set of products derived directly from the well-established zwitterion intermediate and another set upon protonation and nucleophilic trapping of the zwitterion. All in all, the rearrangement and fragmentation pathways available to this system are more numerous and complex than had been anticipated.

The numerous photorearrangements of 2,5-cyclohexadienones have intrigued organic photochemists for many years. Over 20 years ago, a detailed mechanism was postulated[2] to account for formation from such dienones of bicyclo[3.1.0]hexen-2-ones (lumiketones), a reaction of considerable generality. This postulated mechanism (Scheme I) involves the following (1) initial $n \rightarrow \pi^*$ excitation of **1** to give a singlet excited state **2**; (2) intersystem crossing to the triplet excited state **3**; (3) rebonding to give the triplet oxyallyl radical **4**; (4) electronic demotion to a ground-state zwitterion **5**; (5) [1,4]-sigmatropic rearrangement to the bicyclic ketone **6**.

The first direct evidence for the intermediacy of a zwitterionic species in a photochemical system came from a methanol-trapping study using dienone **7**,[3] which gave the solvent adduct **9** (whose structure was later confirmed by X-ray crystal data)[4] which preserves the skeletal structure and orientation of substituents at C_6 in the postulated zwitterion **8** (see Scheme II). The stereochemical relationship between lumiketone **6** and methanol adduct **9** proved that the [1,4]-sigmatropic rearrangement from **8** to **6** goes with inversion of configuration at the migrating carbon.

The richness of the photochemistry of these trichloromethyl-substituted cyclohexadienones (photorearrangement,[5] photoreduction and radical fragmentation,[6] photoaddition of nucleophiles,[7] electron-transfer-induced reaction,[8] and photopolymerization[9]) has provided a versatile probe of reaction mechanism in these systems.[10,11]

Scheme I



The present paper describes the results of a study of UV irradiation of 3,4-dimethyl-4-(trichloromethyl)-2,5-cyclohexadienone **10** in methanolic solutions, as a function of

---

(1) Part 79: Schuster, D. I.; Brown, P. B.; Capponi, L. J.; Rhodes, C. A.; Scaiano, J. C.; Tucker, P. C.; Weir, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 2533. Part 78: Schuster, D. I.; Wilczak, W. A.; Chang, S. P.; Brown, P. B.; Levi, A. *J. Photochem.* **1987**, *37*, 323. Part 77: Wilczak, W. A.; Schuster, D. I. *Tetrahedron Lett.* **1986**, *27*, 5331.

(2) Zimmerman, H. E.; Schuster, D. I. *J. Am. Chem. Soc.* **1961**, *83*, 4486; **1962**, *84*, 4527.

(3) Schuster, D. I.; Abraitys, V. Y. *J. Chem. Soc., Chem. Commun.* **1969**, 419.

(4) Brisimitzakis, A. C.; Schuster, D. I.; van der Veen, J. M. *Can. J. Chem.* **1985**, *63*, 685.

(5) Schuster, D. I.; Patel, D. J. *J. Am. Chem. Soc.* **1966**, *88*, 1825.

(6) Schuster, D. I.; Patel, D. J. *J. Am. Chem. Soc.* **1965**, *87*, 2515

(7) Schuster, D. I.; Liu, K.-C. *J. Am. Chem. Soc.* **1971**, *93*, 6711; *Tetrahedron* **1981**, *37*, 3329.

(8) Schuster, D. I.; Brisimitzakis, A. C. *Tetrahedron Lett.* **1982**, *23*, 4531, 4535.

(9) Brisimitzakis, A. C.; Karydas, A. *J. Polym. Sci. Polym. Lett. Ed.* **1983**, *21*, 565.

(10) Patel, D. J.; Schuster, D. I. *J. Am. Chem. Soc.* **1968**, *90*, 5137. Schuster, D. I.; Patel, D. J. *Ibid.* **1968**, *90*, 5145.

(11) For a review, see: Schuster, D. I. *Acc. Chem. Res.* **1978**, *11*, 65.

0022-3263/87/1952-3644$01.50/0

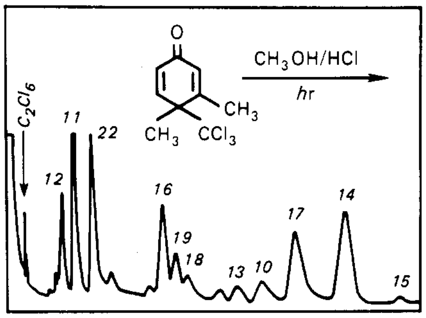
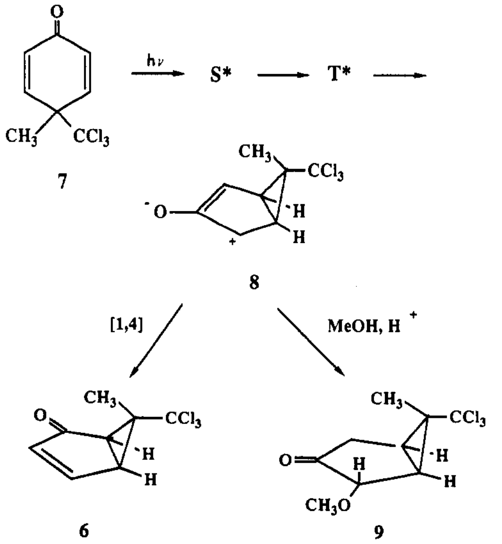


Figure 1. Gas chromatogram of photolysate of dienone 10 in acidified methanol. See Experimental Section for details of procedure.

Scheme II



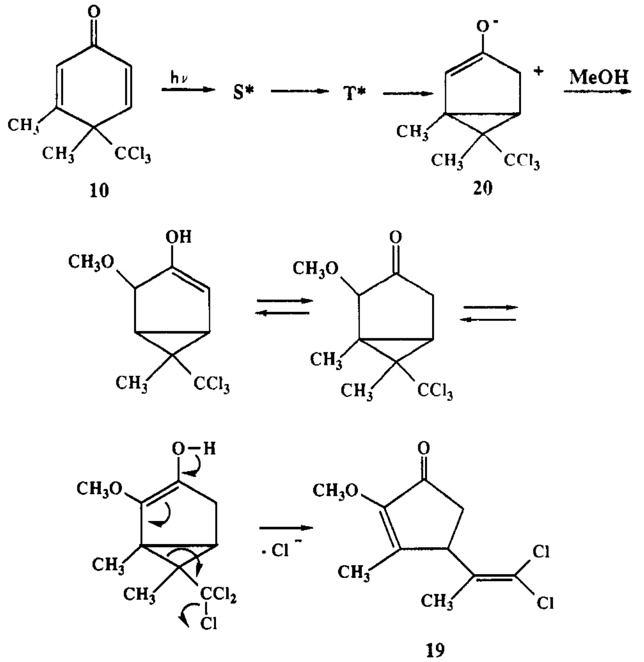
acidity, temperature, and dienone concentration. It focuses on the nature of the reaction products and the mechanisms for their formation, as well as the nature of the reactive excited states. Our initial findings[12] suggested that quite novel reaction pathways are operative under these conditions.

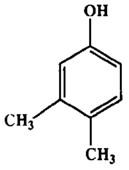
Results and Discussion

A. Isolation and Identification of Photoproducts. Irradiation of dienone 10 in MeOH/HCl solutions of varying acidity and temperature in Pyrex vessels at 300 nm gave a large number of products. A typical vapor chromatogram with structure assignments as made below is given in Figure 1. Twelve of the photoproducts were isolated by utilizing column and preparative vapor chromatographic procedures. Characterization of these materials was made by using IR, ^1H and ^{13}C NMR, and mass spectral data, GC coinjections with authentic samples and independent synthesis. Some of these photoproducts of 10 had been isolated and characterized previously by using other solvent systems (benzene, *tert*-butyl alcohol).[13] However, the plethora of photoproducts resulting from irradiation of 10 in methanol was completely unexpected.

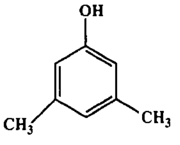
Specific products and product types familiar to us from earlier photochemical studies of 7 and 10 included hexachloroethane, 3,4- and 3,5-dimethylphenol (11 and 12), 4,6-dimethyl-6-(trichloromethyl)bicyclo[3.1.0]hexanone 13 (lumiketone), the bicyclo[3.2.0]heptenone 14, and 2-chloro-3,4-dimethyl-4-(trichloromethyl)cyclohex-2-en-1-one 15.[10,11,13] Three totally unprecedented rearrangement products (16–18) found on ultraviolet irradiation of 10 in acidic MeOH have already been described, and mechanisms for their formation were proposed.[12] Two other novel types of photoproducts (X and Y) have now been isolated and characterized.

Scheme III

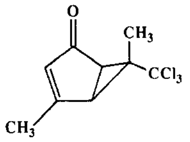




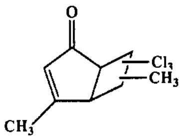
11



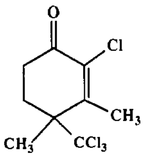
12



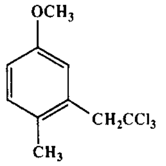
13



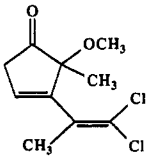
14



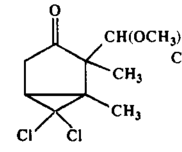
15



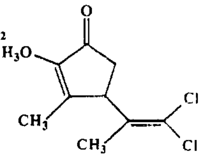
16



17



18



19

Photoproduct X, isolated by column chromatography on Florisil, is a colorless viscous oil. Exact mass analysis (see Experimental Section) indicated a formula of $C_{10}H_{12}Cl_2O_2$. Spectral data (see Experimental Section) suggested a cyclopentenone structure lacking vinyl hydrogens and two uncoupled vinylic methyl groups. From these data and by analogy to previous studies,[10,11] we propose structure 19 for this product. A reasonable mechanism for formation of 19 from 10 is shown in Scheme III, involving protonation of zwitterion 20, attack by methanol, tautomerization, and a Grob-type fragmentation with ring opening.

Photoproduct Y was also isolated by column chromatography. GC/MS analysis indicated molecular ions of mass 144 and 146, corresponding to a molecular formula of $C_7H_9C_{10}$. Spectral data (see Experimental Section) indicate a cyclopentenone structure with two vinylic hydrogens, an uncoupled methyl, and a methyl coupled to CH. These data suggest structures 21 and 22 as possibilities. Differentiation between them was afforded by the independent synthesis of 22 as a mixture of cis and trans isomers by a published procedure,[14] followed by separation of the isomers

---

[12] Schuster, D. I.; Smith, K. J.; Brisimitzakis, A. C.; van der Veen, J. M.; Gruska, R. P. *J. Org. Chem.* 1981, *46*, 473.

[13] Schuster, D. I.; Prabhu, K. V. *J. Am. Chem. Soc.* 1974, *96*, 3511.

Table I. Effect of Acidity and Temperature on Relative Product Yields[a]

solvent[b]	temp, °C	16	17	18	19	22	11	13
MeOH/HCl	−60	1.25	0.11	1.49	0.56	0.94	0.94	0.56
MeOH/HCl	+10	2.08	0.23	0.68	0.64	1.23	1.21	0.64
MeOH/HCl	+60	2.29	0.34	0.32	0.70	1.62	1.49	0.69
MeOH	−60	0.51		0.76		0.16	0.28	1.06
MeOH	+10	1.72	0.71	0.44	0.69	0.46	0.46	1.69
MeOH	+60	2.04	1.15	0.17	1.11	0.67	0.71	2.39
MeOH/$CaCO_3$	−60	0.30		0.23		0.14	0.21	1.28
MeOH/$CaCO_3$	+10	1.39	0.56	0.17	0.70	0.42	0.47	2.01
MeOH/$CaCO_3$	+60	1.81	1.22	0.09	1.27	0.58	0.71	2.93

[a] Relative product yields measured as a ratio of GC product area to area of internal standard. [b] Concentration of dienone 10, 0.042 M.

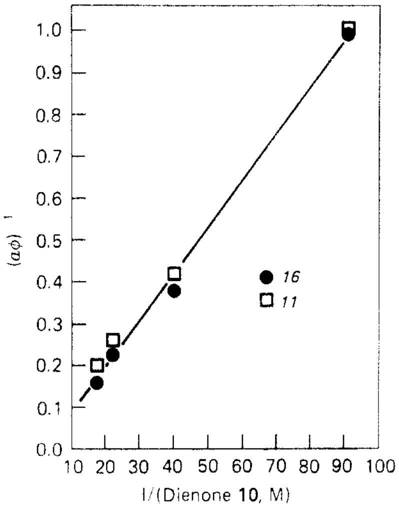
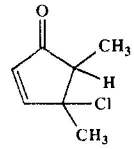
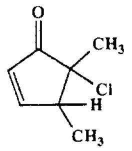


Figure 2. Effect of changes in the concentration of dienone 10 in acidified methanol on the yields of products 11 and 16.

by column chromatography on silica gel. The NMR spectrum of photoproduct Y best matched the spectrum reported[14] for the trans isomer of 22. The trans but not the cis isomer of 22 gave a single peak upon GC coinjection with photoproduct Y on two different analytical columns. Thus, we conclude that photoproduct Y is *trans*-5-chloro-4,5-dimethyl-2-cyclopentenone (22).



21



22

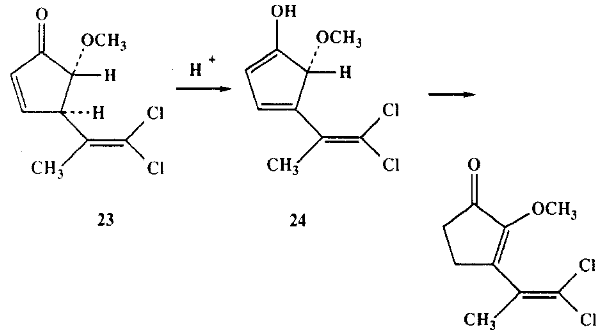
It is obvious that gross skeletal rearrangement and fragmentation must be involved along the reaction pathway leading to 22. However, further mechanistic speculation is deferred at this time.[15]

The NMR spectrum of a sample of 10 in MeOH/Cl, identical in concentration with the solutions used in the above irradiations, did not change after the solution had been heated at reflux in the dark for 24 h, showing that the formation of the above products indeed reflects photochemical rather than thermal transformations of 10 in this medium.

B. Temperature and Acidity Effects. During the course of study of the methanolic irradiations of 10, it became obvious that relatively minor variations in reaction conditions had a profound effect on the product distribution. The results of a systematic study of the effects of temperature and acidity on relative product yields are summarized in Table I. The following is evident from these experiments:

(1) The relative yield of every product studied, with the exception of 18, increased with temperature in acidic, basic, or neutral methanol. Presumably energy barriers along the reaction pathway are overcome more easily at elevated temperatures. The opposite temperature dependence for 18 may be due to a pathway leading to its decomposition at higher temperatures (see section E).

(2) The relative yields of 13, 17, and 19 increased as the solution became less acidic. Lumiketone 13 fragments to 3,5-dimethylphenol (12) under acidic conditions in the dark, thus accounting for its diminished yield at higher acid concentrations. We have shown previously[10] that ketone 23, structurally analogous to 17 and 19, isomerizes thermally in the presence of acid, presumably via intermediate 24, to the fully conjugated ketone 25.



23 24 25

(3) At a given temperature, the relative yields of 11, 16, 18, and 22 increase as solvent acidity was increased, indicating the importance of a proton source along the reaction pathway leading to these products.

C. Concentration Effects. Product Formation via Excimers. Increasing the initial concentration of dienone 10 in methanol led to an increase in the yields of 3,4-dimethylphenol (11) and the rearrangement product 16 (see Figure 2). A similar effect on the yield of 11 had been previously observed in benzene.[13] Since formation of 11 requires a hydrogen donor and since biphenyl was not detected in the benzene studies, we suggested that the hydrogen source was ketone 10 itself.[13] The concentration effects observed in methanol are attributed to an excimeric interaction en route to 11 and 16, resulting in electron transfer from a ground-state dienone molecule to an excited n,π* triplet molecule of 10 with formation of a radical ion pair, as shown in Scheme IV. Photoinduced electron transfer has recently been shown to be the dominant process occurring upon irradiation of 10 in amine solvents, in which case the major product was again 3,4-dimethylphenol (11).[8] The quantum yield of 11 was found to be dependent on the ionization potential of the amine, consistent with an electron-transfer mechanism involving the ground-state amine as the donor and the triplet excited state of dienone 10 as the acceptor.[8]

A proposed mechanism for the formation of 11 from the initial radical ion pair, depicted in Scheme IV, involves initial abstraction by radical anion 26 of a proton from the allylic methyl group of radical cation 27 to give the ketyl radical 28 and the conjugated radical 29. Expulsion of ${}^{\bullet}CCl_3$ from ketyl 28, a well-established process,[5,16] leads directly to 3,4-dimethylphenol (11) and, by dimerization of ${}^{\bullet}CCl_3$, to hexachloroethane, a detected product. H abstraction converts 29 to enol 30, in tautomeric equilibrium

---

[14] Martin, G. J.; Durand, H.; Daviaud, G.; Martin, M. L. *C. R. Seances Acad. Sci., Ser. C.* **1968**, *266*, 478.

[15] For one suggestion, see: Brisimitzakis, A. C., Ph.D. Dissertation, New York University, 1984.

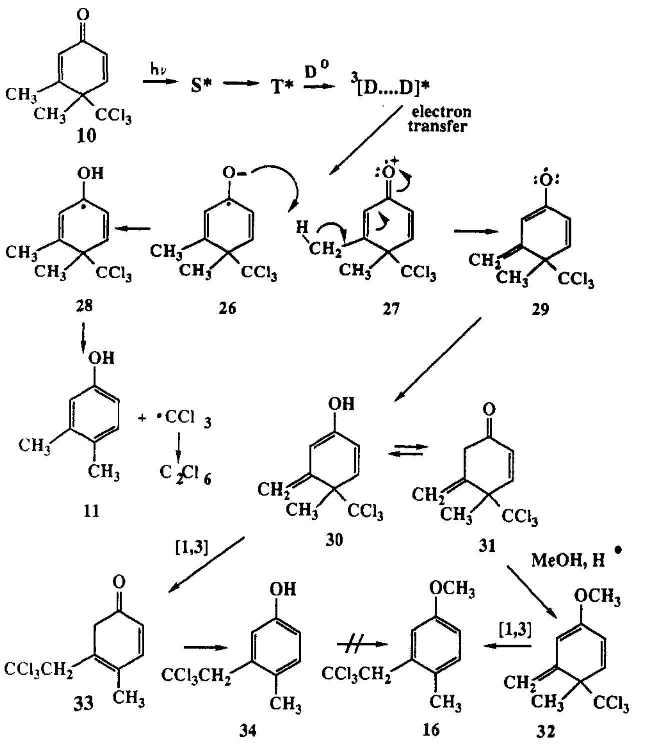
[16] Schuster, D. I.; Barile, G. C. *Tetrahedron Lett.* **1976**, 3017.

Table II. Stern–Volmer Quenching Slopes in Methanol[a]

quencher	product quenching slopes, $k_q\tau_T$, M^{-1} [c]						
	16	17	18	19	22	11	13
naphthalene	40.4	42.5	38.8	36.9	40.2	39.1	38.8
CHD	b	22.2	362.0	24.5	23.2	b	19.6

[a] Dienone concentration = 0.1 M. [b] Quenching is nonlinear. [c] Least-squares fit to data. See Figures 3 and 4.

Scheme IV



with dienone **31**, which can undergo acid-catalyzed addition of methanol to give ether **32**. The [1,3]-sigmatropic shift of CCl_3 to give **16** has ample precedent.[17] Alternatively, [1,3]-sigmatropic shift of CCl_3 could occur first to give **33**, which would tautomerize to give **34**, the phenol analogue of **16**. Phenol **34** was independently synthesized[17] and was detected in the product mixture. However, phenol **34** is not converted to **16** thermally or photochemically in acidic methanol, so that methanol addition to **31** must precede the [1,3]-sigmatropic rearrangement on the pathway to product **16**.

D. Quenching Studies. The formation of photoproducts from dienone **10** in methanol was quantitatively quenched in the presence of the triplet quenchers naphthalene (E_T = 61 kcal/mol) and 1,3-cyclohexadiene (CHD) (E_T = 52.5 kcal/mol). Studies were carried out by using Pyrex filters in a Rayonet reactor containing a merry-go-round apparatus. Product yields were measured by GLPC with internal standards added after photolysis. The quenching data are shown in the form of Stern–Volmer plots in Figures 3 and 4.

Figure 3 shows that in methanol all of the photoproducts of dienone **10** are quenched by naphthalene with the same efficiency (within experimental error), while Figure 4 illustrates differential quenching by CHD. Nonlinear quenching of formation of **11** and **16** by CHD was observed, as well as particularly efficient quenching of formation of **18**. The values of the quenching slopes, from a least-squares fit of the data to eq 1, are summarized in Table II, where k_q is the rate constant for energy transfer and τ_T is the lifetime of dienone triplet in the absence of quencher under the given conditions of solvent, temperature, and concentration.

$$\Phi_0/\Phi_Q = 1 + k_q\tau_T[Q] \qquad (1)$$

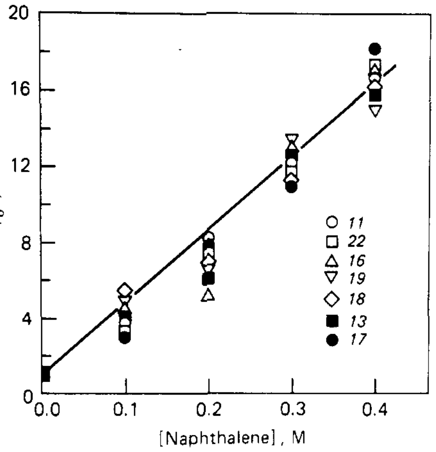


Figure 3. Stern–Volmer plot of the effect of naphthalene concentration on the yield of products of irradiation of dienone **10** in acidified methanol.

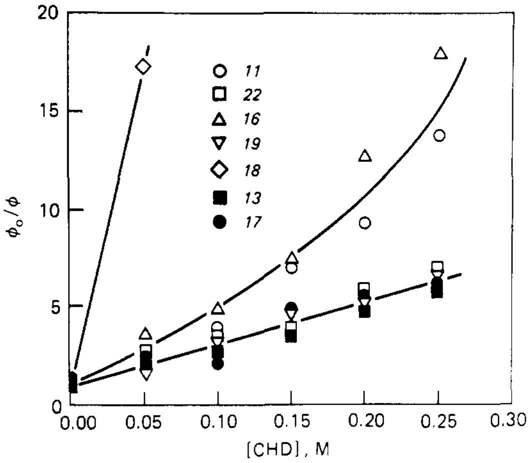


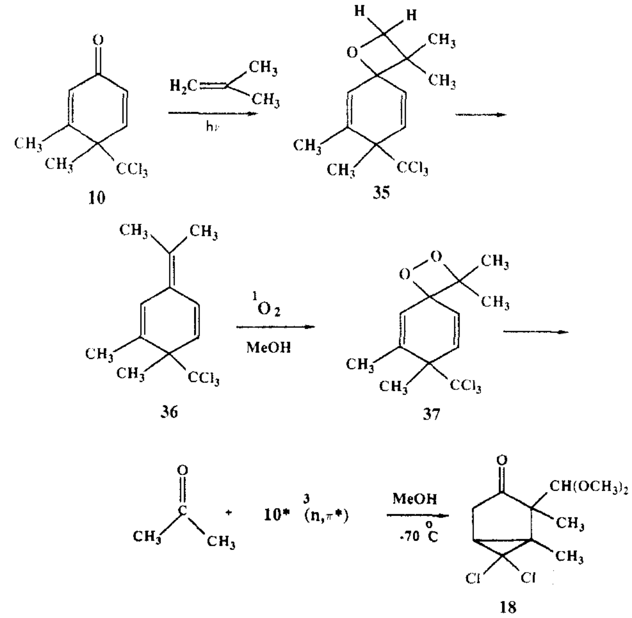
Figure 4. Stern–Volmer plot of the effect of 1,3-cyclohexadiene on the yield of products of irradiation of dienone **10** in acidified methanol.

Previous studies led to the conclusion that the photorearrangements of dienone **10** in benzene arise from a triplet excited state.[13] The naphthalene quenching data indicate that all the photoproducts derive from one triplet excited state of **10**, presumably the originally postulated n,π* triplet state,[2] although we can not exclude the possibility of two or more thermally equilibrated triplets. However, the CHD quenching data suggest that an additional electronically excited intermediate is involved. The nonlinear quenching of products **11** and **16** is consistent with the observed concentration dependence of the yields of these products, which was rationalized above by the intermediacy of a triplet excimer on the pathway leading to these photoproducts. The discrepancies in the effects of CHD and naphthalene on formation of **11** and **16** can be explained in terms of the different triplet excitation energies of these quenchers. Thus, while naphthalene efficiently quenches the higher energy n,π* triplet state of **10**, triplet energy transfer from the lower lying excimeric state would be expected to be relatively inefficient, affording no distinction between products derived directly from the monomer triplet and those (**11**, **16**) formed via the excimer. Since CHD has a much lower triplet excitation energy, triplet energy transfer can take place from both monomeric and excimeric states, resulting in nonlinear quenching kinetics; the limiting slope at low CHD

---

[17] Newman, M. S.; Bayerlein, F. *J. Org. Chem.* **1963**, *28*, 2804. See also: Newman, M. S.; Wood, L. L., Jr. *J. Am. Chem. Soc.* **1959**, *81*, 6450. Newman, M. S.; Bajzer, W. X. *J. Org. Chem.* **1972**, *35*, 270.

Scheme V



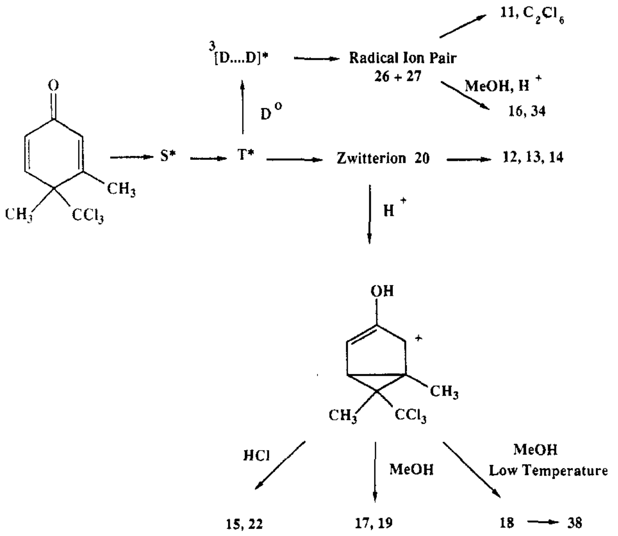
concentration represents quenching only of the monomer triplet.

E. Photoproduct 18: Thermal Behavior and Formation from a Dioxetane. The unique temperature dependence and quenching behavior observed for formation of 18 from 10 prompted a further study of the origin of this product. The anomalous effect of CHD on formation of 18 raised questions about the excited-state precursor(s) of this product. Compound 18 is stable in methanol solutions containing CHD in the dark and upon UV irradiation, eliminating CHD-induced degradation as the source of the striking effect of CHD on formation of 18.

Our approach to this problem was to generate triplet states of dienone 10 by thermal decomposition of appropriate dioxetanes[18] and to see if 18 was formed along with the other photoproducts of the n,π* triplet of 10. Entry toward the required dioxetane 37 was afforded by photooxygenation of triene 36, which was formed by the thermal breakdown of the intermediate oxetane 35 prepared from photoaddition of 2-methylpropene to dienone 10 (Scheme V)[10]. Triene 36 was photooxygenated[19] using methylene blue as the sensitizer in methanol at -70 °C. The progress of the photooxygenation was monitored by thin-layer chromatography at -10 °C, which after 2 h revealed the presence of two new spots. TLC comparison with authentic samples and subsequent GC/MS analysis of the crude photooxygenation mixture established the presence of 18 and parent dienone 10 as the two major reaction products. Bicyclic ketone 18 had previously been found to be the predominant product in the methanolic photolyses of dienone 10 at low temperatures.[12] The presumed dioxetane intermediate 37 is apparently unstable even at relatively low temperatures and decomposes to give acetone and the triplet excited state of dienone 10, which reacts with methanol at -70 °C to give 18. Thus, there is little doubt that 18 is derived from the n,π* triplet state of 10.[18] The pronounced quenching effect on formation of 18 seen with CHD is tentatively attributed at this time to reaction of CHD with one of the ground-state precursors to 18[12] rather than to triplet energy transfer.

While bicyclic ketone 18 was found to be quite stable at room temperature, it readily decomposes upon heating in refluxing xylene. This crude reaction mixture was chromatographed and yielded a white solid, which gave an undepressed mixed melting point with authentic 2,3-dimethyl-4-chlorophenol (38). In addition, spectra (^{1}H NMR, IR, MS) obtained for this thermal decomposition product were identical with those recorded for an authentic sample of 38.

Scheme VI



Summary and Overall Mechanistic Scheme. The course of events occurring on photoexcitation of dienone 10 in methanol is shown in Scheme VI. One triplet excited state of the dienone is the precursor of all the products, according to the naphthalene quenching data. The formation of photoproducts 11, 16, and 34 is proposed to occur via a bimolecular interaction involving sequentially a triplet excimer and a radical ion pair as intermediates (see Scheme IV). The remaining products arise by transformations of a zwitterion intermediate 20 of the type originally postulated by Zimmerman and Schuster[2] 26 years ago. As shown in Scheme VI, zwitterion 20 partitions itself between skeletal rearrangement to lumiketone 13 and reaction with the solvent. Lumiketone 13 undergoes further photochemical changes in methanol to yield 3,5-dimethylphenol (12) and a bicyclo[3.2.0]heptanone (14), while only 12 if formed from 13 in acidic methanol in the dark. Under acidic conditions, protonation of zwitterion 20 followed by reaction with methanol gives ketones 15, 17–19, and 22. Rather complex mechanisms for formation of 12, 14, 15, 17, and 18 have previously been proposed.[12] A mechanism for formation of cyclopentenone 19 is proposed in Scheme III, while that for 22 is deferred until further data is available.[15]

In conclusion, it appears that photoexcitation of dienone 10 in methanol results in a unique competition between excimer formation and electron demotion to a zwitterion from a common n,π* triplet precursor. This partitioning is evident from quenching studies and from the concentration effects on the yields of 11 and 16. Temperature effects reinforce the belief that significant energy barriers exist on the ground-state surface after crossover from the excited-state surface. The dependence of product ratios on the acidity of the medium is consistent with the intermediacy of ionic species such as 20, 26, and 27 on the reaction pathways in this system.

The rearrangement and fragmentation pathways available to this system are clearly far more numerous and complex than we had anticipated based upon earlier studies.[2,10,11]

Experimental Section

Spectral Data. Ultraviolet spectra were recorded on a Perkin-Elmer Coleman 124D double beam spectrophotometer. Matched 1-cm Quarasil cuvettes were used in the sample and reference beams. Infrared spectra were recorded on a Perkin-Elmer Model 734 infrared spectrophotometer. All spectra were calibrated against the 1601-cm^{-1} absorption band of a polystyrene film. Mass spectra were recorded by Mr. C. Strom at New York University on a Du Pont Model 21-492 double focusing mass spectrometer. Proton magnetic resonance spectra were recorded on a Varian Associates EM-360A high-resolution 60-MHz NMR spectrometer, and 100-MHz spectra were recorded by Mr. C. Strom on a Varian Associates XL-100 NMR spectrometer equipped with a Nicolet Fourier transform accessory. Tetramethylsilane was used as an internal standard for spectra taken on the 60-MHz instrument; 100-MHz spectra were taken with $CDCl_3$ as the solvent and internal standard. Carbon-13 magnetic

---

[18] Turro, N. J.; Lechtken, P.; Shore, N. E.; Schuster, G. B.; Steinmetzer, H.-C.; Yekta, A. *Acc. Chem. Res.* **1974**, *7*, 97. Kearns, D. R. *Chem. Rev.* **1971**, *71*, 395. Hastings, J. W.; Wilson, T. *Photochem. Photobiol.* **1976**, *23*, 461.

[19] Zimmerman, H. E.; Keck, G. E.; Pflederer, J. L. *J. Am. Chem. Soc.* **1967**, *18*, 5574.

resonance spectra of dilute samples of $CDCl_3$ were recorded by Mr. C. Strom on a Varian Associates Model XL-100 NMR spectrometer equipped with a Nicolet Fourier transform accessory. $CDCl_3$ was used as an internal standard.

Chromatographic Procedures. Gas-liquid partition chromatography analyses were carried out on two different instruments: (i) a Hewlett-Packard 5710A gas chromatograph equipped with a flame ionization detector, a Model 5702A oven temperature prorammer, a Model 7123A strip chart recorder, and a Model 3373B electronic integrator; (ii) a Hewlett-Packard 5840-A gas chromatograph equipped with a flame ionization detector. The columns used were exclusively 10% XE-60 on Chromosorb W (regular). Analytical work was done with a 6 ft × $^1/_8$ in. column, while preparative work involved the use of a $^1/_4$ in. diameter column. Typical oven temperatures ranged from 110 to 180 °C, with injection port and detector temperatures set at 250 °C. For quantitative measurements an internal standard was used. A known quantity (by volume) of *n*-tetradecane was added to the photolysate after irradiation. Stationary phases used were (i) Florisil, (ii) basic aluminum oxide (Baker analyzed reagent), and (iii) silica gel (60–200 mesh, Davison Chemical Co.). Solvents used were always ether–hexane mixtures. Columns used were 3–4 ft × $^3/_4$ in.

Melting Points. All melting points were taken on a Thomas-Hoover capillary melting point apparatus and are uncorrected.

Irradiation Procedures. Three different light sources were used: (a) an Applied Photophysics Ltd. quantum yield photoreactor and optical bench equipped with a 250-W medium-pressure mercury lamp and quartz Dewar with a merry-go-round apparatus; (b) a Hanovia 450-W high-pressure mercury lamp suspended in a water-cooled Pyrex immersion well; (c) a Rayonet Srinivasan-Griffin photochemical reactor equipped with a merry-go-round apparatus and 16 monochromatic lamps emitting light centered at 3000 Å. Samples to be irradiated were placed in Pyrex test tubes and were purged with nitrogen and sealed with rubber septa.

Reagents and Solvents. All reagents and solvents were reagent grade and were used as received without further purification except where indicated.

Syntheses. The following compounds were prepared according to the literature procedures: 3,4-dimethyl-1,4-(trichloromethyl)-2,5-cyclohexadienone (**10**)[19] and 5-chloro-4,5-dimethyl-2-cyclopentenone (**22**).[14] Physical and spectral properties agreed exactly with those reported in the literature.

Irradiation of Dienone 10 in Methanol. Dienone **10** (10.2 g, 50 mmol) was dissolved in 500 g of methanol in which had been dissolved 20 g of anhydrous HCl (55 mmol). The solution was placed in a large Pyrex tube, which was placed in 300 mL of water (20 °C). This solution was irradiated by using a 450-W Hanovia lamp in a water-cooled Pyrex immersion well for 40 min. During the course of irradiation, the solution was continuously purged with a stream of nitrogen. After photolysis, the solution was concentrated on a rotary evaporator and neutralized with anhydrous calcium carbonate. Isolation of photoproducts was afforded through a series of column chromatography experiments on Florisil (200 mesh) using 5% ether in hexane as eluent. Most products were identified by comparison of spectra and retention times on gas chromatography with properties of authentic samples synthesized independently or available from earlier studies.[13]

Spectra data for new products are as follows. Photoproduct X (**19**): IR (cm^{-1}, CCl_4) 2950, 1710, 1650, 1620, 1455, 1395, 1345, 1300, 1250, 1220, 1120, 1060, 1000, 870; 60-MHz ^1H NMR ($CDCl_3$, ppm) 1.62 (s 3 H), 1.87 (s 3 H), 2.20 (m 3 H), 3.91 (s 3 H); 100-MHz ^{13}C NMR ($CDCl_3$, ppm) 13 (q), 15 (q), 38 (t), 43 (d), 59 (q), 118 (s), 133 (s), 152 (s), 154 (s), 201 (s); exact mass found 234.0198, calcd. for $C_{10}H_{12}Cl_2O_2$ 234.0214. Photoproduct Y (**22**): IR (cm^{-1}, CCl_4) 2990, 2950, 1715, 1600, 1580, 1480, 1455, 1390, 1340, 1260, 1220, 1140, 900, 840, 800; 60-MHz ^1H NMR ($CDCl_3$, ppm) 1.30 (d, 3 H), 1.50 (s, 3 H), 2.90 (q, 1 H), 6.25 (d, 1 H), 7.65 (d, 1 H); 100-MHz ^{13}C NMR ($CDCl_3$, ppm) 12 (q), 20 (q), 48 (q), 64 (s), 133 (d), 164 (d), 207 (s).

Temperature and Acidity Effects. In order to study the effects of temperature and acidity on product distribution, solutions of dienone **10** in methanol (0.042M) were prepared at three different acidities and irradiated over a range of temperatures (see Table I). Methanolic solutions of dienone **10** containing either HCl (0.5 M), methanol alone, or calcium carbonate in Pyrex tubes were irradiated with a medium-pressure mercury lamp through a quartz Dewar with a merry-go-round apparatus. Each of these solutions was irradiated at three different temperatures, namely, −60, 10, and 60 °C. Product yields were determined by GC analysis as the ratio of product area to the area of the internal standard.

Concentration Effects. Solutions of dienone **10** in methanol of 0.011, 0.025, 0.045, and 0.057 M were prepared by successively diluting a standard dienone solution. Samples (2 mL) were pipetted into 1-cm Pyrex test tubes, and the solutions were irradiated at room temperature for 1 h with a 250-W medium-pressure mercury lamp and a quartz Dewar with a merry-go-round apparatus. After photolysis an internal standard was added to each sample, which was then analyzed by GC. The results are depicted in Figure 2.

Quenching Studies. Naphthalene and freshly distilled 1,3-cyclohexadiene were used as quenchers. Studies were done in methanol and involved the addition of 2 mL of dienone **10** (0.1 M) to Pyrex test tubes. Known amounts of these quenchers were added to all but one test tube. The sample tubes were stoppered, purged with nitrogen and irradiated for 1 h by using a Srinivasan-Griffin photochemical reactor equipped with a merry-go-round apparatus and 16 lamps emitting light centered at 3000 Å. After photolysis an internal standard was added to each sample which was then analyzed by GC. Results are shown in Figures 3 and 4 and summarized in Table II.

Photooxidation of Triene 36. A solution of 250 mg of triene **38** and 25 mg of methylene blue in 130 mL of methanol was photooxidized at −70 °C by using a 450-W Hanovia lamp encased in a Pyrex jacket. After 2 h of irradiation, TLC analysis (∼−10 °C) established the presence of starting triene **36** in addition to two new products. The reaction mixture was transferred to a separatory funnel and maintained at low temperature as chilled ether, and cold sodium chloride was added. After the layers were separated, ether extraction was repeated twice, and the ether phases were concentrated in vacuo at −0 °C to give a yellow oil. TLC comparison with authentic samples and subsequent GC/MS analysis established the identity of these two products as dienone **10** and bicyclic ketone **18**.

Acknowledgment. This study was supported in part by a grant from the National Science Foundation (CHE-7819750) for which we are grateful.

Registry No. **10**, 7499-12-9; **18**, 109121-37-1; **19**, 85696-16-8; **22**, 35493-81-3; **35**, 109065-52-3; **36**, 109065-53-4; **37**, 109065-54-5; MeOH, 67-56-1; $CH_2{=}CMe_2$, 115-11-7; naphthalene, 91-20-3; 1,3-cyclohexadiene, 592-57-4; acetone, 67-64-1.