The Photochemistry of 4-Methyl-4-trichloromethyl-2,5-cyclohexadienone. I. The Nature of the Products[1,2]

Dinshaw J. Patel[3a] **and David I. Schuster**[3b]

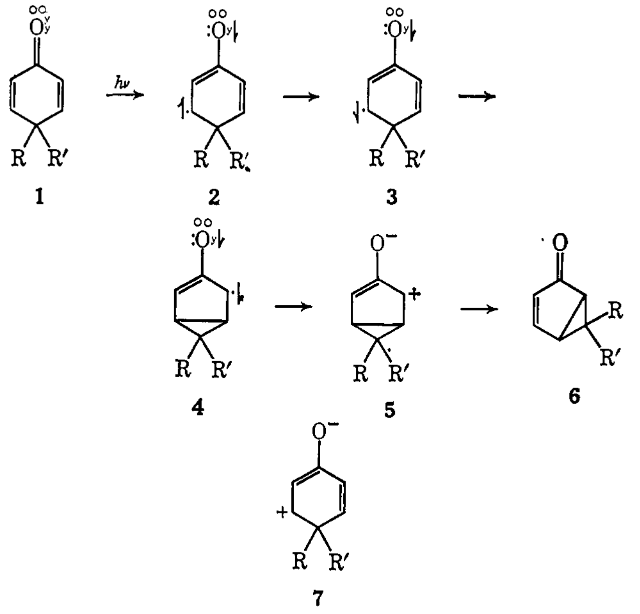
Contribution from the Department of Chemistry, New York University, New York, New York 10453. *Received February 21, 1968*

Abstract: The photochemistry of 4-methyl-4-trichloromethyl-2,5-cyclohexadienone is markedly dependent on the solvent. Irradiation through Pyrex in good hydrogen donor solvents (*e.g.*, ethers, secondary alcohols) gives predominantly *p*-cresol, by a hydrogen abstraction–fragmentation reaction. Chloroform and hexachloroethane are formed concomitantly. In benzene, the usual dienone–lumiketone rearrangement takes place to give stereospecifically one epimer of 6-methyl-6-trichloromethylbicyclo[3.1.0]hex-3-en-2-one (**14**), which subsequently rearranges photochemically to give two isomeric ketones (**20** and **21**) with bicyclo[3.2.0]hex-3-en-2-one structures. In methanol and water, the above reactions do not take place, but an ionic fragmentation reaction occurs to give a cyclopentenone derivative (**22**) with loss of HCl and addition of ROH. In acidified methanol, under conditions where the dienone is stable in the dark, photolysis does not give **22** but rather a saturated ketone tentatively assigned structure **26**, 2-methoxy-6-methyl-6-trichloromethylbicyclo[3.1.0]hexan-3-one. Irradiation in isobutylene or 2-methyl-2-butene gives oxetanes, which subsequently undergo thermal fragmentation and rearrangement. It is shown from irradiations in mixed benzene–ether solvent that the rearrangement and radical fragmentation reactions are competitive. The lumiketone **14** is shown not to be a precursor to the products formed by the radical and ionic fragmentation pathways. Mechanistic discussion is given in the following paper.

Several years ago, a detailed mechanism was postulated[4,5] to account for the formation of bicyclo[3.1.0]hexen-2-ones (so-called "lumiketones") on photolysis of cross-conjugated cyclohexadienones, a reaction of considerable generality.[6] The postulated mechanism[4,5] is outlined in Scheme I: (1) excitation of **1** (n → π^*) to give a singlet state, **2**; (2) intersystem crossing to the triplet state, **3**; (3) rebonding, with geometric changes, to give **4**; (4) electron demotion to the ground-state zwitterion **5**; (5) rearrangement to the bicyclic ketone **6**. Originally, there was little evidence to support the mechanism other than the nature of the products and the electronic transition involved.[4,5] It was pointed out that the formation of the products could be rationalized assuming an intermediate role for a polar state **7**,[6a,c] although the exact nature (ground or excited electronic state) and mode of formation of the polar state were never explicitly defined. This study was undertaken to provide direct experimental evidence for the mechanism proposed in Scheme I.

Our point of departure was to divert the photochemical transformation of a dienone so as to define the sequence of excited states and intermediates involved in the transformation. In almost all cases studied previously the only product of photolysis of a cross-conjugated cyclohexadienone in nonacidic media was the lumiproduct, and the quantum efficiency of the transformation measured in two cases was close to 1.[7,8] In acidic media, the photochemistry of fused ring dienones such as α-santonin and a series of steroidal dienones could be diverted from lumiketone formation to formation of rearranged hydroxy ketones,[6,9–11] impli-

Scheme I



o = 2s electrons
y = $2p_y$ electrons
= $2p_z$ electrons

---

(1) Part XVI of a series on the photochemistry of unsaturated ketones in solution. Part XV: W. V. Curran and D. I. Schuster, *Chem. Commun.*, 699 (1968).

(2) Portions of this work have been published in preliminary form: (a) D. I. Schuster and D. J. Patel, *J. Amer. Chem. Soc.*, **87**, 2515 (1965); (b) *ibid.*, **88**, 1825 (1966); (c) D. J. Patel and D. I. Schuster, *ibid.*, **89**, 184 (1967).

(3) (a) Bell Telephone Laboratories, Inc., Murray Hill, N. J. 07971; (b) Fellow of the Alfred P. Sloan Foundation, 1967–1969.

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

(5) H. E. Zimmerman, *Advan. Photochem.*, **1**, 183 (1963).

(6) For reviews of the abundant literature in this area, see ref 4 and 5 and the following: (a) O. L. Chapman, *Advan. Photochem.*, **1**, 323 (1963); (b) K. Schaffner, *ibid.*, **4**, 81 (1966); (c) P. J. Kropp, *Org. Photochem.*, **1**, 1 (1967); (d) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965.

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

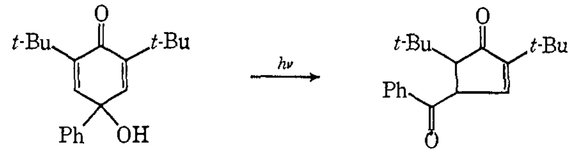
(8) H. E. Zimmerman and J. S. Swenton, *ibid.*, **86**, 1436 (1964); **89**, 906 (1967).

(9) P. J. Kropp and W. F. Erman, *ibid.*, **85**, 2456 (1963).

(10) P. J. Kropp, *ibid.*, **86**, 4053 (1964).

(11) C. Ganter, E. C. Utzinger, K. Schaffner, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, **45**, 2403 (1962).

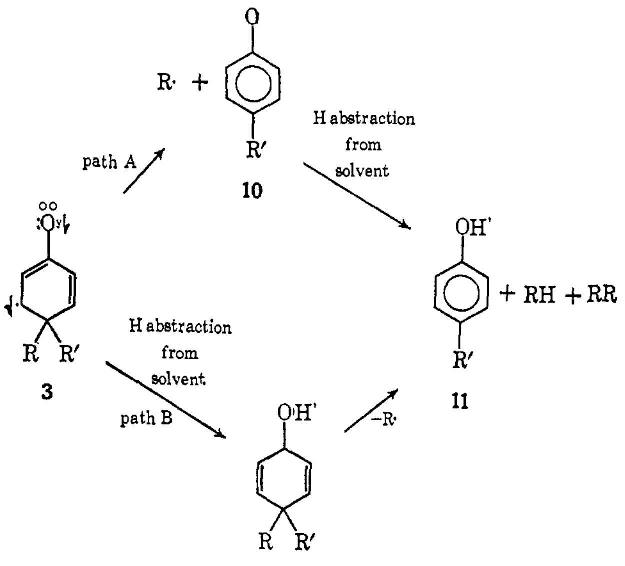
cating a role for ionic intermediates in the photochemical transformations of dienones in acidic media. The phototransformation in 20% yield of **8** to **9** in aqueous dioxane[12] seems also to require ionic intermediates in the product-determining stage of the reaction. In none of these reactions was any evidence provided on the possible role and nature of intermediates formed prior to the ionic intermediates apparently required to explain the nature of the products.



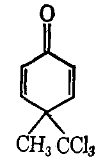
8 **9**

We sought to show experimentally that diradical intermediates such as **2**, **3**, and **4** in Scheme I were precursors for the apparently well-established ionic intermediates. If species such as **2** and **3** were involved, it seemed possible to divert the usual reaction (to give **4** and eventually lumiketone **6**) to a new path (path A, Scheme II) in which cleavage of one of the substituents at C-4 would give a radical R· and a phenoxy radical **10**, leading to radical abstraction and coupling products RH and RR and phenols **11**. A mechanistic alternative to the formation of these products (**11**, RH and RR) is hydrogen abstraction from solvent by **2** or **3** to give the dienone ketyl radical **12** (Scheme II, path B). A 4-substituent R was chosen which might favor cleavage to a radical R·, in contrast with the simple alkyl and aryl 4-substituents in dienones studied heretofore.[4–6] An ideal candidate seemed to be R = CCl_3, since CCl_3· is a stabilized radical whose chemistry is well established,[13] and since dienone **13** could be synthesized readily in high yield.[14]

Scheme II



12



13

This paper describes the products of photolysis of dienone **13** under various conditions, including detailed structure proofs for new compounds. Mechanistic discussion is given in the accompanying paper[15] which presents experimental evidence allowing characterization of the excited states responsible for these reactions and kinetic data which permit evaluation of rate constants for the primary processes.

Results and Discussion

Spectral Properties of 4-Methyl-4-trichloromethyl-2,5-cyclohexadienone (13). The ultraviolet (uv) spectrum of **13** in methanol shows maxima at 230 mμ (ε 15,000), 339 (16), and 350 (15), and infrared (ir) carbonyl absorption at 1685 cm^{-1}. The strong uv maximum is shifted about 10 mμ to the blue compared with other representative cyclohexadienones,[4,11,16] and the ir carbonyl frequency at 1685 cm^{-1} is likewise shifted to higher frequency about 20–25 cm^{-1} compared with other dienones. These small shifts are probably due to dipole interactions between the trichloromethyl group and the dienone chromophore.

Photolysis in Ethyl Ether and Other Hydrogen Donor Solvents. Formation of *p*-Cresol. Irradiation of **13** in ethyl ether through Pyrex filters resulted in the formation in good yield of *p*-cresol, which was isolated and directly compared with an authentic sample. In Table I, yields of *p*-cresol determined by uv spectra are given for irradiation in a number of solvents. Chloroform was identified as a product in ethereal solvents from nmr and glpc analysis of concentrated photolysates, while hexachloroethane was detected in hexane and cyclohexane runs by glpc analysis of concentrated photolysates on four different columns by comparison (co-injection) with authentic materials.

Table I. Yields of *p*-Cresol from Irradiation of Dienone **13**[a]

Solvent	Concn, *M*	% yield, *p*-cresol[b]
Ethyl ether	22.9	73
Dioxane	22.5	39
	7.2	39
Diglyme	21.0	49
Diethyl Carbitol	7.1	55
Hexane	7.0	53
Cyclohexane	7.1	62

[a] Hanovia 450-W high-pressure mercury arc, Pyrex filter. [b] Calculated from absorbance at 282.5 mμ, using ε 2400 for *p*-cresol.

Other ketone photoproducts were indicated by ir spectra of the crude photolysates in runs in hexane and dioxane. These ketones could be separated by chromatography on silica gel, but were more conveniently isolated from the benzene runs described below.

---

[12] E. R. Altwicker and C. D. Cook, *J. Org. Chem.*, **29**, 3087 (1964).

[13] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957.

[14] M. S. Newman and A. G. Pinkus, *J. Org. Chem.*, **19**, 978 (1964). The suggestion to initially study dienone **13** was originally made by Professor Douglas Hennessy of Fordham University during an informal discussion.

[15] D. I. Schuster and D. J. Patel, *J. Amer. Chem. Soc.*, **90**, 5145 (1968).

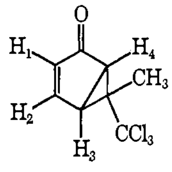
[16] J. Frei, C. Ganter, D. Kägi, K. Kocsis, M. Miljkovic, A. Siewinski, R. Wenger, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **49**, 1049 (1966).

Table II. Nuclear Magnetic Resonance Spectra of Photoproducts[a]

Compound	Proton resonances, ppm (J in Hz) Vinyl	Ring	Methyl	Other
ϕ-I (**14**)	7.50, H_2, J_{12} = 5.5, J_{23} = 2.8, J_{24} = 0.6 6.07, H_1, J_{12} = 5.5, J_{14} = 0.9	3.20, H_3, J_{23} = 2.8, J_{34} = 5.5 2.65, H_4, J_{34} = 5.6, J_{14} = J_{24} = 0.7–0.9	1.55 (s)	...
ϕ-II (**20** or **21**)	7.71, H_2, J_{12} = 5.4, J_{23} = 3.2, J_{24} = 0.6 6.42, H_1, J_{12} = 5.5, J_{13} = 1.5	4.04, H_3, J_{13} = 1.5, J_{23} = 3.3, J_{34} = 6.0 3.20, H_4, J_{24} = 0.7, J_{34} = 6.0	1.98 (s)	...
ϕ-III (**20** or **21**)	7.73, H_2, J_{12} = 5.0, J_{23} = 3.0 6.42, H_1, J_{12} = 5.0, J_{13} = 1.5	4.17, H_3, J_{13} = 1.5, J_{23} = 3.0, J_{34} = 7.0 3.42, H_4, J_{34} = 7.0	1.68 (s)	...
MeOH-I (**22**, R = CH_3)	7.37, H_2, J_{12} = 6.0, J_{23} = 2.5 6.20, H_1, J_{12} = 6.0, J_{13} = 2.5	4.20, H_3, J_{34} = 3.5 J_{13} = J_{23} = 2.5 3.70, H_4, J_{34} = 3.5	1.78 (s)	OCH_3, 3.53 (s)
H_2O-I (**22**, R = H)	7.43, H_2, J_{12} = 6.0, J_{23} ~ 2 6.33, H_1, J_{12} = 6.0, J_{13} ~ 2	4.17, H_3 + OH[b] 3.37, H_4[c]	1.82 (s)	OH, 4.17 (s)
MeOH-II **26**	...	2.0–2.7 (4 H, m)	1.30 (s)	OCH_3, 3.25 (s)
Oxetane **27**	5.8–6.6 (4 H, m)	...	1.03 (s) 1.08 (s), 1.18 (s) 1.28 (s), 1.42 (s) 1.53 (s)	$\overset{CH_3}{\overset{\vert}{O—CH—}}$, 4.48 (q, J = 7)
Oxetane **28**	6.45 (4 H, s)	...	1.20 (s) 1.47 (s)	$O—CH_2—\overset{\vert}{\underset{\vert}{C}}—$, 4.18 (s)

[a] All spectra were taken in carbon tetrachloride or chloroform-*d* with tetramethylsilane as an internal reference. All data reported are from spectra at 60 MHz, except for compounds **14** and **21** which were recorded at 100 MHz. [b] Finely split multiplet. [c] Broadened singlet.

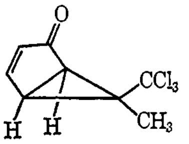
Photolysis of 13 in Benzene. Structures of Isomeric Photoketones. Photolysis of dienone **13** in benzene using either a Hanovia high-pressure mercury lamp with Pyrex filters (exciting light >3000 Å) or at 2537 Å in a Rayonet reactor did not give any *p*-cresol, according to uv spectra and glpc. Three new ketonic products were separated by chromatography on silica gel. As in earlier studies by Kropp[10] and Jeger and Schaffner and their coworkers[11,16] the yield of one ketone, designated ϕ-I (mp 74–76°), could be maximized by irradiation at 2537 Å, conditions under which its rate of disappearance by subsequent photochemical transformation to the other two ketones could be minimized. The lumiketone structure **14** is assigned to ϕ-I from the following spectral and chemical evidence.



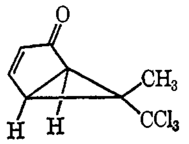
14

The nmr spectrum of ϕ-I is given in Table II, while the ir, uv and mass spectra are summarized in Table III. The mass spectrum and analytical data confirm ϕ-I as an isomer of **13**. The nmr spectrum indicates two vinyl protons, whose coupling constant of 5.5 Hz indicates they are on a five-membered ring.[17] The magnitudes of the other coupling constants (J_{14}, J_{24}, J_{23}, and J_{34}) are in accord with structure **14** and in agreement with couplings reported for other bicyclo[3.1.0]hexenones.[4,10,16,18] Hydrogenation of ϕ-I with uptake of 1 equiv of hydrogen gave a ketone, mp 78–79°, *m/e* 226, which had no vinyl hydrogen from its nmr spectrum. The ir spectrum of the hydrogenated ketone had bands at 3030 and 1030 cm^{-1}, indicating saturation of a carbonyl conjugated double bond. Quantitative ozonolysis[19] with consumption of 0.87 equiv of ozone did not yield the expected cyclopropane diacid on oxidative work-up (see Experimental Section for details). Ketone ϕ-I was inert toward zinc in ethanol and basic or acidic hydrolysis of the CCl_3 group, as was dienone **13**. Sodium methoxide in methanol resulted in addition of methanol across the double bond (see Experimental Section).

These data are consistent only with structure **14** for ketone ϕ-I. The ir and uv data for **14** and other lumiketones are given in Table IV. The large blue shifts seen in the uv and ir spectra of **14** (compare with **13** above) possibly indicate some special interaction between the CCl_3 group and the carbonyl chromophore. Although two diastereomeric structures **14a** and **14b** are possible for this ketone, only one ketone could be isolated whose properties are consistent with structure **14** from irradiations in a variety of solvents in addition



14a



14b

---

[17] O. L. Chapman, *J. Amer. Chem. Soc.*, **85**, 2014 (1963); P. Laszlo and P. von R. Schleyer, *ibid.*, **85**, 2017 (1963); G. V. Smith and H. Kreloff, *ibid.*, **85**, 2016 (1963).

[18] H. Dutler, C. Ganter, H. Ryf, E. C. Utzinger, K. Weinberg, K. Schaffner, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, **45**, 2346 (1962).

[19] These ozonolysis experiments were run at Fordham University with the very kind assistance of Professor E. Moriconi and Dr. L. Saltze.

Table III. Ultraviolet, Infrared, and Mass Spectra of Photoproducts[a]

Compound	Uv spectrum, λ_{max}, mμ (ϵ)	Ir bands,[b] cm^{-1}	Mass spectrum, m/e[c]
ϕ-I (**14**)	216.3 (5600), 253 (3200), 334 (127), 346 (124)[d]	3030 (w), 1725 (s), 1585 (w), 1400 (w), 1350 (m), 1260 (w), 1240 (w), 1170 (m), 1020 (w), 985 (m), 950 (w), 910 (m), 885 (w)	224, 3 Cl (2); 196, 3 Cl (2); 189, 2 Cl (68); 161, 2 Cl (98); 153, 1 Cl (20); 126, 1 Cl (32); 125, 1 Cl (100); 98, 0 Cl (65)
ϕ-II (**20** or **21**)	226 (7200), 334 (29)[e]	1740, 1595, 1455, 1395, 1345, 1230, 1165, 1085, 1050, 990, 950, 910, 865, 700, 650, 600	224, 3 Cl (1.5); 196, 3 Cl (4.2); 189, 2 Cl (100); 161, 2 Cl (20); 153, 1 Cl (30); 144, 3 Cl (26); 125, 1 Cl (55); 91, 0 Cl (68)
ϕ-III (**20** or **21**)	225 (7100), 338 sh (80)[e]	1730, 1590, 1455, 1395, 1345, 1210, 1165, 1085, 1050, 990, 945, 900, 845, 725, 645	224, 3 Cl (1.2); 196, 3 Cl (2.6); 189, 2 Cl (100); 161, 2 Cl (18); 153, 1 Cl (26); 144, 3 Cl (40); 125, 1 Cl (45); 91, 0 Cl (33)
MeOH-I (**22**, R = CH_3)	207.5 (18,300),[f] 347 (45)[e]	2800, 1735, 1625, 1595, 1450, 1395, 1345, 1245, 1225, 1125, 1045, 910, 660	220, 2 Cl (42); 205, 2 Cl (8); 192, 2 Cl (22); 189, 2 Cl (24); 185, 1 Cl (35); 161, 2 Cl (20); 157, 1 Cl (53); 143, 1 Cl (40); 125, 0 Cl (62); 122, 0 Cl (42); 111 (52); 91, 0 Cl (80); 77, 0 Cl (100)
H_2O-I (**22**, R = H)	208.8 (16,500), 327 (67)[d]	3500, 1720, 1625, 1590, 1110, 1085, 910, 655, 615	206, 2 Cl (54); 177, 2 Cl (17); 171, 1 Cl (20); 143, 1 Cl (37); 125, 1 Cl (31); 113 (52); 108, 0 Cl (70); 97 (25); 91, 0 Cl (45); 77, 0 Cl (100); 51, 0 Cl (68)

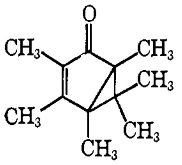
[a] See Experimental Section for details of instrumentation. [b] Infrared spectra taken as solutions in carbon tetrachloride. [c] Mass spectra reported as follows: ion (m/e), number of ^{35}Cl atoms in ion, intensity relative to the most abundant ion as 100 (in parentheses). [d] Methanol solvent. [e] Dioxane solvent. [f] Low-wavelength measurement in methanol kindly made by Professor K. Mislow at Princeton University.

Table IV. Spectral Properties of Bicyclo[3.1.0]hexen-2-ones

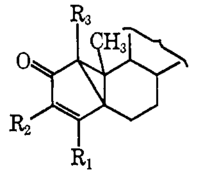
Compound	λ_{max} (ϵ)	$\nu_{C=O}$ cm^{-1}	Ref
ϕ-I (**14**)	216[a] (5600); 253 (3200)	1725[b]	
Lumisantonin	237[c] (5800)	1693[d]	20
15	235[c] (6270); 274 (3240)	1690[b]	21
16a	236[c] (5500); 270 sh (2820)	1686[d]	16
16b	232[c] (6500); 264 sh (3800)	1672[d]	16
16c	238[c] (5400); 269 sh (2500)	1686[d]	16

[a] Methanol. [b] CCl_4. [c] Ethanol. [d] Chloroform.

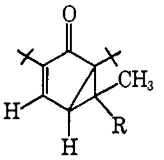
to benzene. Furthermore, analysis of reaction mixtures at various stages of the reaction showed clearly that only one isomer of **14** was formed: glpc analysis on several columns showed initially only one new peak in addition to **13**, while nmr spectra at early stages of the reaction were simulated by mixtures of **13** and the isolated isomer ϕ-I, although the nmr spectra of a mixture of **14a** and **14b** should show two methyl resonances, by analogy with compound **15**[21] and epimeric lumiketones **17**.[22] Thus, the transformation of **13** to **14** is apparently entirely stereospecific. The results do not unequivocally allow an assignment of stereochemistry to **14**, without the second isomer for direct spectral comparison. The ir and uv data, indicating interaction of the CCl_3 group and the carbonyl group, favor but do not demand structure **14a**. Further studies to define the stereochemistry are now in progress.



15



16a, $R_1 = R_2 = R_3 = H$
b, $R_1 = CH_3$; $R_2 = R_3 = H$
c, $R_2 = CH_3$; $R_1 = R_3 = H$



17, R = allyl or *n*-propyl

The main photoproduct on irradiation of dienone **13** in benzene using Pyrex filters is a ketone, mp 62–64°, designated ϕ-II (50% yield), accompanied by a minor ketone product (<5% yield) designated ϕ-III, mp 65.5–68°. ϕ-II and ϕ-III were derived from phototransformations of **14** and were not formed directly from dienone **13**.[23] The two ketones, separated by column chromatography on silica gel, are isomers of dienone **13** from their mass spectral molecular ions, m/e 224, and have extremely similar ir, uv, and mass spectra, Tables II and III, differing in detail from the spectra for ϕ-I. The nmr spectra of ϕ-II and ϕ-III both show two vinyl hydrogens in a five-membered ring (J = 5.5 Hz),[17] and two ring protons deshielded from those in ϕ-I (**14**). The coupling of the saturated ring protons (6.0 and 7.0 Hz, respectively) is larger than that found for **14** (5.5 Hz), while $J_{14} = 0$ and $J_{13} = 1.5$ Hz, further indications of a new bicyclic ring structure in the new ketones. This is further confirmed by an important mass spectral fragment at m/e 144 ($C_3H_3Cl_3$), not found in ϕ-I (**14**). Further chemical studies were carried out only with ketone ϕ-II as ϕ-III was not available in sufficient quantities.

Hydrogenation of ϕ-II gave a saturated ketone (m/e 226, 3 Cl; no vinyl H in nmr; no ir bands at 3030, 1595, or 700 cm^{-1}). The ir carbonyl band shifted from 1740 to 1755 cm^{-1}, indicating conjugation of the double bond with the carbonyl group. Quantitative ozonolysis[19] led to take-up of 0.81 mol of ozone, but no well-characterizable product could be isolated after oxidative treatment of the ozonide. Dechlorination of ϕ-II with zinc in ethanol at reflux gave a new ketone, C_8H_7ClO. The nmr spectrum showed two vinyl protons (δ 7.65 and 6.07 ppm, multiplets), two saturated ring protons (δ 3.95 and 3.30 ppm, multiplets), and a methyl resonance centered at 1.80 ppm, coupled to both H_3 and H_4 (2.1 and 1.4 Hz). The uv spectrum of the dehalogenated ketone has λ_{max} (cyclohexane)

---

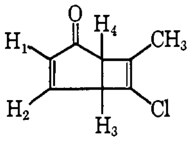
(20) D. Arigoni, H. Bosshard, H. Bruderer, G. Büchi, O. Jeger, and L. J. Krebaum, *Helv. Chim. Acta*, 40, 1732 (1957).

(21) H. Hart, P. M. Collins, and A. J. Waring, *J. Amer. Chem. Soc.*, **88**, 1005 (1966).

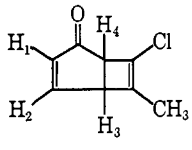
(22) B. Miller and H. Margulies, *ibid.*, **89**, 1678 (1967); B. Miller, *ibid.*, **89**, 1690 (1967).

(23) In our earlier communication, ref 2b, ketone ϕ-II was erroneously assigned structure **14** before ketone ϕ-I was isolated and characterized. Once both ketones were at hand, it became clear from comparison of their spectral and chemical properties that the two ketones had quite different structures and that ketone ϕ-I, mp 74–76°, was indeed one of the epimeric lumiketones **14**.

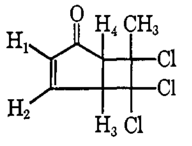
204 mμ (ϵ 7730), a shoulder at 221 mμ (5020), and enhanced intensity from 323 to 390 mμ, *e.g.*, λ_{max} 254 mμ (270), virtually diagnostic of a rigid β,γ-unsaturated ketone.[24–26] These data strongly suggest that the dehalogenated ketone has structure **18** or **19**; thus, ϕ-II and ϕ-III are two of the isomeric ketones **20** or **21**. The large differences in the methyl resonances (Table II), despite near identity of other spectral properties, suggest the ketones are epimers, with the methyl group *syn* to the cyclopentenone ring in ϕ-III and *anti* in ϕ-II, but do not indicate whether they are epimers of structure **20** or **21**. Synthesis and degradation studies are planned to define these structures further.



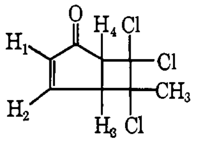
18



19



20

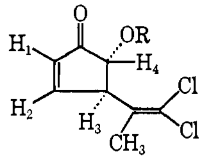


21

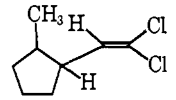
Considerable polymer formation (about 50%) accompanies the formation of ketones ϕ-II and ϕ-III on irradiation of dienone **13** in benzene through Pyrex. This polymer arises during the photoreactions and not the formation of the lumiketone **14**.

Photolysis of Dienone 13 in Methanol and Aqueous Dioxane. Irradiation of dienone **13** in methanol through Pyrex gave neither *p*-cresol nor any of the three isomeric ketones isolated from reactions in benzene, from analyses of photolysates at various stages of reaction. Solutions became acidic as reaction proceeded. Photolyses in the presence of excess calcium carbonate gave in high yield a ketone, mp 59–60°, designated MeOH-I, $C_9H_{10}Cl_2O_2$ (elemental analysis and the mass spectrum molecular ion, *m/e* 220 with 2 Cl). The nmr spectrum (Table II) shows two vinyl hydrogens on a five-membered ring (J_{12} = 6.0 Hz),[17] two saturated ring protons coupled by 3.5 Hz, a methyl group, and a methoxyl group. The carbonyl band at 1735 cm^{-1}, as found in ketones **21**, is shifted to 1770 cm^{-1} on hydrogenation, in which uptake of 1 equiv of hydrogen is rapid and further hydrogen is absorbed slowly. The hydrogenation product had no vinyl hydrogens and had a methyl singlet in its nmr spectrum. The low-wavelength uv maximum for MeOH-I at 208 mμ is noted in several other conjugated cyclopentenones.[27] The high-frequency ir carbonyl band indicates the methoxyl group is probably α to the carbonyl group. The mass spectrum, besides featuring fragment ions from loss separately or together of one or two chlorine atoms (35 and 70), methoxyl (31), carbon monoxide (28), and methyl (15), also exhibits a peak at *m/e* 111, $C_6H_7O_2$, corresponding to an intact methoxycyclopentenone ring.

The ir band at 1625 cm^{-1} is assigned to the $>C{=}CCl_2$ group, by analogy with the band at 1616 cm^{-1} in compound **23**.[28] These data strongly suggest structure **22**, R = CH_3, for ketone MeOH-I. The coupling constant of 3.5 Hz between H_3 and H_4 is consistent with *gauche* but not *cis* hydrogens on a cyclopentane ring.[29]

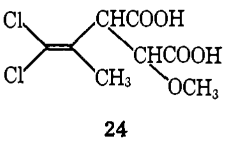


22

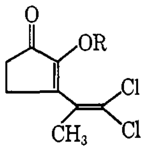


23

Verification for this structure comes from ozonolysis experiments,[19] in which 1.15 equiv of ozone was taken up. Base–hydrogen peroxide treatment of the ozonolysis solution gave a diacid **24**, mp 176–178°, $C_8H_{10}Cl_2O_5$. The nmr spectrum in acetone-d_6 showed singlets at δ 1.97 (methyl), 3.42 (methoxyl), 4.35 (2 H), and 11.17 ppm (2 H, carboxyl). The peak at 4.35 ppm remained a singlet in dimethyl-d_6 sulfoxide and chloroform-d_1, but was split into an AB quartet (J = 7.5 Hz) in benzene-d_6.



24



25

Further evidence for structure **22**, R = CH_3, comes from isomerization of **22**, on standing for extended periods in methanol[30] saturated with hydrogen chloride or on chromatography on neutral alumina, to a new ketone, assigned structure **25**, R = CH_3. This conjugated ketone, *m/e* 220, has its uv maximum (hexane) at 263 mμ (ϵ 14,600) and an ir carbonyl band at 1710 cm^{-1}. The nmr spectrum shows no vinyl hydrogens, a singlet (methyl) at δ 2.03, another singlet (methoxyl) at 3.96, and a symmetrical multiplet (4 H) centered at 2.47 ppm.

While these experiments were being carried out, a report appeared of the photochemistry of dienone **13** in aqueous dioxane[31] in the presence of calcium carbonate, which offered a ketone, mp 91–92°, assigned structure **22**, R = H. Part of the structure proof involved base-catalyzed isomerization to **25**, R = H, ir 1703 cm^{-1}, uv λ_{max}^{EtOH} 275 mμ (ϵ 8800).[31] We obtained the same ketone, mp 91–92°, and the spectral data, given in Tables II and III, strikingly resemble those of the methanol photoproduct. The structure assignment was confirmed by a positive periodate test, the rapid uptake of 1 equiv of hydrogen over 5% Pd–C,[32] and the mass spectrum, which is remarkably like that of the methanol photoproduct, shifted by 14 mass units. The stereochemistry of the water photoproduct is probably as in structure **22**, R = H, as

---

(24) H. Labhart and G. Wagniere, *Helv. Chim. Acta*, **42**, 2219 (1959).

(25) A. Moscowitz, K. Mislow, M. A. W. Glass, and C. Djerassi, *J. Amer. Chem. Soc.*, **84**, 1945 (1962).

(26) D. E. Bays, R. C. Cookson, and S. MacKenzie, *J. Chem. Soc.*, *B*, 215 (1967), and earlier references cited therein.

(27) R. L. Frank, R. Armstrong, J. Kwiatek, and H. A. Price, *J. Amer. Chem. Soc.*, 70, 1379 (1948).

(28) E. I. Heiba and R. M. Dessau, *ibid.*, **88**, 1589 (1966).

(29) M. Karplus, *J. Chem. Phys.*, 30, 11 (1959); H. Conroy, *Advan. Org. Chem.*, 2, 265 (1960).

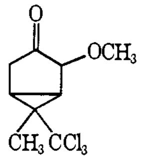
(30) We are grateful to Mrs. V. Abraitys for these experimental results.

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

(32) We are grateful to Mr. Ralph Propper for assistance with the preparation and characterization of the water photoproduct.

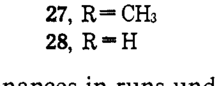
indicated[29] by the very small coupling between H_3 and H_4 seen in the nmr spectrum (Table II).

From experiments in methanol without added calcium carbonate, the nmr spectrum indicated another product was formed in addition to **22**, R = CH_3. Photolysis in methanol saturated with dry hydrogen chloride (dienone **13** does not react in methanol–HCl in the dark) gave this new ketone, designated MeOH-II, as the main product. Subtraction of the spectra of MeOH-I (**22**, R = CH_3) and unreacted dienone gave the spectrum of the new product. Attempts to isolate this product by column chromatography under mild conditions have been fruitless, although it survives prolonged standing in methanol–HCl under which conditions isomerization of **22** occurs.[30] The new product had an infrared carbonyl band at 1760 cm^{-1} and an nmr spectrum (Table II) indicating the complete absence of vinyl hydrogens, a methyl singlet at δ 1.30, a methoxyl singlet at 3.42, a singlet (1 H) at 3.25, and a multiplet from 2.0 to 2.7 ppm. The data are completely consistent with the assignment of structure **26** to MeOH-II, which is attractive from a mechanistic viewpoint, as seen in the accompanying paper.[15] Because of the failure to isolate this compound in pure form, any structure assignment must be regarded as tentative. Experiments to isolate this ketone are continuing.

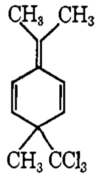


26

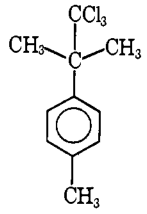
Photolysis of Dienone 13 in Olefins. Oxetane Formation. Dienone **13** was irradiated through Pyrex at low temperatures (Dry Ice–acetone cooling bath) in isobutylene and 2-methyl-2-butene and also at room temperature in the latter case. Oxetane formation is a reaction thought to be characteristic of ketones with an n,π^* configuration for the lowest triplet state[33] (see ref 15 for further discussion). Indeed, solid products were isolated which were clearly oxetanes on the basis of their spectral properties, particularly the nmr data in Table II. In the case of the oxetane from 2-methyl-2-butene, the quartet at δ 4.48 ppm is characteristic of the hydrogen on carbon α to oxygen.[33] A series of methyl singlets at 1.0–1.6 ppm indicates that both diastereomers of structure **27** are formed, further shown by the complex vinyl proton resonances at 5.8–6.6 ppm. From variations in the relative size of the methyl resonances in runs under slightly different conditions, the methyl resonances at 1.03, 1.28, and 1.42 ppm are assigned to one diastereomer, and the other methyl resonances to the other. Broad bands seen in the ir at 1020 and 1040 cm^{-1} are also characteristic of oxetanes.[33] The singlet for the protons α to oxygen at 4.18, the methyl singlets at 1.20 and 1.47, and the vinyl protons at 6.45 ppm (coincidentally appearing as a singlet) characterize oxetane **28**. Other minor nmr peaks may be due to a second diastereomer or some impurity. Again, there are several strong ir bands in the vicinity of 1000 cm^{-1}.[33] Both oxetanes decompose on standing at room temperature or upon column chromatography on alumina to give the same product, a white crystalline solid, mp 73–75°, *m/e* 250 (3 Cl). This compound, $C_{11}H_{13}Cl_3$, is formulated as **29** from its uv spectrum, λ_{max} 269 mμ (ϵ 18,000), characteristic of cross-conjugated trienes,[21] mass spectrum (*m/e* 250, 3 Cl), and nmr spectrum—AB quartet centered at 6.22 ppm (4 H, J = 10.5 Hz, vinyl protons in a six-membered ring),[17] two equivalent methyl groups at 1.88 (6 H, singlet), and a methyl singlet at 1.47 ppm. The triene thermally rearranges on heating or slowly on standing at room temperature to a compound **30** which had the following simple nmr spectrum: AB quartet, 4 H, centered at 7.27 (J = 8 Hz), a singlet (3 H) at 2.33, and a singlet (6 H) at 1.80 ppm. The ir bands at 3060, 3030, 1620, and 1530 cm^{-1} and the uv spectrum are characteristic of a substituted benzene. This thermal 1,5 rearrangement of a halomethyl group has precedent in the literature.[34,35]



27, R = CH_3
28, R = H



29



30

Miscellaneous Photolyses of Dienone 13. The results of a number of irradiations of dienone **13** carried out in solvents other than those discussed in detail above are summarized in Table V. In addition, it was found qualitatively that reaction in ethanol in the presence of calcium carbonate gave a product (not isolated) with retention time close to that of **22**, R = CH_3; little or no *p*-cresol was formed. Irradiation in benzene containing benzhydrol gave *p*-cresol, whose formation in 2-propanol was confirmed by ir and nmr spectroscopy.

Since irradiation in ether gave exclusively *p*-cresol and in benzene gave initially only lumiketone **14**, a study in mixtures of these two solvents was undertaken (Table VI). As benzene is diluted with ether, the yield of *p*-cresol increases at the expense of lumiketone **14**, indicating direct competition in the pathways to these two products.

Photolysis of Lumiketone 14 in Various Solvents. Careful glpc analysis of reaction mixtures from photolyses of lumiketone **14** in benzene, ether, and methanol gave no indication of the formation from **14** of dienone **13**, *p*-cresol, *m*-cresol, or **22**, R = CH_3, under any of the conditions given in Table VII. In methanol, nmr analysis indicated formation of a new product, not isolated, involving reaction with methanol, perhaps due to addition across the double bond.[36,37] Con-

---

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

[34] K. Auwers and W. Julicher, *Chem. Ber.*, **55**, 2167 (1922).

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

[36] P. J. Kropp, *ibid.*, **88**, 4091 (1966); P. J. Kropp and H. J. Krauss, *ibid.*, **89**, 5199 (1967).

[37] T. Matsuura and K. Ogura, *Bull. Chem. Soc. Jap.*, **40**, 945 (1967).

siderable hydrocarbon-insoluble material, assumed to be polymeric, was formed in all the irradiations of lumiketone ϕ-I (**14**).

Ketone ϕ-II was stable to further irradiation in benzene but formed a new unidentified saturated ketone on irradiation in ethyl ether.

Table V. Products of Irradiation of Dienone **13** in Various Solvents[a]

Solvent	Irradiation time, min	Yield, %: Dienone **13**	*p*-Cresol	ϕ-I (**14**)	ϕ-II (**21**)
Ethyl ether[b]	20	11	65	*b*	. .
Tetrahydrofuran[b]	20	17	55	*b*	. .
Dioxane[b]	20	14	21	*b*	9
Cyclohexane[b]	20	22	30	*b*	2
Benzene[b]	20	34	0	*b*	31
Cumene[c]	5	66	2	12	6
	20	23	5	2	24
Toluene[c]	5	82	1	11	5
	24	25	2	3	31
2-Propanol[c,d]	5	64	25	0	0
	20	2	45	0	0

[a] Irradiation of 0.01 mol of dienone **13** in 640 ml of solvent, 450-W Hanovia high-pressure mercury lamp, quartz immersion well, Pyrex filter. [b] Glpc analysis on $^1/_8$ in. × 4 ft. 10% Carbowax 20M on Chromosorb P; dienone **13** and product ϕ-I are not well separated. The peak due to **13** contained no more than 4% of lumiketone ϕ-I (nmr, glpc analysis on other columns). [c] Analysis on $^1/_8$ in. × 4 ft 10% cyanosilicone XF-1150 on Chromosorb P. All products are separated. [d] Solution contains 20 g of calcium carbonate (suspension). Glpc analysis indicates another unidentified product, perhaps (from retention times) the isopropyl analog of the methanol photoproduct, **22**, R = isopropyl.

Table VI. Irradiation of Dienone **13** in Benzene–Ether Mixtures[a]

Benzene, ml	Ether, ml	*p*-Cresol, yield,[b] %	Yield of **14**,[b] %
15	0	0.0	2.3
13	2	0.3	1.8
11	4	0.7	1.5

[a] Tubes were simultaneously irradiated through Pyrex in a merry-go-round apparatus surrounding a 100-W Hanovia high-pressure mercury arc. Each tube contained 1.0 g of dienone **13**. [b] All tubes were analyzed after 15-min irradiation on a 5 ft × $^1/_8$ in. 15% cyanosilicone XF-1150 on Chromosorb P column with acenaphthene as internal standard.

Table VII. Irradiation of Lumiketone ϕ-I (**14**)[a]

Solvent	Filter	Irradiation time, min	Yield,[b] %: ϕ-I (**14**)	ϕ-II (**21**)[c]	ϕ-III (**21**)[d]
Benzene	None[a]	10	28	24	2
Benzene	Pyrex	3	33	30	3
		10	5	49	5
Ethyl ether	Pyrex	3	64	22	3
Methanol	Pyrex	6	0	52	2

[a] Irradiations of 85.5 mg (3.8×10^{-4} mol) of lumiketone ϕ-I (**14**) in 640 ml of solvent, 450-W Hanovia high-pressure mercury lamp, quartz immersion well, Pyrex filters, except for the first entry in the table which was carried out with 2537-Å lamps in a Srinivasan-Griffin Rayonet reactor. [b] Analyses by glpc on a 4 ft × $^1/_8$ in. 10% cyanosilicone XF-1150 on Chromosorb P column. [c] The presence of ϕ-II was confirmed by nmr spectra of crude photolysates. [d] This product has the same glpc retention time under the conditions used as dienone **13**; however, nmr spectra indicated no dienone **13** in the product. Thus, this peak was assumed to be entirely due to ϕ-III.

Experimental Section

Spectra. Nuclear magnetic resonance spectra were taken on a Varian A-60 spectrometer, with tetramethylsilane as an internal standard. Spectra of ϕ-I and ϕ-II were also recorded at 100 MHz by Varian Associates, Pittsburgh, Pa. Infrared spectra were recorded on a Perkin-Elmer Model 337 grating Infracord spectrophotometer, ultraviolet spectra on a Cary 15 spectrophotometer using 1-cm cells, and mass spectra at Columbia University on a Hitachi-Perkin-Elmer Model RMV-6D spectrometer, with the assistance of Miss V. Parmakovich. The chlorine composition of each fragment ion could be determined from the relative intensities of the M, M + 2, M + 4, and M + 6 peaks, etc.[38] Only the M peaks, *i.e.*, those containing only ^{35}Cl, are given in Table III and elsewhere in the text.

Photochemical Apparatus. Most of the irradiations were carried out in a specially designed Pyrex vessel which fitted around a Hanovia quartz immersion well containing 100- or 450-W Hanovia high-pressure mercury lamps and Pyrex filters. The vessel has a capacity of 640 ml and is equipped with a nitrogen inlet, an outlet with a stopcock for removing aliquots for analysis, and a condenser. The solutions were stirred with a magnetic stirring bar. Irradiations at 2537 Å were carried out in a quartz reaction flask inside a Srinivasan–Griffin Rayonet reactor (Southern New England Ultraviolet Co.). The "merry-go-round" apparatus consisted of a circular rack containing either six or twelve Pyrex tubes with ground glass joints on a turntable surrounding a quartz immersion well containing the light source and appropriate filters. The rack was rotated using a motor and reduction gears at adjustable speed.

Photochemical and Analytical Procedures. Nitrogen was bubbled through all solutions for 1 hr prior to irradiation, and a nitrogen atmosphere was maintained during irradiation by passage through the solution or by means of a bypass. Nitrogen used for this purpose was purified by passage through pyrogallol, sulfuric acid, and benzophenone ketyl solution to remove all traces of oxygen and moisture. Samples were removed during irradiation and the progress of the reaction was determined by ultraviolet spectroscopy or gas–liquid partition chromatography (glpc).

All glpc data were obtained on the F & M Model 810 dual-column instrument equipped with a disk chart integrator using flame ionization detection. Initial studies were carried out on a 10% Carbowax 20M on Chromosorb P column ($^1/_8$ in. × 4 ft) at a column temperature of 180°. Later studies were made on columns of cyanosilicone XF-1150 on Chromosorb P (10%, $^1/_8$ in. × 4 ft or 15%, $^1/_8$ in. × 5.25 ft) at column temperatures of 160°. Injections using a microliter syringe were always kept under 3 μl. Details of retention times and exact conditions in each case can be obtained elsewhere.[39]

When aliquots were removed every few minutes, the course of reaction was followed by determining the relative glpc peak areas of product and reactant, correcting for the relative areas of these compounds determined from calibration mixtures of these compounds prepared separately. When an internal standard was used for calibration, the relative glpc peak areas of reactants, products, and internal standard (added after irradiation) were determined, and the amounts of the reactant and products could be calculated using detection response factors determined from analysis of carefully prepared standard solutions of the reactants, products and standard. The relative peak areas in the standard calibration solution were kept as close as possible to those obtained on analysis of the photolysis solution. Details of all procedures are given in ref 39.

4-Methyl-4-trichloromethyl-2,5-cyclohexadien-1-one (13). Dienone **13** was made by the procedure of Newman and Pinkus.[14] The product was recrystallized from hexane, mp 103.5–104° (lit.[14] 103.8–104.2°), and purified by sublimation under high vacuum at bath temperatures below 100°. The spectra are reported in the text, except for the nmr spectrum which shows an AB quartet (J = 11 Hz) centered at δ 6.71 (4 H) and a singlet at 1.68 ppm (3 H).

Photoproduct ϕ-I. 6-Methyl-6-trichloromethylbicyclo[3.1.0]hex-3-en-2-one (14). Using the Srinivasan–Griffin apparatus, 10 g of dienone **13** in 640 ml of purified benzene was irradiated at 2537 Å for 3 hr, consuming only a small portion of dienone. A large part of the unreacted dienone could be separated by crystallization on addition of hexane and a crystal of dienone **13**. The residue was column chromatographed on silica gel. The ketone ϕ-I was eluted first

---

(38) K. Biemann, "Mass Spectrometry: Organic Chemical Applications," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

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

with 80% benzene–20% hexane, followed by the dienone, and was purified by recrystallization from hexane and sublimation, mp 74–76°. *Anal.*[40] Calcd for $C_8H_7Cl_3O$: C, 42.61; H, 3.13; Cl, 47.19. Found: C, 42.96; H, 3.44; Cl, 45.22.[41]

Hydrogenation of lumiketone 14 in ethanol over 5% Pd–C was halted after uptake of 0.95 equiv of hydrogen. The slightly acidic solution, after filtration, was neutralized with calcium carbonate and filtered, and ethanol was removed at reduced pressure. The residue crystallized at refrigerator temperatures, and was vacuum sublimed at 50° to give a white solid, mp 78–79°. *Anal.* Calcd for $C_8H_9Cl_3O$: C, 42.24; H, 3.99; Cl, 46.77. Found: C, 42.44; H, 4.34; Cl, 46.06.

The hydrogenated lumiketone had no resonance in the vinyl hydrogen region, a singlet (3 H) at 1.55 ppm, and a complex multiplet at 1.67–2.83 ppm. The ir spectrum had bands at 3030, 1750, 1180, 1140, 1030, 990, 900, and 870 cm^{-1}. The mass spectrum had prominent peaks at 226 (3 Cl), 191 (2 Cl), 184 (3 Cl), 149 (2 Cl), 144 (3 Cl), 127 (1 Cl), and 113 (1 Cl).

Other Reactions of Lumiketone 14. Quantitative ozonolysis of **14** in methylene chloride with an excess of ozone at −78° led to uptake of 0.86 equiv of ozone.[19] After evaporation of methylene chloride and removal of excess ozone with nitrogen, the mixture was treated dropwise with 4 ml of 30% hydrogen peroxide and 20 ml of 10% sodium hydroxide. There was spontaneous reflux and the contents were allowed to stand overnight. Extraction led to isolation of a yellow-brown oil, whose spectral and analytical data indicated it was not the expected cyclopropanedicarboxylic acid derivative, but rather that one chlorine had been replaced by hydroxyl. Further attempts at purification of this material were not successful.

The lumiketone **14** (0.5 g) could be completely recovered after being heated at reflux for 3 hr with 3 g of zinc in 200 ml of ethanol. Attempts at conversion of **14** to a carboxylic acid derivative by reaction with sodium methoxide in methanol at room temperature led to recovery of starting material and a small amount of an impure product whose spectra indicated addition of methanol across the double bond: nmr, multiplet 2.2–2.8 ppm, singlet 3.33 ppm (methoxyl), singlet 1.5 ppm (methyl); ir, 1755 cm^{-1}.

Photoproducts φ-II and φ-III (20 and/or 21). Dienone **13**, 10 g, was irradiated in 640 ml of benzene with a 450-W high-pressure mercury lamp and Pyrex filter for 3 hr. After removal of benzene at reduced pressure, the residual oil was dissolved in a few milliliters of benzene and hexane was added slowly with stirring, leading to precipitation of a solid, until no further solid precipitated. The apparently polymeric solid was separated by filtration and the solution was concentrated to give a residue which was column chromatographed on silica gel. Early benzene eluents gave ketone φ-II,[23] which was recrystallized from hexane and vacuum sublimed at 50°, mp 62–64°. *Anal.* Calcd for $C_8H_7Cl_3O$: C, 42.61; H, 3.13; Cl, 47.19. Found: C, 43.08; H, 3.74; Cl, 46.73. Later benzene eluents gave a second ketone, φ-III, purified in the same way, mp 65.5–68°, whose small amounts precluded further study. Spectral data for φ-II and φ-III are given in Tables II and III.

Hydrogenation of ketone φ-II over 5% Pd–C resulted in rapid uptake of 1 equiv of hydrogen. The usual work-up gave a white solid, mp 60–62°, with a carbonyl band at 1755 cm^{-1} and no ir bands at 1595 and 700 cm^{-1}. The nmr spectrum had a singlet at 2.0 ppm, a complex resonance at 1.5–2.8 ppm, and no vinyl proton resonance. The mass spectrum had a molecular ion at 226, 3 Cl. *Anal.* Calcd for $C_8H_9Cl_3O$: C, 42.24; H, 3.99; Cl, 46.77 Found: C, 42.05; H, 4.01; Cl, 46.15.

Zinc Dehalogenation of Ketone φ-II. Photoproduct φ-II (500 mg) was heated at reflux for 4 hr with 2 g of zinc in ethanol. The solution was filtered and ethanol removed under reduced pressure. Chloroform was added and the solution dried over magnesium sulfate. After filtration, the chloroform was removed *in vacuo*. Column chromatography on silica gel resulted in isolation of the minor component in hexane–benzene eluents and the major component in benzene eluents. The major liquid product had an elemental analysis consistent with loss of chlorine. *Anal.* Calcd for C_8H_7ClO: C, 62.15; H, 4.53; Cl, 22.98. Found: C, 62.05; H, 4.77; Cl, 23.19. The ir spectrum (CCl_4) showed bands at 1725, 1675, 1585, 1350, 1205, 1160, 1140, 1035, 1020, 930, 895, 860, 735, 615, and 580 cm^{-1}. The uv spectrum (cyclohexane) had maxima at 204 (ε 7730), 221 sh (5020), 323, 338, 354 (270), 368, 371, 388, and 390 mμ. The nmr spectrum (CCl_4) had resonances at δ 7.65 ppm (1 H, J_{12} = 5.9, J_{23} = 2.9 Hz), 6.07 (1 H, J_{12} = 5.8, J' = 1, J'' = 0.5 Hz), 3.95 (1 H, multiplet), 3.27 (1 H, multiplet), and 1.78 ppm (J' = 1.5, J'' = 2.1 Hz). The structure of the product is thus **18** or **19**. The minor reaction product shows an ir carbonyl band at 1755 cm^{-1}, a C=C stretch at 1675 cm^{-1}, but no band at 1585 cm^{-1}, consistent with addition of ethanol across the α,β conjugated double bond of the major component.

Photolysis in Methanol. Photoproduct MeOH-I. 5-Methoxy-4-[2-(1,1-dichloropropenyl)]cyclopent-2-enone (22, R = CH_3). Irradiation of dienone **13** in methanol in the presence of excess calcium carbonate (to neutralize HCl formed in the reaction) gave photoketone MeOH-I. The photolysate was filtered and methanol removed *in vacuo*. Addition of chloroform, drying over magnesium sulfate, filtration, and removal of methanol *in vacuo* gave an oil which was chromatographed on a column of silica gel. The product was collected in benzene–chloroform eluents and was distilled, bp 97–99° (0.3 mm). The distillate crystallized on cooling and was recrystallized from benzene, mp 59–60°. Spectral data are given in Tables II and III. *Anal.* Calcd for $C_9H_{10}Cl_2O_2$: C, 48.91; H, 4.53; Cl, 32.10. Found: C, 48.95; H, 4.70; Cl, 29.4.[41]

Hydrogenation of MeOH-I (22, R = CH_3) over 5% Pd–C resulted in rapid uptake of 1 equiv of hydrogen. Further hydrogen uptake was slow. The ir spectrum (CCl_4) showed no band at 1585 cm^{-1} but the presence of the 1620-cm^{-1} band, while the nmr spectrum showed no vinyl hydrogens; ir, 2800, 1765, 1620, 1105, 900 cm^{-1}; nmr, δ 1.93 (singlet), 3.50 (singlet), 1.1–1.4 (weak multiplet), 1.7–2.5 (multiplet), and 3.3–4.0 ppm (multiplet). The results indicate selective hydrogenation of the carbonyl conjugated double bond. Attempts at crystallization of the material were unsuccessful. The ketone could be quantitatively recovered from reflux with zinc in ethanol for 4.5 hr.

Ozonolysis of MeOH-I (22, R = CH_3, 4.43 mmol) was carried out with a threefold excess of ozone in methylene chloride at −80°, resulting in uptake of 1.15 equiv of ozone. Excess ozone was removed with nitrogen, and the reaction mixture was treated with 20 ml of 10% sodium hydroxide and 4 ml of 3% hydrogen peroxide. After reflux on addition of the reagents, the solution was stirred at room temperature overnight. The layers were separated, and the aqueous layer acidified with 10% hydrochloric acid, saturated with sodium chloride and extracted with three 1-lb portions of ethyl ether. The ether solution was dried over magnesium sulfate and filtered, and ether removed *in vacuo*. The residue was recrystallized from acetone–hexane, mp 176–178°. The nmr spectrum is described in the text, allowing assignment of structure **24** to the ozonolysis product. *Anal.* Calcd for $C_8H_{10}Cl_2O_5$: C, 37.38; H, 3.92; Cl, 27.58. Found: C, 37.51; H, 3.91; Cl, 27.32.

Isomerization of MeOH-I (22) to Ketone 25.[30] When a solution of ketone **22**, R = CH_3, in methanol acidified with hydrogen chloride was allowed to stand for an extended period, the nmr spectrum of the solution changed as ketone **22** disappeared. The spectrum of a new compound appeared, described in the text. The isomerization could also be brought about by chromatography on neutral alumina whereby pure **22** was converted quantitatively into the new ketone, isolated as an oil, assigned structure **25**, R = CH_3, on the basis of the spectral data and analogy with the isomerization studies of King and Leaver.[31]

Photoketone MeOH-II (26). 2-Methoxy-6-methyl-6-trichloromethylbicyclo[3.1.0]hexan-3-one. Irradiation of dienone **13** through Pyrex in 640 ml of methanol acidified with 4 g of gaseous hydrogen chloride was followed by nmr spectroscopy. Spectra indicated the presence of **13** plus a new compound, whose spectrum is given in Table II. The mixture could be distilled *in vacuo* at 110° without change in spectrum, while chromatography on alumina or silica gel led to loss of the new component. On standing for extended periods in methanol–HCl, no change in the nmr spectrum of the new compound was observed, under conditions which caused the isomerization of ketone **22**. The product, which was never isolated in pure form, is tentatively assigned structure **26** on the basis of its spectral data.

Irradiation of Dienone 13 in Isobutylene and 2-Methyl-2-butene. Oxetane Formation. Irradiation of dienone **13** in isobutylene or 2-methyl-2-butene through Pyrex was carried out at low temperatures in the usual reaction flask, equipped with a Dry Ice–acetone condenser, one-third immersed in the cooling bath. Complete reaction of 2 g of dienone **13** required 2 hr. The solvent was removed by

---

[40] Elemental analyses by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

[41] In this and other instances, chlorine analyses were low although carbon and hydrogen analyses were satisfactory. Since the composition of the material is completely defined by its mass spectrum, there can be no question of the correctness of the molecular formula. The reason for the discrepancy in the chlorine analyses is not known.

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

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

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

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

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

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

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

---

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

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

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

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

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

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

---

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

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

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

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