

Photochemical Transformations of 2,2-Dimethylspiro[4,5]deca-6,9-dien-8-one. Solvent Effects on the Stereochemistry of the Lumiketone Rearrangement¹⁻³

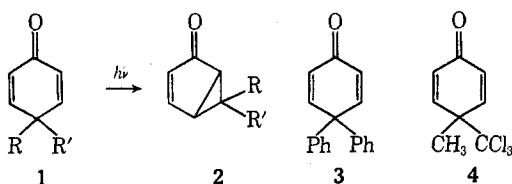
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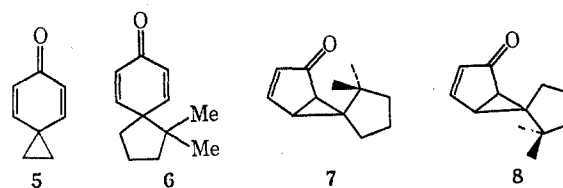
The title compound was prepared by two different routes which have in common a ring closure modeled after the synthesis of the parent unsubstituted compound by Baird and Winstein. Photolysis of the spirodienone **6** gives a product mixture which was separated into a ketonic and a phenolic part. The ketone products were shown to be a mixture of the two epimeric spiro lumiketones **7** and **8**. Assignment of stereochemistry to the ketones is based on nmr and mass spectral data, and spectra of hydrogenation products. An interesting case of nmr deshielding due to steric interactions is reported for these compounds. The phenolic fraction was shown to consist of a mixture of 1,1-dimethyl-7-tetralol (**20**), 1,1-dimethyl-6-tetralol (**25**), and 1,1-dimethyl-8-tetralol (**26**). None of the expected fragmentation product **28** was found, and conclusions with respect to the general occurrence of radical fragmentations in dienone photochemistry are made. Quantum yield, sensitization, and quenching data for conversion of **6** to the lumiketones, as well as conversion of lumiketones to phenols, are given. It is concluded that the dienone-lumiketone reaction occurs exclusively by the lowest triplet, whose energy is 60–69 kcal/mol above the ground state, and whose lifetime in benzene appears to be 1.3×10^{-10} sec from the quenching data. These data are similar to those found for other 2,5-cyclohexadienones. The stereochemistry of the lumiketone rearrangement is discussed in detail, and it is shown that the stereochemistry of the product is determined at the time the bond forms between C₃ and C₅ of the dienone. The steric course of the ensuing [1,4]-sigmatropic shift is discussed, and, while ground state analogy would suggest reaction with inversion of configuration (*i.e.*, maintenance of exo-endo relationships as the reaction proceeds), no firm conclusion with respect to the stereochemistry of the photochemical rearrangement is as yet possible. A solvent effect on the ratio of epimeric ketones is reported and discussed. It is shown that the photochemistry of the lumiketones cannot be quenched by typical triplet quenchers, and it is concluded that the reaction most likely proceeds *via* the excited singlet state, S₁. Some of the results indicate that in this case photochemical reversion of the lumiketones to dienone **6** probably occurs to a small extent. The direction of rearrangement of the lumiketones conforms to the predictions of earlier molecular orbital calculations.

The photochemical transformation of cross-conjugated cyclohexadienones **1** into bicyclo[3.1.0]hexenones **2** (lumiketones) is by now a well-known reaction.⁶ Many aspects of the mechanism are well understood, particularly with respect to the sequence of steps involved in the isomerization, and identification of the n, π^* triplet as the reactive excited state in the model monocyclic cyclohexadienones **3** and **4**.⁷⁻⁹ It has been shown in an intensive study of compound **4**⁹ that in hy-



drogen-donating solvents an abstraction-fragmentation reaction to give *p*-cresol can compete effectively with the lumi rearrangement, and that both reactions originate from the same excited triplet state.¹⁰ In sys-

tems such as **4** where competitive reaction paths exist on excitation, it is possible to obtain considerable information experimentally regarding the structure of the excited state and the sequence of reactive intermediates involved in the reaction.⁹ While photochemical radical fragmentation reactions of cyclohexadienones are known involving loss of trichloromethyl,¹¹ acetoxy,¹² and methoxy¹³ groups, no example illustrating loss of an alkyl radical had been observed when this study began. The only exception is the photochemical cleavage of the cyclopropane ring in the strained spirodienone **5**, which is a special case and mechanistically unrelated to dienone photochemistry in general.^{14,15} It was therefore of interest to study a cyclohexadienone in which such an alkyl radical fragmentation was a reasonable expectation, but in which there were no special considerations of strain or unusual electronic effects to complicate the interpretation. The spirodienone **6** seemed a good candidate for such a study.



An additional intriguing aspect of the study of **6** was the possibility of generating two diastereomeric lumiketones, **7** and **8**, and studying the factors affecting the stereoselectivity of the reaction. Few studies had been

(1) Part XXVI of a series on the photochemistry of unsaturated ketones in solution. Part XXV: D. I. Schuster and D. J. Blythin, *J. Org. Chem.*, **35**, 3190 (1970).

(2) Supported by the U. S. Army Research Office (Durham) by grants under project 4019-C, and by the National Science Foundation, Grant GP-7433.

(3) A portion of this work was communicated earlier: W. V. Curran and D. I. Schuster, *Chem. Commun.*, 699 (1968). Part of this work was presented at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, P-162.

(4) Alfred P. Sloan Fellow, 1967–1969; to whom correspondence should be addressed.

(5) American Cyanamid Junior Educational Award, 1967–1968; this paper is based on the Ph.D. Dissertation of W. V. C., New York University, 1968; Organic Chemical Research Section, Lederle Laboratories, Pearl River, N. Y.

(6) For recent reviews, see (a) P. J. Kropp, *Org. Photochem.*, **1**, 1 (1967);

(b) K. Schaffner, *Advan. Photochem.*, **4**, 81 (1966).

(7) H. E. Zimmerman and D. I. Schuster, *J. Amer. Chem. Soc.*, **84**, 4527 (1962).

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

(9) D. I. Schuster and D. J. Patel, *ibid.*, **90**, 5145 (1968).

(10) D. I. Schuster and S. D. Denver, unpublished results.

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

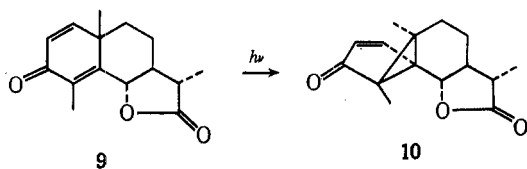
(12) R. Warszawski, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **43**, 500 (1960).

(13) T. Matsuura, *Bull. Chem. Soc. Jap.*, **37**, 564 (1964).

(14) D. I. Schuster and C. J. Polowczyk, *J. Amer. Chem. Soc.*, **88**, 1722 (1966).

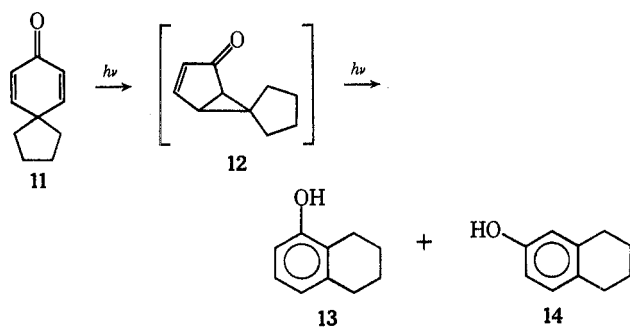
(15) D. I. Schuster and I. S. Krull, *Mol. Photochem.*, **1**, 107 (1969).

made as of the time this work was begun in which more than one lumiketone was possible on photoisomerization of a cyclohexadienone. For example, dienones in which there is a fusion to a six-membered ring, as in α -santonin **9** and steroid dienones, are constrained to give only one lumiketone, *e.g.*, **10**, because of strain restrictions imposed by the ring fusion.¹⁶ In the case of die-



none **4**, the surprising observation was made^{9,17} that the lumi rearrangement was totally stereospecific, although the stereochemistry of the single diastereoisomer formed in the reaction was not rigorously established. The factors influencing the stereochemistry of such rearrangements in systems without steric constraint (such as a ring fusion) are a matter of considerable current interest.¹⁸ It was anticipated that the study of **6** might provide valuable information on this point. Finally, **6** seemed a good system in which to study photochemical dienone-phenol rearrangements, some aspects of which were still puzzling.⁶

In an earlier study, it was shown that photolysis of the unsubstituted spirodienone **11** gave phenols **13** and **14**, presumably *via* lumiketone **12** (not isolated) as an intermediate.¹⁹



Results

Synthesis of 2,2-Dimethylspiro[4,5]deca-6,9-dien-8-one (6).—Two routes to the synthesis of **6** are shown in Scheme I. The critical step, ring closure of the tosylate **15**, was based on the original synthesis of **11** by Baird and Winstein using an A_{r1-5} participation process.²⁰ Some other aspects of the reactions in Scheme I deserve comment. The selective Friedel-Crafts reaction of anisole with diol **16** to give **17** in good yield is a rare use of unsymmetrical diols in such a reaction.²¹ The demethylation of **17** to give **18** under alkaline con-

(16) For discussion of this point, see ref 7 and also H. E. Zimmerman, *Advan. Photochem.*, **1**, 183 (1963).

(17) D. I. Schuster and D. J. Patel, *J. Amer. Chem. Soc.*, **88**, 1825 (1966).

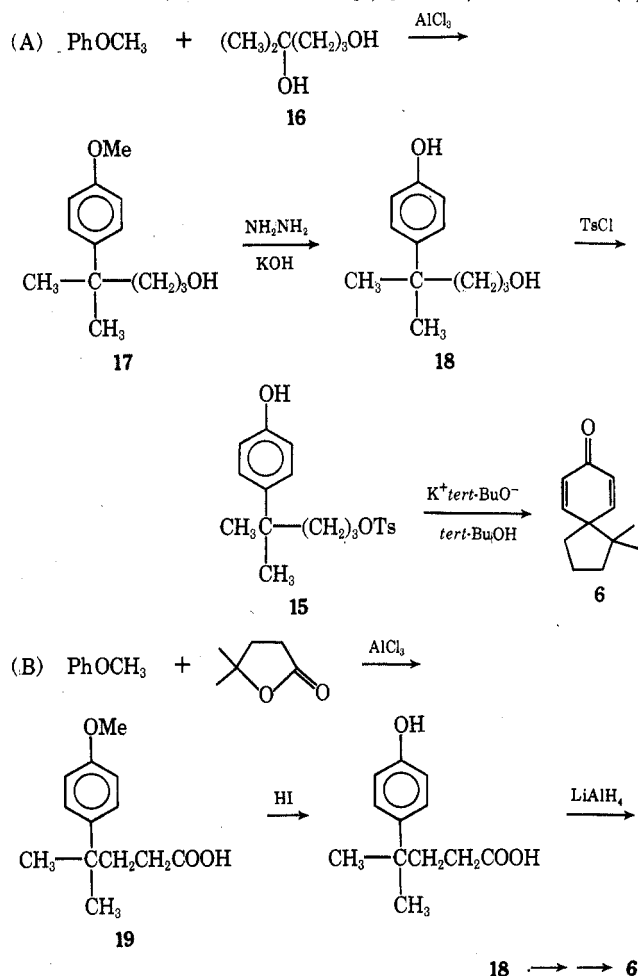
(18) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, GmbH, Academic Press, New York, N. Y., 1970, p 89 ff.

(19) A. A. Griswold, Ph.D. Dissertation, Iowa State University, 1963.

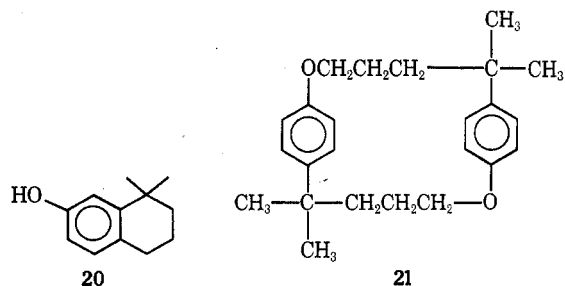
(20) R. Baird and S. Winstein, *J. Amer. Chem. Soc.*, **84**, 788 (1962); **85**, 587 (1963).

(21) (a) G. Olah in "Friedel-Crafts and Related Reactions," Vol. 1, G. Olah, Ed., Interscience, New York, N. Y., 1963, p 903; (b) A. Schriesheim, *ibid.*, Vol. 2, 1964, p 507.

SCHEME I SYNTHESIS OF 2,2-DIMETHYLSPIRO[4,5]DECA-6,9-DIEN-8-ONE (6)



ditions is based on a procedure of Kropp.²² This route turned out to be less than satisfactory in practice, and the alternative route was devised. Lactones are known to undergo carbon alkylation under Friedel-Crafts conditions,²³ and hence reaction of 4,4-dimethylbutyrolactone with anisole gave **19**²⁴ in good yield. The latter was converted by standard reactions into the phenolic alcohol **18**, which in turn was converted to the tosylate **15** by Kropp's method.²² Attempts to crystallize the oily tosylate were without success, but ring closure of crude **15** to **6** by reflux with potassium *tert*-butoxide in *tert*-butyl alcohol²⁰ was successful. Attempts at isolation of **6** by chromatography of the crude reaction mixture on silica gel gave only phenol **20**, presumably by



(22) P. J. Kropp, *Tetrahedron*, **21**, 2183 (1965).

(23) R. V. Christian, Jr., *J. Amer. Chem. Soc.*, **74**, 1591 (1952); W. E. Truce and C. E. Olson, *ibid.*, **74**, 4721 (1952).

(24) H. Hart, J. L. Corbin, C. R. Wagner, and C-Y. Wu, *ibid.*, **85**, 3269 (1963).

TABLE I
SPECTRAL DATA FOR KETONES

Compd	Uv, $\lambda_{\max}^{\text{EtOH}}$, nm (ϵ)	Ir, cm^{-1}	Nmr (CCl_4), δ , ppm, J in Hz	Mass, m/e (% of base)
6	245 (15,150)	2950, 2925, 2840, 1670, 1660, 1620, 1595, 1470, 1460, 1420, 1390, 1370, 1235, 1160, 1100, 862, 846	6.83 (d, $J = 10.5$, 2 H), 6.47 (d, $J = 10.5$, 2 H), multiplet centered at 1.92 (6 H), 0.97 (s, 6 H)	Not taken
7	228 (5,300), 265 (2,040), 335 (200)	2990, 2930, 2840, 1700, 1630, 1575, 1460, 1390, 1375, 1350, 1310, 1160, 960, 880, 860, 845	7.35 (H_2 , $J_{12} = 5.5$, $J_{23} = 2.8$), 5.70 (H_1 , $J_{12} = 5.5$), 2.45 (H_3 , $J_{23} = 2.8$, $J_{34} = 5.5$), 1.92 (H_4 , $J_{34} = 5.5$), 1.08 (s, 3 H), 1.01 (s, 3 H)	176 (31), 161 (75), 133 (14), 120 (26), 107 (48), 96 (57), 95 (100), 91 (22), 81 (48)
8	227 (6,500) 265 (3,350), 335 (272)	3050, 2930, 2840, 1700, 1630, 1580, 1470, 1460, 1390, 1375, 1350, 1310, 1160, 960, 880, 857, 843	7.35 (H_2 , $J_{12} = 5.5$, $J_{23} = 2.8$), 5.73 (H_1 , $J_{12} = 5.5$), 2.44 (H_3 , $J_{23} = 2.8$, $J_{34} = 5.5$), 2.01 (H_4 , $J_{34} = 5.5$), 0.87 (s, 6 H)	176 (59), 161 (100), 133 (14), 120 (79), 107 (23), 95 (53), 91 (12), 81 (14)
22		2960 (sh), 2920, 2840, 1725, 1480, 1420, 1375, 1172, 1130, 1010, 930, 888, 875	Multiplets centered at 2.17 and 1.60, 1.20 (s, 3 H), 1.00 (s, 3 H)	178 (6), 136 (23), 121 (23), 107 (20), 96 (57), 93 (23), 91 (25), 81 (100)
23		2920, 2840, 1725, 1465, 1415, 1385, 1370, 1168, 1125, 1005, 930, 875, 845	1.5-2.3 (multiplet), 0.87 (s, 3 H), 0.82 (s, 3 H)	178 (17), 136 (55), 121 (24), 108 (25), 96 (75), 93 (32), 91 (23), 81 (100)
24		3000, 2960, 2830, 1715, 1475, 1420, 1390, 1370, 1310, 1280	1.8-2.3 (multiplet), 1.55 (multiplet), 0.90 (s, 6 H)	180 (45), 137 (19), 123 (59), 110 (100), 97 (38), 95 (23)

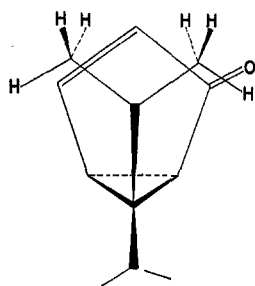


Figure 1.—Perspective drawing of compound 7 indicating the position of the methyl groups.

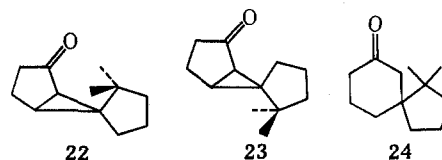
acid-catalyzed rearrangement of 6, but 6 could be isolated after chromatography of the crude mixture on basic alumina. The best yields obtained in the last step were 25–30%. The spectral data on the crystalline spirodienone, mp 50–51.5°, are given in Table I. A high-melting crystalline solid obtained in small amounts as a by-product of the ring closure is assigned structure 21 on the basis of spectral data and analogy with a similar compound isolated by Griswold.¹⁹

Photolysis Products. A. Lumiketones.—Photolyses of the dienone 6 in methanol, at concentrations of about 1.0 g per 600 ml of methanol, were carried out under nitrogen in a quartz vessel at 2537 Å in a Rayonet photochemical reaction chamber. Since satisfactory conditions for analyses of 6 using gas-liquid chromatography (glc) could not be found, due to the ease of thermal dienone-phenol rearrangement, the reaction was followed by infrared spectroscopy. The crude reaction mixture was readily separated into ketonic and phenolic fractions by column chromatography on basic alumina. The ketonic fraction is discussed below, and the phenolic fraction is discussed later. The ketone fraction was shown to be a mixture of two compounds, ratio 2:1, by glc analysis on 15% Carbowax 20M. The compounds could not be separated by column or liquid-liquid chromatography, but small amounts of each com-

pound could be obtained by preparative glc on a Carbowax 20M column.

The spectral data for the two ketones, given in Table I, are very similar. The infrared spectra show small differences only in the fingerprint region. Comparison with earlier data on bicyclo[3.1.0]hex-2-en-1-ones^{25–27} clearly indicates that these two compounds are the isomeric lumiketones 7 and 8. The nmr spectra in carbon tetrachloride show that the methyl groups of one isomer appear together at δ 0.87 while the other isomer shows two resonances at δ 1.01 and 1.08. It might have been anticipated that the methyls in 7 would be shielded relative to those in 8, since in 7 one methyl lies above the carbonyl group while the other is over the carbon-carbon double bond (see Figure 1). However, molecular models show that the methyls in 7 are within the van der Waals radii of the cyclopentenone ring atoms and would probably be shifted to low field, since steric crowding results in a deshielding effect.²⁸ In addition, the methyls in 8 should have more nearly the same chemical shift than those in 7.

Confirmation of the proposed stereochemistry of 7 and 8 was obtained from their dihydro derivatives. A mixture of the two lumiketones was hydrogenated at atmospheric pressure over 10% Pd-C, and two isomeric products 22 and 23 were isolated in small quantities by

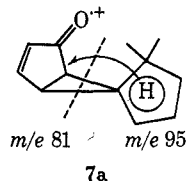


(25) D. J. Patel and D. I. Schuster, *J. Amer. Chem. Soc.*, **90**, 5137 (1968).
 (26) J. Frei, C. Ganter, D. Kägi, K. Kocsis, M. Miljkovic, A. Siewinski, R. Wenger, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **49**, 1049 (1966).
 (27) P. J. Kropp, *J. Amer. Chem. Soc.*, **86**, 4053 (1964); P. J. Kropp and W. F. Erman, *ibid.*, **85**, 2456 (1963).
 (28) Numerous examples of a deshielding effect due to intramolecular steric compression have been reported. For example, see S. Winstein, P. Carter, F. A. L. Anet, and A. J. R. Bourn, *ibid.*, **87**, 5247 (1965), and references cited therein.

preparative glc on Carbowax 20M. Spectral data are given in Table I. In a separate experiment, the lumiketone with the longer glc retention time (7) gave the dihydro compound with the longer retention time (22). Both products had a parent peak in their mass spectra at m/e 178, and a sharp carbonyl band in the ir at 1725 cm^{-1} . The lumiketone which has its methyl resonances at δ 1.01 and 1.08 affords a reduced ketone with resonances at δ 1.00 and 1.20, compared with a corresponding change from δ 0.87 to a split resonance at δ 0.82 and 0.87 for the other isomer. This information supports the stereochemical assignments. The methyl groups in 8 would not be expected to be affected much by saturation of the double bond, while those in 7 should experience even more severe steric compression in the saturated analog 22, leading to increased deshielding.²⁸ Hydrogenation of 7 should produce little change in that methyl which is over the carbonyl group, suggesting that the major change from δ 1.02 to 1.20 ($\Delta\delta$ 0.18) is due to the methyl over the double bond. If the reverse assignment to the methyls in 7 is made, one of the methyls must still experience a deshielding of 0.12 ppm.

Additional support for the stereochemistry assignment to 7 and 8 comes from the further hydrogenation of the more strained dihydro lumiketone 22 under conditions which do not affect 23. The new product is assigned structure 24, 1,1-dimethylspiro[4,5]decan-7-one, on the basis of a parent peak in the mass spectrum at m/e 180, a carbonyl band at 1720 cm^{-1} in the infrared, and a methyl resonance at δ 0.90 in the nmr. The preference for structure 24 over other possible compounds formed by cleavage of one of the other two cyclopropane bonds is based principally on the ir data, since such compounds would have carbonyl bands in the $1740\text{--}1750\text{ cm}^{-1}$ region. Such a preferential reductive ring opening in the more sterically hindered of two epimeric bicyclic compounds has also been observed in the bicyclo[2.1.0]pentane system by Kristinsson and Hammond.²⁹

Further evidence on this point comes from a detailed analysis of the mass spectra of 7 and 8 (Table I). The intensity of the molecular ion is 7.7% Σ_{26} for 8, while only 3.6% Σ_{26} for 7. Biemann and Siebl³⁰ have found that the more crowded isomer of a pair of epimeric polycyclic alcohols always exhibits a molecular ion of lower intensity than the less crowded isomer. Also, the peak at m/e 95 is the base peak in 7 (11.4% Σ_{26}) while in 8 it is 6.9% Σ_{26} . The more crowded molecular ion should provide a greater driving force for fragmentation, according to the schematic process noted in 7a.³¹



(29) H. Kristinsson and G. S. Hammond, *J. Amer. Chem. Soc.*, **89**, 5970 (1967).

(30) K. Biemann and J. Seibl, *ibid.*, **81**, 3149 (1959).

(31) An alternative fragmentation pattern to give m/e 95 involves a McLafferty rearrangement of a methyl group, for which there is no known precedent. Such a process was considered feasible in 7a since the methyl group is held in a fixed position above the carbonyl group, while other cases designed for a test of this type of process have not had this structural advantage.³² However, the high resolution mass spectrum of 7 eliminated this possibility: W. V. Curran and G. van Lear, unpublished results.

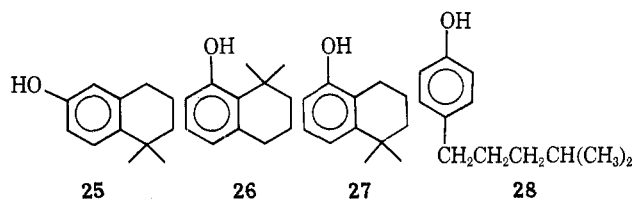
(32) (a) R. R. Arndt and C. Djerassi, *Chem. Commun.*, 578 (1965).

(b) For a recent review of rearrangements produced on electron impact, see P. Brown and C. Djerassi, *Angew. Chem. Int. Ed. Engl.*, **6**, 477 (1967).

In the dihydro lumiketones, it is again the more hindered isomer 22 which has the lower intensity molecular ion. Cleavage of 22 and 23 across the cyclopropane ring accounts for formation of m/e 96 and 81, and the latter is the base peak for both isomers.

Attempts were made to confirm the stereochemistry assigned above with the electron spin resonance (esr) spectra of the corresponding semidiones of 22 and 23, since different hyperfine coupling constants are expected in each case.³³ However, the results were inconclusive since a satisfactory spectrum, which was clearly that of a semidione with a bicyclo[3.1.0]hexane skeleton,³⁴ could only be obtained from one stereoisomer, 23. Since interconversions of the epimeric semidiones is a distinct possibility,³⁵ spectra of both semidiones are required for a structural assignment.

B. Phenolic Products.—The phenolic fraction, obtained as described above from several photolyses of 6 in methanol at 2537 \AA , was separated by column chromatography on silica gel. Three crystalline phenols were isolated: 1,1-dimethyl-7-tetralol (20), 1,1-dimethyl-6-tetralol (25), and 1,1-dimethyl-8-tetralol (26). Compound 20 was shown to be the same isomer as obtained by the acid-catalyzed dienone-phenol rearrangement of 6 (see above). Compound 25 was identified by



comparison of its ir spectrum and glc retention time with those of an authentic sample.^{24,36} The phenol 26, not reported previously, was assigned its structure based on the following information: (a) elemental analysis; (b) similarity of its ir spectrum to those of 20 and 25; (c) the nmr spectrum which shows an aromatic multiplet (3 H) centered at δ 6.5, a hydroxyl proton at 2.7, a multiplet for benzylic protons at 2.7, and methyls at 1.4 [The latter resonance is deshielded compared with those for the methyls in 20 (at δ 1.22) and 25 (at δ 1.21), consistent with the closer proximity of the methyls in 26 to the hydroxyl group, and possibly some steric compression.];²⁸ (d) nonidentity of the product with phenols 27 or 28. Analysis by glc indicated that a trace of phenol 27 might also be present in the photolysate. Since phenol 28 was considered a possible product of photofragmentation of spirodienone 6, an authentic sample was synthesized by a route essentially as reported previously.³⁷ None of this product was discovered in the photolysate.

Effect of Solvents on Photolysis of 6 at 2537 \AA .—The dienone 6 was photolyzed in seven solvents using

(33) G. A. Russell, P. R. Whittle, and J. McDonnell, *J. Amer. Chem. Soc.*, **89**, 5515 (1967).

(34) The semidiones were prepared and esr spectra were taken at Iowa State University through the very kind assistance of Professor G. A. Russell. We are indebted to Professor Russell for his cooperation and interest, and for communication of other results from his laboratory prior to publication.

(35) G. A. Russell, P. R. Whittle, and J. McDonnell, *J. Amer. Chem. Soc.*, **89**, 5515 (1967); G. A. Russell, J. McDonnell, and P. R. Whittle, *ibid.*, **89**, 5516 (1967); G. A. Russell and J. J. McDonnell, *Tetrahedron Lett.*, **39**, 4213 (1968).

(36) We are grateful to Professor Harold Hart of Michigan State University for kindly supplying samples of compounds 20, 25, and 27.

(37) M. Mousseron and M. Mousseron, *Bull. Soc. Chim. Fr.*, 391 (1956).

TABLE II
 SOLVENT EFFECTS ON RELATIVE YIELDS OF PRODUCTS AT 2537 Å

Solvent	Ratio of 7:8			Lumiketones/ phenols after 8.5 hr	Rel yields of ketones 7 and 8 8.5 hr	Phenol distribution, 26:25:20
	1.0 hr	2.2 hr	6.5 hr			
Methanol	2.50	2.26	1.73	0.14	0.21	a
<i>tert</i> -Butyl alcohol	2.04	1.95	1.87	0.34	0.65	0.3:0.6:1.0
Dioxane	1.23	1.19	1.19	1.28	1.00	0.5:1.0:0.6
Ethyl ether	1.11	0.96	0.93	1.24	0.79	a
Hexane	0.91	0.82	0.96	0.35	0.51	a
Cyclohexane	0.79	0.82	0.73	0.52	0.60	0.2:0.4:1.0
Benzene	b	b	1.00 ^c	b	b	a

^a Not measured. ^b Too small to be measured. ^c Measured after 17.5 hr. Reaction very slow under these conditions. Benzene absorbed 77% of the incident light.

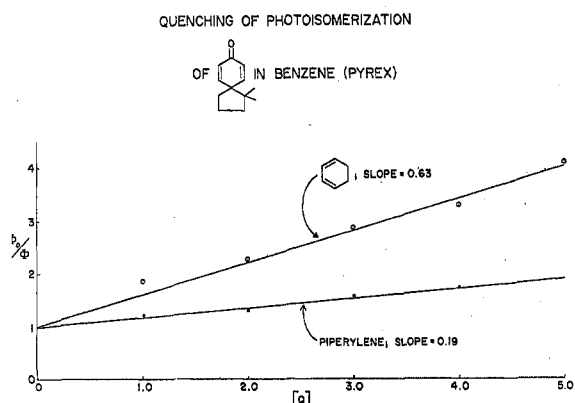


Figure 2.—Stern-Volmer plots for quenching of the photoisomerization of spirodienone (6) by cyclohexadiene and piperylene.

an Hanau NK 6/20 lamp (output almost entirely at 2537 Å) in a merry-go-round apparatus. Tubes were analyzed periodically for lumiketones 7 and 8 by glc, and Table II shows the relative ratio of the lumiketones as a function of time. In the protic solvents, methanol and *tert*-butyl alcohol, there is a preference for 7, which is shown less markedly in dioxane as well. The product ratio is close to unity in ether and benzene, but reverses in favor of 8 in hexane and cyclohexane. The decrease in the ratio of 7:8 with time observed in methanol was experimentally reproducible. The ratio of lumiketones to phenols (Table II) shows a similar pattern. The yield of ketones 7 and 8 after 8.5 hr was largest in dioxane and least in methanol.

As might be expected, some difficulty was encountered in establishing glc conditions for analysis of all five possible isomeric phenols (20, 25, 26, 27, and 28). No column was found which separated all these compounds, and 20 and 25 were not separable on any column used, although their acetates were separable on a UCW-98 column. Using two columns, and authentic samples of the five phenols and their acetates, a complete analysis was possible. Quantitative acetylation of the phenols separately or in a mixture (*e.g.*, the photolysate) was readily accomplished by heating in acetic anhydride-pyridine for 30 min, conditions which did not affect the lumiketones. Results of the analyses are shown in Table II.

Quantum Yields.—The quantum yield for formation of the lumiketones in dioxane at 2537 Å was measured using a Bausch and Lomb high intensity grating monochromator and ferrioxalate actinometry.³⁸ The yields

of lumiketones were quantitatively determined by glc using internal standards. Conversions of starting material were kept low to minimize light absorption by products. Values of Φ of 0.59 and 0.64 were obtained in duplicate experiments. Under these conditions, Φ for formation of phenol 20 was 0.057.

Sensitization and Quenching Experiments.—Photolyses of 6 were carried out through Pyrex in the presence of benzophenone (E_T 69 kcal/mol), acetophenone (E_T 74), and 2-acetonaphthone (E_T 59) with the sensitizers absorbing better than 90% of the incident light at 3130 and 3660 Å. In methanol with short reaction times, benzophenone sensitization was demonstrated by the accelerated rate of disappearance of 6 relative to a blank. After 40 min, the amount of phenols was considerably less than in the blank and some benzophenone had reacted. Probably, photoreduction of benzophenone occurs by hydrogen abstraction from the benzylic carbons of the phenol products, leading to higher molecular weight products which do not appear in the vapor chromatogram. Similar results were obtained using acetophenone. However, 2-acetonaphthone did not sensitize the reaction, the small amount of observed reaction being attributable to that portion of the light directly absorbed by dienone 6. With benzene as solvent and acetophenone as sensitizer, the amount of phenols was again reduced, but an enhancement in the yield of lumiketones 7 and 8 beyond the blank was observed. The ratio of 7 and 8 after 10 min was 0.60 in the presence of the sensitizer and 0.51 in the blank.

Quenching of the reactions of 6 was observed with 2.0 *M* 1,3-cyclohexadiene (CHD) in benzene. More dienone 6 was present than in the blank, and dimers of CHD were formed, identified by comparison with authentic samples using glpc.³⁹ The diene dimers are known to be formed only on triplet energy transfer to the diene.⁴⁰ The yield of lumiketones and phenol 20 were reduced in the presence of the diene. A study of the quantitative dependence of the yield of lumiketones on the concentration of CHD was made, with the product yields determined by quantitative glpc using internal standards. Tubes were photolyzed in a merry-go-round apparatus with a 100-W Hanovia lamp and a Pyrex filter. Reactions were carried to short conversions (4.8% in the blank) to minimize complications due to light absorption by the products. A similar study was made using piperylene as the quencher, with 4.5% reaction in the blank tube in this case. The data are presented graphically in Figure 2.

(39) The dimers were prepared⁴⁰ in this laboratory by D. J. Patel.

(38) C. S. Hatchard and C. A. Parker, *Proc. Roy. Soc. Ser. A*, **235**, 518 (1956).

(40) D. Valentine, N. J. Turro, Jr., and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 5202 (1964).

The line for CHD quenching has a much steeper slope ($0.63 M^{-1}$) than that for piperylene ($0.19 M^{-1}$). Such an effect has been noticed with a number of other cyclohexadienones and is discussed in detail elsewhere.^{41,42} Using the Stern-Volmer slope for CHD quenching ($k_q\tau = 0.63$) and a value of $k_q = 5 \times 10^9 M^{-1} \text{sec}^{-1}$ for the energy transfer rate constant,⁴³ a triplet lifetime for **6** of $1.3 \times 10^{-10} \text{sec}$ is calculated. Together with Φ , one obtains values for the rate constants for triplet processes of k_r (isomerization of the triplet leading to lumiketones) = $5.6 \times 10^9 \text{sec}^{-1}$ and k_d (triplet decay) = $2.4 \times 10^9 \text{sec}^{-1}$. The latter value, as is the case for other cyclohexadienones,^{7-9,41,42} is much too high to be ascribed to radiationless decay directly from the triplet to the ground state⁴⁴ and is probably due to reversal to the ground state of **6** from some later intermediate on the route to products. Recent work of Zimmerman and Jones supports this suggestion.⁴⁵

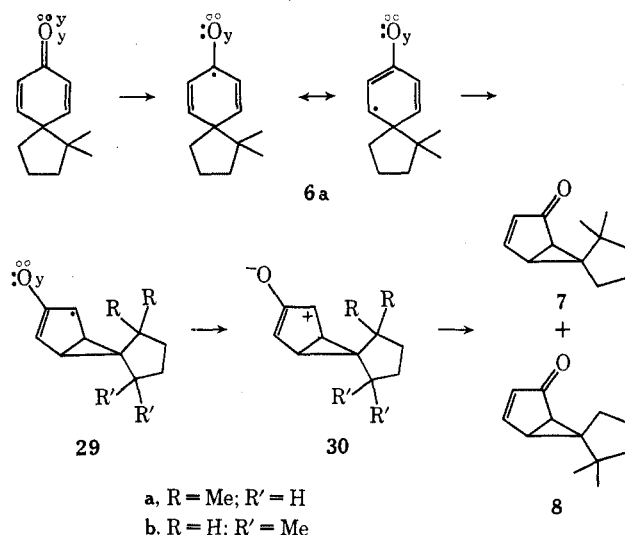
Photochemistry of Lumiketones 7 and 8.—Dilute solutions of the lumiketone mixture were photolyzed in methanol and cyclohexane at 2537 Å; the ratio of **7**:**8** was determined by glc as a function of time. The data indicate a slightly more efficient rate of disappearance of **7** than of **8**, with reaction slightly faster in methanol than in cyclohexane. The yields of the various phenols were determined after nearly all the ketones had reacted. Phenols **25** and **26** were formed, with some indications of a trace of **20**. The **25**:**26** ratio was 2.2 in methanol and 2.4 in cyclohexane. Photolysis of **7** and **8** in benzene through Pyrex gave a similar yield of phenols, with **25**:**26** = 2.4. The **7**:**8** ratio was 0.79 at the start, and after 5.0 min it was reduced to 0.73. On photolysis of a pure sample of **7** under these conditions, no isomeric lumiketone **8** could be detected. Photolysis of the lumiketones in acetic acid gave the usual yields of **25** and **26**, but also an increased yield of phenol **20**.

The quantum yield for disappearance of lumiketones in dioxane at 3660 Å was found to be 0.46. When the lumiproduet mixture was photolyzed in the presence of varying amounts of CHD up to 5.0 *M*, no quenching of the reaction was observed. Analytic conditions were as sensitive as those used to detect the very inefficient quenching in the case of **6**. Surprisingly, the CHD dimers^{39,40} were formed in these reactions, according to glpc, at all CHD concentrations.

Discussion

A. Lumiketone Formation.—The photochemical transformation of spirodienone **6** into the isomeric lumiketones **7** and **8** is outlined in Scheme II, using the mechanism and notation of Zimmerman and Schuster.⁷ The chief point of interest is that stereoisomeric 3,5-bonded intermediates (**29a** and **29b**) and zwitterions (**30a** and **30b**) are possible in the formation of the lumiketones. The final step in lumiketone formation is a sigmatropic change of order [1,4]¹⁸ which could occur in two distinct stereochemical modes. For example,

SCHEME II
MECHANISM AND STEREOCHEMISTRY OF LUMIKETONE
FORMATION



the intermediate **30b** could rearrange concertedly to lumiketone **7** by a pivot mechanism with retention of configuration at the migrating spiro carbon atom. Alternatively, bond formation could occur with inversion of configuration at the spiro atom, as for the conversion of **30b** into **8**. The latter stereochemical mode is predicted for concerted rearrangement of the ground state zwitterion,¹⁸ and inversion of configuration has indeed been observed in several thermal [1,4]-sigmatropic rearrangements of systems analogous to **30**.⁴⁶⁻⁴⁸ It should be noted that several other slightly different mechanisms can produce the same stereochemical result, for example, rearrangement by two successive 1,2-alkyl shifts.¹⁸

In order to interpret the observed solvent effects on lumiketone formations, it is necessary to know the stereochemistry of rearrangement, *i.e.*, inversion or retention. That is, the preferential formation of **7** in alcohol solvents could indicate either (a) a preference for formation of **30b** followed by rearrangement with retention of configuration, or (b) a preference for formation of **30a** followed by rearrangement with inversion of configuration. Since revertibility has at best only a minor role in these reactions (see later), there can be no interconversion of the diastereomeric intermediates, and the stereochemistry of the product is determined on formation of the 3,5 bond in the triplet state to generate **29a** or **29b**.⁴⁹ Assuming only a single specific mode of rearrangement operates subsequently (*i.e.*, inversion or retention), steric interactions in formation of these intermediates determine the stereochemistry of the product,⁴⁹ whereas steric interaction of substituents in the final product should be of little or no influence on the

(46) H. E. Zimmerman and D. S. Crumrine, *ibid.*, **90**, 5612 (1968); T. M. Brennan and R. K. Hill, *ibid.*, **90**, 5614 (1968).

(47) R. F. Childs and S. Winstein, *ibid.*, **90**, 7146 (1968).

(48) H. Hart, T. R. Rodgers, and J. Griffiths, *ibid.*, **91**, 754 (1969).

(49) The same conclusion has been reached independently by T. R. Rodgers and H. Hart, *Tetrahedron Lett.*, 4845 (1969). These workers report the effect on stereoselectivity of rearrangement of substituents at C₃ and C₅ in photolysis of 4-methyl-4-*n*-propyl-2,5-cyclohexadienones. Their interpretation is based on the assumption that rearrangement occurs from the corresponding zwitterions by inversion, analogous to ground state [1,4]-sigmatropic rearrangements.⁴⁶⁻⁴⁸ The predominant lumiketone isomer formed under these conditions has the *n*-propyl group in the endo position. No solvent study was reported.

(41) D. I. Schuster, A. C. Fabian, N. P. Kong, W. C. Barringer, W. V. Curran, and D. H. Sussman, *J. Amer. Chem. Soc.*, **90**, 5027 (1968).

(42) D. I. Schuster and N. K. Lau, *Mol. Photochem.*, **1**, 415 (1969).

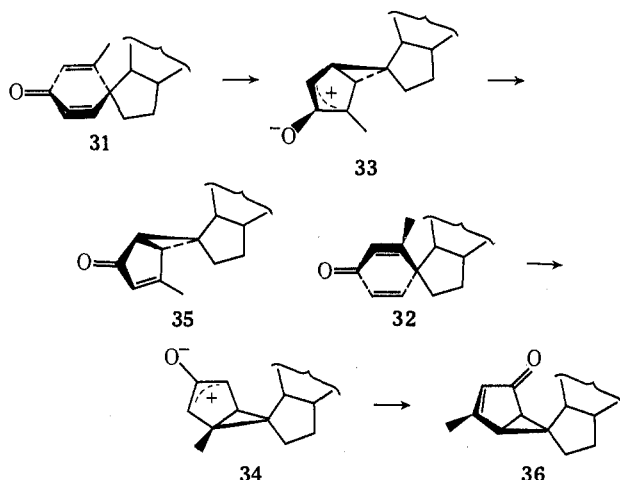
(43) P. J. Wagner and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 1245 (1966).

(44) P. J. Wagner, *Mol. Photochem.*, **1**, 71 (1969); P. J. Wagner and D. J. Bucheck, *J. Amer. Chem. Soc.*, **91**, 5090 (1969).

(45) H. E. Zimmerman and G. Jones, II, *ibid.*, **91**, 5678 (1969).

overall stereoselectivity. It should not be surprising, for instance, if the major product were the more sterically hindered of the two epimers, as is the case for reaction of **6** in alcohol solvents, with the larger substituent at C-6 endo (*i.e.*, syn to the cyclopentenone ring).^{13,49,50}

A case was made in an earlier extensive study of a series of steroid dienones^{5b,26} that the photochemical rearrangement occurs with inversion of configuration when both modes were *a priori* possible. It was reported that the two spirodienones **31** and **32** gave, respectively, lumiketones **35** and **36**, and it was proposed that the reaction occurs *via* intermediates **33** and **34**. If



the absolute configurations of the dienones and lumiketones are correct as shown, the rearrangement must have occurred as shown with inversion of configuration; that is, the endo group in the zwitterion intermediate remains endo in the final product. The absolute configurations were assigned on the basis of a complex argument involving in part the chemical relationship of these molecules to others of known absolute configuration. However, it is important that the absolute stereochemistry of this type of rearrangement be experimentally established with minimum recourse to elaborate arguments and extrapolations in a system which is totally free of steric constraints. Such experiments are now in progress in our laboratories.

If the [1,4]-sigmatropic rearrangement does take place with inversion, then why is the sequence **6a** → **29a** → **30a** → **7** preferred in alcohol solvents, while **6a** → **29b** → **30b** → **8** is preferred in hydrocarbon solvents? The preference is not great in energy terms, but it is necessary to understand such selectivities if the course of reaction in analogous systems is to be predictable. In other published examples,^{13,26,49-51} no studies of the effect of solvent on the stereoselectivity were reported. It should be emphasized that the possibility of direct rearrangement of diradical intermediates (*e.g.*, **29**) to lumiketones without involvement of zwitterion intermediates has not been excluded as a viable mechanism for the photochemical rearrangement of cyclohexadienones especially in nonpolar solvents.⁵² If this were the case, the observation of rearrangement with inversion in [1,4]-sigmatropic rearrangements of ground state molecules analogous to zwitterions⁴⁶⁻⁴⁹ would

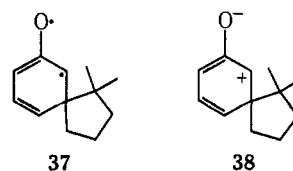
not be a good model for the course of the photochemical reaction. Furthermore, there is no assurance as yet that the stereochemical mode of reaction is independent of the nature of the solvent or that the reaction is even totally concerted.

B. Fragmentation Reactions.—One of the principal reasons for study of **6** was to further investigate the scope of fragmentation reactions in dienone photochemistry. Since the fragmentation product **28** could not be detected by glc under any conditions of photolysis of **6**, such a process is not important in this case. Previous investigations showed that fragmentation of an allyl or *tert*-butyl group also does not occur on photolysis of suitably 4-substituted cyclohexadienones.⁵⁰ It appears that fragmentation of an alkyl group from the 4 position of a 2,5-cyclohexadienone can not, in general, compete with the lumiketone rearrangement, even in solvents which are good H donors, except in special cases where the lumiketone rearrangement is structurally prohibited, or at least retarded.^{14,15,45} This supports the postulate⁹ that, when fragmentation occurs, cleavage of the bond at the 4 position is concerted with H abstraction from the solvent.

C. Photochemical Dienone-Phenol Rearrangements.—The rearrangement of **6** to **20** seems to occur much more readily than similar reactions of previously studied dienones.⁶ The reaction occurs in nearly all of the solvents studied at 2537 Å as well as at longer wavelengths. The detailed solvent and wavelength dependence of this process is difficult to interpret in detail, but seem to indicate that more than one intermediate (excited and/or ground state) may be involved. No mechanistic details of similar reactions have been reported. It is interesting to note that the diphenyl dienone **3** does not undergo a photochemical phenyl migration from C₄ to C₃ in aqueous dioxane.⁸

D. Multiplicity of The Reactive Excited States.—The sensitization and quenching data together indicate that only one reactive excited state is involved in the conversion of **6** to the lumiketones **7** and **8** and that this is the (presumably lowest) triplet state. The lack of sensitization by 2-acetonaphthone (*E_T* 59) places the triplet energy of **6** between 60 and 69 kcal/mol. This triplet energy, as well as the triplet lifetime and rate constants derived from the quenching data of Figure 2, are similar to such values obtained for other 2,5-cyclohexadienones.^{8,9,41,42}

E. Photolysis of Lumiketones 7 and 8.—Both epimeric ketones **7** and **8** afford mainly phenols **25** and **26**, the expected products according to the pathway previously proposed for this type of photorearrangement.⁷ Zimmerman and Grunewald⁵¹ have provided convincing evidence that such rearrangements proceed *via* zwitterionic intermediates. Extrapolation of their results in aqueous alcohol to solvents such as hexane or cyclohexane is not necessarily justified, and in the present case it is expected that the more substituted bond will migrate whether the reactive intermediate is the diradical **37** or the zwitterion **38**. A common in-



(50) B. Miller and H. Margulies, *J. Amer. Chem. Soc.*, **89**, 1678 (1967); B. Miller, *ibid.*, **89**, 1690 (1967).

(51) H. E. Zimmerman and J. O. Grunewald, *ibid.*, **89**, 5163 (1967).

(52) For a full discussion of this point, see ref 9.

intermediate is indicated from the fact that mixtures rich in one or the other lumiketones give the same product distribution, as found also in earlier work.⁵¹ Reclosure of any ring-opened intermediate (37 or 38) is ruled out by lack of interconversion of the epimeric starting materials in this and an earlier study.⁵¹ The decrease in the ratio of 7:8 with irradiation time implies that the relief of strain on ring opening provides some assistance, perhaps in reducing the efficiency of competing radiationless decay processes.

In all solvents, phenol 25 was the predominant product. Preferential migration to the para position is predicted from simple molecular orbital calculations on the intermediate zwitterion,⁵³ although this was not observed in phenol formation from the diphenyl lumiketone (2, R, R' = Ph).

The formation of small amounts of phenol 20 on photolysis of the lumiketones could arise from either (a) migration of the least substituted bond in a ring-opened intermediate, or (b) conversion of lumiketone back to dienone 6 and photoconversion of 6 to 20. Evidence for the latter alternative comes from photolysis of 7 and 8 in aqueous acetic acid where increased yields of 20 were observed, attributable to photochemical reversion to 6 followed by an acid-catalyzed dienone-phenol rearrangement. Precedent for photochemical reversion of lumiketones 2 to 2,5-cyclohexadienones 1 comes from the work of Jeger, *et al.*,²⁶ although no such reaction was found with the diphenyl lumiketones (2, R, R' = Ph).⁵³

The fact that photolysis of lumiketones 7 and 8 could not be quenched by 1,3-cyclohexadiene (CHD) implies that either the direct photolysis occurs *via* an excited singlet state or that the lifetime of the reactive triplet is so short ($\ll 10^{-10}$ sec) that no quenching can be observed. In other studies in this laboratory, it has been possible to detect quenching using dienes even in cases where the triplet lifetime is as low as 10^{-10} sec, with Stern-Volmer slopes as small as 0.02.⁴² Acetophenone sensitized reaction of the lumiketones was observed, but, due to difficulties with determining product distribution, it was not definitely established whether the triplet-sensitized reaction takes the same course as the direct photolysis. Even though quenching by CHD was not observed, CHD dimers were formed in small amounts. These could be formed by triplet energy transfer to CHD from dienone 6 formed from the lumiketones (see above). In the case of phenol formation from the diphenyl lumiketone (2, R, R' = Ph), it was concluded⁵³ that the reaction proceeded mainly *via* the triplet state, although the conclusion was not regarded as rigorous.

Experimental Section

Infrared spectra were taken on a Perkin-Elmer Model No. 337 grating Infracord spectrophotometer. Ultraviolet spectra were recorded on a Cary Model No. 15 spectrophotometer. Nuclear magnetic resonance spectra were taken using a Varian Model A-60 spectrometer using tetramethylsilane as an internal reference. Analytical gas chromatographic analyses were performed on either a F & M Model 810 or 5750 chromatograph, while preparative experiments were conducted on Aerograph Model A-700 and F & M Model 776 chromatographs.

4-Methyl-4-*p*-methoxyphenyl-1-pentanol (17).—Anisole (1.0 l.) and aluminum chloride (52.5 g, 0.357 mol) were stirred in an ice bath and a suspension of 4-methylpentane-1,4-diol (16)⁴⁴ (0.357 mol) in 250 ml of anisole was added dropwise over 45 min. The internal temperature did not exceed 6°. An additional 52.5 g of aluminum chloride was added and the mixture was stirred for 3.0 hr in the ice bath, and then at room temperature overnight. The reaction mixture was poured into 800 ml of cold dilute hydrochloric acid (1:1) and extracted with two 400-ml portions of ether. The combined ether extracts were washed with 250 ml of saturated salt solution and then dried over magnesium sulfate. The ether and anisole were removed by evaporation and the residue was distilled through a 12 in. Vigreux column. Three fractions were collected: (1) 19.4 g, bp 129–140° (0.08–0.10 mm), n_D^{20} 1.5217; (2) 37.0 g, bp 125–139° (0.1–0.07 mm), n_D^{20} 1.5208; (3) 3.7 g, bp 115–125° (0.07 mm), n_D^{20} 1.5207; ν_{\max}^{neat} 3300, 1530, 1235, 1170, 1030, 830 cm^{-1} ; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 1.20 (s, 6 H, gem dimethyl), 3.60 (s, 3 H, methoxyl), A_2B_2 pattern centered at δ 6.90 (4 H, aromatic protons).

4-Methyl-4-*p*-hydroxyphenyl-1-pentanol (18). Method A.—4-Methyl-4-*p*-hydroxyphenyl-1-pentanoic acid (20.0 g, 0.096 mol) was dissolved in 175 ml of dry tetrahydrofuran and added to a stirred mixture of lithium aluminum hydride (12.0 g, 0.32 mol) in 175 ml of dry tetrahydrofuran over 2.0 hr. After having been refluxed for 5.0 hr, the reaction mixture was cooled in an ice bath and the excess reagent was decomposed by carefully adding 100 ml of tetrahydrofuran–water (1:1). The reaction mixture was then poured into 600 ml of 3 *N* hydrochloric acid and extracted with three 200-ml portions of ether. The combined ether extracts were washed with two 150-ml aliquots of saturated salt solution and dried over magnesium sulfate. The ether was evaporated and the residue was crystallized from methylene chloride to yield 13.4 g, mp 60.5–63°, after drying over phosphorus pentoxide *in vacuo*. Incomplete drying of this compound results in a hygroscopic solid of mp 48–51.5°, which is probably a hydrate. For analytical purposes, 1 g was recrystallized from methylene chloride–petroleum ether, mp 62.5–64°.

Method B.—4-Methyl-4-*p*-methoxyphenyl-1-pentanol (12.0 g, 0.058 mol) dissolved in 50 ml of triethylene glycol was added to 150 ml of diethylene glycol containing 45 g of potassium hydroxide and 5.0 ml of hydrazine hydrate. The mixture was refluxed under nitrogen for 7.0 hr and then poured into 250 ml of water and extracted with four 100-ml aliquots of ether which were discarded. The aqueous phase was acidified with 75 ml of concentrated hydrochloric acid and extracted with four 100-ml aliquots of ether. The combined ether extracts were washed with three 100-ml portions of saturated sodium bicarbonate and then four 50-ml portions of 10% sodium hydroxide. The combined sodium hydroxide extracts were acidified with concentrated hydrochloric acid and reextracted with several 100-ml aliquots of ether. The ether extracts were washed with saturated salt solution, dried over magnesium sulfate, and evaporated to an amber oil, yield 8.0 g.

Thin layer chromatography of this product indicated the presence of two compounds. Therefore, it was dissolved in 30 ml of ether and applied to a column of Merck acid-washed alumina (440 g, 6 × 20 cm). The column was eluted with eleven 300-ml aliquots of ether. Thin layer chromatography showed that fractions 3 to 6 were pure, yield 5.4 g, colorless oil, which analyzed for a monohydrate: ν_{\max}^{neat} 3600 (sharp), 3350 (broad), 1510, 1175, 835 cm^{-1} ; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 1.20 (s, 6 H, gem dimethyl), 3.60 (s, 3 H, methoxyl), A_2B_2 pattern centered at 6.80 (4 H, aromatic protons).

Anal. Calcd for $C_{12}H_{18}O_2 \cdot H_2O$ (212): C, 68.0; H, 9.5. Found: C, 68.5; H, 8.8.

4-Methyl-4-*p*-hydroxyphenyl-1-pentanol Bisphenylurethane.—4-Methyl-4-*p*-hydroxyphenyl-1-pentanol (0.66 g) was added to 1.5 ml of phenylisocyanate and heated on a steam bath for 15 min. The reaction mixture was dissolved in 15 ml of hot ethyl acetate, treated with Norit, and filtered. The filtrate was brought to incipient turbidity with hexane which afforded white crystals on cooling to yield 0.87 g, mp 130–132°. Recrystallization from ethyl acetate–petroleum ether gave 0.63 g, mp 131–133°.

Anal. Calcd for $C_{26}H_{28}N_2O_4$ (433): C, 72.1; H, 6.5; N, 6.5. Found: C, 71.7; H, 6.7; N, 6.5.

(53) H. E. Zimmerman, R. Keese, J. Nasielski, and J. S. Swenton, *J. Amer. Chem. Soc.*, **88**, 4895 (1966).

(54) A. Franke and M. Kohn, *Monatsh. Chem.*, **28**, 1006 (1907).

4,4-Dimethyl- α -butyrolactone. Method A.—A solution of 41 g (0.36 mol) of 4-methyl-2-pentenoic acid and 240 g of potassium hydroxide in 500 ml of water was refluxed for 17.0 hr and then acidified with 500 ml of concentrated hydrochloric acid. The mixture was cooled and extracted with six 200-ml portions of ether which were combined, washed with two 250-ml aliquots of saturated salt solution, and dried over sodium sulfate. The crude product, obtained by evaporation of the ether was distilled through a Nester-Faust spinning-band column to afford 20.6 g of the lactone: bp 42–45° (0.35 mm), n_D^{25} 1.4312; ν_{\max}^{neat} 1780, 1255, 1150, 1125, 1100, 950, 930 cm^{-1} ; $\delta_{\text{C}}^{\text{CDCl}_3}$ 1.40 (s, 6 H, gem dimethyl). A small amount of the starting acid was also recovered, 1.7 g, bp 62–64° (0.2–0.3 mm), n_D^{25} 1.4457.

Method B.—A solution of 109.5 g of 4-methyl-2-pentenoic acid in 500 ml of dioxane containing 500 ml of concentrated hydrochloric acid was refluxed for 48 hr, evaporated to a syrup at reduced pressure with the aid of benzene, and distilled through a Nester-Faust spinning-band column. Two fractions were collected: 49.93 g, bp 41–44° (0.2–0.3 mm), n_D^{25} 1.4423, and 38.34 g, bp 43–54° (0.2–0.3 mm), n_D^{25} 1.4454. Both fractions contained some hydroxylated material as shown by infrared spectra. However, this material did not interfere with the next step in the synthetic sequence.

4-Methyl-4-(*p*-methoxyphenyl)pentanoic Acid (19).—To a stirred mixture of 190 ml of anisole and 10 g (0.075 mol) of aluminum chloride in an ice bath was added 20 g (0.17 mol) of 4-methyl-4-hydroxypentanoic acid γ -lactone over 20 min. An additional 10 g of aluminum chloride was added and the mixture was stirred for 3.5 hr in the cold and then overnight at room temperature. The mixture was then heated at 80° for 1.0 hr, cooled, and poured into 150 ml of cold concentrated hydrochloric acid. Water (100 ml) was added and the organic phase was separated and washed with two 100-ml portions of 10% hydrochloric acid, 100 ml of water, and then three 100-ml aliquots of 10% sodium hydroxide solution. The combined basic extracts were washed with two 100-ml portions of ether, and these were acidified with 100 ml of concentrated hydrochloric acid. The insoluble oil was extracted with two 100-ml portions of ether which were combined and dried over magnesium sulfate. Evaporation of the ether afforded an oil which was crystallized from petroleum ether: yield 20.0 g (52.5%), mp 66.5–69° (lit.²⁴ mp 65–66°).

4-Methyl-4-*p*-hydroxyphenyl-1-pentanoic Acid.—4-Methyl-4-*p*-methoxyphenyl-1-pentanoic acid (20.0 g, 0.089 mol) was added to 150 ml of acetic acid containing 60 ml of 57% hydroiodic acid and refluxed for 4.0 hr. The reaction mixture was poured onto ice to afford crystals which were filtered, washed with water, and dried over phosphorous pentoxide and potassium hydroxide at reduced pressure, yield 15.0 g, mp 136–139°. This product was dissolved in 75 ml of warm ethyl acetate, treated with Norit, and filtered. The filtrate was diluted with an equal volume of petroleum ether and the product crystallized as large rosettes, yield 12.4 g, mp 138.5–140°. An additional 1.8 g (77% total yield), mp 137–139°, was obtained from the mother liquor: ν_{\max}^{neat} 3200 (broad), 1690, 1225, 830 cm^{-1} .

Anal. Calcd for $\text{C}_{12}\text{H}_{16}\text{O}_3$ (208): C, 69.3; H, 7.7. Found: C, 69.5; H, 8.2.

1,1-Dimethylspiro[4,5]deca-6,9-dien-8-one (6).—4-Methyl-4-*p*-hydroxyphenyl-1-pentanol (4.8 g, 24.8 mmol) and 4.8 g (25.0 mmol) of *p*-toluenesulfonyl chloride were added to a solution containing 70 ml of chloroform and 70 ml of pyridine (distilled from barium oxide) and stored at –5° for 18 hr. The solution was poured into 500 ml of cold saturated sodium bicarbonate solution and extracted with three 100-ml portions of chloroform. The combined extracts were washed with six 100-ml portions of 5% hydrochloric acid solution, two 100-ml portions of saturated salt solution, and then dried over magnesium sulfate. The solvent was evaporated at reduced pressure and excess pyridine was removed by codistillation using xylene to afford the tosylate derivative as a syrup: ν_{\max}^{neat} 3300 (broad), 1350, 1170, 920, 830, 815, 660 cm^{-1} .

The tosylate was dissolved in 350 ml of *tert*-butyl alcohol and added to a stirred solution of 3.1 g (27.5 mmol) of potassium *tert*-butoxide in 2.0 l. of *tert*-butyl alcohol under nitrogen over 45 min. The mixture was heated at reflux for 5.0 hr, poured into 2.0 l. of ice-water, and extracted with three 600-ml aliquots of ether. The combined ether extracts were washed with 500 ml of saturated salt solution, then dried over magnesium sulfate. The solvent was evaporated and the residue dissolved in 10 ml of ether and added to a column of basic alumina (200 g, 4 \times 15

cm) which was eluted with ten 50-ml portions of ether. Fraction 4 crystallized and was recrystallized from petroleum ether (bp 30–60°) to afford 455 mg of light yellow crystals, mp 50–51.5°. Additional material was obtained from some of the other fractions. This procedure gave yields that were usually about 25% of theoretical. For analysis, a portion of the crystalline material was sublimed at 70° *in vacuo*. Spectra are given in Table I.

Anal. Calcd for $\text{C}_{12}\text{H}_{16}\text{O}$: C, 81.9; H, 9.2. Found: C, 81.8; H, 9.0.

Fraction 1 contained a small amount of crystals, mp 203–204°, which were insoluble in petroleum ether. The structure 21 is assigned on the basis of the ir spectrum: ν_{\max}^{KBr} 1510, 1285, 1265, 1220, 1180, 1060, 1040, 825 cm^{-1} .

Photolysis of 1,1-Dimethylspiro[4,5]deca-6,9-dien-8-one (6) at 2537 Å in Methanol.—The spirodienone (6) (1.1 g) was dissolved in 600 ml of spectral grade methanol in a quartz tube, purged with nitrogen for 10 min, and then photolyzed for 40 min in a Rayonet photochemical reaction chamber. The progress of the reaction was followed by examining the ir spectra at intervals to follow the disappearance of the carbonyl band of the dienone at 1670 cm^{-1} . The photolysis was stopped when this band was reduced to a minor peak. The solvent was removed at reduced pressure and the resulting oil was dissolved in 10 ml of benzene and chromatographed on 105 g of basic alumina (3 \times 20 cm column). The column was eluted with the following solvents and the weights of each fraction are included: (1) 3 l. of benzene (0.305 g), (2) 1 l. of benzene-ether (1:1) (0.258 g), (3) 1 l. of ether (0.016 g), (4) 1 l. of ethyl acetate (0.249 g), (5) 1 l. of methanol (0.224 g ether-soluble portion); material balance = 95%. The benzene and benzene-ether fractions contained the lumiketones (7 and 8) and the ethyl acetate and methanol fractions contained the phenolic material. Several attempts to separate the two lumiketones 7 and 8 by column chromatography were futile. Similarly, liquid-liquid partition chromatography was not successful.⁵⁵ The above procedure was repeated several times with essentially the same result.

Preparative Gas Chromatography of the Lumiketone Mixture.—A mixture of lumiketones (7 and 8) was separated on a Aerograph Model A-700 gas chromatograph using a 10-ft, 0.25-in. column of 15% Carbowax 20M on Chromosorb W, DMCS treated, at a temperature of 185–190°. A mixture (600 mg) afforded 44 mg of 7 and 37 mg of 8. These fractions were shown to be homogeneous by analytical gas chromatography on a 6-ft 15% Carbowax 20M column at 160°. The spectral data for these compounds are given in Table I.

Column Chromatography of the Phenols Obtained from Methanol Photolysis of the Dienone 6.—The combined phenol fractions (1.2 g) obtained from several preparative scale photolysis of the dienone (6) in methanol were combined and chromatographed on 100 g of silica gel (3 \times 22.5 cm column). The column was eluted with the following solvents and the weights of the fractions are given: (1) seven 150-ml aliquots of benzene (0.294 g), (2) three 500-ml aliquots of benzene (0.670 g), (3) 800 ml of benzene (0.019 g), (4) 500 ml of 1:1 benzene-ether (0.252 g). The progress of the column was followed using thin layer chromatograph on silica gel using benzene as solvent. Fractions 2 and 3 were combined and crystallized from petroleum ether (bp 30–60°) to afford 64 mg of product, mp 51–52°. This phenol was assigned structure 26, 1,1-dimethyl-8-tetralol, as discussed previously.

Anal. Calcd for $\text{C}_{12}\text{H}_{16}\text{O}$: C, 81.9; H, 9.1. Found: C, 81.8; H, 9.1.

Fractions 8 and 9 were combined and 29 mg of 1,1-dimethyl-7-tetralol (20) was obtained by seeding a petroleum ether (bp 30–60°) solution. The identity of this compound was shown by comparison of the ir spectrum with an authentic specimen.⁵⁶ The filtrate deposited 48 mg of 1,1-dimethyl-6-tetralol (25) on seeding. The structure of this material was also established by comparison of the ir spectrum with a synthetic sample. Gas chromatographic analysis of the filtrate indicated the possible presence of a small amount of 1,1-dimethyl-5-tetralol (27).⁵⁶

Hydrogenation of Lumiketone Mixture.—A solution of 179 mg of the lumiprodukt mixture (7 and 8) in 15 ml of ethanol containing 40 mg of 10% palladium on carbon was hydrogenated at atmospheric pressure for 10 min. The catalyst was filtered off and the ethanol removed at reduced pressure to afford an oil

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which possessed absorption at 1725 cm^{-1} in the ir. The nmr spectrum showed that no vinyl hydrogens were present. The two dihydro lumiketones **22** and **23** were separated by preparative gas chromatography using the same procedure described for the lumiketones. A total of 21 mg of **22** and 35 mg of **23** were obtained. See Table I for spectral data.

1,1-Dimethylspiro[4,5]decan-7-one (24).—A mixture of the lumiketones (115 mg) was dissolved in 10 ml of methanol containing 50 mg of 10% palladium on carbon and hydrogenated for 1.0 hr at atmospheric pressure. The catalyst was removed by filtration and the solvent was evaporated at reduced pressure. The resulting oil was taken up in 2.0 ml of benzene and added to a column of silica gel (15 g, $1.75 \times 12.5\text{ cm}$) which was eluted with ten 100-ml aliquots of benzene. Fractions 3–6 were combined to afford 40 mg of the spiro derivative **24**. The structure of this compound is based primarily on the ir spectrum which shows carbonyl absorption at 1720 cm^{-1} and the mass spectrum which has a parent peak at m/e 180. Fractions 11–13 were combined and shown to be the dihydro compound **23** by spectral properties.

Quantum Yield Determination.—The method of Hatchard and Parker²⁸ utilizing potassium ferrioxalate as the actinometer was employed. A Bausch and Lomb Model 33-86-25 ultraviolet grating monochromator equipped with a 200-W super pressure mercury source and power supply was used as a light source for these studies. The quantitative determination of the lumiketones was accomplished using cyclododecane as the internal standard by gas chromatography on a UCW-98 column at 165° .

In a typical experiment, 70.3 mg ($4 \times 10^{-4}\text{ mol}$) of dienone **6** was diluted to 100 ml with spectral grade dioxane in a volumetric flask and irradiated for 120 min at 2537 \AA .

Analysis of Phenols by Gas Chromatography.—Each solution to be analyzed was checked for the presence of dienone **6** either by ir spectroscopy or glc on UCW-98. If present, separation was accomplished by adsorption of the phenols onto basic alumina from an ether solution. The phenols were eluted from the alumina with methanol which was evaporated to dryness and the ether soluble portion of the residue was used. This solution was analyzed on the two columns shown in Table III. The mixture of phenols was then acetylated by heating on a steam

TABLE III

GLC RETENTION TIMES OF PHENOLS AND PHENOL ACETATES

Phenol	Retention times (min)		
	UCW-98 ^a	DC-11 ^b	UCW-98 ^{a,c}
20	20	14	26
25	20	14	24
26	16	10	24
27	18	12	30
28	16	12	24

^a 6-ft UCW-98 on Chromosorb W at 130° at a flow rate of 20 ml/min. ^b 6-ft DC-11 on Chromosorb W (DMCS treated) at 115° at a flow rate of 50 ml/min. ^c Data for phenol acetates, same as in *a* but at 50 ml/min.

bath for 0.5 hr in a solution of 2.0 ml of acetic anhydride and 1.0 ml of pyridine and analyzed as shown in Table III. Since authentic samples of all the phenols and their acetates were on hand it was possible, by coinjection techniques, to identify all five isomeric phenols.

Registry No.—**6**, 20691-79-6; **7**, 20674-83-3; **8**, 20674-14-0; **17**, 26315-95-7; **18**, 26315-96-8; **22**, 20674-15-1; **23**, 26315-98-0; **24**, 26315-99-1; **26**, 26316-00-7; 4-methyl-4-hydroxyphenyl-1-pentanol bisphenylurethane, 26316-01-8; 4,4-dimethyl- α -butyrolactone, 3123-97-5; 4-methyl-*p*-hydroxyphenyl-1-pentanoic acid, 23203-47-6.

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Chlorination of 2-Fluoropropene.

3-Chloro-2-fluoropropene and Some of Its Derivatives

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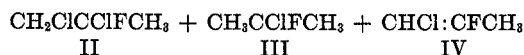
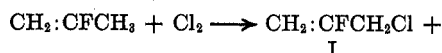
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3-Chloro-2-fluoropropene, a new reactive intermediate, was prepared by chlorination of 2-fluoropropene under a variety of conditions where an ionic mechanism predominated, but not under radical conditions. 3-Amino-2-fluoropropene, 2-fluoro-3-iodopropene, 2-fluoro-2-propenol, and 2-fluoro-2-propenyl ethyl ether were prepared to demonstrate the reactivity. 3-Chloro-2-fluoropropene can be copolymerized to low polymers with acrylonitrile and methyl methacrylate. 3-Chloro-2-fluoropropene and its derivatives are very toxic and should be handled with extreme caution.

It has become evident from the examples which have appeared in the literature¹ that the pathway of chlorination is very much dependent on the conditions which control ionic *vs.* radical reaction. In most cases those molecules of the type $\text{CH}_2\text{CY}=\text{CH}_2$ undergo allylic chlorination under ionic conditions.² The usual examples of compounds which react by allylic chlorination are 2-methylpropene, which yields 3-chloro-2-methylpropene,³⁻⁶ 2-chloropropene, which yields mainly 2,3-di-

chloropropene,⁷⁻⁸ and 2-chlorobutene-2, which yields 2,3-dichlorobutene-1.⁸

The chlorination of 2-fluoropropene under non-free-radical conditions proceeds rapidly to form the new compound 3-chloro-2-fluoropropene (I), 1,2-dichloro-2-fluoropropane (II), 2-chloro-2-fluoropropane (III), and a very small amount of 1-chloro-2-fluoropropene (IV).



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