The Influence of Electron-Withdrawing Substituents on the Photochemical Behavior of Bicyclic 6/6-Fused Cross-Conjugated Cyclohexadienones[1]

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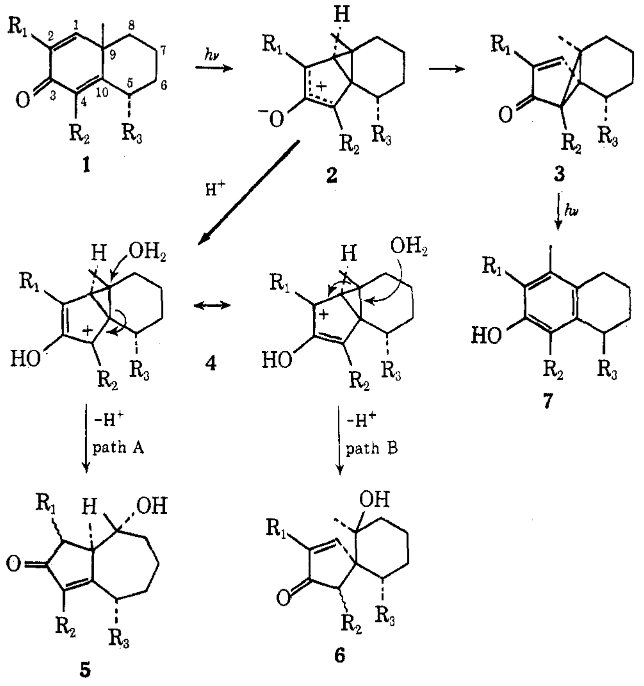
Derivatives of the bicyclic 6/6-fused cross-conjugated cyclohexadienone, 3-keto-9-methyl-$\Delta^{1,4}$-hexahydronaphthalene (**1j**), with electron-withdrawing formyl, carbonyl, and carbomethoxyl groups at positions 2 and 4 were synthesized and irradiated in aqueous acetic acid and in some cases other solvents. Each of the 2-substituted dienones was converted photochemically into a hydroazulene derivative in good yield. The 2-carboxy dienone **1e** proved to be an exceedingly useful compound for the synthesis of ring A unsubstituted hydroazulenes, as decarboxylation of the initial rearrangement products occurred spontaneously. The 4-formyl and 4-carbomethoxy dienones **1i** and **1g** failed to yield identifiable products having a rearranged carbon skeleton. In these cases it is possible that photochemical deconjugation to an enol of a β-dicarboxyl compound took place in preference to the normal cyclohexadienone rearrangement. However, the 4-carboxy dienone **1h** yielded spiro[4.5]decane derivatives on irradiation in aqueous acetic acid and in dioxane. In general, the mode of rearrangement of the substituted dienones can be intrepreted in terms of pathways generally accepted to be involved in cross-conjugated dienone rearrangements provided that the electron-withdrawing influence of the substituent and the ability of carboxyl substituents to act as internal proton donors to carbonyl groups are recognized.

Scheme I



a, $R_1 = R_2 = H$; $R_3 = CH_3$
b, $R_1 = R_3 = H$; $R_2 = CH_3$
c, $R_2 = R_3 = H$; $R_1 = CH_3$
d, $R_2 = R_3 = H$; $R_1 = CHO$
e, $R_2 = R_3 = H$; $R_1 = CO_2H$
f, $R_2 = R_3 = H$; $R_1 = CO_2CH_3$
g, $R_1 = R_3 = H$; $R_2 = CO_2CH_3$
h, $R_1 = R_3 = H$; $R_2 = CO_2H$
i, $R_1 = R_3 = H$; $R_2 = CHO$
j; $R_1 = R_2 = R_3 = H$

The photochemical behavior of ring A unsubstituted and 2- and 4-methyl substituted cross-conjugated cyclohexadienones such as **1** (Scheme I) has been widely studied.[2] The products of irradiation of dienones of this type are generally considered to arise *via* dipolar cyclopropyl intermediates such **2**, first proposed by Zimmerman and Schuster.[3a,4,5] Bicyclo[3.1.0]hex-2-en-3-one derivatives (lumiproducts) **3a–c**, which are obtained in good yield on irradiation of the corresponding dienones in neutral solvents such as dioxane,[6a–c] may be considered to arise *via* a symmetry-allowed 1,4-sigmatropic rearrangement of **2**.[7–9] However, when protic solvents such as aqueous acetic acid are employed, **2** too may be protonated to give the mesoionic species **4** which may undergo solvolytic cleavage to produce 5/7-fused or spiro hydroxy ketones. The mode of cleavage of **4** is apparently controlled by tbe electronic effect of methyl substituents. For example, on irradiation in aqueous acetic acid the 4-methyl dienone **1b** yielded exclusively the 5/7-fused hydroxy ketone **5b**,[10] while the 2-methyl compound **1c** yielded exclusively the spiro hydroxy ketone **6c**.[6c] Under similar conditions the unsubstituted dienone **1a** yielded an approximately 1:1 mixture of **5a** and **6a**.[6a] [In each case the hydroxy ketone products were accompanied by varying amounts of phenols (**7**), considered to arise as secondary photoproducts from the related lumiproducts.][2] Thus the location of an electron-releasing methyl group at C-4 or C-2 appears to increase the stability of the resonance form of **4** having a positive charge at that position and cleavage *via* path A or B takes place; and, when ring A of the dienone is unsubstituted, both resonance forms of **4** are approximately equal in energy so that products derived from both possible cleavage pathways are isolated.

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

(3) (a) H. E. Zimmerman[3b] and D. I. Schuster, *J. Amer. Chem. Soc.*, **84**, 4527 (1962); (b) H. E. Zimmerman and J. S. Swenton, *ibid.*, **86**, 947 (1964); (c) H. E. Zimmerman and J. S. Swenton, *ibid.*, **89**, 906 (1967).

(4) Zimmerman and coworkers[3a–c] have presented a detailed treatment of the mechanistic pathways by which species analogous to **2** may be formed photochemically from the parent dienone.

(5) For recent evidence for the intervention of dipolar intermediates in dienone photolysis see (a) M. H. Fisch, *Chem. Commun.*, 1472 (1969); (b) D. I. Schuster and V. Y. Abraitys, *ibid.*, 419 (1969); (c) D. I. Schuster and K. Liu, *J. Amer. Chem. Soc.*, **93**, 6711 (1971).

(6) (a) P. J. Kropp and W. F. Erman, *ibid.*, **85**, 2456 (1963); (b) P. J. Kropp, *ibid.*, **87**, 3914 (1965); (c) P. J. Kropp, *ibid.*, **86**, 4053 (1964).

(7) (a) H. E. Zimmerman and D. S. Crumrine, *ibid.*, **90**, 5612 (1968); (b) H. E. Zimmerman, D. S. Crumrine, D. Dopp, and P. S. Huyffer, *ibid.*, **91**, 434 (1969).

(8) T. M. Brennam and R. K. Hill, *ibid.*, **90**, 5614 (1968).

(9) R. B. Woodward and R. Hoffman, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

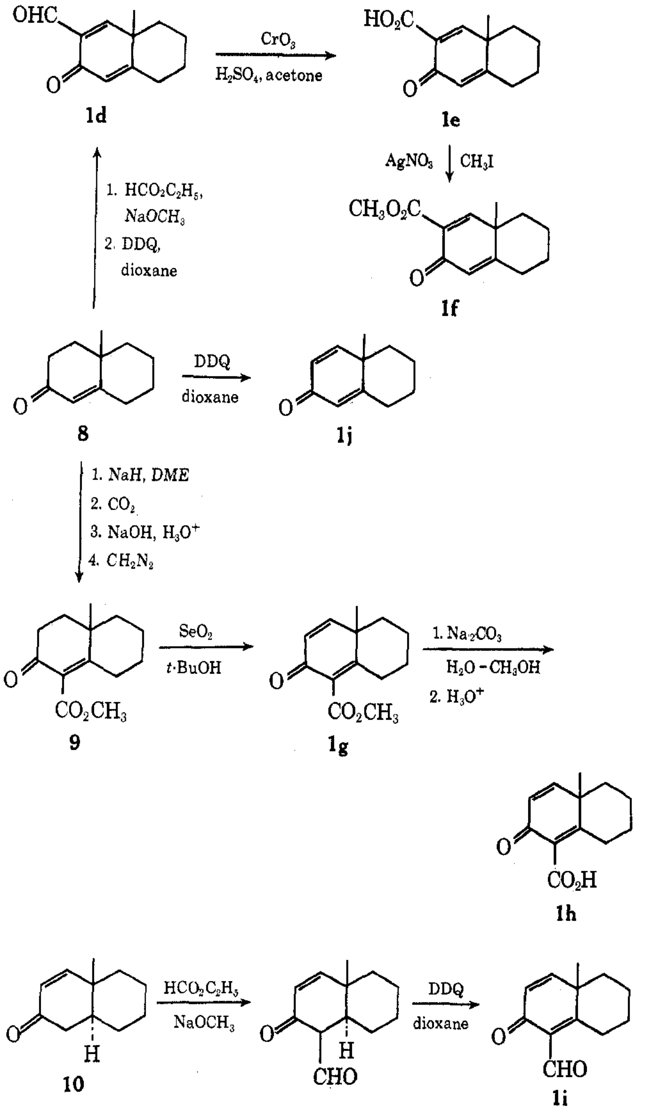
(10) (a) P. J. Kropp, *J. Org. Chem.*, **29**, 3110 (1964); (b) D. Caine and J. B. Dawson, *ibid.*, **29**, 3108 (1964).

The apparent involvement of species such as **4** in the reactions of **1a–c** suggested that substituents other than methyl groups might influence the course of cyclohexadienone photochemical rearrangements in nucleophilic solvents to produce largely or exclusively 5/7-fused or spirocyclic products. For example, electron-withdrawing groups such as formyl, carboxyl, or carbomethoxyl located at C-2 or C-4 would be expected to favor solvolytic cleavage of intermediates analogous to **4** *via* path A or path B to produce 5/7-fused or spirocyclic products, respectively. Furthermore, groups such as these should be easily removable after photolysis so that convenient routes to ring A unsubstituted products such as **5a** or **6a**, which are obtained only in poor yield from direct irradiation of **1a**,[6a] would be provided. However, it was recognized that excited-state species derived from dienones bearing chromophoric groups such as those indicated above might be capable of reactions which would prevent or compete with the formation of intermediates such as **4**. Also, even though such intermediates might be formed, the presence of functional groups on the allylic system might allow the intervention of reactions not normally encountered when simpler unsubstituted or methyl-substituted compounds are involved. The above considerations suggested that a study of the photochemical behavior of functionally substituted dienones related to **1** would be of synthetic and mechanistic interest. Thus the C-2 substituted dienones **1d–f** and the C-4 substituted compounds **1g–i** have been prepared and irradiated under various conditions. Our investigations have mainly involved a study of the photochemical behavior of compounds **1d–i** in nucleophilic solvents, but interesting results have also been obtained on irradiation of some of these compounds, particularly **1e** and **1h**, in dioxane.[11]

Results

The octalone **8**[12] served as the starting material for the synthesis of the ring A substituted dienones **1d–h** as well as the unsubstituted compound **1j**. Condensation of **8** with ethyl formate in the presence of sodium methoxide and reaction of the resulting hydroxymethylene derivative with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in dry dioxane[13] gave **1d** in approximately 50% overall yield. The 2-carboxy dienone **1e** was obtained in 61% yield by oxidation of **1d** with Jones reagent.[14] This material was also prepared in low yield by condensation of 2-formyl-2-methylcyclohexanone with ethyl acetoacetate according to the procedure of Dreiding and Tomasewski.[15] The corresponding methyl ester **1f** was obtained in 88% yield by reaction of **1e** with methyl iodide in the presence of silver oxide.[15]

The 4-carbomethoxy dienone **1g** was obtained by dehydrogenation of the corresponding enone ester **9**. Enone **8** was converted into **9** by a procedure similar to that used by Wenkert and Jackson[16] for the preparation of a related compound. The $\Delta^{3,5}$-conjugated enolate of **8** [prepared from treatment of the enone with sodium hydride in 1,2-dimethoxyethane (DME)] was carbonated at C-4 by treatment with dry, gaseous carbon dioxide, and the 4-carboxy enone, obtained by brief treatment with aqueous sodium hydroxide to isomerize the β,γ double bond into conjugation and careful acidification, was esterified with diazomethane to give **9** in 63% yield. Attempted introduction of the 1,2 double bond by treatment of **9** with DDQ under a variety of conditions gave mixtures which appeared to be composed of the desired cross-conjugated dienone, the related linearly conjugated dienone, and trienone derived from further oxidation of either of the above. Attempted separation of **1g** from the other two products failed. However, the successful preparation of **1g** was carried out by oxidation of **9** with selenium dioxide in *tert*-butyl alcohol.[17] The dienone acid **1h** was obtained by mild hydroxysis of **1g** with aqueous sodium carbonate followed by acidification. The known dienone **1j**[18] was also obtained from **8** by dehydrogenation with DDQ.[19]



The 4-formyl dienone **1i** was prepared from the octalone **10**.[20] Conversion of **10** into its 4-hydroxymethylene derivative was accomplished using ethyl formate

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[11] Preliminary reports which cover portions of this work have appeared: (a) D. Caine and J. F. Debardeleben, Jr., *Tetrahedron Lett.* 4585 (1965); (b) D. Caine, J. F. Debardeleben, Jr., and J. B. Dawson, *ibid.*, 3625 (1966).

[12] N. C. Ross and R. Levine, *J. Org. Chem.*, **29**, 2341 (1964).

[13] J. A. Edwards, M. C. Calzada, L. C. Ibanez, M. E. Cabezas Rivera, R. Urguiza, L. Carbona, J. C. Orr, and A. Bowers, *ibid.*, **29**, 3481 (1964).

[14] K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

[15] A. S. Dreiding and A. J. Tomasewski, *J. Org. Chem.*, **19**, 241 (1954).

[16] E. Wenkert and G. Jackson, *J. Amer. Chem. Soc.*, **81**, 5601 (1959).

[17] A procedure similar to that described by Bloom was employed. See S. M. Bloom, *ibid.*, **81**, 4728 (1959).

[18] R. B. Woodward and T. Singh, *ibid.*, **72**, 494 (1950).

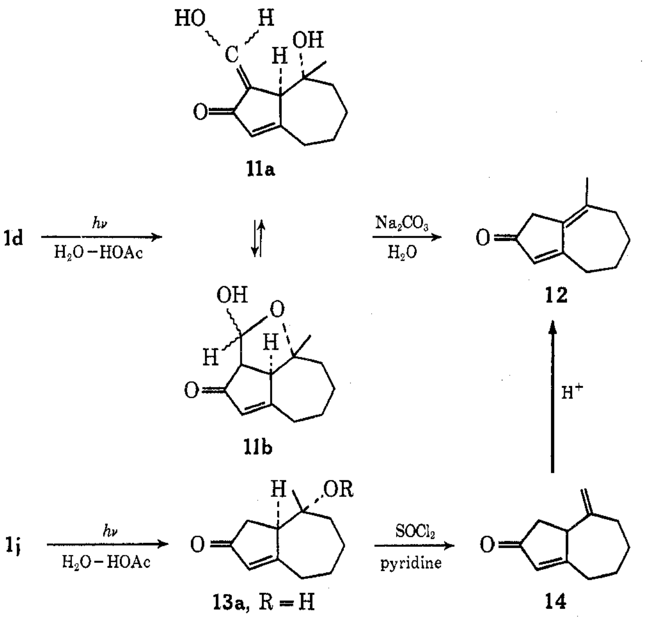
[19] D. Burn, D. M. Kirk, and V. Petrow, *Proc. Chem. Soc.*, 14 (1960).

[20] C. Djerassi and D. Marshall, *J. Amer. Chem. Soc.*, **80**, 3986 (1958).

and sodium methoxide in benzene in a procedure similar to that employed by Woodward and coworkers[21] for the preparation of a related compound, and this product was readily oxidized with DDQ[13] to give **1i**.

All of the new dienones exhibited the expected spectral properties (see Experimental Section). The compounds having substituents at C-4 exhibited a one-proton nmr absorption at a lower field than is normally observed for protons on saturated carbon atoms. This absorption was assigned to the C-6 equatorial proton, which is deshielded by the unsaturated substituent at C-4.[22]

The 2-formyl dienone **1d** was the first compound to be investigated. On irradiation (Pyrex)[23] of this material in 45% aqueous acetic acid for 3.5 hr at room temperature a viscous oil was obtained on removal of the solvent. The material could not be purified sufficiently to permit a positive structural assignment, but, on the basis of spectral and chemical evidence the hydroxymethylene compound **11a** and its related internal hemiacetal **11b** are considered to be the major components of the mixture. The crude product was soluble in dilute sodium hydroxide and it gave positive ferric chloride and Tollens' tests, indicative of an enolizable β-keto aldehyde grouping. It showed strong uv absorption at 235 nm and a weak band at 300 nm which shifted to longer wavelength (340 nm) in basic solution. The ir and nmr spectra also were consistent with the structures **11a** and **11b** (see Experimental Section). Attempts to convert the primary photoproduct to a solid derivative were unsuccessful and attempted purification of the material by chromatography on silica gel led to the isolation of the heteroannular dienone **12**, identified as described below, as the only significant product.



On treatment of the crude photolysis mixture with dilute aqueous sodium carbonate, **12** was obtained in 70% yield from **1d**. This compound was readily identified on the basis of its spectral properties, which were quite similar to those reported for related 5/6-fused bicyclic[24] and steroidal[25] dienones. On catalytic hydrogenation **12** was converted into its tetrahydro derivative, which was capable of exchanging four hydrogen atoms for deuterium on equilibration with deuterium oxide in the presence of potassium carbonate.

Confirmation of the structure of **12** was obtained by its synthesis from the 5/7-fused hydroxy ketone **13a**. Using the conditions described by Kropp and Erman[10a] for the synthesis of **5a**, **13a** was obtained in *ca.* 10% yield by irradiation of **1j**. Dehydration of the hydroxy ketone with thionyl chloride in pyridine[26] gave the dienone **14** having an exocyclio double bond. This compound was readily isomerized into **12** on treatment with a catalytic amount of trifluoroacetic acid (TFA) in carbon tetrachloride.

Compound **1d** was also irradiated (quartz)[23] in dioxane solution. However, thin layer chromatography of the photolysis mixture indicated that at least four products were formed in low yield. In addition, a significant amount of polymeric material was produced. Because of these results and because Schaffner and coworkers[27] had reported that a 2-formyl steroidal dienone related to **1d** was stable to light at 2537 Å and gave a complex mixture composed of mainly phenolic products when irradiated in dioxane with a broad spectrum lamp, further studies on the photochemistry of **1d** in dioxane were not undertaken.

Irradiation (Pyrex)[23] of the 2-carboxy dienone **1e** at room temperature in several solvents gave various mixtures of products **13**, **14**, and **12**, and the enone lactone **15**. The yields of these products and the reaction conditions are shown in Table I.

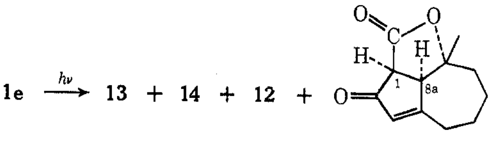


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Table I

Irradiation of 2-Carboxy-3-keto-9-methyl-$\Delta^{1,4}$-hexahydronaphthalene (**1e**) under Various Conditions

Solvent	Time, hr	Product yield, %				
		13a	13b	15	12	14
45% aqueous HOAc	2.0	65		6	5	7
45% aqueous dioxane	2.0	60		12		
Anhydrous dioxane	2.0			16		67
Anhydrous methanol	2.5		48	14		13

The methoxy ketone **13b** was readily identified on the basis of its spectral properties, which were similar to those of **13a** if allowance was made for the presence of the C-8 methoxy rather than the hydroxy group. The

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[21] A procedure similar to that described by Woodward and coworkers was employed. See R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler, and W. M. McLamore, *J. Amer. Chem. Soc.*, **74**, 4223 (1952).

[22] M. Tomoeda, M. Inuzuka, T. Furuta, and T. Takahaski, *Tetrahedron Lett.*, 1233 (1964).

[23] Irradiations were carried out with a 450-W Hanovia high-pressure mercury lamp housed in a quartz or Pyrex probe. The solution was vigorously agitated with a stream of nitrogen for several minutes prior to and during the entire irradiation period.

[24] D. Caine, A. M. Alejandre, K. Ming, and W. J. Powers, III, *J. Org. Chem.*, **37**, 706 (1972).

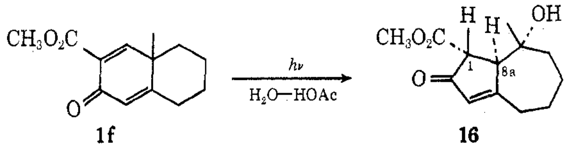
[25] G. Bozzato, H. P. Throndsen, K. Schaffner, and O. Jeger, *J. Amer. Chem. Soc.*, **86**, 2073 (1964).

[26] D. H. R. Barton, P. deMayo, and M. Shafiq, *J. Chem. Soc.*, 929 (1957).

[27] E. Alterburger, H. Wehrli, and K. Schaffner, *Helv. Chem. Acta*, **44**, 2735 (1963).

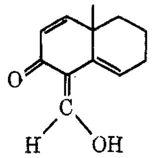
enone lactone **15** exhibited the expected ir absorptions for the γ-lactone (5.61 μ) and conjugated cyclopentenone (5.87 and 6.23 μ) groupings and its nmr spectrum showed a three-proton singlet at δ 1.05 ppm for the CH_3CO grouping, a one-proton multiplet at δ 5.81 ppm for the C-1 vinyl proton, and an AB quartet at δ 3.50 and 4.07 ppm (J = 7.4 Hz) for the C-1 and C-protons, respectively. The peaks of the doublet for the C-8a proton were slightly broadened presumably because of coupling with the C-4 proton which is allylic to it. The coupling constants for the AB quartet, indicating a dihedral angle of 15° or less,[28] are consistent with the stereochemical assignment at the 1 and 8a positions of **15**. On hydrolysis with aqueous sodium carbonate, acidification, and decarboxylation, **15** yielded a mixture of **12** and **13a**. The formation of **13a** served to verify the stereochemical assignment at C-8.

Irradiation (Pyrex)[23] of the 2-carbomethoxy dienone **1f** in 45% aqueous acetic acid at room temperature yielded the hydroazulene derivative **16** in 67% yield. The product exhibited the expected ir absorptions for the ester (5.77 μ) and conjugated cyclopentenone groupings (5.87 and 6.24 μ) and the nmr spectrum (DMSO-d_6) showed three-proton singlets at 0.82 and 3.36 ppm for the C-8 methyl and the methoxyl groups, a multiplet at 5.41 ppm for the C-4 proton, and a one-proton singlet at 3.19 ppm which probably corresponded to the C-1 or to the C-8a proton. Molecular models of **16** having the carbomethoxy group in what appears to be the more stable α configuration show that the dihedral angle between the C-8a hydrogen and the C-1 hydrogen which is trans to it is *ca.* 120°, indicating that a small coupling constant (J = 0–2 Hz) would be expected.[28] Chemical evidence for the structure of **16** was obtained by its conversion into the dihydro derivative of **13a** by catalytic reduction of the carbon–carbon double bond followed by hydrolysis of the ester and decarboxylation.



1f **16**

The results of irradiations of the 4-formyl dienone **1i** and the 4-carbomethoxy dienone **1g** were disappointing, since photoproducts having a rearranged carbon skeleton were not obtained. When **1i** was irradiated (Pyrex)[23] for 1.5 hr in aqueous acetic acid, examination of the nmr spectrum of the crude photolysis mixture indicated that it was composed of an approximately 4:1 mixture of the starting material and what appeared to be the enolic compounds **17** or **18**. Longer irradiation periods produced no new products, and **1i** was recovered unchanged when irradiated in aqueous acetic acid using 2537-Å light source. When **1g** was irradiated (Pyrex)[23] in aqueous acetic acid for 2 hr, nmr analysis of the crude photolysis mixture indicated that a significant amount of the starting material had been consumed. However, chromatography of the photolysis mixture on silica gel failed to yield identifiable compounds other than the starting material.



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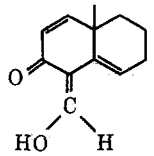

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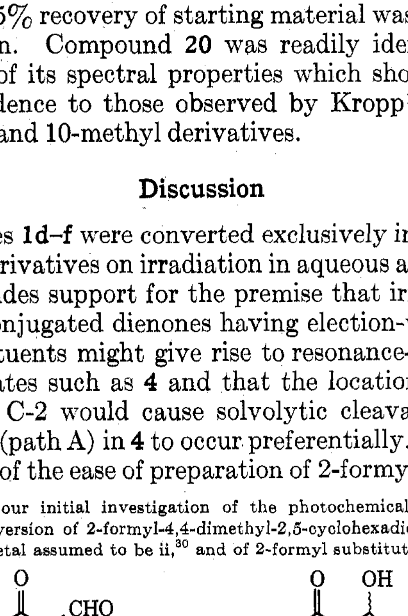
Unlike dienones **1i** and **1g**, the 4-carboxy compound **1h** was smoothly converted into products having a spiro[5.4]decane carbon skeleton when irradiated in aqueous acetic acid or in anhydrous dioxane. Irradiation (quartz)[23] in the former medium for 30 min gave the lactone **19** in *ca.* 40% yield as the only isolated product other than the starting material. Compound **19** exhibited the expected ir absorptions for a γ-lactone (5.65 μ) and cyclopentenone (5.84 and 6.05 μ), and the nmr spectrum ($CDCl_3$) showed a three-proton singlet at 1.15 ppm for the C-6 methyl group, a broad one-proton singlet at 3.38 ppm for the C-1 proton, a one-proton doublet at 6.17 ppm (J = 5.5 Hz) for the C-3 proton, and a broad doublet at 7.58 ppm (J = 5.5 Hz) for the C-4 proton. The broadening of the absorptions for the C-1 and C-4 protons presumably arises as a result of long-range interactions between the two nuclei.



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When irradiated (quartz)[23] in anhydrous dioxane for 25 min, dienone **1h** gave the spiro dienone **20** in *ca.* 60% yield; a 25% recovery of starting material was obtained in this run. Compound **20** was readily identified on the basis of its spectral properties which showed close correspondence to those observed by Kropp[10b] for the related 3- and 10-methyl derivatives.

Discussion

Dienones **1d–f** were converted exclusively into hydroazulene derivatives on irradiation in aqueous acetic acid. This provides support for the premise that irradiations of cross-conjugated dienones having election-withdrawing substituents might give rise to resonance-stabilized intermediates such as **4** and that the location of these groups at C-2 would cause solvolytic cleavage of the 5,10 bond (path A) in **4** to occur preferentially.[29]

In view of the ease of preparation of 2-formyl dienones

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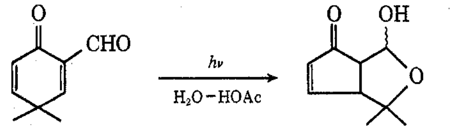
[28] J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Englewood Cliffs, N. J., 1965, p 116.

[29] Since our initial investigation of the photochemical behavior of **1d**[11a] the conversion of 2-formyl-4,4-dimethyl-2,5-cyclohexadienone into an enone hemiacetal assumed to be ii,[30] and of 2-formyl substituted tetracyclic



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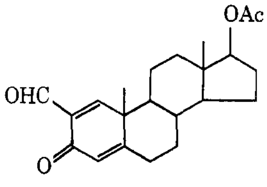
dienones into products having the Grayanotoxin carbon skeleton[31] by irradiations in aqueous acetic acid have been reported. These results are also consistent with the view that the course of solvolytic cleavage of resonance-stabilized intermediates analogous to **4** is controlled by the location of the electron-withdrawing formyl group.

[30] H. V. Secor, M. Bourlas, and J. F. DeBardeleben, *Experientia*, **27**, 18 (1971).

[31] M. Shiozaki, K. Mori, M. Matsui, and T. Hiraoka, *Tetrahedron Lett.*, 657 (1972).

such as **1d** from the corresponding octalone derivatives, the photochemical rearrangement of these compounds in aqueous acetic acid followed by base-catalyzed deformylation provides a convenient route to ring A unsubstituted hydroazulene derivatives. However, the synthetic value of the sequence is limited by the fact that the conditions required for the deformylation step also lead to the elimination of water. Thus **12** was the only product isolated when the crude photolysis mixture derived from irradiation of **1d** was treated with base.

The photolability of 2-formyl dienones in aqueous acetic acid contrasts strikingly with their behavior in dioxane.[27] Kropp[2a] has suggested that the phenol **22** obtained in 9% yield by Schaffner and coworkers[27] by irradiation of the steroidal dienone **21** in dioxane arises from the lumiproduct intermediate **23**. The lumiproduct would be expected to be formed by way of the zwitterionic intermediate **24**. Because of the presence of the electron-withdrawing formyl group, **24** would be expected to be of higher energy than related unsubstituted and methyl-substituted species such as **2a–c**. Clearly charged species such as **24** might be expected to be formed more readily in polar, hydrogen bonding solvents such as aqueous acetic acid than in solvents of low polarily such as dioxane. Also, from a study of the ultraviolet spectrum of 2-formyl-$\Delta^{1,4}$-3-keto steroids in dioxane and in ethanol Edwards and coworkers[13] concluded that in ethanol reversible hemiacetal formation takes place. Thus in aqueous acetic acid it is possible that the hydrate of **1d** is formed and that excitation of this species is more efficient than that of **1d** itself. If the hydrated species were actually involved in the photochemical reaction, the *gem*-dihydroxy C-2 substituent would be expected to exert a similar influence to that of a formyl group on the course of cleavage of a species such as **4**.



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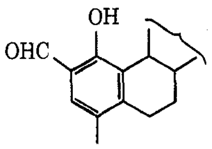

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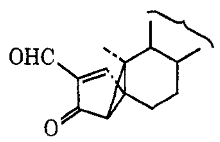

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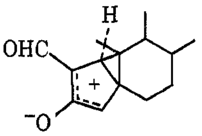
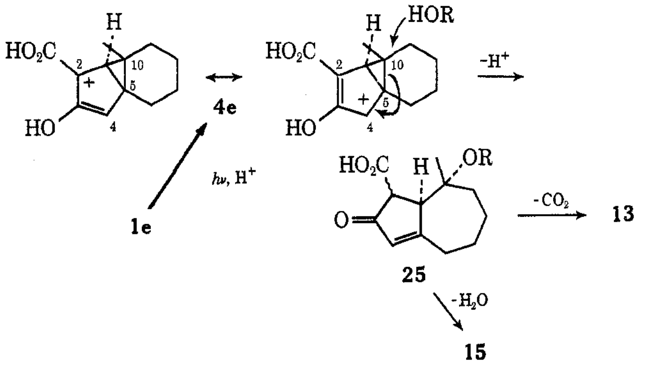


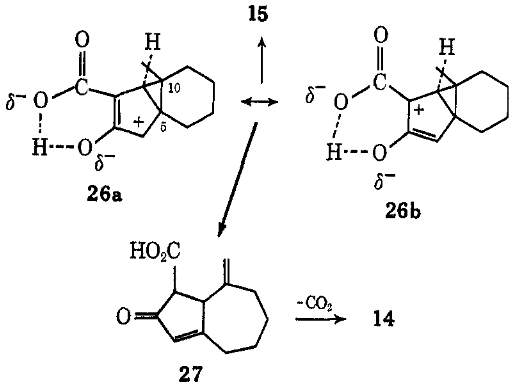
24

The 2-carboxy dienone **1e** proved to be a useful compound for the synthesis of ring A unsubstituted hydroazulenes. Irradiations of this compound in aqueous solvents and in methanol produced good yields of the 5/7-fused hydroxy and methoxy ketones **13a** and **13b**, respectively. The formation of these products can readily be rationalized in terms of the intervention of intermediate **4e**. In this case the structure having the positive charge at C-4 should be the major contributor to the resonance hybrid and solvolytic cleavage of the 5,10 bond would give initially the hydroxy β-keto acid **25**, which could undergo rapid decarboxylation to **13**.



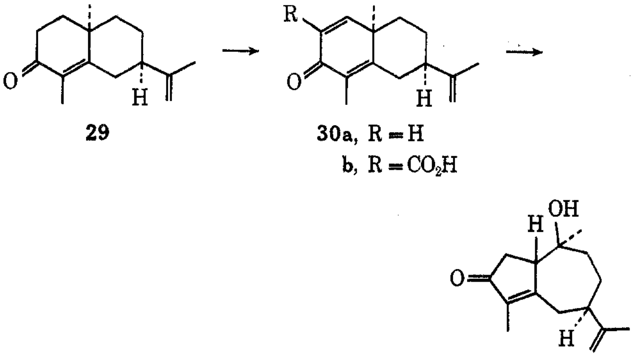
a, R = H
b, R = CH$_3$

Irradiation of **1c** in dioxane is likely to give rise to the dipolar intermediate **26**. The ability of the carboxyl group to internally protonate the carbonyl oxygen atom in **26** is likely to be the major factor contributing to the photolability of **1e** as compared with **1d** in dioxane. The conjugated chelate structure **26a** would be expected to be more stable than the unconjugated one **26b**, and cleavage of the 5,10 bond of the cyclopropane ring in **26** should again be favored. The dienone **14**, the major product of irradiation of **1e** in dioxane, may arise by the conversion of **26** into **27** followed by loss of carbon dioxide. The loss of a proton from the C-10 methyl group and the cleavage of the 5,10 bond is probably concerted, since no product derived from loss of a proton from C-9 was observed. Although we suggested earlier that the carboxyl group might internally assist in the proton abstraction reaction, it seems more likely that the proton loss to give a endocyclic double bond does not occur because neither of the C-9 protons can easily achieve a transoid-coplanar relationship with the 5,10 bond. On the other hand, free rotation readily allows such a relationship to be established between one of the methyl protons and the 5,10 bond. Dienone **14** was also obtained as a minor product of irradiation of **1e** in aqueous acetic acid and in methanol. Apparently, in these solvents proton loss competes to some degree with the nucleophilic attack of the solvent on C-10. Since dienone **13** is readily isomerized into the conjugated system **12**, it seems likely that the small amount of **12** isolated on irradiation of **1e** in aqueous acetic acid results from partial isomerization of **14** during photolysis and workup.



The keto lactone **15** was a minor product of irradiation of **1e** in all of the solvents studied. In the aqueous media this material probably arises as a result of competition between decarboxylation and lactonization of **25a**. Although direct conversion of **4e** into **15** cannot be excluded, the formation of **15** in anhydrous solvents suggests that direct attack of the C-2 carboxyl group at C-10 of intermediates **4e** or **26** may be involved. Examination of models of these species shows that considerable stretching of the 5,10 bond would be required to bring the carboxyl group into the bonding distance of C-10. However, a transition state resembling the product in which breaking of the 5,10 bond is far ahead of formation of the new C–O bond would appear to satisfactorily explain the direct formation of **15**.

The photochemical rearrangement of 2-carboxy dienones such as **1e** provides a convenient method of preparation of synthetically useful hydroazulenes such as **13** and **14**. 2-Carboxy cross-conjugated dienones are relatively easily prepared from the parent octalone derivatives. Indeed, Piers and Cheng[32] have found that a better overall yield of the hydroazulene **28** is obtained from the parent octalone **29** if the 2-carboxy dienone **30b** rather than the unsubstituted dienone **30a** is prepared and irradiated.



29

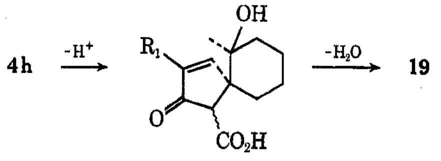
30a, R = H
b, R = CO_2H

28

As expected, irradiation of the 2-carbomethoxy dienone **1f** in aqueous acetic acid produced the hydroxy keto ester **16** having the ring A substituent retained. It appears that compounds such as **16** are potentially useful intermediates for the synthesis of 1-alkyl hydroazulene derivatives, which could be obtained by base-catalyzed alkylation of **16** followed by hydrolysis and decarboxylation.

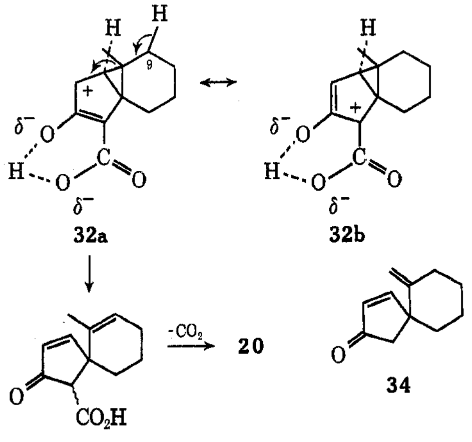
The 4-formyl and 4-carbomethoxy dienones **1i** and **1j**, respectively, failed to yield products having a rearranged carbon skeleton on irradiation under the conditions described above. This may be attributable to the fact that these compounds are capable of undergoing photochemical deconjugation of the 4,5 double bond to produce enols such as **17**.[33]

Although photochemical deconjugation of α,β-unsaturated acids has been observed,[33c,d] irradiation of the dienone acid **1h** both in aqueous acetic acid and in dioxane produced reasonably good yields of spiro[4.5]decane derivatives. The spiro lactone **19**, the product of irradiation of **1h** in aqueous acetic acid, probably arises from lactonization of the hydroxy β-keto acid **31**. Irradiation of **1h** in protic media should lead to the intermediate **4h**. The location of the electron-withdrawing group at C-4 should favor path B cleavage of **4h** and compound **31** would be the initial product of this process. Unexpectedly, no spiro hydroxy ketone derived from decarboxylation of proposed intermediate **31** was obtained.



31

In aprotic media the spiro dienone **20** probably arises from decarboxylation of the β-keto acid **33**, which would be produced from proton loss from C-9 of the chelate intermediate **32**. Resonance structure **32a** should be the major contribution to the resonance hydrid **32** and this factor would be expected to favor cleavage of the 1,10 bond of the cyclopropane ring. Examination of models of **32** reveals that the C-9β proton can easily achieve a transoid-coplanar relationship with the 1,10 bond, providing a concerted pathway for the formation of **33** from **32**. No evidence for the formation of **34**, the possible product derived from proton loss from the C-10 methyl group of **32**, was obtained. Although the C-4 carboxyl group does appear to control the direction of cleavage of the cyclopropane ring in the intermediate **32** it apparently does not play a role in determining the direction of formation of the new B ring double bond. Thus, as suggested above, it seems unlikely that the presence of the C-2 carboxyl group in **26** is the primary factor responsible for the exclusive formation of the exocyclic **14** on irradition of **1e** in anhydrous dioxane. Again, the ability of the carboxyl substituent to act as an internal proton donor probably accounts for the facile rearrangement of **1h** in dioxane.



Experimental Section[34]

2-Formyl-3-keto-9-methyl-$\Delta^{1,4}$-hexahydronaphthalene (1d).—2-Hydroxymethylene-3-keto-9-methyl-Δ^4-octahydronaphthalene

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[32] E. Piers and K. F. Cheng, *Can. J. Chem.*, **48**, 2234 (1970).

[33] (a) M. J. Jorgensen and L. Gundel, *Tetrahedron Lett.*, 4991 (1968); (b) J. A. Barltrop and J. Wills, *ibid.*, 4987 (1968); (c) P. J. Kropp and H. J. Krauss, *J. Org. Chem.*, **32**, 3222 (1967); (d) R. R. Rando and W. von E. Doering, *ibid.*, **33**, 1671 (1968); (e) J. K. Crandall and C. F. Mayer, *ibid.*, **35**, 3049 (1970); (f) J. R. Scheffer and B. A. Boire, *J. Amer. Chem. Soc.*, **93**, 5490 (1971).

[34] Melting points and boiling points are uncorrected. Infrared spectra were taken on Perkin-Elmer Model 457 or 137 infrared spectrophotometers. Ultraviolet spectra were taken on a Cary Model 14 or a Beckman DBGT recording spectrophotometer using 1-cm matched quartz cells. Nmr spectra were determined at 60 MHz with a Varian A-60 spectrometer. Signals are reported in parts per million (δ) downfield from internal tetramethylsilane. Mass spectra were obtained using a Varian M-66 spectrometer. Microanalyses were obtained by Galbreath Laboratories, Inc., Knoxville, Tenn., or by Atlantic Microlab, Inc., Atlanta, Ga. Gas–liquid chromatography was carried out using a Perkin-Elmer 881 or an Aerograph A-90-P3 gas chromatograph. The following columns were used: A (6 ft × 0.125 in., 10% SE-30 on Chromosorb W); B (6 ft × 0.125 in., 10% Carbowax K-20M on Chromosorb W); C (10 ft × 0.025 in., 10% Carbowax K-20M on Chromosorb W); D (5 ft × 0.25 in., 20% SF-96 on Chromosorb W); E (10 ft × 0.25 in., 20% SE-30 on Chromosorb W); F (10 ft × 0.25 in., 10% Apiezon L on Chromosorb W).

was prepared by a method similar to that described by Edwards and coworkers.[13] A mixture of 38.2 g (0.23 mol) of **8**,[12] 17.4 g (0.23 mol) of anhydrous ethyl formate (freshly distilled from P_2O_5), 500 ml of anhydrous benzene, and 21.2 g (0.4 mol) of sodium methoxide was prepared and stirred for 10 days at room temperature under nitrogen. The reaction mixture was extracted with four 25-ml portions of sodium hydroxide (5%) followed by 100 ml of water. The combined aqueous extracts were extracted with two 100-ml portions of ether. The aqueous layer was acidified with cold 1:1 hydrochloric acid and extracted with three 100-ml portions of ether. The solution was dried over anhydrous magnesium sulfate and the solvent was removed *in vacuo* to give 31.0 g (75%) of product: bp 116–118° (0.5 mm); uv $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 250 nm (ϵ 10,500) and 306 (5600), $\lambda_{\max}^{\mathrm{EtOH+NAOH}}$ 240 (11,700) and 360 (8000); ir $\lambda_{\max}^{\mathrm{CHCl_3}}$ 6.08 (unsaturated C=O) and 6.39 μ (conjugated C=C); nmr $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 1.14 (s, 3 H), 1.5–2.7 (broad absorption, 10 H), 5.80 (m, 1 H), and 7.43 ppm (m, 1 H). *Anal.* Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.06; H, 8.60.

The above hydroxymethylene derivative was converted into **1d** by a method similar to that reported by Edwards and coworkers.[13] 2-Hydroxymethylene-3-keto-9-methyl-Δ^4-octahydronaphthalene, 12.0 g (0.063 mol), was dissolved in 200 ml of anhydrous dioxane cooled to 20°. Then DDQ, 21.3 g (0.094 mol), dissolved in 100 ml of anhydrous dioxane was added rapidly while the temperature was maintained at 20° by the use of an ice bath. After 3.5 min, the reaction mixture was poured into 300 ml of methylene chloride and filtered twice through alumina. The light yellow filtrate was evaporated to dryness *in vacuo* to yield an oil, which solidified on standing at room temperature for 1 hr. Recrystallization of the material from hexane gave 9.0 g (76%) of **1d**: mp 82.5–84.0°; uv $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 220 nm (ϵ 11,900) and 244 (11,000); $\lambda_{\max}^{\mathrm{EtOH+NaOH}}$ 242 (12,000) and 347 (9600); ir $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.87 (unsaturated aldehyde), 6.00 (unsaturated ketone), 6.16 and 6.24 μ (conjugated double bonds); nmr $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 1.38 (s, 3 H), 1.25–2.65 (broad absorption, 8 H), 6.06 (m, 1 H), 7.40 (s, 1 H), and 10.10 ppm (s, 1 H). *Anal.* Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.60; H, 7.54.

2-Carboxy-3-keto-9-methyl-$\Delta^{1,4}$-hexahydronaphthalene (1e).—Jones reagent[14] (15 ml) (prepared by dissolving 15.0 g of chromium trioxide in 12.01 ml of concentrated sulfuric acid, and cooling the solution to 0°) was added dropwise with stirring over 25 min to a solution of 5.0 g (0.026 mol) of **1d** in 200 ml of anhydrous acetone while the reaction mixture was maintained at 0°. The reaction mixture was allowed to stand for 5 min at 0°, 600 ml of a saturated solution of sodium chloride was added, and the mixture was extracted with five 100-ml portions of ether. The combined ether extracts were washed with 200-ml portions of a saturated solution of sodium chloride until neutral (*ca.* 1 l. required) and dried over anhydrous magnesium sulfate, and the solvent was removed *in vacuo*. Recrystallization of the residue from ether afforded 3.3 g (61%) of **1e**: mp 130–131° (lit.[15] mp 128–132°); nmr $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 1.40 (s, 3 H), 1.60–2.70 (broad absorption, 8 H), 6.29 (m, 1 H), and 8.13 ppm (s, 1 H). The uv and ir spectra of the sample were identical with those previously reported.[15]

The procedure of Dreiding and Tomasewski[15] was also utilized for the synthesis of **1e**. 2-Methyl-2-formylcyclohexanone,[35] 11.2 g (0.08 mol), 4.8 g of acetic acid, and 100 ml of freshly distilled ethyl acetoacetate were mixed at room temperature and 6.8 g (0.08 mol) of piperidine was added dropwise with cooling under the tap. After standing in a closed reaction vessel for 17 hr at room temperature, the mixture was heated at 55° for 80 hr using an oil bath. Ether (500 ml) was then added, and the organic layer was washed with five 100-ml portions of water, 25 ml of saturated sodium bicarbonate, and three 100-ml portions of saturated sodium chloride solution. The ether was removed *in vacuo* and the excess of ethyl acetoacetate was removed by vacuum distillation using a sand bath maintained at 100°. The residue which remained after distillation was treated overnight at room temperature with a solution of sodium ethoxide, prepared from 8.0 g of 50% of a sodium hydride mineral dispersion and 200 ml of ethanol. The alcoholic solution was heated at reflux for 30 min, 25 ml of water was added, and the alcohol was removed by distillation at atmospheric pressure. Hot water (100 ml) was added, and the reaction mixture was made acidic with 1:1 hydrochloric acid, cooled, and extracted with four 100-ml portions of ether. The combined ethereal extracts were dried over sodium sulfate and the ether was removed *in vacuo*. The residue, 9.4 g, was chromatographed on 70 g of alumina. After elution with 2 l. of benzene, elution with 1 l. of ether gave 3.0 g (18%) of **1e** having identical physical properties with those of the sample prepared above.

2-Carbomethoxy-3-keto-9-methyl-$\Delta^{1,4}$-hexahydronaphthalene (1f).—This compound was prepared according to the method reported by Dreiding and Tomasewski.[15] The dienone acid **1e**, 3.2 g (0.0155 mol), and 50 ml of freshly distilled methyl iodide were allowed to stir at room temperature for 18 hr in the presence of 3.0 g of silver oxide. The solid was removed by filtration through Celite and the filter cake was washed with three 50-ml portions of ether. The combined ether filtrates were washed with 50 ml of a saturated sodium bicarbonate solution and dried over magnesium sulfate, and the ether was removed *in vacuo*. Treatment of the resulting oil with boiling hexane gave 3.0 g (88%) of **1f**: mp 70.5–71.0; nmr $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 1.32 (s, (3 H), 1.5–2.7 (broad absorption, 8 H), 3.77 (s, 3 H), 5.97 (m, 1 H), and 7.29 ppm (s, 1 H). The compound showed identical infrared and ultraviolet spectral properties with those previously reported.[15] *Anal.* Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.66; H, 7.41.

4-Carbomethoxy-3-keto-9-methyl-Δ^4-octahydronaphthalene (9).—A 1000-ml, three-necked flask fitted with dropping funnel, variable takeoff head, mechanical stirrer, thermometer, and nitrogen inlet was charged with 11.2 g (0.25 mol) of 53.4% sodium hydride–mineral oil and 500 ml of dry DME. Compound **8** (47.0 g, 0.28 mol) was added rapidly with stirring. The solution was stirred at room temperature overnight and solvent was removed by distillation until the volume was approximately 200 ml. The solution was cooled to room temperature and 1000 ml of ether was added. Carbon dioxide which had been passed through concentrated sulfuric acid and a calcium chloride drying tube was allowed to bubble through the solution for 1.25 hr while the temperature was maintained at 0–3° by use of an ice bath. To the cold reaction mixture was added 500 ml of 10% sodium hydroxide solution and stirring was continued for 15 min. The solution was washed with three 500-ml portions of ether, acidified to pH 2–3 with 3:1 hydrochloric acid, stirred for 30 min, and extracted with three 100-ml portions of ether. The ether layers were combined and poured slowly into a stirred solution of *ca.* 10.5 g of diazomethane (the diazomethane was freshly prepared from Dupont EXR-101, *N*,*N*-dimethyl-*N*,*N*-dinitrosoterephthalamide, 70% in mineral oil, according to instructions issued by the manufacturer) in 500 ml of ether maintained at 0° with an ice bath. The cold mixture was stirred for 30 min and the excess diazomethane was destroyed by the addition of dilute hydrochloric acid. The organic layer was separated and washed with two 500-ml portions of a saturated sodium bicarbonate solution and one 100-ml portion of a saturated sodium chloride solution. The solution was dried over anhydrous sodium sulfate and the solvents were removed *in vacuo* to give 26.2 g (63%) of the crude product as a yellow oil, bp 123–127° (1.5 mm). Crystallization of the product from ether–hexane gave an analytical sample: mp 77.5–78.5°; ir $\lambda_{\max}^{\mathrm{KBr}}$ 5.76 (α,β-unsaturated ester), 5.98 (α,β-unsaturated ketone), 6.19 μ (conjugated C=C); nmr $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 1.28 (s, 3 H), 1.50–2.62 (broad absorption, 12 H), 3.69 (s, 3 H, OCH_3); mass spectrum (70 eV) *m/e* 222 (M^+), EMD 222.1267 (calcd 222.1256). *Anal.* Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 7.16; H, 8.34.

4-Carbomethoxy-3-keto-9-methyl-$\Delta^{1,4}$-hexahydronaphthalene (1g).—A 5000-ml, three-necked flask fitted with a variable takeoff distilling head and nitrogen inlet tube was flame dried and charged with 22.2 g (0.20 mol) of freshly sublimed selenium dioxide, 3000 ml of *tert*-butyl alcohol (freshly distilled over sodium *tert*-butoxide), and 10 ml of glacial acetic acid. The mixture was stirred until the selenium dioxide dissolved and a solution of 11.5 g (0.05 mol) of **9** in 500 ml of *tert*-butyl alcohol was added. The reaction mixture was then stirred at reflux for 72 hr and 3000 ml of solvent was removed by distillation. The remaining suspension was cooled to 0° and filtered using a fitted glass funnel to remove unreacted selenium dioxide. The filtrate was stirred with 200 ml of saturated sodium carbonate solution and solid sodium carbonate was added slowly with stirring until the evolution of carbon dioxide ceased. The mixture was then filtered with suction and the filter cake was washed well with ether. The layer were separated and the aqueous layer was extracted with two 100-ml portions of ether. The combined ethereal extracts were washed with water and dried over sodium sulfate, and the solvent was removed *in vacuo*. The viscous residue was fractionally distilled and *ca.* 9.0 g of material, bp 120–130° (1.5 mm), was collected which exhibited one peak on glc analysis (column A).[34] Crystallization

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(35) F. D. Gunstone and R. M. Heggie, *J. Chem. Soc.*, 1437 (1952).

of the product from methanol using activated carbon for decolorization gave 7.8 g (55%) of **1g**: mp 53.5–54.5; uv $\lambda_{max}^{95\%\ EtOH}$ 241 nm (ϵ 15,400); ir λ_{max}^{KBr} 5.77 (α,β-unsaturated ester), 6.02 (α,β-unsaturated ketone), 6.22 (conjugated C=C), and 6.52 μ (conjugated C=C); nmr δ_{max}^{CCl} 1.29 (s, 3 H), 1.14–2.06 (broad absorption, 7 H), 2.18–2.58 (broad absorption, 1 H, C_5H) 3.75 (s, 3 H, OCH_3), 6.10 and 6.77 ppm (AB quartet, J_{AB} = 10 Hz, 2 H); mass spectrum (70 eV) *m/e* 220 (M^+); EMD 220.1089 (calcd 220.1099). *Anal.* Calcd for $C_{13}H_{16}O_3$: C, 70.88; J, 7.32. Found: C, 70.96; H, 7.44.

The conversion of **9** into **1g** using DDQ was attempted. In a typical experiment 1.59 g (0.007 mol) of **9** and 2.01 g of DDQ were refluxed in 175 ml of dry dioxane for 48 hr. The dioxane was removed *in vacuo*, 500 ml of benzene was added, and the mixture was filtered through 50 g of alumina. After removal of the solvent *in vacuo*, a mixture which appeared on the basis of its spectral properties to be composed of about equal amounts of **1g**, 4-carbomethoxy-4-keto-9-methyl-$\Delta^{4,6}$-hexahydronaphthalene, and 4-carbomethoxy-3-keto-9-methyl-$\Delta^{1,4,6}$-tetrahydronaphthalene was obtained. Attempted separation of **1g** from the other components of the mixture by both fractional distillation and column chromatography was unsuccessful. Similar results were obtained when **9** was treated with DDQ in benzene or toluene under the conditions described above.

4-Carboxy-3-keto-9-methyl-$\Delta^{1,4}$-hexahydronaphthalene (1h).—A 500-ml three-necked flask fitted with a variable takeoff distilling head, nitrogen inlet tube, and magnetic stirrer was charged with 9.0 g (0.041 mol) of **1g**, 200 ml of 10% aqueous sodium carbonate solution, and 200 ml of methanol. The suspension was maintained for 3 days at 50° using an oil bath, 250 ml of solvent was removed by distillation at atmospheric pressure, 200 ml of water was added, and the solvent was again removed by distillation until the remaining volume was *ca.* 200 ml. The solution was cooled and extracted with three 200-ml portions of ether, and the ethereal extracts were combined and concentrated *in vacuo* to yield 2.60 g (29%) of an oil, which exhibited the same glc (Column A)[34] and spectral properties as those of the starting material. The aqueous layer was acidified to pH 2–3 with 3:1 hydrochloric acid and extracted with three 100-ml portions of ether. The ether extracts were combined and dried over sodium sulfate, and the solvent was removed *in vacuo*. Recrystallization of the residue from ether–hexane gave 6.46 g (79%) of **1h**: melting point undetermined (decomposition began at 90°); uv $\lambda_{max}^{95\%\ EtOH}$ 240 nm (ϵ 13,900); ir $\lambda_{max}^{CHCl_3}$ 5.78 (α,β-unsaturated acid), 6.04 (α,β-unsaturated ketone), and 6.25 μ (conjugated C=C); nmr $\delta_{TMS}^{CDCl_3}$ 1.34 (s, 3 H, 9-CH_3) 1.47–2.70 (broad absorption, 7 H, 6-, 7-, 8-CH_2 and 5-CH), 3.21–3.64 (m, 1 H, C-5 eq H), 6.33 and 7.00 (AB quartet, J_{AB} = 10 Hz, 2 H, 1-, 2-CH), and 10.02 ppm (s, 1 H, 4-CO_2H); mass spectrum (70 eV) *m/e* 162 ($M^+ - CO_2$). *Anal.* Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 70.08; H, 7.01.

Compound **1h** exhibited two peaks of approximately equal size on glc analysis (column C).[34] These peaks were collected separately by preparative glc (column C).[34] The first peak showed identical properties with those of **1h** and the second peak showed identical spectral properties with those of a sample of 3-keto-9-methyl-$\Delta^{1,4}$-hexahydronaphthalene prepared as described below. Thus, partial decarboxylation of **1h** occurred on glc analysis.

3-Keto-9-methyl-$\Delta^{1,4}$-hexahydronaphthalene (1j).—The octalone **8**, 8.2 g (0.05 mol), was dissolved in 140 ml of dry dioxane, 13.6 g (0.06 mol) of DDQ was added, and the reaction mixture was refluxed under nitrogen for 12 hr. After being cooled to room temperature the reaction mixture was filtered through 65.0 g of alumina, the alumina was washed with two 40-ml portions of dioxane, and the solvent was removed *in vacuo* to give 5.42 g of a colorless oil. Glc analysis (column E)[34] of the oil indicated that it was composed of a *ca.* 4:1 mixture of the desired dienone and the starting material. The pure product was obtained by chromatography of the mixture on activity II alumina (100 g). Elution of the column with 1 l. of hexane and 2 l. of 5% ether–hexane removed the starting material and elution with 1 l. of 15% ether–hexane gave **1i**: bp 110–114° (1.8 mm) [lit.[18] bp 123–124° (3 mm)]; ultraviolet and infrared spectra identical with those reported;[18] nmr $\delta_{TMS}^{CCl_4}$ 1.20 (s, 3 H), 1.20–2.30 (broad absorption, 8 H), 5.98 (broad absorption, 1 H), 6.06 and 6.70 ppm (AB quartet, J_{AB} = 10 Hz, 2 H).

4-Formyl-3-keto-9-methyl-$\Delta^{1,4}$-hexahydronaphthalene (1i).—To a stirred suspension of 3.85 g (0.16 mol) of sodium hydride in 100 ml of dry benzene under nitrogen was added dropwise 3.46 g (0.11 mol) of anhydrous methanol. The suspension was refluxed for 15 min and cooled to room temperature, and 11.8 g (0.16 mol) of ethyl formate (freshly distilled from P_2O_5) was added in a thin stream. After stirring for 30 min, the reaction mixture was cooled to 0° in an ice bath, and 10.5 g (0.064 mol) of **10**[20] in 150 ml of dry benzene was added dropwise with stirring at 0°. When the addition was complete, the cooling bath was removed and stirring was continued overnight. The reaction mixture was acidified with 100 ml of ice-cold 5% sulfuric acid and allowed to stir for 5 min. The layers were separated, and the aqueous layer was extracted with 1:1 ether–benzene. The combined organic layers were washed with four 50-ml portions of 2% potassium hydroxide, and the basic extract was washed once with ether and then acidified with dilute hydrochloric acid. The aqueous layer was then extracted thoroughly with several portions of 1:1 ether–benzene. The organic extracts were washed with saturated brine and dried over anhydrous sodium sulfate. After removal of the drying agent the volatile solvents were removed *in vacuo* to leave a viscous yellow oil. The crude product, which was not further purified, exhibited the following spectral properties: uv $\lambda_{max}^{95\%\ EtOH}$ 244 nm (ϵ 4900) and 305 (3900); $\lambda_{max}^{EtOH+NaOH}$ 237 (8750) and 324 (4950); ir $\lambda_{max}^{CHCl_3}$ 6.08 (α,β-unsaturated ketone) and 6.39 μ (conjugated C=C); nmr $\delta_{TMS}^{CCl_4}$ 0.86 (s, 3 H), 1.0–2.5 (broad absorption, 8 H), 5.75 and 6.58 (AB quartet, J_{AB} = 10 Hz, 2 H) 7.09 (d, *J* = 10 Hz, 0.9 H, =CH), 8.5 (d, 0.1 H, =CHO), and 13.9 ppm (d, *J* = 10 Hz, 0.9 H, =COH).

To a solution of 3.54 g (0.018 mol) of the 4-hydroxymethylene derivative of **8** in 100 ml of anhydrous dioxane was added 4.52 g (0.02 mol) of DDQ in 100 ml of anhydrous dioxane. The solution was swirled for 4 min and poured into 300 ml of methylene chloride, and the mixture was filtered under pressure through a column of silica gel. The column was eluted with an additional 300 ml of methylene chloride. The combined eluent was stirred with 5 g of decolorizing carbon for 10 min and the mixture was filtered through Celite. The solvents were removed *in vacuo*, 100 ml of ether was added to the residue, and the ether solution was washed with three 30-ml portions of saturated sodium bicarbonate solution and one 30-ml portion of saturated sodium chloride solution. The ether solution was dried over anhydrous sodium sulfate and the solvent was removed *in vacuo* to give 2.24 g (64%) of **1i**, bp 110–115° (0.1 mm), which could not be induced to crystallize. The sample showed $\lambda_{max}^{95\%\ EtOH}$ 242 nm (ϵ 12,000); ir $\lambda_{max}^{CHCl_3}$ 3.60 (aldehyde), 6.00 (unsaturated carbonyl group), and 6.15 μ (conjugated C=C); nmr $\delta_{TMS}^{CCl_4}$ 1.39 (s, 3 H, 9-CH_3), 1.00–2.40 (broad absorption, 7 H), 3.80 [d (broadened), *J* = 14 Hz, 1 H, C-5 eq H], and 6.17 and 6.81 ppm (AB quartet, J_{AB} = 10 Hz, 2 H, C-1, 2 H); exact mass calcd for $C_{12}H_{14}O_2$, 190.0990; found, 190.0954.

8-Methyl-4,5,6,7,8a-hexahydro-8-hydroxy-2(1*H*)-azulenone (13a).—A solution of 2.8 g of a 4:1 mixture of **1j** and the corresponding enone **8** was dissolved in 220 ml of 45% aqueous acetic acid and irradiated for 5 hr at 22° using a Pyrex probe.[23] The solution was stirred vigorously with a stream of nitrogen during the irradiation. The reaction mixture was diluted with 100 ml of toluene, evaporated to dryness *in vacuo*, and chromatographed on 100 g of silica gel. After the column had been eluted with 2000 ml of benzene and 4000 ml of 1:1 ether–benzene, elution with 1 l. of ether and 1 l. of ethanol gave colorless crystals which on three recrystallizations from 1:5 ether–hexane afforded 0.2214 g (7%) of **13a**: mp 108.5–109.5°; uv λ_{max}^{EtOH} 237 nm (ϵ 13,000); ir $\lambda_{max}^{CHCl_3}$ 2.88 (OH), 5.97 (cyclopentenone), and 6.25 μ (conjugated C=C); nmr $\delta_{TMS}^{CDCl_3}$ 0.92 (s, 3 H, C-8 CH_3), 1.5–3.2 (broad absorption, 12 H), and 5.62 ppm (m, 1 H, C-4 H). *Anal.* Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.45; H, 9.09.

The above alcohol, 0.78 g, was dissolved in 100 ml of absolute ethanol and 0.150 g of 10% palladium on charcoal was added. The mixture was shaken in the presence of hydrogen for 2 hr at room temperature, the catalyst was removed by filtration, and the solvent was removed *in vacuo* to give a quantitative recovery of the dihydro derivative of **13a** as a colorless oil: bp 163–166° (bath temperature, 1.5 mm); ir $\lambda_{max}^{CHCl_3}$ 2.88 (OH) and 5.73 (cyclopentanone); nmr $\delta_{max}^{CDCl_3}$ 1.18 (s, 3 H, C-8 CH_3), 1.40–3.06 (broad absorption, 14 H), and 3.30 ppm (broad singlet, 1 H, C-8 OH). *Anal.* Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.29; H, 10.11.

Dehydration of 13a.—A solution of 0.10 g of **13a** in 3 ml of pyridine was treated with 0.25 g of thionyl chloride at 0° for 10 min. Water was added slowly while the temperature was maintained below 5°, the reaction mixture was extracted with ether, and the ether solution was washed several times with water and dried over anhydrous sodium sulfate. After removal of the solvent, the crude product exhibited an nmr spectrum (CCl_4) essentially identical with that of **14** identified below. On treatment of the nmr sample of this product with 2 drops of trifluoroacetic acid and allowing the solution to stand for 24 hr at room temperature, **14** was completely isomerized in **12** identified as described below.

Irradiation of 2-Formyl-3-keto-9-methyl-$\Delta^{1,4}$-hexahydronaphthalene (1d). A. In 45% Aqueous Acetic Acid.—A solution of 1.01 g of the 2-formyl dienone **1d** in 220 ml of 45% aqueous acetic acid was irradiated for 3.5 hr at room temperature using a Pyrex probe.[23] Removal of the solvent by lyophilization gave a crude amber oil which was soluble in dilute sodium hydroxide and gave positive ferric chloride and Tollens' tests indicative of the presence of an enolizable β-keto aldehyde grouping. The spectral properties of the material suggested that it was likely to be composed of a mixture of the hemiactal enone **11b** and the related hydroxymethylene compound **11a**. The uv spectrum (95% EtOH) showed a strong absorption maximum at 235 nm, and a much weaker band at 300 nm. The latter band inhibited a bathochromic shift in basic solution ($\lambda_{max}^{NaOH+95\%\ EtOH}$ 340 nm). The ir spectrum ($CHCl_3$) showed bands at 2.88 (hydroxy group), 5.90 (cyclopentenone), 6.23 (broad absorption, conjugated C═C) and 6.40 μ (conjugated C═C). The nmr spectrum (CCl_4) exhibited broad singlets at *ca.* 0.9 and 6.02 ppm which could be assigned to the C-8 methyl groups and the C-3 vinyl proton of **11b** and/or **11a**. Other absorption bands ranging from 4.5 to 8.0 ppm which could not be specifically assigned but were consistent with the presence of the hemiacetal and hydroxymethylene alcohol groupings of **11b** and **11a** were also present.

Attempted purification of the crude photoproduct by chromatography on silica gel or alumina resulted in degradation and the only material that could be eluted exhibited strong uv absorption at 300 nm; the species which gives rise to this absorption is identified below. Numerous attempts to convert the photoproduct into a solid derivative which might provide further evidence for the structural assignments were unsuccessful.

In an identical run with that described above the crude photoproduct was dissolved in 70 ml of dioxane and a solution of 2.2 g of sodium carbonate in 100 ml of water was added. The mixture was heated on a steam bath for 18 hr, cooled, and extracted with five 100-ml portions of ether. After drying of the ether solution over magnesium sulfate, removal of the solvent *in vacuo* yielded 8-methyl-4,5,6,7-hexahydro-2(1*H*)-azulenone (**12**): bp 123–127° (bath temperature, 0.9 mm); uv $\lambda_{max}^{95\%\ EtOH}$ 300 nm (ϵ 10,900); ir $\lambda_{max}^{CCl_3}$ 5.99 (α,β-unsaturated ketone) and 6.40 μ (conjugated C═C); nmr $\delta_{TMS}^{CCl_4}$ 1.85 (s, 3 H, C-8 CH_3), 2.83 (s, 2 H, C-1 CH_2), 2.02–2.90 (broad absorption, 8 H), and 5.86 ppm (m, 1 H, C-3 H). *Anal.* Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.62; H, 8.87.

The 2,4-dinitrophenylhydrazone derivative of **12** was prepared in the usual way, mp 174.0–175.3°. *Anal.* Calcd for $C_{17}H_{18}N_4O_4$: C, 59.64; H, 5.30; N, 16.37. Found: C, 59.41; H, 5.28; N, 16.24.

A solution of 1.26 g of **12** in 200 ml of 95% ethanol containing 0.1 g of 10% palladium on charcoal was shaken with hydrogen in a Parr apparatus for 2.5 hr at room temperature and the catalyst was removed by filtration. Evaporation of the solvent *in vacuo* gave the tetrahydro derivative of **12**: bp 95–102° (bath temperature, 0.7 mm); ir $\lambda_{max}^{CCl_4}$ 5.74 μ (cyclopentanone); nmr $\delta_{TMS}^{CCl_4}$ 0.92 (d, 3 H, J = 7 Hz, C-8 CH_3), 1.25–2.65 (broad absorption, 15 H). *Anal.* Calcd for $C_{11}H_{18}O$: C, 79.47; H, 10.91. Found: C, 80.05; H, 10.99.

A mixture of 0.76 g of the saturated ketone and 30 ml of deuterium oxide containing 0.2 g of potassium carbonate was heated on a steam bath for 18 hr. After being cooled to room temperature the mixture was extracted with three 50-ml portions of ether, the ether solution was dried over magnesium sulfate, and the solvent was removed *in vacuo*. The resulting oil was shown to contain greater than 95% of one component by glc analysis (column D).[3] A sample collected by preparative glc (column D)[34] showed (direct deuterium analysis by the falling drop method)[36] atom % D calcd, 22.22; found, 18.75 (*ca.* 84% deuterium substitution based on an incorporation of four deuterium atoms). *Anal.* Calcd for $C_{11}H_{14}D_4O$: C, 77.58; weight $H_2O + D_2O$ (from 3.205-mg sample), 3.127 mg. Found: C, 78.08; weight $H_2O + D_2O$, 3.058 mg.

The mass spectrum of the sample showed peaks at *m/e* 166, 167, 168, 169, 170, and 171 in the region of the molecular ion. The intensity of these peaks indicated the presence of approximately 2% $C_{11}H_{18}O$, 6% $C_{11}H_{18}DO$, 21% $C_{11}H_{16}D_2O$, 40% $C_{11}H_{15}D_3O$, and 31% $C_{11}H_{14}D_4O$.

B. In Anhydrous Dioxane.—A solution of 1.76 g of **1d** in 230 ml of dioxane was irradiated for 2 hr at room temperature using a quartz probe.[23] The solvent was removed *in vacuo* and the residue was subjected to thin layer chromatography. Four new compounds as well as the starting material were observed. In addition a large amount of material remained at the origin of the spot, indicating that a significant amount of polymerization had occurred. Further investigation of the products of this reaction was not carried out.

Irradiation of 2-Carboxy-3-keto-9-methyl-$\Delta^{1,4}$-hexahydronaphthalene (1e). A. In 45% Aqueous Dioxane.—A solution of 0.80 g of **1e** in 220 ml of 45% aqueous dioxane was irradiated for 2 hr at room temperature using a Pyrex probe.[23] The solvents were removed *in vacuo* and the residue was chromatographed on 30 g of alumina (Merch, acid washed). Elution with 200 ml each of benzene, 20:1 benzene–ether, and 1:1 benzene–ether gave a semi solid residue shown to be composed of at least two components by thin layer chromatography. Rechromatography of this material on 30 g of alumina gave, on elution with 500 ml of benzene followed by 150 ml of 20:1 benzene–ether, 0.1 g (12%) of 1β-carboxy-8-methyl-4,5,6,7,8aα-hexahydro-8α-hydroxy-2-(1*H*)-azulenone lactone (**15**), mp 114.0–114.5. Further elution with 500 ml of 2:1 benzene–ether yielded 0.1 g of the hydroxy ketone **13a**. Further elution of the original column with 300 ml of 1:1 benzene–ether and 400 ml of 1:2 benzene–ether afforded 0.32 g of **13a**, bringing the total yield of this compound to 0.42 g (60%). The lactone **15** showed uv $\lambda_{max}^{95\%\ EtOH}$ 246 nm (ϵ 9950) and 271 (7380); ir $\lambda_{max}^{CHCl_3}$ 5.61 (γ-lactone), 5.87 (cyclopentenone), and 6.26 μ (conjugated C═C); nmr $\delta_{TMS}^{CDCl_3}$ 1.05 (s, 3 H, C-8 CH_3), 1.3–2.0 (broad absorption, 8 H), 3.50 and 4.07 (AB quartet, J_{AB} = 7.4 Hz, C-1 and C-8a H), and 5.81 ppm (s, 1 H, C-3 H). *Anal.* Calcd for $C_{12}H_{14}O_3$: C, 69.89; H, 6.84. Found: C, 70.22; H, 6.73.

A solution of 0.037 g of **15**, 16 ml of water, 0.3 g of sodium carbonate, and 16 ml of dioxane was heated for 18 hr on a steam bath. The solution was cooled to room temperature, made acidic with 1:1 hydrochloric acid, and extracted with four 25-ml portions of ether. The ether solution was dried over magnesium sulfate, the solvent was removed *in vacuo*, and the residue was chromatographed on alumina. Elution with 5:1 benzene–ether gave a mixture which appeared to be composed of **13a** and **12** on the basis of its spectral properties. Further elution with 1:1 benzene–ether afforded 0.018 g of material which was identified as **13a** by its spectral properties and mixture melting point (107–109°) with an authentic sample.

B. In Anhydrous Dioxane.—Oxygen-free nitrogen was passed through a solution of 0.71 g of **1e** in a photolysis apparatus[23] and the exhaust gases were passed through a water-cooled condenser, a Dry Ice–acetone trap, and a drying tube filled with Ascarite. After 1 hr at room temprature the Ascarite tube was weighed and the reaction mixture was irradiated for 2 hr using a Pyrex probe. At the end of the irradiation the Ascarite tube weighed an additional 0.134 g, which corresponded to 87% of carbon dioxide which could have been lost from **1e** or its photolysis products. The irradiated solution was divided into two equal parts and treated as follows.

One part was evaporated *in vacuo* and distilled in a micro Hickman apparatus to yield 0.19 g (67%) of an oil, bp 95–100° (bath temperature, 0.25 mm), which solidified on standing overnight. Recrystallization from hexane afforded 8-methylene-4,5,6,7,8aα-hexahydro-2(1*H*)-azulenone (**14**): mp 61.0–61.5°; uv $\lambda_{max}^{95\%\ EtOH}$ 230 mm (ϵ 12,400); ir $\lambda_{max}^{CHCl_3}$ 5.83 and 5.90 (cyclopentenone),[10a] 6.06 (C═C), 6.19 (conjugated C═C), and 11.07 μ (═CH_2); nmr $\delta_{max}^{CDCl_3}$ 1.18–3.06 (broad absorption, 10 H), 3.56–3.82 (broad absorption, 1 H), 4.97 (s, 2 H, ═CH_2), and 5.96 ppm (m, 1 H, vinyl proton). *Anal.* Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.23; H, 8.87.

The solvent was removed from the other portion of the photolysis mixture *in vacuo* and the residue was chromatographed on 30 g of silica gel. Elution with 600 ml of 20:4 benzene–ether yielded dienone **14**, and elution with 450 ml of 2:1 benzene–ether afforded 0.057 g (16%) of crystalline material identical in all respects with the lactone **15** described above.

C. In 45% Aqueous Acetic Acid.—A solution of 1.16 g of **1e** in 310 ml of 45% aqueous acetic acid was irradiated for 2 hr using a Pyrex probe.[23] The solvent was removed *in vacuo* and the residue was chromatographed on 30 g of silica gel. Elution with 300 ml of benzene, 500 ml of 7:1 benzene–ether, and 600 ml of 3:1

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(36) The analysis was performed by Mr. Josef Nemeth, Urbana, Ill.

benzene–ether gave mixtures which by glc (column F)[34] and spectral analysis appeared to be composed of varying amounts of **14**, **12**, and **15**. Continued elution with 600 ml of 3:2 benzene–ether followed by 200 ml of methanol afforded, after recrystallization from ether, 0.66 g (65%) of **13a**.

The above mixture was rechromatographed on 20 g of alumina. Elution with 1200 ml of 1:1 benzene–ether gave 0.11 g of a colorless oil which by glc analysis (column D)[3] was composed of dienones **12** and **14** in a 53:47 ratio. The yield of **12** and **14** were thus *ca.* 7 and 5%, respectively. Further elution with 200 ml of methanol yielded 0.072 g (6%) of lactone **15**.

D. **In Anhydrous Methanol.**—A solution of 0.97 g of **1e** in 310 ml of dry methanol was irradiated for 2.5 hr using a Pyrex probe.[23] The solvent was removed *in vacuo* to afford an oily residue which was chromatographed on 45 g of alumina. Elution with 200 ml of benzene, followed by 500 ml of 100:8 benzene–ether, gave 0.10 g (14%) of **14**, and further elution with 600 ml of 100:8 benzene–ether, 600 ml of 7:3 benzene–ether, and 800 ml of 1:1 benzene–ether gave 0.45 g (50%) of 8β-methyl-8α-methoxy-4,5,6,7,8aα-hexahydro-2(1*H*)-azulenone (**13b**): mp 55.5–56.0°; uv $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 238 nm (ε 12,600); ir $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.90 (cyclopentenone) and 6.23 μ (conjugated C=C); nmr $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 0.91 (s, 3 H), 1.5–2.9 (broad absorption, 11 H), 3.22 (s, 3 H), and 5.90 ppm (m, 1 H). *Anal.* Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.42; H, 9.40.

Continued elution of the column with 500 ml of ether and 500 ml of methanol afforded 0.11 g (13%) of the lactone **15**.

Irradiation of 2-Carbomethoxy-3-keto-9-methyl-$\Delta^{1,4}$-hexahydronaphthalene (1f) in 45% Aqueous Acetic Acid.—A solution of 1.10 g of **1f** in 300 ml of 45% aqueous acetic acid was irradiated for 2 hr at room temperature using a Pyrex probe.[23] The solvent was removed by lyophilization to give 1.14 g of a semisolid residue which was chromatographed on 35 g of alumina (Merck, acid washed). Elution with 400 ml of 1:1 benzene–ether, 200 ml of ether, and 200 ml of methanol afforded 0.81 g (67%) of 1α-carbomethoxy-8β-methyl-8α-hydroxy-4,5,6,7,8aα-hexahydro-2-azulenone (**16**): mp 165.0–166.0°; uv $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 240 nm (ε 11,100); ir $\lambda_{\max}^{\mathrm{CHCl_3}}$ 2.88 (OH), 5.77 (ester C=O), 5.87 (cyclopentenone), and 6.24 μ (conjugated C=C); nmr $\delta_{\mathrm{TMS}}^{\mathrm{DMSO}\text{-}d_6}$ 0.82 (s, 3 H), 0.95–2.80 (broad absorption, 10 H), 3.19 (s, 1 H), 3.36 (s, 3 H), and 5.41 ppm (m, 1 H). *Anal.* Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.35; H, 7.59.

A solution of 0.15 g of **16** in 70 ml of 95% ethanol containing 0.1 g of 10% palladium on charcoal was shaken with hydrogen for 1.5 hr in a Parr apparatus, the catalyst was removed by filtration, and the solvent was removed *in vacuo*. The residue was dissolved in 30 ml of 1:1 water–dioxane containing 0.1 g of sodium carbonate and warmed on a steam bath for 5 hr. The solvents were removed *in vacuo*, 50 ml of water was added, and the mixture was extracted with two 50-ml portions of ether. The ether layer was dried over sodium sulfate and the solvent was removed *in vacuo* to give 0.11 g of material, bp 160–165° (bath temperature, 1.5 mm), which exhibited identical spectral properties with those of the dihydro derivative of **13a** prepared as described above.

Irradiation of 4-Carboxy-3-keto-9-methyl-$\Delta^{1,4}$-hexahydronaphthalene (1h). A. **In Anhydrous Dioxane.**—A solution of 0.96 g of **1h** in 250 ml of anhydrous dioxane was irradiated for 25 min at room temperature using a quartz probe.[23] The solvent was removed *in vacuo*, 20 ml of ether was added to the residue, and 0.12 g of flocculent material which was insoluble in ether was removed by filtration. The ethereal filtrate was extracted with three 20-ml portions of saturated sodium bicarbonate solution and one 20-ml portion of saturated sodium chloride solution. The basic extracts were combined, acidified with 1:1 hydrochloric acid, and treated in the usual way to give 0.25 g of material whose spectral properties were identical with those of the starting dienone acid. The ether solution was concentrated *in vacuo* to yield 0.48 g (62%) of 6-methylspiro[4.5]deca-3,6-dien-2-one (**20**): bp 109–111° (bath temperature, 0.25 mm); ir $\lambda_{\max}^{\mathrm{film}}$ 5.84 (cyclopentenone), 6.02 (C=C), and 6.08 μ (C=C); uv $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 218 nm (ε 9200); nmr $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 1.54 (d, 3 H, C-6 CH_3), 1.60–2.15 (m, 6 H), 2.00 and 2.38 (AB quartet, J_{AB} = 18.5 Hz, 2 H, C-1 CH_2), 5.57 (m, 1 H C-7 H), 6.06 and 7.31 ppm (AB quartet, J_{AB} = 5.5 Hz, 2 H, C-3, 4 H). *Anal.* Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.28; H, 8.90.

B. **In 45% Aqueous Acetic Acid.**—A solution of 1.02 g of **1h** in 250 ml of 45% aqueous acetic acid was irradiated for 30 min at room temperature using a quartz probe.[23] The solvent was removed by lyophilization to yield a semisolid residue. Ether (100 ml) was added and 0.28 g of flocculent material which was insoluble in ether was removed by filtration. The ether solution was washed with three 100-ml portions of saturated sodium bicarbonate solution and one 100-ml portion of saturated sodium chloride solution. The basic extracts were combined, acidified with 1:1 hydrochloric acid, and treated in the usual way to give 0.18 g of material whose spectral properties indicated that it was composed mainly of the starting dienone acid. The ether solution was dried over sodium sulfate and the solvent was removed *in vacuo* to yield a yellow oil which was crystallized from carbon tetrachloride to give 0.41 g (41%) of 1β-carboxy-6β-hydroxy-6α-methylspiro[4.5]deca-3-en-2-one lactone (**19**): mp 125.5–126.0°; uv $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 223 nm (ε 8400); ir $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.65 (γ-lactone), 5.84 (cyclopentenone), and 6.06 μ (C=C); nmr $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 1.15 (s, 3 H, C-6 CH_3), 1.52–2.70 (m, 8 H), 3.38 (broad s, 1 H, C-1 H), 6.17 (d, J_{AB} = 5.5 Hz, 1 H, C-3 H), and 7.58 ppm (broad d, J_{AB} = 5.5 Hz, 1 H, C-4 H). *Anal.* Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found C, 69.94; H, 7.00.

Irradiation of 4-Formyl-3-keto-9-methyl-$\Delta^{1,4}$-hexahydronaphthalene (1i) in 45% Aqueous Acetic Acid.—A solution of 2.24 g of **1i** in 250 ml of 45% aqueous acetic acid was irradiated for 1.5 hr at room temperature using a Pyrex probe.[23] An equal volume of benzene was added and the solvent was removed *in vacuo*. The nmr spectrum (CCl_4) of the crude photoproduct showed absorptions characteristic of the starting material, but in addition absorptions at δ 1.36 (s), 5.32 (m), 6.07 (d, J_{AB} = 10 Hz), 6.74 (d, J_{AB} = 10 Hz), 8.20 (s), and 13.6 ppm (broad absorption) indicated that 10–20% of the enolic compounds **17** and/or **18** were also present. The formation of enolic compounds was not observed when a solution of **1i** in 45% aqueous acetic acid was allowed to stand in the dark and the solvent was removed as before.

Irradiation of 4-Carbomethoxy-3-keto-9-methyl-$\Delta^{1,4}$-hexahydronaphthalene (1g) in 45% Aqueous Acetic Acid.—A solution of 0.88 g of **1g** in 300 ml of 45% aqueous acetic acid was irradiated for 2 hr at room temperature using a Pyrex probe.[23] The solvent was removed by lyophilization. The nmr spectrum of the residue indicated that a significant quantity of the starting material had been consumed and a large number of broad absorption bands were present. The crude photolysis mixture was subjected to chromatography on silica gel. Elution of the column with hexane–ether mixtures yielded a fraction containing 0.29 g of starting material. However, none of the other chromatography fractions yielded material having discrete nmr and ir spectral properties. Spectral evidence indicated that most of the material was polymeric in nature. Further investigation of this reaction mixture was not carried out.

Registry No.—**1d**, 5240-81-3; **1e**, 13258-46-3; **1f**, 37709-23-2; **1g**, 37709-24-3; **1h**, 37709-25-4; **1i**, 37709-26-5; **1j**, 703-02-6; **8**, 826-56-2; **9**, 37709-28-7; **10**, 22844-34-4; **12**, 6505-79-9; **12** (DNP), 5240-83-5; **12** (tetrahydro derivative), 5240-84-6; **12** (tetradeuterio derivative), 30917-38-5; **13a**, 6531-23-3; **13a** (dihydro derivative), 37709-40-3; **13b**, 13258-49-6; **14**, 13258-48-5; **15**, 13258-47-4; **16**, 37709-37-8; **19**, 37709-38-9; **20**, 37709-39-0; ethyl formate, 109-94-4; 2-hydroxymethylene-3-keto-9-methyl-Δ^4-octahydronaphthalene, 5240-82-4; 2-methyl-2-formylcyclohexanone, 37709-42-5; ethyl acetoacetate, 141-97-9; 4-hydroxymethylene-3-keto-9-methyl-Δ^1-octahydronaphthalene (trans), 37709-43-6; 4-carboxaldehyde-3-keto-9-methyl-Δ^1-octahydronaphthalene (trans), 37709-44-7.