TABLE III

LEAST-SQUARES PLANES[a]

	Atoms defining the plane	*A*	*B*	*C*	*D*
Plane I	C(7), C(8), C(9), C(10), C(11), C(12)	7.1773	2.4574	7.2735	3.4945
Plane II	Br, C(7), C(8), C(9), C(10), C(11), C(12), C(1)	7.2141	2.4532	7.1623	3.4674
Plane III	C(1), C(2), C(3), C(6)	6.7074	4.2102	−2.5713	1.6003

	Deviations from the plane (in Å)		
Atoms	Plane I	Plane II	Plane III
Br		0.002	
C(1)		0.016	−0.003
C(2)			0.003
C(3)			0.001
C(6)			−0.003
C(7)	−0.004	−0.016	
C(8)	0.005	−0.002	
C(9)	−0.006	−0.005	
C(10)	0.005	0.011	
C(11)	−0.003	−0.002	
C(12)	0.003	−0.005	

[a] The equations, in the form $Ax + By + Cz = D$, where x, y, and z are fractional coordinates, were calculated [V. Schomaker, J. Waser, R. E. Marsh, and G. Bergman, *Acta Crystallogr.*, **12**, 600 (1959)] with all weights equal to 1.

TABLE IV

SHORTEST INTERMOLECULAR DISTANCES[a]

$\mathrm{Br\cdots Br^{v}}$	3.52
$\mathrm{Br\cdots C(3^{iii})}$	3.90
$\mathrm{Br\cdots C(2^{iv})}$	3.79
$\mathrm{C(7)\cdots C(6^{ii})}$	3.66
$\mathrm{C(11)\cdots C(8^{i})}$	3.75
$\mathrm{C(11)\cdots C(8^{iv})}$	3.73
$\mathrm{C(11)\cdots C(9^{i})}$	3.70
$\mathrm{C(11)\cdots C(9^{iv})}$	3.60
$\mathrm{C(11)\cdots C(10^{iv})}$	3.59
$\mathrm{C(11)\cdots C(11^{iv})}$	3.78
$\mathrm{C(12)\cdots Br^{iv}}$	3.98
$\mathrm{C(12)\cdots C(8^{i})}$	3.76
$\mathrm{C(12)\cdots C(10^{iv})}$	3.68
$\mathrm{O\cdots C(4^{iii})}$	3.74
$\mathrm{O\cdots C(5^{iii})}$	3.78
$\mathrm{O\cdots C(6^{iii})}$	3.54

[a] C···C and C···O contacts are below 3.80 Å; C···Br and Br···Br contacts are below 4.00 Å.

favorable steric interaction between the hydrogen atom linked to C(8) atom at one hand and the two hydrogen atoms linked to C(6) at the other hand; the distances between H(8) and H(6a) (pseudoequatorial) and between H(8) and H(6b) (pseudoaxial) are 2.6 and 2.2 Å, respectively.

Crystal Packing.—The packing of the molecules in the crystal is described by Figure 2. In Table IV we report the short intermolecular distances. In this table the atoms of the different asymmetric units are related to the atoms of the fundamental unit as follows: i, atom at x, $1 + y$, and z; ii, atom at $1 - x$, $^1/_2 + y$, and $^1/_2 - z$; iii, atom at x, $^1/_2 - y$, and $^1/_2 + z$; iv, atom at $-x$, $^1/_2 + y$, and $^1/_2 - z$; v, atom at $-x$, $-y$, and $1 - z$.

As the values reported in Table IV clearly show, the intermolecular interactions are exclusively of the van der Waals type.

All the calculations were performed on the IBM 7090 computer of Centro Nazionale Universitario di Calcolo Elettronico (CNUCE), Pisa.

Registry No.—1-(*p*-Bromophenyl)-1,2-epoxycyclohexane, 1605-15-8.

Photochemical Rearrangements of Bicyclic 6/5-Fused Cross-Conjugated Cyclohexadienones and Related Compounds[1a]

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School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332

Received August 5, 1971

The ring A unsubstituted bicyclic 6/5-fused cross-conjugated cyclohexadienone **7a** and its 4-methyl (**7b**) and 6-methyl (**7c**) derivatives have been prepared and irradiated at 2537 Å in dry dioxane. The major product in each case was the corresponding bicyclo[3.1.0]hex-3-en-2-one (**8**); **7a** and **7b** also gave small amounts of linearly conjugated dienones (**9**). The bicyclo[3.1.0]hex-3-en-2-one **8b**, which has similar substitution to lumisantonin **12**, was irradiated with light of wavelength greater than 3000 Å in both dioxane and ethanol. In the former solvent it gave mainly the homoannular dienone **14**, while in the latter it afforded the 5/6-fused ethoxy ketone **19**. The photochemistry of these compounds is compared with that of related substances and possible mechanistic pathways are discussed.

It is well known that on irradiation at 2537 Å in inert solvents such as dioxane 6/6-fused bicyclic (**1**) and steroidal cross-conjugated cyclohexadienones, for example, **2**, undergo facile rearrangements into the corresponding bicyclo[3.1.0]hex-3-en-2-ones **3** and **4**, respectively, termed lumiproducts.[2] In contrast, Jeger, Schaffner, and coworkers[3] have reported that *B*-nor-1-dehydrotestosterone acetate (**5**), having a five-mem-

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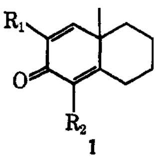
(1) (a) This investigation was supported by Public Health Service Grant No. 15044 from the National Institute of General Medicine and by a NASA Institutional Grant (NsG-657). (b) National Science Foundation Undergraduate Research Participant, summer 1968.

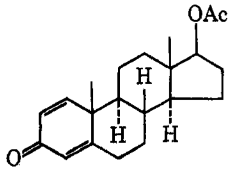
(2) For reviews see (a) P. J. Kropp, *Org. Photo. Chem.*, **1**, 1 (1967); (b) K. Schaffner, *Advan. Photochem.*, **4**, 81 (1966).

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

bered ring fused to the dienone chromophore, is converted directly into the linearly conjugated dienone **6** under similar conditions. In view of these results it appeared of interest to determine the behavior of model bicyclic 6/5-fused dienones such as **7**. Thus we have prepared the ring A unsubstituted indanone **7a**[4] and its 4-methyl (**7b**) and 6-methyl (**7c**) derivatives and have investigated the photochemistry of these compounds in dioxane.[5] In addition, a study of the photochemistry of the bicyclo[3.1.0]hex-3-en-2-one **8b**, the major product of irradiation of **7b**, has been carried out. From mechanistic considerations it appeared that **8b** should exhibit similar photochemical behavior to that of lumisantonin (**12**), which has been studied extensively.[2,6,7] Thus we wished to compare the photochemical behavior of **8b** with that of **12** as well as that of the model lumiproduct **3b** derived from the 6/6-fused dienone **1b**.[2a]



1



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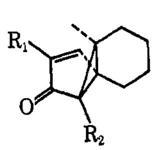

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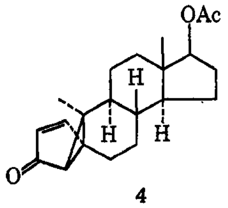

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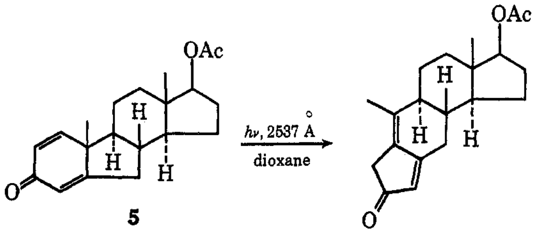
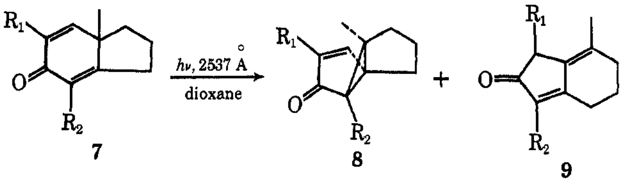


5

6

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



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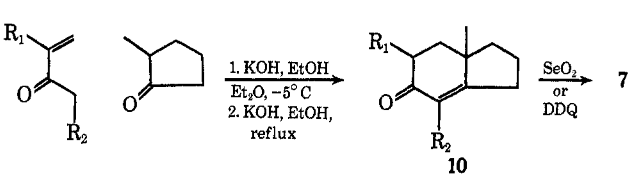
8

9



10

Dienones **7a–c** were obtained from the corresponding enones **10a–c** by dehydrogenation with either 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) or selenium dioxide. Michael addition of 2-methylcyclopentanone to the appropriate vinyl ketone was carried out using potassium hydroxide in ethanol–ether at −5°.[8] These conditions led to the isolation of mixtures of the enones and the corresponding diketone and ketol precursors, and refluxing with potassium hydroxide in ethanol was carried out to complete the aldol cyclization and dehydration reactions. The 4-methyl enone **10b** was readily converted into **7b** on treatment with DDQ in dioxane.[9] However, similar treatment of both **10a** and **10c** gave mixtures of the desired cross-conjugated dienones and the related heteroannular compounds which were difficult to separate. Dienone **7a** was obtained in low yield by treating **10a** with selenium dioxide in *tert*-butyl alcohol according to the procedure of Bloom,[4] and **7c** was obtained from **10c** in a similar manner. The three enones and dienones in this series exhibited the expected physical and spectral properties (see Experimental Section).

Irradiations of dilute solutions of **7a–c** in dry dioxane were conducted at room temperature using a Hanau NK6/20 low pressure mercury lamp which emits *ca.* 90% of its ultraviolet irradiation at 2537 Å. After removal of the solvent under reduced pressure, the photolysis mixtures were subjected to chromatography on silica gel and when necessary the products were further purified by preparative glc.[10] Lumiproducts of the type **8** were the major products of irradiation of each of the dienones, and irradiation periods which led to the optimum yields of these substances were determined by glc analysis[10] of aliquots of the photolysis mixtures taken at various time intervals. In addition to the lumiproducts, linearly conjugated dienones **9a** and **9b** were produced on irradiation of **7a** and **7b**, respectively. No product of the type **9c** could be detected from runs using **7c**. These results are summarized in Table I. The dienones **9a** and **9b** apparently were derived directly from **7a** and **7b** rather than being produced from the lumiproducts in a secondary process. When **8a** and **8b** were isolated and subjected to extended irradiation in dioxane at 2537 Å, products of the type **9** were not formed in significant amounts.

Table I

Products of Irradiation of 6/5-Fused Cross-Conjugated Cyclohexadienones in Dioxane at 2537 Å

Dienone 7	Irradiation time, min	Yield of products, % 8	Yield of products, % 9
a	75	55	21
b	120	50	~5
c	90	67	

The lumiproducts **8a**, **8b**, and **8c** were identified readily on the basis of their uv, ir, and nmr spectral properties, which were quite close to those reported

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(4) S. M. Bloom, *J. Amer. Chem. Soc.*, **81**, 4728 (1959).

(5) A preliminary account of this work has been published: D. Caine, W. J. Powers, III, and A. M. Alejandre, *Tetrahedron Lett.*, 6071 (1968).

(6) M. H. Fisch and J. H. Richards, *J. Amer. Chem. Soc.*, **90**, 1547, 1553 (1968); **85**, 3029 (1963).

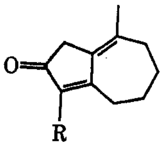
(7) (a) O. L. Chapman and L. F. Englert, *ibid.*, **85**, 3028 (1963); (b) L. Barber, O. L. Chapman, and J. D. Lassila, *ibid.*, **90**, 5933 (1968).

(8) Conditions similar to those described by Ross and Levine [N. C. Ross and R. Levine, *J. Org. Chem.*, **29**, 2341 (1964)] for the synthesis of $\Delta^{1,9}$-octalone and derivatives were employed.

(9) D. Burn, R. Kirk, and V. Petrow, *Proc. Chem. Soc.*, 14 (1960).

(10) A 10 ft × 0.25 in. column containing 15% silicone SE-30 on Chromosorb W was employed.

for the related homologs, **3a**,[11a] **3b**,[11b] and **3c**[11c] The linearly conjugated dienones **9a** and **9b** exhibited absorption maxima at 296 and 302 mμ, respectively, in 95% ethanol which were indicative of the structures. The uv, ir, and nmr spectra of **9a** were quite similar to those of the related 5/7-fused dienone **11** (R = H)[12] and the steroidal dienone **6**[3] having analogous structures, while those of **9b** resembled closely those of **11** (R = CH_3) which can be obtained by dehydration[13] of the 5/7-fused hydroxy ketone produced on irradiation of **1b** in aqueous acetic acid.[14]



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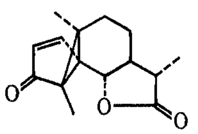
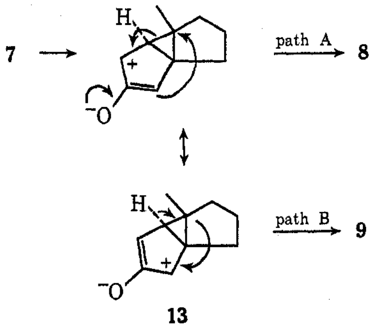


12

The formation of lumiproducts of the type **8** presumably occurs *via* 1,4-sigmatropic rearrangements (path A, Scheme I) in dipolar cyclopropyl intermediates of the type **13**, generally accepted to be involved in dienone photolysis.[2] Jeger, Schaffner, and coworkers[3] have proposed that the formation of **6** from **5** involves the collapse of an intermediate analogous to **13** *via* path B, Scheme I. Since the normal steroidal dienone **2** gave only **4** under similar conditions, they suggested that because of the five-membered B ring an excessive amount of stain would be involved in the formation of a lumiproduct from **5**, and that this accounts for the intervention of the new pathway.[3] In the case of the unsubstituted model dienone **7a**, it appears that the two possible modes of rearrangement compete is indicated by the formation of both **8a** and **9a** in a 5:2 ratio. The exclusive reaction of **5** *via* a path B type process must result from the added strain due to the *trans* fusion of the C ring to the five-membered B ring in the steroidal system.[15]

SCHEME I



The ratio of the tricyclic product to the linearly conjugated one was higher for the 4-methyl substituted dienone **7b** than for the unsubstituted case, and no linearly conjugated dienone product was observed in the irradiation of **7c**. It is possible that products of the type **9** were produced in greater amounts from the methyl-substituted compounds, but that these were rapidly converted into nonvolatile materials. It is also possible that if methyl substituents are present at either position the sigmatropic rearrangement pathway (path A) from **13** to **8** is favored relative to the unsubstituted case. However, the nature of such an effect is not immediately obvious.

While lumiproducts are relatively stable to irradiation at 2537 Å compared with their dienone precursors,[11c] previous work has shown that compounds such as **3**, **4**, and **12** undergo facile rearrangement on irradiation with light of wavelength greater than 3000 Å.[2] Thus a dilute solution of **8b** in dry dioxane was irradiated at room temperature for 90 min using a 450-W Hanovia high-pressure mercury lamp fitted with a Pyrex filter. Analysis of the photolysis mixture by glc[16] revealed the presence of one major product comprising 88% of the volatile components and *ca.* 6% each of the starting material and a minor product. Chromatography of the mixture on silica gel led to the isolation of the major product, which was identified as the homoannular dienone (**14**), in *ca.* 50% yield.

The ir and nmr spectral properties of **14** were consistent with the structure and it exhibited a uv absorption maximum at 335 mμ in 95% ethanol.[17] Catalytic hydrogenation of **14** using 10% palladium on carbon in 95% ethanol led to the isolation of its known tetrahydro derivative having a *cis* ring fusion.[18]

The minor product of irradiation of **8b** proved to be the dienone **7b**. In a separate run, **8b** was irradiated for 30 min and the photolysis mixture was analyzed by glc.[16] The mixture was found to contain **8b**, **14**, and **7b** in an approximately 2:2:1 ratio. Direct irradiation of **7b** under the same conditions as described for **8b** also led to **14**. Monitoring of the reactions by glc[16] revealed that **8b** was formed as an intermediate.

Lumisantonin **12** yields mainly a homoannular dienone **15** when irradiated at wavelengths greater than 3000 Å, and **8b** having the same substitution on the bicyclo[3.1.0]hex-3-en-2-one moiety yields a similar product. Fisch and Richards[6] have proposed that **15** is formed *via* a 1,2-methyl migration in the dipolar intermediate **16** and have presented evidence for the intervention of such a species. However, using infrared spectroscopy Chapman and coworkers[7b] have observed that the ketene **17** is formed on irradiation of **12** at 77°K and that **17** is converted into **15** thermally. These workers have suggested that the ketene pathway is likely to be involved to some degree in the photochemical conversion of **12** into **15** at room temperature.

A ketene intermediate, presumably **18**, believed to be a precursor of **14**, has been observed by infrared spectroscopy when **8b** was irradiated as the neat glass and in hydrocarbon glasses at 77°K.[19] In view of this it appeared possible that **18** might be formed and trapped

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[11] (a) P. J. Kropp and W. F. Erman, *J. Amer. Chem. Soc.*, **85**, 2456 (1963); (b) P. J. Kropp, *ibid.*, **87**, 3914 (1965); (c) P. J. Kropp, *ibid.*, 4055 (1964).

[12] D. Caine and J. F. DeBardeleben, *Tetrahedron Lett.*, 4585 (1965).

[13] D. Caine and J. B. Dawson, unpublished work.

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

[15] We are grateful to Dr. K. Schaffner for a private communication on this point.

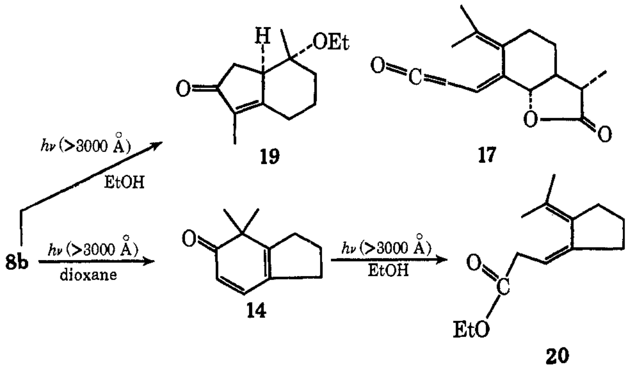
[16] A 10 ft × 0.25 in. column containing Carbowax K-20M on Chromosorb W was employed.

[17] The uv maximum for **14** is close to the predicted value of 338 mμ using the Woodward–Fieser rules. The related homoannular dienones derived from **12** and 6-epilumisantonin show uv absorption maxima at significantly shorter wavelengths.[6] Lack of planarity of the conjugated system and/or electron-withdrawing effects associated with the presence of the lactone rings in the latter compounds may account for this.

[18] J. A. Marshall, N. H. Andersen, and P. C. Johnson, *J. Amer. Chem. Soc.*, **89**, 2748 (1967).

[19] We are indeed grateful to Professor O. L. Chapman for carrying out this experiment and interpreting the results.

at room temperature if **8b** were irradiated in a nucleophilic solvent such as ethanol. However, when **8b** was irradiated under the conditions described above except substituting absolute ethanol for dioxane, the only photoproduct that could be isolated proved to be the ethoxy ketone **19** which was identified on the basis of its spectral properties. The ethanol adduct of the proposed ketene **18**, *i.e.*, **20**, could not be detected in this run. For reference purposes a sample of **20** was prepared by irradiation of **14** in absolute ethanol using the light source described above. The diene ester exhibited the expected nmr spectral properties which in the appropriate regions were very similar to those reported for photosantonic acid.[20] Also, compound **19** was obtained when **7b** was irradiated under the conditions described for **8b**. Apparently, in ethanol **8b** rearranges essentially completely into **7b** which is further converted into **19** *via* attack of the solvent on an intermediate analogous to **13**. Additional work on the photochemical behavior of dienones **7a–c** in nucleophilic solvents is in progress and will be reported later.



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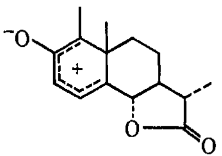
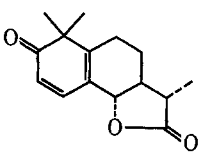
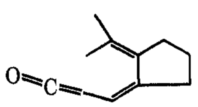


16



15

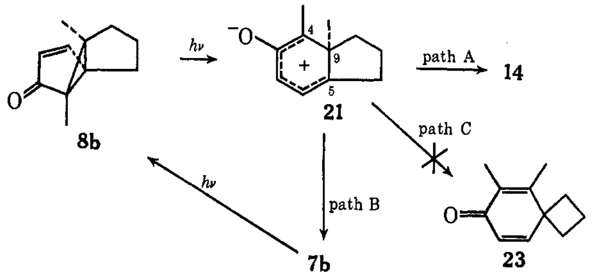


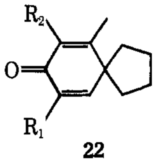
18

The behavior observed for **8b** in dioxane appears to be most readily explained by considering that light excitation leads to cleavage of the 4,5 bond to produce, after electron demotion, the dipolar species **21** (Scheme II). As pointed out above, this type of pathway has been proposed in the conversion of **12** into **15**[6] and analogous pathways have been invoked to explain the photochemistry of number to bicyclo[3.1.0]hex-3-en-2-ones derived from fused ring cross-conjugated cyclohexadienones.[2] In **21** a 1,2-methyl shift from C-9 to C-4 (path A) would give rise of **14**, while a similar shift from C-9 to C-5 (path B) would give **7b**. A minor rearrangement product of **12** which could have arisen *via* a path B type process has been tentatively identified,[6] and the exclusive formation of a cross-conjugated dienone, considered to arise by this type of pathway, has been reported[21] for the irradiation of the lumiproduct derived from 17β-hydroxy-1,4,9(11)-androstrien-3-one.

The results after short irradiation time can be explained by considering that the path A and path B modes of reaction of **21** compete, with the former being somewhat favored. On extended irradiation **14** greatly predominates, since **7b** is photochemically labile, being reconverted into **8b** (Scheme II).

Scheme II





22

The behavior of **8b** in ethanol also can be explained in terms of **21**, if one considers that in going from the aprotic solvent dioxane to the protic one path B becomes greatly favored. Some rather striking solvent effects have been observed in other lumiproduct rearrangements.[2a] In **21** path A rearrangement may be favored in dioxane because in the nonpolar solvent charge separation must be minimized in the dipolar species. However, in ethanol **21** may be protonated on oxygen, giving a mesoionic species in which other factors could favor path B rearrangement.[22]

No significant amounts of products which could be considered to be derived from 1,2-methylene migration (path C) in **21** were observed. Kropp[2a,11] has reported that irradiation of lumiproducts (**3**) in various media leads to photoproducts which are presumably formed by way of spirodienones (**22**). A path C type rearrangement in a species analogous to **21** would lead to **23**. However, path C products are apparently completely eliminated as the size of the ring attached to the bicyclo[3.1.0]hex-3-en-2-one moiety is reduced from six to five members. Kropp[2a,11] has suggested that a methylene shift does not take place in the rearrangement of **12**, because a spirodienone having two trans-fused five-membered rings would be highly strained. The work of Schuster and Fabian,[23] which showed that path A and path C products arise on irradiation of 6-epilumisantonin, supports this suggestion. A spiro[5.3]nonane derivative such as **23** would be expected to be more strained than **22**. Thus the photochemical behavior of **8b** appears to provide excellent additional support for Kropp's hypothesis.

Although a ketene intermediate appears to be ruled out in the irradiation of **8b** in ethanol at room temperature, the results obtained when **8b** was irradiated at 77°K make it necessary to consider the possibility that the ketene pathway is involved in the formation of **14** in the inert solvent, dioxane, at room temperature. Indeed, as has been suggested for the case of lumisantonin,[7b] pathways involving the dipolar intermediate

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(20) E. E. vanTamelen, S. H. Levin, G. Brenner, J. Wolinsky, and P. E. Aldrich, *J. Amer. Chem. Soc.*, **81**, 1666 (1959).

(21) Lj. Lorenc, M. Miljkovic, K. Schaffner, and O. Jeger, *Helv. Chim. Acta.*, **49**, 1183 (1966).

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

(23) D. I. Schuster and A. C. Fabian, *Tetrahedron Lett.*, 4093 (1966).

21 and the ketene **18** may compete when the photolysis is carried out in the inert medium. Also, the possibility exists that a cyclopropanone[24] precursor to **21** intervenes, although the irradiation at 77°K did not provide evidence on this point.[19]

Experimental Section[25]

7,7a-Dihydro-7a-methyl-5(6*H*)-indanone (10a).—Compound **10a** was prepared by a method similar to that reported by Ross and Levine.[8] A dried 500-ml three-necked round-bottom flask equipped with a thermometer, dropping funnel and magnetic stirring bar was placed under positive nitrogen flow. Anhydrous ether (200 ml) was added to the flask and a solution of 2.8 g (0.05 mol) of potassium hydroxide in 20 ml of absolute ethanol was added. The mixture was cooled to −7° with an ice–salt bath and 27.40 g (0.28 mol) of 2-methylcyclopentanone was added. A solution of 9.0 g (0.129 mol) of methyl vinyl ketone in *ca.* 50 ml of anhydrous ether was added at a rate sufficiently slow to keep the reaction temperature at or below −5°. When the addition was complete, the mixture was stirred for 45 min at −5°, then for 45 min with the ice–salt bath removed. The mixture was poured into 200 ml of 10% hydrochloric acid and the layers were separated. The aqueous layer was saturated with salt and extracted with two 50-ml portions of ether. The combined organic layers were dried over magnesium sulfate and the solvents were removed under reduced pressure. Distillation of the residue gave 7.1 g of 2-methylcyclopentanone (26% recovery), bp 41–42° (15 mm), and 14.04 g of a mixture, bp 68–105° (0.25 mm), which appeared by ir and glc[10] to consist of **10a** plus its precursor diketone and ketol. This material was dissolved in 200 ml of 10% ethanolic potassium hydroxide and refluxed under nitrogen for 30 min. The mixture was cooled to room temperature and neutralized with glacial acetic acid. The solvents were removed under reduced pressure, water was added to dissolve the potassium acetate formed in the neutralization, and the layers were separated. The aqueous layer was extracted with two 25-ml portions of ether and the combined organic layers were dried over magnesium sulfate. The solvents were removed under reduced pressure and the product was distilled through a short path distilling head to give 10.9 g (57%) of **10a**, bp 65–67° (0.30 mm) [lit.[4] 112° (4 mm)].

6,7a-Dimethyl-7,7a-dihydro-5(6*H*)-indanone (10c).—In a dried 500-ml three-necked round-bottom flask, fitted with a magnetic stirring bar, dropping funnel, and thermometer and under positive nitrogen flow, a solution of 2.8 g (0.02 mol) of potassium hydroxide in 20 ml of absolute ethanol was dissolved in *ca.* 200 ml of anhydrous ether. The reaction mixture was cooled to −5° with an ice–salt bath and 29.4 g (0.334 mol) of 2-methylcyclopentanone was added. Methyl isopropenyl ketone (14 g, 0.167 mol) in *ca.* 50 ml of anhydrous ether was added dropwise with stirring, while the reaction mixture temperature was maintained at −5°. The ice bath was removed and the mixture was stirred for 45 min. The mixture was poured into 200 ml of 10% hydrochloric acid. The layers were separated and the aqueous layer was extracted with two 25-ml portions of ether. The combined organic layers were dred with magnesium sulfate and the solvents were removed under reduced pressure. Distillation of the residue gave 5.1 g of 2-methylcyclopentanone (17%), bp 41–43° (15 mm). Further distillation gave 18.0 g of tractable material, bp 72–95° (0.07 mm). This was dissolved in 200 of 10% ethanolic potassium hydroxide and refluxed with stirring under nitrogen for 75 min. The mixture was cooled and neutralized with glacial acetic acid, and the solvents were removed under reduced pressure. Water was added to dissolve the potassium acetate formed, the layers were separated, and the aqueous layer was extracted with two 25-ml portions of ether. The combined organic layers were dried over magnesium sulfate. The solvents were removed at reduced pressure and the resulting yellow oil was distilled to yield 12.7 g (46%) of **10c**, bp 61° (0.05 mm). Compound **10c** exhibited the following spectral properties: uv max (95% EtOH) 238 mμ (ε 10,700); ir (CCl_4) 5.97 (conjugated C=O) and 6.32 μ (C=C); nmr (CCl_4) δ 5.65 (m, 1 H), 1.25–2.87 (broad absorption, 9 H), 1.19 (s, 3 H), 1.07 (d, 3 H, J = 7.0 Hz). *Anal.* Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.20; H, 9.84.

4,7a-Dimethyl-7,7a-dihydro-5(6*H*)-indanone (10b).—A dried 1000-ml three-necked round-bottom flask equipped with a dropping funnel, magnetic stirring bar, and thermometer was placed under positive nitrogen flow. Anhydrous ether (400 ml) was added to the flask and a solution of 4.5 g (0.08 mol) of potassium hydroxide in 30 ml of absolute ethanol was added. The mixture was cooled, with stirring to −5° by means of an ice–salt bath, and 52.0 g (0.53 mol) of 2-methylcyclopentanone was added. A solution of 20.5 g (0.244 mol) of ethyl vinyl ketone in *ca.* 150 ml of anhydrous ether was added dropwise while the temperature of the reaction mixture was maintained at −5° or below. Then stirring was continued for an additional 1 hr with the cooling bath removed. The mixture was poured into 300 ml of 10% hydrochloric acid, and the layers were separated. The aqueous layer was extracted with two 25-ml portions of ether, and the combined organic layers were dried over magnesium sulfate. The solvents were removed under reduced pressure. Distillation using a short-path head gave 2-methylcyclopentanone, 25.8 g (49%), bp 43–44° (21 mm), followed by 20.1 g of **10b** and its diketone and ketol precursor, bp 99–113° (1.0 mm). This material was dissolved in 300 ml of 10% ethanolic potassium hydroxide and refluxed for 30 min under nitrogen. The mixture was cooled to room temperature and neutralized with glacial acetic acid, and the solvents were removed under nitrogen pressure. Water was added to dissolve the potassium acetate, the layers were separated, and the aqueous layer was extracted with two 25-ml portions of ether. The combined organic layers were dried over magnesium sulfate and the solvents were removed under reduced pressure. Distillation of the resulting yellow oil through a short path head gave 12.7 g (33%) of **10b**, bp 87° (0.85 mm), which exhibited the following properties: uv max (95% EtOH) 247 mμ (ε 13,700); ir (CCl_4) 5.99 (unsaturated C=O), 6.20 μ (C=C); nmr (CCl_4) δ 1.7–2.91 (broad absorption, 10 H), 1.59 (s, 3 H). *Anal.* Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.84. Found: C, 80.21; H, 10.00.

7a-Methyl-5(7a*H*)-indanone (7a).—Compound **7a** was prepared by the method of Bloom.[4] A dried 1000-ml three-necked round-bottom flask equipped with a reflux condenser and magnetic stirring bar was placed under positive nitrogen flow and 750 ml of freshly distilled *tert*-butyl alcohol and 7 ml of glacial acetic acid were introduced. Freshly sublimed selenium dioxide, 8.4 g (0.076 mol), was added and the mixture was stirred until the selenium dioxide dissolved. Enone **10a**, 11.3 g (0.075 mol), was added and the mixture was refluxed, with stirring, for 46 hr. The mixture was concentrated to *ca.* 200 ml by distillation of solvents under nitrogen. Selenium metal was removed by several filtrations, with suction, and the remaining solvents were removed under nitrogen pressure. The resulting black viscous mass was taken up in 250 ml of ether and filtered with suction. The ethereal solution was washed with five 50-ml portions of 5% sodium hydroxide and dried with magnesium sulfate, and the solvents were removed under nitrogen pressure. Distillation through a short path head gave 2.3 g (21%) of **7a**, bp 70–71° (0.3 mm) [lit.[4] 69–70° (0.65 mm)]. The nmr spectrum of this compound had not been previously reported. It showed absorptions at δ (CCl_4) 7.02 (d, 1 H, J_{AB} = 9.5 Hz), 5.99 (d of d, 1 H, J_{AB} = 9.5 Hz, J_{BX} = 2.0 Hz), 5.89 (m, 1 H), 1.32–3.08 (broad absorption, 6 H), 1.21 (s, 3 H).

6,7a-Dimethyl-5(7a*H*)-indanone (7c).—Dienone **7c** was prepared by a modification of the method of Bloom.[4] A dried 100-ml three-necked round-bottom flask equipped with a reflux condenser and magnetic stirring bar was placed under positive nitrogen flow. Dried, freshly distilled *tert*-butyl alcohol (75 ml) was introduced and 2.45 g (0.022 mol) of freshly sublimed selenium dioxide and 7 ml of glacial acetic acid was added. The mixture was stirred until the selenium dioxide dissolved and 3.2 g (0.02 mol) of **10c** was added. The mixture was refluxed with stirring for 30 hr. The mixture was cooled to room temperature, and the selenium metal was removed by filtration with suction. The solvents were removed under reduced pressure, leaving a viscous black mass that was distilled through a short path head to

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[24] L. Barber, O. L. Chapman, and J. P. Lassila, *J. Amer. Chem. Soc.*, **91**, 3664 (1969).

[25] Melting and boiling points are uncorrected. Infrared spectra were obtained using a Perkin-Elmer Model 457 or 137 infrared spectrophotometer. Ultraviolet spectra were determined using a Cary Model 14 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. All compounds gave appropriate parent ions in their mass spectra at 70 eV using a Varian M-66 spectrometer. Vapor phase chromatography was performed using an Aerograph A-90-P3 with helium as the carried gas. Microanalyses were obtained by Galbreath Laboratories, Inc., Knoxville, Tenn.

give 1 g of a brown oil, bp 65–69° (0.65 mm). Analysis by glc[10] showed that the oil consisted of *ca.* 60% **10c** and 40% unreacted **7c**. The mixture was chromatographed on silica gel. Elution with 300 ml of hexane and 450 ml of 5% ether–hexane gave recovered **10c** mixed with a small amount of the desired compound **7c**. Further elution with 100 ml of 5% ether–hexane and 100 ml of ether gave 519 mg (16%) of **7c** which exhibited the following spectral properties: uv max (95% EtOH) 244 mμ (ϵ 12,900); ir (CCl_4) 5.97 (conjugated C=O) and 6.14 μ (C=C); nmr (CCl_4) δ 6.72 (q, 1 H, $J = 1.5$ Hz), 5.88 (t, 1 H, $J = 1.8$ Hz), 1.41–2.92 (broad absorption, 6 H), 1.79 (d, 3 H, $J = 1.5$ Hz), and 1.18 (s, 3 H). *Anal.* Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.54; H, 8.91.

4,7a-Dimethyl-5(7a*H*)-indanone (7b).—Compound **7b** was prepared by a modification of the method of Burn, Kirk, and Petrow.[9] A 1000-ml three-necked round-bottom flask equipped with a reflux condenser and magnetic stirring bar was placed under positive nitrogen flow. Freshly distilled anhydrous *p*-dioxane (500 ml) was charged into the flask and 9.35 g (0.0413 mol) of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) was added. The mixture was stirred until the DDQ dissolved, and 6.60 g (0.0403 mol) of **10b** was added. The mixture was refluxed with stirring for 30 hr. The solution was cooled to room temperature, and the solid 2,3-dichloro-5,6-dicyanohydroquinone (DDHQ) was collected by filtration with suction. The mixture was concentrated to *ca.* 50 ml by removal of solvents under reduced pressure. The mixture was cooled to room temperature and filtered with suction to remove the remaining DDHQ. It was then poured onto a loosely packed solumn of 70 g of alumina and eluted under pressure with 500 ml of benzene. The solvents were removed under reduced pressure and the resulting yellow oil was distilled through a short path head to give 3.92 (60%) of **7b**, bp 88° (0.5 mm), which exhibited the following spectral properties: uv max (95% EtOH) 243 mμ (ϵ 11,900); ir (CCl_4) 6.01 (conjugated C=O), 6.21 μ (C=C); nmr (CCl_4) δ 6.99 (d, 1 H, $J = 9.5$ Hz), 6.02 (d, 1 H, $J = 9.5$ Hz), 1.15–2.83 (broad absorption, 6 H), 1.72 (s, 3 H), and 1.17 (s, 3 H). *Anal.* Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.29; H, 8.66.

Irradiation of 7a-methyl-5(7a*H*)-indanone (7a) in Dioxane.—The dienone **7a**, 570 mg (0.0038 mol), was dissolved in 300 ml of anhydrous dioxane and irradiated with a Hanau NK 6/20 lamp for 75 min. Using a stream of dry nitrogen, the solution was agitated constantly for 10 min prior to and during the irradiated period. The solvents were removed under reduced pressure, and the crude mixture was chromatographed on silica gel. Elution with 5% ether–hexane (1500 ml) gave 312 g (55%) of 7a-methyl-3,7a-dihydro-3a,7-cyclo-6(7a*H*)-indanone (**8a**) which was greater than 90% pure by glc.[10] The analytical sample was collected by preparative glc[10] and showed uv max (95% EtOH) 236 mμ (ϵ 6300) and 271 (4200); ir (CCl_4) 5.86 μ (C=O); nmr (CCl_4) δ 7.28 (d, 1 H, $J_{AB} = 5.5$ Hz, C-7 H), 5.77 (d of d, 1 H, $J_{AB} = 5.5$, $J_{BX} = 0.8$ Hz, C-6 H), 1.47–2.27 (broad absorption, 7 H), and 1.68 (s, 3 H, C-7a CH_3). *Anal.* Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found; C, 80.99; H, 8.23.

Further elution with 10% ether–hexane (1000 ml) gave a small amount of starting material, and elution with ether (200 ml) gave 120 mg (21%) of the linearly conjugated dienone **9a** which was greater than 90% one component by glc.[10] The analytical sample was collected by preparative glc[10] and showed uv max (95% EtOH) 296 mμ (ϵ 19,000); ir (CCl_4) 5.86 (C=O), 5.97 (C=C), and 6.30 μ (C=C); nmr (CCl_4) δ 5.69 (s, 1 H, C-1 H, 2.72 (s, 2 H, C-3 CH_2), 1.53–2.90 (broad absorption, 6 H), and 1.81 (s, 3 H, C-4 CH_3). *Anal.* Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 80.71; H, 8.47.

Irradiation of 4,7a-Dimethyl-5(7a*H*)-indanone (7b) in Dioxane.—The dienone **7b**, 222 mg (0.0013 mol), was dissolved in freshy distilled dioxane and irradiated for 120 min using a Hanau NK 6/20 lamp. Using a stream of dry nitrogen, the solution was agitated constantly for 10 min prior to and during the irradiation period. Analysis of the mixture by glc[10] showed the presence of starting material and two other volatile components in a *ca.* 2:7:1 ratio. The mixture was subjected to chromatography on silica gel. Elution with hexane (900 ml) gave 110 mg (50%) of **8b**, bp 75–80° (bath temperature) (0.2 mm), which showed uv max (95% EtOH) 247 mμ (ϵ 4820) and 274 (2900); ir ($CHCl_3$) 5.88 (C=O) and 6.36 μ (C=C); nmr (CCl_4) δ 7.28 (d, 1 H, $J_{AB} = 5.5$ Hz, C-7 H), 5.74 (d, 1 H, $J_{AB} = 5.5$ Hz, C-6 H), 1.56–2.80 (broad absorption, 6 H), 1.18 (s, 3 H, C-4 CH_3), and 1.08 (s, 3 H, C-7a CH_3). *Anal.* Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.24; H, 8.40.

Further elution with 10% ether–hexane (200 ml) gave a small amount of starting material, and elution with more 10% ether–hexane gave *ca.* 12 mg (*ca.* 5%) of a solid material having an identical glc[10] retention time with the minor component of the photolysis mixture. This quantity of material was insufficient for complete characterization, but in a separate larger scale run, this component was collected directly by preparative glc.[10] The product identified as **9b** showed mp 85–88°; uv max (95% EtOH) 302 mμ (ϵ 14,000); ir (CCl_4) 5.99 (C=O) and 6.22 μ (C=C); nmr ($CDCl_3$) δ 2.80 (s, 2 H, C-3 CH_2), 2.6–1.9 (broad absorption, 6 H), 1.80 (s, 3 H, C-1 CH_3), and 1.72 (s, 3 H, C-4 CH_3). *Anal.* Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.28; H, 8.78.

Irradiation of 6,7a-Dimethyl-5(7a*H*)-indanone (7c) in Dioxane.—The dienone **7c**, 427 mg (0.0026 mol), was dissolved in 250 ml of anhydrous dioxane and irradiated with a Hanau NK 6/20 lamp for 90 min. Using a stream of dry nitrogen, the solution was agitated constantly for 15 min prior to and during the irradiation period. The reaction was monitored by glc[10] and **7c** had been converted into a single volatile photoproduct after this time. The solvent was removed under reduced pressure, and the crude product was subjected to chromatography on silica gel. Elution of the column with hexane (275 ml) followed by 25% ether–hexane (250 ml) gave 286 mg (67%) of 5,7a-dimethyl-3a,7-cyclo-6(7a*H*)-indanone (**8c**), bp 70–80° (bath temperature) (0.2 mm). The analytical sample was purified by preparative glc[10] and showed the following properties: uv max (95% EtOH) max 235 mμ (ϵ 4630) and 283 (2120); ir (CCl_4) 5.86 (C=O) and 6.18 μ (weak shoulder, C=C), nmr (CCl_4) δ 6.84 (m, 1 H, C-7 H), 1.45–2.33 (broad absorption, 7 H), 1.66 (d, $J = 1.5$ Hz, 3 H, C-6 CH_3), and 1.11 (s, 3 H, C-7a CH_3). *Anal.* Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.16; H, 8.90.

Irradiation of 7,7a-Dimethyl-3a,7a-dihydro-3a,7-cyclo-6(7*H*)-indanone (8b) in Dioxane.—A solution prepared from 300 mg of the bicyclo[3.1.0]hex-3-en-2-one **8b** in 200 ml of anhydrous dioxane was irradiated for 90 min using a 450-W Hanovia high-pressure lamp fitted with a Pyrex filter. Using a stream of dry nitrogen the solution was constantly agitated for 15 min prior to and during the irradiation period. Removal of the solvent under reduced pressure yielded a mixture which by glc analysis[16] was shown to contain one major component and two minor components in an approximately 88:6:6 ratio. The retention time of one of the minor components was identical with that of the starting material. Chromatography of the mixture on silica gel using hexane as the eluting solvent led to the isolation of 151 mg (50%) of the major photoproduct, 4,4-dimethyl-5(4*H*)-indanone (**14**), as a light yellow oil. Compound **14** showed uv max (95% EtOH) 335 mμ (ϵ 3800); ir (CCl_4) 6.00 (C=O) and 6.12 μ (C=C); nmr (CCl_4) 6.86 (d, 1 H, $J_{AB} = 10$ Hz), 5.79 (d, 1 H, $J_{AB} = 10$ Hz), 1.76–2.75 (broad absorption, 6 H), and 1.16 (s, 6 H). *Anal.* Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.52; H, 8.68.

A solution of 102 mg of **14** in 60 ml of 95% ethanol was shaken with 17 mg of 10% palladium on carbon in a hydrogen atmosphere for 16 hr. Removal of the catalyst by filtration and removal of the solvent under reduced pressure gave the cis-fused tetrahydro derivative of **14** as a colorless oil, ir (CCl_4) 5.86 μ. This material was not purified, but ws converted directly into its semicarbazone derivative, mp 203–206° (lit.[18] 207–208°).

The second minor product showed a glc[16] retention time identical with that of **7b**. In a run identical with that described above, **8b** was irradiated for 30 min. After vaporization of the solvents, glc analysis[16] of the photolysis mixture showed that it contained **8b**, **14**, and **7b** in an approximately 2:2:1 ratio. Samples of **8b**, **14**, and **7b** were collected by preparative glc[16] and showed spectral properties identical with those of authentic materials.

Irradiation of 4,7a-Dimethyl-5(7a*H*)-indanone (7b).—A solution of 650 mg of **7b** was irradiated under identical conditions with those described for **8b**. The reaction progress was monitored by glc analysis[16] of aliquots of the photolysis mixture taken at various time intervals. After a short irradiation time **8b** was the major product, but on continued irradiation a peak corresponding to **14** began to develop. After a total irradiation period of 1.5 hr, **14** was the major volatile component in the photolysis mixture.

Irradiation of 8b and 7b in Absolute Ethanol.—A solution of 420 mg (0.0026 mol) of **8b** in 250 ml of absolute ethanol was irradiated for 1 hr using a 450-W Hanovia high-pressure mercury lamp in a Pyrex probe. During the photolysis the mixture was agitated with a stream of dry nitrogen. Removal of the solvents under reduced pressure and glc analysis[16] of the crude mixture showed the presence of the starting material and a major product in a *ca.* 23:77 ratio. Only traces of other volatile products were observed. Distillation of the mixture gave a fraction, bp 75–85° (bath temperature) (0.2 mm), which proved to be mainly starting material. A higher boiling fraction, bp 100–110° (bath temperature) (0.2 mm), weighing 300 mg (55%), was collected. This fraction contained essentially one component, which was identified as the 5/6-fused ethoxy ketone **19**: uv max (95% EtOH) 242 mμ (ε 10,600); ir (CCl_4) 5.91 (C=C) and 6.08 μ (C=C); nmr (CCl_4) δ 3.45 (q, 2 H, J_{AX} = 7 Hz, OCH_2CH_3), 2.9–1.6 (broad absorption, 9 H), 1.63 (broad s, 3 H, C-1 CH_3), 1.10 (t, 3 H, *J* = 7 Hz, OCH_2CH_3), and 0.88 (s, 3 H, C-4 CH_3). *Anal.* Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.72; H, 9.79.

Irradiation of **7b** under identical conditions with those described above gave 19 as the sole photoproduct.

Irradiation of 14 in Absolute Ethanol.—Dienone **14** (380 mg) in 250 ml of absolute ethanol ws irradiated under identical conditions with those described above for **8b**. Removal of the solvent under reduced pressure gave 400 mg of crude liquid which on the basis of its spectral properties appeared to be largely the unconjugated diene ester **20**. Attempted purification of the compound by preparative glc[16] led to extensive isomerization to a mixture of **20** and the corresponding cis- and trans-conjugated diene esters. However, an analytical sample of **20** could be collected from the mixture. The sample showed ir (CCl_4) 5.74 (ester C=O) and 6.06 μ (conjugated diene); nmr (CCl_4) δ 5.42 (broadened t, *J* = 6 Hz, 1 H, vinyl H), 4.17 (q, *J* = 7 Hz, 2 H, $OCHCH_3$), 2.97 (broadened d, *J* = 6 Hz, 2 H, $O{=}CCH_2CH{=}$), 1.70 (s, 3 H, $CH_3C{=}$), 1.65 (s, 3 H, $CH_3C{=}$), and 1.25 (t, 3 H, OCH_2CH_3). *Anal.* Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, C, 75.00; H, 9.45.

Registry No.—**7a,** 22416-99-5; **7b,** 22417-00-1; **7c,** 22417-01-2; **8a,** 22417-02-3; **8b,** 22417-03-4; **8c,** 22417-04-5; **9a,** 22417-05-6; **9b,** 33070-69-8; **10a,** 17299-55-7; **10b,** 33070-71-2; **10c,** 33070-72-3; **14,** 33070-73-4; **19,** 33065-85-9; ***cis*-20,** 33065-86-0; ***trans*-20,** 33065-87-1; 2-methylcyclopentanone, 1120-72-5.

Photocyclizations. II. Synthesis of Iminoethanophenanthridine (Seven-Membered Ring) Homologs[1]

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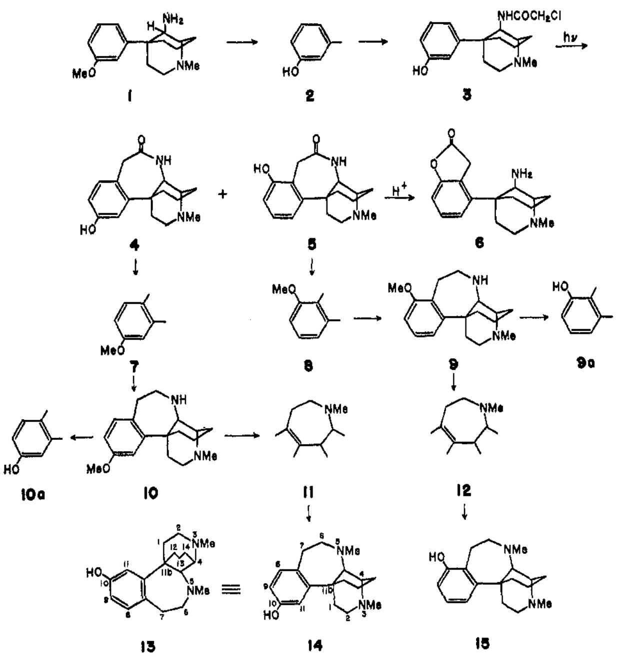
Photolysis of 9-*cis*-chloroacetamino-5-(*m*-hydroxyphenyl)-2-methyl-2-azabicyclo[3.3.1]nonane (**3**) has given both ortho and para ring closure to propanopyridobenzazepinones, **5** and **4**, whose structures were deduced from mass and nmr spectral data and by chemical evidence. The *O*-acetyl derivative of *o*-hydroxy compound **5** formed more slowly than that of **4**. Furthermore, acid treatment of **5** caused lactam ring opening with the formation of a new lactone ring (*cf.* **6**), in effect N → O acyl migration. Methylation of **4** and **5** followed by diborane reduction gave homophenanthridines **10** and **9**, respectively, which were N-methylated then O-demethylated to **14** and **15**.

In paper I of this series[2] we reported the synthesis of 4,5-dihydro-1*H*-naphth[1,8-de]azocin-2(3*H*)-one by irradiation of 1-(2-chloroacetamino)naphthalene. This communication is concerned with the photocyclization of a chloroacetamino group attached to a rigid azabicyclononane system with attack at both the ortho and para positions of a neighboring phenolic ring.[3] The results described here indicate a broadened scope and utility for this reaction especially toward the synthesis of complex heterocyclic systems.

The starting amine **1**[4] was hydrolyzed to **2** with boiling 48% hydrobromic acid. Conversion of **2** to the chloroacetamino compound **3** was effected in high yield by N,O dichloroacetylation with choroacetic anhydride in an aprotic solvent (potassium carbonate) and selective saponification.[5]



Amide **3**, irradiated in dilute aqueous solution, was completely consumed during 90 min to give two products. Preliminary mass spectral data (*m/e* 286 and 243[6] and no higher peaks) and proximate R_f values (for the sublimed mixture) in several solvent systems[7] were

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[1] These compounds are named benzazepines in the Experimental Section in accord with Chemical Abstracts recommendations.

[2] H. H. Ong and E. L. May, *J. Org. Chem.*, **35**, 2544 (1970).

[3] Previously reported photocyclizations of *N*-chloroacetyl compounds (see ref 2 and papers cited therein) have included no examples of alicyclic amines. Furthermore, this appears to be the first record of closure to the ortho position in a monophenolic compound.

[4] H. H. Ong and E. L. May, *J. Heterocycl. Chem.*, **8**, 1007 (1971).

[5] Low yields of **3** (1 mol of chloroacetic anhydride) or extensive quaternization of **2** (with excess reagent) were obtained when the procedure of O. Yonemitzu, T. Tokuyama, M. Chaykovsky, and B. Witkop, *J. Amer. Chem. Soc.*, **90**, 776 (1968), was used.

[6] This is probably due mainly to loss of CH_2NCH_3, but loss of $-NHCO-$ may also contribute; *cf.* A. M. Duffield, H. Budzikiewicz, and C. Djerassi, *J. Amer. Chem. Soc.*, **86**, 5536 (1964).

[7] Silica gel GF plates: system I, $MeNO_2$–AcOH–H_2O (90:28:12), R_f 0.41, 0.35; II, $CHCl_3$–Et_3N (5:1), R_f 0.07, 0.18, for example.