Ground-State and Photochemical Reactions in the Epoxypyrone Series[1-3]

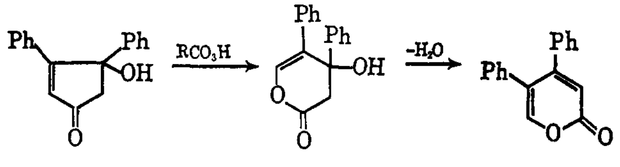
Albert Padwa[4] and Richard Hartman[5]

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received April 11, 1966*

Abstract: Reaction of 4-hydroxy-3,4-diphenyl-2-cyclopenten-1-one with an excess of *m*-chloroperbenzoic acid in methylene chloride produces a quantitative yield of 3,5-dihydroxy-3,4-diphenyl-4,5-epoxypentanoic acid δ-lactone (V). Treatment of V with concentrated sulfuric acid leads to 4-hydroxy-5,6-diphenyl-2-pyrone. Dehydration of V to 5,6-epoxy-4,5-diphenyl-2-pyrone (I) was achieved by the use of thionyl chloride and pyridine in benzene. The reactions of I with acid, base, heat, and light have been investigated. Upon treatment with acid, decarbonylation occurred yielding 4-hydroxy-3,4-diphenylcrotonic acid γ-lactone. With base, extrusion of carbon monoxide gave rise to methyl desylacetate. Thermal decarboxylation yielded 2,3-diphenylfuran whereas irradiation afforded 3,4-diphenylfuran and 2-phenyl-1,4-naphthoquinone. The details of the mechanism of each reaction are described and evidence is presented demonstrating the existence of transient intermediates.

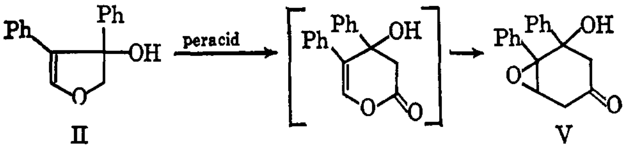
In a previous paper in this series[6] the products obtained from the photolysis of 3,4-diphenyl-4,5-epoxy-2-cyclopenten-1-one were described. It was found that brief irradiation afforded an isomer which had been identified as 4,5-diphenyl-2-pyrone.[7] Consideration of the product distribution obtained in a number of photolyses suggested that the remaining products were derived from the further photoreaction of 4,5-diphenyl-2-pyrone.[8] In connection with our study on the mechanism of this photorearrangement, it was necessary to prepare larger amounts of 4,5-diphenyl-2-pyrone. During the course of this synthesis, we had occasion to prepare reasonable quantities of 5,6-epoxy-4,5-diphenyl-2-pyrone (I). Present detailed knowledge concerning the photochemistry of epoxypyrones is lacking, though attracting considerable attention in the epoxide[9-12] and pyrone series,[13-15] and the present case appeared suitable for further study as regards available photolytic paths. The present paper reports on the photochemistry of this novel oxygenated pyrone, as well as some of the interesting ground-state chemistry.

Earlier reports in the literature have illustrated the use of peracid as a reagent for the oxidation of α,β-unsaturated carbonyl compounds.[16] Conjugated ketones are known to give the Baeyer–Villiger product in which cleavage toward the carbon–carbon double bond occurs.[17] We planned to convert 4-hydroxy-3,4-diphenyl-2-cyclopenten-1-one[18] (II) to 3,5-dihydroxy-3,4-diphenyl-4-pentenoic acid δ-lactone (III) with *m*-chloroperbenzoic acid and then dehydrate the carbinol to the desired 2-pyrone (IV). This two-step sequence was particularly attractive since it appeared readily adaptable to the preparation of a number of 2-pyrone derivatives which would be required in a later investigation.



II III IV

When 4-hydroxy-3,4-diphenyl-2-cyclopenten-1-one (II) was allowed to react with an equimolar amount of *m*-chloroperbenzoic acid, the expected carbinol was not obtained, but rather a new compound (V) was isolated in 48% yield. On the basis of its molecular formula ($C_{17}H_{14}O_4$) and the well-known ability of peracids to epoxidize olefins, it appeared likely that this new material was the further oxidation product of the initially formed enol lactone (III). This possibility was confirmed by the following chemical and spectral evidence which shows conclusively that the compound is 3,5-dihydroxy-3,4-diphenyl-4,5-epoxypentanoic acid δ-lactone (V).



II III V

Compound V exhibited an intense band in the infrared at 5.70 μ, attributable to a δ-lactone group, and its ultraviolet spectrum had $\lambda\lambda_{max}$ 264 mμ (ϵ 286), 261 (290), and 258 (338), characteristic of two isolated benzene rings. The nmr spectrum of V in pyridine as solvent showed an AB quartet at τ 6.83 and 6.25 (J_{AB} =

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[1] Photochemical Transformations of Small Ring Carbonyl Compounds. XI. For part X, see A. Padwa, D. Crumrine, and A. Shubber, *J. Am. Chem. Soc.*, **88**, 3064 (1966).

[2] Support of this research by a grant from the National Science Foundation (Grant GP-3972) is acknowledged with appreciation.

[3] For a preliminary report of this work, see A. Padwa and R. Hartman, *Tetrahedron Letters*, No. 21, 2277 (1966). This work was presented in part at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966.

[4] To whom inquiries should be directed at the Department of Chemistry, State University of New York at Buffalo, Buffalo, N. Y.

[5] National Science Foundation Predoctoral Fellow, 1963–1965; National Institutes of Health Predoctoral Fellow, 1965–1966.

[6] A. Padwa and R. Hartman, *J. Am. Chem. Soc.*, **88**, 1518 (1966).

[7] A. Padwa, *Tetrahedron Letters*, No. 15, 813 (1964).

[8] A. Padwa and R. Hartman, *J. Am. Chem. Soc.*, **86**, 4212 (1964).

[9] C. K. Johnson, B. Dominy, and W. Reusch, *ibid.*, **85**, 3894 (1963).

[10] H. E. Zimmerman, R. B. Cowley, C. Y. Tseng, and J. W. Wilson, *ibid.*, **86**, 947 (1964).

[11] A. Padwa, *ibid.*, **87**, 4205 (1965).

[12] O. Jeger, K. Schaffner, and H. Wehrli, *Pure Appl. Chem.*, **9**, 555 (1964).

[13] E. J. Corey and J. Streith, *J. Am. Chem. Soc.*, **86**, 950 (1964).

[14] P. de Mayo, *Advan. Org. Chem.*, **2**, 394 (1960).

[15] P. de Mayo and R. W. Yip, *Proc. Chem. Soc.*, **84** (1964).

[16] C. H. Hassall, *Org. Reactions*, **9**, 73 (1957).

[17] J. Boeseken and R. Soesman, *Rec. Trav. Chim.*, **52**, 874 (1933).

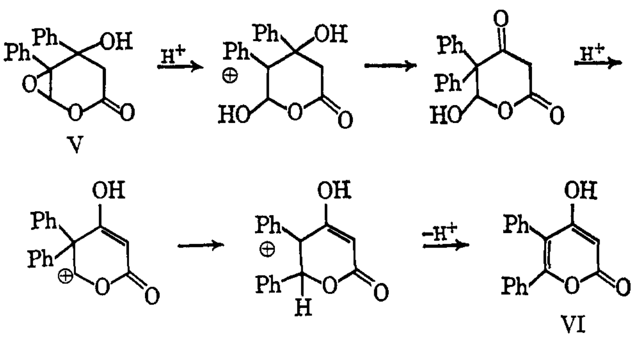
[18] F. R. Japp and G. D. Lander, *J. Chem. Soc.*, **71**, 123 (1897).

16 cps). Using dimethyl sulfoxide as a solvent, the nmr spectrum is characterized by a multiplet at τ 2.74, a singlet at 3.44, and a singlet at 4.08. Addition of a few drops of deuterium oxide was sufficient to remove the hydroxyl hydrogen peak at τ 3.44. The appearance of the hydroxyl proton as a singlet supports the assignment of V as a tertiary alcohol.[19]

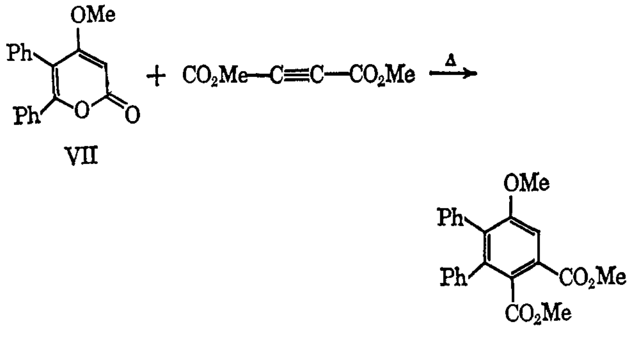
The products obtained from the peracid oxidation of α,β-unsaturated ketones have been shown to vary greatly depending on the reagent used.[20–22] However, for the most part, the product of initial oxygen insertion is the enol lactone rather than the α,β-unsaturated lactone or α,β-epoxy ketone. Conjugation of the double bond is known to reduce the rate of olefin epoxidation since the delocalization of the π electrons with the carbonyl group reduces the electron density at the double bond undergoing electrophilic attack.[23] Evidently, the initially formed enol lactone (III) undergoes further oxidation at a faster rate than starting material. This explanation accounts for the large amount (50%) of starting material that can be recovered when equivalent amounts of peracid were used. When a 2-mole excess of peracid was employed, a quantitative yield of V could be obtained.

In view of the unexpected oxidation of II, our attention was further directed to the acid-catalyzed dehydration of V, since the expected 5,6-epoxy-4,5-diphenyl-2-pyrone (I) would possess a structure that could be deoxygenated to the desired 4,5-diphenyl-2-pyrone. However, treatment of a sample of V with concentrated sulfuric acid at room temperature gave rise, on appropriate work-up, to an acidic substance (VI), $C_{17}H_{12}O_3$, mp 249–251° dec, in 86% yield. Since the acid was exceedingly insoluble in most common solvents, it was converted to its methyl ester (VII) by treatment with diazomethane. This substance exhibited the following nmr chemical shifts (in $CDCl_3$): a methoxyl singlet at τ 6.26, a one-proton singlet at 4.35, and a complex aromatic region (10 protons) centered at 2.81. The ultraviolet spectrum of the ester and acid (see the Experimental Section) indicated the presence of an α-pyrone chromophore.[24] On the basis of the above and ensuing data, we have formulated the acid as 4-hydroxy-5,6-diphenyl-2-pyrone (VI), which can presumably arise *via* the mechanistic path shown in Scheme I. Protonation of V at the epoxide ring can lead to the formation of a relatively stable carbonium ion. Migration of the phenyl group may or may not be synchronous with ring opening and carbonyl formation, but it ultimately affords a product that has undergone a transformation that is closely related to the pinacol rearrangement. Under the acidic conditions employed, the initial product forms a new carbonium ion that rapidly undergoes further phenyl migration and loss of a proton to attain the additional stability of the α-pyrone system.

Scheme I



Evidence supporting structure VI for the acid was obtained by comparison of its ultraviolet spectrum with a number of related 4-hydroxy-2-pyrone derivatives.[24] The compound could be oxidized with hot potassium permanganate to 2 moles of benzoic acid and did not react with bromine in carbon tetrachloride. Attempts to hydrogenate the compound at atmospheric pressure failed. On heating VI with acetic anhydride an acetate VIII was obtained, mp 169–170°, which could be reconverted to VI upon treatment with base in refluxing alcohol. Furthermore, it has been reported that related 4-hydroxy-2-pyrones behave as relatively acidic substrates.[25] The structural assignment of VI was further substantiated by heating methyl ester VII with dimethyl acetylene dicarboxylate at 200° for 1 hr. The product IX obtained in better than 90% yield provides conclusive evidence for the presence of an α-pyrone unit in VI. The proposed structure IX for the dimethyl acetylenedicarboxylate adduct was in accord with the spectral evidence. The infrared spectrum of IX shows a carbonyl band at 5.83 μ and has maxima in the ultraviolet region at 300 mμ (ϵ 10,000) and 275 mμ (ϵ 15,200). The nmr spectrum of IX displayed three singlets at τ 6.03, 6.15, and 6.47 and a multiplet at 2.88.



Final verification of structure VI was obtained by comparison with an authentic sample synthesized by treating diethyl malonate and deoxybenzoin with aluminum chloride by a modification of the procedure used by Gotschel and Mentzer.[26]

The synthesis and acid-catalyzed rearrangement of 5,6-epoxy-4,5-diphenyl-2-pyrone (I) was next studied. A test of the proposed mechanistic reasoning for the formation of VI was therefore at hand; for if the mechanism of the acid-catalyzed rearrangement of V to VI had proceeded *via* I, a similar sequence should occur here.

Compound V reacts smoothly with thionyl chloride in pyridine to produce a colorless solid (mp 134–135°),

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[19] O. L. Chapman and R. W. King, *J. Am. Chem. Soc.*, **86**, 1256 (1964).

[20] G. Pettit and T. Kasturi, *J. Org. Chem.*, **26**, 4557 (1961).

[21] B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, 1525 (1955).

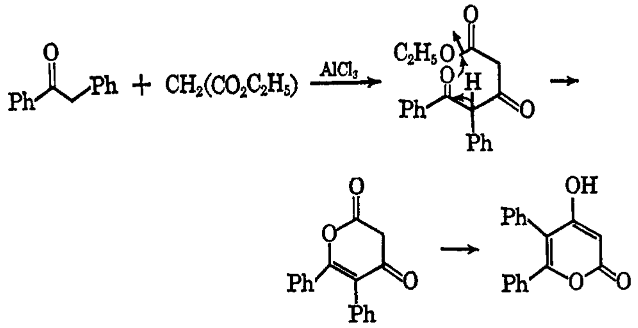
[22] J. T. Pinhey and K. Schaffner, *Tetrahedron Letters*, **No. 10**, 601 (1965).

[23] H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, p 116.

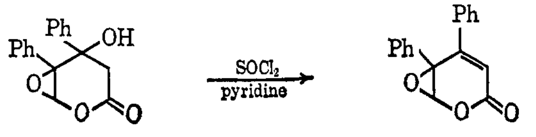
[24] A. I. Scott, "Interpretation of the Ultraviolet Spectra of Natural Products," The Macmillan Co., New York, N. Y., 1964, p 140.

[25] T. A. Giessman and C. F. Koelsch, *J. Org. Chem.*, **3**, 489 (1938).

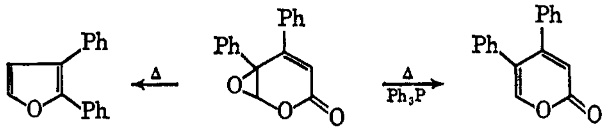
[26] C. Gotschel and C. Mentzer, *Bull. Soc. Chim. France*, 365 (1962).



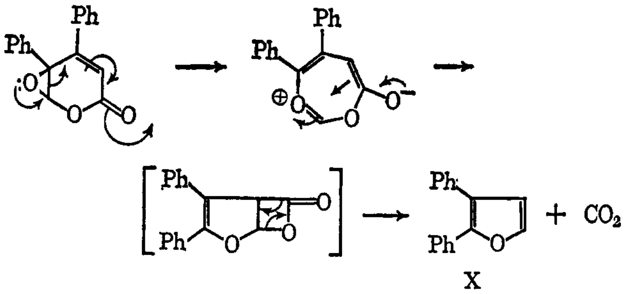
having the composition $C_{17}H_{12}O_3$, in about 70% yield. Chemical and spectral evidence (see the Experimental Section) shows that this new compound is 5,6-epoxy-4,5-diphenyl-2-pyrone (I). Chemical confirmation of the structure of I was obtained by converting it, in low yield, to 4,5-diphenyl-2-pyrone (IV) by heating with triphenylphosphine.[27] This reaction, however, took an unexpected course when lower temperatures were employed; only 2,3-diphenylfuran (X) and recovered starting material were produced. 2,3-Diphenylfuran was identical with an authentic sample independently synthesized.[28] Undoubtedly, the furan resulted from the thermal decarboxylation of I, since this same product was obtained when the reaction was subsequently repeated in the absence of triphenylphosphine. A reasonable mechanism for the formation of X is presented below.



V I

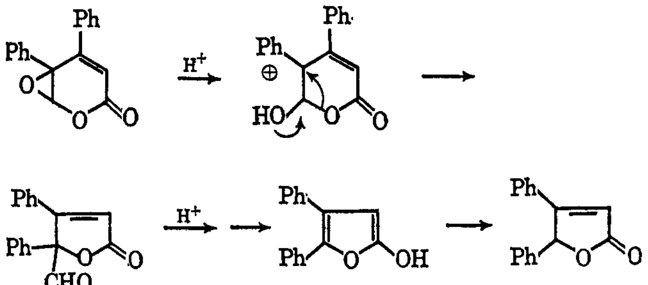


X I IV



X

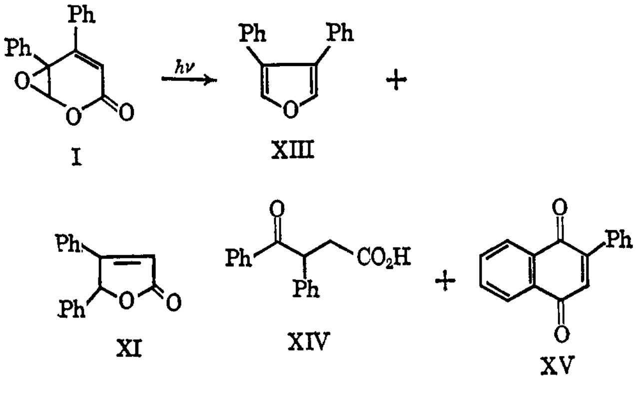
When I was treated with concentrated sulfuric acid for 10 min, followed by aqueous work-up, 4-hydroxy-3,4-diphenylcrotonic acid γ-lactone (XI) was obtained in high yield. Thus, initial dehydration of V to I does not occur in the acid-catalyzed rearrangement of V to VI, presumably because ring opening of the epoxide is faster than dehydration. The formation of lactone XI can arise *via* the mechanistic pathway shown below. Efforts to isolate the proposed aldehyde from the reaction medium were unsuccessful. The reason for this appears to be that the aldehyde, once formed, is rapidly attacked by water leading to the observed product. In order to simplify this problem, it was decided to conduct the acid-catalyzed rearrangement of I in the presence of 2,4-dinitrophenylhydrazine in an effort to trap the aldehyde as rapidly as it is formed. This proved to be very successful and it was possible to gain considerable insight into the mechanism of the over-all decarbonylation. A sample of I, when treated in this manner, gave essentially a quantitative yield of the 2,4-dinitrophenylhydrazone of the above aldehyde (see the Experimental Section), thereby supporting the above mechanistic interpretation.



XI

Inasmuch as both acid and heat caused epoxypyrone I to undergo an unusual decarbonylation and decarboxylation, it became of further interest to investigate the reaction of I with base and ultraviolet light. Treatment of I with sodium methoxide in methanol produced a single component in high yield which was subsequently identified as methyl desylacetate (XII). Basic hydrolysis of the keto ester provided desylacetic acid. The structure of XII was fully established by comparison with an authentic sample of methyl desylacetate. The most likely mechanism for the formation of the observed product seems to involve initial attack of methoxide on the carbonyl group. The resulting alkoxide anion causes the epoxide ring to open, yielding an aldehyde that is rapidly attacked by base giving the observed product.

The photolysis of I was conducted using an internal water-cooled mercury arc lamp (Hanovia, Type L, 450 w) with a Corex filter to eliminate wavelengths below 280 mμ. The photolysis was followed by withdrawal of small samples at fixed intervals and examination of these by thin layer chromatography. Upon irradiation of 1 g of I in anhydrous ether for 4 hr, the spot on a thin layer plate due to I had completely disappeared and four new spots had appeared in its place. Chromatography of the crude photolysis mixture on florisil afforded 3,4-diphenylfuran (XIII, 12%), 4-hydroxy-



I XIII XI XIV XV

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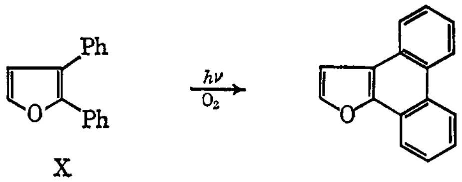
(27) G. Wittig and W. Haag, *Ber.*, **88**, 1654 (1955).
(28) A. Padwa, *Tetrahedron Letters*, **No. 16**, 1049 (1965).

3,4-diphenylcrotonic acid γ-lactone (XI, 35%), desyl acetic acid (XIV, 25%), and 2-phenyl-1,4-napthoquinone (XV, 10%). The structures were substantiated by comparison of infrared and mixture melting points with those of authentic samples.

It is noteworthy that no 2,3-diphenylfuran (X) was obtained upon irradiation of 5,6-epoxy-4,5-diphenyl-2-pyrone (I). The possibility was considered that the formation of 3,4-diphenylfuran (XIII) might proceed through the intermediacy of 2,3-diphenylfuran. Recently, several examples of light-induced rearrangements of five-membered ring heterocycles have appeared in the literature, providing reasonable chemical precedent for the above suggestion.[29-31] As a preliminary step toward verifying this postulation, a search for the possible photoisomerization was made.[32]

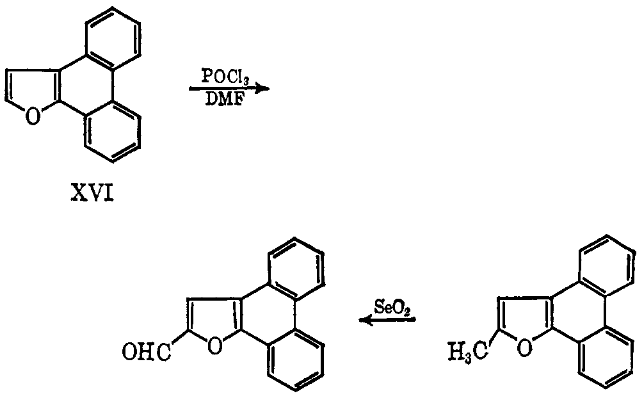
Photolysis of 2,3-diphenylfuran (X) in anhydrous benzene affords a single product to which structure XVI is assigned on the basis of chemical and physical data (see the Experimental Section). Proof of structure XVI was obtained by an application of the Vilsmeier reaction in which [9,10-*b*]phenanthrofuran (XVI) was treated with a 1:1 complex of dimethylformamide and phosphorus oxychloride. The product obtained in better than 90% yield was identical with sample of [9,10-*b*]phenanthrofuran-2-carboxaldehyde (XVII) synthesized by selenium dioxide oxidation of 2-methyl-[9,10-*b*]phenanthrofuran (XVIII).[39] The previously unreported [9,10-*b*]phenanthrofuran-2-carboxaldehyde (XVII), mp 153–154°, was elucidated by elemental analysis, and infrared, ultraviolet, and nuclear magnetic resonance data (see the Experimental Section).



X

XVI

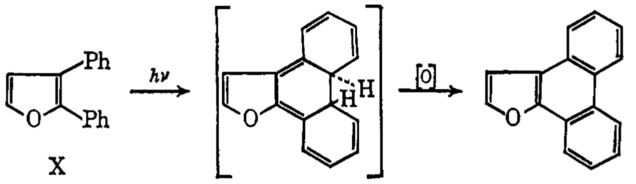
Irradiation with ultraviolet light of solutions containing *cis*-stilbenes in the presence of a suitable oxidant such as molecular oxygen has been demonstrated to lead to formation of phenanthrene derivatives.[40] Evidence which strongly indicates the latter reaction proceeds *via* a dihydrophenanthrene has recently been presented.[41] It is quite reasonable to assume that the formation of XVI from the irradiation of X in the presence of oxygen proceeds *via* a similar mechanism.



XVI

XVII

XVIII



X

XVI

The photoreaction of X was carefully monitored by ultraviolet and gas–liquid chromatography of aliquots withdrawn during the irradiation. We observed that the gas chromatographic peak due to X began to decrease in size immediately on irradiation and a peak corresponding to XVI appeared with a slightly higher retention time. Further irradiation led to the reduction in the amount of X until, after 20 hr, only traces of starting material remained. At no time during the irradiation did any other peak, corresponding to an isomeric diphenylfuran, appear.[42] The formation of XVI rather than photoisomerization of X to XIII may be attributed to a lower energy pathway for phenanthrene formation. We are therefore led to conclude that 2,3-diphenylfuran is not formed from the irradiation of I and that the electronically excited state of I decarboxylates by a route which differs from the decarboxylation of a higher vibrational level of ground state.

It is of interest to speculate on the mechanism for formation of 3,4-diphenylfuran. One possibility is that outlined as follows, involving excitation of the carbonyl group and subsequent cleavage of the carbon–oxygen bond of the oxide ring followed by ring closure at the α position.[43] Decarboxylation may then occur

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(29) H. Tiefenthaler, W. Dorscheln, H. Goth, and H. Schmid, *Tetrahedron Letters* 2999 (1964).

(30) H. Wynberg and H. van Driel, *J. Am. Chem. Soc.*, **87**, 3998 (1965).

(31) E. F. Ullman and B. Singh, *ibid.*, **88**, 1844 (1966).

(32) Recent evidence for Dewar benzene intermediates in aromatic systems[33-36] suggests that the photoisomerizations observed in the five-membered heterocyclic series may proceed by way of bridged valence tautomers[30] related to those found as intermediates in the benzenoid system. In the case of furan X the preferred conrotative mode of thermal stereoisomerization[37,38] cannot operate since an extraordinarily strained *cis,trans* isomer of furan would result. The stereoelectronically less preferred disrotatory ring opening should result in an increase in the transition-state energy for ring opening and consequently lead one to expect Dewar furan to be of comparable stability to related Dewar benzenes. However, Ullman[31] has noted that the photoisomerization of five-membered ring heterocycles may not involve valence bond tautomers but rather unsaturated small ring carbonyl compounds as critical intermediates.

(33) E. E. van Tamelen and S. P. Pappas, *J. Am. Chem. Soc.*, **84**, 3789 (1962).

(34) K. E. Wilzbach and L. Kaplan, *ibid.*, **86**, 2307 (1964).

(35) E. M. Arnett and J. M. Bollinger, *Tetrahedron Letters*, 3803 (1964).

(36) E. E. van Tamelen, *Angew Chem. Intern Ed. Engl.*, **9**, 738 (1965).

(37) R. B. Woodward and R. Hoffman, *J. Am. Chem. Soc.*, **87**, 395 (1965).

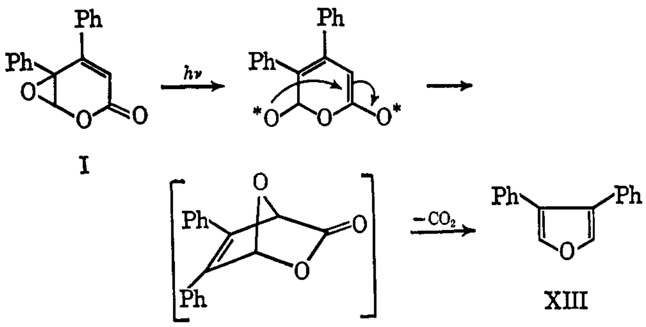
(38) H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, **87**, 2045 (1965).

(39) F. Japp and F. Klingemann, *Ber.*, **21**, 2932 (1888).

(40) F. B. Mallory, C. S. Wood, and J. T. Gordon, *J. Am. Chem. Soc.*, **86**, 3094 (1964), and earlier references cited there.

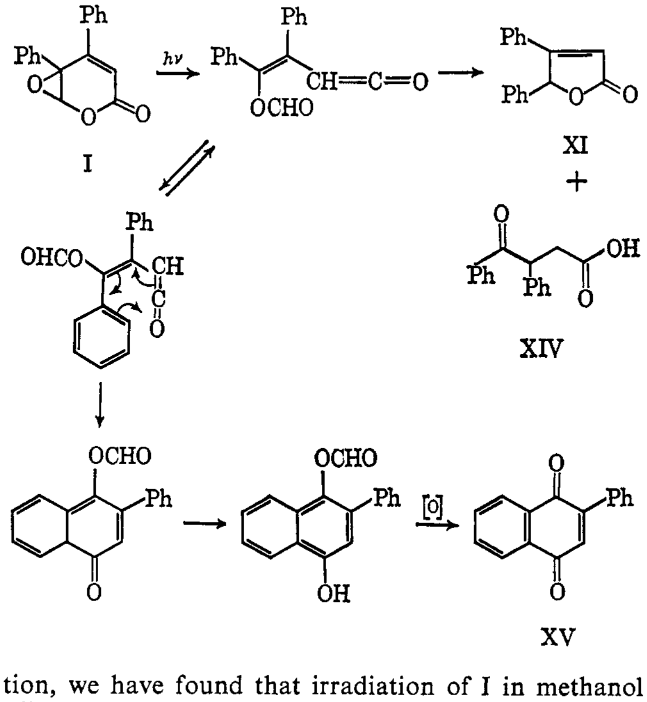
(41) W. M. Moore, D. D. Morgan, and F. R. Stermitz, *ibid.*, **85**, 830 (1963).

(42) By using long irradiation time, it was felt that the formation of XVI from the photolysis of 2,4- 3,4-, and 2,5-diphenylfuran would provide evidence for the intermediacy of a Dewar furan. Experimentally, irradiation of the three isomeric furans afforded either a high molecular weight polymer or recovered starting material without any detectable formation of [9,10-*b*]phenanthrofuran (XVI). Thus, it seems that if a transient Dewar furan is formed by irradiation of disubstituted furans, it does not undergo subsequent transformations related to the phenylthiophene case.[30]



either thermally or photochemically from the transient lactone.

The formation of the remaining products obtained from the irradiation of I may be rationalized on the basis of an initial ring fission giving a *cis*-ene-ketene as a transient intermediate. The opening of I to a ketene by means of appropriate electron movement bears close resemblance to the reported formation of methyl β-acetonylcrotonate from the irradiation of 4,6-dimethyl-2-pyrone, a reaction which has been interpreted as a cycloelimination proceeding *via* a ketene intermediate.[14] Photoisomerization of the *cis*-ene-ketene to the *trans*-ene-ketene and cyclization in the manner described below readily accounts for the formation of XV. Cyclization of the *trans*-ene-ketene is related to the reaction by which diphenylketene and diphenylacetylene form triphenylnapthol,[44] as well as by the formation of 1-phenyl-2-ethoxy-4-hydroxynapthalene from diphenylketene and ethoxyacetylene,[45] and by the large number of known photocyclization reactions of cyclohexadienes.[46] In agreement with this interpretation, we have found that irradiation of I in methanol afforded methyl desylacetate (XII, 60%) and 3,4-diphenylfuran (XIII). Careful examination of the reaction revealed no detectable amounts of XV. The isolation of ester XII strongly suggests the presence of a ketene intermediate which reacts with solvent to give a product different from that previously observed, but which is totally compatible with the mechanism outlined above.



Experimental Section[47]

Peracid Oxidation of 4-Hydroxy-3,4-diphenyl-2-cyclopenten-1-one (II). A solution of 10.0 g of 4-hydroxy-3,4-diphenyl-2-cyclopenten-1-one (0.04 mole) and 24.5 g of *m*-chloroperbenzoic acid (0.12 mole) in 200 ml of methylene chloride was allowed to stand at room temperature for 48 hr. At the end of this time, the precipitated *m*-chlorobenzoic acid was removed by filtration and the solution was washed with saturated sodium carbonate and dried over sodium sulfate. The solvent was removed *in vacuo* to leave a white solid. Recrystallization from benzene–chloroform gave a white, crystalline solid (V), mp 179.5–180°, yield 9.8 g (96%).

Anal. Calcd for $C_{17}H_{14}O_4$: C, 72.33; H, 5.00. Found: C, 72.75; H, 4.91.

The infrared spectrum in a potassium bromide pellet is characterized by bands at 5.70, 8.15, 9.43, and 11.53 μ. The ultraviolet spectrum in 95% ethanol has maxima at 264 mμ (ϵ 286), 261 (290), and 258 (338). The nmr spectrum in pyridine shows a doublet at τ 6.83 and a doublet at 6.25 (J_{AB} = 16 cps). The nmr spectrum in dimethyl sulfoxide shows a singlet at τ 4.08, a singlet at 3.44, and a multiplet at 2.74. The relative intensities are 1:1:1:10. Upon addition of D_2O the peak at τ 3.44 disappears. All the data are consistent with the structure of V as 3,5-hydroxy-3,4-diphenyl-4,5-epoxypentanoic acid γ-lactone.

Treatment of 3,5-Dihydroxy-3,4-diphenyl-4,5-epoxypentanoic Acid δ-Lactone (V) with Concentrated Sulfuric Acid. To 25 ml of concentrated sulfuric acid was added 2.5 g of V and the solution was allowed to stand at room temperature for 15 min. Ice was added to the brown solution and the light tan solid which precipitated was collected by filtration, washed thoroughly with water, and dried to yield 2.1 g (85%) of an acidic material (VI). This acid was very difficult to purify, and a small sample was finally sublimed, mp 249–251° dec. The infrared spectrum is characterized by a broad band at 3.3–3.9, and bands at 5.95, 6.15, 7.48, 8.92, and 12.99 μ. The acid (VI) was converted into a methyl ester by treatment with diazomethane in ether. Recrystallization of the methyl ester (VII) from 95% ethanol gave a white, crystalline solid, mp 189–190°.

Anal. Calcd for $C_{18}H_{14}O_3$: C, 77.68; H, 5.07. Found: C, 77.52; H, 5.07.

The infrared spectrum of the crystalline compound (KBr) is characterized by bands at 5.87 and 6.13 μ. The ultraviolet spectrum in 95% ethanol has $\lambda\lambda_{max}$ 312 mμ (ϵ 8900), 236 (17,000), and 226 (17,200). The nmr spectrum ($CDCl_3$) of the methyl ester shows a multiplet at τ 2.81, a singlet at 4.35, and a singlet at 6.26. The peak areas are in the ratio of 10:1:3.

The acidic material (VI) could be converted to an acetate derivative (VIII) by refluxing a mixture of 2.0 g of VI in 25 ml of acetic anhydride containing a trace of sodium acetate for 12 hr. Removal of the solvent and chromatography of the residual brown oil on a silica column gave 750 mg of a yellow solid. Recrystallization of this material from 95% ethanol gave a pale yellow solid, mp 169–170°.

Anal. Calcd for $C_{18}H_{14}O_4$: C, 74.45; H. 4.60. Found: C, 74.53; H, 4.78.

The infrared spectrum of the acetate (VIII) shows a single carbonyl band at 5.70, and bands at 6.23, 6.25, 7.05, 8.80, and 11.15 μ. The ultraviolet spectrum (95% ethanol) has maxima at 343 mμ (ϵ 16,200) and 227 mμ (ϵ 18,300). The nmr spectrum shows a multiplet at τ 2.60 and a sharp singlet at 7.20 in the ratio of 11:3.

Compound VI was identified as 4-hydroxy-5,6-diphenyl-2-pyrone by comparison with an authentic sample synthesized by the method of Gotschel and Mentzer.[26]

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(43) The nature of the transition involved in the phototransformation is not defined and consequently an asterisk is used to indicate the excited character of this state.

(44) L. I. Smith and H. H. Hoehn, *J. Am. Chem. Soc.*, **63**, 1181 (1941).

(45) J. Druey, E. F. Jenny, K. Schenker, and R. B. Woodward, *Helv. Chim. Acta*, **45**, 600 (1962).

(46) O. L. Chapman, *Advan. Photochem.*, **1**, 345 (1963).

(47) All melting points are corrected and boiling points are uncorrected. Elemental analyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark, and Alfred Bernhardt Laboratories, Hohenweg, Germany. The infrared absorption spectra were determined on a Perkin-Elmer Infracord spectrophotometer, Model 137. The ultraviolet absorption spectra were measured with a Cary recording spectrophotometer, Model 14, using 1-cm matched cells. The nuclear magnetic resonance spectra were determined at 60 Mc with the Varian Associates high-resolution spectrophotometer. Tetramethylsilane was used as an internal standard.

Reaction of 4-Methoxy-5,6-diphenyl-2-pyrone (VII) with Dimethyl Acetylenedicarboxylate. Elucidation of the structure of VI was achieved by reacting its methyl ester (VII) with dimethyl acetylenedicarboxylate. In a sealed tube were placed 1.0 g of VII and 550 mg of dimethyl acetylenedicarboxylate. The sealed tube was heated at 200° for 1 hr and the crude mixture was chromatographed from a silica gel chromatography column. The product was eluted with 5% ethyl acetate in benzene as a pale oil which solidified when scratched. The crude solid was crystallized from benzene–hexane to give white needles, mp 132–133°, 950 mg (72%).

Anal. Calcd for $C_{23}H_{20}O_5$: C, 73.39; H, 5.36. Found: C, 73.85; H, 5.43.

The infrared spectrum of 3,4-diphenyl-5-methoxyphthalic acid dimethyl ester (IX) shows a carbonyl band at 5.72, and bands at 7.45, 8.05, 8.51, and 9.40 μ. The ultraviolet spectrum (95% ethanol) has maxima at 300 mμ (ε 10,000) and 275 mμ (ε 15,200). The nmr spectrum has a multiplet centered at τ 2.88 and three singlets at 6.03, 6.15, and 6.47. The peak areas are in the ratio of 11:3:3:3.

Preparation of 4-Hydroxy-5,6-diphenyl-2-pyrone (VI). The procedure of Gotschel and Mentzer was adopted to the present case.[26] A mixture of 8.0 g of diethyl malonate and 9.8 g of desoxybenzoin in the presence of 500 mg of anhydrous aluminum chloride was heated at 250° for 1 hr. The cold reaction mixture was poured onto water and sodium hydroxide was added. The aqueous solution was extracted with ether and the aqueous layer was acidified with hydrochloric acid. Extraction of the acidic solution with ether followed by drying the ether extracts over sodium sulfate and removal of the solvent left 2.4 g of an oil which solidified upon standing. The solid was triturated with ether to remove soluble impurities. The infrared spectrum of this material was identical in every detail with that of 4-hydroxy-5,6-diphenyl-2-pyrone prepared from the treatment of V with sulfuric acid. The solid was also converted to its methyl ester by treatment with diazomethane. The ester was recrystallized from methanol to give a white solid, mp 187–188°. The infrared and nmr spectra of this material were identical in every feature with that of the methyl ester of VI. The mixture melting points of these two methyl esters were undepressed at 187–189°.

5,6-Epoxy-4,5-diphenyl-2-pyrone (I). To a solution of 4.0 g of V and 6.1 ml of pyridine in 350 ml of benzene was added 2.28 g of thionyl chloride in 100 ml of benzene. The mixture was allowed to stir at room temperature for 12 hr. The yellow solution was then filtered from the precipitated pyridine hydrochloride, washed with 5% hydrochloric acid, and dried over sodium sulfate. Evaporation of the solvent left 2.3 g of a yellow oil which solidified upon the addition of ethanol. Recrystallization from 95% ethanol gave a white solid, mp 134–135°.

Anal. Calcd for $C_{17}H_{12}O_3$: C, 77.26; H, 4.58. Found: C, 77.13; H, 4.63.

The infrared spectrum (KBr) shows a carbonyl band at 5.80, and bands at 8.30, 9.13, 11.85, and 12.34 μ. The ultraviolet spectrum in 95% ethanol has a maximum at 281 mμ (ε 12,500). The nmr spectrum ($CDCl_3$) shows a multiplet at τ 2.83 and a singlet at 4.75. The peak areas are in the ratio of 10:1:1.

Deoxidation of 5,6-Epoxy-4,5-diphenyl-2-pyrone. A sealed tube containing 500 mg of I, 500 mg of triphenylphosphine, and 150 mg of hydroquinone was heated at 185° for 3 hr. Chromatography of the crude residue on Woelm neutral Alumina (Grade No. 3) gave 50 mg (10%) of 4,5-diphenyl-2-pyrone (IV). This material was identified by comparison of melting point, mixture melting point, and infrared spectrum to an authentic sample.

Thermal Decarbonylation of I to 2,3-Diphenylfuran (X). A solution of 1.0 g of I in 25 ml of *sym*-tetrachloroethane was refluxed for 12 hr. The solvent was removed by distillation and the yellow oil (0.83 g, 85%) remaining was purified by filtration through a Florisil chromatography column. Thin layer and vapor phase chromatography revealed the oil to be homogeneous. Molecular distillation of this material at bp 173–174° (0.8 mm) gave crystals, mp 17–18°, which gave a satisfactory elemental analysis.

Anal. Calcd for $C_{16}H_{12}O$: C, 87.24; H. 5.49. Found: C, 87.46; H, 5.61.

The infrared spectrum of 2,3-diphenylfuran (X) is chiefly characterized by a sharp intense band at 11.24 μ. The nmr spectrum in carbon tetrachloride has a sharp doublet at τ 2.57 (J = 2 cps), a multiplet at 2.84, and a doublet at 3.63 (J = 2 cps). The peak areas are in the ratio of 1:10:1. The infrared spectrum and the retention time from two different chromatography columns were identical with an authentic sample of 2,3-diphenylfuran prepared from the copper-catalyzed decarboxylation of 4,5-diphenylfuran-3-carboxylate.[28]

Acid-Catalyzed Rearrangement of 5,6-Epoxy-4,5-diphenyl-2-pyrone (I). To 1.0 g of I was added 10 ml of concentrated sulfuric acid, and the dark brown solution was allowed to stand for 10 min at room temperature. Ice was added to the acidic solution and the aqueous mixture was extracted with ether. The ether extracts were washed with sodium carbonate solution and dried over anhydrous potassium carbonate. Removal of the solvent left a white solid which was recrystallized from ethyl acetate to give 0.84 g (86%) of a white, crystalline solid, mp 152–153°. This material was identified as 4-hydroxy-3,4-diphenyl-2-butenoic acid γ-lactone (XI) by comparison with an authentic sample prepared by the method of Thiele.[48]

A solution of 1.0 g of desylacetic acid in 50 ml of acetic anhydride was refluxed for 2 hr and the cooled solution was poured onto 200 ml of water. The aqueous solution was neutralized to pH 7 by addition of sodium bicarbonate and the neutral solution was extracted with ether. The organic washings were dried over sodium sulfate and the ether was removed *in vacuo*. The remaining oil was crystallized from ethyl acetate–hexane to a constant melting point, 153–154°. The infrared spectrum of this material was identical in every detail with the material obtained from the acid treatment of I. The mixture melting point of the two lactones was undepressed at 152–154°

Acid-Catalyzed Rearrangement of I in the Presence of 2,4-Dinitrophenylhydrazine. To 1.0 g of I was added 10 ml of a 10% solution of 2,4-dinitrophenylhydrazine in concentrated sulfuric acid. The mixture was poured onto 100 g of crushed ice and the yellow precipitate was collected. The material was crystallized repeatedly from ethanol to give a yellow solid, mp 124–125°.

Anal. Calcd for $C_{23}H_{16}N_4O_4$: C, 62.16; H, 3.63; N, 12.61. Found: C, 62.18; H, 3.71; N, 12.59.

The infrared spectrum shows a carbonyl band at 5.72, and a carbon–nitrogen double band at 6.25 μ. The ultraviolet spectrum (95% ethanol) has $\lambda\lambda_{max}$ at 351 mμ (ε 31,500) and 271 mμ (ε 32,800). The material was identified on the basis of spectral data and the method of preparation as 4-hydroxy-3,4-diphenyl-2-penten-5-al-1-oic acid γ-lactone 5-(2,4-dinitrophenylhydrazone).

Decarbonylation of I with Sodium Methoxide–Methanol. A solution of 1.0 g of I in 25 ml of anhydrous methanol containing 1.0 g of sodium methoxide was allowed to stand at room temperature for 12 hr. The solution was poured onto 100 ml of water and acidified to pH 7 with dilute hydrochloric acid. The aqueous layer was extracted with ether and dried over sodium sulfate. Removal of the solvent left 1.0 g of a pale oil which slowly solidified upon standing for several days. Recrystallization from pentane gave a white solid, mp 51–53°, whose infrared spectrum and melting point were identical with an authentic sample of methyl desylacetate (XII). Saponification of the ester using an aqueous ethanolic potassium hydroxide solution gave a white solid, mp 161–163°, whose infrared spectrum was identical with that of an authentic sample of desylacetic acid.

Irradiation of 5,6-Epoxy-4,5-diphenyl-2-pyrone (I). A solution of 500 mg of I in 150 ml of anhydrous ether was irradiated with an internal, water-cooled mercury arc lamp (Hanovia, Type L, 450 w) with a Corex filter to eliminate wavelengths below 260 mμ. Aliquots were removed and analyzed by thin layer chromatography. After 4 hr the photolysis was complete and the solution was washed twice with 10% sodium carbonate solution. Acidification of the aqueous layer followed by ether extraction, drying over sodium sulfate, and removal of the solvent gave 200 mg of a solid. Recrystallization from ethanol afforded desylacetic acid (25%), mp 161–163°.

The organic layer was dried over sodium sulfate and the solvent was removed *in vacuo*. The residue was chromatographed on a 3 × 98 cm Florisil column. The column was eluted with 400 ml of 50% hexane–benzene. The eluent, in 50-ml fractions, was concentrated and dried *in vacuo*. Fractions 4–8 contained 80 mg of 3,4-diphenylfuran (XIII), mp 107–108°. 3,4-Diphenylfuran (XIII), formed in 12% yield, shows infrared absorption at 6.24, 6.50, 9.50, and 11.40 μ, typical of a phenyl-substituted furan. The ultraviolet spectrum in 95% ethanol has a maximum at 225 mμ (ε 18,300). The nmr spectrum has singlets at τ 2.48 (one proton) and 2.76 (five protons). Final verification was obtained by comparison with an authentic sample prepared by a procedure described by Farnum.[49]

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(48) J. Thiele, *Ann.*, **306**, 196 (1894).

(49) D. G. Farnum and M. Burr, *J. Org. Chem.*, **28**, 1387 (1963).

Further elution of the column with benzene gave 100 mg of 2-phenyl-1,4-napthoquinone (XV), mp 111–112°. The quinone, formed in 10% yield, was characterized by the following spectral properties: ultraviolet spectrum had $\lambda\lambda_{max}$ (95% ethanol) 337 mμ (ϵ 4600), 303 (6800), and 249 (24,700); infrared spectrum had λ_{max} (KBr) 6.03, 6.30, 13.19, and 14.50 μ; 60-Mc nmr (deuteriochloroform) showed multiplet at τ 2.17 (nine protons), singlet at 2.97 (one proton). Proof of structure XV was obtained by comparison with an authentic sample.[50] Further elution of the chromatographic column with 10% ethyl acetate–benzene gave 300 mg of 3,4-diphenyl-4-hydroxy-2-butenoic (35%) acid γ-lactone (XI), identified by comparison of its infrared spectrum with that of an authentic sample.

Irradiation of 2,3-Diphenylfuran. A solution of 500 mg of 2,3-diphenylfuran[27] in 100 ml of anhydrous benzene was irradiated with an internal, water-cooled mercury arc lamp (Hanovia, Type L, 450 w) with a Vycor filter. Aliquots were removed and analyzed by gas–liquid chromatography. The analytical gas chromatography was performed on an Aerograph Hy-Fi instrument with nitrogen as the carrier gas on a column of SE-30 (5%) on Chromosorb W at 225°. After 20 hr the peak due to starting material had completely disappeared and a new peak appeared with a slightly higher retention time. At no time during the irradiation did any other peak appear. After the irradiation was completed, the solution was evaporated to dryness to give an orange oil. The crude residue was chromatographed on a 3 × 98 cm silica gel column. The column was eluted with 1 l. of benzene. The eluent, in 50-ml fractions, was concentrated and dried *in vacuo*. Fractions 9–14 contained 200 mg of a white solid, mp 112–114°. Recrystallization from pentane and vacuum sublimation at 0.1 mm in a microsublimation apparatus gave crystals, mp 118.5–119°, which gave a satisfactory elemental analysis for [9,10-*b*]phenanthrofuran (XVI).

Anal. Calcd for $C_{16}H_{10}O$: C, 88.05; H, 4.62. Found: C, 87.80; H, 4.85.

The infrared spectrum of this material showed a strong band at 13.1 μ. The ultraviolet spectrum (95% ethanol) has $\lambda\lambda_{max}$ at 352 mμ (ϵ 1300), 335 (1200), 320 (800), 3.02 (12,300), 290 (10,600), 280 (14,800), 254 (64,600), 249 (52,100), and 237 (30,000). The molecular weight (calcd 218, found 228) is consistent with a monomeric unit. The structure of this material was determined to be [9,10-*b*]phenanthrofuran (XVI) by conversion to [9,10-*b*]phenanthrofuran-2-carboxaldehyde (XVII) and comparison to a sample of XVII independently synthesized as described below.

Preparation of [9,10-*b*]Phenanthro-2-carboxaldehyde (XVII). To 500 mg of dimethylformamide with stirring and cooling in an ice bath was added 142 mg of phosphorus oxytrichloride. The mixture was subsequently stirred for 10 min in the ice bath and then 170 mg of [9,10-*b*]phenanthrofuran (XVI) was added to the cooled solution. The mixture was kept at 0° for 10 min and at 80° for 5 min and then poured onto ice. The aqueous layer was extracted with ether and the extracts were dried over sodium sulfate. Evaporation of the solvent and drying afforded 450 mg of a dark oil. The crude mixture was dissolved in benzene and passed through an alumina column (activity III). Elution of the chromatographic column with 1% ethyl acetate-benzene gave 150 mg of a yellow solid, mp 146–152°. Recrystallization from hexane–benzene gave yellow needles, mp 153–154° dec.

Anal. Calcd for $C_{17}H_{10}O_2$: C, 82.91; H. 4.09. Found: C, 82.79; H, 4.43.

The infrared spectrum of the crystalline compound in a KBr pellet is characterized by a strong band at 5.97 and bands at 8.63, 9.05, 10.52, and 12.31 μ. The ultraviolet spectrum in 95% ethanol has $\lambda\lambda_{max}$ at 358 mμ (ϵ 12,300), 342 (14,900), 333 (15,500), 257 (40,500), 249 (41,700), and 244 (40,800). The nmr spectrum in deuteriochloroform has a singlet at τ 0.33 (one proton) and two complex multiplets at 1.69 and 2.41 (nine protons). The identity of the Vilsmeier product as [9,10-*b*]phenanthrofuran-2-carboxaldehyde (XVII) was further confirmed by comparison with a sample independently prepared by selenium dioxide oxidation of 2-methyl[9,10-*b*]phenanthrofuran (XVIII).

In a sealed tube was placed 1.0 g of XVIII[39] and 480 mg of selenium dioxide. The tube was heated at 140–150° for 30 min. After the oxidation was complete the contents of the tube were taken up in ether and filtered through a glass funnel to remove selenium metal. Evaporation of the solvent left a dark oil which was chromatographed on a 3 × 48 cm column of silica gel. The column was eluted with 1% ethyl acetate–benzene. After elution of starting material (300 mg) with 800 ml of solvent, 200 mg of a yellow solid was eluted with 750 ml of 2% ethyl acetate-benzene. Recrystallization from hexane afforded yellow needles, mp 152–153°. The infrared and nmr spectra of this material were identical in every detail with that of XVII prepared from the Vilsmeier reaction of XVI. The mixture melting point of these two materials was undepressed at 152–154°.

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Photosensitized Reactions of Cyclobutene in Solution

R. Srinivasan and K. A. Hill

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Abstract: Irradiation of a solution of cyclobutene in acetone gives rise to tricyclo[4.2.0.$0^{2,5}$]octane, 5-methyl-4-hexenal, and cyclobutylacetone as the major products. Quantum yields for the formation of these products have been obtained at 2537 and 3130 A as a function of the concentration of cyclobutene. It is believed that 5-methyl-4-hexenal is formed through the addition of an excited acetone molecule to cyclobutene to give an oxetane which subsequently decomposes to this product. The irradiation of acetone and 1-methylcyclobutene gives 6-methyl-5-hepten-2-one in a similar fashion. Cyclobutylacetone is probably formed by a free-radical reaction that is photoinitiated. The formation of all three of the products is quenched by the presence of even a trace of biacetyl. It is estimated that for every collision of a triplet acetone with a cyclobutene that gives an oxetane, there are 11 collisions which result in energy transfer to give a triplet cyclobutene.

The photochemical reactions that cyclic monoolefins undergo on sensitized excitation have been studied quantitatively in a number of instances in the gas phase, but scarcely ever in solution. In particular, the sensitized reactions of cyclobutene have received very little attention in either phase. The photochemistry of cyclobutene is of interest in two ways: (i) since it is in itself a "small-ring" compound, it can be expected to give novel products through addition reactions, and (ii) the rigidity imposed by the four-membered ring would allow very little freedom to the olefinic group to twist in the excited state. As a result, the range of