Photochemical Transformations of Small Ring Carbonyl Compounds. VIII. Photorearrangements in the Cyclopentenone Oxide Series[1,2]

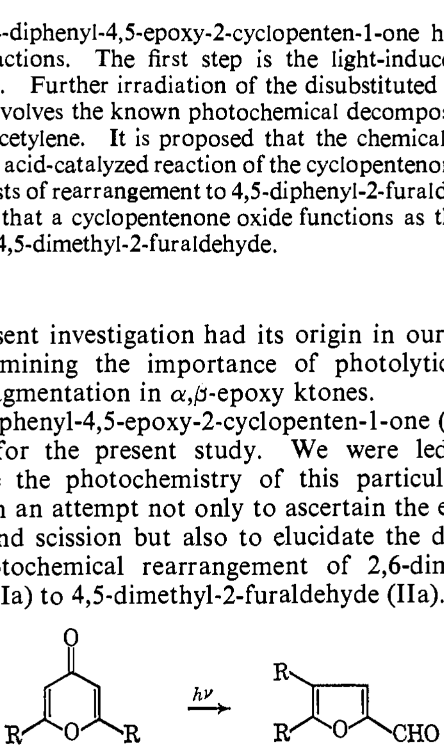
Albert Padwa and Richard Hartman[3]

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received October 18, 1965*

Abstract: The isolation of *p*-terphenyl from the photolysis of 3,4-diphenyl-4,5-epoxy-2-cyclopenten-1-one has been resolved into a sequence of three discrete photochemical reactions. The first step is the light-induced rearrangement of the cyclopentenone oxide to 4,5-diphenyl-2-pyrone. Further irradiation of the disubstituted 2-pyrone led to 1,2,4,7-tetraphenylcyclooctatetraene. The final step involves the known photochemical decomposition of the cyclooctatetraene derivative to *p*-terphenyl and diphenylacetylene. It is proposed that the chemically active excited state of the cyclopentenone oxide is a π–π^* singlet. The acid-catalyzed reaction of the cyclopentenone oxide derivative involves complex processes, but one of the paths consists of rearrangement to 4,5-diphenyl-2-furaldehyde. This result is consistent with and supports the interpretation that a cyclopentenone oxide functions as the initial intermediate in the rearrangement of 2,6-dimethyl-4-pyrone to 4,5-dimethyl-2-furaldehyde.

Spectroscopic evidence of the electronic interaction of small rings with adjacent unsaturated groups has been described thoroughly in the literature.[4] In addition to these spectroscopic studies, increased emphasis has been given during the past few years to the photochemistry of three-membered ring compounds having a carbonyl group attached to one of the ring carbons. In particular, recent investigations of a number of α,β-epoxy ketones have demonstrated that these species are exceptionally reactive under the influence of ultraviolet light.[5] Irradiation may lead to geometrical isomerization,[6] to rearrangement,[7] to internal hydrogen abstraction,[8] to photofragmentation,[9] or to photochemical valence tautomerization.[10] In those cases which have been fully investigated, it has usually been found that the photolysis can be described by a cleavage of the α-C–O bond of the oxide ring followed by a multitude of possible second steps. The driving force for the fission of the epoxide ring was attributed to the tendency of the excited n–π^* state to eliminate α substituents as odd-electron or anionic species according to the reaction medium.[8] However, it has recently been demonstrated that a number of the photochemical reactions in this series may be envisaged as proceeding *via* scission of the α-C-β-C bond.[11–14] The present investigation had its origin in our interest in determining the importance of photolytic C_α–C_β bond fragmentation in α,β-epoxy ktones.

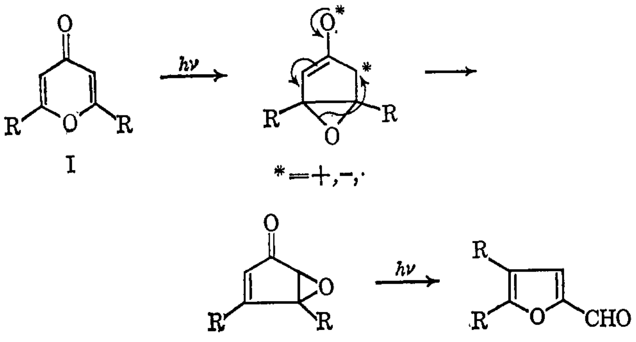
3,4-Diphenyl-4,5-epoxy-2-cyclopenten-1-one (III) was chosen for the present study. We were led to investigate the photochemistry of this particular compound in an attempt not only to ascertain the extent of C–C bond scission but also to elucidate the details of the photochemical rearrangement of 2,6-dimethyl-4-pyrone (Ia) to 4,5-dimethyl-2-furaldehyde (IIa).



I II

Ia, IIa, R = Me
Ib, IIb, R = Ph

Studies of the ultraviolet irradiation of 2,6-dimethyl-4-pyrone (Ia) in either the solid state or in solution have shown that a "head-to-tail" cage dimer was formed exclusively.[15] When the photolysis was carried out under conditions chosen to retard dimerization, a low yield of an unusual rearranged product was detected.[16] Yates has suggested that the mechanism of this trans-



I

* = +, −, ·

III IIa

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(1) For preliminary reports of this work see (a) A. Padwa, *Tetrahedron Letters*, No. 15, 813 (1964); (b) A. Padwa and R. Hartman, *J. Am. Chem. Soc.*, **86**, 4212 (1964); (c) A. Padwa, *Tetrahedron Letters*, No. 16, 1049 (1965).

(2) This work was presented in part at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1964.

(3) National Science Foundation Predoctoral Fellow, 1963–1965; National Institutes of Health Predoctoral Fellow, 1965–1966.

(4) For a summary of leading references see A. L. Goodman and R. H. Eastman, *J. Am. Chem. Soc.*, **86**, 908 (1964).

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

(6) C. K. Johnson, B. Dominy, and W. Reusch, *J. Am. Chem. Soc.*, 3894 (1963).

(7) S. Bodforss, *Chem. Ber.*, **51**, 214 (1918).

(8) H. E. Zimmerman, B. R. Cowley, C. Y. Tseng, and J. W. Wilson, *J. Am. Chem. Soc.*, **86**, 1947 (1964).

(9) H. E. Zimmerman, Abstracts of the 17th National Organic Chemistry Symposium, Atlantic City, N. J., Sept 1962, p 89Q.

(10) E. F. Ullman and J. E. Milks, *J. Am. Chem. Soc.*, **86**, 3814 (1964).

(11) E. F. Ullman, *ibid.*, **85**, 3529 (1963).

(12) J. M. Dunston and P. Yates, *Tetrahedron Letters*, 505 (1964).

(13) A. Padwa, *ibid.*, 813 (1964).

(14) H. E. Zimmerman and R. D. Simkin, *ibid.*, 1847 (1964).

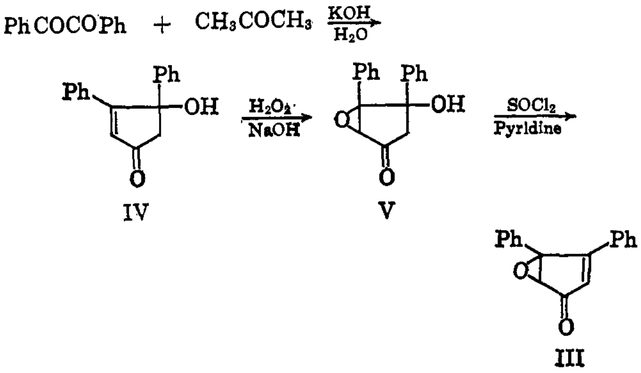
(15) P. Yates and M. J. Jorgenson, *J. Am. Chem. Soc.*, **85**, 2956 (1963).

(16) P. Yates and I. W. J. Still, *ibid.*, **85**, 1208 (1963).

formation proceeds by a route analogous to those cases possessing the corresponding carbocyclic system, *i.e.*, 4,4-diphenyl-2,5-cyclohexadienone (see above).[17,18]

Results

The resolution of this complex photochemical transformation into a sequence of separate photochemical rearrangements necessitates a description of the intermediates involved between starting material and product. In order to confirm the role of a cyclopentenone oxide as an intermediate in the above sequence, 3,4-diphenyl-4,5-epoxy-2-cyclopenten-1-one (III) was chosen for the present study. Cyclopentenone oxides have not been described in the literature, but a convenient three-step synthesis was devised, beginning with benzil. Condensation of equimolar quantities of benzil and acetone afforded 4-hydroxy-3,4-diphenyl-2-cyclopenten-1-one (IV).[19] Treatment of the latter with 10% sodium hydroxide and 30% hydrogen peroxide in methyl alcohol readily gave rise to epoxy alcohol V. Dehydration of the tertiary alcohol with thionyl chloride–pyridine in benzene afforded in excellent yield the desired starting material.



Photolysis of 3,4-diphenyl-4,5-epoxy-2-cyclopenten-1-one (III) in anhydrous ether at 25° for 18 hr with ultraviolet light of wavelength above 260 mμ afforded a mixture of products. The two major components were *p*-terphenyl (VIII), mp 212°, and diphenylacetylene (IX), mp 62°.[20] Irradiation of cyclopentenone oxide (III) for shorter periods of time gave, in addition to VIII and IX, 4,5-diphenyl-2-pyrone (VI) and 1,2,4,7-tetraphenylcyclooctatetraene (VII), separated by alumina chromatogratography. Consideration of the product distribution as a function of time in a number of photolyses showed an initial buildup of an intermediate 4,5-diphenyl-2-pyrone, isomeric with III, followed by a decrease in amount. This contrasted with a steady increase in the yields of diphenylacetylene and *p*-terphenyl (Table I).

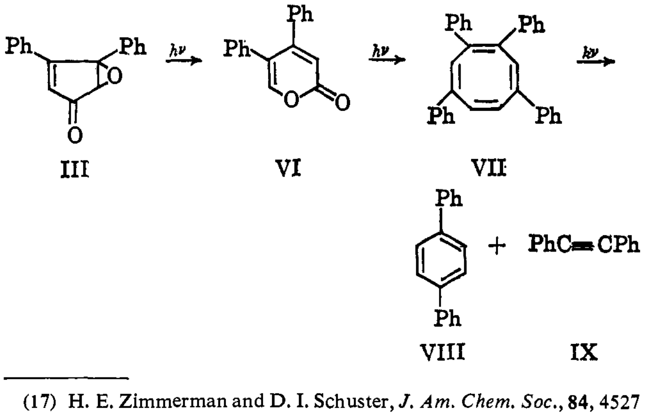
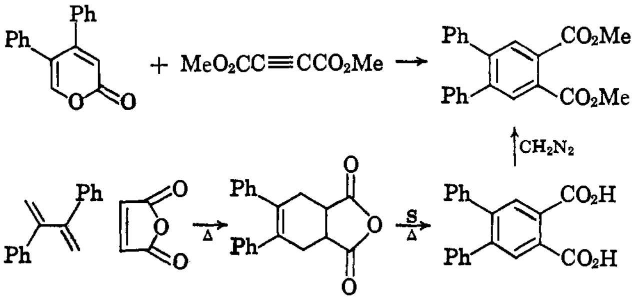


Table I. Product Distribution *vs.* Extent Conversion from the Photolysis of 3,4-Diphenyl-4,5-epoxy-2-cyclopenten-1-one

Run	Time, hr	Products, % yield[a] VI	VII	VIII	IX
1	0.16	96	0	0	0
2	1	52	24	0	0
3	2	38	19	10	6
4	4	11	14	25	17
5	18	0	4	39	34

[a] Material balance did not add up to 100% in the longer photolysis experiments because of the formation of several minor components.

Ultraviolet irradiation of a solution of III in ether for only 10 min, utilizing in this case a Pyrex filter, affords the intermediate VI in almost quantitative yield. Its infrared spectrum shows a strong carbonyl band at 5.78 and a sharp weak spike at 6.13 μ. The nmr spectrum is in excellent agreement with the structure. There is a singlet at τ 2.60, a multiplet at 2.92, and a singlet at 3.79. The peak areas are in the ratio of 1:10:1. Chemical confirmation was obtained by heating VI with dimethylacetylene dicarboxylate at 150° for 12 hr. The product obtained in better than 90% yield was identical with an authentic sample of 1,2-diphenyl-4,5-dicarbomethoxybenzene, synthesized by the method of Alder.[21]



Further evidence that 4,5-diphenyl-2-pyrone (VI) is an intermediate in the formation of the remaining products was confirmed by the finding that the photolysis of VI itself in anhydrous ether afforded VII, VIII, and IX in about the same distribution as found in runs beginning with 3,4-diphenyl-4,5-epoxy-2-cyclopenten-1-one. The yields of these compounds are strongly affected by the length of the irradiation, as shown in Table I. As VI decreases, VII appears and, more slowly, VIII and IX are formed. Continued irradiation gives mostly *p*-terphenyl and diphenylacetylene. The structures of VII, VIII, and IX are based on the following observations. The infrared spectrum of VII showed a weak band at 6.16 μ attributed to the carbon–carbon double bond stretching frequency of the cyclo-

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(17) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, 84, 4527 (1964).

(18) Zimmerman, in his interpretation of the mechanisms of photochemical reactions involving dienones, has written the excitation step as forming a species with both ionic and radical character. The nature of the transition involved in the rearrangement of the 4-pyrone is not defined, and consequently an asterisk is used to indicate the excited character of this state.

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

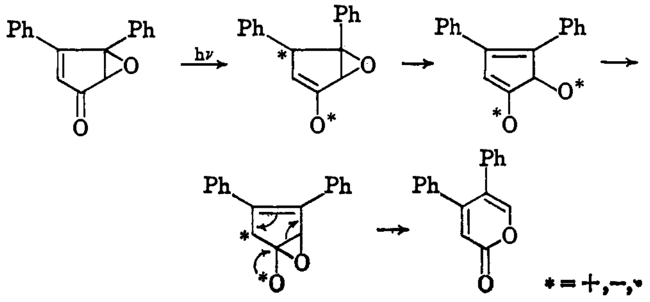
(20) Current work is being directed toward the identification of the minor products, all of which are characterized by the absence of a carbonyl band in the infrared region.

(21) K. Alder and J. Haydn, *Ann.*, 570, 201 (1950).

octatetraene ring.[22] The intense ultraviolet absorption at 263 mμ (log ϵ 4.71) is in accord with structure VII. The nmr spectrum of VII has a multiplet centered at τ 2.68, a singlet at 3.12, and a singlet at 3.39. The peak areas are in the ratio of 1:10:1. Elemental analysis and a molecular weight determination also support structure VII. The infrared spectrum of this substance in a potassium bromide pellet was identical in every detail with that of an authentic sample of 1,2,4,7-tetraphenylcyclooctatetraene.[23] *p*-Terphenyl and diphenylacetylene were identified by comparison of infrared spectra and mixture melting point with those of authentic samples.

Discussion

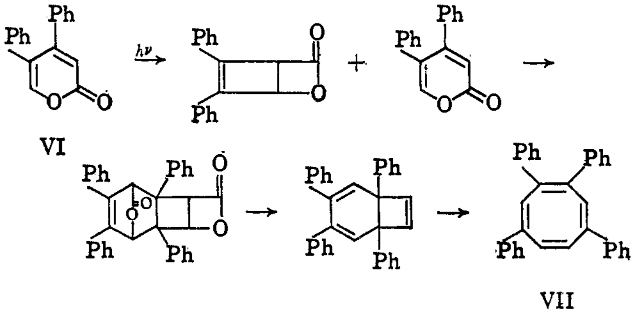
The behavior of III upon irradiation differs considerably from the rearrangement of related cyclopentenone oxides reported by Ullman and Milks.[24] The latter authors found the existence of a photochemical valence tautomerization between starting material and a dipolar pyrylium 3-oxide. Evidence was presented demonstrating that for the case of 2,3-epoxy-2,3-diphenylindanone, the pyrylium 3-oxide is solely responsible for the formation of the observed product.[25] We have found, however, that III proceeds directly to VI without the intervention of a pyrylium oxide. The fact that no coloration appears during the photolysis and that attempts to trap a transient pyrylium oxide were unsuccessful provides evidence against such a species. The photolytic rearrangement of III to VI may be accounted for in the following manner.



The excited state which is directly responsible for rearrangement may be represented as a dipolar state, since the rearrangement seems to be characteristic of a polar process.[26,27] Such a visualization allows one to formulate the excited state in the form of a convenient, although admittedly approximate, valence-bond structure.

The quantum yield for the rearrangement of III to VI is high (ϕ = 0.47), implying that the two most likely steps for deactivation of the lowest excited singlet state (S_1) of III are either photochemical rearrangement to VI or intersystem crossing to the lowest triplet of III, T_1, followed by rearrangement. However, no phosphorescence from III (a yield of 0.002 would have been detected) was observed at 77°K in an ethanol–ether–isopentane glass[28] and the photolysis could not be quenched by a high concentration (see the Experimental Section) of 1,3-pentadiene. These facts imply that T_1 is not involved in these photolyses.[29] So far, the discussion has avoided the problem of identifying the nature of the excited singlet involved in the photorearrangement. The formation and participation of either n–π^* or π–π^* singlets in the photorearrangement studied here remains sufficiently attractive to warrant further investigation.

The light-induced rearrangement of 4,5-diphenyl-2-pyrone to 1,2,4,7-tetraphenylcyclooctatetraene represents the most complex step in the sequence outlined above. A recent report describing an internal photoaddition reaction of α-pyrone suggests a likely mechanism, however. Corey[34] found that the low-temperature ultraviolet irradiation of 2-pyrone in ether afforded in almost quantitative yield a photoisomer to which a bicyclic β-lactone structure was assigned. The intermediacy of a bicyclic β-lactone suggests the sequence shown below as a reasonable series of events in the formation of the cyclooctatetraene derivative.



Attempts to isolate the hypothetical bicyclic β-lactone by irradiation at low temperatures were unsuccessful. Irradiation of VI in the solid state or in a decane matrix at −185° revealed no carbonyl band in its infrared spectrum at wavelengths shorter than 5.65 μ.[35] Experiments designed to trap the transient β-lactone at low temperatures in the presence of dimethylacetylene dicarboxylate or with 2,5-diphenyl-3,4-isobenzofuran were unsuccessful. It is quite conceivable that this particular β-lactone is very photolabile itself, because of the presence of the stilbene chromophore, and reacts instantaneously with additional pyrone to give VII.

The final step in the sequence involves the known photochemical decomposition of 1,2,4,7-tetraphenylcyclooctatetraene (VII).[36] White has reported recently that the irradiation of VIII gave a mixture of com-

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[22] E. H. White and H. C. Dunathan, *J. Am. Chem. Soc.*, **86**, 453 (1964).

[23] A highly purified sample was kindly provided by Professor Emil H. White.

[24] E. F. Ullman and J. E. Milks, *J. Am. Chem. Soc.*, **84**, 1315 (1962).

[25] E. F. Ullman and W. A. Henderson, *ibid.*, **86**, 5050 (1964).

[26] O. L. Chapman, "Advances in Photochemistry," Interscience Publishers, Inc., New York, N. Y., 1963, Chapter IX.

[27] Events leading to the same dipolar intermediates can also be expressed in reasonable terms by the Zimmerman theory.[17]

[28] We wish to thank Professor P. J. Wagner for obtaining this information for us.

[29] However, it has been noted already by several workers that the absence of quenching by triplet acceptors is inconclusive evidence against a triplet mechanism, as photoreaction of T_1 may be more rapid than energy transfer to 1,3-pentadiene.[30-33]

[30] G. S. Hammond, N. J. Turro, and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1144 (1962).

[31] H. E. Zimmerman and J. S. Swenton, *J. Am. Chem. Soc.*, **86**, 1436 (1964).

[32] N. J. Turro, P. A. Leermakers, H. R. Wilson, D. C. Neckers, G. W. Byers, and G. F. Vesley, *ibid.*, **87**, 2613 (1965).

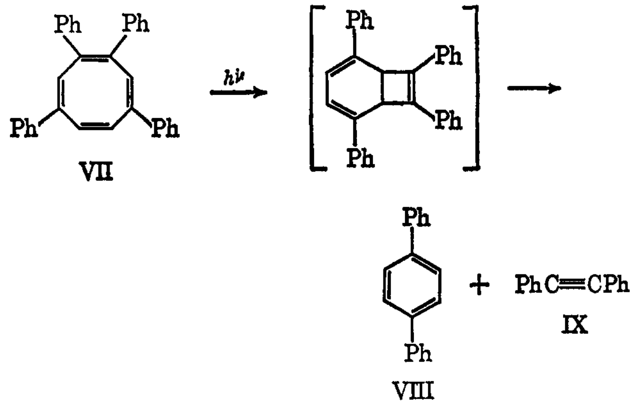
[33] H. E. Zimmerman and J. W. Wilson, *ibid.*, **86**, 4036 (1964).

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

[35] The authors wish to acknowledge Professor Emil White for supplying us with the low-temperature data and for his interest in the work.

[36] E. H. White and R. L. Stern, *Tetrahedron Letters*, No. 4, 193 (1964).

pounds from which *p*-terphenyl and diphenylacetylene could be isolated in moderate yield.



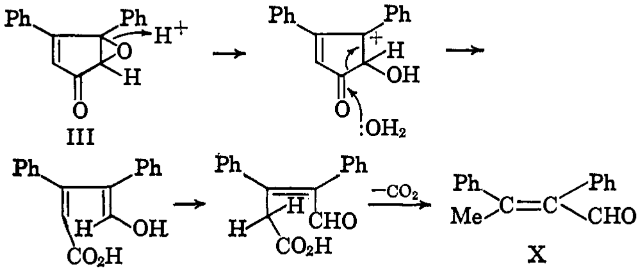
The mechanism for the photochemical transformation of 3,4-diphenyl-4,5-epoxy-2-cyclopenten-1-one to *p*-terphenyl, now firmly established, constitutes an exceedingly complex sequence of photoreactions. Presently we restrict comment to a note of caution of interpreting a complex sequence without at least a knowledge of the number of excitation steps involved and the sequence of these excitations.

The data outlined above clearly establish that III does not rearrange photochemically to a furan derivative. Although the present evidence does not completely rule out the intermediacy of a cyclopentenone oxide in the rearrangement of 2,6-dimethyl-4-pyrone (Ia) to 4,5-dimethyl-2-furaldehyde (IIa), it does appear to cast some doubt on it. The failure to isolate the corresponding 2-furaldehyde from the photolysis of III suggests that another mechanism may obtain. Yang has suggested that there may be a large difference in the photochemistry of molecules, depending whether $n-\pi^*$ or $\pi-\pi^*$ is the low-lying excited state.[37] It is known that β-phenyl substituents have a very marked effect on the level of $\pi-\pi^*$ singlet excited states of α,β-unsaturated ketones.[38] It would not be surprising, therefore, that this substituent might alter the course of the photoreaction for the different cyclopentenone oxides. We have examined the photolysis of 2,6-diphenyl-4-pyrone. Should the reaction proceed by way of a cyclopentenone oxide, then the products from the photolysis of 2,6-diphenyl-4-pyrone would be well defined.

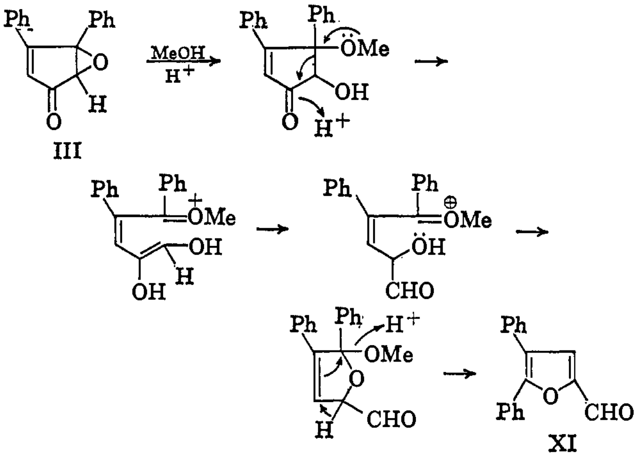
Irradiation of a solution of 2,6-diphenyl-4-pyrone (Ib) in benzene with a medium-pressure mercury lamp gave a single photodimer in high yield.[39] Careful examination of the residue revealed no detectable amounts of monomeric material other than Ib. Control experiments demonstrated that as little as 0.5% of III, VI, VII, or VIII would have been detected by the recording ultraviolet spectrophotometer employed (see the Experimental Section). The isolation of a single photodimer from Ib cannot, therefore, shed any information on the mechanism of the photoisomerization.

In order to evaluate the possible intervention of competing ground-state reactions, we have carried out the acid-catalyzed reaction of III. At the time, it was hoped that the rearrangement of the cyclopentenone oxide to the furan derivative might proceed *via* a nonphotochemical route.

Treatment of III with aqueous acidic methanol resulted in a mixture of two major products. Separation by alumina chromatography gave 2,3-diphenylcrotonaldehyde (X) in addition to 4,5-diphenyl-2-pyrone (VI). 2,3-Diphenylcrotonaldehyde was identified by comparison with an authentic sample.[40] A reasonable mechanism for the formation of X is presented below.



When the reaction was carried out using anhydrous methanol (containing gaseous hydrogen chloride), there was obtained a complex mixture of products, from which was isolated in approximately 10% yield a new unsaturated aldehyde, 4,5-diphenyl-2-furaldehyde (XI). Proof of structure XI was obtained by comparison with an authentic sample prepared by the Vilsmeier reaction of 2,3-diphenylfuran[1c] with a 1:1 complex of dimethylformamide and phosphorus oxychloride.



This result demonstrates that a cyclopentenone oxide is indeed capable of rearranging to a 2-furaldehyde. We cannot yet rule out the posssibility of direct formation of 4,5-dimethyl-2-furaldehyde from the photolysis of 3,4-dimethyl-4,5-epoxy-2-cyclopenten-1-one. As mentioned earlier, more than one kind of excited cyclopentenone oxide may be involved in the rearrangement which leads to photoproduct.

Experimental Section[41]

3,4-Diphenyl-4,5-epoxy-2-cyclopenten-1-one (III). To 20.0 g of 4-hydroxy-3,4-diphenyl-2-cyclopenten-1-one (IV) dissolved in 400

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[37] N. C. Yang and M. J. Jorgenson, *Tetrahedron Letters*, 1203 (1964).

[38] H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p 239.

[39] The structure of this photodimer was not investigated.

[40] R. Breslow, J. Lockhart, and A. Small, *J. Am. Chem. Soc.*, **84**, 2793 (1962).

[41] 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.

ml of methanol was added 90 ml of 30% hydrogen peroxide and 30 ml of 10% sodium hydroxide solution. The mixture was allowed to stand at room temperature for 12 hr. It was then diluted with an equal volume of water, saturated with sodium chloride, and thoroughly extracted with ether. The ethereal extracts were washed with sodium thiosulfate solution and dried over sodium sulfate. Evaporation of the solvent left 16.8 g (80%) of a pale yellow residue, which rapidly crystallized on addition of hexane–benzene to give a colorless solid, mp 115–116°. The material analyzed for 3-hydroxy-3,4-diphenyl-4,5-epoxy-2-cyclopenten-1-one (V).

Anal. Calcd for $C_{17}H_{14}O_3$: C, 76.67; H, 5.30. Found: C, 76.61; H, 5.32.

The infrared spectrum of the epoxy alcohol in carbon tetrachloride has bands at 2.8–3.0 and 5.70 μ. The nmr spectrum in carbon tetrachloride has a multiplet centered at τ 2.84, a singlet at 6.15, a broad singlet at 6.78, and a doublet at 7.08. The integrated peak areas are in the ratio of 10:1:1:2.

A solution of 20.0 g of 3-hydroxy-3,4-diphenyl-4,5-epoxy-2-cyclopenten-1-one and 12.64 g of pyridine in 400 ml of benzene was cooled to 0° and 9.50 g of thionyl chloride in 200 ml of benzene was added dropwise over 45 min. The solution was stirred for an additional 30 min during which time the temperature was allowed to rise to 20°. The mixture was filtered to remove the pyridine hydrochloride. The solution was washed twice with 100-ml portions of water and dried over sodium sulfate. Evaporation of the solvent left 19.0 g of a pale yellow oil. This material was taken up in hexane–benzene and a crystalline solid soon precipitated. The solid amounted to 12.0 g (60%), mp 108–114°, and was repeatedly recrystallized from hexane–benzene to give a solid, 126–127°.

Anal. Calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87. Found: C, 82.27; H, 4.89.

The infrared spectrum of the crystalline compound in carbon tetrachloride is characterized by a carbonyl band at 5.84 and bands at 6.24, 11.4, and 11.6 μ. The ultraviolet spectrum in 95% ethanol has λ_{max} 307 mμ (ϵ 10,300). The nmr spectrum (CCl_4) of the epoxy ketone shows a doublet at τ 6.53 due to the methine proton and a doublet at 3.87 due to the olefinic proton (τ = 3.1 cps) the aromatic protons exhibit a multiplet at τ 2.78. The peak areas are in the ratio of 1:1:10.

Irradiation of 3,4-Diphenyl-4,5-epoxy-2-cyclopenten-1-one. A solution of 1.0 g of III in 1 l. of anhydrous ether[42] was irradiated with an internal water-cooled mercury arc lamp (Hanovia, Type L, 450 w) with a Pyrex filter to eliminate wavelengths below 280 mμ. Aliquots were removed and analyzed by thin layer chromatography. After 15 min the spot on a thin layer plate due to Ib had completely disappeared and a new spot had appeared in its place. Concentration of the solution left an oil, which rapidly crystallized on addition of hexane–benzene to give 4,5-diphenyl-2-pyrone as a colorless solid, mp 118–119°.

Anal. Calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87. Found: C, 82.28; H, 4.98.

The infrared spectrum shows a strong carbonyl band at 5.78 and a sharp weak spike at 6.13 μ. The ultraviolet spectrum in 95% ethanol has maxima at 237 mμ (ϵ 17,500) and 282 mμ (ϵ 7100). The nmr spectrum is in excellent agreement with the structure. There is a singlet at τ 2.60, a multiplet at 2.92, and a singlet at 3.79. The peak areas are in the ratio of 1:10:1.

Diels–Alder Reaction of 4,5-Diphenyl-2-pyrone with Dimethylacetylene Dicarboxylate. A mixture of 100 mg of 4,5-diphenyl-2-pyrone and 57 mg of dimethylacetylene dicarboxylate was heated in a sealed tube at 150° for 12 hr. Vacuum sublimation of the crude reaction mixture at 0.1 mm in a microsublimation apparatus gave crystals, mp 122–123°, which gave a satisfactory elemental analysis for 1,2-diphenyl-4,5-dicarbomethoxybenzene.

Anal. Calcd for $C_{22}H_{18}O_4$: C, 76.28; H, 5.24. Found: C, 76.41; H, 5.29.

The infrared spectrum of the diester is chiefly characterized by a sharp intense carbonyl band at 5.79 μ. The nmr spectrum in carbon tetrachloride has a sharp singlet at τ 2.25, a singlet at 2.83, and a sharp singlet at 6.12. The integrated peak areas are in the ratio of 1:5:3. The mixture melting point of this material (122–123°) with that of 1,2-diphenyl-4,5-dicarbomethoxy benzene prepared independently by the procedure of Alder[21] was undepressed at 121–123°.

Attempted Trapping of 4,5-Diphenylpyrylium 3-Oxide. Photolysis of 3,4-diphenyl-4,5-epoxy-2-cyclopenten-1-one (III) for 20 min with 2900–3900-A light from a 200-w Hanovia medium-pressure lamp gave only 4,5-diphenyl-2-pyrone. The nickel sulfate–cobalt sulfate filter combination was used to isolate the specified wavelength range of light used.[43] During the photolysis it was noted that the usual orange color of related pyrylium 3-oxides did not develop. Attempts to trap the hypothetical 4,5-diphenylpyrylium 3-oxide with dimethylacetylene dicarboxylate were unsuccessful. An ethereal solution of III and a 10-mole excess of dimethylacetylene dicarboxylate was irradiated with 2900–3900-A light. Removal of the solvent followed by chromatography on alumina gave only 4,5-diphenyl-2-pyrone in 95% yield.

Measurement of Quantum Yields. The optical bench described by Pitts and Calvert[44] was used in these experiments. It consisted of a Hanovia (Type 673A) 500-w, medium-pressure mercury lamp whose light was collected and collimated by lenses so that a parallel beam of light would pass through a filter holder and cell holder mounted on an optical bench. Light intensities were monitored just before and just after sample irradiation. After the irradiation the degree of rearrangement was determined by ultraviolet absorption measurements. Details of the measurements are given in Table II.

Table II. Quantum Yields for Photorearrangement of III to VI in Dioxane at 25°[a]

Run	[III], mg l.$^{-1}$	[VI], mg l.$^{-1}$	10^{-15} I, quantum sec^{-1}	$10^3 t$, sec	% conversion	ϕ_{III}
1	50.88	7.75	2.52	2.7	15.3	0.51
2	49.51	4.50	2.77	1.8	9.1	0.45
3	49.07	2.75	2.76	1.2	5.6	0.42
4	49.51	4.60	2.31	1.8	9.4	0.48
5[b]	49.67	4.87	2.58	1.8	9.8	0.47

[a] 3130-A light, quartz reaction cells, and ferrioxalate actinometry. [b] A 25-mole excess of *cis*-piperylene (5 mmoles) was used in an attempt to suppress the quantum yield of the photorearrangement.

Photolysis of 4,5-Diphenyl-2-pyrone (VI). A solution of 4,5-diphenyl-2-pyrone (1.0 g) in anhydrous ether (1 l.) was irradiated with a Hanovia 450-w mercury arc lamp using a Corex filter. The photolysis was followed by withdrawing small samples at fixed intervals without interrupting the system. The samples were analyzed by thin layer chromatography. After 4 hr, 95% of the starting material had disappeared and four new spots had appeared in its place. 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 alumina (Woelm, neutral, grade 2) column. The column was eluted with 4 l. of petroleum ether (bp 60–68°). The eluent, in 50-ml fractions, was concentrated and dried *in vacuo*. Fractions 3–6 contained 117 mg of a white solid, mp 54–61°. Recrystallization from pentane afforded a crystalline solid, mp 62–63°. Fractions 8–12 contained 156 mg of material, mp 198–206°. Recrystallization from pentane gave a white solid, mp 212–213°. Fractions 37–48 contained 138 g of a yellow solid, mp 133–135°. The three major products obtained from the photolysis were assigned structures IX (diphenylacetylene), VIII (*p*-terphenyl), and VII (1,2,4,7-tetraphenylcyclooctatetaene). The yields of these compounds are strongly affected by the length of the irradiation as shown in Table III. As VI decreases, VII appears and, more slowly, VIII and IX are formed. Continued irradiation gives mostly *p*-terphenyl and diphenylacetylene. The amounts of the pure components isolated are reported in Table III.

The structures of VII, VIII, and IX are based on the following observations. The infrared spectrum of VII showed a weak band at 6.16 μ attributed to the carbon–carbon double bond stretching frequency of the cyclooctatetraene ring. The intense ultraviolet absorption at 263 mμ (log ϵ 4.71) is in accord with structure VII. The nmr in deuteriochloroform has a multiplet centered at τ 2.68, a singlet at 3.12, and a singlet at 3.39. The peak areas are in the ratio of 1:10:1.

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[42] The photolysis of methanol, benzene, carbon tetrachloride, and aqueous dioxane solutions of Ib gave similar transformations.

[43] D. J. Trecker and J. P. Henry, *Anal. Chem.*, **35**, 1882 (1963).

[44] J. Pitts and J. Calvert, "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1964.

Table III. Photolysis of 3,4-Diphenyl-4,5-epoxy-2-cyclopenten-1-on (III)

Run	Amount of epoxide photolyzed, g l.$^{-1}$	Time of photolysis, hr	Products, g, %			
			VI[b]	VII	VIII	IX
1	0.53	0.16	0.51, 96[c,d]	*a*	*a*	*a*
2	1.09	1	0.57, 52	0.21, 24	...	...
3	0.97	2	0.37, 38	0.15, 19	0.11, 10	0.04, 6[e]
4	0.86	4	0.09, 11	0.10, 14	0.20, 25	0.10, 17[e]
5	1.13	6	...	0.08, 9	0.35, 34	0.22, 27[e]
6	1.02	18	...	0.05, 4	0.37, 39	0.25, 34[e]

[a] Thin layer chromatography indicated the absence of these materials. [b] Material separated by alumina chromatography; figures represent approximate yields. There are indications that starting material isomerizes to VI on alumina. [c] Infrared of the crude residue indicated that there was no recovered starting material. [d] Pyrex filter was used. [e] Material balance did not add up to 100% in the longer photolysis experiments due to the formation of other products which have not yet been identified.

Anal. Calcd for $C_{32}H_{24}$: C, 94.08; H, 5.92. Found: C, 94.32; H, 5.89.

The infrared spectrum of this substance was identical in every detail with that of an authentic sample of 1,2,4,7-tetraphenylcyclooctatetraene. The mixture melting point of VII with that of 1,2,4,7-tetraphenylcyclooctatetraene was undepressed at 133–135°. *p*-Terphenyl and diphenylacetylene were identified by comparison of infrared and mixture melting point with that of an authentic sample.

Low-Temperature Photolysis of 4,5-Diphenyl-2-pyrone. Ultraviolet irradiation of a solution of VI in ether at −70° followed by evaporation of the solvent under reduced pressure gave a crude mixture which has no carbonyl band in the 5.40–5.70-μ region of its infrared spectrum. Compound VI was also irradiated in the solid state at −185° and in a decane matrix at liquid nitrogen temperatures. The course of the reaction was followed by infrared irradiation and, again, no carbonyl band appeared at wavelengths shorter than 5.70 μ.

Attempted Trapping of the Internal Photoaddition Product. Attempts to trap the hypothetical β-lactone by coirradiation of 4,5-diphenyl-2-pyrone with 2,5-diphenyl-3,4-isobenzofuran[45] were unsuccessful. An equimolar ethereal solution of VI and 2,5-diphenyl-3,4-isobenzofuran was irradiated with a mercury arc lamp (Hanovia, 450-w) equipped with a Corex filter. Removal of the solvent left an orange mushy semisolid. This material was taken up in ether–hexane to give a quantitative yield of the known photodimer of 2,5-diphenyl-3,4-isobenzofuran.[46] The mother liquors when chromatographed on alumina gave the same distribution of products that were obtained in the absence of added isobenzofuran.

Ultraviolet irradiation of an equimolar solution of VI and diphenylacetylene under the same conditions as outlined above gave, after removal of the solvent, an orange oil. The residue was chromatographed on an alumina column to give a 95% yield of recovered diphenylacetylene and the same distribution of products normally obtained.

Photolysis of 2,6-Diphenyl-4-pyrone (Ib). This material was prepared by the procedure of Hauser and Harris using 1,5-diphenyl-1,3,5-pentanetrione prepared from the condensation of the dipotassio salt of benzoylacetone and methyl benzoate.[47] A 10-g sample of the triketone was dissolved in 100 ml of concentrated sulfuric acid at 0°. After 25 min at this temperature, the solution was poured into ice–water. The resulting precipitate was collected on a funnel, washed with water, and recrystallized from ethanol to give 8.4 g (93%) of pyrone Ib, mp 138–139° (lit[48] mp 139–141°).[48]

Photolysis of Ib in anhydrous benzene at 25° for 48 hr with ultraviolet light of wavelength above 260 mμ deposited a solid on the walls of the flask which could be conveniently separated. This material was only sparingly soluble in all common organic solvents and could be recovered as a fine powder by recrystallization from dimethylformamide. Two recrystallizations followed by thorough washing with petroleum ether gave an analytical sample, mp 283–285° dec (sealed capillary); λ_{max}^{KBr} 5.80, 5.86 μ.

Anal. Calcd for $C_{34}H_{24}O_4$: C, 82.24; H, 4.87. Found: C, 82.59; H, 5.06.

The molecular weight (calcd 496; found 478) is consistent with a dimeric species.

The mother liquors were subjected to liquid–liquid partition chromatography. The separation was carried out in a water-jacketed column (150 × 3.5 cm) which was kept at a constant temperature of 29.0 ± 0.05°. The two-phase liquid system (prepared from 1000 ml of cyclohexane, 400 ml of dimethylformamide, 250 ml of ethyl acetate, and 30 ml of water) was allowed to equilibrate for at least 30 min before use. The liquid–liquid apparatus used in these experiments and the processing of the fractions has been described in detail elsewhere.[17] The chromatogram showed two peaks with retention volume of 1700 ml and 3200 ml of mobil phase. The first peak had an infrared spectrum identical with 2,6-diphenyl-4-pyrone. The last peak after workup gave 760 mg of the photodimer described above. There was no indication of any other component in the chromatogram. The material balance was nearly 100% in terms of only recovered starting material and photodimer. Control experiments demonstrated that as little as 0.5% of 3,4-diphenyl-4,5-epoxy-2-cyclopenten-1-one, 4,5-diphenyl-2-pyrone, or *p*-terphenyl would have been detected by the recording ultraviolet spectrophotometer employed.

Acid-Catalyzed Rearrangement of 3,4-Diphenyl-4,5-epoxy-2-cyclopenten-1-one. A. In Aqueous Acidic Methanol. In 10 ml of methanol was dissolved 500 mg of 3,4-diphenyl-4,5-epoxy-2-cyclopenten-1-one. To the mixture was added 0.5 ml of concentrated hydrochloric acid. The mixture was allowed to stand at room temperature for 5 hr and was then diluted with water. The oil which separated was extracted with ether and the extracts were dried over sodium sulfate. Evaporation of the solvent *in vacuo* left 483 mg of a pale oil. The oil was chromatographed on a 69 × 3 cm Woelm neutral alumina (activity III) column. After elution of small amounts of material with 1 l. of benzene, 260 mg (52%) of a colorless oil was eluted with 750 ml of 50% ether–benzene. The oil solidified on standing and recrystallization from 95% ethanol gave white, crystalline material, mp 128–129°.

Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.53; H, 6.33.

The infrared spectrum of this material showed a sharp weak spike at 3.67 and a strong band at 5.96 μ. The ultraviolet spectrum (95% ethanol) has λ_{max} 277 mμ (ε 10,000). The nmr spectrum in deuteriochloroform shows a singlet at τ 0.38, a singlet at 2.67, and a singlet at 7.85. The peak areas are in the ratio of 1:10:3. The material was converted to a 2,4-dinitrophenylhydrazone derivative, orange needles, mp 227–228°.

Anal. Calcd for $C_{22}H_{18}O_4N_4$: C, 65.66; H, 4.51; N, 13.92. Found: C, 65.57; H, 4.66; N, 13.78.

The ultraviolet spectrum of the 2,4-dinitrophenylhydrazone has λ_{max} 387 mμ (ε 32,700). On the basis of these data, the product was considered to be 2,3-diphenylcrotonaldehyde. The physical constants of this material are in excellent agreement with those reported.[40] Final verification was obtained by comparison of an infrared spectrum with an authentic sample.[49] The mixture melting point of this material with that of an authentic sample of 2,3-diphenylcrotonaldehyde was undepressed at 127–128°. On further elution with 50% ether–benzene, 75 mg (15%) of 4,5-diphenyl-2-pyrone was obtained. Further elution afforded intractable material.

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(49) A highly purified sample was kindly provided by Professor R. Breslow.

B. In Anhydrous Methanol Containing Gaseous Hydrogen Chloride. In 15 ml of anhydrous methanol, saturated with gaseous hydrogen chloride, was dissolved 500 mg of 3,4-diphenyl-4,5-epoxy-2-cyclopenten-1-one. The solution was allowed to stand for 2 hr and water was then added. The cloudy solution was extracted with methylene chloride and the extracts were dried over sodium sulfate. Evaporation of the solvent and drying afforded 473 mg of a viscous yellow material. The crude mixture was dissolved in benzene and passed through an alumina column (20 × 4 cm). The first fraction (250 ml) gave 28 mg of an orange residue; the second fraction (600 ml) gave 48 mg of a white solid, mp 64–73°. Recrystallization from hexane–ether gave white crystalline material, mp 77–78° (10%).

Anal. Calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87. Found: C, 82.08; H, 4.99.

The infrared spectrum of the crystalline compound in carbon tetrachloride is characterized by a sharp weak spike at 3.64 and a carbonyl band at 6.03 μ. The ultraviolet spectrum in 95% ethanol has λ_{max} at 329 mμ (ϵ 19,500), 256 (13,900), and 234 (21,000). The nmr spectrum in carbon tetrachloride has a singlet at τ 0.41, a multiplet at 2.69, and a singlet at 2.81. The peak areas are in the ratio of 1:10:1. The structure of this material was determined to be 4,5-diphenyl-2-furaldehyde (IIb) by comparison with a sample independently synthesized as described below.

Preparation of 4,5-Diphenyl-2-furaldehyde (X). The procedure of Hendrickson, Rees, and Templeton was adopted to the present case.[50] In 250 ml of acetone containing 6.5 g of potassium carbonate were heated 10 g of benzoin and 8.0 g of dimethylacetylene dicarboxylate at reflux for 24 hr. The mixture was cooled, poured onto ice, and extracted with ether; drying and evaporating the solvent yielded an oil which congealed crystalline and was recrystallized from methanol, yielding 6.8 g (41%) of white crystals, mp 115–116° (lit[50] mp 116–117°).

The above dimethyl 4,5-diphenyl-4-hydroxy-Δ^2-dihydrofuran-2,3-dicarboxylate (6.1 g) was refluxed for 6 hr in 250 ml of methanol containing 1 ml of sulfuric acid. The mixture was poured onto ice and extracted with ether, yielding 5.2 g of dimethyl 4,5-diphenylfuran-2,3-dicarboxylate. Recrystallization from methanol gave 5.0 g of material, mp 86–88°.

Saponification of the diester was carried out on 4.0 g in 80 ml of methanol and 60 ml of 4 *N* sodium hydroxide at room temperature overnight. Acidification at 0° yielded a white precipitate which was filtered, dissolved in hot methanol, and precipitated slowly by addition of water to give 3.6 g (72%) of 4,5-diphenylfuran-2,3-dicarboxylate, mp 249–251°.

Anal. Calcd for $C_{18}H_{12}O_5$: C, 70.13; H, 3.92. Found: C, 70.58; H, 4.01.

The neutralization equivalent of the crystalline compound is in accord with its assignment as a dicarboxylic acid (Calcd for $C_{18}H_{12}O_5$: neut equiv, 154. Found: neut equiv, 156).

The infrared spectrum of this acidic substance in a potassium bromide pellet had a broad band from 3.2 to 4.1 and bands at 5.86 and 6.20 μ.

The above product (3.0 g) was heated at 250–260° in a sealed tube for 45 min until the evolution of carbon dioxide ceased. Recrystallization from methanol afforded white crystals, mp 200–202°, infrared absorption at 5.93 μ.

Anal. Calcd for $C_{17}H_{12}O_3$: C, 77.26; H, 4.58. Found: C, 77.05; H, 5.04.

To 1.0 g of the above 4,5-diphenylfuran-3-carboxylate in 3 g of quinoline was added 150 mg of copper–bronze and the mixture was heated at 250° for 1 hr. After being cooled, the mixture was filtered from the copper–bronze and was then taken up in ether and extracted with 50 ml of 10% hydrochloric acid and washed with water. Drying and evaporation of the ether gave 575 mg (67%) of an oil whose infrared spectrum showed the absence of a carbonyl band. Molecular distillation of this material at 0.8 mm (bp 173–174°) gave crystals, mp 17–18° (when cooled in ice), 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 4,5-diphenylfuran is chiefly characterized by a sharp intense band at 11.25 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.

To 500 mg of dimethylformamide with stirring and cooling in an ice bath was added 354 mg of phosphorus oxytrichloride. The mixture was subsequently stirred for 10 min in the ice bath. 4,5-Diphenylfuran (500 mg) was then added to the cooled solution. The mixture was kept at 0° for 1 hr and at room temperature for 4 hr and then poured onto ice. The white solid which precipitated was filtered and dried to give 286 mg (57%) of 4,5-diphenyl-2-furaldehyde, mp 60–68°. Recrystallization from hexane gave colorless prisms, mp 77–78°. The infrared and nmr spectra of this material were identical in every detail with those of 4,5-diphenyl-2-furaldehyde prepared from the acid-catalyzed rearrangement of 3,4-diphenyl-4,5-epoxy-2-cyclopenten-1-one. The mixture melting point of these two materials was undepressed at 76–78°.

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