Anal. Calcd for $C_{47}H_{40}O_2$ (636.85): C, 88.64; H, 6.33. Found: C, 88.59; H, 6.32; mol wt, 630.

Spectra.[14]—The infrared spectra were taken on a Perkin-Elmer grating infrared spectrophotometer, Model 521. Proton magnetic resonance spectra were obtained on a Varian A-60 spectrometer using deuteriochloroform solution with tetramethylsilane as an internal standard.

Registry No.—IIIb, 13135-44-9; IIIc, 13118-45-1; IIId, 13118-46-2; IIIe, 13118-47-3; IIIf, 13118-48-4; VIIa, 13118-49-5; VIIb, 13118-50-8; IXa, 13118-51-9; IXb, 13118-52-0; IXc, 13143-75-4; IXd, 13118-21-3; IXe, 13118-22-4.

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[14] Spectra were recorded by Miss Dorothy McClung (infrared) and Miss Mary Ann Olivier (nmr) whose prompt collaboration is kindly acknowledged.

Photochemical Reactions with Phenols. IV. The Benzophenone-Sensitized Disproportionation of Hydroquinone Monoaryl Ethers

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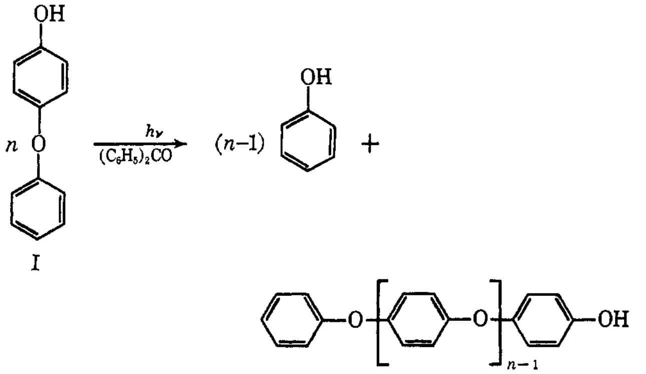
The photochemical reaction of benzophenone with hydroquinone monoaryl ethers results in a smooth disproportionation: *p*-phenoxyphenol yields phenol and poly-*p*-phenylene ether. The mechanism of this reaction as revealed by the disproportionation of various substituted hydroquinone monoaryl ethers is discussed. Triplet-state benzophenone is described as a highly selective oxidizing agent for phenols.

In order to determine the scope of the photochemical reactions of benzophenone with phenols,[1] it appeared desirable to extend the investigation to some *para*-substituted phenols with free *ortho* positions. As a representative of this group of compounds, *p*-phenoxyphenol (hydroquinone monophenyl ether) was chosen to be treated with triplet-state benzophenone. The direct irradiation of *p*-phenoxyphenol at 2537 A in aqueous solution, resulting in the formation of hydroquinone, had been reported earlier.[2] Under the experimental conditions employed in this study, *i.e.*, upon irradiation with ultraviolet light filtered through Pyrex, *p*-phenoxyphenol was found to be stable.

Results and Discussion

Irradiation of a benzene solution of benzophenone (2 mmoles) and *p*-phenoxyphenol (10 mmoles) leads to rapid consumption of *p*-phenoxyphenol (I) and formation of phenol (9 mmoles). From the reaction mixture a benzene-insoluble fraction and a benzene-soluble (but methanol insoluble) fraction of poly-*p*-phenylene ether (II) were obtained. These were identified from analytical and infrared spectroscopic data. The over-all photochemical reaction of *p*-phenoxyphenol in the presence of benzophenone can be formulated as follows.



I

II

By monitoring the reaction by vapor phase chromatography (see Figure 1) the slight formation and subsequent partial consumption of *p*-(*p*-phenoxyphenoxy)phenol (II, $n = 2$) was revealed. Higher homologous compounds were beyond vapor phase chromatographic detection.

In contrast to the reactions with 2,6-disubstituted phenols, benzophenone apparently acted as a photosensitizer since less than a stoichiometric amount was required in order to bring about an essentially complete disproportionation of *p*-phenoxyphenol. Removal of the light source during the course of the reaction terminated the disproportionation. The formation of phenol together with consumption of *p*-phenoxyphenol continued, however, upon further irradiation, even after a 20-hr dark period. Although benzpinacol could be isolated after completion of the disproportionation, benzophenone seemed to be left unreacted as long as *p*-phenoxyphenol was present and as long as the formation of phenol occurred.

Other hydroquinone monoaryl ethers were found to undergo this unique photochemical disproportionation reaction in the same manner. *p*-(*p*-Phenoxyphenoxy)phenol (II, $n = 2$), upon irradiation in the presence of 20 mole % of benzophenone, also yielded phenol and poly-*p*-phenylene ether. Vapor phase chromatographic analysis of the components present during the course of the reaction (see Figure 2) revealed intermediate formation of *p*-phenoxyphenol (I), but its consumption became apparent as soon as its concentration was of the same order of magnitude as that of the starting material.

Illuminating results were obtained by irradiating *p*-phenoxyphenol (always in the presence of 20 mole % of benzophenone) in the presence of other phenols. Photolysis of a mixture of *p*-phenoxyphenol and *p*-(*p*-phenoxyphenoxy)phenol resulted in the consumption of both starting materials at approximately equal rates and formation of phenol (Figure 3). Irradiation of an equimolar mixture of *p*-phenoxyphenol and *p*-(2,6-xylenoxy)-2,6-xylenol (III), however, led to rapid consumption of *p*-(2,6-xylenoxy)-2,6-xylenol and rapid formation of 2,6-xylenol, while most of the *p*-phenoxy-

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[1] For other results on this subject, see the preceding papers I–III: *J. Org. Chem.*, **32**, 2115, 2124, 2131 (1967).

[2] H. I. Joschek and S. I. Miller, Abstract of Papers, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, p 148.

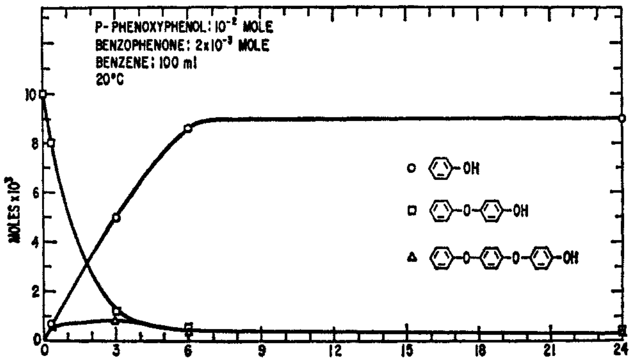


Figure 1.

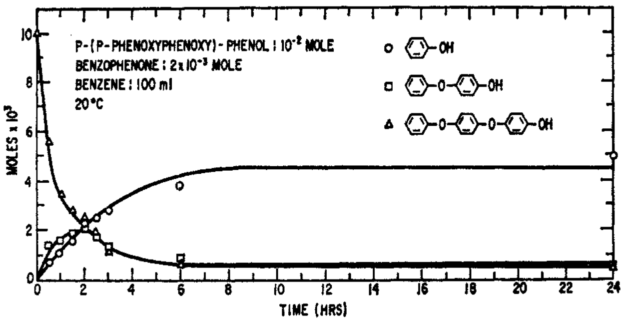
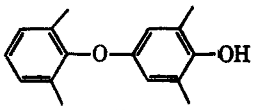


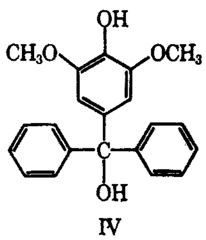
Figure 2.



III

phenol remained unchanged (Figure 4). On the other hand, irradiation of an equimolar mixture of *p*-phenoxyphenol and phenol resulted in the unaffected disproportionation of *p*-phenoxyphenol.

Although *p*-(*p*-phenoxyphenoxy)phenol upon irradiation in the presence of benzophenone disproportionates smoothly, irradiation in a mixture with 2,6-dimethoxyphenol leaves it completely unreacted, while 2,6-dimethoxyphenol is consumed (Figure 5) to give 3,5-dimethoxy-4-hydroxytriphenylcarbinol (IV, *cf.* ref 1)



IV

which crystallized from the reaction mixture upon partial evaporation of the solvent. A similar coupling reaction between benzophenone and 2,6-xylenol can be assumed to occur in the disproportionation of *p*-(2,6-xylenoxy)-2,6-xylenol, since vapor phase chromatographic analysis (Figure 4) during the reaction indicates partial consumption of benzophenone and initially formed 2,6-xylenol. Most of the *p*-phenoxyphenol thus remains unreacted because the sensitizer has been consumed. These codisproportionation experiments with phenols indicate that triplet-state benzophenone is a highly selective oxidizing agent.

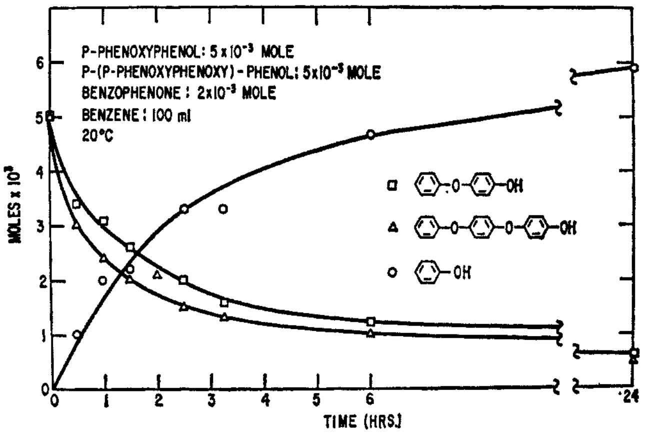


Figure 3.

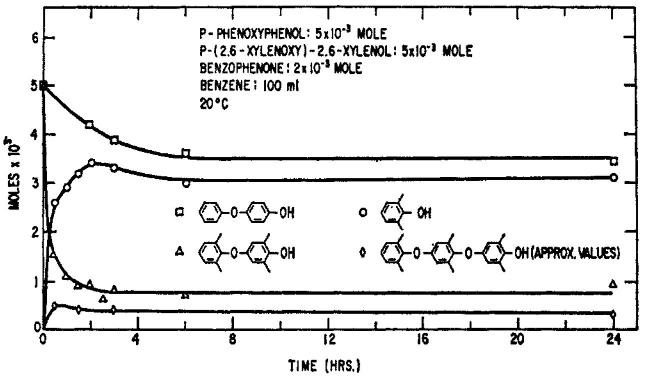
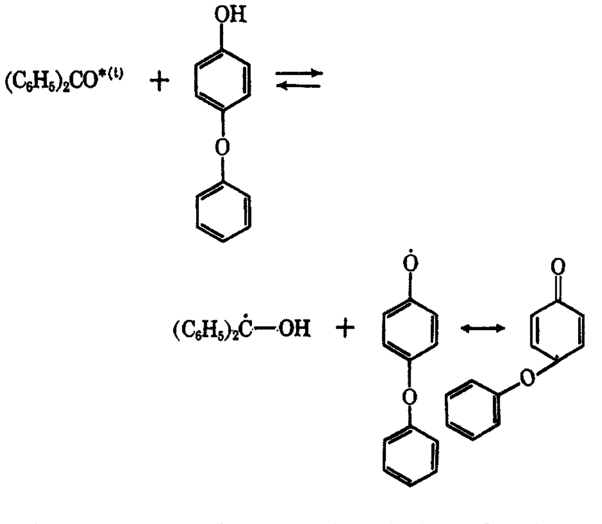


Figure 4.

Considering these experimental results, the following mechanism is proposed for the benzophenone-sensitized disproportionation of hydroquinone monoaryl ethers. Triplet-state benzophenone oxidizes *p*-phenoxyphenol to give a ketyl radical and a phenoxy radical.

$$(C_6H_5)_2CO + h\nu \xrightarrow[\text{excitation}]{n-\pi^*} (C_6H_5)_2CO^{*(s)} \qquad (1)$$

$$(C_6H_5)_2CO^{*(s)} \xrightarrow[\text{crossing}]{\text{intersystem}} (C_6H_5)_2CO^{*(t)} \qquad (2)$$



(3)

As opposed to the examples of photochemical reactions of benzophenone with 2,6-disubstituted phenols, however, no coupling between the ketyl radical and the phenoxy radical occurs, but the phenoxy radical undergoes a dimerization reaction.

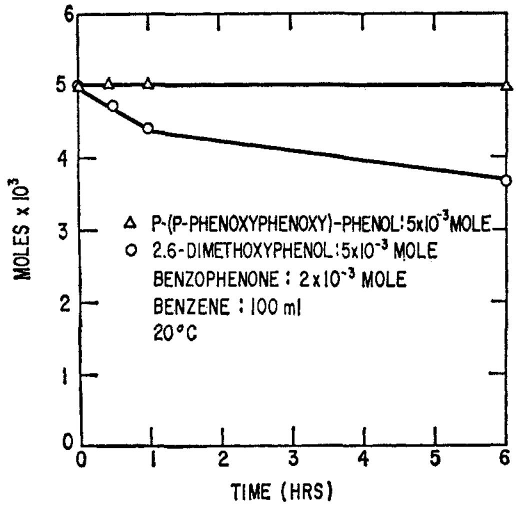
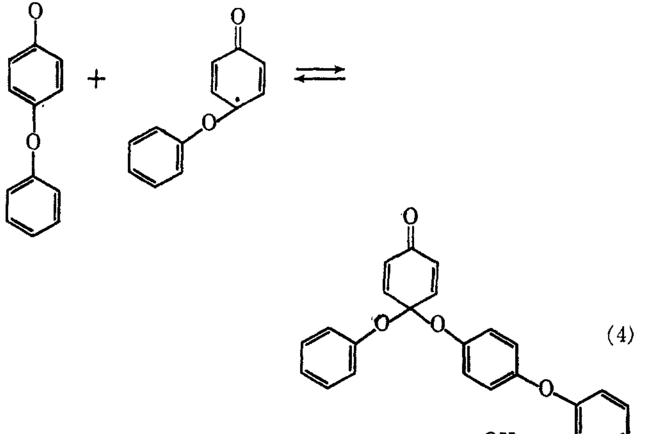


Figure 5.

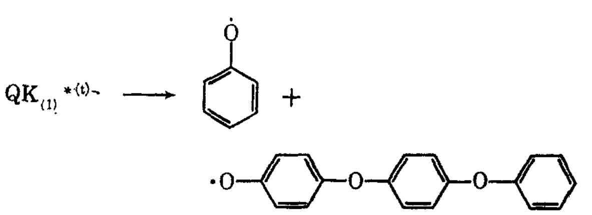


$QK_{(1)}$ (4)

The resulting species ($QK_{(1)}$) is a 4,4-disubstituted cyclohexadienone (a *p*-quinone ketal) which can undergo homolytic fission in the excited state. Since the light employed was filtered through Pyrex and the cyclohexadienone chromophore probably does not have any considerable absorption above 300 mμ, its excitation could be achieved by triplet energy transfer from benzophenone.

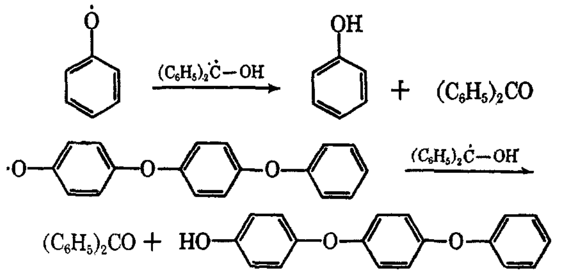
$$(C_6H_5)_2CO^{*(t)} + QK_{(1)} \longrightarrow (C_6H_5)_2CO + QK^{*}_{(1)}{}^{(t)} \quad (5)$$

Homolytic fission would then result in the formation of a phenoxy radical and a trimer–phenoxy radical.



(6)

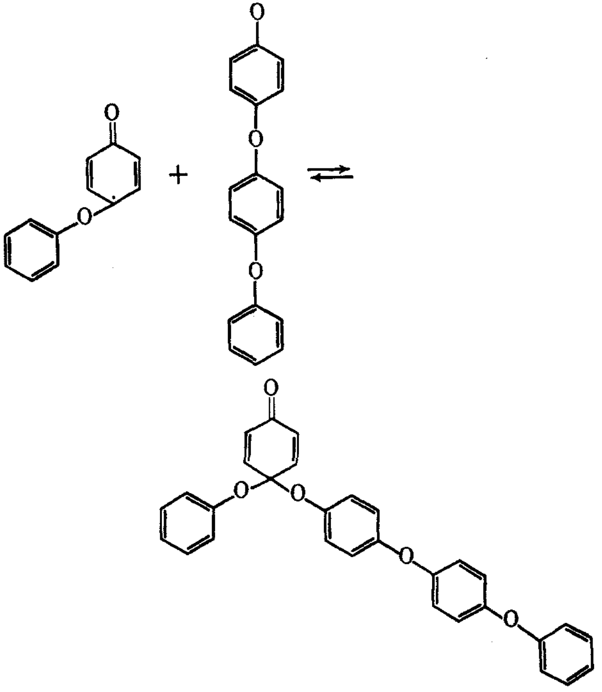
These phenoxy radicals then could be reduced to phenol and "phenol trimer," respectively. The ketyl radical formed in reaction 3 could be a suitable hydrogen donor.[3] Such a reaction accounts for the fact that a deficiency of benzophenone causes complete disproportionation, since benzophenone would then be regenerated. (See reactions 7a and 7b.)



(7a)

(7b)

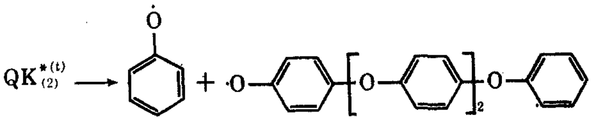
The trimer radical also could react with another dimer radical to give a quinone ketal ($QK_{(2)}$) which, after energy transfer and reduction, could yield phenol and phenoltetramer (reactions 8 through 11). Because of the stoichiometry of the oxidation reaction, for each phenoxy radical formed by dissociation of the quinone ketal intermediate, a ketyl radical is available and can serve as a hydrogen donor for the formation of phenol. Apparently the rate of reduction of phenoxy radicals by ketyl radicals is greater than the rate of dimerization of ketyl radicals. Side reactions, such as *ortho* coupling of phenoxy radicals (either C–C or C–O), which do not regenerate benzophenone, are probably responsible for the less than theoretical yields of monomer. Elevated temperatures apparently introduce this type



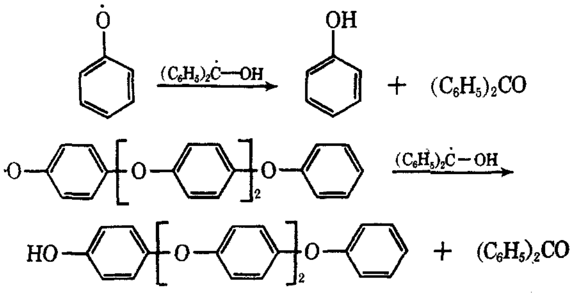
(8)

$QK_{(2)}$

$$QK_{(2)} + (C_6H_5)_2CO^{*(t)} \longrightarrow QK^{*(t)}_{(2)} + (C_6H_5)_2CO \quad (9)$$



(10)



(11a)

(11b)

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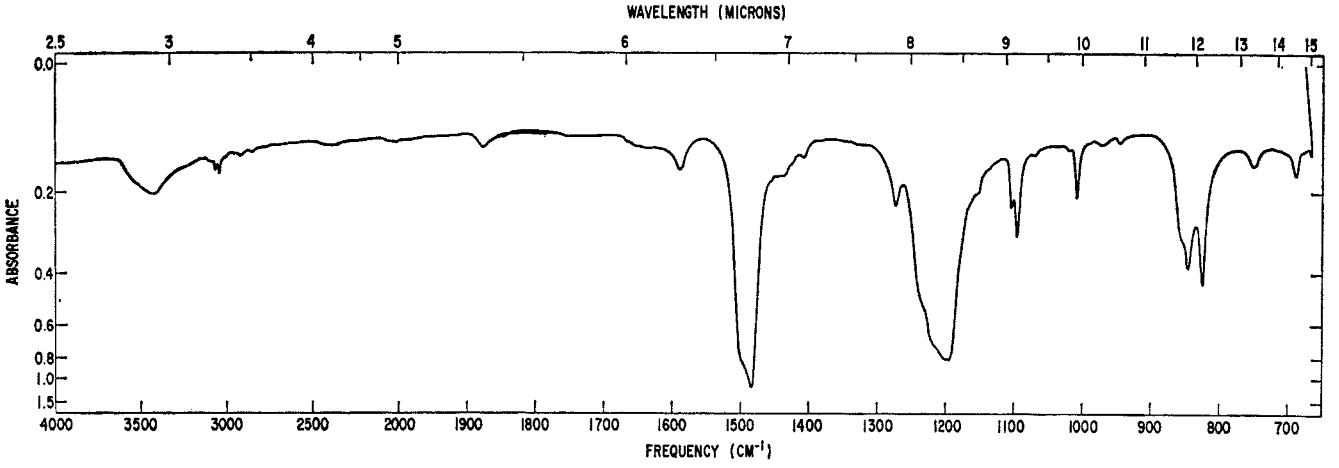
[3] Another source of hydrogen could be *p*-phenoxyphenol itself. Such, a chain mechanism indeed cannot be excluded with certainty without having any knowledge about the quantum yield of the disproportionation reaction.

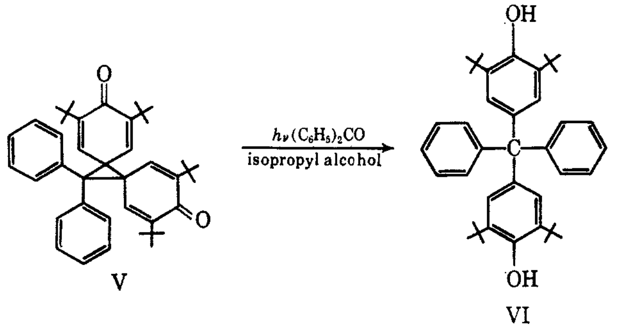


INFRARED SPECTRUM OF POLY-PHENYLENE ETHER (IN KBr)

Figure 6.

side reaction. The formation of phenol in the benzophenone-sensitized disproportionation of *p*-phenoxyphenol was found greatly impaired at a reaction temperature of 50°.

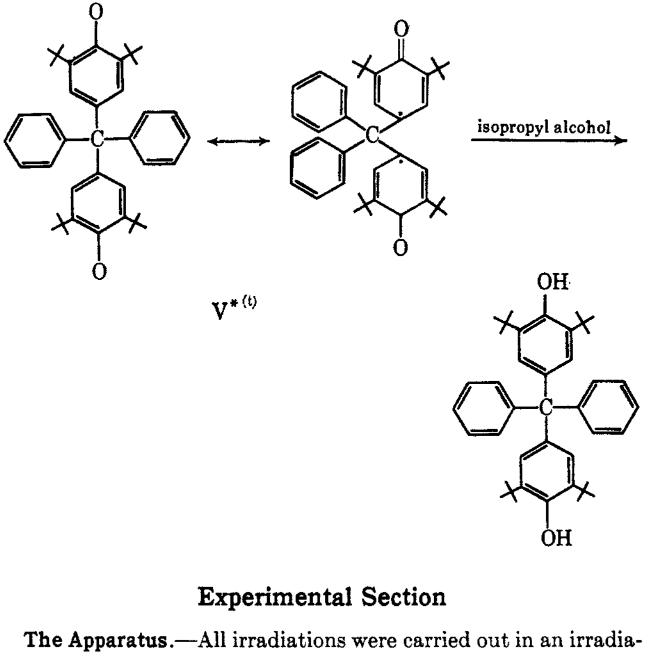
Concerning the proposed homolysis of the intermediate quinone ketals,[4] it should be pointed out that the two known aromatic quinone ketals have been shown to dissociate homolytically in solution either spontaneously or upon heating.[5,11] Evidence also has been presented for light-induced homolytic bond breaking in certain 4,4-disubstituted cyclohexadienones.[12,13] An interesting reaction supporting the suggestion of a benzophenone-sensitized bond breaking–reduction reaction of 4,4-diaryloxycyclohexadienone is presented here. Irradiation of an isopropyl alcohol solution of bispirodienone V[14] and benzophenone with light of a mercury arc filtered through Pyrex leads in high yield to 4,4′-dihydroxy-3,3′,5,5′-tetra-*t*-butyltetraphenylmethane (VI). As in the previously reported benzophenone-sensitized reduction of 3,5-di-*t*-butylfuchsone,[14] formation of benzpinacol is not observed as long as the cyclohexadienone is still present. In the absence of benzophenone, under otherwise identical conditions, bispirodienone V is stable upon irradiation although it absorbs strongly at 335 mμ ($\epsilon \approx 13{,}000$). Thus, the mechanism of the benzophenone-sensitized reduction of V apparently is best interpreted in terms of triplet–triplet energy transfer, followed by reduction of the resulting biradical $V^{*(t)}$ by isopropyl alcohol to give VI and acetone. A reduction mechanism analogous to that of reactions 7 and 11, however, cannot be excluded.



V

VI

$$(C_6H_5)_2CO^{*(t)} + V \longrightarrow (C_6H_5)_2CO + V^{*(t)}$$



$V^{*(t)}$

Experimental Section

The Apparatus.—All irradiations were carried out in an irradiation apparatus made of Pyrex glass as described previously.[14] The lamp used was a G.E. 100-w mercury lamp, Type H-100 A4/T, from which the glass jacket was removed. Nitrogen or argon was used for inert gas blanketing. Constant temperature of the reaction mixture was achieved by connecting the internal immersion cooler to a thermostat.

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[4] A quinone ketal intermediate has been invoked earlier in explaining the formation of polymers derived from pentachlorophenoxy radical.[5,6] Likewise, the formation of small amounts of 2,6-xylenol in the oxidative polymerization of *p*-(2,6-xylenoxy)-2,6-xylenol has been interpreted in terms of dissociation of a *p*-quinone ketal intermediate.[7,8] *Cf.* also the mechanism proposed for the oxidation of *p*-phenoxyphenol with periodate.[9,10]

(5) E. Müller, A. Rieker, and W. Beckert, *Z. Naturforsch.*, **17b**, 567 (1962).

(6) E. Müller, A. Rieker, and A. Schick, *Ann.*, **673**, 40 (1964).

(7) E. J. McNelis, Abstract of Papers, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, p 15S.

(8) C. D. Cooper, H. S. Blanchard, G. F. Endres, and H. L. Finkbeiner, *J. Am. Chem. Soc.*, **87**, 3996 (1965).

(9) E. Adler and R. Magnusson, *Acta Chem. Scand.*, **13**, 505 (1959).

(10) E. Adler, I. Falkehag, and B. Smith, *ibid.*, **16**, 529 (1962).

(11) H.-D. Becker, *J. Org. Chem.*, **29**, 3068 (1964).

(12) G. Scheibe and F. Feichtmair, *J. Phys. Chem.*, **66**, 2449 (1962).

(13) D. I. Schuster and D. J. Patel, *J. Am. Chem. Soc.*, **87**, 2515 (1965); D. L. Schuster and C. J. Polowczyk, *ibid.*, **88**, 1722 (1966).

(14) Paper I.

Materials.—Benzene was reagent grade (thiophene free) and dried over sodium wire. *p*-Phenoxyphenol was obtained from Dow Chemical Co., Midland, Mich., and repeatedly recrystallized from methanol. The melting point was 84°. Traces of hydroquinone as impurity in *p*-phenoxyphenol inhibit the disproportionation. Benzophenone, mp 48–49° (commercial grade), was recrystallized from methanol and occasionally also used without further purification. Other hydroquinone monoarylethers were obtained from this laboratory's stock. All melting points were taken on a Fisher-Johns melting point apparatus and are not corrected.

Vapor Phase Chromatographic Analyses.[15]—The phenols in the reaction mixtures analyzed by vapor phase chromatography were converted into their trimethylsilyl ethers according to the following standard procedure. Samples (2 ml) of the irradiation solution were taken and refluxed for about 1 hr in a mixture of pyridine (3 ml), trimethylchlorosilane (1 ml), and hexamethyldisilazane (1 ml). Measured amounts of this silylation mixture were then subjected to vapor phase chromatographic analysis, using a 2-ft silicon rubber on Chromosorb P column, programmed from 100 to 300°, using helium as a carrier gas. The observed peaks of phenoltrimethylsilyl ethers were integrated by hand. Conversion into moles of material is based on calibrations with standard solutions of silylated phenols.

Photochemical Reaction of Benzophenone with *p*-Phenoxyphenol.—A solution of *p*-phenoxyphenol (1.86 g, 10 mmoles) and benzophenone (364 mg, 2 mmoles) in benzene (100 ml) was purged with argon for 30 min and then irradiated for 18 hr at 18° passing a current stream of argon through the solution. After 3 hr of irradiation a precipitate had started forming. Filtration yielded 350–530 mg (*i.e.*, 47–64% of the theoretically expected) of benzene-insoluble, light tan polymer with a softening range of 200–220°.

Anal. Calcd for a tetradecamer $C_6H_5O(C_6H_4O)_{12}C_6H_4OH$ (1291): C, 78.11; H, 9.55. Found: C, 77.49; H, 4.71; mol wt (in camphor), 1281.

The infrared spectrum of the polymer (Figure 6) resembles those of poly-*p*-phenylene ethers obtained by oxidative coupling of phenols.[16]

The above benzene filtrate was evaporated to about 5 ml and dropped under stirring into 300 ml of methanol containing few drops of hydrochloric acid (in order to speed up coagulation), yielding 150–300 mg (16–32%) of methanol-insoluble polymer, mp 120–140°. Its infrared spectrum is essentially identical with that of the benzene-insoluble material.

Anal. Calcd for a heptadecamer $C_6H_5O(C_6H_4O)_{15}C_6H_4OH$ (1568): C, 78.13; H, 4.51. Found: C, 78.51; H, 4.48; mol wt, 1540 (thermoelectric measurement in warm dioxane).

The lower melting point but higher molecular weight of this polymer fraction, compared with those of the benzene-insoluble fraction, is suggestive of less regularity in the polymer structure.

Photochemical Reaction of Benzophenone with *p*-(*p*-Phenoxyphenoxy)phenol (II).—A solution of II (2.78 g, 10 mmoles) and benzophenone (364 mg, 2 mmoles) in benzene (100 ml) was irradiated for 24 hr. The yield of benzene-insoluble polymer, which started precipitating after 1 hr of irradiation, was 700 mg. From the benzene filtrate 300 mg of polymer was obtained by precipitation with methanol. The infrared spectra of both fractions were identical with those of the poly-*p*-phenylene ethers obtained by disproportionation of *p*-phenoxyphenol.

Benzophenone-Sensitized Reduction of Bispirodienone V.—A solution of benzophenone (9.1 g, 50 mmoles) in isopropyl alcohol (60 ml), in which bispirodienone V (1.43 g, 2.5 mmoles) was suspended and partly dissolved, was irradiated for 40 min. By that time bispirodienone V had completely dissolved and a colorless precipitate had formed. Filtration gave 1.25 g (87%) of 4,4′-dihydroxy-3,3′-5,5′-tetra-*t*-butyltetraphenylmethane, mp 234°. A mixture melting point with authentic material[14] showed no depression.

Control Experiment.—Bispirodienone V (287 mg, 0.5 mmole) was suspended in 60 ml of isopropyl alcohol and irradiated for 5 hr. Filtration gave 260 mg (94%) of unreacted starting material.

Registry No.—II ($n = 13$), 13145-40-9; II ($n = 16$), 13137-30-9; VI, 13135-05-2.

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[15] The author would like to thank Mrs. A. L. Klopfer for carrying out all of the vapor phase chromatographic analyses which are reported in this paper.

[16] A. S. Hay, *J. Polymer Sci.*, **58**, 581 (1962).

Photochemical Reactions with Phenols. V.[1] The Photochemical Oxidative–Reductive Dimerization of Acetophenones

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Received January 4, 1967

Acetophenone has been found to undergo a novel photochemical reaction. In the presence of a small amount of phenol, acetophenone smoothly reacts upon irradiation, using ultraviolet light filtered through Pyrex, to give 1,2-dibenzoylethane and acetophenone pinacol in excellent yields. The reaction has been applied to several methyl-substituted acetophenones. A mechanism for the oxidative–reductive dimerization of acetophenones involving a photochemical, phenol-catalyzed enolization reaction is proposed.

The investigation of photoreactions of dissolved alkyl–aryl ketones has been the subject of several recent papers. Butyrophenone in hydrocarbon solvents, upon irradiation in the 3100 A region, undergoes a type II cleavage to yield ethylene and acetophenone.[2] Similarly, irradiation of valerophenone in acetone solution gives acetophenone as the major product, besides a cyclobutanol.[3] Acetophenone itself has been reported to be stable "when exposed to the full light of a mercury lamp."[4] In alcohol solution, however, acetophenone upon irradiation yields acetophenone pinacol, the alcohol being oxidized to the corresponding carbonyl compound.[5] Irradiation of acetophenone in methylphenylcarbinol gives acetophenone pinacol as the sole product. The inhibition of this reaction by mercaptans and disulfides has recently been studied by Cohen and his co-workers.[6]

In the course of investigations on the reactions of triplet-state ketones with phenols, we found that irradiation of a solution of 2,6-di-*t*-butylphenol in acetophenone gave a mixture of several products, as revealed by vapor phase chromatographic analysis. One component of this mixture was isolated and identified as 1,2-dibenzoylethane. In view of the known

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[1] For paper IV, see *J. Org. Chem.*, **32**, 2136 (1967).

[2] J. N. Pitts, Jr., L. D. Hess, E. J. Baum, E. A. Schuck, J. K. S. Wan, P. A. Leermakers, and G. Vesley, *Photochem. Photobiol.*, **4**, 305 (1965).

[3] R. B. LaCount and C. E. Griffin, *Tetrahedron Letters*, 1549 (1965).

[4] E. J. Bowen and E. L. A. E. de la Praudiere, *J. Chem. Soc.*, 1503 (1934). It should be noted, however, that gas phase photolysis of acetophenone does result in a decomposition reaction. Biphenyl, benzil, and 1,2-dibenzoylethane have been identified as reaction products; *cf.* H. H. Glazebrook and T. G. Pearson, *ibid.*, 589 (1939).

[5] Ch. Weizmann, E. D. Bergmann, and Y. Hirshberg, *J. Am. Chem. Soc.*, **60**, 1530 (1938).

[6] S. G. Cohen, D. A. Laufer, and W. V. Sherman, *ibid.*, **86**, 3060 (1964).