

Photochemical Reactions with Phenols. III. Photosensitized Addition of Phenols to Quinone Methides

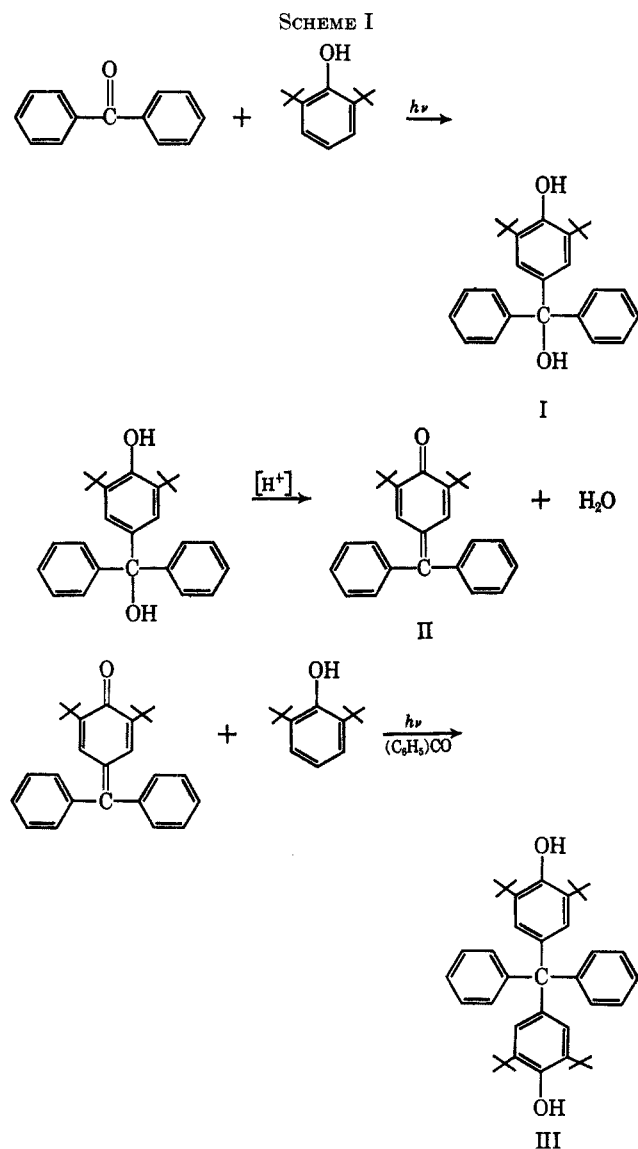
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α,α -Diphenyl-1,4-benzoquinone methides (fuchsones) have been found to undergo an acetophenone- or benzophenone-sensitized photochemical addition reaction with phenols. The reaction leads in high yields to new bisphenols (4,4'-dihydroxytetraphenylmethanes).

In the course of an investigation on the reaction of triplet-state ketones with phenols, we found that the photochemical, acid-catalyzed reaction of benzophenone with 2,6-di-*t*-butylphenol smoothly leads to a bisphenol, 4,4'-dihydroxy-3,3',5,5'-tetra-*t*-butyltetraphenylmethane (III) according to a multistep mechanism involving 3,5-di-*t*-butyl-4-hydroxytriphenylcarbinol (I) and 3,5-di-*t*-butylfuchsonone (II) as intermediates¹ (Scheme I). Analogous products were formed from substituted benzophenones and 2,6-di-*t*-butylphenol.²



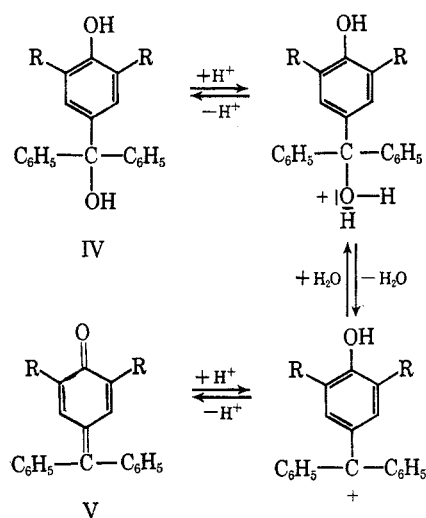
However, bisphenols could not be isolated when benzophenone was treated photochemically in the

(1) H.-D. Becker, *J. Org. Chem.*, **32**, 2115 (1967).

(2) H.-D. Becker, *ibid.*, **32**, 2124 (1967).

presence of mineral acid with other substituted phenols such as 2,6-dicyclohexyl- or diisopropylphenol. Surprisingly, in the absence of acid, the reaction was found to lead to the corresponding 4-hydroxytriphenylcarbinols, which after isolation did eliminate water by treatment with acid (Scheme II).²

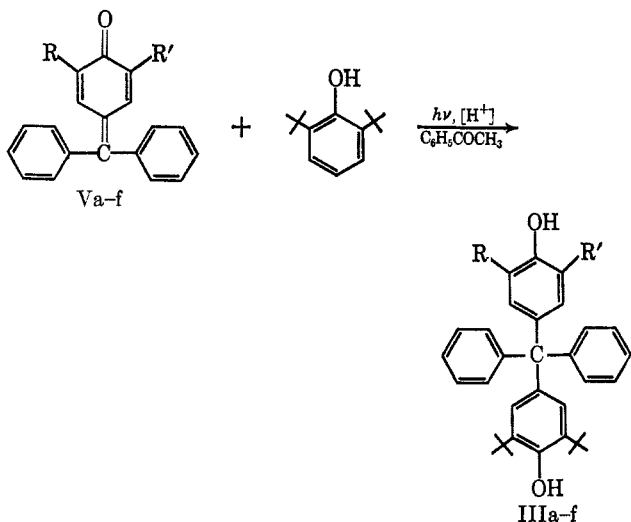
The reason for the extraordinary photochemical behavior of 2,6-di-*t*-butylphenol presumably lies in the extreme acid sensitivity of the intermediate 3,5-di-*t*-butyl-4-hydroxytriphenylcarbinol (I or IV, R = *t*-butyl), which, as revealed by ultraviolet spectroscopy, in the presence of traces of mineral acid, is quantitatively converted into the quinone methide (II or V, R = *t*-butyl) 3,5-di-*t*-butylfuchsonone, *via* the corresponding 4-hydroxytriphenylmethyl cation. Other 4-



hydroxytriphenylcarbinols apparently do not undergo the elimination reaction with the same ease, thus not forming the corresponding quinone methides under the conditions employed in the photochemical reaction. Dilute solutions of 3,5-diphenyl-4-hydroxytriphenylcarbinol, *e.g.*, (IV, R = phenyl), prepared by non-photochemical means, indeed remain colorless in methanol in the presence of a trace of acid, and dilute solutions of 3,5-diphenylfuchsonone (V, R = phenyl) in methanol rapidly decolorize upon treatment with traces of hydrochloric acid.

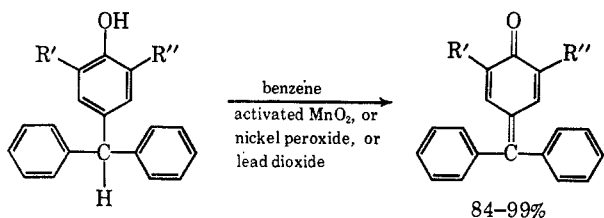
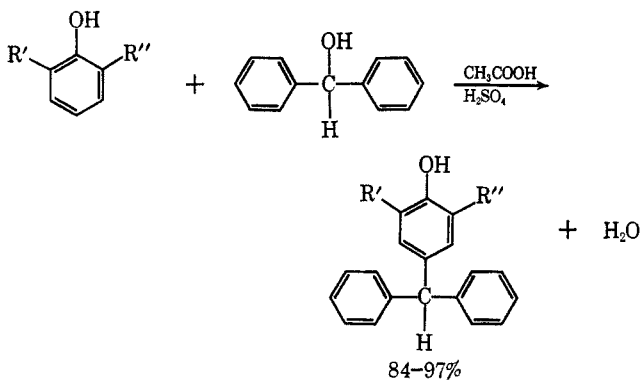
This unique substituent effect seems to limit the direct photochemical synthesis of 4,4'-dihydroxytetraphenylmethanes to the use of 2,6-di-*t*-butylphenol. It appeared conceivable, however, to extend the photochemical formation of 4,4'-dihydroxytetraphenylmethanes to other phenols, provided the second photochemical sequence of the proposed mechanism for the formation of III, outlined in Scheme III, has general applicability. Excitation of any fuchsonone to its triplet state

TABLE I

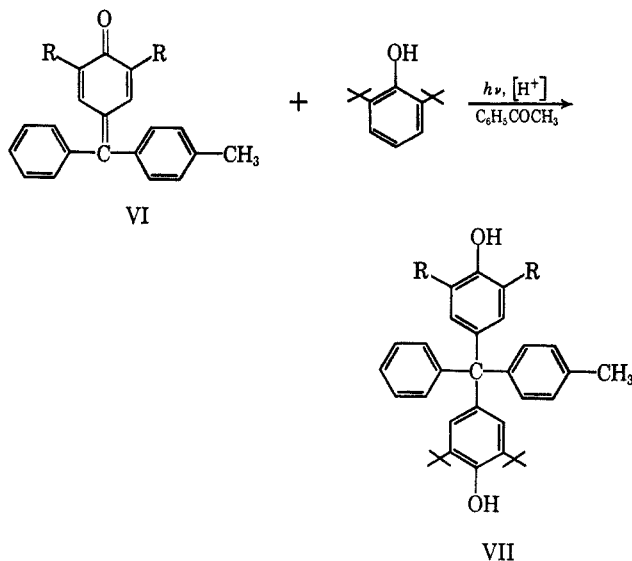


V and III	R	R'	Yield of III, %
a	<i>t</i> -Butyl	<i>t</i> -Butyl	94
b	Cyclohexyl	Cyclohexyl	80
c	Isopropyl	Isopropyl	73
d	Methyl	Phenyl	90
e	Phenyl	Phenyl	90
f	Phenyl	<i>t</i> -Butyl	91

some cases preferable, route to substituted fuchsones exists in the photochemical reaction of substituted benzophenones with 2,6-disubstituted phenols, described in a preceding paper of this series.² Thus, 4,4'-



dihydroxytetraphenylmethanes can be prepared from phenols and diaryl ketones in a two-step synthesis, which consists in the photochemical preparation of a fuchson followed by the photosensitized addition of a phenol. We have used this approach for the preparation of tetraphenylmethanes having an asymmetric carbon atom. Photochemical reaction of 4-methylbenzophenone with 2,6-diisopropylphenol yielded 3,5-diisopropyl-4'-methylfuchson (VIa, R = isopropyl), to which 2,6-di-*t*-butylphenol was added in an acetophenone-sensitized reaction to give 4,4'-dihydroxy-3,5-diisopropyl-3',5'-di-*t*-butyl-4'-methyltetraphenylmethane (VIIa). 2,6-Di-*t*-butylphenol was added in



VI and VIIa, R = isopropyl
b, R = cyclohexyl

the same manner to the photochemically prepared 3,5-dicyclohexyl-4'-methylfuchson (VIb, R = cyclohexyl) to give the bisphenol (VIIb, R = cyclohexyl). Both compounds were found to be racemic. It appears to be an interesting problem for future research, whether the application of an optically active sensitizer will lead to an optically active tetraphenylmethane. The answer to that question may provide a better understanding of the mechanism of photosensitization.⁴

The photosensitized addition reaction is not limited to the use of 2,6-di-*t*-butylphenol, but has been found to be applicable to a variety of phenols (VIII). Thus, symmetrically tetrasubstituted 4,4'-dihydroxytetraphenylmethanes IXa-d were prepared by acetophenone- and/or benzophenone-sensitized addition of 2,6-di-phenyl-, dicyclohexyl-, diisopropyl-, and 2-phenyl-6-*t*-butylphenol to the corresponding fuchsones (see Table II). 2-Phenyl-6-*t*-butylphenol also was added to 3,5-diphenylfuchsones, giving 4,4'-dihydroxy-3-*t*-butyl-3,5,5'-triphenyltetraphenylmethane (IXe) in excellent yield. Asymmetrically substituted tetraphenylmethanes can thus be prepared from two different pairs of reactants.⁵

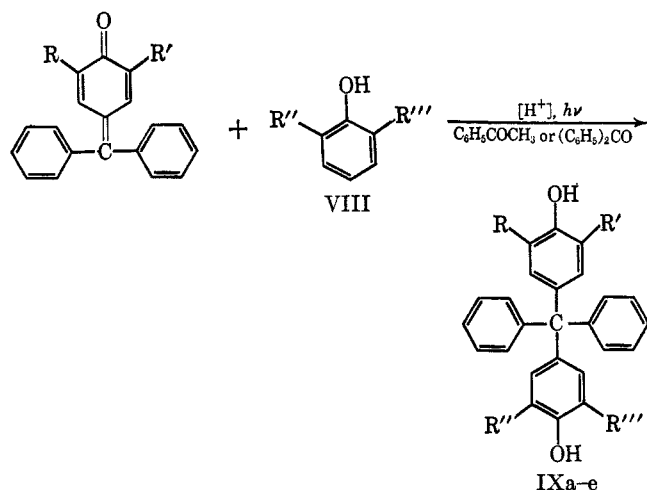
The results presented in this paper support the mechanism which we proposed for the direct photochemical formation of 4,4'-dihydroxy-3,3',5,5'-tetra-*t*-butyltetraphenylmethane from 2,6-di-*t*-butylphenol and benzophenone.¹

Thus, the mechanism of the photosensitized addition of phenols to fuchsones appears to be well represented by the second photochemical reaction sequence outlined in Scheme III, in which the sensitizer benzophenone can be replaced by acetophenone, and in which 3,5-di-*t*-butylfuchson and 2,6-di-*t*-butylphenol stand as one example for a variety of pairs of quinone methides and phenols. To what extent the rate of the addition of phenols to quinone methides is governed by photo-

(4) Cf. G. S. Hammond and R. S. Cole, *J. Am. Chem. Soc.*, **87**, 3256 (1965).

(5) We did notice some peculiarities of the addition reaction: 2-phenyl-6-*t*-butylphenol adds rapidly to 3,5-diphenylfuchson to give bisphenol IXe, but adds rather slowly to 3,5-di-*t*-butylfuchson in the formation of bisphenol IIIf, which in turn is formed smoothly by addition of 2,6-di-*t*-butylphenol to 3-phenyl-5-*t*-butylfuchson (cf. the Experimental Section).

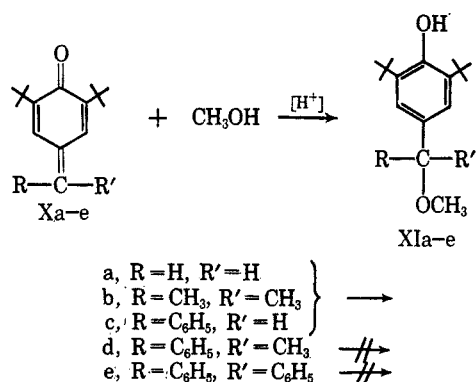
TABLE II



IX	R	R'	R''	R'''	Yield, %
a	Phenyl	Phenyl	Phenyl	Phenyl	60
b	Cyclohexyl	Cyclohexyl	Cyclohexyl	Cyclohexyl	65
c	Isopropyl	Isopropyl	Isopropyl	Isopropyl	74
d	Phenyl	<i>t</i> -Butyl	Phenyl	<i>t</i> -Butyl	89
e	Phenyl	Phenyl	Phenyl	<i>t</i> -Butyl	88

physical factors such as efficiency of energy transfer to the fuchsons, or photochemical factors such as side reactions owing to dehydrogenation of phenols, is not known yet.

Finally, it is of interest to view the photosensitized reaction described here within the field of quinone methide chemistry.⁶ Quinone methides in general are known to undergo nonphotochemical addition reactions with nucleophiles such as water,⁷ alcohols,^{8,9} or phenols.¹⁰ Di-*t*-butyl-substituted quinone methides have been studied in particular because of their formation in the disproportionation reaction of *t*-butyl-substituted phenoxy radicals.^{8,9,11} Thus, quinone methide Xa (R = H, R' = H) rapidly reacts with methanol in the presence of mineral acid to produce 2,6-di-*t*-butyl- α -methoxy-*p*-cresol (XIa, R = H; R' = HF).^{8,9} In the same manner quinone methides Xb (R = CH₃;



R' = CH₃)⁸ and Xc (R = C₆H₅; R' = H)¹¹ rapidly undergo the addition reaction with methanol. How-

ever, quinone methides Xd (R = C₆H₅; R' = CH₃)¹¹ and Xe (R = C₆H₅; R' = C₆H₅)¹¹ are reported to resist the addition of methanol, even under vigorous conditions. These results suggest that steric factors are of importance for the addition of nucleophiles to quinone methides. We, therefore, believe that the photosensitized addition of phenols to α,α -diphenyl-1,4-benzoquinone methides does proceed because the geometry of triplet-state fuchson is favorably different with regard to steric hindrance from the geometry of the ground-state molecule.

Experimental Section

Apparatus.—Irradiations were carried out in a water-cooled immersion apparatus made of Pyrex. For a detailed description, see ref 1. The lamp used was a G.E. 100-w mercury lamp, Type H-100 A4/T, from which the glass jacket was removed. All irradiations were carried out at about 16° under nitrogen passed through a frit into the reaction mixture during irradiation in order to provide agitation of suspension.

Materials.—Phenols¹² were either distilled¹³ or recrystallized before use. Fuchsons were prepared as described elsewhere.³ Melting points were taken on a Fisher-Johns melting point apparatus and are not corrected. All molecular weights were determined by thermoelectric measurement in benzene.

4,4'-Dihydroxy-3,3',5,5'-tetra-*t*-butyltetraphenylmethane (IIIa).—See ref 1, where the sensitized addition of 2,6-di-*t*-butylphenol to 3,5-di-*t*-butylfuchson has been described in detail.

3,5-Dicyclohexyl-4,4'-dihydroxy-3',5'-di-*t*-butyltetraphenylmethane (IIIb).—3,5-Dicyclohexylfuchson (1.055 g, 2.5 mmoles) was suspended in a solution of 2,6-di-*t*-butylphenol (1.03 g, 5 mmoles) and acetophenone (15 g, 125 mmoles) in methanol (50 ml) containing 0.1 ml of concentrated hydrochloric acid. After 5 hr of irradiation the clear solution turned suddenly almost colorless (very light yellow). The solvent was then removed by evaporation *in vacuo* and the acetophenone was removed by distillation at about 1 mm (bath temperature 90°). The residual, light yellow, crystalline solid was recrystallized by dissolving in little hot acetone and adding methanol. Addition of few drops of water to the solution causes rapid crystallization (yield 1.3 g, 80%) as colorless crystals, mp 199–201°.

Anal. Calcd for C₄₈H₅₆O₂ (628.95): C, 85.94; H, 8.97. Found: C, 85.83; H, 8.95; mol wt, 615.

4,4'-Dihydroxy-3,5-diisopropyl-3',5'-di-*t*-butyltetraphenylmethane (IIIc).—A solution of 3,5-diisopropylfuchson (1.713 g, 5 mmoles), 2,6-di-*t*-butylphenol (2.06 g, 10 mmoles), and acetophenone (12.0 g, 100 mmoles) in methanol (60 ml) containing 0.2 ml of concentrated hydrochloric acid was irradiated for 18 hr. Vapor phase chromatographic analysis of the reaction mixture showed a trace of residual fuchson and a trace of 4,4'-dihydroxy-3,3',5,5'-tetra-*t*-butyldiphenyl besides one reaction product, and the starting materials used in excess. The light yellow reaction mixture was evaporated *in vacuo* and the acetophenone was removed by distillation at 1 mm. The solid residue thus obtained was triturated with few milliliters of methanol and filtered, yielding 2.0 g (73%) of colorless crystals, mp 196–197°. Recrystallization from hot methanol and a few drops of water raised the melting point to 196–198°.

Anal. Calcd for C₃₉H₄₈O₂ (548.82): C, 85.35; H, 8.62. Found: C, 85.16; H, 8.72; mol wt, 508.

4,4'-Dihydroxy-3,5-di-*t*-butyl-3'-methyl-5'-phenyltetraphenylmethane (III'd).—A solution of 2,6-di-*t*-butylphenol (2.06 g, 10 mmoles), 3-methyl-5-phenylfuchson (1.92 g, 5 mmoles) (partially suspended), acetophenone (15 g, 125 mmoles), and concentrated hydrochloric acid (0.1 ml) in methanol (50 ml) was irradiated for 11.5 hr. At that time the yellow solution suddenly appeared almost completely colorless. Removal of the methanol, acetophenone, and excess 2,6-di-*t*-butylphenol by vacuum distillation at 1 mm (bath temperature about 100°) gave an almost colorless, crystalline residue which was recrystal-

(6) For a recent review on quinone methides, see A. B. Turner, *Quart. Rev. (London)*, **18**, 347 (1964).

(7) E. Adler and B. Stenemur, *Chem. Ber.*, **89**, 291 (1956).

(8) C. D. Cook and B. E. Norcross, *J. Am. Chem. Soc.*, **78**, 3997 (1956).

(9) H.-D. Becker, *J. Org. Chem.*, **30**, 982 (1965).

(10) K. Freudenberg and M. Friedmann, *Chem. Ber.*, **93**, 2138 (1960).

(11) C. D. Cook and N. D. Gilmour, *J. Org. Chem.*, **25**, 1429 (1960); see also E. Muller, *et al.*, *Ann.*, **645**, 66 (1961).

(12) Thanks are due to Drs. A. S. Hay and J. R. Ladd for providing the author with some phenols.

(13) Thanks are due to Mr. W. Ruminski for the distillation of phenols.

lized by dissolving in little ether and adding methanol (yield 2.75 g, 90%), mp 186–187°.

Anal. Calcd for $C_{40}H_{42}O_2$ (554.78): C, 86.60; H, 7.63. Found: C, 86.83; H, 7.73; mol wt, 540.

4,4'-Dihydroxy-3,5-diphenyl-3',5'-di-*t*-butyltetraphenylmethane (IIIe).—3,5-Diphenylfuchsonone (2.05 g, 5 mmoles) was suspended in a solution of 2,6-di-*t*-butylphenol (2.06 g, 10 mmoles), acetophenone (15 g, 125 mmoles), and concentrated hydrochloric acid (0.1 ml) in methanol (50 ml). After 4 hr of irradiation the by then clear, yellow reaction mixture suddenly turned colorless. The reaction mixture was then worked up by removing the solvent and the acetophenone by distillation *in vacuo* (bath temperature 80–100° at 1 mm). The resulting crystalline, colorless residue was recrystallized by dissolving in warm ether and adding methanol (yield 2.72 g, 90%), mp 195–196°.

Anal. Calcd for $C_{48}H_{44}O_2$ (616.86): C, 87.63; H, 7.19. Found: C, 87.64; H, 7.23; mol wt, 601.

Attempted Acid-Catalyzed, Nonphotochemical Addition of 2,6-Di-*t*-butylphenol to 3,5-Diphenylfuchsonone.—A suspension of 3,5-diphenylfuchsonone (1.025 g, 2.5 mmoles) in a solution of 2,6-di-*t*-butylphenol (1.03 g, 5 mmoles) in acetic acid (20 ml) was acidified with concentrated sulfuric acid (0.1 ml) and stirred for 3 days. Upon dilution of the red suspension with little methanol, 1.00 g of 3,5-diphenylfuchsonone was recovered.

4,4'-Dihydroxy-3-phenyl-3',5,5'-tri-*t*-butyltetraphenylmethane (III_f). **A. Photosensitized Addition of 2,6-Di-*t*-butylphenol to 3-Phenyl-5-*t*-butylfuchsonone.**—A solution of 3-phenyl-5-*t*-butylfuchsonone (1.95 g, 5 mmoles, partially suspended), 2,6-di-*t*-butylphenol (2.06 g, 10 mmoles), acetophenone (15 g, 125 mmoles) and concentrated hydrochloric acid (0.1 ml) in methanol (50 ml) was irradiated for 15.5 hr. At that time the yellow solution suddenly appeared almost completely colorless. Removal of solvent, acetophenone, and excess 2,6-di-*t*-butylphenol by vacuum distillation at 1 mm (bath temperature 100°) gave a light yellow, crystalline residue which was washed with methanol and recrystallized by dissolving in little warm ether and adding methanol (yield 2.70 g, 91%) as colorless crystals, mp 188–189°.

Anal. Calcd for $C_{48}H_{48}O_2$ (596.86): C, 86.53; H, 8.11. Found: C, 86.48; H, 8.19; mol wt, 566.

B. Photosensitized Addition of 2-Phenyl-6-*t*-butylphenol to 3,5-Di-*t*-butylfuchsonone.—A suspension of 3,5-di-*t*-butylfuchsonone (1.85 g, 5 mmoles) in a solution of 2-phenyl-6-*t*-butylphenol (2.26 g, 10 mmoles), acetophenone (18 g, 150 mmoles), and hydrochloric acid (0.1 ml) in methanol (60 ml) was irradiated for 48 hr. By then the solution was clear but still quite yellow. The solvent, acetophenone, and excess phenol were removed by distillation *in vacuo* at 1 mm (bath temperature 185°) and the glassy, brown residue was treated with 100 ml of boiling methanol. The light yellow, crystalline substance thus precipitating was removed by filtration of the warm solution (yield 1.65 g, 55%) as light yellow crystals, mp 188–189°. Mixture melting point with authentic 4,4'-dihydroxy-3'-phenyl-3',5,5'-tri-*t*-butyltetraphenylmethane showed no depression.

From the above filtrate no 250 mg (13.5%) of 3,5-di-*t*-butylfuchsonone crystallized upon cooling.

4,4'-Dihydroxy-3,5-diisopropyl-3',5'-di-*t*-butyl-4'-methyltetraphenylmethane (VIIa).—A solution of 2,6-di-*t*-butylphenol (2.06 g, 10 mmoles), 3,5-diisopropyl-4'-methylfuchsonone (1.78 g, 5 mmoles), and acetophenone (18 g, 150 mmoles) in methanol (50 ml) containing 0.1 ml of concentrated hydrochloric acid was irradiated for 18 hr. The irradiation was stopped when the yellow solution turned almost colorless. The solvent was evaporated *in vacuo* and the acetophenone was removed by distillation at about 1 mm (bath temperature 100°). The solid, light yellow residue was recrystallized from a mixture of acetone, methanol, and a little water (yield 2.25 g, 80%), mp 185–188°.

Anal. Calcd for $C_{46}H_{50}O_2$ (562.85): C, 85.36; H, 8.95. Found: C, 85.04; H, 8.89; mol wt, 559.

3,5-Dicyclohexyl-4,4'-dihydroxy-3',5'-di-*t*-butyl-4'-methyltetraphenylmethane (VIIb).—A suspension of 3,5-dicyclohexyl-4'-methylfuchsonone (1.09 g, 2.5 mmoles) in a solution of 2,6-di-*t*-butylphenol (1.03 g, 5 mmoles) and acetophenone (15 g, 125 mmoles) in methanol (50 ml) containing 0.1 ml of concentrated hydrochloric acid was irradiated for 5 hr. By then the clear solution had turned suddenly almost colorless. Evaporation of the solvent *in vacuo* and removal of the acetophenone by distillation at about 1 mm (bath temperature 90°) gave a colorless, crystalline residue. The substance was recrystallized by dis-

solving in hot acetone, adding methanol, and boiling off the acetone (yield 1.34 g, 84%), mp 210–212°.

Anal. Calcd for $C_{48}H_{58}O_2$ (642.98): C, 85.93; H, 9.09. Found: C, 85.71; H, 9.21; mol wt, 625.

4,4'-Dihydroxy-3,3',5,5'-tetraphenyltetraphenylmethane (IXa). **A. Acetophenone-Sensitized Preparation.**—A suspension of 3,5-diphenylfuchsonone (1.025 g, 2.5 mmoles) in a solution of 2,6-diphenylphenol (1.23 g, 5 mmoles), acetophenone (15 g, 125 mmoles), and concentrated hydrochloric acid (0.03 ml) in methanol (50 ml) was irradiated for 22 hr. By then the solution was clear and yellow. Removal of solvent by distillation *in vacuo* at 1 mm (bath temperature 140–150°) yielded a yellow, oily residue which upon treatment with boiling methanol gave colorless to light yellow crystals, mp 230–232°. Recrystallization by dissolving in hot ether and adding methanol raised the melting point to 233–234° (yield 1.00 g, 61%).

Anal. Calcd for $C_{48}H_{38}O_2$ (656.84): C, 89.60; H, 5.52. Found: C, 89.35; H, 5.36; mol wt, 630.

B. Benzophenone-Sensitized Addition of 2,6-Diphenylphenol to 3,5-Diphenylfuchsonone.—A suspension of 3,5-diphenylfuchsonone (2.05 g, 5 mmoles) in a solution of 2,6-diphenylphenol (1.84 g, 7.5 mmoles), benzophenone (9.1 g, 50 mmoles), and concentrated hydrochloric acid (0.1 ml) in methanol (50 ml) was irradiated for 9 hr. By then the reaction mixture was clear and very light yellow in color. The usual distillative work-up at 1 mm (bath temperature 145°) gave a light yellow, oily residue which yielded 1.25 g (38%) of 4,4'-dihydroxy-3,3',5,5'-tetraphenyltetraphenylmethane, mp 231–232°, upon treatment with methanol.

4,4'-Dihydroxy-3,3',5,5'-tetracyclohexyltetraphenylmethane (IXb).—A suspension of 3,5-dicyclohexylfuchsonone (1.055 g, 2.5 mmoles) in a solution of 2,6-dicyclohexylphenol (1.29 g, 5 mmoles), acetophenone (15 g, 125 mmoles), and concentrated hydrochloric acid (0.1 ml) in methanol (50 ml) was irradiated for 13 hr. By then the solution was clear and only very slightly yellow. Distillative removal of all solvents at about 1 mm (bath temperature 130°) gave a light yellow, solid residue which yielded colorless crystals upon treatment with methanol (yield 1.15 g, 67%), mp 252–254°. Recrystallization from a boiling ether-methanol mixture did not raise the melting point.

Anal. Calcd for $C_{48}H_{60}O_2$ (681.03): C, 86.42; H, 8.88. Found: C, 86.51; H, 8.86; mol wt, 637.

4,4'-Dihydroxy-3,3',5,5'-tetraisopropyltetraphenylmethane (IXc).—A solution of 3,5-diisopropylfuchsonone (1.029 g, 3 mmoles), 2,6-diisopropylphenol (1.05 g, 6 mmoles), benzophenone (9.1 g, 50 mmoles), and concentrated hydrochloric acid (0.04 ml) in methanol (50 ml) was irradiated for 3 hr. By then the yellow solution turned colorless. Removal of the solvent by evaporation and distillation at about 1 mm (bath temperature 145°) *in vacuo* yielded a solid, colorless to light yellow residue which was recrystallized from aqueous methanol (yield 1.15 g, 74%), mp 192–193°.

Anal. Calcd for $C_{37}H_{44}O_2$ (520.77): C, 85.34; H, 8.52. Found: C, 85.44; H, 8.30; mol wt, 501.

4,4'-Dihydroxy-3,3'-diphenyl-5,5'-di-*t*-butyltetraphenylmethane (IXd).—A solution of 3-phenyl-5-*t*-butylfuchsonone (1.95 g, 5 mmoles) (partially suspended), 2-phenyl-6-*t*-butylphenol (2.26 g, 10 mmoles), acetophenone (18 g, 150 mmoles), and concentrated hydrochloric acid (0.1 ml) in methanol (50 ml) was irradiated for 26 hr. The by then clear, light yellow solution was subjected to vacuum distillation at 1 mm (bath temperature 135°) in order to remove methanol, acetophenone, and excess phenol. The light yellow, crystalline residue thus obtained was treated with methanol, filtered, and recrystallized by dissolving in little warm ether and adding methanol (yield 2.75 g) as colorless crystals (89%), mp 181–182°.

Anal. Calcd for $C_{46}H_{44}O_2$ (616.86): C, 87.63; H, 7.19. Found: C, 87.79; H, 7.35; mol wt, 582.

4,4'-Dihydroxy-3-*t*-butyl-3',5,5'-triphenyltetraphenylmethane (IXe).—A suspension of 3,5-diphenylfuchsonone (1.025 g, 2.5 mmoles) in a solution of 2-phenyl-6-*t*-butylphenol (1.13 g, 5 mmoles), acetophenone (15 g, 125 mmoles), and concentrated hydrochloric acid (0.1 ml) in methanol (50 ml) was irradiated for 2 hr. By then the solution was clear and almost completely colorless. Methanol was removed by evaporation *in vacuo* and the residual solution was subjected to vacuum distillation at 1 mm (bath temperature 185°). The light yellow, glassy residue yielded colorless crystals upon treatment with methanol which were recrystallized by dissolving in little hot ether and adding methanol. The yield of two combined work-ups was 2.80 g (88%), mp 205–206°.

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

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

spectrometer using deuteriochloroform solution with tetramethylsilane as an internal standard.

Registry No.—IIIb, 13135-44-9; IIIc, 13118-45-1; IIIId, 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.

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

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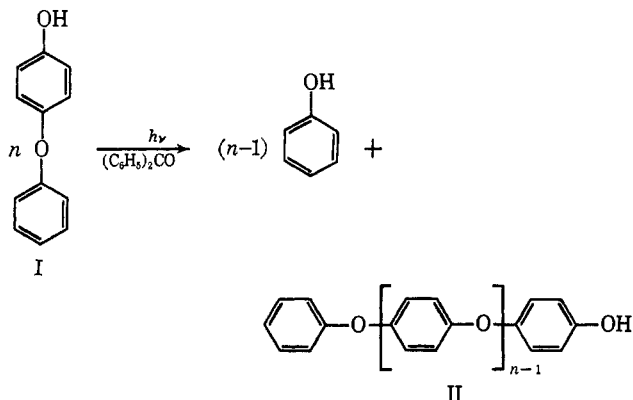
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The photochemical reaction of benzophenone with hydroquinone monoaryl ethers results in a smooth disproportionation: *p*-phenoxyphenol yields phenol and poly-*p*-phenylene ether. The mechanism of this reaction as revealed by the disproportionation 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 Å 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.



(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.

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-xyleneoxy)-2,6-xyleneol (III), however, led to rapid consumption of *p*-(2,6-xyleneoxy)-2,6-xyleneol and rapid formation of 2,6-xyleneol, while most of the *p*-phenoxy-