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.

---

[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

HANS-DIETER BECKER

General Electric Research and Development Center, Schenectady, New York

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

---

[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).

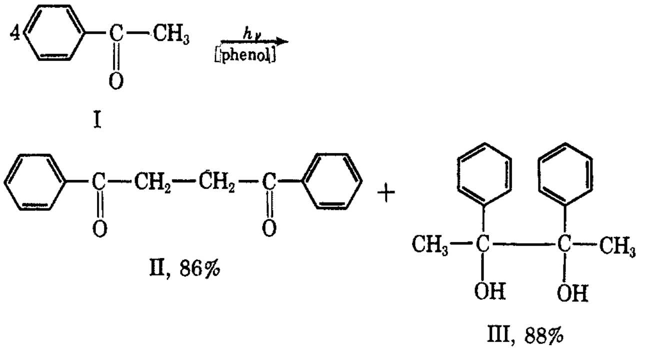
[5] Ch. Weizmann, E. D. Bergmann, and Y. Hirshberg, *J. Am. Chem. Soc.*, **60**, 1530 (1938).

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

stability of acetophenone toward direct irradiation, it appeared worthwhile to investigate the unexpected formation of 1,2-dibenzoylethane in more detail. The result of that investigation is this report on the photochemical oxidative–reductive dimerization of acetophenone, 4-methylacetophenone, 3,4-dimethylacetophenone, 2,4-dimethylacetophenone, and 2,5-dimethylacetophenone.

Results and Discussion

Irradiation of liquid acetophenone (I) containing a catalytic amount of phenol, using light from a high-pressure mercury arc filtered through Pyrex, results in a smooth oxidative–reductive dimerization of acetophenone according to the following reaction path.


I

II, 86%

III, 88%

This novel photochemical reaction of acetophenone is remarkably clean. Vapor phase chromatographic analysis indicates that no side products are formed. The oxidation product, 1,2-dibenzoylethane (II), isolated in 86% yield, precipitates during the irradiation in high state of purity, while the acetophenone pinacol (III), isolated in 88% yield, is easily separated from a small amount of nonvolatile material by means of distillation.

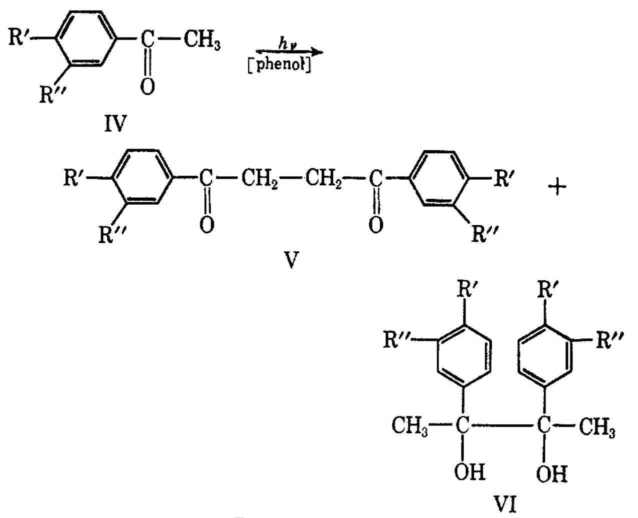
The presence of phenol is quite essential in the photochemical oxidative–reductive dimerization of acetophenone. At a concentration of about 1%, phenol—preferably adsorbed on silica gel suspended in acetophenone—catalyzes the photochemical formation of 1,2-dibenzoylethane and acetophenone pinacol on a preparatively useful scale. Other phenols, such as 2,6-di-*t*-butylphenol and 2,6-diphenylphenol also can act as catalysts; however, the unsubstituted phenol was found to be far more efficient. The photochemical oxidative–reductive dimerization of acetophenone, catalyzed by phenol, also proceeds in acetone solution, but irradiation without a solvent appears preparatively advantageous. Some experimental data on the effect of different phenols on the yield of 1,2-dibenzoylethane are listed in Table I.

TABLE I

I, g	Catalyst[a] (g)	Time, hr	Yield of II, g
60	A (4.12)	23	0.3
60	A (2.06)	21	0.7
50	B (1.23)	21	0.5
12[b]	C (3.0)	17	1.1
50	C (2.0)	14	2.6
75	C (1.0 g on 5 g of SiO_2)	24	10.65

[a] A, 2,6-di-*t*-butylphenol; B, 2,6-diphenylphenol; C, phenol.
[b] Dissolved in 75 ml of acetone.

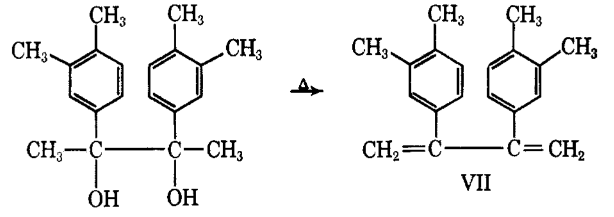
4-Methylacetophenone (IVa) in the presence of phenol reacts photochemically in the same manner as described for acetophenone. 1,2-Bis-*p*-toluylethane (Va) and 4-methylacetophenone pinacol (VIa) were isolated in 89 and 99%, respectively. Similarly, irradiation of 3,4-dimethylacetophenone (IVb) in the presence of phenol results in the formation of 1,2-bis(3,4-dimethylbenzoyl)ethane (Vb) and 3,4-dimethylacetophenone pinacol (VIb). As a by-product, 2,3-bis(3,4-dimethylphenyl)butadiene (VII), probably formed by elimination of water from 3,4-dimethylacetophenone pinacol (VIb) during the distillative work-up, was isolated from the reaction mixture.


IV

V

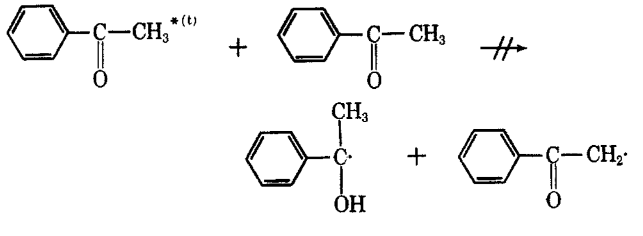
VI

a, R′ = CH_3; R″ = H
b, R′ = CH_3; R″ = CH_3


VIb

VII

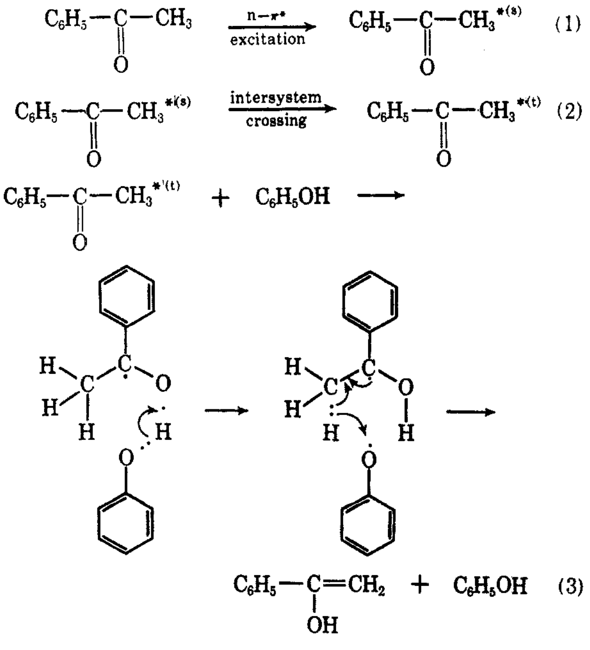
Irradiation of acetophenone in the absence of phenol only yields traces of 1,2-dibenzoylethane and acetophenone pinacol as revealed by vapor phase chromatographic analysis. Thus, the necessity of having a catalyst present and, furthermore, the absence of 4,4′-diacetylbibenzyl in the photochemical reaction of 4-methylacetophenone suggest that direct oxidation of ground state acetophenone by triplet-state acetophenone is a very inefficient process. It rather appears plausible that the observed reaction products derive from a hydrogen abstraction by triplet-state acetophenone from the enol of acetophenone. The carbon–carbon coupling observed in the homolytic oxidative dimerization of enolizable ketones lends support to this



view.[7] Since the addition of a trace of hydrochloric acid, however, does not show any effect on the photochemical reaction of acetophenone (in the absence of phenol) a simple, ground-state enolization of acetophenone due to the acidity of phenol appears very unlikely. An attempt to exchange the hydrogen atoms of the acetyl group for deuterium by shaking acetophenone with D_2O in the presence of phenol indeed was unsuccessful. Thus, phenol seems to play a unique photochemical role in the enolization of acetophenone.

We would like to propose and discuss the following mechanism for the oxidative–reductive dimerization reaction involving a phenol-catalyzed, photoenolization of acetophenone.

Photochemically excited acetophenone reacts with phenol by abstracting a hydrogen atom to produce a phenoxy radical and a semipinacol radical. Quite different from the reaction of triplet-state benzophenone with 2,6-disubstituted phenols described in the preceding papers, however, no radical coupling occurs. Instead a redox reaction, conceivably favored by a six-membered transition state, leads to the enol form of acetophenone and regeneration of phenol. The observed advantageous effect of having the phenol adsorbed on silica gel presumably lies in the restriction of mobility of phenoxy radicals, thus inhibiting the dissociation of the intermediate radical pair and suppressing the possible side reaction of irreversible phenol oxidation.[8]



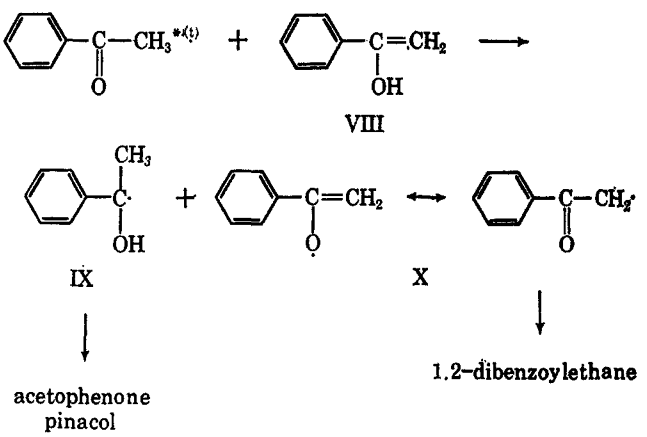
$$\mathrm{C_6H_5-\underset{\underset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow[\text{excitation}]{n-\pi^*} C_6H_5-\underset{\underset{\displaystyle O}{\|}}{C}-CH_3^{*(s)}} \qquad (1)$$

$$\mathrm{C_6H_5-\underset{\underset{\displaystyle O}{\|}}{C}-CH_3^{*(s)} \xrightarrow[\text{crossing}]{\text{intersystem}} C_6H_5-\underset{\underset{\displaystyle O}{\|}}{C}-CH_3^{*(t)}} \qquad (2)$$

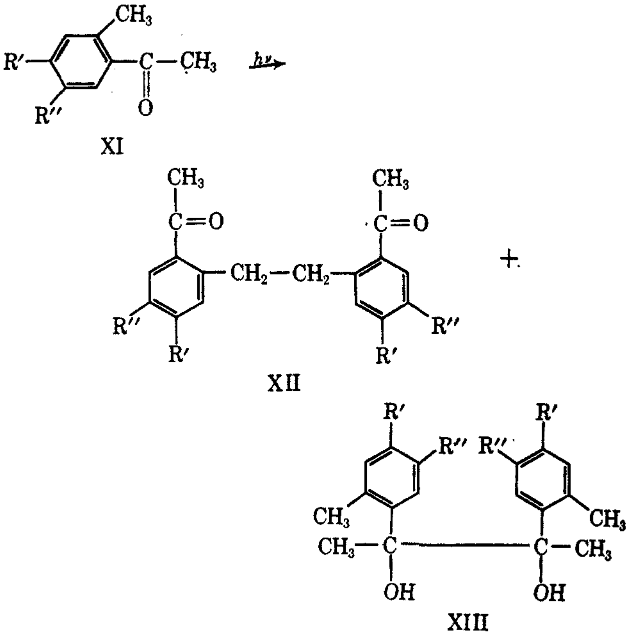
$$\mathrm{C_6H_5-\underset{\underset{\displaystyle O}{\|}}{C}-CH_3^{*(t)} + C_6H_5OH \longrightarrow}$$

$$\mathrm{C_6H_5-\underset{\underset{\displaystyle OH}{|}}{C}=CH_2 + C_6H_5OH} \qquad (3)$$

Oxidation of acetophenone enol (VIII) by triplet-state acetophenone then produces a semipinacol radical (IX) which dimerizes to give acetophenone pinacol, and an enoxy radical (X) which dimerizes to give 1,2-dibenzoylethane. 4-Methyl- and 3,4-dimethylacetophenone react accordingly. We have observed earlier that triplet-state benzophenone is a highly selective oxidizing agent for phenols.[1] Acetophenone most likely exhibits a similar photochemical behavior. Thus, the assumption that triplet-state acetophenone preferentially oxidizes the acetophenone enol rather than the also present phenol appears to be fully justified.



The participation of phenol in the formation of an intermolecular six-membered transition state with triplet-state acetophenone represents an attractive explanation for the photoenolization of acetophenone. Intramolecular photoenolization of *o*-alkylaryl ketones involving a six-membered transition state has been demonstrated earlier in the case of *o*-methylbenzophenone by Yang and Rivas[9] and has recently been shown to occur with a variety of *o*-alkyl-substituted aryl ketones.[10] Spectroscopic evidence has also been presented for the reversible photoenolization of *o*-methyl-substituted acetophenones.[11] We have now found that 2,4-dimethylacetophenone (XIa), in the absence of phenol, does undergo a photochemical reaction leading to 2,2′-diacetyl-5,5′-dimethylbibenzyl (XIIa, yield 21%) and 2,4-dimethylacetophenone pinacol (XIIIa). The major product of the reaction, however, was found to be a polymeric material. Similar results were obtained by irradiating 2,5-dimethylacetophenone (XIb) in the absence of phenol. The



a, R′ = CH_3; R″ = H
b, R′ = H; R″ = CH_3

---

[7] H.-D. Becker, *J. Org. Chem.*, **30**, 989 (1965).

[8] Vapor phase chromatographic analysis of the irradiated reaction mixtures does reveal the presence of phenol; however, no attempt has been made to determine the yield of recoverable phenol.

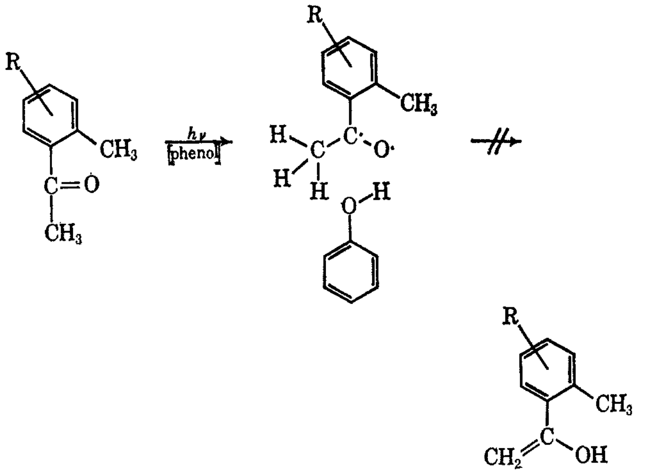
[9] N. C. Yang and C. Rivas, *J. Am. Chem. Soc.*, **83**, 2213 (1961).

[10] M. Pfau, N. D. Heindel, and T. F. Lemke, *Compt. Rend.*, **261**, 1017 (1965).

[11] G. Wettermark, *Photochem. Photobiol.*, **4**, 621 (1965).

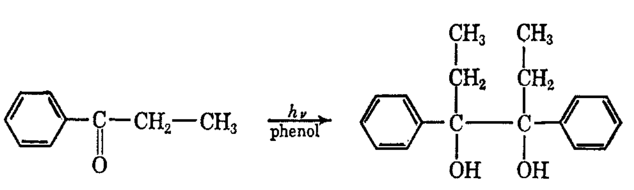
oxidative dimerization product, 2,2′-diacetyl-4,4′-dimethylbibenzyl (XIIb), was isolated in 18% yield from a large amount of nonvolatile reaction products. The addition of phenol was found to be without any effect on the course of the photoreactions of *o*-methyl-substituted acetophenones.

Obviously different from acetophenones I and IV, intramolecular photoenolization of *o*-methyl-substituted acetophenones appears to be favored over intermolecular hydrogen abstraction from phenol by triplet-state acetophenone XI which subsequently would lead to the structurally different enol XIV.[12] In agreement with the mechanistic scheme proposed for the formation of 1,2-dibenzoylethane from acetophenone, the formation of bibenzyl derivatives from acetophenones XI is readily explained by oxidation of the photoenol XV by triplet-state *o*-methyl-substituted acetophenone (Scheme I). The observed polymeric reaction products probably arise from successive coupling reactions of the primarily formed bifunctional, photoenolizable reaction products.



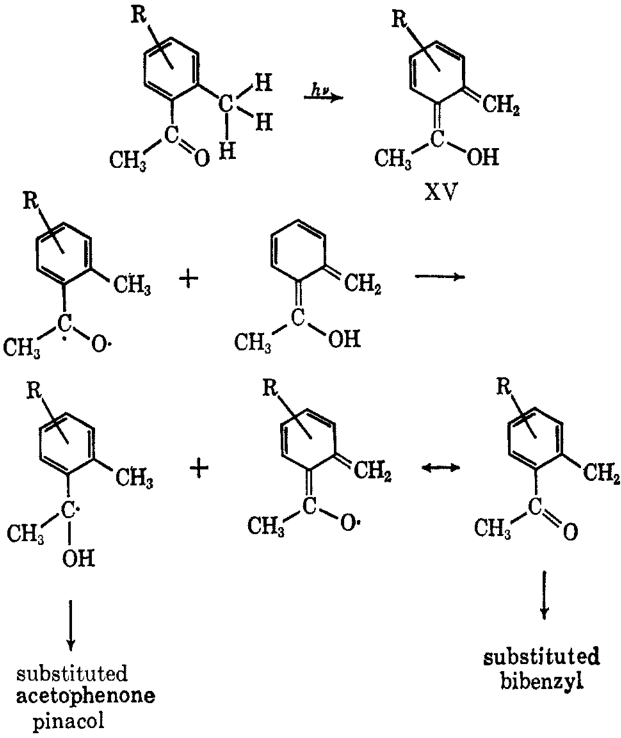
XIV

An attempt to extend the photochemical, phenol-catalyzed oxidative–reductive dimerization to propiophenone was unsuccessful. Propiophenone (XVI) did not yield any isolable products when irradiated in the absence of phenol. The only reaction product isolated after the irradiation of propiophenone in the presence of phenol was propiophenone pinacol (XVII).[13] The dark color of the reaction mixture indicated that phenol had been oxidized irreversibly, thus serving only as a hydrogen donor for the reductive dimerization of propiophenone rather than as a catalyst for a photoenolization.



XVI XVII

Scheme I



Experimental Section

The Apparatus.—All irradiations were carried out in a Pyrex apparatus described in a preceding paper.[14] The lamp used was a G.E. 100-w mercury lamp, Type H-100 A 4/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.

Materials.—Acetophenones were distilled before use. Phenol (Loose Crystals, Analytical Reagent) was obtained from Mallinckrodt Chemical Works. According to its specifications, it contained approximately 0.15% H_3PO_2 as preservative. Silica gel (Fisher Laboratory Chemical) was 28–200 mesh. The phenol was adsorbed onto silica gel by warming under stirring. All melting points were taken on a Fisher-Johns melting point apparatus and are not corrected. Molecular weights were determined by thermoelectric measurement in solvents as indicated in each case. Vapor phase chromatographic analyses were carried out on a 2-ft silicone rubber column using temperature programming (7.5°/min) between 100 and 300°. Infrared and proton magnetic resonance spectra were obtained on all compounds reported in this paper.

Photolysis of Acetophenone.—A suspension of phenol (1 g) adsorbed on silica gel (5 g) in acetophenone (75 g) was irradiated for 24 hr. By then the reaction mixture contained a colorless, crystalline precipitate which was removed by filtration. Separation of the precipitate from the silica gel was effected by treatment with chloroform, filtration, and evaporation to yield 9.15 g of 1,2-dibenzoylethane, mp 144–145° (lit.[15] 144–145°).

Anal. Calcd for $C_{16}H_{14}O_2$ (238.29): C, 80.65; H, 5.92. Found: C, 80.64; H, 6.09; mol wt, 239 (in benzene).

Vacuum distillation (1 mm) of the original filtrate gave 50 g of recovered acetophenone. Treatment of the viscous residue of the distillation with methanol (30 ml) caused the precipitation of additional 1.5 g of 1,2-dibenzoylethane (total yield 10.65 g, 86%, based on consumed acetophenone).

The filtrate was subjected to vacuum distillation (1 mm), yielding a mixture of stereoisomer acetophenone pinacols as colorless, oily distillate (bp 160–165°) which crystallized at room temperature (yield 11.1 g, 88%), mp 85–95°. Partial separation of one isomer was accomplished by treatment of the mixture with boiling petroleum ether (bp 30–60°), thus extracting a crystalline

---

(12) We have unsuccessfully attempted to treat *o*-methylbenzophenone photochemically with 2,6-di-*t*-butylphenol in acetone solution. Thus, photoenolization of *o*-methylbenzophenone also appears to be favored over intermolecular hydrogen abstraction from 2,6-di-*t*-butylphenol.

(13) It is worth mentioning that the hydrogens of the CH_2 groups in propiophenone pinacol are magnetically nonequivalent, owing to the asymmetry of the adjacent carbon atom.

(14) Paper I: H.-D. Becker, *J. Org. Chem.*, **32**, 2115 (1967).

(15) S. Kapf and C. Paal, *Ber.*, **21**, 3053 (1888).

acetophenone pinacol which was recrystallized from petroleum ether (bp 65–110°) (yield 3 g), mp 123–125° (lit.[5] 123°).

Anal. Calcd for $C_{16}H_{18}O_2$ (242.32): C, 79.31; H, 7.49. Found: C, 79.46; H, 7.64; mol wt, 244 (in chloroform).

The undissolved part of the crystalline distillate (mp 85–95°) was analyzed by nmr spectroscopic means and found to consist of a mixture of two acetophenone pinacols, one of which was identical with the pure isomer described above.

Anal. Calcd for $C_{16}H_{18}O_2$ (242.32): C, 79.31; H, 7.49. Found: C, 79.51; H, 7.68; mol wt, 241 (in chloroform).

The yield of nonvolatile brown residue of the distillative work-up was 1.6 g.

Photolysis of 4-Methylacetophenone.—A suspension of phenol (3 g) adsorbed on silica gel (15 g) in 4-methylacetophenone (73 g) was irradiated for 15 hr and then worked up in the same manner as described above: precipitated 1,2-bis-*p*-toluylethane (4.8 g), second fraction (1.4 g) (total yield 6.2 g, 89%), mp 159–160° (lit.[16] 159°).

Anal. Calcd for $C_{18}H_{18}O_2$ (266.34): C, 81.17; H, 6.81. Found: C, 81.21; H, 6.99; mol wt, 266 (in benzene).

The 4-methylacetophenone recovered was 59 g. The yield of a distilled liquid mixture of isomer pinacols [bp 165° (1 mm)] was 7 g (99%). Treatment of the distillate with petroleum ether (bp 30–60°) caused the crystallization of one isomer pinacol (yield 1.8 g), mp 135–136°.

Anal. Calcd for $C_{18}H_{22}O_2$ (270.38): C, 79.96; H, 8.20. Found: C, 79.76; H, 8.26; mol wt, 268 (in benzene).

The noncrystallizable fraction of the distillate was analyzed by nmr spectroscopic means and found to consist of a mixture of two 4-methylacetophenone pinacols, one of which was identical with the crystalline isomer.

Anal. Calcd for $C_{18}H_{22}O_2$ (270.38): C, 79.96; H, 8.20. Found: C, 80.03; H, 8.22; mol wt, 266 (in benzene).

Photolysis of 3,4-Dimethylacetophenone.—A suspension of phenol (1 g) adsorbed on silica gel (5 g) in 3,4-dimethylacetophenone (80 g) was irradiated for 22 hr. The reaction mixture was then worked up in the same manner as described under the photolysis of acetophenone: precipitated 1,2-bis(3,4-dimethylbenzoyl)ethane (2.1 g), second fraction (0.75 g) (total yield 2.85 g, 96%), mp 157°.

Anal. Calcd for $C_{20}H_{22}O_2$ (294.40): C, 81.60; H, 7.53. Found: C, 81.44; H, 7.64; mol wt, 289 (in benzene).

The 3,4-dimethylacetophenone recovered was 74 g. Further distillative work-up gave 3 g of a colorless liquid distillate [bp 200–240° (1 mm)], from which one stereoisomer 3,4-dimethylacetophenone pinacol precipitated upon treatment with petroleum ether (bp 30–60°) (yield 0.35 g), mp 129–131° (recrystallized from petroleum ether, bp 65–110°).

Anal. Calcd for $C_{20}H_{26}O_2$ (298.43): C, 80.50; H, 8.78. Found: C, 80.32; H, 8.82; mol wt, 292 (in benzene).

Additional crystalline material which separated from the original petroleum ether filtrate consisted of a mixture of stereoisomer 3,4-dimethylacetophenone pinacols (nmr) (yield 750 mg), mp 100–120°.

Anal. Calcd for $C_{20}H_{26}O_2$ (298.43): C, 80.50; H, 8.78. Found: C, 80.20; H, 8.96; mol wt, 292 (in benzene).

The oily residue obtained from the final petroleum ether filtrate after evaporation of solvent gave 0.25 1 g of 2,3-bis(3,4-dimethylphenyl)butadiene upon treatment with methanol as colorless crystals, mp 73°.

Anal. Calcd for $C_{20}H_{22}$ (262.40): C, 91.55; H, 8.45. Found: C, 91.52; H, 8.71; mol wt, 263 (in benzene).

Photolysis of 2,4-Dimethylacetophenone.—2,4-Dimethylphenol (97 g) was irradiated for 40 hr. Distillative work-up of the yellow reaction mixture gave unreacted starting material (70 g), a yellowish, oily distillate [12.8 g, bp 215–225° (1 mm)], and a brown nonvolatile, polymeric residue (13 g). Treatment of the distillate with petroleum ether (bp 30–60°) caused the precipitation of 2,2′-diacetyl-5,5′-dimethylbibenzyl, which was recrystallized from boiling methanol (yield 2.88 g, 21%), mp 117–118°.

Anal. Calcd for $C_{20}H_{22}O_2$ (294.40): C, 81.60; H, 7.53. Found: C, 81.57; H, 7.78; mol wt, 290 (in benzene).

Evaporation of the petroleum ether filtrate and treatment of the oily residue with petroleum ether (bp 65–110°) caused the crystallization of one isomer, 2,4-dimethylacetophenone pinacol (nmr). It was recrystallized from boiling petroleum ether (bp 65–110°) (yield 1.75 g, 13%), mp 117–118°.

Anal. Calcd for $C_{20}H_{26}O_2$ (298.43): C, 80.50; H, 8.78. Found: C, 80.35; H, 8.63; mol wt, 297 (in chloroform).

Photolysis of 2,5-Dimethylacetophenone.—2,5-Dimethylacetophenone (75 g) was irradiated for 30 hr. Vapor phase chromatographic analysis of the reaction mixture indicated the presence of at least eight products. Distillative work-up yielded unchanged starting material (58 g), a distillate [10 g, bp 220–250° (1 mm)] containing all products detected by vpc analysis, and an undistillable polymeric residue (7 g). The distillate was treated with little methanol, yielding 2,2′-diacetyl-4,4′-dimethylbibenzyl as colorless crystals. It was removed by filtration and recrystallized from boiling methanol (yield 1.5 g, 18%), mp 127–128°.

Anal. Calcd for $C_{20}H_{22}O_2$ (294.40): C, 81.60; H, 7.53. Found: C, 81.80; H, 7.49; mol wt, 291 (in benzene).

Attempts to characterize any other products in the oily distillate were unsuccessful. Infrared spectroscopic analysis of the oily mixture indicated the presence of hydroxyl group containing compounds.

Photolysis of Propiophenone.—A solution of phenol (3 g) in propiophenone (65 g) was irradiated for 30 hr. Vapor phase chromatographic analysis of the reaction mixture indicated the formation of only one major reaction product. Vacuum distillation gave unchanged propiophenone (50 g) and a light yellow, oily fraction [bp 175–200° (1 mm), yield 4 g] from which one isomer, propiophenone pinacol, crystallized upon treatment with petroleum ether (bp 30–60°). The pinacol was recrystallized from boiling petroleum ether (bp 65–110°) (yield 1.0 g), mp 137–138°.

Anal. Calcd for $C_{18}H_{22}O_2$ (270.38): C, 79.96; H, 8.20. Found: C, 79.84; H, 8.17; mol wt, 278 (in chloroform).

Spectra.[17]—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.—II, 495-71-6; III, 1636-34-6; Va, 13145-56-7; Vb, 13145-57-8; VIa, 13145-58-9; VIb, 13131-79-8; VII, 13145-59-0; XIIa, 13145-60-3; XIIb, 13145-61-4; XIIIa, 13145-62-5; XVII, 10442-33-8.

---

[16] J. B. Conant and R. E. Lutz, *J. Am. Chem. Soc.*, **45**, 1303 (1923).

[17] Thanks are due to Miss Dorothy McClung and Miss Mary Ann Olivier for their prompt collaboration in recording the spectra.