(4) Solid aluminum chloride can form liquid complexes with the polyethylation products which are formed during prolonged contact of the reactants with the surface (exp. III, Table I). Since hydrogen chloride also is produced it may be a necessary part of the complex, as Brown and coworkers[5] have demonstrated to be the case for aluminum chloride complexes with toluene. Because of their low vapor pressure it is quite possible that the polyethylated compounds condensed as liquids on the surface before complex formation occurred in the present work. It has been demonstrated by Mr. James Reavis in our laboratory that neither gaseous mixtures of hydrogen chloride with benzene or with ethyl chloride show appreciable reaction with solid aluminum chloride.

It would be premature to attempt to state a detailed mechanism depicting the manner in which the reacting molecules become attached to the aluminum chloride surface, and undergo reaction. It may be that the localized centers of coulombic attraction on the surface of the ionic lattice play an important role.[2] Alternatively it may be that the initial step involves adsorption of the ethyl chloride and benzene by the aluminum atom acting as an acid.[6]

Acknowledgments.—We should like to thank Donald R. Johnson, working in the departmental instrument laboratory, which is under the direction of Prof. V. W. Meloche, for making the infrared analyses we have reported.

This work was supported in part by the Atomic Energy Commission, in part by the University Research Committee with funds made available by the Wisconsin Alumni Research Foundation, and in part by a Visking Corporation Fellowship.

[5] (a) H. C. Brown, H. W. Pearsall and L. P. Eddy, THIS JOURNAL, **72**, 5347 (1950); (b) H. C. Brown and H. W. Pearsall, *ibid.*, **74**, 191 (1952).

[6] For discussions of such interactions in solution and references, see for example: (a) H. C. Brown and J. D. Brady, *ibid.*, **74**, 3570 (1952); (b) M. Tamres, *ibid.*, **74**, 3375 (1952).

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, NEW MEXICO HIGHLANDS UNIVERSITY, AND FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF MISSOURI]

Condensations of Aromatic Aldehydes and Aryl Carbinols with Aluminum Chloride and Aromatic Systems

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RECEIVED FEBRUARY 14, 1953

The reaction of aryl carbinols and aromatic aldehydes with aromatic hydrocarbons and excess aluminum chloride has been extended to include substituted benzyl alcohols as donors and mesitylene, biphenyl and diphenyl ether as acceptor molecules. An unexpected reaction occurred with diphenyl ether. The implications of the experimental results are discussed.

Various aromatic aldehydes, benzyl alcohol and benzhydrol can be cleaved with excess aluminum chloride at 60° to give carbon monoxide. When the reaction is carried out in benzene the carbon monoxide is not evolved but reacts with the solvent to give anthracene and triphenylcarbinol. With toluene and diphenylmethane a condensation occurs which yields dimethyl- and dibenzylanthracenes as end-products.[4] In these reactions the oxygenated carbon of the donor molecule furnishes only the *meso* carbons of the anthracenes and the carbinol carbon of triphenylcarbinol. The aryl portion of the donor molecule is generally isolated as ArH.[4-6]

The reaction with biphenyl, benzaldehyde and excess (2 moles) aluminum chloride furnishes a diphenylanthracene, m.p. 202–203° (diphenylanthraquinone, m.p. 270–271°), which differs from the substance obtained previously under somewhat different conditions,[7] but is doubtless formed in the same fashion.[8]

The three xylenes were shown to react with benzaldehyde and excess aluminum chloride to give different tetramethylanthracenes,[7] evidently without appreciable rearrangement of the methyl groups. A reaction of this sort is not possible with mesitylene. The product of the reaction was identical with the tetramethylanthracene prepared from *m*-xylene.[7,9] The volatile fraction from the reaction contained xylenes as well as tetramethylbenzenes, further establishing the cleavage of a methyl group in mesitylene.

When the reaction takes place in diphenyl ether the same solid product (I) is formed from benzaldehyde, benzyl alcohol or benzhydrol. This substance is not an anthracene but has been identified as 9-phenylxanthydrol by degradation and synthesis. Its formation in these reactions is unique since the oxygenated compounds apparently

[1] Chemistry Department, Purdue University, Lafayette, Ind.

[2] From the master's thesis of E. F. Kline, N. M. Highlands University, 1952.

[3] In part from the Ph.D. thesis of E. W. Crandall, University of Missouri, 1950.

[4] H. E. Ungnade and E. W. Crandall, THIS JOURNAL, **71**, 2209, 3009 (1949).

[5] D. H. Hey, *J. Chem. Soc.*, 72 (1935).

[6] For an understanding of the reaction it is necessary to point out that the reaction mixtures are decomposed with ice and hydrochloric acid and separated by steam distillation. Under these conditions tertiary halides analogous to triphenylchloromethane will be rapidly hydrolyzed to carbinols (W. Hemilian, *Ber.*, **7**, 1208 (1874)). The non-volatile products usually contain tar and oily by-products without characteristic absorption spectra in the ultraviolet or visible region. These may represent hydrogen acceptors.

[7] H. Ellison and D. H. Hey, *J. Chem. Soc.*, 1847 (1938).

[8] The absorption spectrum of this substance indicates that the phenyl substituents will be in beta positions.

[9] A precedent for this reaction is the formation of hexamethylanthracene from isodurene and pivalyl chloride (D. Nightingale, R. L. Sublett, R. A. Carpenter and H. D. Radford, *J. Org. Chem.*, **16**, 658 (1951)).

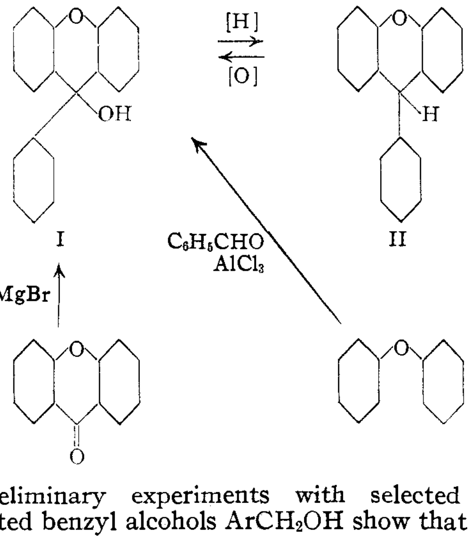
donate one benzene nucleus and one carbon, *i.e.*, they undergo condensation rather than cleavage. Moreover this condensation takes place at the normally unreactive *ortho* positions of the diphenyl ether molecule.

The structure of I is derived as follows. The colorless crystalline solid, m.p. 156–157°, $C_{19}H_{14}O_2$ (or $C_{20}H_{14}O_2$) is reduced in good yield to a colorless solid II, m.p. 142–143°, $C_{19}H_{14}O$ (or $C_{20}H_{14}O$) under various conditions. It reacts with phenylhydrazine, hydroxylamine and semicarbazide with elimination of water. The formation of the semicarbazide derivative (III) does not alter the ultraviolet absorption spectrum. The parent compound is regenerated from III by action of nitrous acid.

The reduction product II can be oxidized to I but the latter is stable to further oxidation under ordinary conditions. Methylmagnesium iodide reacts with I giving an orange solution from which I is completely recovered on hydrolysis. These reactions are compatible with a tertiary aryl carbinol structure with one inert (ether) oxygen.

The ultraviolet absorption spectra of I and II,[10] while somewhat similar to that of diphenyl ether, differ from the curves obtained for diphenyl ethers with appropriate *para* substituents, but the spectrum of II resembles that of xanthene thus indicating a xanthene structure for II and a xanthydrol type of structure for I.

To distinguish between $C_{19}H_{14}O$ and $C_{20}H_{14}O$, 9-benzyl- and 9-phenylxanthene were synthesized. The reduction product II proved identical with the latter and quite different from the homolog. The reactions can therefore be written[6]



Preliminary experiments with selected substituted benzyl alcohols $ArCH_2OH$ show that these can serve as carbon monoxide donors as well as the aromatic aldehydes[4] and will furnish anthracene when benzene is used as solvent. The aryl group is recovered as an ArH compound but there is a difference in the products from aldehydes and carbinols with the same substituents. *p*-Methoxybenzaldehyde yields phenol whereas *p*-methoxybenzyl alcohol gives anisole. 3,4-Dimethoxybenzyl alcohol is cleaved to give guaiacol while veratric aldehyde is only demethylated to a vanillin. It appears therefore that benzyl alcohols are not dehydrogenated to give the corresponding aromatic aldehydes as intermediates.

o-Benzylbenzyl alcohol (IV) has been investigated because of the possibility of intramolecular cyclization. The carbinol IV fails to react with only 1 mole of aluminum chloride. The product of the reaction with benzene and 3 moles of aluminum chloride is anthracene. The reaction is predominantly a cleavage reaction rather than an intramolecular cyclization because the product from IV and toluene is the eutectic mixture of the dimethylanthracenes and the aryl portion of IV is largely recovered as diphenylmethane.

Acknowledgment.—This work was supported by a grant from the Research Corporation to whom the authors wish to express their gratitude.

Experimental[11]

Diphenylanthracene.—Benzaldehyde (30 g., 0.28 mole) was added during 0.5 hour to a stirred mixture of 20 g. (0.13 mole) of biphenyl and 79 g. (0.59 mole) of aluminum chloride at 60°. The mixture was stirred at 60° for 3.5 hours, decomposed and steam distilled. The non-volatile fraction (32.39 g.) was distilled under reduced pressure. The distillate (6.02 g., 28%) boiling at 170–210° (0.001 mm.) was crystallized three times from ligroin; m.p. 202–203°. Its absorption spectrum in cyclohexane had maxima at 230, 257.5, 277.5, 332.5, 347.5, 365 and 385 mμ (log ϵ 4.65, 4.97, 5.09, 3.67, 3.91, 4.01 and 3.89). (Absorption spectrum by Dr. E. E. Pickett.)

Anal. Calcd. for $C_{26}H_{18}$: C, 94.52; H, 5.49. Found: C, 94.25; H, 5.46.

Diphenylanthraquinone.—Diphenylanthracene (1.0 g., 0.003 mole) dissolved in 14 cc. of glacial acetic acid, was refluxed gently over a low flame. A solution of 4.0 g. of chromic anhydride in 4 cc. of water and 16 cc. of acetic acid was added slowly during 0.5 hour. The solution was cooled, diluted with 200 cc. of water and filtered. The crude green solid was washed with water, dilute aqueous sodium hydroxide and again with water. The pure substance crystallized in yellow needles from 95% ethanol. It was filtered and dried *in vacuo* at 100°; yield 1.02 g. (93.5%), m.p. 270–271°.

Anal. Calcd. for $C_{26}H_{16}O_2$: C, 86.60; H, 4.47. Found: C, 86.92; H, 4.56.

The Reaction of Benzaldehyde with Aluminum Chloride and Mesitylene.—Benzaldehyde (25 g., 0.24 mole) was added over a period of 0.5 hour to a mixture of 67 g. (0.5 mole) of aluminum chloride in 60 cc. (51.9 g., 0.43 mole) of mesitylene. The reaction mixture was stirred for 3.5 hours at 60°, decomposed and steam distilled. The distillate, taken up in benzene, was washed with saturated aqueous sodium bisulfite. The insoluble adduct furnished 7.86 g. (31%) of benzaldehyde (oxime, m.p. 32–33°). The benzene solution was rectified through a micro Vigreux column giving 1.0 g. (2%) of xylenes, b.p. 140–150° (598 mm.), $n^{23}D$ 1.4970, λ_{max} (alc.) 266 mμ (log ϵ 2.36), 8.7 g. (17%) of trimethylbenzenes, b.p. 150–160° (600 mm.), $n^{23}D$ 1.5005, λ_{max} (alc.) 266 mμ (log ϵ 2.40), which on nitration gave 2,4,6-trinitromesitylene, m.p. 230–232° and 2.6 g. (4%) of tetramethylbenzenes, b.p. 180–185° (600 mm.), $n^{23}D$ 1.5105, λ_{max} 269 mμ (log ϵ 2.57).

When a portion (12.86 g.) of the non-volatile residue (22.50 g.) was refluxed with ligroin (b.p. 70–90°), 2.74 g. remained undissolved. The ligroin solution was adsorbed on alumina. Three bands with blue fluorescence (under ultraviolet light) were eluted with ligroin and gave 7.34 g. (45.7%) of oily solid. Repeated crystallizations from ligroin raised the melting point from 132–138° to 148–148.7°. The absorption spectrum of this substance in cyclohexane showed four maxima at 338, 350, 366 and 386

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[10] For the complete spectra for the substances referred to in this paper order Document 3953 from ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C., remitting $1.25 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.25 for photoprints readable without optical aid.

[11] All temperatures uncorrected.

mμ (log ε 3.45, 3.66, 3.78 and 3.68) at precisely the same wave lengths at which the tetramethylanthracene from *m*-xylene[7] absorbed.

9-Phenylxanthydrol was obtained from benzyl alcohol, benzhydrol or benzaldehyde by reaction with diphenyl ether and aluminum chloride. The procedure is given in detail only for benzaldehyde.

Benzaldehyde (25 g., 0.24 mole) was added during 0.5 hour to a mixture of 67 g. (0.50 mole) of aluminum chloride and 75 cc. (0.47 mole) of diphenyl ether. The mixture was allowed to stir for 3.5 hours at 60°. It was decomposed with ice and concentrated hydrochloric acid and steam distilled until no diphenyl ether appeared in the distillate. The steam distillate was extracted with ether; the extract was washed with water and dried over anhydrous sodium sulfate, filtered and distilled through a Vigreux column. The solvent boiled at 32–33° (610 mm.). The remaining liquid, distilled at 19 mm., gave 1.2% of unreacted benzaldehyde (b.p. 96–98°, identified as benzoic acid) and 44.3% of recovered diphenyl ether, b.p. 162–164°; 4,4′-disulfonamide, m.p. 157–158°.

The non-volatile semi-solid residue from the steam distillation was taken up in benzene, washed, dried and distilled to remove the solvent; yield 32.2 g. It was worked up as follows: (a) Adsorption of the material (2.18 g.), dissolved in benzene on aluminum oxide gave four distinct bands. The bulk of the product was contained in three bands which were eluted with benzene and contained in order: 0.12 g. of red viscous oil, 1.48 g. of red-brown oil and 0.46 g. of crystalline solid, m.p. 149–154° (after crystallization from ligroin). The solid was identical with 9-phenylxanthydrol.

(b) Distillation of the residue (9.55 g.) at 190–210° (0.001 mm.) gave 4.15 g. of a red oil which solidified on standing. Crystallization from benzene–ligroin yielded 9-phenylxanthydrol, m.p. 156–157° (3.02 g.).

Anal. Calcd. for $C_{19}H_{14}O_2$: C, 83.12; H, 5.14; mol. wt., 274.30. Found: C, 83.53; H, 5.34; mol. wt. (Rast), 262.0.

On vacuum distillation of larger quantities pyrolysis and reduction occurred. The isolated products were phenol and 9-phenylxanthene.

The over-all yields of 9-phenylxanthydrol isolated according to method (b) were: (1) from benzaldehyde 15.5%; (2) from benzyl alcohol 15%; (3) from benzhydrol 27%. In the last case the amount of aluminum chloride was increased to 3 moles per mole of benzhydrol.

Synthetic 9-phenylxanthydrol, prepared in 76% yield from xanthone and phenylmagnesium bromide,[12] melted at 157–158° and did not depress the melting point of the above specimens. Their ultraviolet absorption spectra were identical.

9-Phenylxanthydrol dissolved in concentrated sulfuric acid with green-yellow color and fluorescence. It reacted with semicarbazide, hydroxylamine and phenylhydrazine to give solid derivatives, m.p. 206–207°, 194–195° and 127–128° but was recovered unchanged (in 99.3% yield) from its reaction mixture with methylmagnesium iodide. Acylating and oxidizing agents failed to attack it under ordinary conditions. It was pyrolyzed at 282° to give phenol.

9-Phenylxanthene.—9-Phenylxanthydrol can be reduced to the xanthene by the following methods in the yields indicated: (1) Clemmensen reduction (91.3%); (2) Schmidt reaction (96.6%); (3) refluxing with ethanolic hydrochloric acid (87.7%). The product so obtained melted at 142–143° (lit. m.p. 145°)[12c] after crystallization from ligroin.

Anal. Calcd. for $C_{19}H_{14}O$: C, 88.35; H, 5.46; mol. wt., 258.30. Found: C, 88.45; H, 5.08; mol. wt. (Rast). 242.0.

The substance was insoluble in concentrated sulfuric acid. When oxidized with potassium permanganate in aqueous pyridine it was converted to 9-phenylxanthydrol, m.p. and mixed m.p. 155–156° (from ligroin).

9-Benzalxanthene.—Xanthone (5 g., 0.025 mole), dissolved in dry benzene, was added to benzylmagnesium chloride (0.025 mole) in dry ether. The complex, decomposed with ice and ammonium chloride solution, furnished 6.11 g. of yellow oil which solidified when triturated with petroleum ether. Recrystallization from ligroin or chromatographic adsorption on alumina yielded 89% of crystalline benzalxanthene (yellow needles, m.p. 110–111°, lit. 114–115°[13]) from the crude product. The pure compound dissolved in cold concentrated sulfuric acid with yellow color and green fluorescence.

9-Benzylxanthene.—The reduction of benzalxanthene with hydriodic acid and acetic anhydride was accompanied by cleavage of the 9,10 double bond.[13] The reaction products from 2.65 g. (0.009 mole) of benzalxanthene when crystallized from ligroin gave 0.11 g. of xanthone, m.p. 158–160° (recrystallized m.p. 173–174°), and 0.74 g. of 9-benzylxanthene, recrystallized, m.p. 69–70° (lit. m.p. 71°[13]).

4-Phenoxytoluene and 4-phenoxy-*o*-xylene were prepared from potassium phenoxide and potassium 3,4-dimethylphenoxide and the appropriate bromides in 70 and 38% yields according to the method described previously.[14]

4-Phenoxybenzophenone prepared according to Kipper[15] melted at 69.2–69.4°. It dissolved in cold concentrated sulfuric acid with yellow color[16] and was unchanged under the conditions of the cyclodehydration procedure of Bradsher.[17] On fusion with sodium hydroxide at 350° it cleaved to give benzoic acid and diphenyl ether plus traces of phenol and *p*-hydroxybenzophenone (m.p. 132–133°). Its structure was further established by strong absorption at 6.05 μ (C=O) and 8.02 μ (ether) and ten additional bands common to benzophenone or diphenyl ether. (Infrared absorption spectra in carbon tetrachloride and carbon disulfide by Dr. V. Koenig, Los Alamos, N. M.)

4-Phenoxybenzhydrol.—4-Phenoxybenzophenone (2.0 g., 0.0072 mole), dissolved in 100 cc. of 95% ethanol, was reduced under a pressure of 30 mm. of hydrogen with 3 g. of Raney nickel catalyst and one drop of 50% aqueous potassium hydroxide. The mixture was filtered from catalyst and solvent. The remaining solid, crystallized from petroleum ether, weighed 1.70 g. (85%), m.p. 75.8–76.9° (lit. m.p. 76.5°).[18]

Anal. Calcd. for $C_{19}H_{16}O_2$: C, 82.50; H, 5.78. Found: C, 82.41; H, 6.17.

4-Phenoxydiphenylmethane.—*p*-Phenoxybenzophenone (20 g.) was added to a mixture of amalgamated zinc (from 100 g. of zinc and 10 g. of mercuric chloride) and 100 cc. of concentrated hydrochloric acid. The mixture was refluxed for 12 hours during which time three fresh 50-cc. portions of concentrated hydrochloric acid were added. The product was extracted with benzene, washed neutral, dried and distilled to remove the solvent. The residue (19.67 g.) was sublimed from a molecular still at 0.001 mm. The colorless distillate (9.34 g.) was resublimed to give 8.61 g. of colorless liquid which solidified on standing, m.p. 41–42°. (The literature reports the substance as a colorless liquid.[19])

Anal. Calcd. for $C_{19}H_{16}O$: C, 87.65; H, 6.19. Found: C, 87.41, 87.59; H, 6.37, 6.33.

The second fraction from the molecular distillation, a viscous oil, which set to a glassy solid in the side arm, is believed to be the corresponding pinacol.

The Reaction of Substituted Benzyl Alcohols with Benzene and Aluminum Chloride.—***p*-Methoxybenzyl alcohol** (33 g., 0.18 mole) was added over a period of 1 hour to 75 g. (0.56 mole) of aluminum chloride in 160 cc. (1.80 moles) of benzene. The deep red solution was stirred for 3.5 hours at 60°. The mixture was decomposed and steam distilled. The distillate was extracted with ether and the extract was washed, dried and fractionally distilled from a micro Vigreux column. The products were unreacted benzene, b.p. 72–75° (606 mm.), n^{25}_{D} 1.4952, anisole, b.p. 75–78° (19 mm.), n^{23}_{D} 1.5147, yield 11.8 g. (redistilled: b.p. 144° (606 mm.), n^{22}_{D} 1.5157, yield 8.4 g. (43%), identified as 2,4-dinitroanisole, m.p. 84–85°) and anthracene, b.p.

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(12) (a) M. Gomberg and L. H. Cone, *Ann.*, **370**, 183 (1909); (b) H. Bünzli and H. Decker, *Ber.*, **37**, 2934 (1904); (c) F. Ullmann and G. Engi, *ibid.*, **37**, 2367 (1904).

(13) H. Decker, *ibid.*, **38**, 2505 (1905).

(14) H. E. Ungnade and E. F. Orwoll, *Org. Syntheses*, **26**, 50 (1946).

(15) H. Kipper, *Ber.*, **38**, 2490 (1905).

(16) W. Dilthey, E. Bach, H. Grütering and E. Hausdorfer, *J. prakt. Chem.*, **117**, 337 (1927).

(17) C. K. Bradsher, THIS JOURNAL, **62**, 488 (1940).

(18) M. P. Balfe, E. A. W. Rowner, A. A. Evans, J. Kenyon, J. Poplett, C. E. Searle and A. L. Tarnoky, *J. Chem. Soc.*, 471 (1946).

(19) W. D. Schroeder and R. Q. Brewster, THIS JOURNAL, **60**, 752 (1938).

155–160° (19 mm.), yield 3.2 g. The anthracene fraction solidified on standing. Recrystallization from ligroin gave colorless plates, m.p. 212–213°. The still residue, decolorized with Nuchar and crystallized, gave an additional quantity of anthracene, m.p. 210–211°. The combined fractions (4.68 g.) were identified by mixed melting points and absorption spectra.

Since anthracene was isolated from the steam distillate, it was desirable to establish the composition of its binary mixture with water. Steam distillation of pure anthracene (1.0 g.) at 97° (603 mm.) furnished 0.49 g. of anthracene in 5 liters of distillate during 1 hour. The binary mixture thus contained 0.0098% anthracene. A mixture of 1 g. of anthracene and 10 g. of anisole, steam distilled at 605 mm. (98°), yielded 5 liters of distillate (in 1 hour) which contained 0.30 g. of anthracene. Each substance therefore steam distilled independently.

3,4-Dimethoxybenzyl alcohol[20] (0.148 mole) with 0.297 mole of aluminum chloride and 150 cc. (1.69 moles) of thiophene-free benzene under identical conditions gave 1.34 g. of guaiacol (phenylurethan, m.p. 134°) and 1.03 g. of anthracene, m.p. 211–212°, from the volatile portion of the reaction products.

***o*-Hydroxybenzyl alcohol** (0.20 mole) yielded 0.61 g. of phenol and 2.47 g. of anthracene with aluminum chloride (0.40 mole) and benzene (150 cc., 1.69 moles). In this case only the addition was reversed, the aluminum chloride being added in small portions to the *o*-hydroxybenzyl alcohol dissolved in benzene.

***o*-Benzylbenzyl Alcohol.**—Lithium aluminum hydride (10 g., 0.26 mole) was dissolved in 180 cc. of anhydrous ether. A solution of 34.50 g. (0.16 mole) of *o*-benzylbenzoic acid (m.p. 110–111°)[21] in 100 cc. of ether was added with stirring at such a rate that the mixture was gently refluxing. Stirring was continued for 0.5 hour after completed addition. Water (100 cc.) was added cautiously while the mixture was cooled in an ice-bath followed by 150 cc. of a solution of 10% aqueous sulfuric acid. The ether layer was separated, washed with 10% aqueous sodium carbonate solution and dried over anhydrous sodium sulfate. Removal of the ether left nearly pure *o*-benzylbenzyl alcohol, b.p. 130–132° (0.001 mm.), yield 20.47 g. (64.5%).

Anal. Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.11. Found: C, 84.73; H, 6.95.

The Reaction of *o*-Benzylbenzyl Alcohol with Benzene and Aluminum Chloride.—A solution of 10 g. (0.05 mole) of *o*-benzylbenzyl alcohol in 50 cc. (0.56 mole) of benzene was added over a period of 0.5 hour with stirring to a mixture of 20 g. (0.15 mole) of anhydrous aluminum chloride and 25 cc. (0.28 mole) of benzene. The mixture was stirred at 60° for 3.5 hours, decomposed and steam distilled in the usual manner. The dry, non-volatile residue weighed 12.60 g. and furnished 5.00 g. of anthracene, m.p. and mixed m.p. 212–214° on sublimation at 160–200° (1–2 mm.).

The Reaction of *o*-Benzylbenzyl Alcohol with Toluene and Aluminum Chloride.—*o*-Benzylbenzyl alcohol (10 g., 0.05 mole) treated in exactly analogous manner with 75 cc. (0.70 mole) of toluene and 0.15 mole of aluminum chloride yielded 11.08 g. of non-volatile residue which gave 4.76 g. (0.023 mole) of sublimed and crystallized dimethylanthracene, m.p. 215–217° (from ligroin), in all respects identical with the eutectic mixture described previously,[4] which can be oxidized to the quinone, m.p. 154–155°.[22]

The volatile fraction contained 4.02 g. (47.8%) of diphenylmethane, b.p. 260–262°, identified as benzophenone, m.p. 47–48°.

Ultraviolet absorption spectra were determined in the solvents indicated with a model DU Beckman spectrophotometer as described previously.[23] The experimental data are given in Table I.

TABLE I

ABSORPTION SPECTRA IN 95% ETHANOL

Compound	λ_{max}[b]	log ϵ	λ'_{max}[c,d]	log ϵ	λ''_{max}	log ϵ
Diphenyl ether	225[a]	4.01	271	3.31	...	...
4-Phenoxytoluene	225	4.06	278	3.30	...	...
4-Phenoxy-*o*-xylene	226[a]	4.05	278	3.32	...	...
4-Phenoxybenzhydrol	233	4.18	265	3.27	...	...
4-Phenoxydiphenylmethane	228[a]	4.21	271	3.47	...	...
4-Phenoxybenzophenone	286[f]	4.24	...	...	...	...
Xanthene	247	3.88	283	3.36	...	...
9-Phenylxanthene	250	3.91	284	3.47	...	...
9-Benzylxanthene	243	3.94	283	3.50	338	2.37[d]
9-Benzalxanthene	252[a,e]	4.10	284	3.89[b]	341	4.08[b]
Xanthydrol	239	4.17	290	3.59[b]	336	2.69[d]
9-Phenylxanthydrol	244	4.10	290	3.61	...	...
1-(9-Phenylxanthyl)-semicarbazide	245	4.11	290	3.69	...	...
Xanthone	260	4.11	288	3.66[b]	336	3.85[b]

[a] Shoulder. [b] Concentration $1-10 \times 10^{-5}$ mole/l. [c] Only the most intense of the fine structure bands is listed. [d] Concentration $1-14 \times 10^{-4}$ mole/l. except as noted. [e] In agreement with the findings of E. D. Bergmann, *et al.*, (*Bull. soc. chim.*, [5] 18, 693(1951)) a strong band was also observed at 222 mμ (log ε 4.74). [f] The absorption spectrum of 4-phenoxybenzophenone differed considerably from the literature data (H. H. Szmant and C. M. McGinnis, THIS JOURNAL, 74, 240 (1952)). Comparison of our sample with one kindly furnished by Dr. Szmant showed them to be different chemically although both had the same melting point. Evidence given in the experimental section for the substance measured above makes it reasonably certain that the assigned structure is correct.

LAS VEGAS, N. M.

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[20] The authors are indebted to the Monsanto Chemical Company, St. Louis, Mo., for a generous sample of this substance.

[21] E. C. Horning and D. B. Reisner, THIS JOURNAL, **71**, 1036 (1949).

[22] J. Lavaux, *Compt. rend.*, **139**, 976 (1909); *Ann. chim.*, **20**, 433 (1910); G. T. Morgan and E. A. Coulson, *J. Chem. Soc.*, 2203 (1929).

[23] H. E. Ungnade and R. Lamb, THIS JOURNAL, **74**, 3789 (1952).