2. In the instance of substitution within the phthalic anhydride residue the displacement of the maxima is influenced by the nature of the halogen concerned in a definite, but appreciably less decided, degree than is the case in the instance of substitution within the resorcinol residues.

3. The effect of substitution in the resorcinol residues is not constant in degree under all conditions but is modified by substitution within the phthalic anhydride residue.

4. Substitution in the 1 and 8 (h and i) positions in the resorcinol residues is without appreciable effect upon the absorption.

5. Substitution within the resorcinol residues increases the stability of the dyes in aqueous solution to the hydrogen ion, whereas substitution within the phthalic anhydride residue is of opposite effect.

6. The relative stability of the dyes to acids is increased by the replacement of iodine by bromine and by that of bromine by chlorine.

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ACTION OF AROMATIC ALCOHOLS ON AROMATIC COMPOUNDS IN THE PRESENCE OF ALUMINUM CHLORIDE. III. CONDENSATION OF BENZYL ALCOHOL AND PHENOL

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RECEIVED JUNE 30, 1924 PUBLISHED DECEMBER 13, 1924

Earlier publications in this series[1] described the condensation of primary and secondary aromatic alcohols with benzene to form diphenylmethane and its derivatives. In this article is described the application of the method to the preparation of benzylphenol and its ethers.

The condensation of benzyl alcohol and phenols has been accomplished by the use of zinc[2] and sulfuric and acetic acids[3] and zinc chloride.[4] Zinc and zinc chloride have also been used in the condensation of simple aliphatic alcohols with phenols.[5]

Merz and Weith[6] found that aluminum chloride reacted with phenol to give a 10 to 12% yield of diphenyl ether. This reaction takes place when the mixture is heated under a reflux condenser. The present in-

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[1] THIS JOURNAL, **38**, 2525 (1916); **40**, 785 (1918).

[2] Paterno, (a) *Gazz. chim. ital.*, **2**, 2 (1872); (b) *Ber.*, **5**, 288 (1872). (c) Paterno and Mazzara, *Gazz. chim. ital.*, **8**, 303 (1878).

[3] Paterno and Fileti, *Gazz. chim. ital.*, **5**, 381 (1875).

[4] Liebmann, *Ber.*, **14**, 1844 (1881). Venturi, *Gazz. chim. ital.*, **31**, 1, 469 (1901).

[5] Dennstedt, *Ber.*, **23**, 2569 (1890). Auer, *Ber.*, **17**, 669 (1884). Senkowski, *Ber.*, **24**, 2974 (1891). Bauer, *Ber.*, **27**, 1614 (1894). Anschütz and Beckerhoff, *Ber.*, **28**, 407 (1895).

[6] Merz and Weith, *Ber.*, **14**, 189 (1881).

vestigation has shown that diphenyl ether is not formed to an appreciable extent if the phenol is suspended in petroleum ether and the temperature kept below 30°.

When a mixture of one molecular equivalent of benzyl alcohol and 1.1 equivalents of phenol was suspended in petroleum ether and treated with 0.5 molecular equivalent of aluminum chloride, a vigorous reaction occurred. By decomposition of the dark red intermediate product there was obtained a good yield (43–45%) of *p*-benzylphenol.

$$C_6H_5CH_2OH + C_6H_5OH \xrightarrow{AlCl_3} C_6H_5CH_2C_6H_4OH + H_2O$$

The yield of *p*-benzylphenol was not increased by the use of a full molecular equivalent of aluminum chloride. When the petroleum ether was omitted the reaction started more slowly, then the temperature rose rapidly to 65°. The yield of *p*-benzylphenol was lessened. Carbon disulfide was used in several experiments in place of petroleum ether with good results.

The condensation of benzyl alcohol with anisole takes place readily under the same conditions as described for benzyl alcohol and phenol.

$$C_6H_5CH_2OH + C_6H_5OCH_3 \xrightarrow{AlCl_3} C_6H_5CH_2C_6H_4OCH_3 + H_2O$$

The yield of the methyl ether of *p*-benzylphenol was about 46%. The compound boiled at 305° under atmospheric pressure[7] and at 133–135° under 4 mm. pressure. This last value differs from that given by Paterno[2b] but is the same as that obtained when the ether was prepared from *p*-benzylphenol, methyl iodide and potassium hydroxide.

Condensation of benzyl alcohol with phenetole gave a 57% yield of the ethyl ether of *p*-benzylphenol.

$$C_6H_5CH_2OH + C_6H_5OC_2H_5 \xrightarrow{AlCl_3} C_6H_5CH_2C_6H_4OC_2H_5 + H_2O$$

The reaction proceeded smoothly below 20° and the formation of high-boiling by-products was considerably reduced. The product boiled after five fractionations at 315–317° under atmospheric pressure and at 171–173° under 12 mm. pressure. Klages and Allendorff give[8] 205° at 12 mm. As a check, the ether was prepared from *p*-benzylphenol, ethyl bromide and potassium hydroxide. The properties corresponded in every way with those of the ether prepared from benzyl alcohol and phenetole.

In order to throw some light on the course of this condensation, experiments were made to determine the effect of aluminum chloride on benzyl alcohol. When the temperature was kept below 35°, 96% of the benzyl alcohol was recovered. When the temperature was not kept below 40°, vigorous reaction set in with the formation of a complex mixture from which was isolated 25 to 30% of the calculated amount of benzyl chlor-

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[7] Renni, *Trans. Chem. Soc.*, **41**, 37 (1882).

[8] Klages and Allendorff, *Ber.*, **31**, 1001 (1898).

ide. From these experiments it is concluded that the formation of benzyl chloride is not a necessary intermediate in the condensation of benzyl alcohol with phenols or aromatic hydrocarbons.

It was rather surprising to find that the literature contains no definite data on the condensation of benzyl chloride and phenol by means of aluminum chloride.[9] An experiment gave 36% of the calculated amount of *p*-benzylphenol.

$$C_6H_5CH_2Cl + C_6H_5OH \xrightarrow{AlCl_3} C_6H_5CH_2C_6H_4OH + HCl$$

Experimental Part

Phenol and Aluminum Chloride.—A mixture of 50 g. of phenol and 100 cc. of petroleum ether was stirred vigorously during the addition of 30 g. of aluminum chloride. Although the chloride was added quite rapidly, the temperature did not rise above 20°. Hydrogen chloride was given off copiously. A colorless viscous mass was formed which solidified on standing (probably aluminum phenolate). This was decomposed with ice and hydrochloric acid and extracted with ether; 48 g. of phenol was recovered by distillation of the ether extract.

Benzyl Alcohol, Phenol and Aluminum Chloride. I.—Fifty g. of benzyl alcohol and 50 g. of phenol were added to 100 cc. of petroleum ether and the mixture was stirred vigorously with a motor stirrer while 30 g. of aluminum chloride was added in small portions. The temperature was maintained at 20–30°. A great deal of hydrogen chloride was given off while a dark red, pasty mass formed in the lower part of the vessel. After all of the aluminum chloride had been added (about an hour) the stirring was continued for about 30 minutes and the mixture was allowed to stand overnight at room temperature. It was then decomposed with ice and hydrochloric acid and extracted with ether. The ether extract was dried over potassium carbonate and the ether distilled. The residue was fractionated; on the third refractionation 15.2 g. was obtained between 150° and 220°; 38.6 g. between 120° and 180° (4 mm.); 26.6 g. between 180° and 230° (4 mm.); and 10 g. of residue.

Most of the first fraction distilled between 180° and 183°. It solidified in the receiver and was identified as phenol. The second fraction, 120–180° (4 mm.), nearly all distilled at 141–143° and solidified in the receiver. It was freed from an oily impurity by pressing between filter papers and recrystallized from petroleum ether, forming in clusters of long, flat, glistening needles; m. p., 83.58° (Paterno[2a]).

Anal. Subs., 0.2122: CO_2, 0.6615; H_2O, 0.1206. Calc. for $C_{13}H_{12}O$: C, 84.74; H, 6.57. Found: C, 84.99; H, 6.36.

The ethyl ether was prepared by dissolving 25 g. of the compound in absolute alcohol and treating with 3 g. of sodium and 15 g. of ethyl bromide. The mixture was warmed on the water-bath and left at room temperature overnight—most of the alcohol was distilled, the residue treated with water and extracted with ether. Practically all of the product came over on the second distillation at[8] 315–317°.

The fraction boiling at 180–230° (4 mm.) did not solidify. It gave the characteristic phenol reactions and was probably a mixture of dibenzylphenols.

Benzyl Alcohol, Phenol and Aluminum Chloride. II.—A mixture of 50 g. of benzyl alcohol with an equal weight of phenol was stirred constantly while 60 g. of aluminum chloride was added. In order to start the reaction the mixture was warmed to 40°. A vigorous evolution of hydrochloric acid set in and the temperature rose to 65°. After two days the red semi-solid mass was decomposed and extracted in the usual manner.

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[9] Rennie, *Trans. Chem. Soc.*, **41,** 220 (1882). Liebmann, *Ber.*, **15,** 152 (1882).

The second redistillation of the extract gave the following fractions: 14 g. (phenol) at 120–220°; 30.4 g. (*p*-benzylphenol) at 120–180° (4 mm.); 16.4 g. at 180–230°; 12 g. of residue.

Benzyl Alcohol, Phenol and Aluminum Chloride. III.—A solution of 50 g. of benzyl alcohol and 50 g. of phenol in 100 g. of carbon disulfide was treated with 35 g. of aluminum chloride. The reaction proceeded smoothly at 20°; there was a tendency to froth. The mixture did not separate into layers. After it had been stirred for an hour it was allowed to stand overnight when it solidified into a porous mass that almost filled the jar. This was decomposed with ice and hydrochloric acid and extracted with ether. The ether extract was dried over potassium carbonate and distilled. The second refractionation gave 22 g. (phenol) at 120–220°; 28.8 g. (*p*-benzylphenol) at 120–180° (4 mm.); 18.2 g. at 180–230° (4 mm.); and 10.2 g. of residue.

Benzyl Alcohol, Anisole and Aluminum Chloride.—Fifty g. of benzyl alcohol, 70 g. of anisole, 100 cc. of petroleum ether and 35 g. of aluminum chloride were mixed under the usual conditions. The temperature did not rise above 22°. In this case the intermediate compound was a dark red solid. After 48 hours, decomposition, extraction and distillation gave upon the third refractionation 36 g. (anisole) at 130–170°; 44.2 g. at 230–330°; 6 g. at 330–360°; and 23 g. of residue.

Practically all of the fraction obtained at 230–330° distilled between 305° and 308°. After four distillations it distilled at 133–135° (4 mm.).

Benzyl Alcohol, Phenetole and Aluminum Chloride.—Fifty g. of benzyl alcohol and 75 g. of phenetole in 100 cc. of petroleum ether were treated with 30 g. of aluminum chloride. The temperature was not allowed to rise above 20°. Two layers were formed, the lower one of which was red and tarry. The decomposition, extraction and distillation were carried out as in the preceding experiments. The third refractionation gave 38 g. (phenetole) at 150–220°; 2 g. at 220–280°; 56 g. at 280–330°; and 6.1 g. of residue.

Practically all of the fraction obtained at 280–330° distilled at 315–317°. Its properties correspond in every way with those of the ethyl ether of *p*-benzylphenol, prepared from this last compound, ethyl bromide and sodium. After six distillations the compound distilled at 171–173° (12 mm.).

Benzyl Chloride, Phenol and Aluminum Chloride.—Fifty g. of benzyl chloride and 50 g. of phenol were added to 100 cc. of petroleum ether, in which they completely dissolved; 30 g. of aluminum chloride was then added in small portions. The reaction was quite vigorous and was retarded by placing the vessel in cracked ice. The temperature rose to 35°. Two layers were formed, the lower one of which was dark red and rather viscous. After 24 hours the entire mixture was decomposed.

The third refractionation gave 28.4 g. at 150–220°; 26 g. at 120–180° (4 mm.); 10.2 g. at 180–230° (4 mm.); and 21.2 g. of residue. The fraction obtained at 120–180° was *p*-benzylphenol.

Benzyl Alcohol and Aluminum Chloride.—Fifty g. of benzyl alcohol was added to 100 g. of petroleum ether and the mixture was stirred while 30 g. of aluminum chloride was added in small portions. Hydrogen chloride was slowly evolved and the lower layer became rather pasty. After all of the chloride had been added, the mixture was heated to 30–35° for two hours and allowed to stand for five days at room temperature. It was then decomposed with dil. hydrochloric acid and extracted with ether; 47 g. of benzyl alcohol was recovered from the extract. When the aluminum chloride was added too rapidly and the temperature rose above 40°, a more vigorous reaction set in. The lower layer turned dark red and formed a semi-solid mass. When decomposed with ice, a considerable amount of yellow precipitate separated, which was insoluble in ether. The ether extract yielded 14 g. of impure benzyl chloride and 12 g. of condensation products which distilled above 250°.

Conclusions and Summary

1. Benzyl alcohol reacts with phenol at low temperatures in the presence of aluminum chloride to form *p*-benzylphenol.

$$C_6H_5CH_2OH + C_6H_5OH \xrightarrow{AlCl_3} C_6H_5CH_2C_6H_4OH + H_2O$$

2. The methyl and ethyl ethers of *p*-benzylphenol may be prepared in good yield by condensing benzyl alcohol with anisole or phenetole.
3. The phenolic hydroxyl group does not interfere with the substitution of the benzyl group in the benzene ring by means of aluminum chloride under the described conditions.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MINNESOTA]

NAPHTHALENE AND THE CENTROID STRUCTURE

BY REYNOLD C. FUSON[1]

RECEIVED JULY 7, 1924 PUBLISHED DECEMBER 13, 1924

Using the Lewis theory of atomic structure[2] as a basis, Huggins has recently evolved a new theory of conjugated double bonds.[3] Applying this theory to benzene (regarded as a triply conjugated system), he has arrived at the conclusion that the centroid model first proposed by Körner[4] is the correct configuration for benzene, naphthalene and other aromatic nuclei. The X-ray experimental data of Hull[5] and of Debye and Scherrer[6] for graphite have been interpreted by Huggins as constituting a *proof* of the correctness of this model;[7] and the more recent measurements made by Mark and Weissenberg[8] on triphenylmethane crystals are also in agreement with this theory.

Considering the centroid structure as *proved* for benzene, Huggins has applied it to numerous benzene derivatives including naphthalene, to which he has assigned a structure differing from that of Kekulé[9] in several

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[1] The work described in this paper formed a part of a thesis presented by Reynold C. Fuson in June, 1924, to the Faculty of the Graduate School of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy. The original thesis is on file in manuscript in the Library of the University of Minnesota.—W. H. Hunter.

[2] Lewis, THIS JOURNAL, **38**, 762 (1916).

[3] Huggins, *ibid.*, **44**, 1607 (1922).

[4] Körner, *Gazz. chim. ital.*, **4**, 444 (1874). See also Marsh, *Phil. Mag.*, **26**, 426 (1888). Vaubel, *J. prakt. Chem.*, [2] **44**, 137 (1891); **49**, 308 (1894); **50**, 58 (1894).

[5] Hull, *Phys. Rev.*, [2] **10**, 692 (1917).

[6] Debye and Scherrer, *Physik. Z.*, **18**, 294 (1917).

[7] Huggins, THIS JOURNAL, **45**, 264 (1923).

[8] Mark and Weissenberg, *Z. Physik*, **17**, 347 (1923).

[9] The Kekulé structure is referred to here merely as a *type* of structure; this type includes most of the models which have received any considerable favor among chemists.