

ice-cold hydrobromic acid and dried *in vacuo* over solid sodium hydroxide. A 66% yield (6.5 g.) of light gray material was obtained.

Anal. Calcd. for $C_8H_{10}ONBr \cdot HBr$: C, 32.4; H, 3.73; Br, 53.8. Found: C, 32.7; H, 3.79; Br, 54.6.

Attempted Synthesis of 3-Amino-4-hydroxystyrene: (a) **By Elimination of Water from 3-Aminotyrosol.**—(1) With aqueous sodium hydroxide: One gram of 3-aminotyrosol, 1.5 g. of sodium hydroxide, and 3 ml. of water were heated slowly in a nickel crucible to 300° where the temperature was held for twenty minutes. After cooling, the contents of the crucible were dissolved in water and saturated with carbon dioxide. Without filtering, the mixture was extracted with ether, the extract dried, clarified with charcoal and evaporated. Only a trace of thick tarry material remained.

(2) **By fusion with sodium hydroxide:** One gram of 3-aminotyrosol and 1 g. of crushed sodium hydroxide pellets were heated together in a Pyrex test-tube immersed in a fused salt-bath. The final temperature of 300° was held for one half hour. After cooling and dissolving the mass in water the solution was saturated with carbon dioxide, the fluffy precipitate filtered off, washed with water and dried *in vacuo*. It was light gray in color, insoluble in water, benzene and carbon tetrachloride, but soluble in alcohol. The weight was only 0.1 g., an 11% yield if it represented the desired aminohydroxystyrene.

Anal. Calcd. for C_8H_9ON : C, 71.1; H, 6.71. Found: C, 69.0; H, 6.86.

(3) **By sublimation over hot alumina:** An apparatus was constructed to allow aminotyrosol, vaporized at low pressure, to be carried by a stream of nitrogen admitted by a capillary leak through a column of granular activated alumina ("Hydralo") heated to 350°. Results indicated that the aminotyrosol had decomposed and deposited a carbonaceous residue on the alumina.

(b) **By Elimination of Hydrogen Bromide from β -(3-Amino-4-hydroxyphenyl)-ethyl Bromide (I).**—(1) With sodium ethylate: Three modifications of a procedure in which (I) was treated with sodium ethylate solution were examined. While sodium bromide was definitely produced, no product analyzing higher than 68% carbon could be obtained. Aminohydroxystyrene contains 71.1% carbon.

(2) With alcoholic potassium hydroxide: Two experiments in which (I) was treated with potassium hydroxide gave a product analyzing only 67% carbon.

Attempted Conversion of β -(4-Aminophenyl)-ethyl Bromide to 4-Aminostyrene.—The hydrobromide of β -(4-aminophenyl)-ethyl bromide was prepared by dissolv-

ing 2.5 g. of 4-aminophenylethanol in 25 ml. of constant-boiling hydrobromic acid and refluxing four hours. White crystals melting at 199–201° were obtained.

Anal. Calcd. for $C_8H_{10}NBr \cdot HBr$: C, 34.2; H, 3.95. Found: C, 33.8; H, 3.95.

Two grams of the above in 20 ml. of absolute alcohol was mixed with 1.35 g. of potassium hydroxide in 15 ml. of alcohol. After twenty-four hours the potassium bromide was removed, the solution saturated with carbon dioxide and filtered, and the alcohol evaporated *in vacuo* at room temperature. A viscous yellow liquid remained.

4-Aminostyrene should be easily purified by vacuum distillation but half of the viscous liquid gave only 2–3 drops of distillate at 1 mm. up to 250°. This analyzed C, 70.7; H, 8.92. Aminostyrene contains 80.6% C, 7.61% H. The other half of the viscous liquid hardened to a glassy solid in a few days. Analysis gave C, 71.0; H, 7.65.

3-Amino-4-hydroxytoluene, 3-Aminocresol.—Ten grams of 3-nitro-4-hydroxytoluene in 200 ml. of water and 50 ml. of concentrated ammonium hydroxide was added slowly to a solution of 75 g. of sodium hydrosulfite in 300 ml. of water. After a few minutes white flaky crystals appeared and the red color of the solution turned to pale yellow. Without filtering, the entire mixture was extracted with ether. The extract, dried, treated with charcoal and evaporated gave 6.5 g. (81% yield) of light tan crystals, melting 134–135°.

Attempts to reduce the nitrocresol by sodium sulfide or sodium hydroxide and hydrogen sulfide, by phenylhydrazine, and by catalytic hydrogenation were unsuccessful.

Acknowledgment is made to Dr. Groves H. Cartledge at whose suggestion this work was initiated.

Summary

1. Satisfactory methods for the synthesis of the following new compounds have been worked out and are described: β -(3-nitro-4-hydroxyphenyl)-ethanol, β -(3-amino-4-hydroxyphenyl)-ethanol, the hydrobromide of β -(3-amino-4-hydroxyphenyl)-ethyl bromide, and the hydrobromide of β -(4-aminophenyl)-ethyl bromide.

2. Unsuccessful attempts to prepare 3-amino-4-hydroxystyrene are noted.

BUFFALO, N. Y.

RECEIVED OCTOBER 26, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF BUFFALO]

Some Metal Compounds of Aminocresol and Aminotyrosol

BY CALVIN F. STUNTZ^{1,2} AND HENRY M. WOODBURN

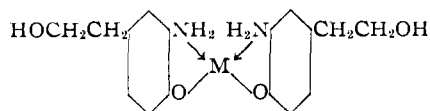
In the course of work involving 3-amino-4-hydroxytoluene and β -(3-amino-4-hydroxyphenyl)-ethanol,³ referred to hereafter as aminocresol and aminotyrosol, respectively, it was desired to prepare salts of these compounds with certain divalent metals. Since the amino and hydroxyl groups are ortho to one another, it

(1) Abstracted from a portion of a thesis submitted in partial fulfillment of the requirements for the Ph.D. degree at the University of Buffalo, August, 1946.

(2) Present address: Department of Chemistry, University of Maryland, College Park.

(3) For the synthesis of this compound, see Woodburn and Stuntz, *THIS JOURNAL*, **72**, 1361 (1950).

might be expected that chelate ring compounds of the inner complex type would be formed, one metal atom combining with two organic molecules, replacing the hydroxyl hydrogens and forming coordinate bonds with the amino nitrogen



Compounds of this general structure have been reported by Hieber and Schnackig,⁴ who pre-

(4) Hieber and Schnackig, *Z. anorg. allgem. Chem.*, **226**, 209 (1936).

pared inner complexes, as well as addition complexes, of divalent cobalt, copper, nickel, cadmium and zinc with *o*-aminophenol. The compounds described as inner complexes all conformed to the general formula $M(-ONH_2C_6H_4)_2$; they were anhydrous, insoluble in water and organic solvents, but soluble in mineral acids. Their colors were typical of these metals, *i. e.*, red-violet with cobalt, green with copper and nickel, and colorless with cadmium and zinc. The solid compounds, with the exception of the nickel salt, did not absorb gaseous ammonia; Hieber and Schnackig presented this as evidence of complete coordinate saturation.

We have prepared and identified some complexes of trivalent cobalt, and divalent copper, nickel and cadmium with aminocresol and aminotyrosol. They are insoluble in water and organic solvents, but soluble in mineral acids. Their other properties, however, differ markedly from those reported by Hieber and Schnackig. Our compounds are all hydrates, containing either one or two molecules of water. The trivalent cobalt compounds are red-violet, as might be expected, but all of the divalent metal complexes are colorless when pure, although some darken to gray or brown on standing. This indicates some difference in the type of bonding between the metal and organic molecules in our compounds and those of Hieber and Schnackig, since it is improbable that the addition of a methyl or ethanol group to the benzene ring would cause the disappearance of the color. We did not test our compounds for reactivity with gaseous ammonia; however, they were quite resistant to attack by 6 *M* ammonium hydroxide, requiring several hours before decomposition was complete. Hieber and Schnackig did not mention trivalent cobalt complexes at all; we have not only prepared such complexes, but experienced considerable difficulty in preventing the oxidation of the cobalt in attempts to prepare the divalent compounds, as will be described further in the experimental section. This strong tendency toward formation of cobaltic compounds is evidence for the true coordinate nature of the aminocresol and aminotyrosol compounds, since cobalt oxidizes in the air to the cobaltic state only when complex formation is possible. In melting point determinations, the copper compounds with aminocresol and aminotyrosol melted quite sharply with decomposition to black liquids at 195 and 193°, respectively. All the others were stable up to temperatures near 275° and charred without melting at higher temperatures. Hieber and Schnackig did not mention the melting points of their compounds.

Experimental

Materials.—Aminocresol and aminotyrosol were synthesized as described elsewhere.³ All other reagents were commercial C. P. chemicals, used without special treatment.

Triaminocresolcobalt Monohydrate.—A procedure based upon that of Hieber and Schnackig was used for the initial experiments, with the expectation that the product would be diaminocresolcobalt. Solutions of 0.002 mole of cobalt chloride (0.48 g. of the hexahydrate), 0.005 mole (0.62 g.) of aminocresol and 0.015 mole (1.50 g.) of potassium acetate, each in 40 ml. of 95% alcohol, were prepared. The quantity of aminocresol used represented a 25% excess. The solutions were filtered, heated nearly to boiling, and the cobalt chloride added to the aminocresol. A dark brown color developed. The potassium acetate was added dropwise; potassium chloride and an extremely fine red-violet material precipitated. After standing several hours without further heating, the mixture was filtered with suction on sintered glass; the solid was washed with alcohol until the washings were colorless, then with water until chloride free, and finally with alcohol and ether. After drying *in vacuo* over sulfuric acid, the product was brown in color and weighed only 0.09 g. The individual particles were too small to be resolved under a microscope at 550X. The analysis indicated a carbon-hydrogen ratio of roughly 7:8, the expected ratio for aminocresol with the phenolic hydrogen replaced. However, the cobalt-carbon ratio was much closer to 1:21 than the anticipated 1:14, indicating that there were three aminocresol molecules associated with each cobalt atom. This would require trivalent cobalt with a coordination number of six; apparently there was air oxidation of the cobalt, the poor yield resulting from incomplete oxidation and a deficiency of aminocresol, which is also slowly oxidized by air. The preparation was repeated, with conditions and quantities of materials adjusted to favor the formation of the trivalent cobalt complex. Cobalt acetate was used instead of the chloride to avoid contamination of the product with potassium chloride, and the potassium acetate was omitted. Solutions of 0.004 mole of cobalt acetate (1.00 g. of the tetrahydrate) and 0.016 mole (2.00 g.) of aminocresol, each in 40 ml. of 80% alcohol were filtered, heated, and the cobalt solution added dropwise to the aminocresol solution in an open beaker with vigorous stirring. The color gradually darkened nearly to black, and a fine precipitate appeared. The stirring was continued for about three hours, after which the precipitate was collected by centrifugation and washed repeatedly with 80% alcohol by suspension and centrifuging until the washings were colorless. The product was finally washed with 95% alcohol, absolute alcohol and ether. After drying *in vacuo* over sulfuric acid, the product weighed 0.40 g. It was violet-pink in color, and under the microscope appeared as tangled masses of splintery fibrous crystals. The analysis indicated a cobalt-carbon ratio of 1:21, and a cobalt-nitrogen ratio of 1:3, correct for triaminocresolcobalt. However, the cobalt-hydrogen ratio was 1:26 instead of the expected 1:24. This indicated the presence of one molecule of water. Attempts to determine this water by vacuum drying over phosphorus pentoxide at 140° were unsuccessful, the loss in weight being less than 1%, whereas a monohydrated triaminocresolcobalt contains 4.06% water. However, the analysis fits the monohydrate formula quite well, and water of hydration was definitely established in some of the complexes to be described below.

Anal. Calcd. for $Co(-ONH_2C_6H_4CH_3)_3 \cdot H_2O$: C, 56.9; H, 5.91; N, 9.48; Co, 13.3. Found: C, 57.2; H, 5.80; N, 9.61; Co, 13.0.

Triaminotyrosolcobalt Monohydrate.—This experiment was carried out before the preparation and analysis of the preceding product was completed, so the procedure was still based on the expectation of a product with two organic molecules per divalent cobalt atom. Solutions of 0.002 mole of cobalt acetate (0.50 g. of the tetrahydrate) and 0.005 mole (0.765 g.) of aminotyrosol, each in 20 ml. of 80% alcohol, were filtered, heated, and the cobalt acetate solution added dropwise to the aminotyrosol solution. A very dark color formed, and the solution gradually became cloudy. After standing overnight in a refrigerator, the extremely fine precipitate was filtered with suction,

washed with 80, 95% and absolute alcohol, and ether. The product was dried *in vacuo* over sulfuric acid; 0.15 g. was obtained. It was very similar in appearance and in analytical results to the corresponding aminocresol complex described above.

Anal. Calcd. for $\text{Co}(\text{—ONH}_2\text{C}_6\text{H}_3\text{CH}_2\text{CH}_2\text{OH})_2\cdot\text{H}_2\text{O}$: C, 54.0; H, 6.05; Co, 11.1. Found: C, 54.0; H, 6.13; Co, 11.0.

In an attempt to prepare the divalent cobalt complex analogous to that of Hieber and Schnackig, a few runs were made similar to those described above, but with a stream of commercial nitrogen passing through the reaction flask to prevent air oxidation. Products varying from dark brown to very pale pink were obtained, none of which gave analyses corresponding to any reasonable formulas. When the nitrogen was purified by bubbling through Fieser solution⁵ to remove any oxygen present, more definite results were obtained. A colorless, needle-like product was isolated which, however, was unstable, and while its analysis pointed strongly toward that of diaminyrosolcobalt monohydrate, agreement was not sufficiently close to establish its identity with certainty.

An atmosphere of purified nitrogen was maintained in the reaction flask for all the preparations described below.

Diaminyrosolcadmium Monohydrate.—A solution of 0.0015 mole of cadmium acetate (0.40 g. of the dihydrate) in 25 ml. of water was heated to 80°, and a solution of 0.003 mole (0.50 g.) of aminotyrosol in 25 ml. of alcohol was added dropwise. This was followed by a solution of 0.5 ml. of concentrated ammonium hydroxide in 5 ml. of alcohol likewise introduced very slowly. No precipitate formed in the hot solution even after all the ammonium hydroxide was added, but on cooling a considerable quantity of pure white crystalline material formed. The mixture was cooled to 0° for a half-hour, after which the solid was filtered with suction and washed with 50% alcohol, water, 95% and absolute alcohol, and ether. The pure white color was unaffected as long as the product was covered with wash liquid. However, when air was drawn through it after the ether wash, it began to turn violet. The discoloration stopped when the material was placed in a vacuum desiccator, and it appeared to be quite stable after drying, showing only a slight darkening over a period of two years. The yield was 0.20 g. Under the microscope the crystals appeared as colorless, splintery lath-like individuals, with occasional radiating groups. The presence of one molecule of water of hydration was verified by heating a sample in a drying pistol at 110° for six hours, under a vacuum of better than 1 mm., and with anhydrous magnesium perchlorate as drying agent. The loss in weight agreed closely with that calculated for one molecule of water. The dried complex was very hygroscopic; after standing on the balance pan exposed to the air for ten or fifteen minutes, it gained in weight almost exactly the amount which had been lost on drying. On standing for a half-hour longer, the additional gain in weight was negligible.

Anal. Calcd. for $\text{Cd}(\text{—ONH}_2\text{C}_6\text{H}_3\text{CH}_2\text{CH}_2\text{OH})_2\cdot\text{H}_2\text{O}$: C, 44.2; H, 5.10; N, 6.44; Cd, 25.8; H₂O, 4.15. Found: C, 43.5, 43.3; H, 5.09, 5.05; N, 6.20; Cd, 26.3, 26.1; H₂O, 3.9.

Diaminyrosolnickel Monohydrate.—The same procedure and conditions were used, but substituting 0.0015 mole of nickel acetate (0.265 g. of the anhydrous salt) for the cadmium acetate. The yield was 0.46 g. of light gray product. Under the microscope it appeared as colorless, splintery needles and thin irregular and rectangular plates. These were all isotropic, appearing dark between crossed nicols of a polarizing microscope. The complex appeared to be completely stable, showing no change in two years.

Anal. Calcd. for $\text{Ni}(\text{—ONH}_2\text{C}_6\text{H}_3\text{CH}_2\text{CH}_2\text{OH})_2\cdot\text{H}_2\text{O}$: C, 50.4; H, 5.82; N, 7.36; Ni, 15.4. Found: C, 51.0; H, 5.74; N, 7.65; Ni, 15.6.

(5) Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Co., New York, N. Y., 1941, p. 395.

Diaminocresolnickel Dihydrate.—A solution of 0.004 mole of nickel chloride (1.00 g. of the hexahydrate) and 1.00 g. of ammonium acetate in 100 ml. of alcohol was heated to 80° and a solution of 0.010 mole (1.20 g.) of aminocresol in 50 ml. of alcohol was added dropwise. The mixture became quite dark in color, but no precipitate formed. The addition, in succession, of 1.0 g. of ammonium acetate, 0.5 ml. of concentrated ammonium hydroxide, and 50 ml. of water had no immediate effect, but on standing overnight in a refrigerator a small amount of light tan precipitate formed. This was separated and washed with alcohol, water, alcohol, and finally ether, and dried *in vacuo* over sulfuric acid. The product weighed 0.17 g. Under the microscope it appeared as spherical aggregates, remarkably uniform in size and regular in shape. On crushing, irregular fragments of colorless crystalline material resulted, with occasional rectangles. The analysis indicated a nickel-carbon ratio of 1:14, and a nickel-nitrogen ratio of 1:2 as expected, but a nickel-hydrogen ratio of 1:20, suggesting the presence of two molecules of water of hydration. This was verified by the loss in weight on heating *in vacuo* as previously described. Again the dried material was very hygroscopic and gained almost exactly the weight it had lost, but no more.

Anal. Calcd. for $\text{Ni}(\text{—ONH}_2\text{C}_6\text{H}_3\text{CH}_3)_2\cdot 2\text{H}_2\text{O}$: C, 49.7; H, 5.97; N, 8.26; Ni, 17.4; H₂O, 10.7. Found: C, 49.4; H, 5.92; N, 8.40; Ni, 17.6; H₂O, 10.5.

Diaminocresolcopper Monohydrate.—A solution of 0.004 mole of copper acetate (0.80 g. of the monohydrate) in 150 ml. of 65% alcohol was heated to 80°, and a solution of 0.010 mole (1.20 g.) of aminocresol in 50 ml. of alcohol was added dropwise. A fine, silky, white precipitate appeared, while the color of the mixture darkened until it was nearly black. After thirty minutes at 80°, the mixture was allowed to cool to room temperature and the precipitate was removed by centrifuging. Three washes with alcohol removed all the dark color, leaving a light gray product. There was a small amount of red-brown impurity which proved to be cuprous oxide. It was removed by washing with 3 M ammonium hydroxide, followed by water, alcohol and ether. After drying *in vacuo* over sulfuric acid, the yield was 0.95 g. of light gray lumpy material which was difficult to pulverize, tending to spread into flakes very much like graphite. Under the microscope it was too finely divided to show any individual crystals. The analysis indicated one molecule of water, which was verified by drying *in vacuo* as previously described.

Anal. Calcd. for $\text{Cu}(\text{—ONH}_2\text{C}_6\text{H}_3\text{CH}_3)_2\cdot\text{H}_2\text{O}$: C, 51.6; H, 5.57; N, 8.60; Cu, 19.5; H₂O, 5.5. Found: C, 51.5; H, 5.53; N, 8.44; Cu, 19.4; H₂O, 5.9.

It should be mentioned that in a preliminary trial using very nearly the same procedure and conditions, but omitting the ammonium hydroxide wash, a product was obtained in the form of glistening silvery scales. No cuprous oxide was observed; the material appeared to be homogeneous, both macroscopically and microscopically. Under the microscope it appeared as colorless thin flakes of usually irregular shape, but with many well-formed, elongated, pointed boat-shaped individuals. All the flakes were anisotropic, showing low order interference colors when viewed between crossed nicols. The analysis indicated a carbon-hydrogen ratio of 7:9, which would be expected for a monohydrated diaminocresolcopper. However, when the copper-carbon-hydrogen ratio was calculated, the smallest whole numbers were 3:28:36. The homogeneous appearance and well-formed crystals suggested the possibility of a double salt containing one cuprous oxide to four diaminocresolcopper monohydrate molecules, although the exact 1:4 ratio indicated by the close agreement of the analysis with the calculated values may be fortuitous.

Anal. Calcd. for $\text{Cu}_2\text{O}\cdot 4[\text{Cu}(\text{—ONH}_2\text{C}_6\text{H}_3\text{CH}_3)_2\cdot\text{H}_2\text{O}]$: C, 46.5; H, 5.02; Cu, 26.4. Found: C, 46.3, 46.4; H, 5.03, 5.01; Cu, 26.3, 26.1.

Diaminotyrosolcopper Monohydrate.—Solutions of 0.001 mole of copper acetate (0.20 g. of the monohydrate) in 50 ml. of 50% alcohol, and 0.002 mole (0.30 g.) of aminotyrosol in 25 ml. of 95% alcohol were treated exactly as described for diaminocresolcopper monohydrate, including the ammonium hydroxide wash to eliminate cuprous oxide. The observations were very similar; a yield of 0.10 g. of a product with a brilliant silvery luster was obtained.

Anal. Calcd. for $\text{Cu}(\text{—ONH}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{OH})_2\cdot\text{H}_2\text{O}$: C, 49.8; H, 5.75; N, 7.26; Cu, 16.5. Found: C, 49.7; H, 5.87; N, 7.33; Cu, 16.6.

Analytical Methods.—Carbon and hydrogen were determined by a standard semi-micro combustion procedure. Nitrogen was determined by the Kjeldahl or micro Dumas method. The analyses for metal content were carried out by weighing the oxide residue remaining in the boat after combustion. Copper was weighed as cupric oxide, cobalt as Co_2O_4 , nickel as nickel oxide, and cadmium as cadmium oxide. When the residue could not be recovered quantitatively, the metal was determined on a separate sample. This was done also with complexes of each metal to establish the validity of the method of weighing the oxide. Samples were brought into solution with a

mixture of nitric, perchloric and sulfuric acids. Copper then was determined electrolytically, nickel with dimethylglyoxime and cadmium as cadmium sulfate. Cobalt was determined colorimetrically by the method of Cartledge and Nichols,⁶ and also gravimetrically as sulfate. In all but one or two instances, the results of these analyses checked the values obtained by weighing the oxides within the experimental error of the weighing.

Acknowledgment.—Acknowledgment is made to Dr. Groves H. Cartledge, upon whose suggestions this work was based.

Summary

Complex compounds of cobalt, copper, nickel and cadmium with 3-amino-4-hydroxytoluene (aminocresol) and β -(3-amino-4-hydroxyphenyl)-ethanol (aminotyrosol) have been prepared and described.

(6) Cartledge and Nichols, *Ind. Eng. Chem., Anal. Ed.*, **13**, 20 (1941).

BUFFALO, N. Y.

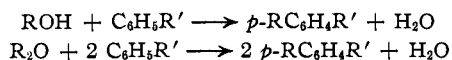
RECEIVED SEPTEMBER 15, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

Reaction Rates by Distillation. II. The Alkylation of Aromatic Compounds by Phenylcarbinols and Their Ethers¹

BY ERNEST F. PRATT, ROBERT K. PRESTON AND J. DANIEL DRAPER

A study of alkylations by benzyl alcohol, benzhydrol and their symmetrical ethers as well as by certain *p*-substituted benzyl alcohols has been made. The general reactions in which R' may be —H, —CH₃ or —OCH₃ are



A solution of the alcohol or ether and some *p*-toluenesulfonic acid in an excess of the aromatic compound being alkylated was refluxed in an apparatus equipped with an automatic water separator.^{2,3} The reactions were followed by observing the rate at which the by-product water collected.

Most of these reactions proceeded smoothly to give 80 to 95% yields of the products indicated by the above equations. In the alkylation of benzene by benzhydrol or its ether, however, the yields were only about 50%. It may be noted that benzhydrol and its ether require much less catalyst than benzyl alcohol and its ether for the alkylation of anisole, but that these relations do not hold for the alkylation of toluene or benzene. For seven of the products the alkylations could theoretically have occurred at either the ortho or para positions; three of the seven were solids, however, and all of these melted at the known temperatures

for the para isomers. The refractive index or melting point of all known products was determined and found to agree closely with the recorded values.

Purification of Materials.—All starting materials were purified by the usual methods until their physical constants agreed closely with the values in the literature. The physical constants for compounds not used in the preceding investigation⁴ were as follows: dibenzyl ether, n_D^{25} 1.5592; dibenzhydrol ether, m.p. 109–110°; *p*-chlorobenzyl alcohol, m.p. 70–71°; *p*-methylbenzyl alcohol, m.p. 59–60°; anisyl alcohol, n_D^{25} 1.5414; toluene, n_D^{25} 1.4928; anisole, n_D^{25} 1.5176; *p*-xylene, b.p. 136–137°; mesitylene, n_D^{25} 1.4948.

Standard Procedure.—The precautions previously described² were taken and the same apparatus and procedure were used except for the following modifications. An excess of the aromatic compound being alkylated was used as the solvent. The reaction mixture consisted of 500 ml. of solution containing the catalyst and 0.125 mole of the alcohol or 0.0625 mole of the ether. The liquid separator was filled with additional solvent before refluxing was begun. The highest voltages which would not cause flooding of the condenser were applied to the heating mantle. Test runs in benzene, toluene and anisole at lower voltages gave the same reaction rates. The yield of water was 98 to 100% unless otherwise noted. Within a given experiment the temperature variation for the 20 to 80% portion of the reaction was less than half the total variation indicated below for all the reactions in a given solvent. After the reactions were complete the catalyst was removed by washing the reaction mixture with sodium bicarbonate solution and with water. The solvents were distilled off and the products isolated by crystallization or distillation. This standard procedure was followed in all cases unless otherwise noted. Most of the experiments were repeated and close checks on the results were obtained except in the one case noted below.

Alkylation of Benzene.—The reaction temperature for these reactions in benzene was $83 \pm 0.8^\circ$. For the alkylation of benzene by benzyl alcohol (BA) the catalyst con-

(1) From portions of the Ph.D. theses of R. K. Preston, June 1948, and J. D. Draper, September 1947.

(2) Pratt and Draper, *THIS JOURNAL*, **71**, 2846 (1949).

(3) Recent related papers are: Huston, Langdon and Snyder, *ibid.*, **70**, 1474 (1948); Monacelli and Hennon, *ibid.*, **63**, 1722 (1941); Simons and Archer, *ibid.*, **62**, 1623 (1940); O'Connor and Sowa, *ibid.*, **60**, 125 (1938); Tsukervanik and Poletaev, *J. Gen. Chem. (U. S. S. R.)*, **17**, 2240 (1947).