

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_3 , 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.

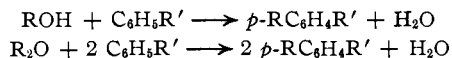
RECEIVED SEPTEMBER 15, 1949

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

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

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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^{27} 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).

centration was 0.128 molar, the time for 50% reaction was 1.37 hr., the time for 90% reaction was 2.94 hr. and the yield of once-distilled diphenylmethane was 78%. Since the time for 90% reaction was more accurately determinable it is given in preference to the time for complete reaction. A 6% yield of *m*-dibenzylbenzene (m.p. 58–59°) was also isolated. The data for the alkylation by dibenzyl ether (BE), in the same order, were: 0.128 molar, 1.20 hr., 2.38 hr. and 83%. In an experiment with benzhydrol (BH) the data were: 0.128 molar, 0.18 hr.,⁴ — hr. and 9%. The main product was benzhydrol ether which was isolated in 55% yield (m.p. 108–109°). The evolution of water ceased at 1.8 hr.; the yield of water, calculated for alkylation, was 71%. For another experiment with benzhydrol the data were: 0.512 molar, 0.46 hr.,⁴ — hr. and 52%. *p*-Dibenzhydrylbenzene (m.p. 167–169°) was also isolated in 4% yield. The evolution of water stopped at four hours; yield 85%. The cause of the increase in time for 50% reaction with increase in catalyst concentration shown in these two experiments is being further investigated. With benzhydryl ether (BHE) the data were: 0.256 molar, 0.23 hr., — hr. and 54%. *p*-Dibenzhydrylbenzene was again isolated in low (5%) yield. The evolution of water ceased at 3.9 hr.; yield 78%.

Alkylation of Toluene.—The reaction temperature here was 113 ± 0.5°. The data are given as above. BA: 0.064 molar, 1.42 hr., 2.38 hr. and 90%. BA: 0.128 molar, 0.18 hr., 0.37 hr. and —%. The product from this experiment was not isolated. BE: 0.064 molar, 1.40 hr., 2.78 hr. and 90%. BH: 0.064 molar, 0.21 hr.,⁴ 25.0 hr. and 91%. BHE: 0.064 molar, 7.76 hr., 14.4 hr. and 90%. The sources of irregularities in the rate curves discussed below do not appear adequate for explaining the extreme distortion of the curve for this experiment. The times for 20, 30, 40, 50, 60, 70, 80, 90 and 100% reaction were 0.12, 0.35, 4.52, 7.76, 10.4, 12.8, 13.8, 14.4 and 15.5 hr., respectively.

Alkylation of Anisole.—The reaction temperature was 157.5 ± 0.5°. BE: 0.128 molar, 0.57 hr., 1.53 hr. and 97%. BH: 0.001 molar, 2.24 hr., 12.3 hr. and 93%. BHE: 0.004 molar, 1.02 hr., 1.92 hr. and 85%.

Alkylation of *p*-Xylene and Mesitylene.—In order to indicate further the scope of the method these two compounds were also alkylated by benzyl alcohol. The reaction temperatures were 140 ± 0.3° for *p*-xylene and 165.5 ± 1.5° for mesitylene. For *p*-xylene the data were: 0.064 molar, 0.27 hr., 0.50 hr. and 84%. The data for mesitylene were: 0.064 molar, 0.08 hr., 0.15 hr. and 89%. In this experiment the water was evolved so rapidly that the temperature fluctuations were excessive and the time readings were inaccurate.

Alkylations by alcohols proceed in some cases chiefly *via* the formation of the corresponding symmetrical ethers. Thus when a low catalyst concentration was used for the reaction of benzhydrol in benzene² or toluene the reaction stopped when only half the theoretical volume of water for alkylation had been evolved and benzhydryl ether was isolated in 85 to 90% yields. If instead of isolating the product more catalyst was added, or if a higher catalyst concentration was used at the start, the reaction would proceed to give the alkylation product. At these higher catalyst concentrations the shapes of the rate curves (or comparisons of the times for 50 and 90% reaction) showed that in the alkylation of toluene and benzene most of the benzhydrol was converted to the ether which then served as the alkylating

(4) It is evident from the reaction rate curves that this is approximately the time for complete etherification in these cases in which little alkylation occurs before etherification is complete (see later discussion).

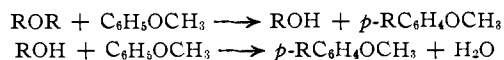
agent.⁵ It has not been established whether ether formation occurs in the alkylation of anisole by benzhydrol.

The alkylation of benzene by benzyl alcohol also proceeds to a significant extent *via* the ether. It was found, for example, that if the process was interrupted when only partially complete the molar ratio of dibenzyl ether to diphenylmethane was about three to one, while if the process was allowed to proceed to completion, diphenylmethane was obtained in 78% yield. The shapes of the rate curves here also gave some indications that the benzylation of both benzene and toluene proceeded partly by way of dibenzyl ether.

Study of Intermediate Ether Formation.—When the reaction of benzhydrol in toluene was carried out at a catalyst concentration of only 0.032 molar the reaction stopped when the yield of water was only 56% (calculated for alkylation). An 85% yield of benzhydryl ether (m.p. 109–110°) was isolated together with 1 to 2 g. of *p*-benzhydryltoluene. In a similar experiment at a catalyst concentration of 0.0128 molar the reaction stopped when the yield of water was 51%. Upon the addition of 0.064 mole of catalyst the reaction proceeded rapidly to completion. *p*-Benzhydryltoluene was isolated in 89% yield.

In an experiment with benzyl alcohol in benzene 0.625 mole of alcohol and 0.064 mole of catalyst were used. Refluxing was stopped when 20% of the theoretical volume of water for etherification had been evolved; this required four and one-half hours. Fractional distillation of the products, freed of solvent and catalyst in the usual way, gave 2.5 g. of diphenylmethane and 9.3 g. of dibenzyl ether, *n*_D²⁰ 1.5592. The refractive index of authentic dibenzyl ether prepared from benzyl alcohol and benzyl chloride⁶ was *n*_D²⁰ 1.5597. It should be noted that the quantitative yields of water obtained in alkylations by benzyl alcohol show that no dibenzyl ether remains in the reaction mixture.

Irregularities in the rate curves arise from causes other than the etherifications just discussed. When hydrocarbon solvents are used irregularities arise which appear to be due to an increase in catalyst activity as the basic oxygen atoms are removed from the system as water.⁷ In the experiments in which anisole was alkylated by dibenzyl or benzhydryl ether the rate of water evolution increased over about the first 25% of the process. This suggests that in these alkylations by ethers the reaction in which water is formed is preceded by one in which no water is evolved, *e. g.*



A similar increase in rate, ascribable to similar causes, was observed in transesterification reactions.² In view of these considerations it is not surprising that in none of the foregoing experiments was the steadily decreasing rate typical of a

(5) Ether intermediates appear not to have been previously considered. For a discussion of the mechanism of alkylation by alcohols see Luder and Zuffanti, "The Electronic Theory of Acids and Bases," John Wiley and Sons, Inc., New York, N. Y., 1946, pp. 117–121.

(6) Bennett and Willis, *J. Chem. Soc.*, **133**, 2305 (1928).

(7) In the etherification studies (ref. 2) there was probably little if any increase in catalyst activity because even at the end of the reaction the ratio of basic oxygen atoms to catalyst molecules in the reaction mixture was high.

single rate controlling process of constant order observed.

When anisole was alkylated by benzyl alcohols the rate curves did agree satisfactorily with those calculated for a reaction which is first order with respect to the alcohol. This suggests that the "leveling effect" of the oxygen atom of the anisole maintains constant catalytic activity and that the dibenzyl ethers are not significant intermediates in these reactions.

Alkylation of Anisole by Benzyl Alcohols.—The reaction temperatures were the same as given above for anisole and the data are given in the same manner as before except that the rate constants are listed in place of the time for 90% reaction. The values given are the arithmetic mean of the constants calculated, as previously described,² for 30, 40, 50, 60, 70 and 80% reaction plus or minus the average deviation of a single value from this mean. Close checks were obtained in repeat runs except that with anisyl alcohol the ease of oxidation or some unknown factor made it very difficult to obtain reproducible data. With benzyl alcohol the data were: 0.032 molar, 2.34 hr., $0.00554 \pm 0.00006 \text{ min.}^{-1}$ and 89%. The data at a higher catalyst concentration were: 0.064 molar, 0.57 hr., $0.0229 \pm 0.0014 \text{ min.}^{-1}$ and —%. This product was not isolated. For *p*-chlorobenzyl alcohol: 0.032 molar, 4.94 hr., $0.00235 \pm 0.00004 \text{ min.}^{-1}$ and 92%. In this experiment the yield of water dropped to 95%. With *p*-methylbenzyl alcohol: 0.016 molar, 0.65 hr., $0.0228 \pm 0.0013 \text{ min.}^{-1}$ and 77%. With anisyl alcohol: 0.00025 molar, 0.45 hr., $0.0260 \pm 0.0012 \text{ min.}^{-1}$ and 85%. The reactivity of the *p*-methyl- and *p*-methoxybenzyl alcohols was much greater than would have been predicted on the basis of the reactivity of benzyl and *p*-chlorobenzyl alcohols.⁸ Because of the great differences in reactivity it was impractical to use the same catalyst concentration throughout.

Since these reactions followed the same course valid comparisons of their rates can be made. The order of decreasing activation by the para substituent is $\text{CH}_3\text{O}-$, CH_3- , $\text{H}-$ and $\text{Cl}-$ which is the order of decreasing ability to release electrons. *p*-Nitrobenzyl alcohol, as might have been expected on the basis of this series, reacted very sluggishly to give a mixture of unidentified products.

The foregoing data on the alkylation of anisole by benzyl alcohol show that the rate is approximately quadrupled when the catalyst concentration is doubled. It may be noted that in the alkylation of toluene by benzyl alcohol a larger than proportional increase in rate with catalyst concentration was also observed. Investigations to determine the significance of this fact are in progress.

When attempts were made to alkylate benzene, toluene or anisole with triphenylcarbinol a mixture of several products which have not been identified

was obtained in each case. Considerable alkylation of benzene occurred when attempts were made to use it as an inert solvent for the alkylation of mesitylene or phenol. *p*-Triphenylmethylphenol was, however, prepared in 73% yield in benzene solution.

Attempts to Use Benzene as an Inert Solvent.—One-eighth mole of mesitylene and an equivalent amount of benzyl alcohol were allowed to react in the presence of 0.064 mole of *p*-toluenesulfonic acid in 500 ml. of benzene solution. The theoretical volume of water was evolved in six hours. A 15% yield of benzylmesitylene and a 64% yield of diphenylmethane were isolated by fractional distillation.

When phenol was used in place of mesitylene at a catalyst concentration of 0.064 molar the theoretical volume of water was evolved in nine hours. A 28% yield of *p*-benzylphenol and a 50% yield of diphenylmethane were isolated.

When 250 ml. of a benzene solution containing 0.07 mole of triphenylcarbinol, 0.20 mole of phenol and 0.00025 mole of *p*-toluenesulfonic acid was refluxed for twenty-four hours, 73% of the theoretical volume of water was evolved. A solid precipitated during the refluxing. A 71% yield of *p*-triphenylmethylphenol was isolated by recrystallization from 95% alcohol.

New Compounds.—Physical constants and analytical results for the new products follow. *p*-Benzylanisole, b.p. 121–123° (1.5 mm.), $n_D^{25} 1.5723$. *Anal.* Calcd. for $\text{C}_{14}\text{H}_{14}\text{O}$: C, 84.81; H, 7.12. Found: C, 84.70; H, 7.45.⁹ 2,5-Dimethylbenzylbenzene, b.p. 124–125° (1.0 mm.), $n_D^{25} 1.5694$. *Anal.* Calcd. for $\text{C}_{15}\text{H}_{16}$: C, 91.84; H, 8.16. Found: C, 91.91; H, 8.30. 4-Chloro-4'-methoxydiphenylmethane, b.p. 170–175° (5.0 mm.), $n_D^{25} 1.5820$. *Anal.* Calcd. for $\text{C}_{14}\text{H}_{13}\text{ClO}$: C, 72.26; H, 5.26. Found: C, 72.26; H, 5.71. 4-Methyl-4'-methoxydiphenylmethane, b.p. 140–145° (2.7 mm.), $n_D^{25} 1.5671$. *Anal.* Calcd. for $\text{C}_{15}\text{H}_{16}\text{O}$: C, 84.86; H, 7.60. Found: C, 84.85; H, 7.68.

This investigation is being continued with emphasis on the mechanism of alkylation and the scope of this distillation method.

Acknowledgment.—It is a pleasure to acknowledge generous financial support by the Research Corporation which greatly aided the progress of this work.

Summary

A number of aromatic compounds have been alkylated smoothly by benzyl alcohol, benzhydrol and their symmetrical ethers. Certain of the alkylations by alcohols were found to proceed to a considerable extent *via* the formation of the symmetrical ethers. The rate of alkylation of anisole by *p*-substituted benzyl alcohols was found to increase as the electron releasing ability of the substituent increased.

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RECEIVED MAY 7, 1949

(8) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 188.

(9) Microanalyses by Mrs. Mary Aldridge and Dr. Eleanor Werble. Values given are averages of duplicates.