

**Solubility Determinations.**—The water solubilities<sup>14</sup> of the compounds listed in Table I were determined according to the following general method. An excess of the compound was put into a vessel and shaken with 150 cc. of water in a constant temperature bath overnight at 30°. The vessel was then taken out and shaken in another constant temperature bath for several hours at 25°. It is realized that these conditions do not necessarily ensure equilibrium, yet it was felt that the procedure was accurate enough for the purpose in question. Following this, an aliquot of the liquid was removed from the vessel with a pipet, the tip of which was protected by a piece of filter paper. The clear liquid was transferred quantitatively into a weighing bottle, which was then kept in a vacuum desiccator over calcium chloride at room temperature to remove most of the water. The

(14) The authors are grateful to Dr. C. W. Ewing of these laboratories for the determination of some of the water solubilities.

samples were dried to constant weight at 60° *in vacuo*.

### Summary

The preparation of water-insoluble, biologically active forms of thiamine and niacin for the enrichment of certain cereals is described.

The thiamine derivatives were obtained by interaction with various high molecular carboxylic and sulfonic acids; the latter also were used to obtain salts with alkyl nicotinates.

Water-insoluble derivatives of nicotinamide were prepared by interaction with *p*-aminobenzoic acid, phenyl isocyanate and 6-methoxy-8-aminoquinoline.

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## Catalytic Alkylation of Chlorobenzenes

BY GERTRUDE VERMILLION AND MARTHA A. HILL<sup>1</sup>

The reversibility of the Friedel-Crafts reaction has been demonstrated by Boedtger and Halse.<sup>2</sup> By heating polyethyl- and polyisopropylbenzenes with benzene and a small quantity of aluminum chloride, they succeeded in recovering good yields of the corresponding monoalkylated compounds. Interconversion between mono- and polyalkylbenzenes with exchange of substituent groups, in the presence of aluminum chloride, has been reported more recently by Hoffmann, Farlow and Fuson<sup>3</sup> as additional proof of reversibility. This alkyl migration has been utilized by Reid and his associates to alkylate naphthalene by means of polyethylbenzene<sup>4</sup> and diisopropylbenzene.<sup>5</sup> Cline and Reid<sup>6</sup> have also employed a "transalkylation" method to prepare mono- from polyethylbenzene, with a high degree of conversion.

Alkyl transfer in the presence of anhydrous aluminum chloride occurs even when benzene is not added to the alkylated compound. Heise and Töhl<sup>7</sup> report the conversion of cumene at 100° to propane, benzene, diisopropylbenzene and tar. Near refluxing temperature, traces of toluene and substantial quantities of xylenes are produced, according to Moore and Egloff.<sup>8</sup>

In this investigation, the reaction of cumene with chlorobenzene, catalyzed by aluminum chloride, was studied as a new method of alkylating halobenzenes. Attempts to alkylate dichlorobenzenes by modifications of the same method were unsuccessful.

(1) This paper is taken from part of a thesis submitted to the Graduate Faculty of Rutgers University in partial fulfillment of the requirements for the degree of Master of Science.

(2) Boedtger and Halse, *Bull. soc. chim.*, **19**, 444 (1916).

(3) Hoffmann, Farlow and Fuson, *THIS JOURNAL*, **55**, 2000 (1933).

(4) Milligan and Reid, *ibid.*, **44**, 206 (1922).

(5) Berry and Reid, *ibid.*, **49**, 3142 (1927).

(6) Cline and Reid, *ibid.*, **49**, 3150 (1927).

(7) Heise and Töhl, *Ann.*, **270**, 155 (1892).

(8) Moore and Egloff, *Met. Chem. Eng.*, **17**, 61 (1917).

### Experimental

**Reagents.**—Paragon cumene, of b. r. 150.0–151.5°<sup>9</sup> (758 mm.), *n*<sup>20</sup><sub>D</sub> 1.4918, monochlorobenzene of b. r. 130.0–130.7° (759 mm.), *n*<sup>20</sup><sub>D</sub> 1.5246, and sublimed aluminum chloride were used.

**Procedure.**—The catalyst was weighed into a one-liter, three-necked flask, to which the measured, liquid organic reagents were quickly added. A 360° thermometer, a mercury-sealed, motor-driven stirrer and a reflux condenser closed by a calcium chloride tube, were attached to the flask by silicone-lubricated, ground glass joints. All heating was done on a constant-level water-bath. At the end of the heating period the flask was cooled and the contents were poured into ice water (300 g. per 0.05 mole of aluminum chloride), with stirring to break up the complexes. The oily product was washed with 100 ml. of 5% sodium bicarbonate and 200 ml. of distilled water before drying over calcium chloride. The dried samples were fractionated through a 91-cm., vacuum-jacketed, Vigreux column.

In the preliminary run, 0.1 mole of aluminum chloride, 2 moles of cumene and 2 moles of chlorobenzene were taken. After an eight-hour reaction period at 90 ± 5°, the product consisted of 19% benzene, 6% high-boiling material, and 25% of an oil containing chlorocumene, with traces of diisopropylbenzene. Unreacted chlorobenzene, 38%, and 13% of unreacted cumene, were recovered.

Other experiments indicated that the conversion of chlorobenzene was increased by reducing the mole ratio of chlorobenzene to cumene, to 0.5:2. Reduction of temperature and reaction time caused lower yields, while an increase in catalyst concentration had no effect.

Cumene, alone, reacted in the presence of aluminum chloride yielding 18% benzene and 24% diisopropylbenzene in the oily top layer of product.

**Identification of Products.**—The fractions boiling below 83° were refractionated. The portion of b. r. 80.2–80.3° (762 mm.) was identified as benzene by its physical properties, *d*<sup>20</sup> 0.8768 and *n*<sup>20</sup><sub>D</sub> 1.5015.

A purified sample of diisopropylbenzene from the cumene digestion was found to have a b. r. of 195–197°, *d*<sup>20</sup> 0.8580 and *n*<sup>20</sup><sub>D</sub> 1.4897, checking the literature values.

Chlorocumene was isolated from the combined 188–196° distillation cuts. Three fractionations at 100 mm., followed by two at 11 mm., yielded a sample of b. r. 72–

(9) All boiling temperatures given in this paper are uncorrected

74°,  $d^{20}$  1.0141 and  $n_D^{20}$  1.5127. *Anal.*<sup>10</sup> Calcd. for  $C_9H_7Cl$ : C, 69.90; H, 7.17; Cl, 22.93. Observed: C, 71.66; H, 8.11; Cl, 22.4. Oxidation with chromic acid in glacial acetic acid solution yielded a small quantity of acid, m. p. 230–235°. The physical constants checked fairly closely those of *p*-chlorocumene prepared by a boron fluoride alkylation method in this Laboratory,<sup>11</sup> but the discrepancies seemed to indicate that a mixture of isomeric chlorocumenes were present, among which the para predominated.

A higher-boiling chlorocumene fraction, b. r. 125–126 (100 mm.), was observed to have  $d^{20}$  0.9816 and  $n_D^{20}$  1.5075. The acid derivative was prepared and purified by sublimation, m. p. 239–241°, checking the literature for *p*-chlorobenzoic acid. Diisopropylbenzene impurities probably caused the depression of specific gravity and refractive index values.

(10) The microanalyses were carried out by Miss L. Baker and Miss L. May in the Laboratories of Columbia University.

(11) Vermillion and Hill, *THIS JOURNAL*, **67**, 2209 (1945).

To determine whether xylenes<sup>8</sup> were formed, a 2-g. sample of the refractionated cumene digestion products was used in an attempt to prepare a derivative by the method of Baril and Hauber.<sup>12</sup> No xylene picrates were obtained and 98% of the picric acid was recovered unchanged.

### Summary

The method of alkylation by transfer of alkyl groups has been applied successfully to the alkylation of monochlorobenzene by transfer of isopropyl groups from cumene, in the presence of aluminum chloride. The para isomer has been shown to be present among the chlorocumenes thus prepared.

(12) Baril and Hauber, *ibid.*, **53**, 1087 (1931).

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## Condensation of Aliphatic Alcohols with Aryl Hydrocarbons in the Presence of Chlorosulfonic Acid<sup>1</sup>

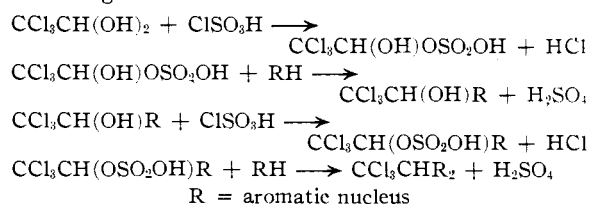
BY WALTER H. C. RUEGGERBERG,<sup>2</sup> MERCHANT L. CUSHING<sup>3</sup> AND WALTER A. COOK<sup>4</sup>

The alkylation of benzene and some of its derivatives with aliphatic alcohols under the catalytic influence of sulfuric acid,<sup>5</sup> boron trifluoride,<sup>6</sup> mixed catalysts containing boron trifluoride,<sup>7</sup> hydrogen fluoride<sup>8</sup> and aluminum chloride<sup>9</sup> has been previously reported. Although the use of halosulfonic acids has not been previously described for this type of condensation, both chlorosulfonic acid<sup>10</sup> and fluorosulfonic acid<sup>11</sup> have been employed by the petroleum industries as alkylation catalysts in reactions between a saturated and an olefinic hydrocarbon.

In connection with the insecticide program conducted by the Chemical Warfare Service during the war, it was found that chlorosulfonic acid is a good condensing agent for the synthesis of 1-trichloro-2,2-bis-(*p*-chlorophenyl)-ethane (DDT) from chloral hydrate and chlorobenzene.<sup>12</sup>

Furthermore, the behavior of chlorosulfonic acid in the condensation between the above named reagents is believed to throw some light on the mechanism by which this condensation takes place. The proposed over-all mechanism in-

volves the formation of an alkyl hydrogen sulfate which undergoes condensation with the aromatic hydrocarbon. In the case of the DDT type compound, this scheme is postulated to consist of the following reactions



In view of these facts, it appeared worth while to extend this condensation to monohydric alcohols with the aim of preparing alkylated benzenes directly. It was found that secondary and tertiary aliphatic alcohols undergo the desired condensation readily, while primary alcohols, except benzyl alcohol, are extremely sluggish, producing only a trace of product under conditions identical with those used for the secondary and tertiary alcohols. The results obtained are given in Table I.

An attempt to prepare bis-(2-phenylethyl) sulfide from thiodiglycol and benzene resulted in the formation of much mustard gas, bis-(2-chloroethyl) sulfide.

Because of the urgency of more important war research and development problems, this method of alkylation has by no means been fully explored. It is our aim, however, to point out at this time the nature of the reaction and the ease with which alkylated benzenes can be prepared from alcohols and aryl hydrocarbons in the presence of chlorosulfonic acid. The method is generally applicable to other halosulfonic acids.

(1) Published with the permission of the Chief, Chemical Warfare Service.

(2) Captain, C. W. S., Army of the United States.

(3) Captain, C. W. S., Army of the United States.

(4) Present address: University of Akron, Akron, Ohio.

(5) Meyer and Bernhauer, *Monatsh.*, **53–54**, 721 (1929).

(6) McKenna and Sowa, *THIS JOURNAL*, **59**, 470 (1937).

(7) Toussaint and Hennion, *ibid.*, **62**, 1145 (1940); Welch and Hennion, *ibid.*, **63**, 2603 (1941).

(8) Simons and Archer, *ibid.*, **62**, 1623 (1940).

(9) Suter and Ruddy, *ibid.*, **65**, 762 (1943).

(10) Vesterdal, U. S. Patent 2,282,505; *C. A.*, **36**, 5832 (1942).

(11) Ipatieff and Linn, U. S. Patent 2,366,731; *C. A.*, **39**, 2642 (1945).

(12) Rueggeberg, Cook, Dawson, Wearn and Mitchell, report on file at Edgewood Arsenal.