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The Catalytic Isopropylation of *o*-Dichlorobenzene

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Boron fluoride, assisted by phosphorus pentoxide, has been shown to be an effective catalyst in the alkylation of benzene[2] and halobenzenes[3] with isopropyl alcohol. The method has not been previously applied to the alkylation of dihalobenzenes.

In this investigation *o*-dichlorobenzene was used since chlorinated benzenes are least subject to halogen migration. Isopropyl alcohol, a secondary alcohol; was used because it undergoes the reaction more readily than primary alcohols.[4]

Three parallel runs, alkylating benzene, chlorobenzene and *o*-dichlorobenzene, were made. All three compounds underwent appreciable alkylation. The experimental conditions and percentage yields, based on the alcohol, are described in Table I.

TABLE I

EXPERIMENTAL CONDITIONS AND PRODUCTS OBTAINED

Starting materials, moles							Yield, %	
Alkylated compound		Isopropyl alcohol	P_2O_5	BF_3	Time, hr.	Temp., °C.	Monoisopropyl	Diisopropyl
Benzene	2	1	0.2	Sat.	4	75–85	50	14
Chlorobenzene	2	1	0.2	Sat.	4	100–110	25	
o-Dichlorobenzene	1	0.5	0.1	Sat.	4	150–160	53	

Experimental

Reagents.—Isopropyl alcohol of b. p. 81.8–82.3° (761 mm.), thiophene-free benzene, monochlorobenzene of b. p. 131.0–131.7° (759 mm.) and $n^{20}D$ 1.5246, *o*-dichlorobenzene b. p. 175.0–177.5° (763 mm.) and $n^{20}D$ 1.5513, boron fluoride and reagent grade phosphorus pentoxide were used.

Procedure.—The apparatus consisted of a one-liter, 3-necked, round-bottom flask fitted with a mercury-sealed stirrer, a 360° thermometer, and a Y-shaped addition tube. The addition tube carried a water-cooled, reflux condenser closed by a calcium chloride tube and a removable gas-inlet tube, which extended to the bottom of the flask and directed the gas toward the stirrer.

The weighed liquid reagents were poured into the reaction flask and boron fluoride was slowly bubbled in with constant stirring and cooling. Addition of the gas was continued until the separation of a white phase and the appearance of white fumes above the condenser, indicated saturation. The gas inlet tube was removed, and a weighed quantity of phosphorus pentoxide was introduced before resealing the addition tube. The temperature was slowly raised to a point just below refluxing where it was maintained for four hours while stirring was continued. The mixture was then cooled and the upper layer separated and washed successively with 250–300 g. of crushed ice, 200 ml. of 5% sodium bicarbonate solution and 200 ml. of distilled water. The oily product was dried over calcium chloride, filtered and fractionated through a vacuum-jacketed, 36-in. Vigreux column.

Three runs were made with the mole ratio of benzene derivative, isopropyl alcohol and phosphorus pentoxide of 2:1:0.2.

Products.—The cumene, diisopropylbenzene and chlorocumene were identified by their physical constants which checked the literature values.

A sample isolated from the 153–170° (100 mm.) distillation cuts of the *o*-dichlorobenzene run had b. p. 159–161° (100 mm.), $n^{20}D$ 1.5336 and d^{20}_4 1.1646. No literature values are given for the constants of either isomer of *o*-dichlorocumene. From the specific gravity and refractive index, the observed molar refractivity was found to be 65.48. The calculated value was 65.48, based on observed values for an isopropyl group (18.69) and *o*-dichlorobenzene (46.79).

Anal.[5] Calcd. for $C_9H_{10}Cl_2$: C, 57.17; H, 5.33; Cl, 37.50. Found: C, 57.57; H, 5.01; Cl, 37.15.

Two isomeric dichlorocumenes with adjacent chlorine atoms are theoretically possible. The orientation was established by chromic acid oxidation of a 0.5-g. sample in glacial acetic acid solvent. The recrystallized acid melted at 203–204°, checking the literature for 3,4-dichlorobenzoic acid. The compound was thus shown to be 3,4-dichlorocumene (1,2-dichloro-4-isopropylbenzene).

Summary

Alcohol–condensation alkylation catalyzed by boron fluoride and an assistant has been applied to the isopropylation of benzene, monochlorobenzene and *o*-dichlorobenzene; in the last case affording the novel preparation of 3,4-dichlorocumene (1,2-dichloro-4-isopropylbenzene) whose physical properties have been ascertained and whose orientation has been demonstrated by oxidation to 3,4-dichlorobenzoic acid.

NEW BRUNSWICK, NEW JERSEY RECEIVED JULY 23, 1945

(1) This paper is taken from part of a thesis submitted to the graduate faculty of Rutgers University by Martha A. Hill in partial fulfillment of the requirements for the degree of Master of Science.

(2) Toussaint and Hennion, THIS JOURNAL, **62**, 1145 (1940).

(3) Hennion and Pieronek, *ibid.*, **64**, 2751 (1942).

(4) McKenna and Sowa, *ibid.*, **59**, 470 (1937).

(5) Analysis performed in the microcombustion laboratories of Dr. Carl Tiedcke, New York City.