

A number of erroneous conclusions in Dostal and Raff's paper have been pointed out. The relation of the previously published molecular size

distribution equations to kinetic problems has been discussed.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

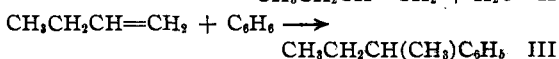
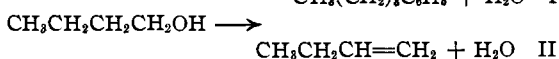
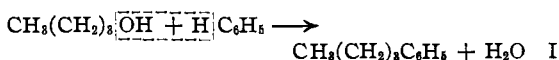
Organic Reactions with Boron Fluoride.¹ XIII. The Alkylation of Benzene with Alcohols

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Sulfuric acid² and aluminum chloride^{3,4} have been used to accomplish the condensation of alcohols with benzene.

It was the purpose of this investigation to treat benzene with various alcohols in the presence of boron fluoride. An attempt was also made to determine the course of the reaction by subjecting primary, secondary and tertiary alcohols to the same treatment.

The reaction of alcohols with benzene might proceed by the direct elimination of water from the hydroxyl group of the alcohol and the hydrogen of the aromatic ring (see equation I below) or by first dehydrating the alcohol to an unsaturated compound with subsequent condensation into the aromatic nucleus (equations II and III).



Both *n*-propyl and isopropyl alcohols reacted with benzene to give identical alkylation products, namely: mono-, di-, and tri-isopropylbenzenes. Likewise *n*-butyl and *s*-butyl alcohol both yielded *s*-butylbenzene derivatives. Both isobutyl and *t*-butyl alcohols gave *t*-butylbenzene derivatives.

Since neither *n*-propyl, *n*-butyl nor isobutylbenzenes were isolated from the corresponding primary alcohols, the reaction did not take place to any appreciable extent according to equation (I). The direct elimination of water from the hydroxyl of the alcohol and the hydrogen of the aromatic nucleus therefore does not suggest itself as a plausible mechanism. On the other hand,

however, the products of alkylation of benzene with alcohols all indicated that an unsaturated compound was first formed with subsequent condensation into the aromatic nucleus. It is, therefore, proposed that the mechanism of the reaction of benzene with an alcohol is first by dehydration to an unsaturated compound with subsequent condensation of the olefin with benzene according to equations (II) and (III).

Other alcohols besides the *n*-propyl, isopropyl, *n*-butyl, *s*-butyl and *t*-butyl were treated with benzene in the presence of boron fluoride. Cyclohexanol gave mono- and dicyclohexylbenzene; benzyl alcohol yielded mono- and dibenzylbenzene; allyl alcohol gave a small quantity of allylbenzene with a much larger quantity of light brown, high boiling material.

The disubstituted benzenes were the para derivatives with very small quantities of the ortho compounds. The positions were determined by oxidation. Sulfuric acid and boron fluoride both gave the para-substituted dialkylbenzene as the main product with a little ortho and no meta dialkylbenzene. When aluminum chloride is used, as an alkylation agent, in the Friedel-Crafts reaction, however, the main product is most often the meta dialkylbenzene.

The *t*-butyl, benzyl, cyclohexyl, allyl, *s*-butyl and isobutyl alcohols reacted very readily with benzene in the presence of boron fluoride while *n*-propyl and *n*-butyl reacted with more difficulty. Ethylene chlorohydrin reacted only very slightly to give a halogenated compound the structure of which was not determined. Phenol, as would be expected, did not react with benzene. Methyl and ethyl alcohols did not react under the conditions used in this investigation.

Experimental Part

Since the procedure was quite uniform for all of the reactions, only a general one will be described.

(1) For previous paper see Sowa and Nieuwland, *THIS JOURNAL*, **58**, 271 (1936).

(2) Meyer and Bernbauer, *Monatsh.*, **53-54**, 721 (1929).

(3) Huston and Hsieh, *THIS JOURNAL*, **58**, 439 (1936).

(4) Tzukervanik, *J. Gen. Chem. (U. S. S. R.)*, **5**, 117-120 (1935); *C. A.*, **29**, 4746 (1935).

One mole of either *n*-propyl, isopropyl, *n*-butyl, *s*-butyl, isobutyl, *t*-butyl, benzyl, cyclohexyl or allyl alcohol and one mole of benzene were weighed into a 500-cc. Erlenmeyer flask which was fitted with an inlet tube that extended to within 2 cm. of the bottom and an outlet tube. Boron fluoride was then added, the quantity varied from 20 to 65 g. depending upon the alcohol used. For *t*-butyl alcohol only 20 g. of boron fluoride was necessary and two layers appeared during the addition while *n*-butyl alcohol required 63 g. of boron fluoride and was heated at 60° for a period of nine hours in a closed Pyrex bottle. The most common quantity was 47 g. of boron fluoride; if two layers had not separated after standing overnight it was warmed.

After the reaction mixture was cooled the lower layer was separated and proved to be water, hydroxyfluoboric acid (b. p. 160°) and hydrofluoric acid. The upper layer was washed several times with 75-cc. portions of a 10% solution of sodium hydroxide, then water, dried over calcium chloride, and carefully fractionated through a Widmer column.

TABLE I
ALKYLBENZENES FROM ALCOHOL AND BENZENE

Alcohols used	Nature of alkyl group in benzene	Yield of alkylbenzenes, g.		
		Mono	Di	Poly
<i>n</i> -Propyl	Isopropyl	23.5	14.2	17.6
<i>i</i> -Propyl	Isopropyl	24.4	13.0	10.0
<i>n</i> -Butyl	<i>s</i> -Butyl	42.5	21.0	20.0
<i>s</i> -Butyl	<i>s</i> -Butyl	35.9	16.9	14.6
<i>i</i> -Butyl	<i>t</i> -Butyl	16.2	8.9	21.2
<i>t</i> -Butyl	<i>t</i> -Butyl	32.0	21.8	10.1
Cyclohexyl	Cyclohexyl	56.2	27.4	6.4
Benzyl	Benzyl	23.2	15.1	34.0 (Above 250° at 15 mm.)
Allyl	Allyl	8.7	31.1	(Above 165°)

TABLE II
PHYSICAL PROPERTIES OF ALKYLBENZENES

Alkylbenzene	B. p., °C.	n_D^{25}	Sp. gr., 25°
<i>n</i> -Propylbenzene	157	1.4925	0.8656
<i>i</i> -Propylbenzene	151	1.4885	.8581
Diisopropylbenzene	204	1.4892	.8550
<i>s</i> -Butylbenzene	171	1.4880	.8577
<i>s</i> -Dibutylbenzene	237	1.4880	.8548
<i>t</i> -Butylbenzene	167	1.4905	.8623
<i>t</i> -Dibutylbenzene	M. p. 77°		
Cyclohexylbenzene	235	1.5190	.9338
Dicyclohexylbenzene	M. p. 100-102°		
Benzylbenzene	261	1.5697	1.0043
Dibenzylbenzene	M. p. 84-85°		
Allylbenzene	156-159	1.5042	0.8812

The results of several runs are given in Table I and the physical properties are tabulated in Table II.

Oxidation of Dialkylbenzenes.—In order to determine the position of the alkyl group in the dialkylbenzenes, oxidation of the side chains to well-known benzene derivatives was used. The phthalic acids or their methyl esters differ widely in melting points.

Several methods of oxidation of diisopropylbenzene were tried but the only successful method was by the use of dilute nitric acid.

Two grams of diisopropylbenzene was refluxed with 300 cc. of 25% nitric acid for twenty hours. An 85% yield of a phthalic acid was obtained. After recrystallization from hot water and drying the acid sublimed without melting above 300°, indicating terephthalic acid. This acid was heated with absolute methyl alcohol in the presence of hydrogen chloride. On cooling a mass of white crystals separated in the form of thin plates. The crystals melted at 140°, which checks with the dimethyl ester of terephthalic acid. No metaphthalic ester could be detected. A separate sample of the acid was tested for ortho phthalic acid by conversion to fluorescein. The test indicated the presence of the ortho isomer but in very small quantity.

The structure of *p*-*s*-dibutylbenzene and of *p*-*t*-dibutylbenzene was best determined by oxidation with chromic acid in acetic acid solution.

The structures of most of the other para dialkylbenzenes have been determined previously and the physical properties of the compounds in this investigation checked well with them.

Summary

Benzene has been alkylated by normal and iso as well as secondary and tertiary alcohols in the presence of boron fluoride.

Normal and secondary alcohols give identical products; iso- and *t*-alcohols also give identical alkylation products.

A mechanism for the alkylation of benzene with alcohols has been proposed.

Boron fluoride, in general, gives different dialkylbenzenes than aluminum chloride, as the main product, when used as an alkylating agent.

The ease of reaction has been found to be dependent upon the ease of dehydration of the alcohol.

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