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

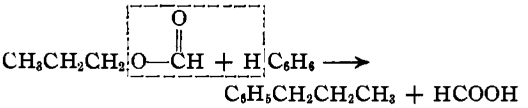
Organic Reactions with Boron Fluoride.[1] XV. The Alkylation of Benzene with Esters

BY JAMES F. McKENNA[2] AND FRANK J. SOWA

Kane and Lowy[3] in a recent publication showed that benzene could be alkylated by esters in the Friedel and Crafts syntheses.

The purpose of this investigation was to show that benzene could likewise be alkylated in the presence of boron fluoride and also to determine the mechanism of this general type reaction.

Recently[4] it was shown that alcohols reacted with benzene, not by double decomposition, but first by dehydration of the alcohol with subsequent condensation of the olefin into the benzene nucleus. As in the case of the alcohols, esters could react with benzene by double decomposition (equation I) or by the intermediate olefin formation (equations II and III).



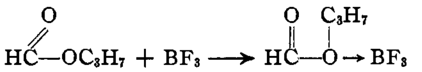
$$CH_3CH_2CH_2O\!-\!\overset{\overset{O}{\|}}{C}H + HC_6H_6 \longrightarrow C_6H_5CH_2CH_2CH_3 + HCOOH \qquad \text{I}$$

$$HCOOCH_2CH_2CH_3 \longrightarrow CH_3CH{=}CH_2 + HCOOH \qquad \text{II}$$

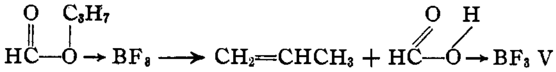
$$C_6H_6 + CH_3CH{=}CH_2 \longrightarrow C_6H_5CH(CH_3)_2 \qquad \text{III}$$

It should be noted that if the reaction followed the course given in equation (I), then *n*-propyl formate should give *n*-propylbenzene. Instead of this product, however, isopropylbenzene resulted from the reaction of *n*-propyl formate withbenzene. Likewise, *n*-butyl and isobutyl formates gave *s*-butyl and *t*-butyl substituted benzenes, respectively. The results of these experiments definitely indicate that the mechanism of the reaction of esters with benzene proceeds according to equations (II) and (III), namely, by the intermediate olefin formation with subsequent condensation into the benzene nucleus, rather than by double decomposition (equation I).

The role played by the boron fluoride in this reaction is to coördinate with the oxygen of the ester which apparently weakens the carbon to oxygen linkage and results in an olefin formation. The olefin then condenses with benzene.



$$H\overset{\overset{O}{/\!/}}{C}\!-\!OC_3H_7 + BF_3 \longrightarrow H\overset{\overset{O}{\|}}{C}\!-\!\overset{\overset{C_3H_7}{|}}{O}\rightarrow BF_3 \qquad \text{IV}$$



$$H\overset{\overset{O}{\|}}{C}\!-\!\overset{\overset{C_3H_7}{|}}{O}\rightarrow BF_3 \longrightarrow CH_2{=}CHCH_3 + H\overset{\overset{O}{/\!/}}{C}\!-\!\overset{\overset{H}{/}}{O}\rightarrow BF_3 \qquad \text{V}$$

The yield of alkylated benzenes was directly proportional to the quantity of boron fluoride used. The yield also increased with the time of heating.

The esters *s*-butyl formate, isobutyl formate, isopropyl acetate, *s*-butyl acetate, cyclohexyl acetate, and isopropyl trichloroacetate reacted very readily with benzene in the presence of boron fluoride while *n*-propyl formate, ethyl formate and *n*-butyl formate reacted with more difficulty. Ethyl, *n*-propyl, *n*-amyl and isoamyl acetates and methyl and ethyl benzoates, *n*-butyl propionate and ethyl and butyl carbonates did not react under the conditions employed in this study. The inorganic esters *n*-butyl phosphate and *n*-propyl and isopropyl sulfates[5] also were treated with benzene in this study. Vinyl acetate reacted with benzene with explosive violence even when only very small quantities of boron fluoride were used. The products were indefinite and resinous in character. As in the experiments with alcohols,[4] the disubstituted benzenes consisted mainly of the para derivatives with very small quantities of the ortho isomers.

Experimental Part

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

One mole of ester 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 of the flask and an outlet tube. Boron fluoride was then added, the quantity varying from 1 to 65 g. depending upon the ester used. Vinyl acetate required only 1 g. to react with explosive violence while *n*-butyl formate required 65 g. and was refluxed for a period of five hours before two layers separated. If the layers had not separated after standing overnight, the flask was heated for a period of thirty minutes after the layers had separated or for a maximum of twenty hours.

After the reaction mixture had cooled, the lower layer was separated and proved to be acid-boron fluoride and a small quantity of tarry matter. 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.

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(1) For previous papers see Sowa and Nieuwland, THIS JOURNAL, **59**, 1202 (1937).

(2) Garvan fellow.

(3) Kane and Lowy, THIS JOURNAL, **58**, 2605 (1936).

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

(5) Wunderly, Sowa and Nieuwland, *ibid.*, **58**, 1007 (1936).

The results of several runs are given in Table I.

TABLE I

ALKYLBENZENES FROM ESTERS AND BENZENE

Ester used	Nature of alkyl group in benzene	BF_3, g. used	Yield of alkylbenzenes, g. Mono	Di	Poly.
Ethyl formate	Ethyl	65.0	6.4		4.1
n-Propyl formate	Isopropyl	55.9	33.4	21.8	10.1
Isopropyl acetate	Isopropyl	65.0	16.4	7.8	4.4
Isopropyl trichloroacetate	Isopropyl	23.6	34.8	18.7	9.3
n-Butyl formate	*s*-Butyl	65.0	33.2	26.8	16.0
s-Butyl formate	*s*-Butyl	65.0	26.0	15.0	8.0
s-Butyl acetate	*s*-Butyl	60.3	29.6	16.4	18.9
Isobutyl formate	*t*-Butyl	65.0	30.6	29.4	7.4
Cyclohexyl acetate	Cyclohexyl	22.9	36.8	14.8	22.0
n-Butyl phosphate	*s*-Butyl	65.0	11.0	22.5	22.0
n-Propyl sulfate	Isopropyl	5.0	45	18	10
Isopropyl sulfate	Isopropyl	3.0	38	20	13

The physical properties of the alkylbenzenes checked those as previously reported,[4] the ethylbenzene had b. p. 134.5°, $n^{25}\mathrm{D}$ 1.4949, sp. gr. 0.8629 (25°), in moderately good agreement with values recorded in the literature.

Summary

Benzene has been alkylated by various esters both organic and inorganic in the presence of boron fluoride.

Normal and secondary butyl esters both gave secondary substituted benzenes while isobutyl ester gave tertiary butylbenzenes.

A mechanism for the reaction has been proposed.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

Glycofuranosides and Thioglycofuranosides. I. A Method of Preparation and its Application to Galactose and Glucose

BY JOHN W. GREEN[1] AND EUGENE PACSU

Twenty years after the synthesis[2] of the "normal" α- and β-methylglucosides, E. Fischer found that the sirupy by-product of the reaction was a third methylglucoside, which he designated as a "γ-form."[3] Extensive constitutional studies of the simple glycosides of the sugars by Haworth and co-workers[4] have shown that all the "normal" glycosides are related to the parent form, pyran, whereas the "γ-forms" are derivatives of the parent form, furan. Unlike the α- and β-pyranosides, which can be prepared in crystalline form by several methods, the α- and β-furanosides are only difficultly available substances, and frequently occur as uncrystallizable sirups.

A review of the literature reveals that only seven alkyl-furanosides, obtained by three distinct methods, are known in crystalline form. Fischer's original method, treatment of the sugar with alcoholic hydrogen chloride at room temperature, usually yields an inseparable sirupy mixture of isomeric glycosides. Although this method has been employed for almost all the monoses, only α-methylmannofuranoside[5] and α-methyl-[6] and α-benzylfructofuranoside[7] have been thus prepared in crystalline form. A second method, characterized by the temporary protection of the 5,6-positions in the sugars with a carbonate group, has been worked out by Haworth and co-workers. Crystalline α- and β-ethylglucofuranoside[8,9] representing the first α,β-pair in the furanoside series, crystalline α-methylglucofuranoside,[9] and also the previously mentioned α-methylmannofuranoside[10] have been obtained by this procedure. The third method, employed by Schlubach in the preparation of the crystalline β-ethylgalactofuranoside,[11] requires furanoid acetohalogenoses as starting materials.

Since these procedures are either involved or of no general applicability, further work in the field of the glycofuranosides will be aided by a method which makes this class of sugar derivatives more available for investigation.

In a preliminary report,[12] a brief outline of the

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[1] This paper is based upon a thesis submitted by John W. Green, Chemical Foundation Research Assistant, to the Faculty of Princeton University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Fischer, *Ber.*, **26**, 2400 (1893); **27**, 2478 (1894); **28**, 1145 (1895).

[3] Fischer, *ibid.*, **47**, 1980 (1914).

[4] W. N. Haworth, "The Constitution of Sugars," Edward Arnold & Co., London, 1929.

[5] Haworth, Hirst and Webb, *J. Chem. Soc.*, 651 (1930).

[6] Purves and Hudson, THIS JOURNAL, **56**, 708 (1934).

[7] Purves and Hudson, *ibid.*, **59**, 49 (1937).

[8] Haworth and Porter, *J. Chem. Soc.*, 2796 (1929).

[9] Haworth, Porter and Waine, *ibid.*, 2254 (1932).

[10] Haworth and Porter, *ibid.*, 649 (1930).

[11] Schlubach and Meisenheimer, *Ber.*, **67**, 429 (1934).

[12] Pacsu and Green, THIS JOURNAL, **58**, 1823 (1936).