

fraction was obtained, b. p. 120–121° at 24 mm. The yield was 2 g., or 92% of the theoretical amount based on tri-*n*-butylborine. The boiling point of a specimen of *n*-butyl dibutylborinate synthesized from di-*n*-butylboron oxide and *n*-butyl alcohol³ was 110° at 19 mm., which agrees satisfactorily with the boiling point observed in this case. Previous observations showed that this ester does not react appreciably with either water or 10% sodium hydroxide, and this explains the failure of the ester to be hydrolyzed appreciably by the water present during the oxidation.

The small residue from this distillation, when absorbed on cotton and exposed to air, became hot and the cotton was charred. This behavior is characteristic of di-*n*-butylboron oxide, which would be formed by hydrolysis of the butyl ester of di-*n*-butylborinic acid and subsequent dehydration. The amount of residue obtained in this case was too small for a determination of its boiling point.

Summary

The behavior of tri-*n*-butylborine toward hydrogen peroxide, perbenzoic acid and molecular oxygen has been studied.

Hydrogen peroxide and perbenzoic acid oxidize the borine quantitatively with the formation of *n*-butyl alcohol and boric acid.

In the absence of water tri-*n*-butylborine combines with one mole of oxygen to form di-*n*-butyl *n*-butylboronate, C₄H₉-B(OC₄H₉)₂. In the presence of water only half as much oxygen is consumed and the product is *n*-butyl di-*n*-butylborinate, (C₄H₉)₂B-OC₄H₉.

The mechanism of the oxidation process and of the inhibiting action of water is discussed.

ITHACA, NEW YORK

RECEIVED AUGUST 12, 1937

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

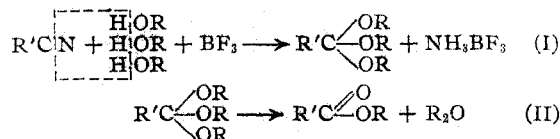
Organic Reactions with Boron Fluoride.¹ XVII

BY JAMES F. MCKENNA² AND FRANK J. SOWA

The purpose of this paper is to present several short investigations that were performed in the presence of boron fluoride. The reactions considered are: the formation of phenolphthalein and fluorescein from the action of phthalic anhydride with phenol and resorcinol, the formation of ethers and esters from the reaction of nitriles and alcohols; the formation of anilides from the reaction of esters with aniline and the alkylation of phenols by alcohols.

Fluorescein and phenolphthalein were prepared at a low temperature and in a short period of time by using boron fluoride as a condensing agent.

In previous publications^{3,4} boron fluoride has been shown to function very desirably as an agent to remove the elements of ammonia. The boron fluoride appeared as monoamminoboron fluoride. In the present study monoamminoboron fluoride was eliminated in the reaction of nitriles with alcohols



(1) Original manuscript received June 25, 1937. For previous paper see Croxall, Sowa and Nieuwland, *J. Org. Chem.*, **2**, 253 (1937).

(2) Garvan Fellow.

(3) Sowa and Nieuwland, *THIS JOURNAL*, **55**, 5052 (1933).

(4) *Idem.*, **59**, 1202 (1937).

Under the conditions of the reaction the assumed ortho ester (equation I) decomposed to an ester and an ether (equation II). The latter reaction was confirmed by treatment of ethyl orthoformate with boron fluoride to give diethyl ether-boron fluoride and ethyl formate-boron fluoride.

Aniline reacts with esters to give very poor yields of anilides and alcohols. The yields of anilides were only 2 to 10%.

t-Butyl alcohol and *i*-butyl alcohol reacted with phenol to give the identical product, *p*-*t*-butylphenol as the main product. This gives further confirmation of the intermediate olefin formation before alkylation of the phenol.⁵

Experimental Part

Preparation of Fluorescein.—By refluxing a mixture of phthalic anhydride (60 g.), resorcinol (50 g.) and boron fluoride (8 g.) in 100 g. of benzene for three hours, a reddish mass insoluble in benzene was obtained. The benzene was removed and the remaining mass purified in the usual manner.⁶ Practically the theoretical yield of fluorescein was obtained. The diacetate derivative⁷ melted at 203–205°.

Preparation of Phenolphthalein.—This procedure was somewhat similar to the preparation of fluorescein except that no benzene was used. Phthalic anhydride (0.75 mole), phenol (1.5 moles) and 50 g. of boron fluoride were heated carefully for one hour. A 72% yield of crude phenolphthalein was isolated.

(5) Sowa, Hennion and Nieuwland, *ibid.*, **57**, 709 (1935).

(6) Baeyer, *Ann.*, **133**, 3 (1876).

(7) Von Liebig, *J. prakt. Chem.*, **85**, 241 (1912).

Nitriles with Alcohols.—One mole of acetonitrile was mixed with three moles of *n*-propyl alcohol and one mole of boron fluoride in a 500-cc. Erlenmeyer flask. After refluxing for one hour the contents was treated with a solution of sodium carbonate and the compounds, excess *n*-propyl alcohol, *n*-propyl acetate, and *n*-propyl ether were separated, respectively, in the usual manner. A yield of *n*-propyl acetate of 28% and of *n*-propyl ether of 27% was obtained.

An analogous experiment with *n*-butyl alcohol gave 40% yield of *n*-butyl acetate and a 38% yield of *n*-butyl ether.

With benzonitrile, *n*-propyl alcohol and boron fluoride a 30% yield of *n*-propyl benzoate and a 26% yield of *n*-propyl ether resulted.

Ethyl Orthoformate with Boron Fluoride.—One-third mole of ethyl orthoformate was saturated with boron fluoride (0.56 mole). The unreacted ethyl orthoformate separated in an upper layer and was removed. Upon careful distillation of the lower layer 0.28 mole of ether-boron fluoride and 0.28 mole of ethyl formate-boron fluoride was recovered. These compounds were identified by agreement of physical properties as described by Gassel⁸ and Bowls and Nieuwland,⁹ respectively.

Esters with Aniline.—Aniline, an ester and boron fluoride were refluxed for a period of time, then cooled and the boron fluoride hydrolyzed off with sodium carbonate solution. Upon steam distillation of the mixture a poor yield of the

(8) Gassel⁸, *Bull. soc. chim.*, [3] 7, 17 (209) (1892).

(9) Bowls and Nieuwland, *THIS JOURNAL*, 53, 3835 (1931).

anilide was recovered. Ethyl acetate gave 1.8% acetanilide; isopropyl acetate gave 5.9% of acetanilide; *n*-butyl propionate gave 10% of propionanilide and ethyl benzoate yielded 9.6% of benzanilide.

Butyl Alcohols with Phenol.—Thirty grams of boron fluoride was passed into 188 g. of phenol contained in a Florence flask. To this mixture 150 g. of *t*-butyl alcohol was added and then refluxed for one hour. Two layers appeared after about thirty minutes. After purification in the usual manner⁵ several small fractions were isolated that contained substituted phenyl ethers, the main fraction being *p*-*t*-butylphenol 165 g., b. p. 233–36°, m. p. 98°.

By repeating the above experiment with *i*-butyl alcohol, 205 g. of *p*-*t*-butylphenol, b. p. 233–36°, m. p. 98°, was isolated.

Summary

A method for the preparation of fluorescein and phenolphthalein using boron fluoride as the condensing agent has been outlined.

The reactions of alcohols with nitriles and phenols in the presence of boron fluoride have been studied.

Esters reacted with aniline in the presence of boron fluoride to give poor yields of anilides.

NOTRE DAME, INDIANA

RECEIVED NOVEMBER 8, 1937

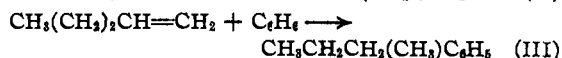
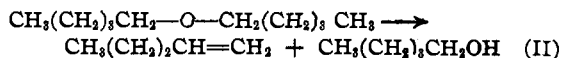
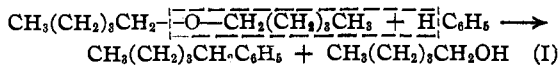
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Organic Reactions with Boron Fluoride.¹ XVIII. The Reaction of Ethers with Benzene

BY MICHAEL J. O'CONNOR AND FRANK J. SOWA

In previous articles^{2,3} it has been shown that alcohols and esters react with benzene in the presence of boron fluoride to give alkylbenzenes through the olefin stage rather than by double decomposition.

The purpose of this work was to investigate the cleavage of various ethers in the presence of boron fluoride and to determine the mechanism these reactions undergo. The reaction of ethers, as in the case of alcohols and esters, with benzene to give alkylbenzenes might proceed by double decomposition (equation I), or by the intermediate olefin formation (equations II and III):



It was noted that if the reaction followed the course given in equation (I), then *n*-amyl ether should give *n*-amylbenzene. Instead, *s*-amylbenzene resulted. Likewise, isoamyl ether gave *t*-amylbenzene. The results of these experiments definitely indicate that the mechanism of the reaction of ethers with benzene proceeds according to equations (II) and (III), that is, by the intermediate olefin formation, with subsequent condensation into the benzene nucleus, rather than by double decomposition as shown in equation (I). Thus, the products of alkylation of benzene with ethers indicate that an unsaturated compound was first formed, and this compound then condensed with benzene.

(1) For previous paper see McKenna and Sowa, *THIS JOURNAL*, 60, 124 (1938).

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

(3) McKenna and Sowa, *ibid.*, 60, 124 (1938).