

g. of benzoic acid (C. P.) in 30 cc. of concentrated sulfuric acid (1.84) and heating for the desired length of time, namely, three, one, one-third and one-twelfth hours. The influence of mercuric sulfate was again studied in a similar fashion by the addition of 0.5 g. of this salt to the reaction mixture. The subsequent procedure was identical with the isomerization experiments except for the removal of the unreacted benzoic acid. This was accomplished by extraction of the acid solution of the sulfobenzoic acids reduced to about 125 cc. three times with 25 cc. of ether. The benzoic acid was weighed and the percentage sulfonation calculated. Finally, to identify absolutely the presence of the ortho isomer, the chloroform soluble residue was powdered in the small extraction flask, placed on a boiling water-bath with a water filled test-tube held in the neck of the flask through a stopper, and the ortho isomer or salicylic acid allowed to sublime onto the outside of the test-tube. In this way the presence of the least trace of salicylic acid could be demonstrated, since it gave the characteristic purple color in a water solution when tested with ferric chloride. This procedure was found necessary both on account of the slight amount of residue and since the melting point method was not completely satisfactory.

The percentage sulfonation was determined not only by the recovered unreacted benzoic acid, but also by the recovered potassium salts and the yield of hydroxybenzoic acids.

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Summary

A reaction scheme for the sulfonation of benzoic acid has been proposed and supported by a study of the isomerization of *o*-sulfobenzoic acid and the actual sulfonation reaction.

A new relation between ortho, meta and para substitution has been proposed and evidence from the sulfonation of benzoic acid added to that already found in the literature.

BALTIMORE, MARYLAND

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

ORGANIC REACTIONS WITH BORON FLUORIDE. I. THE PREPARATION OF ESTERS

By H. D. HINTON AND J. A. NIEUWLAND

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Bowlus and Nieuwland¹ found that boron fluoride united with acetic acid in the proportion of one mole of boron fluoride to two moles of acetic acid. This compound is a heavy liquid, fuming strongly in moist air. Analyses pointed to the formula $(\text{CH}_3\text{COOH})_2\text{BF}_3$. By the use of this compound as a catalytic agent a series of esters has been prepared. The question as to whether the catalytic effect observed is due to the acid-boron fluoride compound, or to the reaction of this substance with some of the alcohol to form the boron fluoride compound, is at present unanswered.

¹ Bowlus and Nieuwland, THIS JOURNAL, 53, 3835 (1931).

If the alcohol-boron fluoride compound is formed, it probably catalyzes the reaction in a manner similar to hydrochloric or sulfuric acid, since it has been shown to be acidic in character.²

Experimental

Ethyl Acetate.—The acetic acid-boron fluoride compound was prepared by passing boron fluoride gas into two moles of glacial acetic acid until one mole of the gas was absorbed. A flask containing 25 g. of acetic acid, 19.18 g. of ethyl alcohol and the catalyst was attached to a reflux condenser, and the contents refluxed from one to nine hours. After refluxing, a saturated solution of sodium carbonate was added to the reaction mixture, and the ester layer was recovered. A yield of 47-50% was obtained. An increase of the catalyst above one or two per cent. concentration did not increase the yield of ethyl acetate. One hour of refluxing produced practically the same amount of ester as a reflux of nine hours.³

Propyl Acetate.—Seven grams of boron fluoride was passed into a mixture of 59.4 g. of propyl alcohol and 60 g. of glacial acetic acid. After refluxing for one-half hour, two layers separated, the top layer containing the ester. A yield of 53.5% of the ester was obtained.

Bowlus and Nieuwland¹ found that propionic acid absorbed one mole of boron fluoride to form a propionic acid-boron fluoride compound boiling at 62-63° (17 mm.). A series of alcohols was refluxed with this propionic acid-boron fluoride compound, each for forty-five minutes, and the corresponding esters were obtained in yields varying from 37 to 66%. Ethyl, propyl, *n*-butyl and *n*-amyl alcohols were used.⁵

Bowlus and Nieuwland did not report a butyric acid-boron fluoride compound. Experiments are being conducted in this Laboratory at the present time to determine if such a compound can be prepared. If it can, a series of esters with this compound should be possible. It was also found that on passing boron fluoride into aliphatic alcohols other than methyl and ethyl, hydrocarbon oils were obtained. After removing the oils, a strongly acid, fuming liquid similar to the methyl and ethyl alcohol solutions of boron fluoride was obtained. This solution, possibly, could be used as a catalytic agent for the preparation of esters. Experiments are being carried out in this Laboratory to find out if the reaction is possible. Evidence obtained up to the present time seems to prove that the above reaction can be used in the preparation of esters.

Summary

Using an acetic acid-boron fluoride compound, and a propionic acid-boron fluoride compound with a series of aliphatic alcohols, the corresponding series of esters has been prepared.

NOTRE DAME, INDIANA

² Nieuwland, Vogt and Foohey, *THIS JOURNAL*, **52**, 1018 (1930).

³ Terre, "Thesis," University of Notre Dame, 1931.

⁴ Seelinger, "Thesis," University of Notre Dame, 1932.

⁵ Sullivan, "Thesis," University of Notre Dame, 1932.