shown to be a convenient synthesis. β-Pyridyl-γ-ethoxypropyl ketone and 1-[β-pyridyl]-1-amino-4-ethoxybutane are reported for the first time.

A complete new synthesis from pyridine of nornicotine and racemic nicotine is reported.

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Organic Reactions with Boron Fluoride. IV. Ether Cleavage in the Presence of Organic Acids

BY G. F. HENNION, H. D. HINTON AND J. A. NIEUWLAND

Introduction

Hinton and Nieuwland have recently shown that boron fluoride catalyzes the reaction between alcohols and acids to form esters.[1] In view of the fact that alcohols, acids and esters form covalent compounds[2] with boron trifluoride, the esterification reaction reported by them may be looked upon as an alkylation reaction depending upon the presence of an alcohol-boron fluoride compound of the type $ROH{\cdot}BF_3$. These compounds possess marked acid properties[3,4] and may be considered to be alkoxy fluoboric acids.

Boron fluoride also forms covalent compounds with ethers.[2,5] With diethyl ether a compound of the formula $(C_2H_5)_2O{\cdot}BF_3$ is formed which boils at 126°. Looking upon the latter compound as the ethyl ester of ethoxyfluoboric acid[6] it was thought that it too should show certain alkylation properties. In a broader sense such a reaction would be a case of ether cleavage. To test this hypothesis a study of esterification of organic acids with ether and boron fluoride was undertaken.

The literature reports numerous cases of ether cleavage. Such reactions occur with acid chlorides[7] at elevated temperatures in the presence of certain catalysts, with acid bromides at high temperatures without catalysts, and with acid iodides still more readily.[8] Meerwein and Maier-Hüser[7] showed that ethers can be cleaved with acid anhydrides in the presence of certain catalysts. In this manner they obtained ethyl acetate from diethyl ether and acetic anhydride in the presence of boron fluoride. In the presence of anhydrous hydrogen bromide ether reacts with certain

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(1) Hinton and Nieuwland, THIS JOURNAL, **54**, 2017 (1932).
(2) Bowlus and Nieuwland, *ibid.*, **53**, 3835 (1931).
(3) Vogt, Foohey and Nieuwland, *ibid.*, **52**, 1018 (1930).
(4) Vaughn, Bowlus and Nieuwland, *Proc. Ind. Acad. Sci.*, **40**, 203 (1930).
(5) Gasselin, *Ann. chim. phys.*, [7] **3**, 11 (1894).
(6) Sugden and Waloff, *J. Chem. Soc.*, 1492 (1932).
(7) Reviewed by Meerwein and Maier-Hüser, *J. prakt. Chem.*, **134**, 51 (1932).
(8) Gustus and Stevens, THIS JOURNAL, **55**, 378 (1933).

acids to produce esters[9] and with phenols and aromatic amines, in the presence of aluminum chloride, to produce ring substitution products.[10]

Experimental

Reagents. Preparation of Ether–Boron Fluoride.—Into a clean, dry 1-liter Florence flask was weighed 148 g. (2 moles) of anhydrous ethyl ether. The flask was equipped with an inlet tube passing through a two-holed stopper. Boron fluoride, generated by heating an intimate mixture of 200 g. of boric oxide, 400 g. of calcium fluoride and 1300 ml. of concentrated sulfuric acid,[2] was passed into the ether, kept cool in an ice-bath. When about 85–112 g. (1.25–1.5 moles) had been absorbed, the reaction was stopped and the flask contents distilled. The fraction boiling at 125–126°, consisting of pure $(C_2H_5)_2O \cdot BF_3$, was retained and kept in a dark, glass-stoppered bottle; yield, theoretical on the basis of BF_3 used.

Acids.—All other reagents used were C. P. anhydrous chemicals and were either distilled or crystallized before use.

Procedure

Ethyl Propionate.—Into a long, soft glass tube (24″ × 0.75″) was weighed 37 g. of propionic acid (0.4 mole plus 25% excess), 10 g. of $(C_2H_5)_2O \cdot BF_3$ (equivalent to 4.78 g. BF_3), and 9.6 g. of ether (total ether 14.8 g. or 0.2 mole). The tube was sealed and heated in gas-fired bomb furnace at 200° for three hours. The tube was allowed to cool to room temperature overnight and then opened. The somewhat pasty product was poured into a 400-ml. beaker. The tube was rinsed out with 40 ml. of water and the rinsings added to the main product. A concentrated solution of sodium carbonate was slowly added until neutralization was complete. The ester layer was removed with a separatory funnel, washed with a small amount of water, dried over calcium chloride and fractionated; yield of ethyl propionate, b. p. 98–99°, was 22 g. or 54% of the theoretical on the basis of ether used.

To show that the pressure incidentally obtained in the above experiment was not essential to the ether cleavage, several experiments were performed with acid–ether combinations of higher boiling point, so that heating at reflux temperature was suitable in place of heating in a sealed tube. The following procedure is typical.

Isoamyl Propionate.—Into a tared flask was weighed 25 g. of propionic acid (excess), 13 g. of diisoamyl ether, and 5 g. of $(C_2H_5)_2O \cdot BF_3$ (equivalent to 2.4 g. of boron trifluoride). The mixture was refluxed for four hours, cooled, neutralized with sodium carbonate solution and the ester layer removed in a separatory funnel, washed with

TABLE I

Ether used	Acid used	Product	Yield, %	B. p., °C.	n_D^{20}
Diethyl	Acetic	Ethyl acetate[a]	47	76– 77	1.3722
Diethyl	Propionic	Ethyl propionate[a,b]	54	98– 99	1.3842
Diethyl	Cinnamic	Ethyl cinnamate[a]	43	269–271	1.5600
Diethyl	Phenol	Phenetole[a,b,c]	26	172–173	1.5075
n-Butyl	Acetic	*n*-Butyl acetate[d]	40	126–128	1.3975
Isoamyl	Propionic	Isoamyl propionate[d]	32	160–163	1.4078
Isoamyl	Benzoic	Isoamyl benzoate[d]	21	259–262	1.4950

[a] Heated in sealed tube for three hours at 200°. [b] See discussion. [c] Separated into phenolic and ether constituents with sodium hydroxide solution. [d] Refluxed in open system for four hours.

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(9) Fenton and Gostling, *J. Chem. Soc.*, **73**, 554 (1898).

(10) Jannasch and Rathjen, *Ber.*, **32**, 2391 (1899).

water, dried over calcium chloride, and fractionated; yield of isoamyl propionate, b. p. 160–163°, was 7.5 g. or 32% of the theoretical on the basis of isoamyl ether used. A small amount of ethyl propionate was also formed, due to the presence of diethyl ether.

Table I shows the substances prepared by the above procedures.

Discussion

Preliminary experiments indicated that the extent of ether cleavage was dependent upon the concentration of boron trifluoride. Assuming that the following reactions take place

$$\text{R—O—R} + \text{R—COOH} \longrightarrow \text{R—COOR} + \text{R—O—H} \qquad \text{(I)}$$
$$\text{R—O—H} + \text{R—COOH} \longrightarrow \text{R—COOR} + \text{H—O—H} \qquad \text{(II)}$$

and that the boron trifluoride reacts with the water formed in equation II it was thought that high yields of esters could be obtained.

A series of experiments on the formation of ethyl propionate, as described above, was performed, regularly increasing the boron trifluoride concentration from 0 to 1 mole per mole of ether used. It was found that when the boron trifluoride concentration was so increased from 0 to one-third mole per mole of ether, the corresponding yield of ester rose from 0% to about 55%. Higher concentrations of boron trifluoride, *i. e.*, above one-third mole per mole of ether, did not influence the ester yield. Gasselin[5] has shown that at high temperatures alcohols react with boron trifluoride as follows.

$$x\text{R—O—H} + \text{BF}_3 \longrightarrow \text{RO—BF}_2 + \text{HF} \longrightarrow (\text{RO})_2\text{BF} + \text{HF} \longrightarrow (\text{RO})_3\text{B} + \text{HF} \qquad \text{(III)}$$

Since the glass tubes used were generally etched during our experiments, it is thought that the reactions expressed by equation III take place, inhibiting the extent of reaction II, and thereby partially accounting for the low yields of esters.

In all cases the crude reaction product was more or less of a pasty nature due to the separation of a solid covalent compound of ester and boron trifluoride. These compounds were spontaneously decomposed upon treatment with carbonate solution, liberating the free ester.

In the experiments in which phenol was treated with ether and boron trifluoride, yields of phenetole were invariably low. Appreciable amounts of various ethylphenols and ethyl phenyl ethyl ethers were always observed but could not be individually isolated. It is believed that phenetole is the intermediate stage in the formation of these compounds, the phenetole formed then rearranging and further etherifying, etc., to yield a mixture of many substances. Boron trifluoride has been shown to catalyze such rearrangements.[11]

Attempts at the cleavage of diphenyl ether to produce phenyl esters were not successful. It is interesting to note in this connection that diphenyl ether does not form a compound[2] with boron trifluoride.

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(11) Sowa, Hinton and Nieuwland, THIS JOURNAL, **54**, 2019 (1932).

Summary

1. In the presence of boron fluoride and organic acids, aliphatic ethers react to form esters. High temperatures are necessary for the ether cleavage.

2. In no instance did the yield of ester exceed 55%. This point is discussed.

3. An alkylation mixture containing approximately one-third mole of boron fluoride per mole of ether was found to be most satisfactory.

4. Phenol reacts with ether in the presence of boron fluoride to form a mixture of ethylphenols and phenyl ethers. Phenetole was the only constituent isolated.

5. Diphenyl ether did not react with organic acids in the presence of boron fluoride as did the aliphatic ethers.

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Studies of Conjugated Systems. XIII. The Preparation and Properties of 1-Phenyl-4-bromobutadiene

BY IRVING E. MUSKAT AND LOREN B. GRIMSLEY

While studying the preparation of conjugated amines it was found desirable to prepare 1-phenyl-4-bromobutadiene. Muskat and Huggins[1] had previously prepared the corresponding 1-phenyl-4-chlorobutadiene by treating the 3,4-dichloride of phenylbutadiene with aqueous potassium hydroxide, and we therefore attempted to use a similar method for the preparation of the bromo derivative. However, this reaction is much more complicated than it first appeared. On treating the 3,4-dibromide of phenylbutadiene with aqueous alkali there is formed some phenylbutadiene, tetrabromide of phenylbutadiene, styrylacetaldehyde, and an oily residue from which we were not able to isolate pure 1-phenyl-4-bromobutadiene. The monobromide, in contrast with the corresponding monochloride, could not be distilled without considerable decomposition, even under reduced pressure.

This peculiar reaction was investigated further and it was found that on treating the 3,4-dibromide of phenylbutadiene with almost any aqueous alkaline reagent, varying amounts of phenylbutadiene and tetrabromide of phenylbutadiene in corresponding molecular quantities are formed in addition to other products. If pyridine in non-aqueous solvents or a suspension of silver oxide in benzene is used, then both bromine atoms are removed to give phenylbutadiene. The expected elimination of hydrogen bromide to give 1-phenyl-4-bromobutadiene was not observed.

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[1] Muskat and Huggins, THIS JOURNAL, **51**, 2496 (1929).