3-Bromopseudocumene (IX) was obtained by hydrolysis of the sulfonic acid (VIII) with sulfuric acid at 150°. The yield was 80% and the product boiled at 94.5–95.5° under 8 mm.

2,3,6-Trimethylbenzoic Acid (X).—3-Bromopseudocumene (5 g.) was converted into the Grignard reagent by dissolving it in ethyl bromide (2.7 g.) and ether (25 cc.) and dropping the mixture slowly onto magnesium (2.4 g.) in an atmosphere of dry nitrogen. The Grignard reagent was carbonated by passing into it a stream of dry carbon dioxide until no further precipitate was formed. The acid, isolated in the usual way and crystallized from water, melted at 110.5–112°, alone and when mixed with the acid X prepared from prehnitene.

Summary

1. When brominated at 140° in direct sunlight and in the absence of a solvent, prehnitene forms 2,3,6-trimethylbenzyl bromide. A number of 2,3,6-trimethylbenzyl derivatives were prepared from this bromide, and the proof of the orientation of the methyl groups is given.

MINNEAPOLIS, MINN. RECEIVED DECEMBER 6, 1937

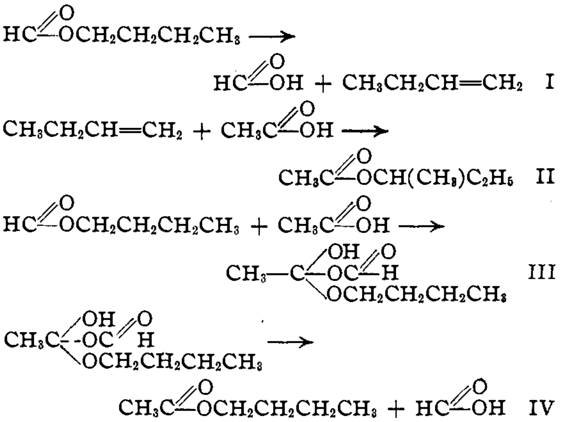
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Organic Reactions with Boron Fluoride.[1] XX. Acidolysis of Esters

BY FRANK J. SOWA

It has been shown that esters[2] react with benzene through the intermediate olefin stage and also that olefins[3] and alcohols[4a] react with acids in the presence of boron fluoride.

The purpose of this investigation was first to study the acidolysis of esters in the presence of boron fluoride and second to determine the course of the reaction. In studying the course of the reaction, it was necessary to determine whether it proceeded through the olefin stage as in equations (I) and (II) to give secondary alkyl esters, or by a mechanism that would not permit olefin formation as in equations (III) and (IV) to give normal alkyl esters.



$$\mathrm{H\overset{O}{\overset{/\!/}{C}}{-}OCH_2CH_2CH_2CH_3 \longrightarrow H\overset{O}{\overset{/\!/}{C}}{-}OH + CH_3CH_2CH{=}CH_2} \qquad \text{I}$$

$$\mathrm{CH_3CH_2CH{=}CH_2 + CH_3\overset{O}{\overset{/\!/}{C}}{-}OH \longrightarrow CH_3\overset{O}{\overset{/\!/}{C}}{-}OCH(CH_3)C_2H_5} \qquad \text{II}$$

$$\mathrm{H\overset{O}{\overset{/\!/}{C}}{-}OCH_2CH_2CH_2CH_3 + CH_3\overset{O}{\overset{/\!/}{C}}{-}OH \longrightarrow CH_3{-}C\begin{matrix}\diagup OH \\ {-}O\overset{O}{\overset{/\!/}{C}}{-}H \\ \diagdown OCH_2CH_2CH_2CH_3\end{matrix}} \qquad \text{III}$$

$$\mathrm{CH_3C\begin{matrix}\diagup OH \\ {-}O\overset{O}{\overset{/\!/}{C}}\;H \\ \diagdown OCH_2CH_2CH_2CH_3\end{matrix} \longrightarrow CH_3\overset{O}{\overset{/\!/}{C}}{-}OCH_2CH_2CH_2CH_3 + H\overset{O}{\overset{/\!/}{C}}{-}OH} \qquad \text{IV}$$

The effect of the quantity of boron fluoride upon the yield of the new ester and the relative efficiencies of sulfuric acid, zinc chloride, boron fluoride, and dihydroxyfluoboric acid as catalysts was also considered.

Experimental Part

Acidolysis Procedure.—The procedure was quite uniform throughout this study and will be described as a general method.

One half mole of an ester, 40 g. of acetic acid and 50 g. of the acetic acid–boron fluoride compound, $(CH_3COOH)_2 \cdot BF_3$, b. p. 142°, were weighed in a 200-cc. round-bottomed flask. The flask was fitted with a two-holed stopper into which was inserted a reflux condenser and a thermometer that extended into the liquid. The contents were heated to 100° on a constant temperature bath. At the end of one hour the reaction flask was cooled in an ice-bath while a solution of sodium carbonate was poured slowly through the top of the reflux condenser until the contents were neutral. The ester layer was separated, dried and carefully fractionated through an efficient 45-cm. Widmer column that was packed with glass beads in the inside tube.

When *n*-propyl esters were treated with acetic acid two fractions were collected, the first from 84 to 90° and the second from 98 to 102°. The first fraction collected from several runs was proved to be isopropyl acetate from its physical properties and by saponifying it to isopropyl alcohol which was further identified. In a similar manner the second fraction proved to be *n*-propyl acetate. By the acidolysis of the three esters, *n*-propyl propionate, benzoate and salicylate 3 g. (3%), 3.6 g. (4%) and 2 g. (2%), respectively, of isopropyl acetate and 40.8 g. (40%), 24.3 g. (24%) and 67.3 g. (66%) of *n*-propyl acetate were formed.

Similarly fractions boiling at 108–113° and 122–126° were proved to be the products *s*-butyl acetate and *n*-butyl acetate, respectively, when the esters *n*-butyl propionate, benzoate and salicylate were each treated with acetic acid as described above. *n*-Butyl propionate gave 4.6 g. (4%) of *s*-butyl and 50 g. (43%) of *n*-butyl acetate; *n*-butyl benzoate gave 5.8 g. (5%) of *s*-butyl and 80.1

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[1] For previous article see Dorris and Sowa, THIS JOURNAL, **60**, 358 (1938).

[2] McKenna and Sowa, *ibid.*, **59**, 1204 (1937).

[3] Dorris, Sowa and Nieuwland, *ibid.*, **56**, 2689 (1934).

[4] (a) Hinton and Nieuwland, *ibid.*, **54**, 2017 (1932); (b) Sowa and Nieuwland, *ibid.*, **58**, 271 (1936).

(69%) of *n*-butyl acetate while *n*-butyl salicylate yielded 5.5 (5%) of *s*-butyl and 73.1 g. (63%) of *n*-butyl acetate.

Likewise by treating the *i*-butyl esters of propionic, benzoic and salicylic acids with acetic acid the products in each case were *t*-butyl acetate (b. p. 91–98°) and *i*-butyl acetate (b. p. 112–117°). The *i*-butyl propionate gave 4.6 g. (4%) of *t*-butyl and 10.5 g. (9%) of *i*-butyl benzoate and salicylate gave 2.3 g. (2%) and 5.8 g. (5%) of *t*-butyl acetate, respectively, along with 10 g. (6%) and 14 g. (12%) of the respective yields of *i*-butyl acetate.

Comparison of Agents for Acidolysis.—*n*-Butyl propionate was treated with acetic acid in the presence of various agents as described above. The products, regardless of the agent used, were *n*-butyl acetate and a small quantity of *s*-butyl acetate. The yields of *n*-butyl acetate by using the agents concd. sulfuric acid, zinc chloride, boron fluoride, and dihydroxyfluoboric acids were 24.4 g. (21%), 36 g. (31%), 46.4 g. (40%) and 70 g. (60%), respectively.

Acidolysis of Ethyl Esters.—The results in Table I were obtained by heating one-half mole of ethyl malonate and one mole of acetic acid at 100° for one hour in the presence of various quantities of boron fluoride. The ethyl acetate was purified in the manner described above.

Three runs of the ethyl malonate–acetic acid system without any boron fluoride were made for one-half, one and two hours, respectively, but no ethyl acetate was recovered.

TABLE I

ACIDOLYSIS OF THE SYSTEM ETHYL MALONATE–ACETIC ACID

$(CH_3COOH)_2 \cdot BF_3$ g. used	Acetic acid g. used	Ethyl acetate yield G.	%
2.8	58.2	3.5	4
6.9	55.6	16.7	19
13.8	51.2	20.3	23
27.8	42.2	27.3	31
41.3	33.7	29.1	33
56.6	24.4	30.0	34
83.1	6.9	30.8	35
127.8	0.0	25.5	29

By heating ethyl sulfate (0.5 mole) and acetic acid (one mole) to 100° for various periods of time in the absence of boron fluoride the following yields of ethyl acetate were formed: (hours, %) 0.5, 6; 1.0, 13; 2.0, 36; 3.0, 43; 4.0, 44; 5.0, 44 and 15, 41.

Table II below gives the yields of ethyl acetate when one mole of ethyl formate and one mole of acetic acid were heated to 100° for one hour in the presence of various quantities of boron fluoride.

TABLE II

SYSTEM ETHYL FORMATE–ACETIC ACID

$(CH_3COOH)_2 \cdot BF_3$ g. used	Ethyl acetate yield G.	%
3	8.8	10
5	29.0	33
11	37.8	43
23	41.4	47
45	45.7	52
60	41.4	47

Ethyl benzoate, ethyl chloroacetate, ethyl phenylacetate and *n*-butyl formate also underwent acidolysis with the acetic acid–boron fluoride compound.

Discussion

The acidolysis of several esters with acetic acid in the presence of boron fluoride has been demonstrated. The mechanism of the reaction seems to proceed principally according to equations (III) and (IV) since *n*-butyl formate and *n*-butyl propionate both gave *n*-butyl acetate as the main product. Steps (I) and (II) would have given *s*-butyl acetate as the main product. Although in general the same alkyl group is found in the acetate as was present in the original ester, there was always a small quantity (not over 4% of total yield) of the secondary or tertiary alkyl ester obtained. This latter result suggests that a small amount of the reaction probably took place through the competitive reactions[3] (I) and (II). The process of acidolysis seems to be quite analogous in this respect to alcoholysis.

The process that involves the acidolysis of ethyl sulfate by acetic acid with and without catalysts might have a practical angle when one considers that olefins can be condensed with sulfuric acid to give alkyl sulfates and that these esters undergo acidolysis to give organic esters. This reaction was definitely proved by the reaction of propylene with acetic acid, in the presence of sulfuric acid. The first part of the reaction could be represented as

$$2C_3H_6 + H_2SO_4 \longrightarrow (C_3H_7O)_2SO_2 \qquad \text{V}$$

$$(C_3H_7O)_2SO_2 + CH_3CO_2H \longrightarrow C_3H_7OSO_2OH + CH_3CO_2C_3H_7 \qquad \text{VI}$$

The isopropyl acid sulfate could then react with a second molecule of acetic acid to give another molecule of isopropyl acetate or it could react with propylene to give isopropyl sulfate and again proceed according to equation (VI).

The quantity of ester formed by acidolysis is proportional to the quantity of catalyst used until a maximum yield is obtained, after which an excess of catalyst seems to diminish the yield. The effect of time also increases the yield of ester formed until a maximum is reached after which the yield seems again to diminish.

In comparative experiments, hydroxyfluoboric acid showed a greater efficiency than sulfuric acid, zinc chloride or boron fluoride in the acidolysis of *n*-butyl propionate with acetic acid.

Summary

The acidolysis of esters by acetic acid in the presence of boron fluoride has been described.

The effect of the concentration of catalyst and time upon the yield of esters by acidolysis has been determined.

The acidolysis of ethyl sulfate has been studied with and without catalysts.

A mechanism of the reaction has been proposed.

NOTRE DAME, INDIANA RECEIVED SEPTEMBER 17, 1937

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

Organic Reactions with Dihydroxyfluoboric Acid[1]

BY T. B. DORRIS, F. J. SOWA AND J. A. NIEUWLAND

Dihydroxyfluoboric acid[2] is a liquid with the formula $HB(OH)_2F_2$ (or $HBO_2H_2F_2$). It possesses acid properties and at the same time it is a potential source for boron fluoride under certain conditions. These properties indicate that it should exhibit desirable catalytic activity.

The purpose of this investigation was to study the use of dihydroxyfluoboric acid as a catalyst in organic reactions. A rough comparison with the catalytic activity of boron fluoride was also made.

With very few exceptions it was found that dihydroxyfluoboric acid could be substituted for boron fluoride as a catalyst. This fact can be explained when it is considered that dihydroxyfluoboric acid gives rise to boron fluoride under various conditions. This is particularly true in its reaction with acetyl chloride, with acetic anhydride, with benzenediazonium chloride and with compounds containing oxygen.[3] Two separate experiments, however, have shown quite conclusively that dihydroxyfluoboric acid is not dependent on boron fluoride for its catalytic activity in all cases. In the presence of boron fluoride, phenol and isopropyl alcohol combine to form isopropylphenols and phenyl ethers.[4] This reaction fails to proceed in any concentration of the new catalyst even after very long periods of heating. In esterification reactions, moreover, boron fluoride is decomposed by the water formed while dihydroxyfluoboric acid may be recovered and reused to catalyze further esterifications.[5]

In general it might be stated that boron fluoride is a more powerful catalyst while dihydroxyfluoboric acid is a milder catalyst that promotes less polymerization. Boron fluoride rearranges isopropyl phenyl ether spontaneously,[6] while 30 to 40% of this ether is unchanged after refluxing for two hours with dihydroxyfluoboric acid. The rate of absorption of propylene by phenol is considerably greater when using boron fluoride.[7] This comparison of rates, however, must be interpreted cautiously, due to the very slight miscibility of dihydroxyfluoboric acid with most organic liquids.

Experimental Part

Preparation of Dihydroxyfluoboric Acid.—Dihydroxyfluoboric acid, b. p. 160°, was prepared by action of anhydrous hydrogen fluoride on boric oxide as previously described.[2]

Olefins with Phenol.—One mole of phenol was weighed in a liter Florence flask that was fitted with a two-hole rubber stopper into which were inserted an inlet tube extending to the bottom of the flask and an outlet tube. The outlet tube was connected to a mercury safety trap that also served the purpose of maintaining a safe pressure in the system. After adding 0.1 mole of dihydroxyfluoboric acid, propylene was passed in under a pressure of 7 to 10 cm. of mercury above atmospheric until 28 g. of propylene was absorbed. The solution was transferred to a separatory funnel and washed several times with a solution of potassium hydroxide. The alkaline extracts were acidified in order to recover the phenolic compounds while the alkali insoluble portion contained the alkyl phenyl ethers. The phenols, 2-isopropylphenol (30 mole %) and 4-isopropylphenol (3.4%) along with traces of higher substituted phenols and ethers were isolated. About 63.5% of the original phenol was recovered. The 2-isopropylphenol was shown to be identical with the 2-isopropylphenol formed by the rearrangement of isopropyl phenyl ether. The two phenols gave the same isopropyl phenyl ether derivative.

By using butylene, which was about 80% isobutylene and about 20% *n*-butylene, in place of propylene in an experiment similar to that described above the products were: butylphenol (8.1%), butyl phenyl ether (5.4%), butylphenyl butyl ether (26.8%) residue (55.8%) and recovered phenol (3.8%). The butyl phenyl ethers were proved by the "Zeisel" reaction.

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(1) Original manuscript received June 28, 1937.

(2) Sowa, Kroeger and Nieuwland, THIS JOURNAL, **57**, 454 (1935).

(3) Kroeger, Sowa and Nieuwland, *ibid.*, **59**, 965 (1937).

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

(5) Kroeger, Sowa and Nieuwland, *Ind. Acad. Science*, Dec. (1937).

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

(7) Sowa, Hinton and Nieuwland, *ibid.*, **54**, 3694 (1932).