The melting points of all of the 2,4-dinitro amides, except that derived from β-naphthylamine, were approximately 20 to 70° higher than the corresponding mononitro amides. All of the amines tested yielded satisfactory solids except *n*-amylamine, which formed an oil.

The 2,4-dinitrobenzenesulfenyl chloride was found to react more rapidly with amines than with water, and it could be used in testing for amines in aqueous solution having a concentration of 30% of the amine.

To study the effect of acid upon the amides, hydrogen chloride was passed for three minutes through ethereal solutions of the amides formed from aniline, *p*-anisidine, ethylamine, *n*-butylamine and N-methylcyclohexylamine. The hydrochlorides were then filtered off, dried and weighed. All were found to have been decomposed by this treatment to yield 90–92% of the original amine hydrochlorides.

The authors wish to thank The Sharples Solvents Corporation and Commercial Solvents Corporation for some of the amines used in this work.

Summary

1. 2,4-Dinitrobenzenesulfenyl chloride has been found to form desirable solid derivatives of both aliphatic and aromatic amines.

2. The reaction was instantaneous and practically quantitative, one-half of the amine going to form amine hydrochloride, the other half to produce the sulfenamide derivative.

3. Aqueous as well as anhydrous amines may be used.

4. The amide derivatives were readily cleaved with hydrogen chloride to the corresponding amine hydrochloride.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Hydrogen Fluoride as a Condensing Agent. XV. The Preparation of Esters and Ethers[1]

BY J. H. SIMONS AND A. C. MEUNIER

In this series of papers the use of hydrogen fluoride to promote a number of organic chemical reactions has been described. It has now been found that esters and ethers can be made by the action of this catalytic agent. Secondary olefins reacted with acetic and normal butyric acids to give good yields of esters, whereas the tertiary olefin, trimethylethylene, gave no detectable quantity of amyl acetate when treated with acetic acid, polymerization of the olefin overshadowing any reaction with the acid. It was found that hydrogen fluoride also promoted the esterification of glacial acetic acid with ethyl alcohol, as well as the reverse hydrolysis reaction. All these experiments were performed at atmospheric pressure and approximately 0°.

In a previous paper[2] it was reported that anisole was formed by the action of hydrogen fluoride upon a mixture of phenol and methanol. It has now been found that dicyclohexyl ether can be obtained by the action of cyclohexene on a mixture of cyclohexanol and hydrogen fluoride at 0°. In other attempted preparations of ethers, either there was no appreciable reaction at this temperature or excessive amounts of polymers were formed.

Experimental

Reactions of Acids with Olefins.—The technique was essentially the same as that hitherto employed with hydrogen fluoride in these laboratories.[3]

Molar quantities were used. The olefin was added dropwise to a solution of the acid or alcohol in the catalyst held in an ice-bath. A ratio of at least five moles of catalyst per mole of acid or alcohol was used, due to the reduction of the catalytic activity caused by both the reacting acid or alcohol and the water produced. Esterification was effected with a few hours stirring at 0°. In some cases, redistillation was necessary to obtain a pure product. Acetic acid reacted with cyclohexene to form cyclohexyl acetate, b. p. 173.5° at 735, $n^{19.5}_{\mathrm{D}}$ 1.4405, d^{20} 0.9732, in a yield of approximately 70%, and with no tar formation. Normal butyric acid reacted with the same olefin to give cyclohexyl *n*-butyrate, b. p. 207.6° at 735, n^{20}_{D} 1.4423, d^{20} 0.9431, in the same yield. Acetic acid reacted with a mixture of octenes 1 and 2 to give octyl acetate, b. p. 192° at 721, n^{20}_{D} 1.4146, d^{20} 0.8628, in approximately 29% yield and *n*-

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[1] For the previous paper of this series see Simons and Bassler, THIS JOURNAL, **63**, 880 (1941).

[2] Simons and Passino, *ibid.*, **62**, 1624 (1940).

[3] Simons and Archer, *ibid.*, **60**, 2952 (1938).

butyric acid reacted with the same olefins to give a 47% yield of octyl ester of *n*-butyric acid, b. p. 221.8° at 735, $n^{20}D$ 1.4213, d^{20} 0.8593. With the octenes polymerization was a greater factor than it was with cyclohexene, but here also there was an absence of tar formation.

Reaction of Ethyl Alcohol with Acetic Acid.—Thirty-five grams (0.76 mole) of absolute ethanol was added over a period of twelve hours to a solution of 0.8 mole of glacial acetic acid in 7.5 moles of hydrogen fluoride, the reactants being kept at 0°. There was recovered a 17.5% yield of ethyl acetate (based on alcohol), b. p. 74–75.5° (735 mm.), $n^{20}D$ 1.3700–1.3740.

Hydrolysis of Ethyl Acetate.—A mixture of 106 g. of ethyl acetate and 18 g. of water (molar quantities) was stirred with 157 g. of hydrogen fluoride at ice temperatures for eleven hours. The products were poured onto ice and neutralized with solid sodium carbonate, the temperature not being allowed to exceed 5°. The liquid was then packed in ice as it was saturated with potassium carbonate. There was obtained 17 g. of liquid, b. p. 75.5–83° (735 mm.), $n^{20}D$ 1.3659. A 3,5-dinitrobenzoate derivative was prepared, m. p. 90°; mixed melting point with an authentic sample of the 3,5-dinitrobenzoate of ethyl alcohol, 89°. This quantity represents a 35% conversion to ethyl alcohol.

Reactions of Alcohols with Olefins.—To one mole of alcohol dissolved in 5–7 moles of hydrogen fluoride kept near 0° by external cooling was added dropwise one mole of olefin over a period of seven to eleven hours. The products were usually neutralized shortly after complete addition of the olefin, although in the case of dicyclohexyl ether, the yield was slightly increased by a few hours of additional stirring at 0°. After separation of layers and neutralizing with cold dilute sodium carbonate solution, the oil was dried over anhydrous potassium carbonate and distilled first through a Claisen flask to separate unreacted materials and polymer from the principal product. Then the ether or middle fraction was distilled through an efficient column. The following reactions were carried out: (1) cyclohexene and cyclohexanol; (2) cyclohexene and isopropyl alcohol; (3) propylene and ethyl alcohol (the propylene was passed through the alcohol solution under 10 mm. pressure for one and one-half hours).

From (1), using 5.5 moles of hydrogen fluoride, addition time of five hours and reaction time of eight hours, there were obtained a 12% yield of dicyclohexyl ether, 61.5% cyclohexyl fluoride (based on olefin), 43.5% recovered alcohol, and 1.6% residual tar.

From (2) using 7.5 moles hydrogen fluoride, and eleven hours addition and reaction time, there were obtained 45% low boiling materials, probably consisting of unreacted olefin, alcohol, and some cyclohexyl fluoride, 2% cyclohexanol, 3.5% dicyclohexyl ether, and 35% residual tar.

From (3) there were obtained only unreacted alcohol and high boiling polymer.

Summary

Secondary olefins reacted with acids in the presence of hydrogen fluoride to give good yields of esters. A tertiary olefin reacted unfavorably.

Hydrogen fluoride promoted the esterification of acetic acid with ethanol and also the reverse hydrolysis reaction.

The reaction of cyclohexene with cyclohexanol in the presence of hydrogen fluoride produced a small yield of dicyclohexyl ether. In other reactions involving secondary olefins, the desired ether was not produced.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSIOLOGICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

Quantitative Studies of the Oxidation of Fatty Acids with Hydrogen Peroxide and an Interpretation of the Reaction Mechanism*

BY ROVELLE H. ALLEN AND EDGAR J. WITZEMANN

More than thirty years ago Dakin reported a series of pioneering studies of the oxidation of fatty acids *in vitro*, that along with the fundamental work of Knoop laid the basis of our present conceptions of these processes as they occur both *in vitro* and *in vivo*. The new data here reported constitute an extension of a portion of these earlier results of Dakin.

In Dakin's studies the materials were placed in a distillation apparatus and in the course of the distillation volatile materials passing over were condensed or absorbed. The multiplicity of products obtained and the lack of suitable analytical methods made quantitative studies impractical at that time. By placing the condenser in the refluxing position, the nature of the end-products was so greatly simplified that an approximately quantitative account can now be given of the fate of the fatty acids oxidized.

Dakin had suggested that perhaps such oxidations could be influenced by "a suitable catalyst,"[1] without realizing that the ammonia of his ammonium salt was just such a catalyst, as was

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* The first part of this paper is an abstract of a part of the Ph. D. dissertation of R. H. Allen.

(1) Dakin, *J. Biol. Chem.*, **4**, 227 (1908)