

Catalysis in Organic Chemistry. V. Decompositions of Esters and Acids by Anhydrous Zinc Chloride¹

BY H. W. UNDERWOOD, JR., AND O. L. BARIL

The catalytic decomposition of esters and acids by anhydrous zinc chloride has been described in previous papers.² The transformations observed were represented by three different types of decomposition which involved the elimination of an aliphatic unsaturated hydrocarbon or carbon dioxide or both. In order to substantiate these results, additional experiments of a similar nature were performed, from which the following regularities and generalities may be concluded.

The methyl, ethyl, propyl and butyl esters of monobasic aliphatic acids were not affected by the catalyst under the conditions of the experiment. The esters derived from amyl alcohol and from a monobasic aliphatic acid decomposed very slowly into an unsaturated hydrocarbon and the aliphatic acid. The rate of decomposition increases with a rise in the number of carbon atoms in the alcohol group. The aliphatic monobasic acids themselves are not affected by the catalyst. Esters of aliphatic dibasic acids are all decomposed, the dibasic acid reacting with the zinc chloride to form the zinc salt of the dibasic acid with evolution of hydrogen chloride. The hydrogen chloride in turn forms the alkyl halide with the liberated unsaturated hydrocarbon.

Esters of aromatic acids decompose into an unsaturated hydrocarbon and the aromatic acid, which in turn decomposes into carbon dioxide and a saturated aromatic hydrocarbon, providing the aromatic acid is monobasic. If the aromatic acid is a dibasic acid, the anhydride of the acid is formed. Benzyl esters decompose into the acid, and the benzyl groups polymerize, forming a dark tarry residue. All unsaturated hydrocarbons evolved, whether aliphatic or aromatic, polymerize, the polymerization increasing with the rise in the number of carbon atoms in the hydrocarbon.

Esters and acids readily decomposed by heat were not used. Those which were used could be distilled or fused without decomposition. In every case, decomposition of the ester or acid was

effected, in the presence of anhydrous zinc chloride, at a much lower temperature than if heated alone. Zinc chloride dissolved in the ester or acid before any evidence of decomposition appeared. Esters and acids which did not dissolve the zinc chloride on heating were not themselves decomposed. This peculiar phenomenon was also noted in the experiments described in previous papers. During the decomposition, there was always a color change from colorless to yellow to orange to red to brown and finally black. The temperature in every case was raised until the ester or acid dropped freely from the end of the reflux condenser. There was often evidence of decomposition in the reaction flask before this temperature was reached. The tests described by Mulliken ["Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York City, 1904, 1916, 1922, Vols. I, II and IV] were used for the identification of all the products of decomposition.

Experimental

No evidence of decomposition was found in experiments with ethyl chloroacetate, dichloroethyl acetate, trichloroethyl acetate, ethyl isovalerate, *n*-butyl formate, *n*-propyl acetate, propyl formate, isopropyl formate and methyl *m*-nitrobenzoate.

Esters Decomposing with Evolution of Carbon Dioxide.—Methyl cinnamate yielded styrene and its polymers; ethyl cyanoacetate gave ethylene and methyl cyanide; amyl chlorocarbonate decomposed into amylene and its polymers, amyl chloride and hydrogen chloride; amyl chloroacetate into amylene and its polymers, chloroacetic acid and hydrogen chloride; ethyl anisate into ethylene, anisic acid, anisole and *p*-ethyl cresyl ether; ethyl phenylacetate into ethylene, phenylacetic acid, propylbenzene and acetic acid; isoamyl valerate into valeric acid, isopropylethylene and its dimer; *n*-amyl acetate into acetic acid, amylene and its polymers; isoamyl propionate into propionic acid, isopropyl ethylene and its dimer; ethyl *m*-aminobenzoate into ethylene and aniline; and ethyl *p*-nitrobenzoate into ethylene and *p*-nitrobenzoic acid.

Ethyl acetoacetate yielded acetone, ethyl acetate and propyl methyl ketone; and isobutyl acetoacetate gave isobutylene, acetone, isobutyl acetate and methyl isoamyl ketone. Ethyl diethylmalonate gave ethylene and ethyl diethylacetate; while ethyl dipropylmalonate gave ethylene and ethyl dipropylacetate. Methyl carbonate yielded methyl alcohol; cyclohexyl acetate gave cyclohexane and acetic anhydride; while ethyl orthoformate decomposed into ethyl ether and ethyl formate when distilled over anhydrous zinc chloride, but on refluxing the mixture for one hour at 60°, ethyl alcohol and paraldehyde were obtained.

Acetal and ethylal gave ethyl alcohol and paraform, whereas dimethyl acetal yielded methyl alcohol and par-

(1) Due to the death of Professor Underwood, this paper has been prepared by the junior author.

(2) Underwood and Baril. *THIS JOURNAL*, **52**, 395 (1930); **53**, 2200 (1931).

aldehyde. Benzene was obtained from both the iso- and terephthalic acids. Anisic acid gave anisole; *p*-toluic acid yielded toluene and the zinc salt of *p*-toluic acid; and diphenylacetic acid decomposed into diphenylmethane.

Esters Decomposing without Evolution of Carbon Dioxide.—Benzyl benzoate and benzyl butyrate decomposed into their respective acids, benzoic and butyric. The benzyl groups polymerized, forming a dark colored and tarry residue. Dimethyl phthalate gave phthalic anhydride, and *n*-amyl phthalate gave phthalic anhydride, amylene and its polymers. Phenyl acetate yielded phenol; and phenyl salicylate gave phenol at a temperature of 177° in presence of the catalyst, although a temperature of 280° is required to decompose it without a catalyst. Phenylacetic acid yielded acetic acid; *m*- and *p*-nitrobenzoic acid reacted with the catalyst to form the zinc salt of the acid with evolution of hydrogen chloride. The *p*-nitrobenzoic acid mixture blew up after fifteen minutes of heating, leaving a deposit of soot over the entire apparatus.

A new type of decomposition has been observed with the elimination of carbon monoxide instead of carbon dioxide from halogenated aliphatic acids. Monochloroacetic acid decomposed into carbon monoxide, formaldehyde and hydrogen chloride; and the trichloroacetic acid decomposed into carbon monoxide, carbonyl chloride and hydrogen chloride.

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Reduction of Nitroguanidine. III. Synthesis of Aminoguanidine¹

By G. B. L. SMITH AND EDWARD ANZELMI

Aminoguanidine has been prepared by the reduction of nitroguanidine with zinc in a solution

(1) For more full details see B.S. thesis by Edward Anzelmi, Polytechnic Institute of Brooklyn, 1933. Contribution No. 27 from the Department of Chemistry of the Polytechnic Institute of Brooklyn.

of acetic acid,² by the interaction of hydrazine hydrochloride and cyanamide,³ and by the electrolytic reduction of nitroguanidine.⁴ We have prepared aminoguanidine in high purity and excellent yield by the hydrazinolysis of methyl isothioureia sulfate. To 139 g. of methyl isothioureia sulfate in 200 ml. of water at 10° is added 119 ml. of a 42% solution of hydrazine hydrate⁵ diluted with an equal volume of water. The methyl mercaptan liberated can be absorbed in a solution of sodium hydroxide.⁶ Finally the aminoguanidine sulfate is precipitated by addition of an equal volume of 95% ethanol to the solution concentrated to 200 ml. A second crop of crystals separates on concentration of the filtered solution. The water of crystallization (1 molecule) may be removed by drying *in vacuo* or at 105°; yield 90%; m. p. 206° with decomposition (Thiele, 207–208°). Aminoguanidine sulfate was identified through conversion to the picrate and bicarbonate, by liberation in alkaline solution of one-half of the nitrogen as ammonia and by hydrolysis to hydrazine.⁷ *Anal.* calcd. for (CH₆N₄)₂H₂SO₄: SO₄, 39.83; NH₃, 27.67; N₂H₄, 26.02. Found: SO₄, 39.3, 39.7; NH₃, 27.2, 27.5, 27.7; N₂H₄, 26.03, 25.93. The fact that aminoguanidine bicarbonate has the composition CN₄H₆H₂CO₃ has been established by analysis. A solution of aminoguanidine is a strong base *K*_B estimated as 1.1 × 10⁻³. Further work on aminoguanidine and alkylaminoguanidines is in progress.

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(2) Thiele, *Ann.*, **270**, 1 (1892).

(3) Pellizzari and Cuneo, *Gazz. chim. ital.*, [2] **21**, 405 (1901).

(4) Boehringer, German Patent 167,637. We have as yet been unable to confirm this observation.

(5) From the Eastman Kodak Company.

(6) Phillips and Clarke, *THIS JOURNAL*, **45**, 1755 (1923).

(7) Jamieson, *Am. J. Sci.*, [4] **33**, 353 (1912).