[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE REACTION OF SODIUM PHENOXIDE WITH ALPHA-CHLOROHYDRACRYLIC ACID

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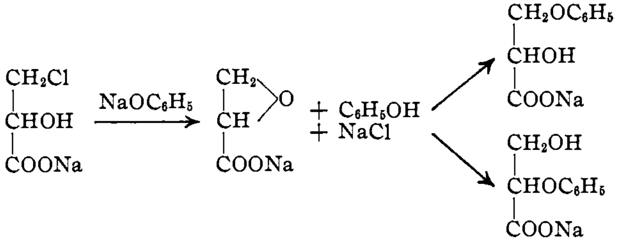
RECEIVED MAY 16, 1930 PUBLISHED AUGUST 5, 1930

In a recent paper[1] it was reported that the reaction between sodium phenoxide and β-chlorolactic acid led to the formation of a mixture of the two isomeric monophenyl ethers of glyceric acid, the amount of β-phenoxylactic acid isolated being some one hundred times greater than that of α-phenoxyhydracrylic acid. The occurrence of α-phenoxyhydrarylic acid was explained on the basis of the following formulation, involving the intermediate formation of glycidic acid



As was pointed out, it was possible that the β-chlorolactic acid used in the reaction was contaminated with a small quantity of α-chlorohydracrylic acid, and that the direct replacement of the chlorine in the latter compound gave rise to α-phenoxyhydracrylic acid; but since the reaction between α-chlorohydracrylic acid and ammonia had been reported[2] to yield only *iso*-serine, $CH_2NH_2CHOHCOOH$, it was argued that even if α-chlorohydracrylic acid were present, it would react with sodium phenoxide to give glycidic acid, which would then add phenol, forming a mixture of monophenylated glyceric acids. Since the addition of phenol to glycidic acid could take place in two different ways, two isomers would be formed in a ratio dependent on factors which are discussed by Michael[3] in his "Partition Principle." The positions of the phenoxyl and hydroxyl in the product would thus be independent of the positions of the chlorine and hydroxyl in the reactant containing these.

Such reasoning, based on analogy, might easily lead to false conclusions. Accordingly, it was deemed advisable to verify the statement that α-chlorohydracrylic acid and sodium phenoxide would react to form mainly β-phenoxylactic acid. The results obtained, which are the subject of this paper, are in complete accord with the prediction.

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[1] Koelsch, THIS JOURNAL, **52**, 2430 (1930).

[2] Melikoff, *Ber.*, **13**, 1265 (1880).

[3] Michael, *J. prakt. Chem.*, [2] 60, 290 (1899).

The α-chlorohydracrylic acid taken was prepared by a method similar to that used for the preparation of the corresponding bromo acid[4] by the action of silver carbonate on α,β-dichloropropionic acid. Although it was obtained as a non-volatile, uncrystallizable sirup, it was shown to be reasonably pure by analysis. That it was quite free from β-chlorolactic acid was shown by dehydration to form α-chloro-acrylic acid which crystallized in needles that melted at 65°.[5] The dehydration of β-chlorolactic acid would be expected to give β-chloro-acrylic acid which crystallizes in plates that melt at 84°.[6] The formation of the latter acid was not observed.

α,β-Dichloropropionic Acid.[7]—A mixture of 50 g. of red fuming nitric acid (d. 1.5) with 100 g. of nitric acid (d. 1.4) was added to 50 g. of glycerol α,β-dichlorohydrin;[8] the temperature was kept below 15° during the addition by external cooling. The mixture was then allowed to come to room temperature, when a vigorous reaction set in. After the mixture had stood overnight, it was distilled under reduced pressure. The part boiling above 100° (15 mm.) was redistilled, giving 38 g. boiling at 112–115° (12 mm.), which soon solidified to a mass of colorless needles melting at 47–50°.

α-Chlorohydracrylic Acid.—A solution of 37 g. of silver nitrate was treated with a slight excess of sodium carbonate (32 g. of $Na_2CO_3 + 10H_2O$) solution. The silver carbonate was washed repeatedly by decantation, suspended in 100 ml. of water, and added to a solution of 30 g. of α,β-dichloropropionic acid in 50 ml. of water. The mixture was heated on a steam-bath for two hours and then filtered. Since the filtrate still contained silver, the heating was continued for two hours. The solution, then free from silver, was filtered and evaporated to a sirup on a steam-bath. After standing for three days in a vacuum desiccator over sulfuric acid and sodium hydroxide, the product was analyzed; yield, 16.5 g.

Anal. Subs., 0.1862: AgCl, 0.1988. Calcd. for $C_3H_5O_3Cl$: Cl, 28.44. Found: Cl, 26.42.

α-Chloro-acrylic Acid.—To a mixture of 2.5 ml. of sulfuric acid (d. 1.84) with an equal volume of water was added 1.0 g. of α-chlorohydracrylic acid. The mixture was refluxed for one hour, cooled, diluted with 7 ml. of water, filtered from carbonaceous material, and extracted with five 2-ml. portions of alcohol-free ether. The ether was evaporated from the combined extracts, and the brown residue, which was almost completely crystalline, was purified by slow sublimation at 10 mm. The product formed colorless monoclinic prisms melting at 64–66°; yield, 0.3 g.

β-Phenoxylactic and α-Phenoxyhydracrylic Acids from α-Chlorohydracrylic Acid.—To a mixture of 15 g. of phenol with 10 g. of α-chlorohydracrylic acid and 20 ml. of water was added a solution of 9 g. of sodium hydroxide in 30 ml. of water. The mixture was refluxed for thirty minutes, acidified with hydrochloric acid, and steam distilled until a test with ferric chloride showed the absence of phenol from the distillate. The separation of α-phenoxyhydracrylic and β-phenoxylactic acids was carried out as described previously.[1]

After recrystallization from water there was obtained 4.6 g. of β-phenoxylactic

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[4] Neuberg and Mayer, *Biochem. Z.*, **3**, 119 (1907).

[5] Otto and Beckurts, *Ber.*, **18**, 242 (1885).

[6] Otto, *Ann.*, **239**, 270 (1887).

[7] *Cf.* Henry, *Ber.*, **7**, 414 (1874).

[8] Prepared according to the directions of King and Pyman, *J. Chem. Soc.*, **105**, 1257 (1914).

acid which crystallized in plates that melted at 157–159°. The anilide prepared from this acid, after crystallization from alcohol and from water, melted at 122–123°.

The α-phenoxyhydracrylic acid obtained was purified by crystallization from toluene and from water, the usual crystallization from chloroform being omitted because of the small quantity in hand; the product formed needles melting at 102–106°; yield, 0.083 g. A mixture with an equal amount of the pure acid (m. p. 109–110°) melted at 103–106°.

The assistance of Professor S. M. McElvain is gratefully acknowledged.

Summary

The reaction between sodium phenoxide and α-chlorohydracrylic acid is shown to yield a mixture of α-phenoxyhydracrylic acid and β-phenoxylactic acid in which the latter predominates greatly.

This is in agreement with the prediction based on the behavior of α-chlorohydracrylic acid toward ammonia and indicates that the α-phenoxyhydracrylic acid formed in the reaction between sodium phenoxide and β-chlorolactic acid does not owe its origin to the presence of α-chlorohydracrylic acid as an impurity in the β-chlorolactic acid.

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THE DETERMINATION OF THE PURITY OF ACETIC ANHYDRIDE

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Received May 19, 1930 Published August 5, 1930

Introduction

A rapid and accurate method for the quantitative determination of acetic anhydride is of great practical importance because of the extensive industrial uses of this reagent. In a publication by Whitford[1] and the senior author of this paper it was shown that anhydrous oxalic acid is decomposed quantitatively in the presence of pyridine, acting as a catalyst, according to the equation

$$(COOH)_2 + (CH_3CO)_2O = CO_2 + CO + 2CH_3COOH$$

This reaction had been reported by Dr. Schierz[2] of this Laboratory, who observed that various tertiary bases such as picolines, butidine, collidine, etc., could also be used as catalysts. Whitford found that the pyridine acts as a catalyst for the reaction through the formation of pyridine acid oxalate $C_5H_5N \cdot (COOH)_2$ which is subsequently decomposed by the acetic anhydride.

The carbon dioxide and carbon monoxide evolved in the reaction were measured by Whitford to give a gasometric method for the determination of acetic anhydride. He found his method to be accurate to within 0.1%

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[1] Whitford and Walton, This Journal, **47**, 2934, 2939 (1925).

[2] Schierz, *ibid.*, **45**, 455 (1923).