[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA]

NITROGEN TRICHLORIDE AND UNSATURATED ACIDS

BY GEORGE H. COLEMAN AND GEORGE M. MULLINS[1]

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The addition of nitrogen trichloride to unsaturated hydrocarbons,[2] unsaturated ketones,[3] and diphenylketone[4] has been reported previously.

Nitrogen trichloride also reacts with unsaturated acids to form small yields of stable addition products and large amounts of nitrogen and chlorine. The chlorine is taken up in part by the excess of unsaturated acid present. Very small amounts of ammonium chloride are formed and in this respect the reaction differs from most of the other reactions of nitrogen trichloride with unsaturated compounds.

The reaction was studied with crotonic acid and cinnamic acid. With crotonic acid the α-chloro-β-dichloro-aminobutyric acid first formed is converted by the hydrochloric acid produced in the solution to β-amino-α-chlorobutyric acid, which precipitates slowly from the carbon tetrachloride solution as the hydrochloride. A similar precipitation of the hydrochloride has been observed with benzalacetone,[3b] methylpropene[2b] and toluene,[5] although this is not characteristic of many of the reactions of nitrogen trichloride with unsaturated compounds. At 20° ten days or longer is required for the complete precipitation of the hydrochloride. It seems probable, however, that the primary addition takes place more rapidly than this. At lower temperatures a longer time is required for the completion of the reaction, but the yields are better and the product slightly purer. The free aminochloro acid was prepared from the hydrochloride and its structure established by reduction to β-aminobutyric acid.

In the case of cinnamic acid the limited solubility of the compound in carbon tetrachloride made it necessary to use a suspension of the finely powdered acid and required the separation of the product from the excess cinnamic acid. Carbon tetrachloride is probably the best solvent for use with nitrogen trichloride, particularly when the reaction mixture is to stand several days. The reaction rate of cinnamic acid is not far different from that of crotonic acid. The dichloro-amino group again enters the β-position. The structure of the product was established by reduction to β-amino-β-phenylpropionic acid.

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[1] This paper is an abstract of a part of the thesis submitted by George M. Mullins in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the State University of Iowa.

[2] (a) Coleman and Howells, THIS JOURNAL, **45**, 3084 (1923); (b) Coleman, Mullins and Pickering, *ibid.*, **50**, 2739 (1928).

[3] (a) Coleman and Craig, *ibid.*, **49**, 2593 (1927); (b) **50**, 1816 (1928).

[4] Coleman and Campbell, *ibid.*, **50**, 2754 (1928).

[5] Coleman and Noyes, *ibid.*, **43**, 2211 (1921).

Experimental

The Reaction of the Crotonic Acid

The Preparation of the Hydrochloride of β-Amino-α-chlorobutyric Acid.—Nitrogen trichloride was prepared and analyzed as described in previous papers.[2b] Solutions containing about 1.5 mg. moles of nitrogen trichloride per gram of solution were used. The crotonic acid was dissolved in enough carbon tetrachloride for complete solution, the nitrogen trichloride was added and the apparatus arranged for collecting the gas evolved. Eighteen runs were made using varying proportions of crotonic acid and nitrogen trichloride and carrying out the reaction at different temperatures. It was found that about 1.5 moles of crotonic acid was required for each mole of nitrogen trichloride. Very little increase in yield was observed when a larger excess of acid was used. In the following table several representative yields obtained at different temperatures are given. For each mole of nitrogen trichloride 1.5 moles or more of crotonic acid was used.

TABLE I

PERCENTAGE YIELDS OF β-AMINO-α-CHLOROBUTYRIC ACID FROM NITROGEN TRICHLORIDE AND CROTONIC ACID

Yields at 0°, %	14.6	9.3	14.6
Yields at 13°, %	18.4	16.4	19.7
Yields at 20°, %	10.5	13.1	12.8

The solutions remained clear for a short time after mixing but soon became opalescent and a slow precipitation of the hydrochloride of the aminochloro acid continued for some days. At 20° ten days or longer was required for complete precipitation. The rate of evolution of nitrogen indicated, however, that the primary reaction was more rapid than this. At the lower temperatures a longer time was required. The product obtained at 0 and 13° was soluble in absolute ethyl alcohol and analysis indicated that it was the hydrochloride with only traces of impurities. The reaction product at 20° contained a small amount of ammonium chloride. For analysis the slightly impure product was purified by dissolving in absolute *n*-propyl alcohol, filtering and reprecipitating with anhydrous ether. If necessary this was repeated.

Anal. Subs., 0.1355, 0.1285: 15.38, 15.03 cc. of 0.1008 *N* $AgNO_3$. Subs., 0.0629, 0.0126: 35.75, 7.21 cc. of 0.01 *N* HCl. Calcd. for $C_4H_9O_2NCl_2$: Cl, 40.80; N, 8.05. Found: Cl, 40.61, 40.75; N, 7.96, 8.01.

β-Amino-α-chlorobutyric Acid.—The free aminochloro acid was prepared by dissolving the hydrochloride in absolute methyl, ethyl or *n*-propyl alcohol and adding pyridine[6] or by adding the calculated amount of lithium hydroxide to an aqueous solution of the hydrochloride, evaporating until crystals formed and adding ten volumes of alcohol.[7] The highest yields obtained by each method were as follows: CH_3OH and C_5H_5N, 63%; C_2H_5OH and C_5H_5N, 70%; C_3H_7OH and C_5H_5N, 80%; LiOH and C_2H_5OH, 60%. After several recrystallizations from 80% ethyl alcohol, the acid was obtained as white needles melting at 161–161.5° (uncorr.).

Anal. Subs., 0.1229, 0.1673: 8.61, 11.85 cc. of 0.1032 *N* $AgNO_3$. Subs., 0.3818, 0.0905: 28.32, 6.88 cc. of 0.0964 *N* HCl. Calcd. for $C_4H_8O_2NCl$: Cl, 25.82, N, 10.18, Found: Cl, 25.66, 25.95; N, 10.00, 10.25.

Benzoyl-β-amino-α-chlorobutyric Acid.—0.3 g. of the purified hydrochloride was dissolved in 10 cc. of water, three times the theoretical amount of benzoyl chloride

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[6] "Organic Syntheses," John Wiley and Sons, Inc., New York, **4,** 31 (1924).

[7] Fischer and Raske, *Ber.*, **40,** 3720 (1907).

and 5 cc. of a 45% solution of sodium hydroxide were added and the mixture was thoroughly shaken. After several hours the solution was acidified and the precipitate filtered off and dried. When the precipitate was thoroughly dry the benzoic acid was removed by repeated extraction with boiling petroleum ether (b. p. 120–140°). After several recrystallizations from water the product melted at 174–174.5° (uncorr.).

β-Aminobutyric Acid.—Several attempts were made to reduce the aminochloro acid to the amino acid with sodium amalgam in both acid and alkaline aqueous solution at room temperature and at 0°. The chlorine was not completely removed. The reduction was finally carried out in an alkaline methyl alcohol solution. The hydrochloride was dissolved in about 20 times its weight of methyl alcohol and several times the theoretical amount of sodium amalgam (2.5%) added very slowly with constant stirring. When the reaction was complete the alcohol was evaporated on a water-bath. The residue was taken up with water and concentrated hydrochloric acid added. The solution was evaporated to dryness as before and the residue extracted with *n*-propyl alcohol. Pyridine was then added and the product thus obtained was recrystallized from 80% ethyl alcohol. After several recrystallizations the compound melted at 184–185° (uncorr.). The melting point recorded for β-aminobutyric acid is 184° and that for α-aminobutyric acid 292° (decomp.). The product gave no test for chlorine by the Beilstein method.

Anal. Subs., 0.0167, 0.0204: 16.07, 19.51 cc. of 0.01 *N* HCl. Calcd. for $C_4H_9O_2N$: N, 13.59. Found: N, 13.50, 13.39.

The Reaction with Cinnamic Acid

Preparation of the Hydrochloride of β-Amino-α-chloro-β-phenylpropionic Acid.—The reaction with cinnamic acid was carried out in much the same manner as that with crotonic acid. The limited solubility of cinnamic acid in carbon tetrachloride made it necessary to use the acid partly dissolved and partly suspended in finely powdered form in the solution. The reaction mixtures were allowed to remain at room temperature for two weeks. Dry hydrogen chloride was then passed into the solution and the product, together with some unchanged cinnamic acid, was filtered off. This was shaken several times with anhydrous ether to free it from the cinnamic acid. The yields of crude product varied from 5 to 8.5%, calculated from the nitrogen trichloride.

The crude hydrochloride was purified by a method similar to that used by Posner[8] with β-phenylalanine. The crude product was treated with a little concentrated hydrochloric acid and the mixture evaporated to dryness on a water-bath. The residue was taken up with methyl alcohol, the solution decolorized with charcoal and the hydrochloride reprecipitated by the addition of five volumes of ether. The product melted at 228–230° (uncorr.).

Anal. Subs., 0.1365, 0.1706: 5.86, 7.35 cc. of 0.0983 *N* HCl. Subs., 0.2037, 0.1422: 17.07, 11.94 cc. of 0.1008 *N* $AgNO_3$. Calcd. for $C_9H_{11}O_2NCl_2$: N, 5.93; Cl, 30.08. Found: N, 5.91, 5.85; Cl, 29.99, 30.05.

β-Amino-α-chloro-β-phenylpropionic Acid.—The free aminochloro acid was prepared by dissolving 0.77 g. of the hydrochloride in 15 cc. of methyl alcohol and adding 4 cc. of pyridine; 0.40 g. of white precipitate formed on standing. After recrystallizing from 80% ethyl alcohol, the product melted at 199–200° (uncorr.).

Anal. Subs., 0.0202, 0.0514: 10.10, 25.63 cc. of 0.01 *N* HCl. Subs., 0.1157, 0.0551: 5.70, 2.73 cc. of 0.1008 *N* $AgNO_3$. Calcd. for $C_9H_{10}O_2NCl$: N, 7.01; Cl, 17.79. Found: N, 7.00, 6.98; Cl, 17.60, 17.69.

Benzoyl-β-amino-β-phenylpropionic Acid.—The hydrochloride of the aminochloro

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[8] Posner, *Ber.*, **38**, 2321 (1905).

acid was dissolved in a small amount of water and six times the theoretical amount of sodium amalgam added very slowly with constant stirring. When the reaction was complete the solution was acidified with hydrochloric acid and evaporated to dryness on a water-bath. The residue was taken up with methyl alcohol, the solution filtered and evaporated as before. The product was weighed and the calculated amount of 0.1 *N* sodium hydroxide added to free the acid from the hydrochloride. This was evaporated until crystals began to form and then allowed to stand at 0° for twenty-four hours. This method was used since β-amino-β-phenylpropionic acid is soluble in alcohol and the methods used for the other acids were not applicable. A 65% yield of crude product was obtained which contained no chlorine. The melting point was, however, too low and the compound could not be readily purified. The benzoyl derivative was prepared as described for β-amino-α-chlorobutyric acid. The melting point of the purified product was 194–195° (uncorr.). A mixed melting point was taken with the known compound prepared by another method.

Anal. Subs., 0.0200, 0.0201: 7.65, 7.66 cc. of 0.01 *N* HCl. Calcd. for $C_{16}H_{15}O_3N$: N, 5.21. Found: N, 5.36, 5.34.

Summary

Nitrogen trichloride reacts with crotonic acid to form, among other products, α-chloro-β-dichloro-aminobutyric acid, which is changed by hydrochloric acid to β-amino-α-chlorobutyric acid. The structure of the compound was established by reduction to the corresponding amino acid.

A similar reaction occurs with cinnamic acid. The dichloro-amino group again enters the β-position.

IOWA CITY, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE]

SOME DERIVATIVES OF 3,4-PHENANTHRENEQUINONE

BY LOUIS FREDERICK FIESER

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In the belief that a knowledge of the reduction potentials of ortho- or para-quinones derived from phenanthrene, but isomeric with 9,10-phenanthrenequinone, would throw some additional light on the general problem of the relationship between the oxidizing power and the structure of the various quinones, the author undertook to prepare one or two compounds of the isophenanthrenequinone type, and to compare them, by the potentiometric method, with the corresponding naphthoquinones. In the course of this work it soon became evident that the isophenanthrenequinones, which have received scarcely any attention up to the present time, are interesting from several points of view other than that of the original problem, and the work has thus developed into a rather extensive study of the general chemistry and the methods of obtaining various isophenanthrenequinones and compounds derived from them. The presentation of the results of investigations which are concerned solely with the chemistry of phenanthrene derivatives will be followed with an account of the electrochemical data which have accumulated.