[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NEBRASKA]

The Influence of the Stibono Group on the Reactivity of Nuclear Chlorine

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In this investigation a study was made of the nuclear chlorine in 2-chlorophenylstibonic acid and 2-chloro-5-nitrophenylstibonic acid in order to compare the reactivity of the halogen with that in analogous arsonic acids.[2] The results showed that the influence of the stibono group is less than that of the arsono group.

Preliminary experiments were carried out to establish the best conditions for condensing 2-chloro-5-nitrophenylstibonic acid with aniline. A small piece of freshly polished sheet copper, when used as a catalyst, produced better results than did copper powder, cuprous iodide or copper acetate. Temperatures ranging from 90 to 140° were tried and the optimum reaction temperature was found to be about 120°. Amyl alcohol and nitrobenzene were the only solvents investigated, the former giving the more satisfactory results.

2-Chlorophenylstibonic acid would not condense with aniline under any of the above conditions; in addition the chlorine was not hydrolyzed when the compound was heated with 6 *N* sodium hydroxide solution at 100° for ten hours.

The arylstibinic chlorides and ammonium arylchlorostibonates not only showed the amphoteric nature of the stibonic acids, but also furnished a very convenient method for their purification since water readily hydrolyzed them to the corresponding acids. The formation of a double salt by the addition of an excess of ammonium chloride to a concentrated hydrochloric acid solution of the arylstibinic chloride is evidence in support of the belief that the chlorides separate as arylchlorostibonic acid, $ArSbCl_5H$, and lose a molecule of hydrogen chloride upon drying.

Experimental

5-Nitro-2-alkylaminophenylstibonic Acids

General Procedure.—Ten grams of 2-chloro-5-nitrophenylstibonic acid, 10 g. of anhydrous potassium carbonate, 10 g. of the amine, 30 cc. of amyl alcohol and a small piece of freshly polished copper plate were introduced into a 125-cc. Erlenmeyer flask fitted with a condenser with ground glass connection. The mixture was agitated by means of a mechanical stirrer which extended down through the condenser, and the flask and contents were heated in an oil-bath at 120° for twenty hours. The mass was cooled to room temperature and filtered. The filtrate was evaporated as nearly as possible to dryness by heating in a water-bath under reduced pressure. The residue was dissolved in 50 cc. of amyl alcohol, cooled to room temperature and filtered. The filtrate was again evaporated to dryness, the residue dissolved in about 40 cc. of warm glacial acetic acid and precipitated by adding slowly, while stirring, a solution of 6 *N* sulfuric acid. The amorphous solid which separated was collected on a suction filter, washed well with water and dried at about 40°. The yields may not represent the extent to which condensation took place, since isolation and purification of the products were difficult.

TABLE I

5-Nitro-()- -aminophenyl- stibonic acid	Yield, %	Dec. p., °C.	Formula	Antimony analyses, %[3] Calcd.	 Found
2-Phenyl-	25	250	$C_{12}H_{11}O_5N_2Sb$	31.72	31.76
2-*n*-Propyl-	50	220	$C_9H_{13}O_5N_2Sb$	34.70	34.91
2-*n*-Butyl-	50	170	$C_{10}H_{15}O_5N_2Sb$	33.37	33.36
2-Iso-butyl-	55	200	$C_{10}H_{15}O_5N_2Sb$	33.37	33.40
2-*n*-Amyl-	30	120	$C_{11}H_{17}O_5N_2Sb$	32.13	32.00
2-Iso-amyl-	55	200	$C_{11}H_{17}O_5N_2Sb$	32.13	32.36

2-Chlorophenylstibonic Acid $3(2\text{-}ClC_6H_4SbO_2)H_2O$.[4]—A freshly diazotized solution of *o*-chloroaniline (0.25 mole) was added slowly, with vigorous stirring, to a cold (0°) alkaline solution of antimony trioxide, prepared by dissolving 75 g. of antimony trichloride in 15 cc. of warm concentrated hydrochloric acid and 100 cc. of glycerol and adding this solution to 300 cc. of 6 *N* sodium hydroxide solution, followed by diluting with ice and water to four liters. After neutralizing and filtering off the unchanged antimony trioxide, the product was precipitated by acidifying the solution with acetic acid and the crude stibonic acid purified by converting it to the stibinic chloride with subsequent hydrolysis.

2-Chloro-5-nitrophenylstibonic Acid $(2\text{-}Cl\text{-}5\text{-}NO_2C_6H_3\text{-}SbO_2)\cdot H_2O$.—A slight modification of the method of Morgan and Micklethwait[5] for the nitration of phenylstibinic acid was used in the preparation of this compound. The 2-chlorophenylstibonic acid was stirred slowly into the nitrating mixture, not allowing the temperature to rise above 50°. The crude product was purified by converting it into the aryl stibinic chloride which was subsequently hydrolyzed with water. The dried product was further purified by precipitating it from hot ethanol. The structure of the compound was indicated by the formation of *p*-nitrochlorobenzene when digested with concentrated sulfuric acid.

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(1) Parke, Davis and Company Fellow.

(2) Etzelmiller and Hamilton, THIS JOURNAL, **53**, 3085 (1931); Hall and Hamilton, *ibid.*, **56**, 1779 (1934).

(3) The potentiometric method of Cislak and Hamilton, THIS JOURNAL, **52**, 638 (1930), was used for the quantitative determination of antimony in all the compounds prepared.

(4) The formulas used to represent some of the compounds were adapted from a method proposed by Schmidt, *Ann.*, **421**, 174 (1920); **429**, 123 (1922).

(5) Morgan and Micklethwait. *J. Chem. Soc.*, **99**, 2286 (1911).

2-Chloro-5-aminophenylstibonic Acid ($2-Cl-5-NH_2-C_6H_3SbO_2)H_2O$.—The method employed for the preparation of this compound was that described by Jacobs, Heidelberger and Rolf.[6] It consisted in the reduction of the nitroarylstibonic acid by means of freshly prepared ferrous hydroxide. The product was purified by precipitating it from an alkaline solution with sulfur dioxide.

2-Hydroxy-5-nitrophenylstibonic Acid ($2-HO-5-NO_2C_6H_3SbO_2)H_2O$.—This compound was prepared by heating 2-chloro-5-nitrophenylstibonic acid with 6 *N* potassium hydroxide solution at about 97° for seven hours. The crude product was purified by dissolving it in about 9 *N* hydrochloric acid, boneblacking the solution and diluting the clear filtrate with a large volume of water. The product gave the characteristic ferric chloride test for phenols and showed no qualitative test for halogen.

TABLE II

All of these compounds were obtained as amorphous products not melting below 250°.

-Phenylstibonic acid	Yield, %	Formula	Antimony analyses, % Calcd.	Found
2-Chloro-	52	$C_{18}H_{14}O_7Cl_3Sb_3$	44.89	44.90
2-Chloro-5-nitro-	90	$C_6H_5O_5NClSb$	37.09	37.12
2-Chloro-5-amino-	40	$C_6H_7O_3NClSb$	41.02	41.00
2-Hydroxy-5-nitro-	35	$C_6H_6O_6NSb$	39.30	39.29

2-Chlorophenylstibinic chloride ($2-Cl-C_6H_4SbCl_4)H_2O$ and **2-chloro-5-nitrophenylstibinic chloride** ($2-Cl-5-NO_2-C_6H_3SbCl_4$) were prepared by dissolving the respective acids in concentrated hydrochloric acid (sp. gr. 1.18) and cooling the resulting solutions. The products, crystallizing as pale yellow needles, were dried over solid sodium hydroxide and then placed in the air to reach a constant analysis.

Ammonium 2-chlorophenylchlorostibonate ($2-Cl-C_6H_4-SbCl_5NH_4$) **and ammonium 2-chloro-5-nitrophenylchlorostibonate** ($2-Cl-5-NO_2C_6H_3SbCl_5NH_4$) were prepared according to the method of Schmidt.[4] It consisted of adding an excess of ammonium chloride to a solution of arylstibonic acid in concentrated hydrochloric acid.

TABLE III

	Yield, %	M. p., °C.	Formula	Sb analyses, % Calcd.	Found
2-Chlorophenylstibinic chloride	95	82[a]	$C_6H_6OCl_5Sb$	30.98	30.98
2-Chloro-5-nitrophenylstibinic chloride	95	250	$C_6H_3O_2NClSb$	28.99	28.90
Ammonium 2-chlorophenylchlorostibonate	98	87–89	$C_6H_8NCl_6Sb$	28.41	28.48
Ammonium 2-chloro-5-nitrophenylchlorostibonate	98	250	$C_6H_7O_2N_2Cl_6Sb$	25.71	25.90

[a] Melted with previous sintering.

Summary

1. 2-Chloro-5-nitrophenylstibonic acid was condensed with aniline and with a series of aliphatic amines, namely, *n*-propyl, *n*-butyl, *i*-butyl, *n*-amyl and *i*-amylamine.

2. Hydrolysis of 2-chloro-5-nitrophenylstibonic acid was carried out in 6 *N* potassium hydroxide solution, producing 2-hydroxy-5-nitrophenylstibonic acid.

3. 2-Chloro-5-aminophenylstibonic acid was prepared by reduction of the nitro compound.

4. 2-Chlorophenylstibonic acid, 2-chloro-5-nitrophenylstibonic acid, and the chlorides and ammonium chlorostibonates of each were also prepared for the first time.

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[6] Jacobs, Heidelberger and Rolf, THIS JOURNAL, **40**, 1581 (1918).

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The Chlorinated Ethylamines—A New Type of Vesicant

BY KYLE WARD, JR.

This paper describes the preparation and properties of β-chloroethylamine, β,β′-dichlorodiethylamine, β,β′,β″-trichlorotriethylamine and a few of their derivatives. The primary[1] and secondary[2] derivatives have been prepared previously. The tertiary derivatives are new. Both the tertiary amine and its hydrochloride exhibit a marked vesicant action.

These three bases have all been prepared from the corresponding ethanolamines or their hydrochlorides. This is very easily accomplished by means of thionyl chloride. Phosphorus pentachloride also proved suitable in the only case where it was tried, namely, with triethanolamine.

The chlorination of monoethanolamine hydrochloride proceeds much more smoothly than that of the free base. The yield is better, also, and the purification of the chlorinated product easier. Formation of thionylamine may be causing the difficulty in this case.

While this paper was being written, an article[3] by F. G. Mann appeared describing the preparation of β,β′-dichlorodiethylamine by the same method used in the present work. The only

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[1] Gabriel, *Ber.*, **21**, 566, 1049 (1888); Seitz, *ibid.*, **24**, 2624 (1891).

[2] Prelog, Dřiza and Hanousek, *Coll. Czech. Chem. Comm.*, **3**, 578 (1931).

[3] Mann, *J. Chem. Soc.*, 464 (1934).