also separated which was not dissolved by ether and finally crystallized in yellow prisms. This substance dissolved easily in warm water and alcohol and separated from alcohol, on cooling, in hexagonal prisms melting at 200–201°. It was not decomposed by warm sodium hydroxide solution and gave a strong test for iodine. The properties of the compound and the analytical determination proved that it was the quaternary salt, *viz.*: *trimethyl-p-nitrophenylethylammonium iodide*, $NO_2C_6H_4CH_2CH_2N(CH_3)_3I$.

Calculated for $C_{11}H_{17}O_2N_2I$: I, 37.85; found: I, 37.79.

When the ether extract (above) was allowed to evaporate a base was obtained which reacted immediately with phenylisothiocyanate at ordinary temperature, giving a thiourea melting at 133–4°. It was identified as 1-phenyl-2-paranitrophenylethylthiourea.[1] A mixture of this compound and the above thiourea melted at the same temperature. A mixture of the compound and 1-phenyl-2,2-methyl-*p*-nitrophenylethylthiourea (see above) melted below 110°.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA.]

THE BROMINATION OF ANTHRANILIC ACID.

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The monobromoaminobenzoic acids have been prepared in most cases by the reduction of the bromonitrobenzoic acids in acid solution with tin, zinc or stannous chloride. The 5-bromoanthranilic acid was obtained in two other ways by Alt,[2] *viz.*: (1) by the oxidation of 5-bromo-2-acetotoluide by potassium permanganate and (2) by the bromination of acetoanthranilic acid. The latter reaction was conducted in aqueous and in acetic acid solution, the only product isolated being the monobromoanthranilic acid. We find that in brominating anthranilic acid directly in acetic acid solution at as low a temperature as possible one-third of the product consists of the 3,5-dibromoanthranilic acid. We[3] find it a most excellent method for preparing both acids. Bogert and Hand[4] employed methods similar to those of Alt.

The dibromoaminobenzoic acids have been prepared similarly. In addition Wachendorff[5] heated *o*-nitrotoluene with bromine at 170°. Bogert and Hand[6] prepared 3,5-dibromoanthranilic acid by treating a

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[1] Johnson and Guest, *Loc. cit.*

[2] Alt, *Ber.*, **22**, 1645 (1889).

[3] Wheeler and Oats, THIS JOURNAL, **31**, 568 (1909).

[4] Bogert and Hand, *Ibid.*, **27**, 1476 (1905).

[5] Wachendorff, *Ann.*, **185**, 281.

[6] Bogert and Hand, THIS JOURNAL, **25**, 935 (1903).

dilute hydrochloric solution of anthranilic acid with a mixture of potassium bromide and potassium bromate. No yield is given. The few tri- and tetraaminobenzoic acids which have been described were obtained by the action of bromine upon the amines or anil.

We have studied the action of bromine upon anthranilic acid in glacial acetic acid solution, (1) near freezing point and (2) near the boiling point of acetic acid. In the first case two-thirds of the product consists of the 5-bromoanthranilic acid and one-third of the 3,5-dibromoanthranilic acid. Under the other conditions the results are reversed almost exactly. The two acids are readily separated by boiling water in which the dibromoanthranilic acid is nearly insoluble. The separated acids may be brought upon drying plates within an hour after the preparation is begun.

The monobromoanthranilic acid is converted by short boiling with acetic anhydride into the anil and the latter on treatment with water is very rapidly hydrolyzed to bromoacetoanthranilic acid. Bogert and Hand prepared the anil by boiling the bromoacetoanthranilic acid with acetic anhydride. We found the barium salt to contain 4 molecules of water as did Alt. The salt obtained by Bogert and Hand was anhydrous. We have prepared also the silver salt, ethyl ester, 2-chloro-5-bromobenzoic acid and its barium salt. The latter acid has only been described by Cohen[1] but he gave no analysis. Our preparation recrystallized from glacial acetic acid gave the melting point stated by Cohen, 155–6°, but we could get no satisfactory analysis. Then on recrystallizing from water we raised the melting point ten degrees. In view of this discrepancy we shall postpone the description until we have made the acid by Cohen's somewhat tedious method. In this paper we also describe the anil and acetyl derivative of the dibromoanthranilic acid as well as the silver salt and ethyl ester.

5-Bromo-2-Aminobenzoic Acid. Bromination of Anthranilic Acid below the Freezing Point of Glacial Acetic Acid.—Twenty grams of anthranilic acid were dissolved in 250 cc. glacial acetic acid and cooled below 16°. After 9.5 cc. bromine had been run in, the reddish color of the liquid persisted. Before this point was reached the mixture had been converted into a thick mush of white glistening crystals, consisting of the hydrobromides of the mono- and dibromoanthranilic acids. The product was filtered off, washed with benzene and after drying was found to weigh 54.7 grams. It was then boiled up with 500 cc. water containing 25 cc. concentrated hydrochloric acid and filtered hot with suction. The insoluble residue was extracted twice more with 500 cc. of boiling water. The filtrates upon cooling yielded abundant precipitates of the monobromoanthranilic acid. The insoluble residue consisted of the 3,5-dibromoanthranilic acid, amounting to one-third of the product. In the

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[1] Cohen, *J. Chem. Soc.*, 85, 1267 (1904).

glacial acetic acid filtrate we found a little tribromoaniline. We also tried the bromination of the hydrochloride of anthranilic acid in glacial acetic acid and also a hydrochloric acid solution of anthranilic acid but the results were less satisfactory.

Barium 5-Bromo-2-aminobenzoate.—Alt who prepared this salt by boiling the acid with barium carbonate states that it crystallizes with 4 molecules of water. Bogert and Hand did not obtain this salt but an anhydrous one crystallizing in prisms. We employed Alt's method and obtained the same salt crystallizing in needles and containing 4 molecules of water. It was impossible to determine the water since the salt began to decompose before the requisite amount of water was expelled. This occurs at about 170°.

Calculated for $C_{14}H_{10}O_4N_2Br_2Ba.4H_2O$: Ba, 21.48; found: 21.78.

Silver 5-Bromo-2-aminobenzoate.—The neutral ammonium salt was treated with silver nitrate, which caused a dense white precipitate. The salt is anhydrous.

Calculated for $C_7H_5O_2NBrAg$: Ag, 33.43; found: 33.69, 33.51.

Ethyl 5-Bromo-2-aminobenzoate.—The silver salt was boiled with an excess of ethyl iodide. After distilling off the excess the residue was extracted with chloroform. The ester crystallizes from alcohol in yellow needles which melt at 187°.

Calculated for $C_9H_{10}O_2NBr$: Br, 33.10; found: 32.79.

5-Bromoacetoanthranil.—Bogert and Hand obtained this anil by boiling the 5-bromoacetoanthranilic acid with acetic anhydride.[1] We obtained it by boiling 4 grams of 5-bromoanthranilic acid with 40 cc. acetic anhydride for 15 minutes. On cooling the solution an abundant crystallization of colorless scales took place. The filtrate contained a mixture of the anil and the acetyl derivative. The anil is very soluble in hot benzene, alcohol and ligroin but difficultly soluble when cold. It is not readily soluble in ether. It melts at 134°. Bogert gives 131° (cor.). It is instantly hydrolyzed to the bromoacetoanthranilic acid by hot water. The same result is obtained by boiling with glacial acetic acid, 99–100 per cent., for two hours.

Calculated for $C_9H_6O_2NBr$:	C, 45.00	H, 2.50	Br, 33.30
Found:	45.00	2.62	33.40

3,5-Dibromo-2-aminobenzoic Acid. Bromination of Anthranilic Acid in Boiling Glacial Acetic Acid.—Fifty grams of anthranilic acid were dissolved in 500 cc. glacial acetic acid and while boiling 27.5 cc. bromine were run in. An abundant separation of colorless crystals took place. After cooling, the product was filtered off, washed with glacial acetic acid and then with benzene. The weight of the hydrobromides was 116 grams.

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[1] Bogert and Hand, THIS JOURNAL, **27**, 1484 (1905).

The mixture was boiled up five times successively with 500 cc. water, each filtration being made rapidly with suction. The insoluble residue consisting of the dibromoanthranilic acid constituted two-thirds of the product. The pure acid was obtained by recrystallizing from alcohol. The melting point was 232° (uncor.). Bogert and Hand give 235–5.5° (cor.).

3,5-Dibromoacetoanthranil.—Ten grams 3,5-dibromoanthranilic acid were boiled 15 minutes with 100 cc. acetic anhydride. Upon cooling an abundant mass of long colorless needles were deposited, some being an inch long. The weight was 9 grams and the melting point 176°, the substance being pure. On concentrating the filtrate another gram was obtained, melting at 173°.

Calculated for $C_9H_6O_2NBr_2$: Br, 50.14; found: 49.99, 49.99.

The anil is easily soluble in benzene, glacial acetic acid, chloroform, toluene and fairly soluble in alcohol. It is insoluble in water, cold or hot. Its conversion back to the dibromoanthranilic acid is effected by warming in 15 per cent. sodium hydroxide for 15 minutes and neutralizing with acid. A 1 per cent. solution of sodium hydroxide introduces water into the anil, giving the dibromoacetoanthranilic acid.

3,5-Dibromoacetoanthranilic Acid.—The free acid was obtained by boiling the anil a moment in dilute sodium hydroxide and immediately acidifying with hydrochloric acid. It is also obtained by long boiling with glacial acetic acid. The crude product melts at 217°. On recrystallizing from alcohol-benzene the melting point is raised to 218–9°. It crystallizes from glacial acetic acid in microscopic needles. It is easily soluble in alcohol and glacial acetic acid. It is insoluble in ether, chloroform, benzene and toluene.

Calculated for $C_9H_7O_3NBr_2$: Br, 47.47; found: 47.36, 47.42.

Silver 3,5-Dibromo-2-aminobenzoate.—A neutral ammonium salt solution of the acid was treated with silver nitrate. A dense white precipitate was thrown down. This is anhydrous and decomposes at about 270°.

Calculated for $C_7H_4O_2NBr_2$: Ag, 26.84; found: 26.70.

Ethyl 3,5-Dibromo-2-aminobenzoate.—The ester was prepared by boiling the silver salt with excess of ethyl iodide. After distilling off the unused ethyl iodide the residue was extracted with cold chloroform. The chloroform extract on evaporation to dryness left a white but somewhat oily residue. This was recrystallized from alcohol. It forms fan-shaped groups of needles which melt at 74°.

Calculated for $C_9H_9O_2NBr_2$: Br, 49.53; found: 49.34, 49.46.

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