

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE PRESIDENCY COLLEGE AND THE UNIVERSITY COLLEGE OF SCIENCE OF CALCUTTA]

## HALOGENATION. XXII. THE ACTION OF BROMINE AND NITRIC ACID ON ORGANIC COMPOUNDS. PREPARATION OF NITROSYL TRIBROMIDE AND THE FORMATION OF TETRABROMOQUINONE

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It has been shown in a previous communication<sup>1</sup> that chloropicrin and tetrachloroquinone are formed by the exhaustive action of aqua regia on organic compounds. It has now been found that bromine and nitric acid act similarly on organic compounds, giving rise to tetrabromoquinone and a mixture of bromonitro derivatives of methane. Tetrabromoquinone has been found to form readily in the case of aromatic compounds in which the *para* positions are substituted by easily replaceable groups. A mixture of hydrobromic and nitric acids gives the same results, but in this case, nitrosyl tribromide,  $\text{NOBr}_3$ , is formed in the first instance as a dark red oil. This is interesting, as it carries analogy to the action of hydrochloric acid on nitric acid in which case nitrosyl chloride and chlorine are formed. The reaction may be represented thus:  $3\text{HBr} + \text{HNO}_3 = \text{NOBr}_3 + 2\text{H}_2\text{O}$ . Nitrosyl tribromide has been prepared previously by Landolt<sup>2</sup> by passing nitrous fumes into bromine.

For the preparation of tetrabromoquinone, hitherto either aromatic compounds with easily replaceable groups in the *para*-positions have been treated with bromine, or aromatic compounds containing the necessary bromine atoms have been oxidized with nitric acid. For example, Graebe and Weltner<sup>3</sup> prepared tetrabromoquinone by the action of bromine and acetic acid on *p*-phenylenediamine, and Losanetoch<sup>4</sup> obtained bromanil from 1,3,5-tribromobenzene by treatment with conc. nitric acid. The simultaneous oxidation and bromination by means of bromine and nitric acid has not been described before.

The following compounds, on treatment with bromine and nitric acid, have been found to give varying yields of bromanil: hydroquinone, *p*-phenylenediamine, *p*-amidophenol, aniline, aniline black, phenylhydrazine, *p*-nitrophenol, *p*-amido-diphenylamine. The action was also studied with the following compounds: resorcinol,  $\alpha$ -naphthol, phthalic anhydride, *m*-phenylene-diamine, *m*-cresol, *p*-cresol, mesitylene, cymene, styrolene, naphthalene, anthracene, acetone, ethyl alcohol, methyl alcohol, ether, allyl alcohol, hexamethylene-tetramine; but in no case could the

<sup>1</sup> Datta and Chatterjee, *THIS JOURNAL*, **33**, 1814 (1916).

<sup>2</sup> Landolt, *Ann.*, **116**, 177 (1860).

<sup>3</sup> Graebe and Weltner, *ibid.*, **263**, 33 (1891).

<sup>4</sup> Losanetoch, *J. Chem. Soc.*, **61**, 568 (1892).

formation of tetrabromoquinone be shown; a mixture of bromonitromethanes was all that was produced, due to a rupture of the molecule of the organic compound.

## Experimental Part

### Preparation and Analysis of Nitrosyl Tribromide

Five cc. of 47% redistilled hydrobromic acid is taken in a test-tube and cooled. To it conc. nitric acid is added drop by drop by means of a pipet, as long as a brown cloudiness is produced; this settles to a dark red, heavy oil. The oil is stable when kept underneath the cold acid mixture, but it decomposes with the evolution of nitric oxide when brought into contact with water.

*Analyses.* Subs., 0.3196: AgBr, 0.6625. Subs., 0.1750: 15.4 cc. of NO (30°, 755 mm.). Calc. for NOBr<sub>3</sub>: Br, 88.88; NO, 11.1. Found: Br, 88.20; NO, 10.52.

Nitrosyl tribromide is taken in a sealed capillary bulb-tube. This is then placed in a hard glass tube, half of which is filled with leaves of Dutch metal, and the tube connected to a cylinder filled with mercury. At first the air inside the apparatus is displaced by passing through it dry carbon dioxide from a tube containing bicarbonate. When the air is completely removed, as shown by a nitrometer tube, the cock of the bicarbonate tube is closed and the capillary bulb is then heated, when it gives way. Nitrosyl tribromide, on passing through the heated Dutch metal, is decomposed and the bromine is all absorbed, while the nitric oxide is collected in the mercury tube. The nitric oxide is finally displaced by carbon dioxide. When all the nitric oxide is collected, it is treated with solid caustic potash to free it from carbon dioxide.

### Action of Bromine and Nitric Acid on Aromatic Compounds

**Hydroquinone.**—Ten cc. of nitric acid and 8 cc. of bromine are mixed and to the mixture 2 g. of hydroquinone is added in small quantities at a time, when an immediate reaction takes place with evolution of brown fumes and rise of temperature. The mixture in a vessel carrying a reflux condenser is warmed on the water-bath for about 6 hours, and the bromine and nitric acid are renewed. During the progress of the reaction, a pungent odor of bromonitro derivatives of methane is also evident. At the end of the reaction, a yellow crystalline solid is deposited at the bottom of the vessel. It consists mainly of tetrabromoquinone mixed with smaller quantities of the lower bromoquinones. It is purified by sublimation, when a good yield of beautiful yellow crystals is obtained melting at 298° in a sealed capillary tube. The identity was further established by a halogen determination.

*Analysis.* Subs., 0.1735: AgBr, 0.3050. Calc. for C<sub>6</sub>Br<sub>4</sub>O<sub>2</sub>: Br, 75.47. Found: 74.82.

***p*-Phenylenediamine.**—To a mixture of bromine and nitric acid, a few grams of *p*-phenylenediamine is added. The reaction is continued on the water-bath with the addition of more bromine and nitric acid. In about 3 hours, sulfur-yellow crystals are formed which, on purification by sublimation, give a good yield of pure crystals of tetrabromoquinone melting at 298° in a sealed capillary tube.

*Analysis.* Subs., 0.1497: AgBr, 0.2636. Calc. for C<sub>6</sub>Br<sub>4</sub>O<sub>2</sub>: Br, 75.47. Found: 74.92.

***p*-Amidophenol.**—One g. of *p*-amidophenol is gradually added in small quantities to a mixture of 4 cc. of bromine and 10 cc. of nitric acid; a reaction occurs at once. When its vigor slackens to some extent the mixture is warmed on the water-bath. After continuing this operation for 4 hours, a dark brown solid is obtained which melts first to

a dark-colored liquid, and ultimately pure tetrabromoquinone sublimes in beautiful yellow crystals melting at 298°. The yield is poor.

**Aniline.**—To a mixture of bromine and nitric acid, aniline is added gradually, when a vigorous reaction takes place. The mixture is then warmed on the water-bath for 15 to 20 hours with the occasional addition of further quantities of bromine and nitric acid. The solid gradually passes through black and becomes brown. The brown mass is subjected to sublimation when pure crystals of bromanil are obtained melting at 298°, leaving the other products behind as a charred mass. The yield is very poor, as much of the original substance is decomposed to give bromonitro derivatives of methane.

**Aniline Black.**—Two g. of aniline black is placed in a flask and to it 10 cc. of conc. nitric acid and excess of bromine are added. The mixture is then warmed on the water-bath, when a deep brown, oily product is obtained. This oily product is subjected to the prolonged action of bromine and nitric acid for 10 to 12 hours. The resulting dark colored product, on sublimation, gives pure crystals of tetrabromoquinone, melting at 298°.

**Phenyldiazine, *p*-Nitrophenol and *p*-diamido-diphenylamine.**—All these substances when treated with bromine and nitric acid on the water-bath gradually change to a brown or yellow mass which on sublimation yields tetrabromoquinone. In all cases, a considerable portion of the material is converted into bromonitro derivatives of methane.

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[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, UNITED STATES DEPARTMENT OF AGRICULTURE, AND THE DEPARTMENT OF CHEMISTRY OF THE GEORGE WASHINGTON UNIVERSITY]

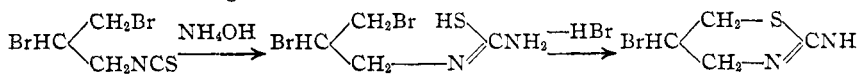
## THE INTERACTION OF ALIPHATIC ALCOHOLS AND BETA-GAMMA-DIBROMOPROPYL ISOTHIOCYANATE<sup>1</sup>

By RAYMOND M. HANN

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Dibromopropyl isothiocyanate was first isolated and purified by Dixon<sup>2</sup> who prepared it by the addition of bromine to allyl isothiocyanate.

In pursuing his study of the substance he attempted to prepare the corresponding dibromopropyl-thio-urea, which had already been described by Maly<sup>3</sup> as resulting from the addition of bromine to allyl-thio-urea. Failure to obtain the expected derivative led to a comprehensive study, and some time later Dixon<sup>4</sup> published work which left little doubt that Maly's compound was the hydrobromide of the base resulting from the action of ammonia on dibromopropyl isothiocyanate. From further study of the carbimide and its reactions with various bases, and in consideration of the work of Gabriel<sup>5</sup> and others upon the ring-closing tendency of mono- and disubstituted thio-ureas containing monobrominated paraffin radicals, it seemed probable that ammonia reacted in the following manner.



<sup>1</sup> Presented at the Pittsburgh meeting of the American Chemical Society, September 4-8, 1922.

<sup>2</sup> Dixon, *J. Chem. Soc.*, **61**, 545 (1892).

<sup>3</sup> Maly, *Z. Chem.*, **1867**, 42.

<sup>4</sup> Dixon, *J. Chem. Soc.*, **69**, 22 (1896).

<sup>5</sup> Gabriel, *Ber.*, **22**, 1140 (1889).