VII.—*Action of Chloroform and Alkali Hydroxides
on the Nitrobenzoic Acids.*

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IN a former communication (Trans., 1896, 69, 1513), it was shown that potassium hydroxide in aqueous solution and chloroform, by their conjoint action on metamidobenzoic acid, produced a substance allied to the aldehydes. The action of these agents on other substituted benzoic acids is now being investigated, this communication dealing with their action on the nitro-acids.

As in the previous research the amido-group had not been attacked, it was thought that the nitro-group would also remain unchanged but this has not proved to be the case. When the attempt was made to bring about a change under the conditions obtaining in the case of the

amido-acid, no action occurred; however, on varying the proportions and the time, products were eventually obtained from the meta- and para-acids which proved to be products of reduction, azoxy-acids, in fact. No compound was formed from the ortho-acid, although some slight action apparently takes place. The yield in every case is small.

Preparation of Metazoxybenzoic Acid.

After many trials, the following method was found to give the best yield. Both potassium hydroxide and sodium hydroxide were used, but no difference in their action could be detected.

To 10 grams of metanitrobenzoic acid dissolved in a solution of 40 grams of sodium hydroxide in 250 c.c. of water, 30 grams of chloroform were added, and the whole heated by a small flame for 6 hours in a flask fitted with a reflux condenser. The solution, after being filtered, diluted, and acidified with dilute sulphuric acid, was boiled, and again filtered; the filtrate contains the greater part of the unaltered nitro-acid, which can be easily recovered by crystallisation; the crystals had the melting point of the nitro-acid (141°), and, on analysis, gave numbers corresponding with 8.37 per cent. of nitrogen. The precipitate, after being well washed with boiling water to remove the rest of the nitro-acid, was boiled with alcohol, which removed the last traces, filtered, and washed with hot alcohol. As the residue was only slightly soluble in alcohol and insoluble in water, it was purified by dissolving it in dilute ammonia and precipitating with dilute sulphuric acid; after washing with hot water and hot alcohol and drying at 100° , a product was obtained which gave concordant results on analysis.

The purified product is a yellowish powder slightly soluble in alcohol, from which it separates as a crystalline powder, slightly soluble in ether, insoluble in water. It does not melt below 300° , but becomes darker in colour above 250° .

The following numbers were obtained on analysis.

- I. 0.1703 gave 0.0556 H_2O and 0.3658 CO_2 . C = 58.58; H = 3.62.
 - II. 0.1892 „ 0.0603 H_2O „ 0.4082 CO_2 . C = 58.83; H = 3.54.
 - III. 0.1806 „ 15.6 c.c. moist nitrogen at 17° and 760.6 mm. N = 9.96.
 - IV. 0.1651 „ 14.2 c.c. moist nitrogen at 16° and 762.6 mm. N = 9.94.
- $\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_5$ requires C = 58.74. H = 3.49; N = 9.79 per cent.

It is therefore metazoxybenzoic acid. This acid was prepared by Griess (*Annalen*, 1864, 131, 92) by the action of alcoholic potash on metanitrobenzoic acid. A specimen prepared by Griess's method was found to have properties similar to those of the acid described above.

The silver salt was obtained as a flocculent, faintly-yellow pre-

cipitate on adding silver nitrate solution to a neutral solution of the ammonium salt; it is slightly soluble in boiling water, and separates as a flocculent precipitate which is very stable in air, and is not affected by light at the ordinary temperature. The silver salt, dried at 100° , was analysed.

- I. 0.1460 gave 0.0626 Ag. $\text{Ag} = 42.87$.
 II. 0.2754 „ 0.1182 Ag. $\text{Ag} = 42.91$.
 $\text{C}_{14}\text{H}_8\text{N}_2\text{O}_5\text{Ag}_2$ requires $\text{Ag} = 43.2$ per cent.

The barium salt, obtained as a yellow, crystalline precipitate on adding barium chloride solution to a neutral solution of the ammonium salt, is almost insoluble in water, and was purified by repeated washing with boiling water; the crystals are in the form of minute plates. The salt was dried at 120° and analysed.

- I. 0.4385 gave 0.2419 BaSO_4 . $\text{Ba} = 32.43$.
 II. 0.5367 „ 0.2953 BaSO_4 . $\text{Ba} = 32.35$.
 $\text{C}_{14}\text{H}_8\text{N}_2\text{O}_5\text{Ba}$ requires $\text{Ba} = 32.54$ per cent.

Preparation of Parazoxybenzoic Acid.

This acid was obtained and purified by the methods used in the case of the meta-acid. It is a bright yellow, amorphous powder, insoluble in all solvents; it does not melt, but becomes darker in colour when heated to a high temperature. The purified acid, dried at 100° , gave the following numbers on analysis.

- 0.1933 gave 0.0636 H_2O and 0.4148 CO_2 . $\text{C} = 58.52$; $\text{H} = 3.65$.
 0.2504 „ 22 c.c. moist nitrogen at 17° and 759 mm. $\text{N} = 10.06$.

The silver and barium salts were obtained by the methods used for the preparation of similar salts of the meta-acid.

The silver salt is a bright yellow, amorphous substance, insoluble in water, and very stable in air. It was dried at 100° and analysed.

- 0.2315 gave 0.1002 Ag. $\text{Ag} = 43.28$.
 0.4172 „ 0.1792 Ag. $\text{Ag} = 42.95$.

The barium salt is precipitated in minute, dark yellow plates insoluble in water. It was dried at 120° and analysed.

- 0.2928 gave 0.1617 BaSO_4 . $\text{Ba} = 32.47$.

After many trials with varying quantities of the interacting substances, nothing but the original nitro-acid was obtained from ortho-nitrobenzoic acid. Some slight action takes place, since there is considerable change of colour on prolonged heating, but all attempts to isolate a definite product have failed; from this it would seem that the nitro-

group in the ortho-position is less easily reduced than when it is in the meta- or para-position.

In the cases where the azoxy-acid is produced, there is brisk effervescence on acidifying the solution after boiling with chloroform, carbon dioxide being evolved in considerable quantity; this fact seems to show that the reduction of the nitro-group is accompanied by oxidation of the alkali formate to carbonate.

The investigation of the conjoint action of chloroform and alkali hydroxides on other substituted benzoic acids, such as the chlorinated acids and the ortho-amido-acid, is now being attempted, and I hope to communicate the results to the Society in a short time.

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