

LXXXIII.—*Note on the Preparation of certain Iodo-compounds.*

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THE authors, having occasion to attempt the preparation of certain 2:6-derivatives of iodobenzene from the corresponding amino-compounds, were confronted with the well-known difficulty that a number of the latter are only very incompletely diazotised under the conditions usually employed. The yield, however, of iodo-compound obtained was usually very satisfactory when allowance was made for the proportion of amino-derivative unchanged. It therefore only remained to achieve complete diazotisation, and it was decided to apply the process specially recommended by Witt

in such cases (*Ber.*, 1909, **42**, 2953), and consisting in the addition of a mixture of the base with a molecular proportion of potassium metabisulphite to fuming nitric acid. By pouring the product on ice, as described by Witt, and adding a solution of iodine in potassium iodide, extremely satisfactory yields of great purity were achieved in the cases of 2-iodo*isophthalic* acid, 2-iodo-3-nitrobenzoic acid, and 5-chloro-4-iodo-3-nitrotoluene. 5-Iodo*isophthalic* acid is more satisfactorily prepared by the ordinary process, which involves no difficulty as regards diazotisation. Attempts to prepare picryl iodide were unsuccessful, probably owing to instability of the diazonium compound, and the method is also obviously unsuitable for compounds like benzidine, which are easily nitrated.

When the diazotised solution, prepared by Witt's process from 3-nitroanthranilic acid, was added to a large excess of cuprous chloride solution, the product contained, besides the desired chloro-nitrobenzoic acid, a considerable amount of hydroxy-compound. Apparently, therefore, the method is unsuitable for the preparation of chloro-derivatives. For many purposes, however, iodo-compounds are at least equally suitable, and it was considered that the successful outcome of the experiments now described might more usefully be separately recorded than as an incident in the syntheses for which the compounds in question were required.

EXPERIMENTAL.

2-Iodoisophthalic Acid.

The starting point for the preparation of this compound was 2-nitro-*m*-toluic acid. The oxidation of this compound to 2-nitro-*isophthalic* acid, referred to by Noelting and Gachot (*Ber.*, 1906, **39**, 73), by neutral potassium permanganate solution is only complete after the mixture has been boiled for some hours. Noelting and Gachot also describe the preparation of 2-amino-*isophthalic* acid from the nitro-acid by means of tin and hydrochloric acid; it is more conveniently carried out by the addition of stannous chloride to a suspension of the nitro-derivative in a boiling mixture of acetic and hydrochloric acids. The free amino-acid separates on cooling the solution.

The conversion of 2-amino-*isophthalic* acid into 2-iodo-*isophthalic* acid was carried out by Mayer (*Ber.*, 1911, **44**, 2301), but, as he admits, the product was very impure. On repeating the process, which consisted in the very slow addition of a solution of the sodium salt of the acid and of sodium nitrite to dilute sulphuric acid, a purer product was obtained, but only about 25 per cent. of the material was diazotised after thirty hours. Witt's process

was therefore adopted, a finely ground mixture of aminoisophthalic acid (20 grams) and potassium metabisulphite (12.5 grams) being gradually added to fuming nitric acid (45 c.c.) below 10°. After four hours, the mixture was poured on ice (220 grams), and to the resulting clear solution was added a solution of iodine (17 grams) in potassium iodide (33 grams) in the minimum quantity of water. The product (29 grams) melted at 229°. By crystallisation from water, the melting point rose to 236—238°, but a determination of the equivalent showed the acid still to contain 5 per cent. of hydroxyisophthalic acid. Mayer gives a melting point of 205—222°, even after purification of the acid through its methyl ester. The probable explanation of the discrepancy became obvious when a small portion of the acid was submitted to hydrolysis by boiling alcoholic sodium hydroxide. As a result, pure hydroxyisophthalic acid, $C_6H_3(OH)(CO_2H)_2, H_2O$ (m. p. 244°; equivalent, 99.3), was obtained, and further characterised by its red coloration with ferric chloride.

3-Nitroanthranilic Acid.

3-Nitroaceto-*o*-toluidide was easily obtained by the addition of sulphuric acid (2 grams) to a mixture of 3-nitro-*o*-toluidine (20 grams) and acetic anhydride (26 grams). A clear solution resulted, accompanied by a rise in temperature to 70°, and almost immediately after the whole set to a mass of crystals, which were collected after the addition of water. The product (25.5 grams) melted at 156°, which was raised to 157—158° by recrystallisation from dilute acetic acid.

3-Nitroacetylanthranilic acid was prepared by oxidising 3-nitroaceto-*o*-toluidide (10 grams) at 100° with a solution of potassium permanganate (22 grams) and magnesium sulphate (16 grams) in water (1100 grams). For some unexplained reason, the melting point of the product (9 grams) varied considerably. By fractional crystallisation from dilute acetic acid, the product of several preparations was separated into two distinct substances, one in the form of stout, golden-yellow prisms (m. p. 244.5°), the other in yellow needles (m. p. 178°), which it is hoped to discuss in a subsequent communication.

By boiling 3-nitroacetylanthranilic acid, either the crude oxidation product or the separate compounds above described, for thirty-five minutes with 50 per cent. sulphuric acid (4 parts), almost pure 3-nitroanthranilic acid (m. p. 205°) is obtained in a yield of more than 90 per cent. The yield is diminished if the strength of acid or the duration of boiling is increased. The acid has been previously described by Hübner (*Annalen*, 1879, 195,

776 NOTE ON THE PREPARATION OF CERTAIN IODO-COMPOUNDS.

37), who obtained it in the form of its ester by the action of ammonia on ethyl 3-nitrosalicylate.

It is noteworthy that the esterification of the acid is only accomplished with difficulty under ordinary conditions. Thus, after the acid (10 grams) had been boiled with alcohol (50 c.c.) and sulphuric acid (5 c.c.) for twenty-four hours, 5 grams remained unchanged, and 5.8 grams of ester had been produced.

2-Iodo-3-nitrobenzoic Acid.

(a) When a suspension of 3-nitroanthranilic acid (10 grams) in sulphuric acid (11 grams) and water (53 grams) was diazotised in the usual manner, 5.5 grams of acid remained undissolved, whilst from the solution 7 grams of crude idonitrobenzoic acid were obtained. A similar, but less satisfactory, result was obtained when the ester was used in place of the free acid.

(b) 202.5 Grams of nitrobenzoic acid, when submitted to the treatment already described in the case of aminoisophthalic acid, gave 321 grams of idonitrobenzoic acid (m. p. 203—206°), a yield of 98 per cent. of the theoretical.

By crystallisation from water, the acid is obtained in prisms melting at 206° (Found: N=4.82. $C_7H_4O_4NI$ requires N=4.78 per cent.).

5-Chloro-4-iodo-3-nitrotoluene.

(a) In an experiment by Mr. C. W. Judd, from 15 grams of 5-chloro-3-nitro-*p*-toluidine, which had been treated with nitrous acid and potassium iodide in the usual manner, 9 grams were recovered unchanged, whilst 6.5 grams of chloriodonitrotoluene (m. p. 83°) were generated from the remainder.

(b) Three grams of the base, treated as described for 2-aminoisophthalic acid, gave 3.7 grams of iodo-derivative (m. p. 92°).

5-Chloro-4-iodo-3-nitrotoluene separates from light petroleum in plates melting at 92°, which are colourless when pure, but usually red (Found: N=4.85. $C_7H_5O_2NClI$ requires N=4.71 per cent.).

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