

XIX.—*Action of Chloroform and Potassium Hydroxide on o-Aminobenzoic Acid.*

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IN a previous communication (Trans., 1896, 69, 1513), it has been shown that when chloroform and potassium hydroxide act on *m*-aminobenzoic acid under certain conditions, a compound is produced which condenses with phenylhydrazine, but does not yield a hydrazone. The results of analysis pointed to the formation of a compound of the formula $\text{NH}_2 \cdot \text{C}_6\text{H}_3(\text{CO}_2\text{H}) \cdot \text{CHO}$.

The study of the action taking place when *o*-aminobenzoic acid is substituted for the meta-derivative has afforded further evidence of the formation of aldehydes, a hydrazone and semicarbazone having been isolated. Unfortunately, the yield is so small and the substance so soluble that the pure aldehyde has not been obtained, but derivatives have been prepared and analysed. Numerous attempts have been made to increase the yield with but slight success. The product, however, is more stable than that obtained from the meta-acid.

It has been shown (Trans., 1898, 73, 145) that *o*-nitrobenzoic acid is far more stable towards chloroform and potassium hydroxide than the meta- and para-acids; the *o*-amino-acid has also proved to be more stable towards these agents than its isomerides.

The compound obtained from the meta-acid readily decomposes when boiled with water, yielding *m*-aminobenzoic acid again, and it was suggested (Trans., 1896, 69, 1517) that the decomposition was preceded by oxidation to aminophthalic acid, which, according to Miller (*Annalen*, 1881, 208, 245), decomposes with the formation of *m*-aminobenzoic acid. The greater stability of the compound formed from the ortho-acid can be understood if the aldehyde group does not enter the molecule in the ortho-position relatively to the carboxyl group as it does probably in the product from the meta-acid. Experiments have been carried out with *p*-aminobenzoic acid which promise interesting results bearing on this point, and I hope shortly to resume the work.

EXPERIMENTAL.

The method adopted in the case of *m*-aminobenzoic acid (*loc. cit.*) was tried. 10 grams of *o*-aminobenzoic acid were added to a solution of 20 grams of potassium hydroxide in about 200 c.c. of water, and the solution was boiled with 14 grams of chloroform for 45 minutes.

After acidifying with acetic acid, no precipitate was at first obtained, but on standing, crystals separated, which proved to be unchanged *o*-aminobenzoic acid (m. p. 144°). Numerous similar experiments were made with varied proportions of the reacting substances and of water, but with similar results. When concentrated solutions were boiled for a long time, a small quantity of a reddish, resinous substance was precipitated by acetic acid; the amount, however, was too small to admit of further examination.

As no insoluble product had been obtained, dilute sulphuric acid was substituted for acetic acid, and the product, after acidification, was shaken with ether. The residue, after distilling off the ether, was crystallised from water; *o*-aminobenzoic acid separated out at first, but on concentrating the mother liquor, crystals were obtained having a melting point considerably below that of this substance. A solution of phenylhydrazine in acetic acid gave, with the mother liquor, a yellow precipitate at once. All attempts to isolate the aldehydo-acid from the ether extract have failed, as no medium has been found to separate it from *o*-aminobenzoic acid. The phenylhydrazone, however, has been prepared in sufficient quantity for examination and analysis, although the task has been laborious, the yield being very small.

Phenylhydrazone of Aldehydo-o-aminobenzoic Acid,
 $\text{NH}_2 \cdot \text{C}_6\text{H}_3(\text{CO}_2\text{H}) \cdot \text{CH} : \text{N} \cdot \text{NH} \cdot \text{C}_6\text{H}_5.$

The method finally adopted for the preparation of the phenylhydrazone was as follows: 10 grams of *o*-aminobenzoic acid were dissolved in a solution of 30 grams of potassium hydroxide in 150 c.c. of water, and the solution heated to a temperature of 60° in a flask fitted with a reflux condenser; 16 grams of chloroform were added gradually, and the mixture heated for 3 hours. When cold, the product was acidified with excess of acetic acid, allowed to stand for an hour, filtered from crystals of the original acid, and treated with a solution of phenylhydrazine in acetic acid. The phenylhydrazone separated on standing as a bulky, yellow precipitate. It was washed with hot water, and crystallised twice from alcohol. The filtrate from the phenylhydrazone, when evaporated to a small bulk, treated with dilute sulphuric acid, and shaken with ether, yielded a large quantity of the original *o*-amino-acid.

The recrystallised phenylhydrazone separated in small, yellow needles which melted at 230°. It was insoluble in water, but fairly easily soluble in alcohol. The yield of the pure substance obtained from 10 grams of the acid never exceeded 0.5 gram.

On analysis, the following numbers were obtained :

0.1445 gave 0.3476 CO_2 and 0.0700 H_2O . $\text{C} = 65.60$; $\text{H} = 5.09$.

0.1997 „ 0.4827 CO_2 „ 0.0946 H_2O . $\text{C} = 65.91$; $\text{H} = 5.25$.

0.1092 „ 14.9 c.c. moist nitrogen at 13° and 763 mm. $\text{N} = 16.04$.

0.1134 „ 16.2 c.c. „ „ 15° „ 752 mm. $\text{N} = 16.37$.

$\text{C}_{14}\text{H}_{13}\text{O}_2\text{N}_3$ requires $\text{C} = 65.88$; $\text{H} = 5.09$; $\text{N} = 16.47$ per cent.

Numerous attempts have been made to obtain the aldehydo-acid from the hydrazone but without success. When boiled with dilute hydrochloric or sulphuric acid, the hydrazone dissolved, but was reprecipitated unchanged on carefully neutralising the solution. Decomposition apparently occurred with concentrated hydrochloric acid, but no definite product could be isolated, possibly owing to the small quantity of hydrazone available.

One remarkable property of this substance is its power of forming salts sufficiently stable for analysis. The barium and silver salts have been prepared and analysed.

Barium Salt.—A dilute solution of ammonia was neutralised by excess of the hydrazone, filtered and treated with barium chloride solution. A yellow, crystalline precipitate separated, which was washed well with water and dried in a vacuum. It was found impossible to recrystallise the salt, as decomposition occurred on heating with water.

0.2574 gave 0.0957 BaSO_4 . $\text{Ba} = 21.86$.

$(\text{C}_{14}\text{H}_{12}\text{O}_2\text{N}_3)_2\text{Ba}$ requires $\text{Ba} = 21.24$ per cent.

Silver Salt.—This salt is unstable but can be isolated if care is taken to exclude light during the preparation and to use cold solutions only. The hydrazone was dissolved in dilute ammonia solution, very dilute nitric acid was added until a precipitate just appeared, the solution was then filtered and silver nitrate solution added. The light yellow precipitate obtained was washed well with cold water and dried in a vacuum.

0.1244 gave 0.0378 Ag . $\text{Ag} = 30.38$.

$\text{C}_{14}\text{H}_{12}\text{O}_2\text{N}_3\text{Ag}$ requires $\text{Ag} = 29.83$ per cent.

Semicarbazone of Aldehydo-o-aminobenzoic Acid.

When a solution of semicarbazide hydrochloride was added to the filtrate obtained after acidifying the condensation product, as already described, a yellow precipitate separated on standing, which proved on analysis to be the semicarbazone of an aldehydo-o-aminobenzoic acid. The yield is even smaller than that of the phenylhydrazone.

The semicarbazone is insoluble in water, and only sparingly soluble in alcohol, from which it separates in greenish-yellow, microscopic crystals melting at 246° .

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0.1462 gave 33.5 c.c. moist nitrogen at 22° and 757 mm. $N = 25.39$.

$C_9H_{10}O_3N_4$ requires $N = 25.22$ per cent.

All attempts to prepare the aldehydo-acid from the semicarbazone have failed.

I hope to be able to publish in due course the results of an investigation of the action of chloroform and potassium hydroxide on *p*-aminobenzoic acid.
