XXXIX.—10-*Chloro*-5 : 10-*dihydrophenarsazine and its Derivatives. Part IV. Carboxy-derivatives.*

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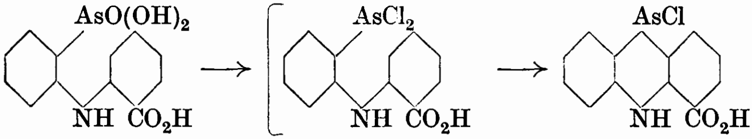
APART from the synthesis of 10-chloro-5 : 10-dihydrophenarsazine (J., 1926, 452), the parent substance and all its analogues so far described have been prepared by the action of arsenious chloride on diphenylamine and its analogues, respectively (*ibid.*, pp. 450, 464, 2241, where all references are given). Owing to the difficulty of obtaining diphenylaminomonocarboxylic acids, carboxy-derivatives of 10-chloro-5 : 10-dihydrophenarsazine could not be obtained directly and it was necessary to study the condensation of *o*-bromophenylarsinic acid with different aminobenzoic acids.

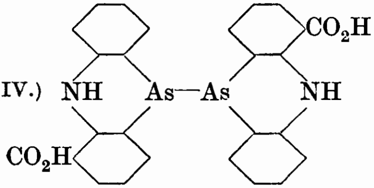
Anthranilic acid condenses readily with *o*-bromophenylarsinic acid in boiling nitrobenzene in presence of anhydrous potassium carbonate and a small quantity of copper powder, forming 2-*carboxydiphenylamine*-6′-*arsinic acid* (I). This acid, on reduction with sulphur dioxide in alcoholic-hydrochloric acid solution, is readily converted into 2-*carboxydiphenylamine*-6′-*arsenic dichloride* (II), which, however, cannot be isolated in the pure condition owing to the ease with which it loses hydrogen chloride. Complete conversion of this compound into 10-*chloro*-5 : 10-*dihydrophenarsazine*-4-*carboxylic acid* (III) can be accomplished either by boiling the acetic acid solution of the reduction product or by dissolving the latter in hot sodium hydroxide solution, boiling for a few minutes, and then precipitating the final product by the addition of an excess of concentrated hydrochloric acid.

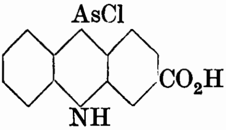


(I.) (II.) (III.)

Whilst its solubility in neutral solvents is much less, as far as its chemical properties are concerned, 10-chloro-5 : 10-dihydrophenarsazine-4-carboxylic acid is very similar to the parent compound. When reduced with hypophosphorous acid, it yields a cacodyl derivative, *viz.*, 10 : 10′-*bis*-4-*carboxy*-5 : 10-*dihydrophenarsazine* (IV), and this compound is soluble in sodium hydroxide.

(IV.)





(V.)

By a similar procedure, starting from *m*-aminobenzoic acid and *o*-bromophenylarsinic acid, 10-*chloro*-5 : 10-*dihydrophenarsazine*-3-*carboxylic acid* (V) was obtained which was even less soluble than the isomeric compound.

We have not succeeded in isolating the corresponding condensation products, using *p*-aminobenzoic acid and *N*-methylanthranilic acid.

EXPERIMENTAL.

2-*Carboxydiphenylamine*-6′-*arsinic Acid* (I).—A mixture of anthranilic acid (13·6 g.), *o*-bromophenylarsinic acid (14·0 g.), anhydrous potassium carbonate (14·0 g.), nitrobenzene (100 c.c.), and a trace of copper powder was boiled under reflux for 7 hours. After all volatile matter had been removed by distillation in steam, the resulting solution was boiled with charcoal, filtered, and acidified. The crude acid (11·0 g.) crystallised from acetic acid in colourless, silky needles, m. p. 243° (decomp.) (Found : As, 22·3. $C_{13}H_{12}O_5NAs$ requires As, 22·25%).

Reduction of 2-*Carboxydiphenylamine*-6′-*arsinic Acid*.—A solution of the acid (5 g.) in alcohol (20 c.c.) and concentrated hydrochloric acid (20 c.c.) containing a trace of iodine was heated to boiling, and sulphur dioxide passed into it for a few minutes. A yellow precipitate formed immediately. The mixture was cooled rapidly, and the solid material separated. This substance was not homogeneous, since on recrystallisation from acetic acid it gave two types of crystals, yellow needles and transparent needles. This result indicated that reduction had taken place and that a partial elimination of hydrogen chloride had been effected.

10-*Chloro*-5 : 10-*dihydrophenarsazine*-4-*carboxylic acid* (III) was prepared by working up the crude reduction product in two ways : (*a*) A solution of the crude reduction product in the minimum quantity of hot acetic acid was boiled under reflux for 3 hours. On cooling, a homogeneous mass of yellow crystals separated. These were recrystallised from acetic acid and obtained in yellow needles, m. p. 243° (decomp.). (*b*) The crude material from the reduction of 5 g. of the original acid was dissolved in 3*N*-sodium hydroxide (75 c.c.), and the colourless solution boiled for a few minutes. On acidifying the cold solution with an excess of concentrated hydrochloric acid, the product separated as a yellow powder. This, after recrystallisation from acetic acid, was identical with the product previously obtained (Found : As, 23·4. $C_{13}H_9O_2NClAs$ requires As, 23·3%).

10 : 10′-*Bis*-4-*carboxy*-5 : 10-*dihydrophenarsazine* (IV).—A solution of 10-chloro-5 : 10-dihydrophenarsazine-4-carboxylic acid (2 g.) in acetic acid (20 c.c.) containing a trace of iodine was mixed with a solution of hypophosphorous acid (5 c.c.; *d* 1·136). Almost immediately an orange-coloured precipitate separated. This was filtered off, washed with acetone, and dried. The compound, m. p. 253° (decomp.), was practically insoluble in the usual organic solvents, but dissolved in sodium hydroxide, giving an orange-coloured solution (Found : As, 25·9. $C_{26}H_{18}O_4N_2As_2$ requires As, 26·2%).

3-*Carboxydiphenylamine*-6′-*arsinic acid*,

$$CO_2H\cdot C_6H_4\cdot NH\cdot C_6H_4\cdot AsO(OH)_2,$$

was prepared from *o*-bromophenylarsinic acid and *m*-aminobenzoic acid in a similar manner to the corresponding 2-carboxydiphenylamine-6′-arsinic acid, amyl alcohol being used instead of nitrobenzene for the condensation. It crystallised from dilute acetic acid in colourless needles, m. p. 238—239° (decomp.) (Found : As, 21·9. $C_{13}H_{12}O_5NAs$ requires As, 22·25%).

10-*Chloro*-5 : 10-*dihydrophenarsazine*-3-*carboxylic Acid* (V).—The reduction of 3-carboxydiphenylamine-6′-arsinic acid was carried out in a similar manner to that of the isomeride. The crude chloro-compound was dissolved in hot sodium hydroxide solution, and precipitated from the cold solution with an excess of concentrated hydrochloric acid. The yellow precipitate was very sparingly soluble in all organic solvents and therefore difficult to obtain pure. It did not melt below 300° (Found : As, 22·8. $C_{13}H_9O_2NClAs$ requires As, 23·2%).

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