CCCCLIII.—10-*Chloro*-5 : 10-*dihydrophenarsazine and its Derivatives. Part XVII. Constitution of the Nitro-derivatives produced from* 3-*Nitrodiphenylamine*-6′-*arsonic Acid and its Homologues.*

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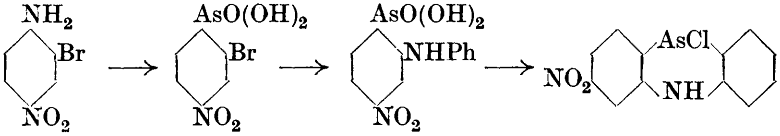
REDUCTION of 3-nitrodiphenylamine-6′-arsonic acid (J., 1927, 2514) in the presence of hydrochloric acid produces a homogeneous, deep red, nitro-10-chloro-5 : 10-dihydrophenarsazine in which the nitro-group may occupy the 1- or the 3-position in the phenarsazine nucleus. The evidence brought forward (J., 1929, 1229) that this compound is 10-chloro-1-nitro-5 : 10-dihydrophenarsazine depended on the comparison of its colour, supplemented by spectroscopic examination (J., 1930, 1622), with the orange-yellow 10-chloro-3-nitro-4-methyl-5 : 10-dihydrophenarsazine and the deep red 10-chloro-1-nitro-4-methyl-5 : 10-dihydrophenarsazine, the constitution of the latter two compounds resting on a definite synthetic basis.

10-*Chloro*-3-*nitro*-5 : 10-*dihydrophenarsazine* (II) has now been definitely synthesised by the following series of reactions :



(I.) (II.)

This compound is orange-yellow and decomposes some 10° above the melting point of the red reduction product of 3-nitrodiphenylamine-6′-arsonic acid. Of the four possible mononitro-derivatives of 10-chloro-5 : 10-dihydrophenarsazine, the 2-, 3-, and 4-derivatives have now been synthesised (compare J., 1927, 2513, 2515). Since the reduction product of 3-nitrodiphenylamine-6′-arsonic acid is different from all of these, its constitution must be 10-chloro-1-nitro-5 : 10-dihydrophenarsazine.

This evidence is supplemented by the preparation of 4-*methyl*-, 1(*or* 3)-*methyl*-, and 2-*methyl*-10-*chloro*-7-*nitro*-5 : 10-*dihydrophenarsazines* by the reduction (cyclisation) of 2-*methyl*-, 3-*methyl*-, and 4-*methyl*-3′-*nitrodiphenylamine*-6′-*arsonic acids*.* All these dihydrophenarsazines which are derivatives of (II) and in which the nitro-

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* There are 46 possible nitromethyldiphenylamine-6′-arsonic acids, not 34 as previously stated (J., 1929, 1231); the total number of nitromethyldiphenylaminearsonic acids theoretically possible is 120.

group is in the *p*-position to the arsenic atom are orange-yellow, in satisfactory confirmation of the views regarding colour and the position of the nitro-group previously expressed. Further, no dichloroarsine as an intermediate product of ring closure was isolated in any case, which is in keeping with the hypothesis we have put forward (J., 1929, 1229) in explanation of the reduction (cyclisation) process. Finally, the present work confirms the correctness of the constitution provisionally assigned to the dihydrophenarsazine derivatives obtained as reduction products of the nitromethyldiphenylamine-6′-arsonic acids.

We have not yet succeeded in synthesising 10-chloro-1-nitro-5 : 10-dihydrophenarsazine by a series of reactions analogous to those formulated above, for we have not been able to determine the conditions for isolating 2-bromo-6-nitrophenylarsonic acid, theoretically obtainable by the Bart–Schmidt reaction from 2-bromo-6-nitroaniline (J., 1928, 3092).

EXPERIMENTAL.

2-*Bromo*-4-*nitrophenylarsonic acid* (I).*—A suspension of finely sieved 2-bromo-4-nitroaniline (J., 1928, 3092) (44 g.) in water (162 c.c.) and hydrochloric acid (61 c.c.) was treated with ice (61 g.) and immediately diazotised by the rapid addition, with stirring, of sodium nitrite solution (20%; 71 c.c.). The diazo-solution was run moderately rapidly into a stirred solution of arsenious oxide (40·5 g.) in sodium hydroxide solution [NaOH (12·2 g.) in water (101 c.c.)] to which a solution of copper sulphate (3·05 g.) in water (30·5 c.c.) had been previously added. Sodium hydroxide solution (20%) was added simultaneously at such a rate that the mixture was kept just alkaline to phenolphthalein paper. At this stage it was necessary to break up the froth to some extent by addition of ether. After the coupling, the mixture was made strongly alkaline to phenolphthalein by addition of a little 20% sodium hydroxide solution and, after being stirred for some time, it was heated on the water-bath for about 15 minutes, treated with charcoal, and filtered. On acidification of the warm filtrate some dark tarry matter was precipitated, and separated mechanically; on further acidification and inoculation the required *acid* was precipitated as a yellow microcrystalline powder. A further quantity was obtained by making the mother-liquor alkaline and concentrating and acidifying it. The total yield of crude material (which was used in all the following condensations except that in which aniline was employed)

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* The method of preparation is similar to that used for the preparation of 2-bromo-5-nitrophenylarsonic acid (J., 1929, 2335) by Dr. H. J. Barber, to whom we are greatly indebted for details not available in his published account of the work.

was 27·5 g. (42%). The compound crystallised from water, in which it was somewhat sparingly soluble, in pale orange-yellow needles, decomp. 240—242° (Found: Br, 23·85. $C_6H_5O_5NBrAs$ requires Br, 24·5%). The sodium salt is precipitated in thin pale orange needles from a solution in 20% aqueous sodium hydroxide. A dilute alkaline solution of the sodium salt is deep red. The ammonium salt separates in clusters of pale orange-yellow needles from moderately concentrated solutions of ammonia. The other salts are not so well defined.

3-*Nitrodiphenylamine*-6-*arsonic Acid*.—A mixture of the preceding acid (13·0 g.), aniline (3·8 g.), potassium carbonate (8·3 g.), amyl alcohol (40 c.c.), and a trace of copper powder was boiled for 4½ hours. The volatile materials were removed in steam, and the aqueous solution filtered after treatment with charcoal. The solid precipitated from the filtrate by acidification was recrystallised from aqueous alcohol (charcoal) and obtained in orange-coloured plates, decomposing at 193° after shrinking at 135° (Found: As, 22·1. $C_{12}H_{11}O_5N_2As$ requires As, 22·2%).

10-*Chloro*-3-*nitro*-5 : 10-*dihydrophenarsazine* (II).—The preceding acid (crude and slightly moist, 4 g.) was dissolved in a hot mixture of alcohol (25 c.c.) and hydrochloric acid (25 c.c.) and, after addition of a trace of iodine, sulphur dioxide was passed through the hot liquid. The orange-coloured precipitate was dried under reduced pressure in the presence of potassium hydroxide. Its sparing solubility indicated that it could not be a dichloroarsine and it was crystallised from a large volume of acetic acid and obtained in thin orange-coloured needles, decomp. 268—271° (Found: Cl, 11·2. $C_{12}H_8O_2N_2ClAs$ requires Cl, 11·0%).

3′-*Nitro*-4-*methyldiphenylamine*-6′-*arsonic acid*, orange-red needles (from aqueous alcohol), showing a colour change at 132° and decomposing at 194° (Found: As, 20·5. $C_{13}H_{13}O_5N_2As$ requires As, 21·3%); 3′-*nitro*-3-*methyldiphenylamine*-6′-*arsonic acid*, small orange-coloured plates (from aqueous alcohol), decomposing at 116° (Found: As, 20·7%); 3′-*nitro*-2-*methyldiphenylamine*-6′-*arsonic acid*, small orange-coloured plates (from dilute acetic acid), decomposing at 127—132° (Found: As, 20·5%), were all prepared by condensing the appropriate amine with 2-bromo-4-nitrophenylarsonic acid (I) under conditions similar to those used in the preparation of 3-nitrodiphenylamine-6-arsonic acid.

These three acids on reduction in the manner described for the preparation of 10-chloro-3-nitro-5 : 10-dihydrophenarsazine (II) furnished respectively 10-*chloro*-7-*nitro*-2-*methyl*-5 : 10-*dihydrophenarsazine*, orange needles (from acetic acid) decomposing at 263° (Found: Cl, 10·4. $C_{13}H_{10}O_2N_2ClAs$ requires Cl, 10·5%), 10-*chloro*-

7-*nitro*-1(or 3)-*methyl*-5 : 10-*dihydrophenarsazine*, apparently homogeneous, orange needles (from acetic acid), decomposing at 292—294° after previous darkening (Found : Cl, 10·4%), and 10-*chloro*-7-*nitro*-4-*methyl*-5 : 10-*dihydrophenarsazine*, orange prisms (from nitrobenzene; this substance is sparingly soluble in all the usual organic solvents), decomposing at about 305—307° after previous darkening (Found : Cl, 10·2%).

Treatment of a hot saturated solution of 10-chloro-7-nitro-2-methyl-5 : 10-dihydrophenarsazine in acetic acid with an excess of hydrogen peroxide, followed by heating for 30 minutes on the water-bath and subsequent dilution with water, gave a precipitate of 7-*nitro*-2-*methylphenarsazinic acid*. This was purified by recrystallising its slightly soluble sodium salt from 5% aqueous sodium hydroxide and subsequently acidifying an aqueous solution of the purified salt. The somewhat gelatinous acid precipitated was yellow, unmelted at 285°, and almost insoluble in the usual solvents (Found : As, 22·1. $C_{13}H_{11}O_4N_2As$ requires As, 22·45%).

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