CXLIII.—10-*Chloro*-5 : 10-*dihydrophenarsazine and its Derivatives. Part VIII. The Bromination of* 10-*Chloro*-5 : 10-*dihydrophenarsazine and Some of its Derivatives.*

By Leslie Alderman Elson, Charles Stanley Gibson, and John Dobney Andrew Johnson.

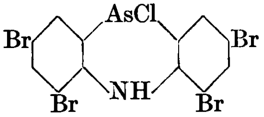
2 : 10-Dichloro-, 1 (or 3) : 10-dichloro-, and 2 : 8 : 10-trichloro-5 : 10-dihydrophenarsazines have been prepared by the condensation of the appropriate halogenated diphenylamine and arsenious chloride in *o*-dichlorobenzene solution (J., 1926, 2246). An attempt to prepare 2 : 4 : 6 : 8 : 10-pentachloro-5 : 10-dihydrophenarsazine by condensing arsenious chloride with 2 : 4 : 2′ : 4′ : tetrachlorodiphenylamine was, however, unsuccessful (*loc. cit.*, p. 2243, footnote). Three explanations of the latter observation may be advanced, *viz.*, (*a*) that the formation of the additive compound of the substituted diphenylamine and arsenious chloride which has been assumed to precede the formation of the phenarsazine derivative (J., 1926, 454; 1928, 2208) might be inhibited if the basicity of the :NH group were diminished by negative substituents in the diphenylamine nucleus, (*b*) the steric effect of the *oo*′-chlorine atoms might prevent the formation of this additive compound, and (*c*) the pentachloro-5 : 10-di-

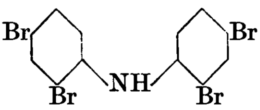
hydrophenarsazine might be too unstable to exist. The fact that *o*-, *m*-, and *p*-nitrodiphenylamines do not condense with arsenious chloride (*loc. cit.*, footnote) seems to support (*a*), but, on the other hand, the more basic *o*-aminodiphenylamine also does not condense with arsenious chloride. That the steric effect mentioned in (*b*) can have little effect on this reaction would appear to be proved by the facts that phenyl-α-naphthylamine (Lewis and Hamilton, *J. Amer. Chem. Soc.*, 1921, **43**, 2218) and di-α-naphthylamine (J., 1926, 463) condense readily with arsenious chloride.

In order to test the third explanation it seemed desirable to ascertain whether halogenated derivatives of 10-chloro-5 : 10-dihydrophenarsazine and related compounds can be obtained by direct halogenation and, for this purpose, we have studied the bromination of some typical compounds of this series.

10-Chloro-5 : 10-dihydrophenarsazine in hot glacial acetic acid solution (it is not very soluble in the cold) was treated with bromine (4 mols.), and a colourless well-defined crystalline substance isolated from the cooled solution. Since the nitration of 10-chloro-5 : 10-dihydrophenarsazine produces the 2- and 4-mononitro-derivatives (Wieland and Rheinheimer, *Annalen*, 1921, **423**, 1; Gibson and Johnson, J., 1927, 2515), it was anticipated that the fully brominated product would be 10-chloro-2 : 4 : 6 : 8 -tetrabromo-5 : 10-dihydrophenarsazine (I); but the colourless product isolated was arsenic-free and analysis showed it to be tetrabromodiphenylamine. It was identical with the tetrabromodiphenylamine obtained by brominating diphenylamine under the same conditions. Although the exact constitution of this tetrabromodiphenylamine has not been determined, there can be little doubt from analogy with the well-known tetrachlorodiphenylamine recently synthesised by Chapman (this vol., p. 570) that it is 2 : 4 : 2′ : 4′-tetrabromodiphenylamine (II). Bromination of 10-bromo-5 : 10-dihydrophenarsazine gave the same product.

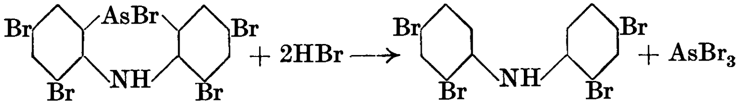
(I.)



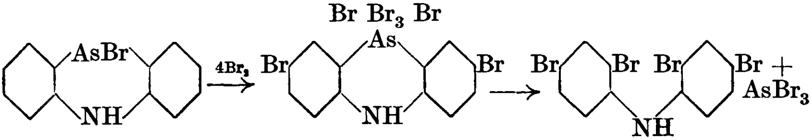


(II.)

Under the conditions of the experiment, only four molecular proportions of bromine react with 10-chloro (or bromo)-5 : 10-dihydrophenarsazine and only tetrabromodiphenylamine and not hexabromodiphenylamine is isolated, although the latter compound is obtained when diphenylamine is brominated (in more dilute solution) with six molecular proportions of bromine, tetrabromodiphenylamine being much less soluble than the hexabromo-compound. In view of this, it was at first thought that the formation of tetrabromodiphenylamine was the result of the reaction (i) :

(i) 

This was investigated more closely by carrying out the bromination in acetic acid solution containing an excess of sodium acetate : tetrabromodiphenylamine was still the only isolable product. When the bromination was carried out in cold *o*-dichlorobenzene solution and also in cold carbon tetrachloride solution, hydrogen bromide was evolved as before and a red microcrystalline solid separated in each case. This red substance itself could not be investigated, since it slowly gave off bromine and white fumes, leaving a yellow crystalline solid which proved to be slightly impure tetrabromodiphenylamine. The red substance had the properties of an arsenic perbromide, and, in spite of the probable instability of such a compound at the temperature of boiling acetic acid, the transitory existence of such a substance in the bromination as carried out in the present work may well be assumed. In this case the formation of tetrabromodiphenylamine is explained as follows :

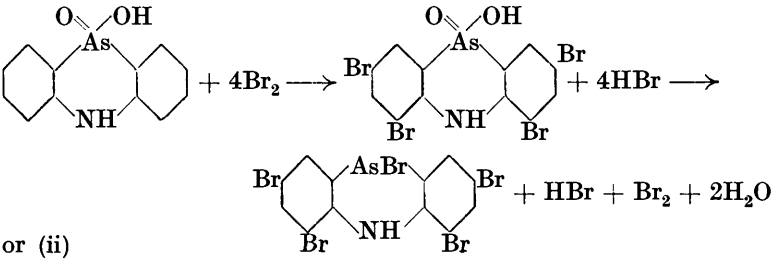


in this scheme hydrogen bromide is not represented as taking part in the production of the tetrabromodiphenylamine. When only two molecular proportions of bromine were used for the bromination of one molecular proportion of 10-bromo-5 : 10-dihydrophenarsazine, the product contained tetrabromodiphenylamine and unchanged initial material.

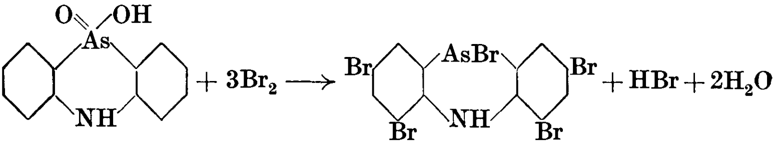
The behaviour towards bromine of some six homologues of 10-chloro-5 : 10-dihydrophenarsazine in acetic acid solution has also been studied and, in each case, dearsenication of the compound took place with the production of a tetrabromodiphenylamine homologue. The constitution of these bromodiphenylamines is not clear, but the substances, whatever their constitution may be, are identical with the direct bromination products of the diphenylamines as far as we have been able to investigate them.

When phenarsazinic acid was submitted to the action of bromine in hot acetic acid solution, comparatively little hydrogen bromide was evolved, the hot solution acquiring a permanent yellow colour.

As far as the experimental conditions allowed them to be determined, three molecular proportions appeared to be the amount required for each molecular proportion of the acid. The main product of this reaction was the tetrabromodiphenylamine already mentioned, 2 : 4 : 6 : 8 : 10 - *pentabromo* - 5 : 10 - *dihydrophenarsazine* being obtained in smaller quantity, and 2 : 4 : 6 : 8-*tetrabromophenarsazinic acid* (there seems every reason for assuming these constitutions) in still less quantity. It is suggested that the formation of the pentabromodihydrophenarsazine is explained by equation (ii). This

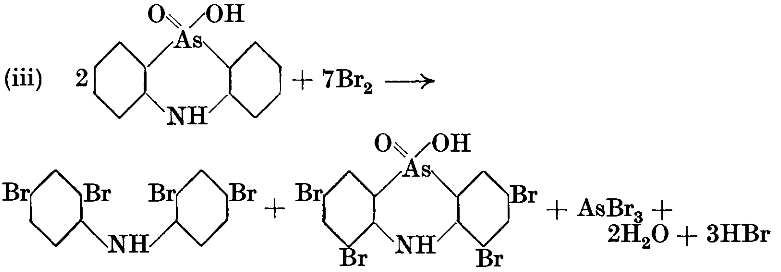


or (ii)



reaction involves hydrogen bromide acting as a reducing agent; another example of this has already been indicated (this vol., p. 782); 3-nitro-*o*-tolylarsinic acid when boiled in a concentrated solution of hydrogen bromide oxidises the latter to bromine. The stability of the pentabromodihydrophenarsazine towards hydrogen bromide (although an aqueous solution was used) and acetic acid may be regarded as evidence against hydrogen bromide playing a part in the production of tetrabromodiphenylamine as was first suggested.

(iii)



It is suggested that the production of tetrabromodiphenylamine and in less quantity of tetrabromophenarsazinic acid is represented by equation (iii), which summarises reactions consisting of (*a*) bromination of phenarsazinic acid to a dibromophenarsazinic acid, (*b*) reduction of part of the latter to tribromo-5 : 10-dihydrophenarsazine, (*c*) the action of bromine on this, yielding tetrabromodiphenylamine and arsenious bromide, and (*d*) further bromination of part of the dibromophenarsazinic acid to tetrabromophenarsazinic acid. Actually this equation does not represent the final stage, because there is still the probability of the hydrogen bromide and the tetrabromophenarsazinic acid reacting to produce 2 : 4 : 6 : 8 : 10-pentabromo-5 : 10-dihydrophenarsazine and bromine by reduction, and the action of this bromine on the original compound, so that the relative amount of tetrabromodiphenylamine will be greater than that indicated. This explanation of the reactions taking place is in substantial agreement with the experimental results.

2 : 4 : 6 : 8 : 10-Pentabromo-5 : 10-dihydrophenarsazine is readily oxidised by hydrogen peroxide to 2 : 4 : 6 : 8-tetrabromophenarsazinic acid. This also is a stable substance and identical with that isolated in small quantity from the mixture of products of the action of bromine on phenarsazinic acid in hot acetic acid solution.

Direct halogenation of aromatic arsenical compounds frequently leads to dearsenication, and the action of potassium iodide and dilute sulphuric acid has been used in orienting these substances, the arsenic group being replaced by an iodine atom. On the other hand, Michaelis (*Annalen*, 1902, **320**, 334) has shown that 2 : 4-dimethylphenyldichloroarsine when chlorinated in aqueous suspension yields a mono- and a di-chloro-2 : 4-dimethylphenylarsinic acid; Bertheim (*Ber.*, 1910, **43**, 531) also showed that acetyl-*p*-arsanilic acid and *p*-arsanilic acid can be directly halogenated, and Fisher and Raiziss (*J. Amer. Chem. Soc.*, 1929, **51**, 529) have brominated 3-nitro-4-hydroxyphenylarsinic acid.

It would appear from the present work that bromination of compounds of the phenarsazine type (which may be considered to be derivatives of *o*-aminophenylarsinic acid) is accompanied by dearsenication, bromine replacing the arsenic group. The reaction belongs, therefore, to the same class as that of the action of halogens on aromatic compounds generally, causing a direct replacement of a substituting group. The production of 2 : 4 : 6-tribromoaniline by the action of bromine on sulphanilic acid (Heinrichen, *Annalen*, 1889, **253**, 268) has long been known and a summary of the more important typical examples of bromine replacement has been given by Sudborough and Lakhumalani (*J. Ind. Inst. Sci.*, 1914—1918, I, 133).

EXPERIMENTAL.

Bromination of 10-*Chloro*-5 : 10-*dihydrophenarsazine*.—A boiling solution of 10-chloro-5 : 10-dihydrophenarsazine (5·55 g.) in glacial acetic acid (222 c.c.) was treated with bromine (4 c.c.; 4 mols.) drop by drop. The colour of the bromine was immediately discharged and hydrogen bromide evolved in considerable quantity. The liquid was boiled for some time to drive off as much as possible of the hydrogen bromide. Even while hot, colourless needles began to separate, and these almost filled the cold solution. The solid product after recrystallisation from glacial acetic acid (charcoal) had m. p. 186° (Found : Br, 65·1. Calc. : Br, 66·0%) and was identical with the tetrabromodiphenylamine, m. p. 186°, obtained from diphenylamine (4·2 g.), boiling glacial acetic acid (300 c.c.), and bromine (5 c.c.; 4 mols.) under the same conditions.

Hexabromodiphenylamine was prepared by treating diphenylamine (16·9 g.) in boiling acetic acid (1183 c.c., this large volume being necessary on account of the sparing solubility of tetrabromodiphenylamine) with bromine (30 c.c.; 6 mols., the last 2 mols. of which were less rapidly absorbed). The greenish crystalline product which separated on cooling was twice crystallised from benzene (charcoal) and obtained in colourless prisms, m. p. 221—222° (Gnehm, *Ber.*, 1875, **8**, 926, gives m. p. 218°). The melting points of this and some of the other brominated diphenylamines described in this communication are not very sharp, softening taking place before the substances actually melt.

Bromination of 10-*Bromo*-5 : 10-*dihydrophenarsazine*.—10-Bromo-5 : 10-dihydrophenarsazine (10 g.) in acetic acid (250 c.c.) was treated with bromine (6·2 c.c.; 4 mols.) under exactly similar conditions. More bromine than the above was not absorbed and was simply expelled with hydrogen bromide from the boiling solution. The product was identical with the tetrabromodiphenylamine described above (Found : Br, 66·7%).

Bromination of 10-*Chloro*-2 : 8-*dimethyl*-5 : 10-*dihydrophenarsazine*.—The quantities used were : chloro-compound (6·11 g.), glacial acetic acid (420 c.c.), bromine (4 c.c.; 4 mols.), and the reaction was carried out in the same manner. The first half of the bromine reacted more readily than the second half. The greater part of the solvent was distilled off, and the product recrystallised from acetic acid. To obtain it colourless and free from the merest trace of arsenic it was necessary to add a few drops of hydrogen peroxide to the acetic acid; experience has shown that the yellow colour was probably due to a small quantity of the intermediate bromo-compound of the chloro-phenarsazine which had escaped the action of further bromine. The product crystallised in colourless flat plates, m. p. 161—162° (Found : Br, 61·4. Calc. : Br, 62·3%). Although the melting point of the compound was somewhat low, it did not depress the melting point (166°) of the product obtained when di-*p*-tolylamine (3·94 g.) in acetic acid (78 c.c.) was treated with bromine (4 c.c.; 4 mols.) under similar conditions, which undoubtedly was tetrabromodi-*p*-tolylamine (Found: Br, 61·6%) (*Ber.*, 1880, **13**, 1545).

Bromination of 7-*Chloro*-12 : 7-*dihydrobenzophenarsazine.*—The chloro-compound (13 g.), dissolved in boiling acetic acid (786 c.c.), was treated with bromine (8 c.c.; 4 mols.), and the product worked up in the usual manner. The *tetrabromophenyl-α-naphthylamine* obtained formed colourless needles, m. p. 150° (Found: Br, 59·8. $C_{16}H_{11}NBr_4$ requires Br, 59·8%), and was identical with the product obtained by treating phenyl-α-naphthylamine (4·38 g.) in boiling acetic acid solution (220 c.c.) with bromine (4 c.c.; 4 mols.).

Bromination of 12-*Chloro*-7 : 12-*dihydrobenzophenarsazine.*—This chloro-compound (6·5 g.) was dissolved as far as possible in boiling acetic acid (650 c.c.) and treated with bromine (4 c.c.; 4 mols.) in the usual manner. The colourless silky needles which separated had m. p. 205°, and this remained unchanged when the substance was recrystallised from acetic acid and then three times from benzene. Several specimens were analysed (Found: Br, 56·0, 57·7, 56·4, 55·5, 56·7, 56·45. Calc. for tetrabromophenyl-β-naphthylamine: Br, 59·8%. Calc. for tribromophenyl-β-naphthylamine: Br, 52·6%). The product was free from arsenic. A tetrabromophenyl-β-naphthylamine, m. p. 202—203°, has been described by Zincke and Lawson (*Ber.*, 1887, **20**, 1170).

Bromination of 7-*Chloro*-9-*methyl*-7 : 12-*dihydrobenzophenarsazine.*—The chloro-compound (6·85 g.), dissolved in boiling acetic acid (544 c.c.), readily absorbed bromine (4 c.c.; 4 mols.). The resulting solution deposited pale brown plates. This product was recrystallised from acetic acid and, although the final product was free from arsenic, it still retained a small amount of colour. It had m. p. 167—170° (Found: Br, 57·8. Calc.: Br, 58·25%), and was identical with the tetrabromo-*p*-tolyl-α-naphthylamine obtained by treating *p*-tolyl-α-naphthylamine (4·66 g.) in boiling acetic acid solution (150 c.c.) with bromine (4 c.c.; 4 mols.) (*J. pr. Chem.*, 1901, **64**, 510).

Bromination of 12-*Chloro*-10-*methyl*-7 : 12-*dihydrobenzophenarsazine.*—The tetrabromo-*p*-tolyl-β-naphthylamine which crystallised from the solution obtained by adding bromine (4 c.c.; 4 mols.) to the chloro-compound (6·85 g.) in boiling acetic acid (500 c.c.) was isolated in colourless silky needles, m. p. 165° (Found: Br, 58·6. Calc.: Br, 58·25%). It was identical with the tetrabromo-*p*-tolyl-β-naphthylamine obtained by brominating *p*-tolyl-β-naphthylamine as described for the isomeric substance (compare Friedländer, *Ber.*, 1883, **16**, 2078; bromination in carbon disulphide solution).

Bromination of 10-*Chloro*-5 : 10-*dihydrophenarsazine in* o-*Dichlorobenzene and in Carbon Tetrachloride at the Ordinary Temperature.*—When the chloro-compound (2·0 g. in 200 c.c. of *o*-dichlorobenzene or 1·4 g. in 300 c.c. of carbon tetrachloride) was treated with bromine (1·44 c.c. and 1 c.c., respectively; 4 mols.), hydrogen bromide was evolved and a red crystalline material separated. This was filtered off and washed with the solvent. On exposure to air, it lost bromine and left a yellow solid, from which, after recrystallisation from acetic acid or from acetone, only tetrabromodiphenylamine was obtained.

After 2 : 4 : 2′ : 4′(?)-Tetrabromodiphenylamine (9·7 g.), arsenious chloride (7·3 g.), and *o*-dichlorobenzene (25 c.c.) had been boiled for 14 hours, only unchanged materials were isolated.

Bromination of 10-*Bromo*-5 : 10-*dihydrophenarsazine in Presence of Sodium Acetate.*—The bromo-compound (2·0 g.) together with fused sodium acetate (5·0 g.) was dissolved in boiling acetic acid (50 c.c.), and the mixture treated with bromine (1·24 c.c.; 4 mols.). No hydrogen bromide was evolved, but crystalline material (inorganic) separated. The hot filtrate from this deposited tetrabromodiphenylamine (m. p. 186°) on cooling.

Bromination of Phenarsazinic Acid : Isolation of 2 : 4 : 6 : 8 : 10-*Pentabromo*-5 : 10-*dihydrophenarsazine.*—The following description is typical of several experiments. Phenarsazinic acid (11 g.) in boiling acetic acid (350 c.c.) was treated slowly with bromine (6 c.c.; 3 mols.). The bromine was decolourised, the liquid became yellow, and only a small quantity of hydrogen bromide was evolved. At the same time a yellow crystalline solid began to separate and after the addition of the bromine was completed it was separated from the boiling solution. The filtrate deposited tetrabromodiphenylamine in long needles on cooling. The yellow solid was repeatedly extracted with boiling acetic acid, in which it was only sparingly soluble, and so obtained free from tetrabromodiphenylamine. Finally it was recrystallised from benzene, in which also it was sparingly soluble, but more soluble than in acetic acid.

2 : 4 : 6 : 8 : 10-*Pentabromo*-5 : 10-*dihydrophenarsazine* (the yield varied from 2·5 to rather more than 4 g. in different experiments) was thus obtained in yellow needles, m. p. 275° (Found : C, 23·1; H, 1·0; N, 2·3; Br, 62·6, 62·6; As, 11·7, 11·6.* $C_{12}H_5NBr_5As$

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* Owing to the possibility of loss of volatile arsenic halide during the estimation of arsenic in this compound of high bromine content by the ordinary method, the determination of arsenic (and of bromine) was carried out as follows: The substance (about 0·6 g.) was heated in a sealed tube at 200—255° with fuming nitric acid (2 c.c.) and silver nitrate (about 1 g.) for 7 hours. The diluted contents of the tube were washed through a Gooch crucible, the silver halide was collected and weighed, and the filtrate and washings were

requires C, 22·6; H, 0·8; N, 2·2; Br, 62·7; As, 11·8%). The compound is not affected when boiled with a mixture of concentrated hydrobromic acid and acetic acid, and does not appear to be acted upon by bromine in acetic acid solution.

During the crystallisation of the pentabromo-compound from benzene, a colourless substance remained undissolved. It was obtained only in small quantity and proved to be 2 : 4 : 6 : 8-tetrabromophenarsazinic acid, described below.

2 : 4 : 6 : 8-*Tetrabromophenarsazinic Acid*.—The preceding substance (2·0 g.) in acetic acid (160 c.c.) was treated with hydrogen peroxide (20 vols.; 14 c.c.), and the mixture heated to boiling. Bromine was evolved and the yellow colour of the solid disappeared. Water (200 c.c.) was added and the mixture allowed to cool. The solid was filtered off and dissolved in boiling very dilute aqueous sodium hydroxide. The hot filtered solution was mixed with 20% aqueous sodium hydroxide until it just remained clear at the boiling point. On cooling, sodium 2 : 4 : 6 : 8-tetrabromophenarsazinate crystallised in colourless soft plates. It was dissolved in water, and the free *acid* precipitated as a somewhat gelatinous mass by the addition of hydrochloric acid. The acid crystallised from 90% acetic acid in colourless needles which began to decompose at about 294° (Found : Br, 54·2. $C_{12}H_6O_2NBr_4As$ requires Br, 54·1%).

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