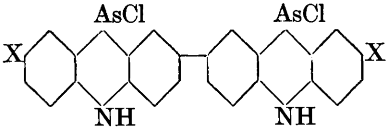
CCLXXXVII.—10 - *Chloro* - 5 : 10 - *dihydrophenarsazine and its Derivatives. Part VI. Compounds containing Two Nitrogen and Two Arsenic Atoms in Six- and Five-ringed Systems.*

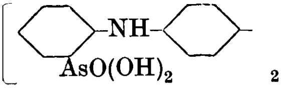
By Charles Stanley Gibson and John Dobney Andrew Johnson.

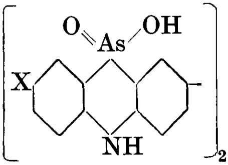
By employing and extending the methods of preparation and synthesis described in previous papers (J., 1926, 450, 464, 2241; 1927, 247, 2499), compounds of the type I (X = H or Me) can be obtained. If, for example, benzidine (1 mol.) be condensed with *o*-bromophenylarsinic acid (2 mols.), 4 : 4-*bis*(*diphenylamine*-2′-*arsinic acid*) (II) is obtained. This acid when reduced with sulphur dioxide in the presence of alcohol, hydrochloric acid, and a trace of iodine is readily converted into 2 : 2′-*bis*(10-*chloro*-5 : 10-*dihydrophenarsazine*) (I; X = H). The compound so obtained appears to be identical with that prepared by condensing *NN′*-diphenylbenzidine (1 mol.) with arsenious chloride (2 mols.). The only means of comparing these two products is by microscopic examination, since they are insoluble and their melting points cannot be determined in the ordinary way. By the methods already described, the chloro-

(I.)



(II.)





(III.)

compound (I; X = H) has been oxidised to 2 : 2′-*bis*(*phenarsazinic acid*) (III; X = H), and from the latter the corresponding *bromo*-compound is readily obtained by the usual method of reduction.

The condensation of *NN*′-di-*p*-tolylbenzidine with arsenious chloride gave 2 : 2′-*bis*(10-*chloro*-8-*methyl*-5 : 10-*dihydrophenarsazine*) (I; X = Me), from this 2 : 2′-*bis*(8-*methylphenarsazinic acid*) (III; X = Me) was obtained by oxidation, and the chloro-, *bromo*-, and *iodo*-compounds were prepared from the acid by reduction.

The above halogen compounds are intensely coloured, do not melt below 320°, and are practically insoluble in all the usual organic solvents. An acid of the type (II) can be recrystallised from dilute acetic acid, but acids of the type (III; X = H or Me) are insoluble in all solvents. They can, however, be purified conveniently through their crystalline disodium salts. This makes it possible to obtain the reduced halogen derivatives from them in a state of purity and, in the case of the chloro-compounds (I), these can be compared with the products of condensation of arsenious chloride and the di-secondary amines.

o-Bromophenylarsinic acid condensed with *o*-, *m*-, and *p*-phenylenediamines to give (IV) 1 : 2-, (V) 1 : 3-, and (VI) 1 : 4-*phenylenediaminodi*-o-*phenylarsinic acid*, respectively, but only the condensation with *m*-phenylenediamine was really satisfactory. The compound (IV) could not be purified and was reduced immediately in the presence of hydrochloric acid to 5 : 8-*dichloro*-13 : 14* : 5 : 8-*tetrahydro*iso*benzarsazinephenarsazine* (VII). This is the only possible constitution of a compound formed in this way. Owing to its sparing solubility, this compound could not be purified in the

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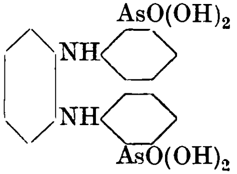
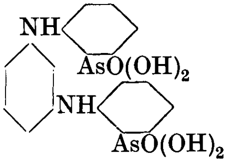
* For simplicity, it is preferred for these complex compounds to write the numbers of the hetero-atoms of lower atomic weight before those of the hetero-atoms of higher atomic weight in spite of the ordinary rule of order of numbering. This system is adhered to throughout this paper.

ordinary way, but by oxidising it to the diarsinic acid, freeing the latter from non-acidic impurities by solution in sodium hydroxide,

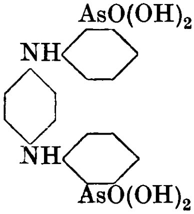
(IV.)

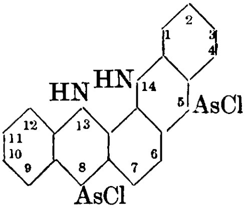




(V.)

(VI.)



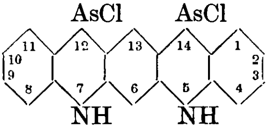


(VII.)

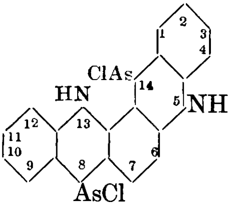
and again reducing the precipitated acid, it was obtained in a reasonable state of purity. Contrary to expectation, this compound was not produced by condensing *NN′*-diphenyl-*o*-phenylenediamine (1 mol.) (Clemo, Perkin, and Robinson, J., 1924, **125**, 1780; Gibson and Johnson, this vol., p. 1988) with arsenious chloride (2 mols.), but the preliminary change in colour noticed might indicate the formation of an intermediate compound (compare Burton and Gibson, J., 1926, 454).

After purification by crystallisation from acetic acid, the diarsinic acid (V), when reduced in the presence of hydrochloric acid, yielded without difficulty a compound which can have either formula (VIII) or (IX). The product was highly crystalline and bright yellow. It differed from the bright red compound, obtained by condensing pure *NN′*-diphenyl-*m*-phenylenediamine (1 mol.) with arsenious chloride (2 mols.) under the usual conditions, not only in colour but also in crystalline form when viewed under the microscope. The latter condensation product could also have a constitution represented by either (VIII) or (IX). When these two dichloro-compounds were separately oxidised to the diarsinic acids and these acids

(VIII.)



12 : 14-*Dichloro*-5 : 7 : 12 : 14-*tetrahydrobenzarsazinephenarsazine.*



(IX.)

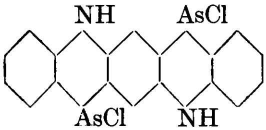
8 : 14-*Dichloro*-5 : 13 : 8 : 14-*tetrahydrobenzarsazinephenarsazine.*

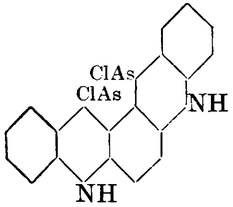
separately reduced back to dichloro-compounds, products having the same colour (yellow) but different properties were obtained. The insolubility of the compounds and the absence of melting points, however, prevented absolute comparisons being made. In spite of the apparent differences between the two dichloro-compounds, specimens of the diarsinic acid [5 : 7 : 12 : 14(or 5 : 13 : 8 : 14)-*benzarsazinicphenarsazinic acid*] prepared from both, when purified through the highly crystalline *disodium salt*, appeared to be identical. From this acid, by reduction in the presence of hydrobromic acid and hydriodic acid respectively, the sparingly soluble, highly crystalline, and coloured *dibromo-* and *di-iodo-*compounds were easily obtained.

When the above diarsinic acid was treated with hypophosphorous acid, no reduction took place until iodine was added, and the substance then precipitated was not the cacodyl compound but the above di-iodo-compound. The necessity for the presence of iodine (or hydriodic acid) for reduction of quinquevalent arsenic in organic compounds by hypophosphorous acid to take place has been pointed out by previous workers.

NN'-Diphenyl-*p*-phenylenediamine (1 mol.) condenses readily with arsenious chloride (2 mols.) and the compound produced may be either 7 : 14-*dichloro*-5 : 12 : 7 : 14-*tetrahydrobenzarsazinephenarsazine* (X) or 13 : 14-*dichloro*-5 : 8 : 13 : 14-*tetrahydrobenzarsazinephenarsazine* (XI). The product appeared to be homogeneous, and being sparingly soluble, was oxidised to the corresponding 5 : 12 : 7 : 14(or 5 : 8 : 13 : 14)-*benzarsazinicphenarsazinic acid*, which again was purified through its *disodium* salt. The acid when reduced in the presence of hydrochloric acid gave the above-mentioned dichloro-compound, an orange-red, highly crystalline substance which, like the isomeric substances, does not melt below 320°. Similarly, the *dibromo*-compound with analogous properties was obtained by reducing the acid in the presence of hydrobromic acid, but the di-iodo-compound could not be obtained pure.

(X.)





(XI.)

The work now described emphasises the highly crystalline nature and intense colour of the homologues of 10-chloro-5 : 10-dihydrophenarsazine and of the corresponding bromo- and iodo-compounds, even when these derivatives possess a much more complicated structure which renders them insoluble and high-melting solids.

EXPERIMENTAL.

4 : 4-*Bis*(*diphenylamine-2′-arsinic acid*) (II).—A mixture of benzidine (3·45 g.; 1 mol.), *o*-bromophenylarsinic acid (11·3 g.; 2 mols.), anhydrous potassium carbonate (8·8 g.), amyl alcohol (40 c.c.), and a trace of copper powder was boiled under reflux for 5 hours; the product was steam-distilled to remove amyl alcohol and filtered while hot. On acidifying the filtrate with dilute hydrochloric acid, a discoloured acid was precipitated. This was obtained as a white powder, unmelted at 320°, by recrystallisation from dilute acetic acid (Found : As, 25·3. $C_{24}H_{22}O_6N_2As_2$ requires As, 25·7%).

2 : 2′-*Bis*(10-*chloro*-5 : 10-*dihydrophenarsazine*) (I; X = H).—(*a*) The preceding compound (crude, 1·2 g.), dissolved in a hot mixture of alcohol (25 c.c.) and hydrochloric acid (20 c.c.) to which a trace of iodine had been added, was reduced by passing sulphur dioxide for a few minutes. The precipitated *chloro-compound* was washed with alcohol and ether and dried at 120° (Found : Cl, 12·7. $C_{24}H_{16}N_2Cl_2As_2$ requires Cl, 12·8%).

(*b*) *NN′*-Diphenylbenzidine (m. p. 250°; from toluene) was prepared from diphenylamine by the method described by Wieland and Wecker (*Ber.*, 1922, **55**, 1804) for the preparation of *NN′*-di-*p*-tolylbenzidine; yield, 60%. The method described by Wieland and Müller (*Ber.*, 1913, **46**, 3296) gives a poor yield, as Marqueyrol and Muraour (*Bull. Soc. chim.*, 1914, **15**, 186) have shown.

A mixture of *NN′*-diphenylbenzidine (23·1 g.; 1 mol.), arsenious chloride (27·8 g.; 2·2 mols.), and *o*-dichlorobenzene (100 c.c.) was boiled under reflux for 5 hours. (The mixture while still cold developed a greenish-blue coloration : this has been frequently noticed in other condensations of this type and it may indicate the formation of a primary addition compound which is subsequently transformed into the ring condensation product; compare Burton and Gibson, J., 1926, 454.) Hydrogen chloride was freely evolved as soon as boiling commenced, and solid matter began to separate after about 30 minutes. The liquid was filtered while hot, the residue washed several times with hot *o*-dichlorobenzene to remove unchanged soluble materials, and the last trace of *o*-dichlorobenzene removed from the product by heating at 160° for a short time. In this condensation, it is important that carefully purified materials should be used; otherwise, highly coloured by-products are formed and these render the purification of the main product a matter of considerable difficulty. Yield, 58% (Found : As, 26·9. $C_{24}H_{16}N_2Cl_2As_2$ requires As, 27·1%).

2 : 2′-*Bis*(10-*chloro*-5 : 10-*dihydrophenarsazine*) formed by either of the above methods is a pale orange-yellow, microcrystalline powder, insoluble in all the usual organic solvents and such solvents as acetylene tetrachloride, *o*-dichlorobenzene, and nitrobenzene. It is slightly soluble in boiling naphthalene and crystallises from it in minute prisms on cooling. It remains unmelted at 325°.

(*c*) 2 : 2′-Bis(10-chloro-5 : 10-dihydrophenarsazine) was also prepared from 2 : 2′-bis(phenarsazinic acid) by a similar method to that used for the corresponding bromo-compound (see below).

2 : 2′-*Bis*(*phenarsazinic acid*) (III; $X = H$).—The use of chloramine-T (Burton and Gibson, J., 1924, **125**, 2275) for the oxidation of the preceding compound was impracticable because of the insolubility of the latter in acetone or water. 2 : 2′-Bis-(10-chloro-5 : 10-dihydrophenarsazine) (5 g.) was boiled with acetic acid (100 c.c.) in order to obtain the substance in a fine state of division. To the cooled suspension, hydrogen peroxide (20 vol.; 16 c.c.) was added and the mixture carefully heated to boiling. The colour of the chloro-compound changed to greyish-brown and in about 5 minutes oxidation was completed. (Because of their insolubility in acetic acid, oxidation of the chloro-compounds described in this communication does not proceed so readily and completely as in the case of the substances previously described; compare J., 1927, 2514.) Water (250 c.c.) was added to the cooled mixture and the solid matter was filtered off, well washed with water, and boiled with dilute aqueous sodium hydroxide. The solution obtained was filtered from non-acidic substances and treated with 20% aqueous sodium hydroxide until the hot, deep brown solution began to deposit the colourless crystalline *disodium* salt. This was filtered off when cold, well drained on the filter, dissolved in a small quantity of hot water, and reprecipitated as before with 20% sodium hydroxide solution. The disodium salt prepared in this way was obtained in short colourless needles, slightly soluble in cold water and more soluble in hot. For analysis, it was well washed with ice-cold water and dried at 160—165° (Found: Na, 7·6. $C_{24}H_{16}O_4N_2As_2Na_2$ requires Na, 7·8%). From a solution of the disodium salt in warm water, dilute hydrochloric acid precipitated 2 : 2′-*bis*(*phenarsazinic acid*) as a white and somewhat gelatinous precipitate (3·5 g.). It was washed with water and dried at 140—145° (Found: As, 27·3. $C_{24}H_{18}O_4N_2As_2$ requires As, 27·35%).

2 : 2′-Bis(phenarsazinic acid) is a white amorphous powder insoluble in the ordinary organic solvents and remains unmelted at 325°. As it was insoluble in a hot mixture of alcohol and hydrochloric acid, attempts to prepare a hydrochloride were unsuccessful. The potassium salt resembles the sodium salt; the magnesium,

calcium, and barium salts are white microcrystalline precipitates; the mercurous and mercuric salts are heavy white precipitates, the latter somewhat crystalline; the silver salt is a white curdy precipitate soluble in ammonia; and the cupric salt is a pale greenish-blue, curdy precipitate. The acid itself is soluble in ammonia, but, being such a weak acid, is precipitated on boiling, ammonia escaping. Attempts to reduce the acid in acetic acid suspension to a cacodyl compound by means of hypophosphorous acid were unsuccessful.

2 : 2′-*Bis*(10-*bromo*-5 : 10-*dihydrophenarsazine*) (formula as I) was prepared by reducing with sulphur dioxide a suspension of 2 : 2′-bis-(phenarsazinic acid) (1·8 g.) in a hot mixture of alcohol (20 c.c.) and hydrobromic acid (const. b. p.; 12 c.c.) to which a trace of iodine had been added, an orange-yellow colour being developed; the precipitate was washed with alcohol and dried at 140° (Found : Br, 24·7. $C_{24}H_{16}N_2Br_2As_2$ requires Br, 24·9%).

2 : 2′-*Bis*(10-*chloro*-8-*methyl*-5 : 10-*dihydrophenarsazine*) (I; X = Me) was prepared from arsenious chloride (10·5 g.), *NN*′-di-*p*-tolylbenzidine [prepared according to the method of Wieland and Wecker (*loc. cit.*) and obtained as colourless plates, m. p. 234°, much more soluble in toluene than *NN*′-diphenylbenzidine] (9·5 g.), and *o*-dichlorobenzene (38 c.c.) as described for 2 : 2′-bis(10-chloro-5 : 10-dihydrophenarsazine); yield, 64%. It was obtained in small orange-red crystals (Found : Cl, 12·4. $C_{26}H_{20}N_2Cl_2As_2$ requires Cl, 12·2%).

It was also prepared by reducing with sulphur dioxide a hot suspension of 2 : 2′-bis(8-methylphenarsazinic acid) (1·2 g.; see below) in alcohol (25 c.c.) and hydrochloric acid (20 c.c.) containing a trace of iodine. Owing to the insolubility of the acid and of the chloro-compound it was necessary to heat the mixture for 30 minutes on the water-bath and to shake it frequently in order to obtain complete reduction. The product was washed with alcohol–hydrochloric acid and with alcohol and dried at 140° (Found : Cl, 12·1. $C_{26}H_{20}N_2Cl_2As_2$ requires Cl, 12·2%).

2 : 2′-*Bis*(8-*methylphenarsazinic acid*) (III; X = Me) was prepared in 64% yield by oxidising the preceding compound (9·5 g.) in acetic acid (150 c.c.) suspension with hydrogen peroxide (20 vol.; 32 c.c.) as described for 2 : 2′-bis(phenarsazinic acid). It was purified through its *disodium* salt, which forms short colourless needles closely resembling in properties the disodium salt of 2 : 2′-bis(phenarsazinic acid). The salt was washed with 90% alcohol, absolute alcohol, and ether and dried at 140—150° (Found : Na, 7·5. $C_{26}H_{20}O_4N_2As_2Na_2$ requires Na, 7·4%). When a warm aqueous solution of the disodium salt was acidified with dilute

hydrochloric acid, 2 : 2′-*bis*(8-*methylphenarsazinic acid*) was precipitated as a white amorphous powder. It does not melt at 320° (Found: As, 26·0. $C_{26}H_{22}O_4N_2As_2$ requires As, 26·0%).

2 : 2′-*Bis*(10-*bromo*-8-*methyl*-5 : 10-*dihydrophenarsazine*) (formula as I; X = Me) was prepared from the preceding acid (1·0 g.), suspended in a boiling mixture of alcohol (25 c.c.) and hydrobromic acid (const. b. p.; 20 c.c.) containing a trace of iodine, as described for the preceding chloro-compound. It was a red micro-crystalline substance. For analysis it was dried at 140° (Found: Br, 22·8. $C_{26}H_{20}N_2Br_2As_2$ requires Br, 22·7%).

2 : 2′-*Bis*(10-*iodo*-8-*methyl*-5 : 10-*dihydrophenarsazine*) was prepared in a similar manner to the corresponding chloro-compound from 2 : 2′-bis(8-methylphenarsazinic acid) (1·4 g.), alcohol (25 c.c.), and hydriodic acid (approx. 30%; 20 c.c.). It was a purplish-red solid which was unmelted at 320° (Found: I, 32·9. $C_{26}H_{20}N_2I_2As_2$ requires I, 33·2%).

5 : 8-*Dichloro*-13 : 14 : 5 : 8-*tetrahydro*iso*benzarsazinephenarsazine* (VII).—The condensation of *o*-phenylenediamine (5·3 g.; 1 mol.) with *o*-bromophenylarsinic acid (27·4 g.; 2 mols.) by boiling with potassium carbonate (21·4 g.), a trace of copper powder, and amyl alcohol (100 c.c.) for 5 hours gave a very discoloured product. All attempts to purify it in the ordinary way were unsuccessful. The crude product (2·0 g.), dissolved in a boiling mixture of alcohol (20 c.c.) and hydrochloric acid (16 c.c.) containing a trace of iodine, was reduced with sulphur dioxide in the usual way and a discoloured product again resulted. Since this could not be crystallised, it (3·4 g.) was suspended in acetic acid (30 c.c.) and oxidised with hydrogen peroxide (20 vol.; 4·2 c.c.) as previously described. The insoluble product was dissolved in hot dilute aqueous sodium hydroxide, the solution filtered, and the filtrate acidified. The precipitated acid was reduced again as just described. The precipitated *chloro-compound* was dark brown, insoluble in all the usual solvents, and remained unmelted at 320° (Found: Cl, 15·15. $C_{18}H_{12}N_2Cl_2As_2$ requires Cl, 14·9%).

1 : 3-*Phenylenediaminodi*-o-*phenylarsinic Acid* (V).—A mixture of *m*-phenylenediamine (m. p. 95°; 5·26 g.; 1 mol.), *o*-bromophenylarsinic acid (27·4 g.; 2 mols.), anhydrous potassium carbonate (21·4 g.), amyl alcohol (100 c.c.), and a trace of copper powder was boiled under reflux for 5 hours. The product was worked up as described for 4 : 4-bis(diphenylamine-2′-arsinic acid). The somewhat discoloured *acid* obtained (22% yield) was crystallised with difficulty from dilute acetic acid and dried at 160° (Found: As, 29·25. $C_{18}H_{18}O_6N_2As_2$ requires As, 29·5%). It is a colourless solid, unmelted at 325°, insoluble in water, sparingly soluble in

glacial acetic acid and in dilute mineral acids. Its ready solubility in a mixture of hydrochloric acid and alcohol distinguishes it from the corresponding ring acid.

12 : 14(or 8 : 14)-*Dichloro*-5 : 7 : 12 : 14(or 5 : 13 : 8 : 14)-*tetrahydrobenzarsazinephenarsazine* (VIII or IX) was prepared by reducing a boiling solution of the preceding acid (5·4 g.) in alcohol (54 c.c.) and hydrochloric acid (43 c.c.) in the usual way. The precipitated chloro-compound (69% yield) was washed with alcohol and dried at 140°. It formed clusters of slender yellow prisms (Found: As, 31·25; Cl, 14·5. $C_{18}H_{12}N_2Cl_2As_2$ requires As, 31·4; Cl, 14·9%).

When *NN'*-diphenyl-*m*-phenylenediamine (5·95 g.), arsenious chloride (9·17 g.), and *o*-dichlorobenzene (34 c.c.) were boiled for 5 hours, stout red prisms formed, which were filtered off from the hot solution, washed with hot *o*-dichlorobenzene and with benzene, and dried at 140° (yield, 7·75 g.; 71%) (Found: Cl, 15·1%).

The products of these two preparations remained unmelted at 320° but did not appear to be identical. Apart from their differences in colour and crystalline form when viewed under the microscope, the former had a more pronounced effect on the mucous membrane than the latter. The diarsinic acid obtained from each on oxidation (see below) gave on reduction a chloro-compound: that derived originally from 1 : 3-phenylenediaminodi-*o*-phenylarsinic acid had a marked tendency to crystallise and a marked effect on the mucous membrane, whereas that derived originally from *NN'*-diphenyl-*m*-phenylenediamine was amorphous and had no effect on the mucous membrane. Both substances were sufficiently soluble in acetone to impart to it a yellow colour, which was discharged on addition of an equal volume of a dilute aqueous solution of chloramine-T, a small quantity of a white substance (unmelted at 325°) being precipitated.

5 : 7 : 12 : 14(or 5 : 13 : 8 : 14)-*Benzarsazinicphenarsazinic acid* was prepared from either form of the foregoing compound by oxidation with hydrogen peroxide in glacial acetic suspension, as described for 2 : 2'-bis(phenarsazinic acid), the quantities being proportional. The product was purified through the *disodium* salt, which formed colourless soft needles, almost insoluble in cold or hot 20% aqueous sodium hydroxide and but slightly soluble in cold water. For analysis, the salt was washed with 90% alcohol, absolute alcohol, and ether and dried at 140—145° (Found: Na, 9·1. $C_{18}H_{12}O_4N_2As_2Na_2$ requires Na, 8·9%). When first precipitated, the free *acid* was somewhat gelatinous, but it was finally obtained as a white amorphous powder similar in properties to the other arsinic acids described in this communication (Found: As, 31·8. $C_{18}H_{14}O_4N_2As_2$ requires

As, 31·8%). The acid also forms crystalline calcium and barium salts, both insoluble in hot and in cold water, a white gelatinous silver salt soluble in aqueous ammonia, heavy white gelatinous lead and mercuric salts, a pale yellow gelatinous mercurous salt, and a brown gelatinous ferric salt.

12 : 14(or 8 : 14)-*Dibromo*-5 : 7 : 12 : 14(or 5 : 13 : 8 : 14)-*tetrahydrobenzarsazinephenarsazine.*—A hot suspension of the preceding compound (1·0 g.) in alcohol (20 c.c.) and hydrobromic acid (const. b. p.; 16 c.c.) containing a trace of iodine was reduced in the usual way. The product was washed with a mixture of alcohol and hydrobromic acid, then with alcohol and ether, and dried at 150° (Found: Br, 27·95. $C_{18}H_{12}N_2Br_2As_2$ requires Br, 28·3%). It crystallised in deep yellow prisms and remained unmelted at 325°.

12 : 14(or 8 : 14)-*Di-iodo*-5 : 7 : 12 : 14(or 5 : 13 : 8 : 14)-*tetrahydrobenzarsazinephenarsazine.*—(*a*) This was prepared in a similar manner to the preceding dibromo-compound (Found: I, 38·1. $C_{18}H_{12}N_2I_2As_2$ requires I, 38·5%). It was a deep red, microcrystalline powder resembling the bromo- and chloro-compounds in general properties. It is somewhat interesting that when 5 : 7 : 12 : 14(or 5 : 13 : 8 : 14)-benzarsazinicphenarsazinic acid is boiled with a mixture of alcohol and concentrated hydriodic acid no reduction of the arsenic takes place.

(*b*) 5 : 7 : 12 : 14(or 5 : 13 : 8 : 14)-Benzarsazinicphenarsazinic acid (0·8 g.) was boiled with acetic acid (20 c.c.) and to the hot suspension hypophosphorous acid (*d* 1·136; 10 c.c.) was added. No reduction took place. On addition of iodine (3·3 g.) in small portions to the boiling suspension, a vigorous reaction took place and a deep red, microcrystalline powder was precipitated. This substance was formed as soon as the first trace of iodine was added and no signs of the preliminary formation of a cacodyl compound were observed. When all the iodine had been added, the liquid was treated with a further 30 c.c. of acetic acid, cooled, and filtered. The product, washed with acetic acid, alcohol, and ether and dried at 140°, appeared to be identical with that obtained as described under (*a*) (Found: I, 38·0%).

On warming the above dichloro-compound with dilute ammonia on the water-bath for an hour, the colour changed from yellow to greyish-white. The product was readily soluble in hot or cold *n*-propyl and benzyl alcohols and also in hot glacial acetic acid, thus behaving exactly like 10 : 10′-oxy-5 : 10-dihydrophenarsazine (Burton and Gibson, J., 1926, 462).

The condensation of *p*-phenylenediamine with *o*-bromophenylarsinic acid, carried out as described for *m*-phenylenediamine, gave a much discoloured product which it was found impossible to purify.

7 : 14(or 13 : 14)-*Dichloro*-5 : 12 : 7 : 14(or 5 : 8 : 13 : 14)-*tetrahydrobenzarsazinephenarsazine* (X or XI) was prepared by boiling *NN'*-diphenyl-*p*-phenylenediamine (m. p. 145°; 15·6 g.; 1 mol.), arsenious chloride (24·1 g.; 2·2 mols.), and *o*-dichlorobenzene (90 c.c.) for 5 hours under reflux. The product (yield, 49%) was worked up as in similar condensations, being finally washed with benzene and dried at 130° (Found: Cl, 14·9. $C_{18}H_{12}N_2Cl_2As_2$ requires Cl, 14·9%). It was unmelted at 320°. When it was oxidised to the arsinic acid (see below), and this reduced in the manner described for similar substances, the chloro-compound was reobtained in orange-red, doubly refracting, prismatic needles (Found: Cl, 14·6%).

5 : 12 : 7 : 14(or 5 : 8 : 13 : 14)-*Benzarsazinicphenarsazinic Acid*.—The oxidation of the preceding compound (12·2 g.) with hydrogen peroxide (20 vol.; 20 c.c.) in acetic acid (122 c.c.) suspension was carried out as described for 2 : 2'-bis(phenarsazinic acid), but the reaction took a somewhat longer time. Water (244 c.c.) was added and, after cooling, the crude acid was filtered off and purified through the *disodium* salt. On addition of 20% sodium hydroxide solution to the hot discoloured solution of the disodium salt, the latter was precipitated in large flat plates. This particular disodium salt appeared to crystallise the most easily of all the disodium salts in this series. The salt was purified by dissolving it in warm water, adding 33% sodium hydroxide solution, and allowing the salt to crystallise slowly; it was then obtained in colourless flat plates and needle-shaped crystals. The salt can also be crystallised from aqueous acetone. For analysis, it was washed with 90% alcohol and absolute alcohol and dried at 140° (Found: Na, 8·8. $C_{18}H_{12}O_4N_2As_2Na_2$ requires Na, 8·9%).

5 : 12 : 7 : 14(or 5 : 8 : 13 : 14)-*Benzarsazinicphenarsazinic acid* was precipitated by the addition of hydrochloric acid to a warm aqueous solution of the preceding sodium salt. It was recrystallised with difficulty from dilute acetic acid and obtained in colourless rhomb-shaped plates, which did not melt at 320° although slight darkening took place somewhat above 290° (Found: As, 31·6. $C_{18}H_{14}O_4N_2As_2$ requires As, 31·8%). It was sparingly soluble in hot glacial acetic acid and insoluble in water. Although the acid was slightly soluble in a mixture of alcohol and hydrochloric acid, the hydrochloride was not isolated. The salts resemble those of the isomeric acid except that the calcium salt appears to be slightly soluble in water.

7 : 14(or 13 : 14)-*Dibromo*-5 : 12 : 7 : 14(or 5 : 8 : 13 : 14)-*tetrahydrobenzarsazinephenarsazine*.—The preceding acid (0·75 g.), suspended in a hot mixture of alcohol (18 c.c.) and hydrobromic acid (38%; 15 c.c.) containing a trace of iodine, was reduced as described

for the chloro-compound. The product formed deep red, doubly refracting, prismatic needles resembling those of the chloro-compound. It was unmelted at 320° and insoluble in all the usual solvents (Found: Br, 27·9. $C_{18}H_{12}N_2Br_2As_2$ requires Br, 28·3%).

The di-iodo compound was prepared in an analogous manner or by the hypophosphorous acid reduction method but could not be purified.

We wish to thank Mr. C. M. Roberts, Assistant in the Chemistry Department, for valuable help in some of the preparative work connected with this investigation.

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[*Received, June 6th*, 1928.]