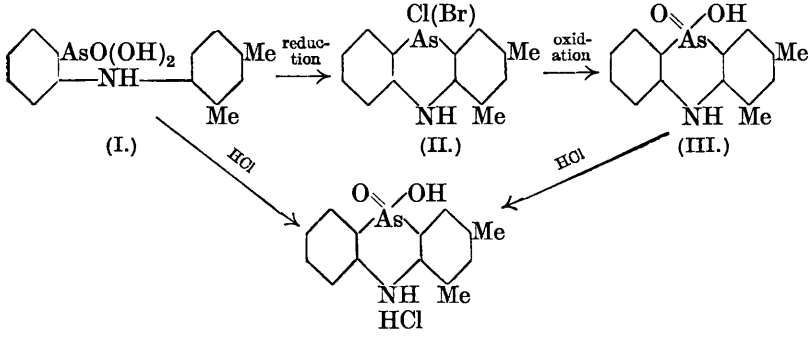
CCCLXVI.—10-*Chloro*-5 : 10-*dihydrophenarsazine and its Derivatives. Part XI. Mono-, Di-, and Tri-methyl Derivatives.*

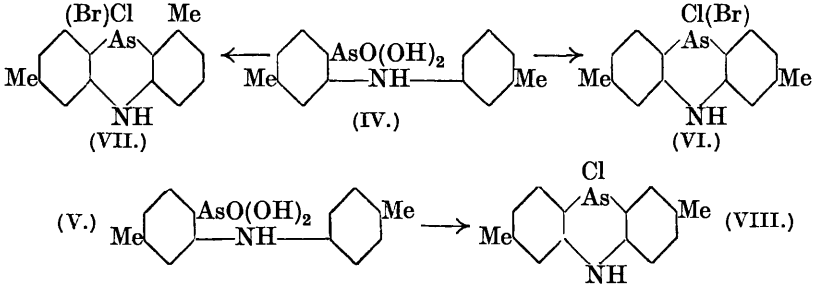
By CHARLES STANLEY GIBSON and JOHN DOBNEY ANDREW JOHNSON.

IN Part IX (this vol., p. 1229) the hypothesis was developed that, when substituted diphenylamine-6′-arsinic acids are reduced in hydrochloric acid–alcohol solution, the nature of the isolable product is dependent upon the nature of the substituting group or groups. Only those diphenylamine-6′-arsinic acids in which a nitro-group is in the ortho-position to the :NH group yield isolable dichloroarsines, with one exception, 5-nitro-2-methyldiphenylamine-6′-arsinic acid, an explanation of the anomalous behaviour of which was given on a stereochemical basis (*loc. cit.*, p. 1241). It is a consequence of the hypothesis that diphenylamine-6′-arsinic acids containing only methyl groups as substituents should yield derivatives of 10-chloro-5 : 10-dihydrophenarsazine directly on reduction, the intermediate dichloroarsines being too unstable to exist. The reduction of a number of monomethyldiphenylamine-6′-arsinic acids has already been described (Gibson and Johnson, J., 1927, 2508, 2510; this vol., pp. 779, 785, 786) and that work has now been extended to di- and tri-methyldiphenylamine-6′-arsinic acids.

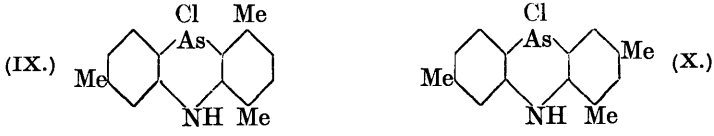
The condensation of *o*-bromophenylarsinic acid and 4-amino-*m*-xylene gave a good yield of 2 : 4-*dimethyldiphenylamine-6′-arsinic acid* (I), purified through its ammonium salt. On reduction under the conditions previously described, 10-*chloro*(*bromo*)-2 : 4-*dimethyl*-5 : 10-*dihydrophenarsazine* (II) was obtained, no dichloro- or dibromo-arsine being isolated. On oxidation, the chloro-compound yielded the corresponding *phenarsazinic acid* (III), which gave a hydrochloride identical with that obtained by boiling 2 : 4-dimethyldiphenylamine-6′-arsinic acid (I) with concentrated hydrochloric acid.



In a similar manner, by condensing 3-bromo-*p*-tolylarsinic acid with *m*-toluidine and with *p*-toluidine, 3 : 3′-*dimethyldiphenylamine*-6′-*arsinic acid* (IV) and 4 : 3′-*dimethyldiphenylamine*-6′-*arsinic acid* (V), respectively, were obtained, and these acids on reduction gave 10-*chloro*(*bromo*)*dimethyl*-5 : 10-*dihydrophenarsazines* directly. In the case of the former arsinic acid (IV), ring closure might lead to the formation of two isomeric cyclic substances, (VI) and (VII), but the reduction product appeared to be homogeneous. Ring closure of the arsinic acids (IV) and (V) was also readily effected by boiling with concentrated hydrochloric acid, the *hydrochlorides* of the cyclic acids being formed.



The crude condensation products of 3-bromo-*p*-tolylarsinic acid with 2-amino-*p*-xylene and with 4-amino-*m*-xylene could not be readily purified, but on reduction of the crude acids, 10-*chloro*-1 : 4 : 7-*trimethyl*-5 : 10-*dihydrophenarsazine* (IX) and 10-*chloro*-2 : 4 : 7-*trimethyl*-5 : 10-*dihydrophenarsazine* (X), respectively, were obtained.



2 : 4 : 7-*Trimethylphenarsazinic acid hydrochloride* was also obtained on boiling the crude condensation product of 3-bromo-*p*-tolylarsinic acid and 4-amino-*m*-xylene with concentrated hydrochloric acid. The 10-chlorotrimethyl-5 : 10-dihydrophenarsazines are characterised by having much greater solubilities in benzene than that of the parent substance.

The above results seem to be in accordance with the views previously expressed. Careful observations showed that during the reduction of the diphenylamine-6′-arsinic acids, unless care be taken to ensure otherwise, the hydrochlorides of the cyclic phenarsazinic acids separate from the liquids and may escape reduction. It would

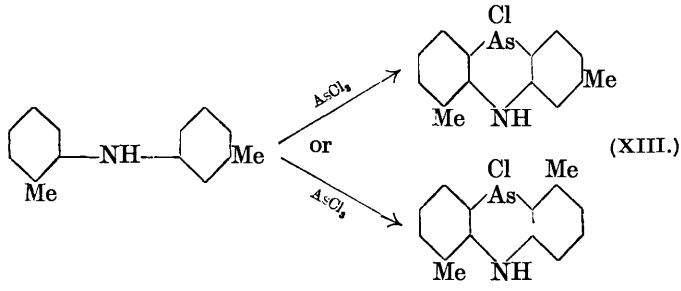
appear, then, that cyclisation of the methyldiphenylamine-6′-arsinic acids is effected by means of the concentrated hydrochloric acid, the hydrochloride of the phenarsazinic acid then being reduced to the 10-chloro-5 : 10-dihydrophenarsazine derivative. This view was foreshadowed in Part VII (this vol., p. 773).

From the results obtained in the earlier stages of these investigations (J., 1926, 2243, footnote) it appeared that the condensation of arsenious chloride with substituted diphenylamines only took place when all the ortho-positions relative to the :NH group were free, except in the case of phenylene-substituting groups. The preparation of many substituted diphenylamines having been greatly facilitated by the work of Chapman (J., 1925, **127**, 1992; 1927, 1743; this vol., p. 569), it has been possible to carry out further work on the condensation of methyldiphenylamines with arsenious chloride and so to test more completely the previous conclusions. Phenyl-*o*-tolylamine was prepared by the hydrolysis of its *benzoyl* derivative (XII), produced by the isomerisation of N-o-*tolylbenziminophenyl ether* (XI).

$$\underset{\text{(XI.)}}{C_7H_7\cdot N{:}CPh\cdot OPh} \xrightarrow{280\text{—}300^\circ} \underset{\text{(XII.)}}{C_7H_7\cdot NPh\cdot COPh} \longrightarrow C_7H_7\cdot NHPh$$

It readily condensed with arsenious chloride in *o*-dichlorobenzene solution, the product, 10-chloro-4-methyl-5 : 10-dihydrophenarsazine, being identical with that prepared by reducing 2-methyldiphenylamine-6′-arsinic acid (Gibson and Johnson, J., 1927, 2510).

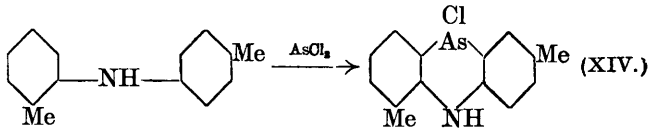
Similarly, o-*tolyl*-m-*tolylamine* prepared by hydrolysis of its *benzoyl* derivative, produced by the isomerisation of N-o-*tolylbenzimino*-m-*tolyl ether* and of *N*-*m*-tolylbenzimino-*o*-tolyl ether (which could not be obtained in the crystalline condition), condensed readily with arsenious chloride to give an apparently homogeneous product, 10-*chloro*-1(or 3) : 6-*dimethyl*-5 : 10-*dihydrophenarsazine* (XIII).



(XIII.)

o-*Tolyl*-p-*tolylamine*, prepared similarly from N-p-*tolylbenzimino*-o-*tolyl ether*, also condensed readily with arsenious chloride to give

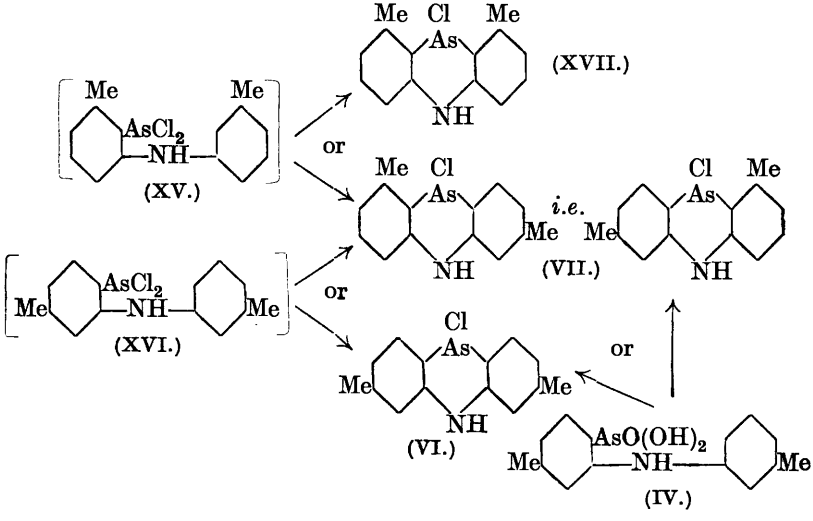
10-*chloro*-2 : 6-*dimethyl*-5 : 10-*dihydrophenarsazine* (XIV). From this it appears that the factors underlying the condensation of



(XIV.)

substituted diphenylamines with arsenious chloride are somewhat different from those previously postulated and it is proposed to review this problem in a future communication.

Recently Rasuwajew (*Ber.*, 1929, **62**, 1218) described the condensation product of di-*m*-tolylamine and arsenious chloride as a yellow crystalline substance, m. p. 250—252°. This product could be one of three substances, *viz.*, 1 : 9-, 1 : 7-, or 3 : 7-dimethyl-10-chloro-5 : 10-dihydrophenarsazine, (XVII), (VII) or (VI), respectively. Rasuwajew mentions the possibility of the formation of only two of the isomerides, *viz.*, the 1 : 9- (described as the 4 : 5-) and the 3 : 7- (described as the 2 : 7-) compounds. We have found that the reduction of 3 : 3′-diphenylamine-6′-arsinic acid (IV) gave a chloro-compound, decomposing at 225—226°, which is different from that obtained by Rasuwajew. It seems reasonable to assume that when a diphenylamine condenses with arsenious chloride a



dichloroarsine is the intermediate stage (compare J., 1926, 454). This intermediate stage in the condensation of di-*m*-tolylamine and arsenious chloride must be either (XV) or (XVI). Now the intermediate stage cannot be (XVI), because then the final product would

be either (VII) or (VI) and identical with the product which we have obtained by the reduction of (IV). Rasuwajew's product, being different, must be derived from the intermediate stage (XV) and therefore at least one of the methyl groups in his condensation product must be in the ortho-position to the :AsCl group, provided that one can assume, which seems reasonable, that the direction of ring closure of (IV) by hydrochloric acid is the same as the direction of ring closure of (XVI).

EXPERIMENTAL.

N-o-Tolylbenziminochloride (Just, *Ber.*, 1886, **19**, 982) has b. p. 164°/6 mm. and 189°/18 mm. (yield, 76%). *N-p*-Tolylbenziminochloride (*ibid.*, p. 980) has b. p. 186°/10 mm. (yield, 72%).

N-2 : 4-*Dimethylphenylbenziminochloride*, $CPhCl{:}N{\cdot}C_6H_3Me_2$, was obtained in 70% yield by heating on the water-bath a mixture of 4-benzamido-*m*-xylene (22·8 g.) and phosphorus pentachloride (21·1 g.) until a homogeneous liquid resulted and then distilling this under reduced pressure. The product distilled at 175°/6 mm. and solidified to a pale yellow substance, m. p. 42° (Found : Cl, 15·1. $C_{15}H_{14}NCl$ requires Cl, 14·6%).

N-p-*Tolylbenzimino*-o-*tolyl ether* was prepared from *N-p*-tolylbenziminochloride (45·9 g.) in ether (100 c.c.), *o*-cresol (21·6 g.), sodium (4·6 g.), and alcohol (80 c.c.) as previously described (this vol., p. 1475) for *N-m*-tolylbenziminophenyl ether. It was recrystallised from alcohol and obtained in colourless prisms, m. p. 54° (Found : N, 4·8. $C_{21}H_{19}ON$ requires N, 4·65%). The yield was moderately good.

N-o-*Tolylbenzimino*-o-*tolyl ether*, prepared in a similar manner, crystallised, on standing under reduced pressure, after one week. When recrystallised from alcohol, it was obtained in colourless prismatic needles, m. p. 63—64° (yield, 68%) (Found : N, 4·5%).

N-m-*Tolylbenzimino*-o-*tolyl ether* crystallised after standing under reduced pressure for 6 days. When recrystallised from alcohol, it was obtained in colourless needles, m. p. 51—52° (Found : N, 4·6%).

N-m-*Tolylbenzimino*-p-*tolyl ether* was obtained in 58% yield in colourless prismatic needles when crystallised from alcohol. It had m. p. 52—53° (Found : N, 4·6%).

N-o-Tolylbenzimino-*p*-tolyl ether and *N-p*-tolylbenzimino-*m*-tolyl ether were not obtained in the crystalline condition.

N-o-*Tolylbenziminophenyl ether*, prepared from *N-o*-tolylbenziminochloride (68·7 g.) in ether (150 c.c.), phenol (28·2 g.), sodium (6·9 g.), and alcohol (120 c.c.), was obtained in colourless prismatic needles, m. p. 54—56°, from methyl alcohol (yield, 68%) (Found : N, 4·8. $C_{20}H_{17}ON$ requires N, 4·9%).

N-*o*-Tolylbenzimino-*m*-tolyl ether could not be induced to crystallise; it isomerised completely, however, on being heated at 280—300° for 2 hours. The product, which crystallised readily from a small quantity of alcohol in colourless prisms, m. p. 103–104°, was identical with the *benzoyl*-o-*tolyl*-m-*tolylamine* prepared by heating *N*-*m*-tolylbenzimino-*o*-tolyl ether under similar conditions (Found: N, 4·7. $C_{21}H_{19}ON$ requires N, 4·65%).

The isomerisation of all the above ethers to the benzoyl derivatives of the substituted diphenylamines was effected by heating at 280—300° for 2 hours.

Benzoylphenyl-o-*tolylamine* crystallised in clusters of colourless prisms, m. p. 110—111°, from alcohol (Found: N, 5·0. $C_{20}H_{17}ON$ requires N, 4·9%).

Benzoyldi-o-*tolylamine*, m. p. 114—115° (Found: N, 4·8. $C_{21}H_{19}ON$ requires N, 4·65%), and *benzoyl*-m-*tolyl*-p-*tolylamine*, m. p. 118—119° (Found: N, 4·65%), both crystallised from alcohol in small colourless prisms.

The product of the isomerisation of *N*-*p*-tolylbenzimino-*o*-tolyl ether (31 g.) could not be obtained crystalline, but it was readily hydrolysed under the conditions previously described (this vol., p. 1475). The o-*tolyl*-p-*tolylamine* (12·3 g.) distilled at 183°/19 mm. as a pale yellow liquid, which did not crystallise when cooled in a freezing mixture (Found: N, 7·2. $C_{14}H_{15}N$ requires N, 7·1%).

Phenyl-*o*-tolylamine (b. p. 175—177°/22 mm.) and o-*tolyl*-m-*tolylamine* [b. p. 187°/22 mm. (Found: N, 7·6. $C_{14}H_{15}N$ requires N, 7·1%)] were obtained in satisfactory yield by the hydrolysis of the corresponding benzoyl derivatives. Both compounds were obtained as pale yellow oils which remained unsolidified at −15°, although they became very viscous at that temperature. The benzoyl derivative of di-*o*-tolylamine was not hydrolysed by the usual method even when the boiling was continued for 12 hours.

Condensation of Phenyl-o-*tolylamine and Arsenious Chloride.*—A mixture of phenyl-*o*-tolylamine (26 g.), arsenious chloride (28·4 g.), and *o*-dichlorobenzene was boiled for 4 hours. Hydrogen chloride was freely evolved and the liquid became green. On cooling, 10-chloro-4-methyl-5:10-dihydrophenarsazine was deposited. It was recrystallised from benzene and obtained in yellow needles, m. p. 191—192° (yield, 63%) (Found: As, 26·0. Calc. for $C_{13}H_{11}NClAs$: As, 25·7%. Compare Gibson and Johnson, J., 1927, 2510).

10-*Chloro*-2:6-*dimethyl*-5:10-*dihydrophenarsazine* (XIV) was similarly prepared from *o*-tolyl-*p*-tolylamine (5·1 g.), arsenious chloride (5·2 g.), and *o*-dichlorobenzene (10 c.c.), the crude product being washed with *o*-dichlorobenzene and with benzene and crystal-

lised from acetic acid. It was obtained in yellow needles, m. p. indefinite, about 226° (decomp.) (Found : As, 25·0. $C_{14}H_{13}NClAs$ requires As, 24·5%).

2 : 5-*Dimethylphenarsazinic acid* was obtained by oxidising the preceding substance (4·2 g.) in boiling acetic acid solution (50 c.c.) with hydrogen peroxide (20-vol.; 17 c.c.) in the manner already described (this vol., p. 780). It crystallised from slightly diluted acetic acid in small colourless needles, which remained unmelted at 310°. It is insoluble in water and moderately easily soluble in acetic acid. It dissolves in concentrated sulphuric acid to a deep olive-green solution (Found : As, 24·8. $C_{14}H_{14}O_2NAs$ requires As, 24·8%). The sodium salt is sparingly soluble in 20% sodium hydroxide solution, the barium salt forms colourless needles, and the silver and mercuric salts are white amorphous precipitates. When the acid was dissolved in a hot mixture of alcohol and concentrated hydrochloric acid, concentrated hydrochloric acid added until crystals began to separate, and the solution allowed to cool, the *hydrochloride* was deposited in colourless needles, which turned green at 208° and finally decomposed vigorously, turning black at 266—268°. This hydrochloride differs in composition from many hydrochlorides of the same class (Found : Cl, 15·05, 15·3. $2C_{14}H_{14}O_2NAs$, 3HCl requires Cl, 14·9%).

10-*Chloro*-1(or 3) : 6-*dimethyl*-5 : 10-*dihydrophenarsazine* (XIII) was obtained by condensing *o*-tolyl-*m*-tolylamine (18·8 g.) and arsenious chloride (19·2 g.) in *o*-dichlorobenzene solution (36 c.c.) in the usual way. It crystallised from benzene in bright yellow needles, m. p. 216—218° (decomp.) after slight shrinking and darkening. The main product appeared to be homogeneous and only a small quantity of a lower-melting and more soluble fraction was obtained. The indefinite melting point (190—196°) of this fraction was raised on admixture with the main product (Found in pure substance : As, 24·7. $C_{14}H_{13}NClAs$ requires As, 24·5%).

1(or 3) : 6-*Dimethylphenarsazinic Acid*.—The preceding substance was oxidised in acetic acid suspension by means of hydrogen peroxide; the *acid* obtained crystallised from slightly diluted acetic acid in small colourless needles, unmelted at 309° (Found : As, 24·1. $C_{14}H_{14}O_2NAs$ requires As, 24·8%). The sodium salt (from 20% sodium hydroxide solution) and the ammonium salt (from 0·880 ammonia solution) both crystallised in thin colourless needles.

2 : 4-*Dimethyldiphenylamine*-6′-*arsinic Acid* (I).—A mixture of 4-amino-*m*-xylene (10·8 g.), *o*-bromophenylarsinic acid (25·0 g.), potassium carbonate (19·4 g.), amyl alcohol (78 c.c.), and a trace of copper powder was boiled for 5 hours. Volatile substances were

removed by steam distillation and the aqueous solution, after treatment with decolorising charcoal, was filtered, cooled, and acidified with dilute hydrochloric acid. For purification, the crude acid (52% yield) was dissolved in a small volume of ammonia solution (equal volumes of water and 0·880 ammonia solution) by gentle warming, care being taken to avoid loss of much ammonia by excessive heating. Ammonia solution (*d* 0·880) was then added in moderate excess, and the liquid cooled. The ammonium salt, which separated from the green solution in colourless flat plates, was filtered off, washed with a little concentrated ammonia solution, well drained, and dissolved in a little warm water, the solution was acidified with glacial acetic acid, and a further quantity of acetic acid was added until a homogeneous solution was obtained at the boiling point. The boiling liquid was treated with decolorising charcoal to remove impurities which would otherwise cause the acid to separate as a gum and was then allowed to cool slowly. 2:4-*Dimethyldiphenylamine*-6′-*arsinic acid* was deposited in slender colourless needles and after recrystallisation from dilute acetic acid had m. p. 135° (Found: As, 23·05. $C_{14}H_{16}O_3NAs$ requires As, 23·4%). The acid is readily soluble in alcohol, acetone, and acetic acid, but insoluble in water. The sodium salt is precipitated slowly from its solution in 20% aqueous sodium hydroxide in colourless, short, flat prisms. The calcium salt, which forms colourless flat plates, is more soluble in cold than in hot water; the barium salt is similar in appearance to the calcium salt; and the salts of the heavy metals are amorphous precipitates.

10-*Chloro*-2:4-*dimethyl*-5:10-*dihydrophenarsazine* (II).—A boiling solution of the preceding acid (crude, 11·6 g.) in a mixture of alcohol (45 c.c.) and hydrochloric acid (30 c.c.) containing a trace of iodine was reduced with sulphur dioxide. The reduction *product* crystallised from benzene in yellow needles, m. p. 216—217° (Found: Cl, 11·8. $C_{14}H_{13}NClAs$ requires Cl, 11·6%). It is readily soluble in acetone and hot benzene, but only sparingly soluble in alcohol and ligroin. The corresponding *bromo*-compound was obtained by reducing a boiling solution of 2:4-dimethylphenarsazinic acid (see below; 0·75 g.) in a mixture of alcohol (10 c.c.) and hydrobromic acid (36%; 10 c.c.) in a similar manner. It crystallised from benzene in orange-coloured needles, decomposing at 198° after softening from 195° (Found: Br, 23·2. $C_{14}H_{13}NBrAs$ requires Br, 22·8%).

2:4-*Dimethylphenarsazinic acid* (III) was obtained by oxidising 10-chloro-2:4-dimethyl-5:10-dihydrophenarsazine with hydrogen peroxide in the manner described above. It crystallised from dilute acetic acid (75%) in colourless flat prisms, unmelted at 300° (Found: As, 24·4. $C_{14}H_{14}O_2NAs$ requires As, 24·8%). With

concentrated sulphuric acid, it gives a deep olive-green colour. It is insoluble in water and alcohol. The salts are very well defined. The sodium salt, from 20% sodium hydroxide solution, crystallises in soft colourless needles; the ammonium salt crystallises in colourless prismatic needles even from somewhat dilute solutions; the barium salt also crystallises in colourless needles; the calcium salt crystallises in clusters of colourless needles; and the magnesium salt, formed only on boiling, forms clusters of colourless prisms. The silver salt is slightly soluble in hot water and crystallises on cooling in colourless nodules. The *hydrochloride* of the phenarsazinic acid was obtained either by allowing a solution of the acid in a hot mixture of alcohol and hydrochloric acid to cool, or by boiling 2 : 4-dimethyldiphenylamine-6'-arsinic acid with concentrated hydrochloric acid for 2 minutes, adding alcohol until a homogeneous solution was obtained, and allowing this to cool. Its melting point, or rather, its decomposition point, varies greatly with the rate of heating, the average value being about 200° (Found : Cl, 10·4. $C_{14}H_{14}O_2NAs,HCl$ requires Cl, 10·4%).

4 : 3'-*Dimethyldiphenylamine*-6'-*arsinic Acid* (V).—A mixture of 3-bromo-*p*-tolylarsinic acid (23·6 g.), *p*-toluidine (8·62 g.), potassium carbonate (17·6 g.), amyl alcohol (70 c.c.), and a trace of copper powder was boiled for 5 hours. The crude *acid* (75% yield), isolated as described for the above isomeric acid, was purified through the ammonium salt in the manner already described. It crystallised from 20% acetic acid in colourless thin needles, m. p. 153—154° (slight decomp.) (Found : As, 23·7. $C_{14}H_{16}O_3NAs$ requires As, 23·4%). The sodium salt, long prismatic needles from 20% sodium hydroxide solution, and the barium salt, rhombic plates slightly soluble in hot water, are the most characteristic salts. When the acid was boiled with concentrated hydrochloric acid, the hydrochloride of the cyclic acid (below) was obtained.

10-*Chloro*-2 : 7-*dimethyl*-5 : 10-*dihydrophenarsazine* (VIII) was prepared by reducing the preceding acid in the usual manner. It crystallised from acetic acid in clusters of yellow needles containing one molecule of acetic acid of crystallisation, not removed on heating at 120°. It turned green at 190—195° and decomposed vigorously at 195—198° (Found : Cl, 9·8. $C_{14}H_{13}NClAs,C_2H_4O_2$ requires Cl, 9·7%).

10-*Bromo*-2 : 7-*dimethyl*-5 : 10-*dihydrophenarsazine*, prepared in an analogous manner, crystallised from benzene in orange needles, m. p. 179—180° (Found : Br, 23·0. $C_{14}H_{13}NBrAs$ requires Br, 22·8%).

2 : 7-*Dimethylphenarsazinic acid*, prepared by the oxidation of 10-chloro-2 : 7-dimethyl-5 : 10-dihydrophenarsazine (2·5 g.) in acetic

acid solution (50 c.c.) with hydrogen peroxide (20-vol.; 10 c.c.) in the usual manner, was purified by conversion into its sodium salt, which was insoluble in 20% sodium hydroxide solution. The acid regenerated from the crystalline sodium salt could not be recrystallised from the usual media. Its m. p. was above 295° (Found : As, 24·6. $C_{14}H_{14}O_2NAs$ requires As, 24·8%). The salts are characteristic. The ammonium salt crystallises even from dilute solutions in soft colourless needles; the calcium, barium and magnesium salts crystallise in glistening colourless needles. The acid gives with concentrated sulphuric acid a blue colour, turning red on addition of concentrated nitric acid. The *hydrochloride* forms clusters of colourless needles, decomp. 219—221° (Found : Cl, 10·6. $C_{14}H_{14}O_2NAs,HCl$ requires Cl, 10·4%).

3 : 3′-*Dimethyldiphenylamine*-6′-*arsinic acid* (IV) was prepared from 3-bromo-*p*-tolylarsinic acid and *m*-toluidine as described above for the isomeric 4 : 3′-dimethyldiphenylamine-6′-arsinic acid. The purification of the crude acid (73% yield) was effected through the ammonium salt in a similar manner. The acid tended to separate from its solution in dilute acetic acid first as an oil and then as a solid. After decantation from the oil, the hot clear liquid deposited the arsinic acid in a crystalline form on cooling. The oily matter later solidified and by further purification through the ammonium salt a further quantity of the crystalline arsinic acid was obtained. Recrystallised from dilute acetic acid, 3 : 3′-dimethyldiphenylamine-6′-arsinic acid was obtained in clusters of feathery needles, m. p. 145—146° after slight softening (Found : As, 23·1. $C_{14}H_{16}O_3NAs$ requires As, 23·4%). The ammonium salt, soft colourless needles, the barium salt, colourless, rhomb-shaped, flat plates, and the sodium salt, deposited slowly in colourless needles from its solution in 20% aqueous sodium hydroxide, are the most characteristic salts.

10-*Chloro*-1(or 3) : 7-*dimethyl*-5 : 10-*dihydrophenarsazine* (VI or VII) was prepared by reducing the preceding acid in the usual manner. When crystallised from acetic acid, it appeared homogeneous and was obtained in yellow needles, turning green at 218° and decomposing at 225—226°. It was sparingly soluble in acetone and in benzene (Found : Cl, 11·5. $C_{14}H_{13}NClAs$ requires Cl, 11·6%). The *bromo*-compound, prepared in an analogous manner, crystallised from benzene in orange-coloured needles, m. p. 255—256° (decomp.) (Found : Br, 21·4. $C_{14}H_{13}NBrAs$ requires Br, 21·0%).

1(or 3) : 7-*Dimethylphenarsazinic acid* was prepared by oxidation of the preceding chloro-compound in the usual manner. It was purified through its sodium salt as described for 2 : 7-dimethyl-

phenarsazinic acid. It could not be recrystallised and remained unmelted at 295° (Found : As, 24·8. $C_{14}H_{14}O_2NAs$ requires As, 24·8%). The *hydrochloride*, prepared either from the cyclic acid or by boiling 3 : 3′-dimethyldiphenylamine-6′-arsinic acid with concentrated hydrochloric acid, had no melting point, but darkened and shrank at 217—219° (Found : Cl, 10·6. $C_{14}H_{14}O_2NAs,HCl$ requires Cl, 10·4%).

The condensation of 3-bromo-*p*-tolylarsinic acid and *o*-toluidine gave a product which could not be purified and the reduction product was also unsatisfactory.

10-*Chloro*-2 : 4 : 7-*trimethyl*-5 : 10-*dihydrophenarsazine* (X).—A mixture of 3-bromo-*p*-tolylarsinic acid (23·6 g.), 4-amino-*m*-xylene (8·0 g.), potassium carbonate (17·6 g.), amyl alcohol (70 c.c.), and a trace of copper powder was boiled for 5 hours. The acid, isolated in the usual manner, could not be purified directly and most of it was reduced in the usual way. During the reduction, there was a marked tendency for the hydrochloride of the cyclic acid to separate and the quantities of alcohol and of hydrochloric acid had therefore to be somewhat larger than usual. The *product* crystallised from a little benzene in yellow needles, m. p. 220—222° (decomp.) (Found : Cl, 11·15. $C_{15}H_{15}NClAs$ requires Cl, 11·1%). It is soluble in acetone, remarkably soluble in hot benzene, and appreciably soluble in the cold solvent.

2 : 4 : 7-*Trimethylphenarsazinic acid hydrochloride* was prepared by boiling the crude condensation product of 4-amino-*m*-xylene and 3-bromo-*p*-tolylarsinic acid with concentrated hydrochloric acid for a few minutes, adding alcohol until a homogeneous solution was obtained, and allowing this to cool. The crystalline material which separated was recrystallised from alcohol–concentrated hydrochloric acid and obtained in colourless needles, decomp. 235—236° (turning green) (Found : Cl, 10·5. $C_{15}H_{16}O_2NAs,HCl$ requires Cl, 10·0%).

10-*Chloro*-1 : 4 : 7-*trimethyl*-5 : 10-*dihydrophenarsazine* (IX), prepared in the usual manner by reducing the crude condensation product from 3-bromo-*p*-tolylarsinic acid and 2-amino-*p*-xylene, was recrystallised from benzene, in which it was remarkably soluble, and obtained in yellow needles, m. p. 200—202° after slight softening (Found : As, 23·5. $C_{15}H_{15}NClAs$ requires As, 23·5%).

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