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

By LESLIE ALDERMAN ELSON and CHARLES STANLEY GIBSON.

PREVIOUS work in this series has shown that condensation between arsenious chloride and substituted diphenylamines ordinarily produces 5 : 10-dihydrophenarsazine derivatives, but that it does not take place (i) when at least one nitro-group is present, as in *o*-nitro-, *m*-nitro-, *p*-nitro-, 4 : 4′-dinitro-, and 2 : 4-dinitro-diphenylamines, (ii) when an amino-group occupies one ortho-position, as in *o*-aminodiphenylamine, (iii) when two amino-groups are present, *e.g.*, the cases of 2 : 4-diamino- and 4 : 4′-diamino-diphenylamines, (iv) when an alkyl or acyl group is substituted for the hydrogen in the NH group, *e.g.*, *N*-methyl-, *N*-formyl-, *N*-acetyl-, and *N*-benzoyl-diphenylamines, (v) when the benzene nuclei are fully reduced, *e.g.*, di*cyclo*hexylamine, and (vi) in the unique case of *NN′*-diphenyl-*o*-phenylenediamine, the corresponding *m*-phenylene- and *p*-phenylene-compounds readily undergoing condensation.

The last failure may be due to steric hindrance; (ii), (iii), and (v) may be explained by the stability of the addition compounds of arsenious chloride and highly basic diphenylamine derivatives, for the initial formation of which, in the reaction, evidence has been brought forward (J., 1926, 454; *Rec. trav. chim.*, 1930, **49**, 1021), and (iv) may be due to the hydrogen of the NH group playing an essential part in the changes leading to the final condensation product. As regards (i), it may be that the nitro-group reduces the basicity of diphenylamine to such an extent that the initial compound formation mentioned above does not take place at all.

To obtain more information regarding the reaction we have made a systematic study of the condensation of arsenious chloride and eleven chlorine-substituted diphenylamines: the condensations with *m*-chloro-, *p*-chloro-, and 4 : 4′-dichloro-diphenylamines to give 1(or 3) : 10-dichloro-, 2 : 10-dichloro-, and 2 : 8 : 10-trichloro-5 : 10-dihydrophenarsazines respectively have already been described (Burton and Gibson, J., 1926, 2243).

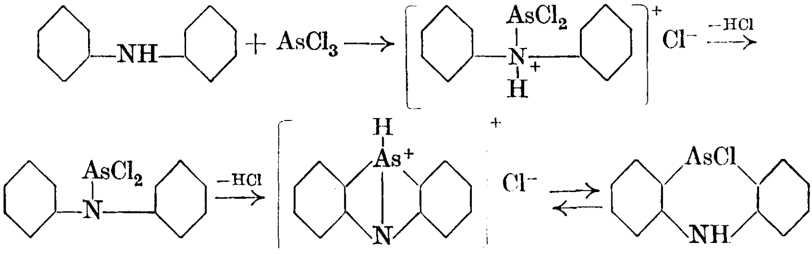
The following new substituted diphenylamines have been prepared. (*a*) By Ullmann's method (*Annalen*, 1907, **355**, 312): o-*chlorodiphenylamine*,* 2 : 5-*dichlorodiphenylamine*, 3 : 4-*dichlorodiphenylamine* (from 3 : 4-*dichlorodiphenylamine*-2′-*carboxylic acid*), 3 : 5-*dichlorodiphenylamine* (from 3 : 5-*dichlorodiphenylamine*-2′-*carboxylic acid*), 3 : 4 : 5-*trichlorodiphenylamine* (from 3 : 4 : 5-*trichlorodiphenylamine*-2′-*carboxylic acid*), and 5-*chloro*-2-*methyldiphenylamine* (from 5-*chloro*-2-*methyldiphenylamine*-2′-*carboxylic acid*); (*b*) by Chapman's method (J., 1929, 569): 3 : 4′-*dichlorodiphenylamine* (from N-3-*chlorophenylbenzimino*-4-*chlorophenyl ether*), 3 : 3′-*dichlorodiphenylamine*, 3′-*chloro*-2-*methyldiphenylamine* (by hydrolysis of *benzoyl*-3′-*chloro*-2-*methyldiphenylamine*), 4′-*chloro*-2-*methyldiphenylamine* (from N-4-*chlorophenylbenzimino*-2-*methylphenyl ether*),

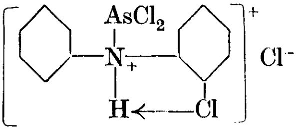
---

* Although described by several authors (compare Chapman, *loc. cit.*), this compound does not appear to have been analysed previously.

and 2′ : 4′-*dichloro-2-methyldiphenylamine* (from N-o-*tolylbenzimino-2 : 4-dichlorophenyl ether*).*

Condensation with arsenious chloride, producing derivatives of 5 : 10-dihydrophenarsazine, proceeded in all but four cases, *viz.*, *o*-chlorodiphenylamine, 2 : 4-dichlorodiphenylamine, 2 : 5-dichlorodiphenylamine, and 2′ : 4′-dichloro-2-methyldiphenylamine. A chlorine atom, therefore, unlike a nitro-group, prevents condensation taking place only when it is in the ortho-position in a diphenylamine. This is strong evidence in favour of the view (Gibson, Johnson, and Vining, *Rec. trav. chim.*, 1930, **49**, 1011) that, if the mechanism of the condensation of a diphenylamine and arsenious chloride is as follows, the reaction in the case of an *o*-chlorodiphenylamine does not proceed beyond the first stage because of the formation of the chelate compound (A) (compare Gibson and Johnson, J., 1929, 1229; Gibson, Hiscocks, Johnson, and Jones, J., 1930, 1622; for confirmatory analogies in the anthracene series, see Barnett and Wiltshire, *Ber.*, 1930, **63**, 1114).





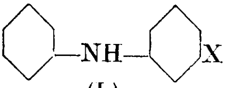
(A)

The possibility of the production of two isomeric 5 : 10-dihydrophenarsazines from substituted diphenylamines (by condensation with arsenious chloride) of type (I) or from diphenylamine-6′-arsinic acids (by ring closure, accompanied by reduction) of type (II) has been discussed (J., 1926, 2242; 1927, 1229, 2499; 1928, 2204; 1929, 757, 1473, 2743; 1930, 1124, 1622). Compounds of types (III) and (IV) can also each give rise theoretically to two

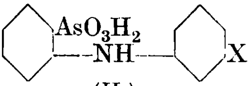
---

* *Benzoyl-2′-chloro-2-methyldiphenylamine* (from N-o-*tolylbenzimino-2-chlorophenyl ether*) could not be hydrolysed to 2′-chloro-2-methyldiphenylamine and therefore the condensation of this compound with arsenious chloride could not be investigated. From the results described in this paper, it may be predicted that the condensation will not proceed.

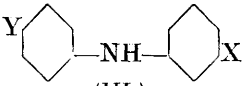
isomeric 5 : 10-dihydrophenarsazines, and from compounds of type (V) three such isomerides are possible if X and Y are identical,



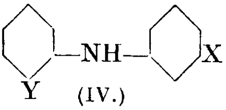
(I.)



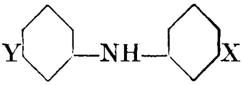
(II.)



(III.)



(IV.)



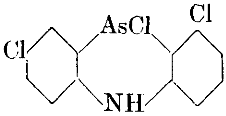
(V.)

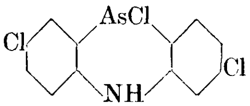
(X and Y may or may not be identical)

and four if they are different. So far, in no case have two isomerides been obtained from a compound of type (I) or (II).

The condensation of 3 : 4′-*dichlorodiphenylamine* (type III) with arsenious chloride gave a mixture of two isomeric compounds, which must be the 1 : 8 : 10 and 3 : 8 : 10-*trichloro*-5 : 10-*dihydrophenarsazines* (VI*a* and *b*). On the other hand, the product from

(VI*a*.)

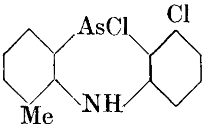


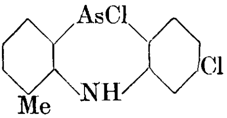


(VI*b*.)

3′-chloro-2-methyldiphenylamine (type IV) was apparently homogeneous, and must be 1(or 3) : 10-*dichloro*-6-*methyl*-5 : 10-*dihydrophenarsazine* (VII*a* or *b*). The condensation product of 3 : 3′-

(VII*a*.)



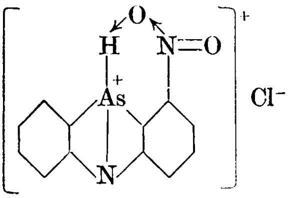


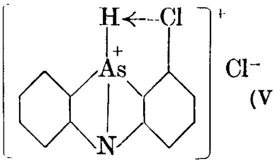
(VII*b*.)

dichlorodiphenylamine (type V) with arsenious chloride was also apparently homogeneous and, as far as our information goes, it must be described as 1 : 7 : 10 (or 1 : 9 : 10 or 3 : 7 : 10)-*trichloro*-5 : 10-*dihydrophenarsazine* (compare the production of a homogeneous 5 : 10-dihydrophenarsazine from 3-nitro-3′-methyldiphenylamine-6′-arsinic acid, where two isomerides are theoretically possible; Gibson and Johnson, J., 1929, 1236).

The difficulties which may arise in attempting to orientate the homogeneous product from a reaction which theoretically should give rise to at least two isomeric compounds have been discussed at length in one particular case (J., 1929, 767, 1473). It has had to be concluded, however, that the homogeneous 5 : 10-dihydrophenarsazine derivative produced from 3-nitrodiphenylamine-6′-arsinic acid (type II) is 10-chloro-1-nitro-5 : 10-dihydrophenarsazine and not the 3-nitro-compound because of its colour and especially because of the nature of its absorption spectra (Gibson and Johnson, J., 1929, 1229; Gibson, Hiscocks, Johnson, and Jones, *loc. cit.*), and, further, that those heterocyclic arsenic compounds which have the nitro-group in the 1-position have, as salts, a constitution which, in the case of the compound referred to above, is represented as (VIII*a*).

(VIII*a*.)



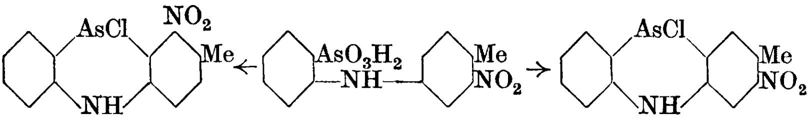


(VIII*b*.)

From this it would appear that the possibility of chelation involving a chlorine atom makes it probable that the isomeride most likely to be produced from the compounds now under discussion is that in which the chlorine atom is in the 1-position and, in the simplest example, the homogeneous product from the condensation of arsenious chloride and *m*-chlorodiphenylamine (Burton and Gibson, *loc. cit.*) is 1-chloro-5 : 10-dihydrophenarsazine having, as a salt, the constitution (VIII*b*).

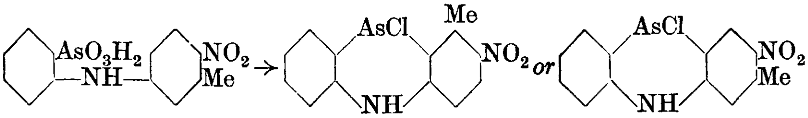
On account of such chelation, the 1-chloro-compounds should have lower melting points than the isomeric 3-chloro-compounds and it is suggested that, of the two compounds (VI), the one having the lower melting point should be given the constitution (VI*a*). Further, if, as appears from the analogous nitro-compounds, there is a greater tendency to form that isomeride (when at least two are theoretically possible) which can yield a chelate substance, then the constitution (VII*a*) should be assigned to compound (VII) and the trichlorodihydrophenarsazine mentioned above should be the 1 : 7 : 10- or the 1 : 9 : 10-trichloro-compound.

Prior to the isolation of the two compounds (VI*a* and *b*), in only one case had the simultaneous production of the two possible isomerides been realised, *viz.*, the production of the two compounds (X*a* and *b*) from compound (IX) (of a more complicated type than the above compounds) by ring closure, accompanied by reduction, in the presence of hydrochloric acid. To the red, lower-melting



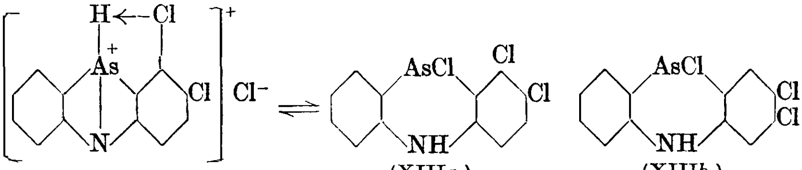
(X*a*.) (IX.) (X*b*.)

(with decomposition) isomeride Gibson and Johnson (*loc. cit.*) assigned the constitution (X*a*) and to the yellow, higher-melting (with decomposition) isomeride the constitution (X*b*), additional evidence in favour of these constitutions being obtained from the absorption spectra of the compounds (Gibson, Hiscocks, Johnson, and Jones, *loc. cit.*). This is another example of the production of two possible isomerides in one of which (X*a*) chelation is possible. It is significant that the product of the same reaction with compound (XI) was apparently homogeneous and, whether its constitution is (XII*a*) or (XII*b*), no chelation of the above kind is possible.



(XI.) (XII*a*.) (XII*b*.)

The two possible isomerides are also produced in the condensation of arsenious chloride with 3 : 4-*dichlorodiphenylamine*. Their constitutions must be as shown (XIII), and to the isomeride of lower melting point and higher solubility is assigned the constitution of 1 : 2 : 10-*trichloro*-5 : 10-*dihydrophenarsazine* (XIII*a*), in which chelation of the type mentioned above is possible. The same two isomerides have been isolated by ring closure, accompanied by reduction, in the presence of hydrochloric acid of 3 : 4-*dichlorodiphenylamine*-6′-*arsinic acid* [belonging to the same type as compound (IX)].



(XIII*a*.) (XIII*b*.)

EXPERIMENTAL.

o-*Chlorodiphenylamine*, obtained by heating 2-chlorodiphenylamine-2′-carboxylic acid (Ullmann, *Annalen*, 1907, **355**, 312) at 300—320° for 5 hours, distilled under reduced pressure as a colourless oil, b. p. 174—175°/12 mm., which solidified on cooling; m. p. 15—16° (Found : Cl, 17·5. $C_{12}H_{10}NCl$ requires Cl, 17·4%).

2 : 5-*Dichlorodiphenylamine*, prepared similarly from 2 : 5-dichlorodiphenylamine-2′-carboxylic acid (Gomberg and Tabern, *J. Amer. Chem. Soc.*, 1926, **48**, 1356), had b. p. 195°/17 mm. (yield, 85%). It did not solidify when cooled to − 16° (Found : Cl, 29·2. $C_{12}H_9NCl_2$ requires Cl, 29·8%).

3 : 4-*Dichlorodiphenylamine-2′-carboxylic Acid.*—A mixture of 3 : 4-dichloroaniline (60 g.), potassium *o*-chlorobenzoate (40 g.), amyl alcohol (96 c.c.), and a trace of copper powder was boiled for 6 hours. The mixture was made alkaline with sodium hydroxide, amyl alcohol and unchanged amine were removed by steam distillation, the residue was boiled with charcoal, and the filtrate acidified with hydrochloric acid. The precipitated *acid* was recrystallised from benzene and obtained in pale yellow, flat prisms, m. p. 178° (Found : Cl, 25·0. $C_{13}H_9O_2NCl_2$ requires Cl, 25·2%).

3 : 4-*Dichlorodiphenylamine.*—The preceding compound was heated for 4 hours at 280—290°, and the product distilled under reduced pressure. It had b. p. 218—220°/20 mm. (yield, 75%). The solidified product crystallised from alcohol in colourless plates, m. p. 69° (Found : Cl, 29·2. $C_{12}H_9NCl_2$ requires Cl, 29·8%).

3 : 5-*Dichlorodiphenylamine-2′-carboxylic acid*, prepared from 3 : 5-dichloroaniline by the method described for the analogous 3 : 4-dichloro-compound, crystallised from alcohol in colourless soft needles, m. p. 245° (Found : Cl, 24·8. $C_{13}H_9O_2NCl_2$ requires Cl, 25·2%).

3 : 5-*Dichlorodiphenylamine*, obtained by heating the preceding compound at 280—290° for 4 hours, had b. p. 200°/12 mm.; it did not solidify when cooled to − 16° (yield, 74%) (Found : Cl, 29·5. $C_{12}H_9NCl_2$ requires Cl, 29·8%).

3 : 4 : 5-*Trichlorodiphenylamine-2′-carboxylic acid*, prepared from 3 : 4 : 5-trichloroaniline in the usual manner, crystallised from alcohol in colourless needles, m. p. 238° (Found : Cl, 33·1. $C_{13}H_8O_2NCl_3$ requires Cl, 33·6%).

3 : 4 : 5-*Trichlorodiphenylamine*, prepared by heating the preceding compound at 290—300° for 2½ hours, distilled at 248°/20 mm. It crystallised from alcohol in colourless prisms, m. p. 83—85°, and when recrystallised from ligroin (b. p. 60—80°) it had m. p. 85° (Found : Cl, 39·2. $C_{12}H_8NCl_3$ requires Cl, 40·0%).

5-*Chloro-2-methyldiphenylamine-2′-carboxylic acid* was prepared from 4-chloro-*o*-toluidine and potassium *o*-chlorobenzoate. It crystallised from acetic acid in pale yellow needles, m. p. 200° (Found : N, 5·6. $C_{14}H_{12}O_2NCl$ requires N, 5·4%).

5-*Chloro-2-methyldiphenylamine*, obtained by heating the preceding acid at 290° for 4 hours, had b. p. 205—207°/23 mm.; it did not solidify when cooled to − 16° (Found : N, 6·6. $C_{13}H_{12}NCl$ requires N, 6·4%).

Benz-*m*-chloroanilideiminochloride (Chapman, J., 1927, 1746), b. p. 199—200°/10 mm., was obtained from benz-*m*-chloroanilide and phosphorus pentachloride in 92% yield.

N-3-*Chlorophenylbenzimino-4-chlorophenyl Ether.*—*p*-Chlorophenol

(12 g.) was added to a solution of sodium (1·7 g.) in alcohol (26 c.c.); to this solution, after cooling, was added a solution of the preceding compound (18 g.) in ether (36 c.c.), and the mixture kept for 16 hours. After evaporation of most of the solvents, the residue was poured into water, the oil which separated was extracted with ether, and the extract washed with aqueous sodium hydroxide and with water and dried with calcium chloride. After evaporation of the ether, the product solidified on cooling. It was recrystallised from alcohol and obtained in colourless prisms, m. p. 77° (Found: Cl, 20·0. $C_{19}H_{13}ONCl_2$ requires Cl, 20·7%).

3 : 4′-*Dichlorodiphenylamine.*—The preceding ether was isomerised by being heated for 2 hours at 290°. The benzoyl derivative of 3 : 4′-dichlorodiphenylamine thus obtained, being resinous and difficult to crystallise, was not purified but was hydrolysed by boiling for 2 hours with alcoholic potassium hydroxide (alcohol, 200 c.c.; potassium hydroxide, 50% aqueous solution, 80 c.c.). The alcohol was evaporated, the residue treated with water and extracted with ether, and the extract washed with water and dried with calcium chloride. After evaporation of the ether, the *diphenylamine* was distilled under reduced pressure. It had b. p. 235°/25 mm. and solidified on cooling. When recrystallised from alcohol it was obtained in almost colourless prisms, m. p. 63—64° (Found: Cl, 29·1. $C_{12}H_9NCl_2$ requires Cl, 29·8%).

3 : 3′-*Dichlorodiphenylamine.*—*N*-3-Chlorophenylbenzimino-3-chlorophenyl ether, prepared from benz-*m*-chloroanilideiminochloride and *m*-chlorophenol, did not solidify after standing for 4 months. It was isomerised by being heated at 290° for 2 hours and the benzoyl derivative thus obtained was hydrolysed by boiling with alcoholic potassium hydroxide. 3 : 3′-*Dichlorodiphenylamine* was obtained as a colourless oil rapidly darkening on exposure to air. It had b. p. 225—230°/18 mm. and did not solidify when cooled to − 16° (Found: Cl, 29·2. $C_{12}H_9NCl_2$ requires Cl, 29·8%).

N-o-*Tolylbenzimino-2-chlorophenyl ether*, prepared from benz-*o*-toluidideiminochloride and *o*-chlorophenol, solidified on being mixed with water. It crystallised in colourless well-formed prisms, m. p. 64° (Found: N, 4·7. $C_{20}H_{16}ONCl$ requires N, 4·4%).

Benzoyl-2′-chloro-2-methyldiphenylamine, obtained by heating the preceding compound at 290° for 2 hours, crystallised from alcohol in colourless prisms, m. p. 132° (Found: Cl, 10·9. $C_{10}H_{16}ONCl$ requires Cl, 11·0%). The compound could not be hydrolysed by the usual methods.

Benzoyl-3′-chloro-2-methyldiphenylamine.—*N*-*o*-Tolylbenzimino-3-chlorophenyl ether, prepared from benz-*o*-toluidideiminochloride and *m*-chlorophenol, did not solidify after prolonged standing and was isomerised by heating at 290° for 2 hours. The *benzoyl* derivative was obtained in colourless prisms, m. p. 106°, by recrystallisation from alcohol (Found : N, 4·8%).

3'-*Chloro*-2-*methyldiphenylamine* was obtained by hydrolysis of the preceding compound with alcoholic potassium hydroxide. It had b. p. 203°/20 mm. and did not solidify in a freezing mixture (Found : N, 6·55. $C_{13}H_{12}NCl$ requires N, 6·4%).

N-4-*Chlorophenylbenzimino*-o-*tolyl ether*, prepared from benz-4-chloroanilideiminochloride and *o*-cresol, solidified when mixed with water; it crystallised from alcohol in colourless prisms, m. p. 65° (Found : Cl, 10·6. $C_{20}H_{16}ONCl$ requires Cl, 11·0%).

4'-*Chloro*-2-*methyldiphenylamine*.—The benzoyl derivative obtained by the isomerisation of the preceding ether was not obtained crystalline and was hydrolysed in the usual way, 4'-*chloro*-2-*methyldiphenylamine* being obtained as a colourless oil, b. p. 200—205°/20 mm. It rapidly darkened on exposure to air and did not solidify when cooled to − 16° (Found : Cl, 16·1. $C_{13}H_{12}NCl$ requires Cl, 16·3%).

N-o-*Tolylbenzimino*-2 : 4-*dichlorophenyl ether*, obtained from benz-*o*-toluidideiminochloride and 2 : 4-dichlorophenol, solidified after standing for 10 days in a vacuum desiccator. When recrystallised from methyl alcohol, it was obtained in colourless prisms, m. p. 53° (Found : N, 4·0. $C_{20}H_{15}ONCl_2$ requires N, 3·9%).

2' : 4'-*Dichloro*-2-*methyldiphenylamine*.—Benzoyl-2' : 4'-dichloro-2-methyldiphenylamine, the product of the isomerisation of the preceding compound, was not obtained crystalline and was hydrolysed in the usual manner. 2' : 4'-*Dichloro*-2-*methyldiphenylamine* had b. p. 205°/20 mm. and crystallised from alcohol in colourless prisms, m. p. 48° (Found : N, 5·5; Cl, 28·1. $C_{13}H_{11}NCl_2$ requires N, 5·6; Cl, 28·1%).

Condensation of 3 : 4-*Dichlorodiphenylamine and Arsenious Chloride*.—The product obtained by boiling 3 : 4-dichlorodiphenylamine (28 g.) with arsenious chloride (24 g.) in *o*-dichlorobenzene (98 c.c.) for 8 hours consisted of yellow crystals (8·5 g.; 20%), and was a mixture. Part of it was very sparingly soluble in toluene and was thus separated. This portion was recrystallised from acetic acid and obtained in yellow prisms, m. p. 263—265°; on further crystallisation from acetone it had m. p. 265—268°, which was constant (Found : Cl, 30·5. $C_{12}H_7NCl_3As$ requires Cl, 30·7%).

The larger portion of the product crystallised from toluene in yellow prisms, m. p. 210—220°, and the melting point was not made more definite or raised by further crystallisation. During further recrystallisation from acetic acid products having m. p. 223—227° and 230—240° were obtained. This was, however, due to some oxidation or acetylation taking place, for the crystalline substance obtained on reduction of the whole of the lower-melting product in alcohol–hydrochloric acid solution with sulphur dioxide in the presence of a trace of iodine began to shrink at 205° and melted at 220° after two crystallisations from carbon tetrachloride (Found: Cl, 30·1; As, 21·9. $C_{12}H_7NCl_3As$ requires Cl, 30·7; As, 21·6%).

Although it is probable that the lower-melting product has not been obtained free from the higher-melting isomeride, there is no doubt that the two compounds 1 : 2 : 10- (XIII*a*) and 2 : 3 : 10-*trichloro*-5 : 10-*dihydrophenarsazines* (XIII*b*) are formed in the above reaction. The same two compounds are formed by the reduction of 3 : 4-dichlorodiphenylamine-6′-arsinic acid described below.

3 : 4-*Dichlorodiphenylamine*-6′-*arsinic Acid.*—A mixture of 3 : 4-dichloroaniline (12 g.), *o*-bromophenylarsinic acid (21 g.), potassium carbonate (16·3 g.), amyl alcohol (115 c.c.), and a trace of copper powder was boiled for 8 hours. The volatile organic substances were removed by steam distillation, the residue was boiled with charcoal, and the filtrate acidified with hydrochloric acid. The precipitated acid was converted into its ammonium salt, which crystallised from a concentrated solution of ammonia. This salt was dissolved in water and the *acid* precipitated by means of hydrochloric acid was recrystallised from dilute acetic acid and obtained in colourless needles, m. p. 150° (Found: As, 20·8. $C_{12}H_{10}O_3NCl_2As$ requires As, 20·7%).

Reduction of 3 : 4-*Dichlorodiphenylamine*-6′-*arsinic Acid.*—The acid, dissolved in a mixture of equal volumes of alcohol and concentrated hydrochloric acid, was reduced with sulphur dioxide in the presence of a trace of iodine. The yellow crystalline product was washed with hydrochloric acid and, after drying, recrystallised from carbon tetrachloride. That portion which was less soluble was filtered off, recrystallised from acetone, and obtained in yellow prisms, m. p. 273—274° (Found: As, 22·3. $C_{12}H_7NCl_3As$ requires As, 21·6%). It was proved identical with the higher-melting and less soluble product from the condensation of 3 : 4-dichlorodiphenylamine and arsenious chloride by the method of mixed melting points.

The more soluble portion crystallised from carbon tetrachloride in yellow prisms, m. p. 230—250°. From the mother-liquor, a fraction having m. p. 225—240° was obtained and this after recrystallisation from acetone had m. p. 230—235° (Found: As, 21·2. $C_{12}H_7NCl_3As$ requires As, 21·6%). When it was mixed with the lower-melting and more soluble product from the condensation of 3 : 4-dichlorodiphenylamine and arsenious chloride there was no depression of melting point. A mixture containing a large excess of the product of lower melting point showed only a small depression of the melting point, whereas a mixture containing a large excess of the higher-melting isomeride had a melting point markedly lower than that of the higher-melting isomeride.

1 : 3 : 10-*Trichloro*-5 : 10-*dihydrophenarsazine* (1·8 g.) was obtained by boiling 3 : 5-dichlorodiphenylamine (8 g.) with arsenious chloride (6·8 g.) in *o*-dichlorobenzene solution (28 c.c.) for 8 hours. From the mother-liquor, after addition of a further quantity of arsenious chloride and another 8 hours' boiling, 1·9 g. were obtained and after the mother-liquor had been boiled again for another 8 hours a further 1·6 g. was isolated. The product crystallised from acetone in yellow prisms, m. p. 251—252° (Found : Cl, 30·7. $C_{12}H_7NCl_3As$ requires Cl, 30·7%).

The trichloro-compound (1·3 g.) was boiled for 10 minutes with acetic acid (12 c.c.) and hydrogen peroxide (20 vols., 6 c.c.). 1 : 3-*Dichlorophenarsazinic acid*, which separated on cooling, crystallised from dilute acetic acid in colourless needles which did not melt below 280° (Found : As, 21·0. $C_{12}H_8O_2NCl_2As$ requires As, 21·8%).

1 : 2 : 3 : 10-*Tetrachloro*-5 : 10-*dihydrophenarsazine* separated in small yield (0·8 g., 6%) when 3 : 4 : 5-trichlorodiphenylamine (10·5 g.) was boiled with arsenious chloride (7·8 g.) in *o*-dichlorobenzene (32 c.c.) for 7 hours, but 5 g. were also obtained when the mother-liquor was boiled for 20 hours with a further quantity of arsenious chloride. When recrystallised from acetone, the compound was obtained in yellow needles, m. p. 260° (Found : Cl, 36·9. $C_{12}H_6NCl_4As$ requires Cl, 37·2%). When boiled for 15 minutes with acetic acid and hydrogen peroxide, it was converted into 1 : 2 : 3-*trichlorophenarsazinic acid*. This was converted into its sodium salt, which crystallised from a solution in concentrated aqueous sodium hydroxide. This salt was separated, its aqueous solution treated with hydrochloric acid, and the precipitated acid recrystallised from acetic acid (90%) and obtained in colourless needles which did not melt below 290° (Found : As, 19·0. $C_{12}H_7O_2NClAs$ requires As, 19·8%).

1 : 9 : 10- or 1 : 7 : 10- or 3 : 7 : 10-*Trichloro*-5 : 10-*dihydrophenarsazine* was obtained in small yield (1·7 g., 15%) by boiling 3 : 3′-dichlorodiphenylamine (8 g.) with arsenious chloride (6·8 g.) in *o*-dichlorobenzene (28 c.c.) for 8 hours. The homogeneous product crystallised from acetic acid in soft yellow needles, m. p. 298° (Found : Cl, 30·8. $C_{12}H_7NCl_3As$ requires Cl, 30·7%).

Condensation of 3 : 4′-*Dichlorodiphenylamine with Arsenious Chloride.*—3 : 4′-Dichlorodiphenylamine (5 g.) was boiled with arsenious chloride (4·5 g.) in *o*-dichlorobenzene (18 c.c.) for 8 hours. The yellow product—a mixture of 1 : 8 : 10- (VI*a*) and 3 : 8 : 10- (VI*b*) *trichloro*-5 : 10-*dihydrophenarsazines*—separated in small yield (1·4 g., 20%). Recrystallised from acetone, it had m. p. 260—280° and after further recrystallisation the product had a constant m. p. 292°. For macro-analysis, this had to be mixed with the lower-melting isomeride, as only a small quantity was obtained (Found for the mixture: Cl, 30·7. $C_{12}H_7NCl_3As$ requires Cl, 30·7%): The mother-liquors from the higher melting product yielded a substance which after recrystallisation had m. p. 240—242° (Found: Cl, 31·3. $C_{12}H_7NCl_3As$ requires Cl, 30·7%).

2 : 10-*Dichloro*-4-*methyl*-5 : 10-*dihydrophenarsazine* (4·7 g., 70%) was obtained by boiling 4-chloro-2-methyldiphenylamine (5 g.) with arsenious chloride (5 g.) in *o*-dichlorobenzene (20 c.c.) for 8 hours. It crystallised from acetone in bright yellow prisms, m. p. 245° (decomp.) (Found: Cl, 21·9. $C_{13}H_{10}NCl_2As$ requires Cl, 21·8%).

1(or 3) : 10-*Dichloro*-6-*methyl*-5 : 10-*dihydrophenarsazine* (VII) (3·6 g., 53%) was obtained as a homogeneous product by boiling 3′-chloro-2-methyldiphenylamine (5 g.) with arsenious chloride (5 g.) in *o*-dichlorobenzene (20 c.c.) for 8 hours. When recrystallised from acetone, it was obtained in bright yellow plates, m. p. 262° (decomp.) (Found: Cl, 21·7. $C_{13}H_{10}NCl_2As$ requires Cl, 21·8%).

2 : 10-*Dichloro*-6-*methyl*-5 : 10-*dihydrophenarsazine* (1·6 g., 25%) was produced on boiling 4′-chloro-2-methyldiphenylamine (5 g.) with arsenious chloride (5 g.) in *o*-dichlorobenzene (20 c.c.) for 8 hours. It was obtained in deep yellow prisms, m. p. 199°, by recrystallisation from acetone (Found: Cl, 22·2. $C_{13}H_{10}NCl_2As$ requires Cl, 21·8%).

GUY'S HOSPITAL MEDICAL SCHOOL (UNIVERSITY OF LONDON),
LONDON, S.E.1.
[*Received, December* 15*th*, 1930.]