LVIII.—10-*Chloro*-5:10-*dihydrophenarsazine and its Derivatives. Part I. The Synthesis, Preparation, and Some Properties of* 10-*Chloro*-5:10-*dihydrophenarsazine.*

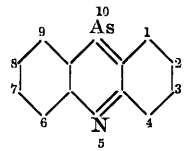
By HAROLD BURTON and CHARLES STANLEY GIBSON.

THE reaction between arsenious halides and secondary aromatic amines was the subject of a patent of F. Bayer & Co. (D.R.-P. 281049, Friedländer, " Fortschritte," 1914, XII, 843), and Wieland and Rheinheimer (*Annalen*, 1921, **423**, 1) made a comprehensive study of the derivatives of the compound obtained by condensing arsenious chloride and diphenylamine. To this compound, Wie-

land and Rheinheimer gave the name " phenarsazine chloride " and ascribed to it the constitution

which is the same as that ascribed to it by the patentees.*

* Wieland and Rheinheimer (*loc. cit.*) prepared the compound phenarsazine, which undoubtedly has the structure



The product of the reaction between diphenylamine and arsenious chloride is derived from phenarsazine by the addition of hydrogen chloride. This compound has hitherto been variously known as " diphenylamine arsenious chloride " (Contardi, *Giorn. Chim. Ind. Appl.*, 1920, i, 11; ii, 100), " phenarsazine chloride " (Wieland and Rheinheimer, *loc. cit.*), and " 6-chlorophenarsazine " (Lee Lewis and Hamilton, *J. Amer. Chem. Soc.*, 1921, **43**, 2218; Lee Lewis, Lowry, and Bergeim, *ibid.*, p. 891). In systematically describing this class of compounds, the name phenarsazine is retained for the parent substance and the atoms are numbered as indicated. The product of the reaction between diphenylamine and arsenious chloride and its simple derivatives are regarded as substitution products of 5 : 10-dihydrophenarsazine, at present unknown. " Phenarsazinic acid," which is already in use for the oxidation product of these derivatives, still applies.

Although the patent referred to was taken out in 1913 and issued in the German Empire in December, 1914, the specification was not available in this country until September, 1920. Our knowledge of this type of heterocyclic compound up to 1918 was limited to that contained in a brief abstract of the patent, which referred only to the general reaction between arsenious chloride and diarylamines without mentioning any specific compound (*J. Soc. Chem. Ind.*, 1915, **34**, 636). It ought to be pointed out that Dr. W. C. Ball independently prepared the compound early in 1918 (unpublished report of the Anti-gas Department) by the action of arsenious chloride on diphenylamine and examined a number of its simpler derivatives. Professor G. T. Morgan in 1918 (unpublished report) also studied the reaction and prepared certain analogues of 10-chloro-5 : 10-dihydrophenarsazine. In preparing his " diphenylamine arsenious chloride," Contardi (*loc. cit.*) heated diphenylamine hydrochloride and arsenious oxide together in the proportions for the following reaction to take place :

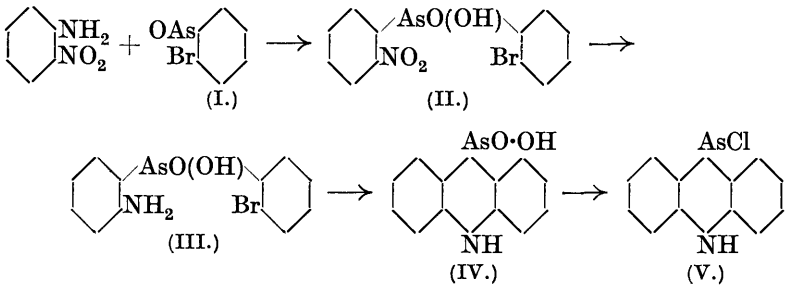
$$2NH(C_6H_5)_2,HCl + As_2O_3 = 2NH(C_6H_4)_2AsCl + 3H_2O.$$

The reaction as described by Contardi does take place, but we have not been able to obtain the high yield recorded, probably because the product of the reaction is decomposed rapidly by water at the temperature employed.

The compound so easily obtained in almost quantitative yield by heating

The work now described was in progress before the paper by Wieland and Rheinheimer (*loc. cit.*) was available, and it seems desirable to describe our results, which supplement those of these two workers.

The constitution ascribed to 10-chloro-5 : 10-dihydrophenarsazine has been proved to be correct by the following synthesis, which may be represented diagrammatically :



The first stage consisted in diazotising *o*-nitroaniline and coupling the diazo-compound with *o-bromophenylarsenious oxide* (I). The resulting compound, *2-bromo-6′-nitrodiphenylarsinic acid*, is reduced to the corresponding *amino*-compound (III) by means of ferrous hydroxide. By heating in amyl alcohol with potassium carbonate and a small quantity of copper powder, the amino-compound is readily converted into phenarsazinic acid (IV), and this, when reduced in hydrochloric acid–alcohol solution by sulphur dioxide, is readily converted into 10-chloro-5 : 10-dihydrophenarsazine identical with the substance prepared by the action of arsenious chloride on diphenylamine according to the equation

$$NH(C_6H_5)_2 + AsCl_3 = NH\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\rangle AsCl + 2HCl.$$

The preparation by Burton and Gibson (J., 1924, **125**, 2277) of the *N*-acetyl, *N*-propionyl, and *N*-benzoyl derivatives is confirmatory evidence of the presence of the :NH group in 10-chloro-5 : 10-dihydrophenarsazine.* Wieland and Rheinheimer (*loc. cit.*) also have described the preparation of the *N*-methyl derivative from

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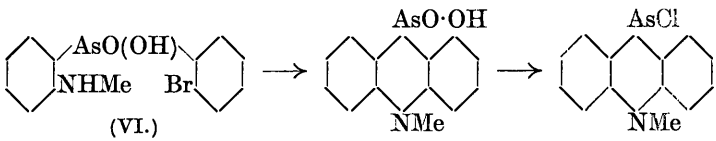
together arsenious chloride and diphenylamine under the conditions described by previous workers is systematically described as 10-chloro-5 : 10-dihydrophenarsazine.

* Whilst 10 : 10′-oxy-5 : 10-dihydrophenarsazine reacts with acetyl chloride to give 10-chloro-5-acetyl-5 : 10-dihydrophenarsazine, benzoyl chloride and the oxy-compound react quantitatively as follows :

$$[NH(C_6H_4)_2As]_2O + 2C_6H_5{\cdot}COCl = 2NH(C_6H_4)_2AsCl + (C_6H_5{\cdot}CO)_2O.$$

arsenious chloride and *N*-methyldiphenylamine. In connexion with our work on the phenarsazinic acids of this group of compounds, it was important to prepare the corresponding acid (Burton and Gibson, *loc. cit.*) with a view to investigate its trypanocidal properties. The only substance we have obtained by condensing arsenious chloride with *N*-methyldiphenylamine and working up the product under the conditions described by Wieland and Rheinheimer is 10-chloro-5 : 10-dihydrophenarsazine and not 10-chloro-5-methyl-5 : 10-dihydrophenarsazine (the *N*-methyl derivative). The melting point of the material we isolated from this reaction (about 10% of the theoretical quantity) was unaffected on admixture with an authentic specimen of 10-chloro-5 : 10-dihydrophenarsazine. Whilst the melting point, quoted by Wieland and Rheinheimer, of the supposed *N*-methyl derivative is 203° (some 8—10° higher than that of 10-chloro-5 : 10-dihydrophenarsazine), its further characterisation is somewhat inconclusive.* Like Wieland and Rheinheimer, we have failed to obtain the *N*-methyl derivative by attempting to methylate 10-chloro-5 : 10-dihydrophenarsazine and we therefore attempted to synthesise the compound according to the following scheme based on the method for obtaining the parent substance :



(VI.) (VII.) (VIII.)

Whether the compound (VII) is actually formed we are unable to say, but when the product obtained by heating *2-bromo-6'-methylaminodiphenylarsinic acid* (VI) in amyl alcohol with potassium carbonate and copper powder is reduced in hydrochloric acid–alcohol solution with sulphur dioxide 10-chloro-5-10-dihydrophenarsazine, *o*-bromophenylarsenious chloride and methylaniline are obtained (see p. 459). While the *N*-acyl derivatives of 10-chloro-5 : 10-dihydrophenarsazine are prepared quite readily, the fact that we have been unable to prepare the *N*-methyl derivative either directly or by synthesis is not easily explained.

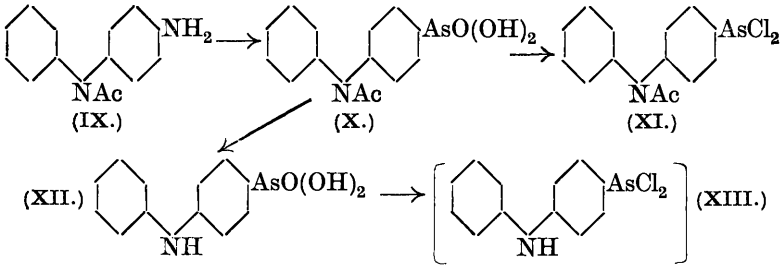
The most convenient way for preparing 10-chloro-5 : 10-dihydrophenarsazine in the laboratory is by heating one molecular proportion of diphenylamine with rather more than one molecular proportion of freshly distilled arsenious chloride in dichlorobenzene. The

* The micro-analysis quoted by the above authors showed a nitrogen content of 5·0%, the calculated values for $NH(C_6H_4)_2AsCl$ and $NMe(C_6H_4)_2AsCl$ being 5·05 and 4·95% of nitrogen, respectively.

product crystallises from the solution on cooling and is rapidly purified by extraction with carbon tetrachloride. The fact that the reaction between arsenious chloride and diphenylamine takes place slowly at the ordinary temperature * (actually a yield of 10% of the theoretical was obtained after 16 months) has enabled us to study the reaction somewhat closely. When the two reacting substances are mixed in the presence of a solvent, a white, crystalline substance having the composition $HCl,NH(C_6H_5)_2,AsCl_3$, is slowly deposited. In a sealed apparatus no development of pressure was recorded, but the solution became dark green and crystals of 10-chloro-5 : 10-dihydrophenarsazine were slowly deposited. The same white crystalline substance was formed immediately on mixing diphenylamine hydrochloride and arsenious chloride, but no further reaction took place. On heating a mixture of arsenious chloride and diphenylamine or its hydrochloride in high-boiling solvents, the additive compound dissolves, a copious evolution of hydrogen chloride takes place, and 10-chloro-5 : 10-dihydrophenarsazine is rapidly formed. From these results, it appears that at the ordinary temperature diphenylamine and arsenious chloride react to liberate hydrogen chloride which combines with unchanged diphenylamine, forming its hydrochloride which then crystallises as the additive compound with arsenious chloride. The substitution product is soluble and has not been isolated, but it is clear that this soluble compound is intermediate in the formation of the final product. If the mixture is not heated and no escape for the hydrogen chloride is provided, it is obvious that the reaction cannot go to completion. In view of the results of the large number of investigations on the action of arsenious chloride on aniline (summarised by Schmidt, *J. Amer. Chem. Soc.*, 1921, **43**, 2449) it is quite probable that the soluble intermediate compound may have the composition $(C_6H_5)_2N{\cdot}AsCl_2$. The ease of formation of 10-chloro-5 : 10-dihydrophenarsazine is very striking in view of the fact that usually para-substitution takes place when arsenic is introduced into the nucleus of aromatic amines. This is the case, not only in the formation of arsanilic acid, but also when arsenious chloride reacts with dialkylanilines (Michaelis and Rabinerson, *Annalen*, 1892, **270**, 139; Michaelis, *Ber.*, 1908, **41**, 1514); with monoalkylanilines and arylglycines (Poulenc Frères and Oechslin, French Patents 450214, 462276, and 473704). The following scheme of reactions was therefore studied with a view to the preparation of *p*-phenylaminophenylarsenious chloride (diphenylamine-*p*-arsenious chloride), which obviously

* The investigation of the reaction between diphenylamine and arsenious chloride at the ordinary temperature was carried out by the late Mr. D. C. Vining and one of us (C. S. G.).

cannot be prepared directly from arsenious chloride and diphenylamine :

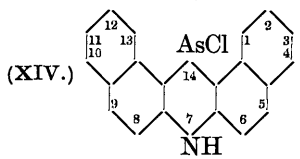


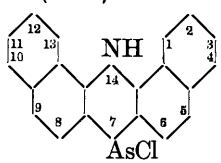
The reduction of the arsinic acid (XII) in the usual manner causes the elimination of the arsenic, and diphenylamine is the main product of the reaction. Consequently it has not been possible to prepare *p*-phenylaminophenylarsenious chloride (XIII), although its *N*-acetyl derivative (XI) is easily obtainable. In view of the ease with which 10-chloro-5 : 10-dihydrophenarsazine is obtained, this result is not unexpected.

In studying the action of arsenious chloride on aniline, Schmidt (*loc. cit.*) isolated trianilinoarsine hydrochloride, $(C_6H_5{\cdot}NH,HCl)_3As$, which was first described by Schiff (*Compt. rend.*, 1863, **56**, 268, 1095). By heating this compound for a long time, either alone or in the presence of an excess of aniline, Schmidt claimed to have obtained 10-chloro-5 : 10-dihydrophenarsazine, which he identified as the corresponding oxy-compound.* Schmidt states that the reaction which takes place may be expressed as follows :

$$(C_6H_5{\cdot}NH,HCl)_3As = NH(C_6H_4)_2AsCl + C_6H_5{\cdot}NH_2,HCl + NH_4Cl.$$

Since we have been able to isolate diphenylamine from the product obtained by heating the trianilinoarsine hydrochloride with an excess of aniline, it is possible that the formation of 10-chloro-5 : 10-dihydrophenarsazine may be due to the action of arsenious chloride on diphenylamine which is formed under these conditions. This possibility is supported by the fact that when arsenious chloride and β-naphthylamine are heated together in *o*-dichlorobenzene solution 14-*chloro*-14 : 7-*dihydrodibenzophenarsazine* (XIV)





* Schmidt states that the oxy-compound is crystallised from acetic acid. It has been known for some time (Wieland and Rheinheimer, *loc. cit.*) that under such conditions the oxy-compound is converted into the 10-acetyl-5 : 10-dihydrophenarsazine.

is readily obtained with elimination of ammonium chloride, and is identical with the product obtained by heating di-β-naphthylamine with arsenious chloride under identical conditions (D.R.-P., *loc. cit.*). α-Naphthylamine and arsenious chloride do not react to give a compound analogous to 10-chloro-5 : 10-dihydrophenarsazine; the compound *7-chloro*-7 : 14-*dihydrodibenzophenarsazine* (XV) is, however, readily obtained from di-α-naphthylamine (D.R.-P., *loc. cit.*).

The ease of the *oo'*-substitution in diphenylamine is also well illustrated by the preparation in good yield of 10 : 10'-oxy-5 : 10-dihydrophenarsazine from diphenylamine and arsenious oxide according to the equation :

$$2NH(C_6H_5)_2 + As_2O_3 = [NH(C_6H_4)_2As]_2O + 2H_2O.$$

The reaction takes place readily at temperatures above 130° in the presence of phosphorus pentoxide.

Regarding 10-chloro-5 : 10-dihydrophenarsazine, one of its most striking properties is its power of forming molecular compounds. Molecular compounds with acetic acid, *s*-tetrachloroethane, chlorobenzene, *o*-dichlorobenzene, acetone, carbon tetrachloride, and arsenious chloride have been isolated.

The chlorine atom in 10-chloro-5 : 10-dihydrophenarsazine can be easily replaced by other atoms or groups. Some of these derivatives have been described by Wieland and Rheinheimer (*loc. cit.*). The most convenient way of preparing the corresponding bromo- and iodo-compounds—we have not succeeded in preparing the latter compound directly from diphenylamine and arsenious iodide—is by adding the corresponding concentrated halogen acid to the solution of the oxy-compound in acetic acid. The bromo- and iodo-compounds are formed almost quantitatively in a state of purity. The iodo-compound resembles the chloro-compound in showing a similar tendency to form molecular compounds with, for example, benzene and acetic acid. Wieland and Rheinheimer noticed the solubility of the oxy-compound in methyl alcohol and isolated the colourless 10-methoxy-5 : 10-dihydrophenarsazine. The analogous n-*butoxy*- and *benzyloxy*-compounds described in the present paper are also colourless and being more soluble than the methoxy-derivative are more useful in preparing other derivatives, for example, the sulpho-compound.

EXPERIMENTAL.

o-Bromophenylarsinic Acid, $C_6H_4Br{\cdot}AsO(OH)_2$.—*o*-Aminophenylarsinic acid (36 g.) dissolved in hydrobromic acid (126 c.c.; *d* 1·265) and water (63 c.c.) was diazotised at 0° with sodium nitrite (12·6 g.)

in water (25 c.c.). The cold diazo-solution was added gradually, with stirring, to a solution of cuprous bromide at 30—40°. (The cuprous bromide solution was made by boiling 16·5 g. of copper carbonate, 165 c.c. of hydrobromic acid, and copper until the solution was clear.) The solid matter was filtered off, and extracted with hot alcohol. The alcoholic extract was evaporated to dryness, boiled with sodium carbonate solution and filtered. On acidifying with concentrated hydrochloric acid, *o*-bromophenylarsinic acid (27 g.) separated in nearly colourless crystals, m. p. 201° (decomp.). The acid crystallises from aqueous alcohol in colourless prisms, m. p. unchanged (Found: As, 26·4. Calc., As, 26·7%).

o-*Bromophenylarsenious Oxide* (I).—*o*-Bromophenylarsinic acid (14 g.) was dissolved in alcohol (14 c.c.) and concentrated hydrochloric acid (14 c.c.) containing a trace of iodine. Sulphur dioxide was passed into the boiling mixture for 30 minutes; the chloroarsine then separated as a heavy oil. After evaporation of the alcohol, the oil was extracted with benzene. The benzene solution was shaken with ammonia (14 c.c.; *d* 0·880) and, after the mixture had cooled, the solid matter was filtered off. This was washed with water until free from ammonium chloride and dried. The benzene filtrate on evaporation gave a small quantity of the oxide. The yield was 92·5% of the theoretical. o-*Bromophenylarsenious oxide* is insoluble in most neutral solvents and melts at 234—238° (Found: As, 30·25. C_6H_4OBrAs requires As, 30·4%).

2-*Bromo*-6′-*nitrodiphenylarsinic Acid* (II).—A suspension of *o*-nitroaniline (13·8 g.) in concentrated hydrochloric acid (80 c.c.) and water (250 c.c.) was cooled to 0° and diazotised with a solution of sodium nitrite (7·6 g.) in water. The filtered solution was added with stirring to a solution, at 20°, of *o*-bromophenylarsenious oxide (27·2 g.) in 5*N*-sodium hydroxide solution (174 c.c.) diluted to 500 c.c. with water, and containing 10 c.c. of 10% aqueous copper sulphate solution to which ammonia had been added to form the soluble complex. The mixture was stirred for 2 hours, made faintly acid to litmus, and filtered. On adding concentrated hydrochloric acid to the filtrate, until Congo-paper turned blue, 2-*bromo*-6′-*nitrodiphenylarsinic acid* (19·6 g.) was precipitated. It crystallised from dilute alcohol in pale yellow prisms, m. p. 254—255° (decomp.) (Found: Br, 20·9; As, 19·2. $C_{12}H_9O_4NBrAs$ requires As, 19·4; Br, 20·7%).

2-*Bromo*-6′-*aminodiphenylarsinic Acid* (III).—Ferrous hydroxide was precipitated from a hot solution of ferrous sulphate (50 g.) in water (150 c.c.) by adding an excess of 25% sodium hydroxide solution. To the boiling suspension a solution of 2-bromo-6′-nitrodiphenylarsinic acid (11·5 g.) in dilute sodium hydroxide was added

slowly with stirring. The mixture was then boiled for 15 minutes. After filtration from the ferric hydroxide, the colourless solution was acidified with concentrated hydrochloric acid (Congo-paper), and the precipitated amino-acid (9·8 g.) filtered. It crystallised from dilute alcohol in colourless prisms, m. p. 213—214° (decomp.) (Found: As, 20·7; Br, 22·3. $C_{12}H_{11}O_2NBrAs$ requires As, 21·1; Br, 22·45%).

2-Bromo-6′-methylaminodiphenylarsinic Acid (VI).—2-Bromo-6′-aminodiphenylarsinic acid (21·4 g.) was suspended in water (150 c.c.) and mixed with 7·6 g. of methyl sulphate. After thorough mixing, a solution of sodium hydroxide (5 g.) in water (20 c.c.) was added in five portions at intervals of 30 minutes. The mixture was well shaken after each addition. The solution was then acidified with hydrochloric acid, and the crude acid filtered. This was dissolved in the minimum quantity of hot alcohol and allowed to cool; a crop of unchanged material (6·0 g.) was then obtained. The alcoholic solution was evaporated and a fraction (10·8 g.), m. p. 192—193°, obtained. This fraction on recrystallisation from alcohol melted at 193—194° (decomp.) (Found: C, 42·3; H, 3·7; Br, 21·6. $C_{13}H_{13}O_2NBrAs$ requires C, 42·2; H, 3·5; Br, 21·6%).

2-Bromo-6′-dimethylaminodiphenylarsinic Acid.—A mixture of 2-bromo-6′-aminodiphenylarsinic acid (4·3 g.) and methyl sulphate (10 c.c.) was heated on the steam-bath for 3 hours. After decomposition of the resulting solution with sodium carbonate solution, the acid was precipitated by hydrochloric acid. It crystallised from aqueous alcohol in clusters of colourless needles, m. p. 220—221° (decomp.) (Found: C, 43·8; H, 4·2; Br, 21·0. $C_{14}H_{15}O_2NBrAs$ requires C, 43·75; H, 3·9; Br, 20·8%).

The Formation of Phenarsazinic Acid (IV) *from 2-Bromo-6′-aminodiphenylarsinic Acid. Isolation of 10-Chloro-5 : 10-dihydrophenarsazine* (V).—A mixture of 2-bromo-6′-aminodiphenylarsinic acid (10·8 g.), dry potassium carbonate (4·4 g.), amyl alcohol (80 c.c.), and a trace of copper powder was boiled under reflux for 12 hours. The amyl alcohol was removed with steam, and the aqueous residue filtered from the copper. The solution was acidified with hydrochloric acid, and the precipitated acid (8·9 g.) filtered off, well washed with water, and dissolved in a mixture of alcohol (20 c.c.) and concentrated hydrochloric acid (20 c.c.) containing a trace of iodine. Sulphur dioxide was passed into the boiling solution for 10 minutes; yellow solid matter then began to separate. After cooling, the crude 10-chloro-5 : 10-dihydrophenarsazine (8·6 g.) was filtered off and extracted with carbon tetrachloride. This solution, on cooling, deposited yellow needles, melting at 191—192° alone or mixed with an authentic sample of 10-chloro-5 : 10-dihydrophenarsazine.

Reduction of 2-Bromo-6′-aminodiphenylarsinic Acid. Isolation of o-Bromophenylarsenious Chloride.—A hot solution of 2-bromo-6′-aminodiphenylarsinic acid (5 g.) in alcohol (5 c.c.), concentrated hydrochloric acid (5 c.c.), and a trace of iodine was treated with sulphur dioxide for 45 minutes. On cooling, a gummy solid separated which slowly solidified. It was filtered off, and found to be *o*-bromophenylarsenious chloride, m. p. 65—66°, the melting point being unchanged by admixture with an authentic sample. 2-Bromo-6′-methylaminodiphenylarsinic acid and 2-bromo-6′-dimethylaminodiphenylarsinic acid under similar conditions yield methylaniline and dimethylaniline, identified as acetomethylanilide and *p*-nitrosodimethylaniline, respectively, together with *o*-bromophenylarsenious chloride.

Attempted Preparation of N-Methylphenarsazinic Acid (VII).—A mixture of 2-bromo-6′-methylaminodiphenylarsinic acid (11·1 g.), dry potassium carbonate (4·2 g.), amyl alcohol (80 c.c.), and a trace of copper powder was boiled under reflux for 12 hours. After steam distillation of the volatile products the aqueous residue was acidified and the crude acid (6·5 g.) filtered off. This was dissolved in alcoholic hydrochloric acid, and the boiling solution, to which a trace of iodine had been added, was saturated with sulphur dioxide for 20 minutes. A tarry precipitate was obtained which on extraction with carbon tetrachloride gave a crop of yellow needles, m. p. 191°. This substance was 10-chloro-5 : 10-dihydrophenarsazine, identified by comparison with an authentic sample.

The mother-liquors from the alcoholic hydrochloric acid treatment were evaporated, made alkaline with ammonia, and extracted with ether. This ethereal extract on evaporation gave a small quantity of an oil, smelling of methylaniline. On acetylation a small amount of acetomethylanilide, m. p. 101°, was obtained.

Action of Arsenious Chloride on Methyldiphenylamine.—(*a*) Attempts to prepare 10-chloro-5-methyl-5 : 10-dihydrophenarsazine from methyldiphenylamine and arsenious chloride in the presence of dichlorobenzene resulted in decomposition of the reacting substances and no crystalline matter could be isolated.

(*b*) Methyldiphenylamine (36·6 g.) and arsenious chloride (36·2 g.) were heated under reflux at 200° for 2 hours. The coloured residue was cooled, extracted with light petroleum, and the solid residue (46·2 g.) worked up, following as closely as possible the details described by Wieland and Rheinheimer (*loc. cit.*). The only compound isolated (yield 10%) was 10-chloro-5 : 10-dihydrophenarsazine, m. p. 187—190°, identical in every respect with an authentic specimen.

10-Chloro-5 : 10-dihydrophenarsazine.—A mixture of diphenyl-

amine (17 g.), arsenious chloride (20 g.), and *o*-dichlorobenzene (40 c.c.) was boiled under reflux for 5 hours, hydrogen chloride escaping steadily. On cooling, the dark green solution deposited a mass of crystals which were filtered off, washed with petrol, dried, and crystallised from carbon tetrachloride. 10-Chloro-5 : 10-dihydrophenarsazine prepared in this way melts at 191—192° and is bright yellow (yield almost theoretical).

The Reaction between Diphenylamine and Arsenious Chloride at the Ordinary Temperature.—Arsenious chloride (8·3 g.) was dissolved in dry benzene (10 c.c.) and treated with diphenylamine (7·8 g.). Solution resulted, and after 1 hour crystallisation commenced. After 24 hours the crystalline matter was filtered off rapidly in the absence of air, washed with dry benzene, and dried on porous tile in a vacuum (Found : Cl, 35·9. $C_{12}H_{12}NCl_4As$ requires Cl, 36·7%).

The crystals formed above, on filtration in the ordinary manner, become opaque and then consist for the most part of diphenylamine hydrochloride. The same compound is produced when diphenylamine hydrochloride and arsenious chloride are mixed in the presence of a solvent.

In an experiment using arsenious chloride (20 g.), diphenylamine (17 g.) and *s*-tetrachloroethane (40 c.c.), the mixture was kept for 16 months. No change of pressure in the flask was observed. After making alkaline with sodium carbonate solution, the volatile products were distilled in steam. The residue (3·0 g.) was converted into 10-chloro-5 : 10-dihydrophenarsazine by treating it in hot acetic acid solution with dry hydrogen chloride. On cooling, the chloroarsine separated in greenish-yellow needles, m. p. 189—190°.

p-*Phenylacetylaminophenylarsinic Acid* (N-*Acetyldiphenylamine*-p-*arsinic acid*) (X).—A solution of *N*-acetyl-*p*-aminodiphenylamine (22·6 g.) in dilute hydrochloric acid (25 c.c. of concentrated acid and 150 c.c. of water) was cooled to 0° and diazotised with sodium nitrite (7·4 g.) in water (20 c.c.). The diazo-solution was added gradually, with vigorous stirring, to a solution of sodium arsenite made by dissolving arsenious oxide (15 g.) in sodium carbonate solution (24 g. of anhydrous sodium carbonate in 105 c.c. of water) containing a small amount of copper sulphate. The arsenite solution was maintained at 30—35° and kept alkaline by addition of sodium hydroxide solution. After the evolution of nitrogen had ceased, the solution was filtered from tarry matter and made slightly acid to litmus. This procedure caused a further quantity of dark-coloured, tarry matter to be precipitated. After filtration, and evaporation to small bulk, the crude acid (16·5 g.), m. p. 121°, was obtained by making the solution strongly acid. The pure acid, m. p. 126° (decomp.), crystallises from water in almost colour-

less prisms containing $1H_2O$ (Found: H_2O, 4·7; As, 21·2. $C_{14}H_{16}O_5NAs$ requires H_2O, 5·1; As, 21·2%).

p-*Phenylaminophenylarsinic Acid* (*Diphenylamine*-p-*arsinic acid*) (XII).—The crude acetyl-arsinic acid (15 g.) was boiled for one hour with a mixture of concentrated hydrochloric acid (30 c.c.) and alcohol (30 c.c.). The solution turned green and the required arsinic acid was precipitated by water. The crude acid (13 g.) contained some green matter very difficult to separate. Purification was conveniently accomplished by treating a concentrated solution of the ammonium salt with magnesium sulphate solution, when the sparingly soluble magnesium salt was precipitated. Extraction of the magnesium salt with successive quantities of hot water and treatment of the solution with dilute sulphuric acid resulted in the formation of almost colourless, hair-like crystals of the arsinic acid, m. p. 265° (decomp.) (Found: As, 25·5. $C_{12}H_{12}O_3NAs$ requires As, 25·6%).

p-*Phenylacetylaminophenylarsenious Chloride* (N-*Acetyldiphenylamine*-p-*arsenious chloride*) (XI).—A hot solution of the acetylarsinic acid (9 g.) in alcohol (30 c.c.) and concentrated hydrochloric acid (9 c.c.) containing a trace of iodine was saturated with sulphur dioxide. On cooling, solid matter separated, and the mother-liquors on evaporation yielded a further crop of crystals. The *arsenious chloride*, after filtration and drying, crystallised from benzene–ligroin in colourless needles, m. p. 141° (Found: Cl, 20·0. $C_{14}H_{12}ONCl_2As$ requires Cl, 20·0%).

Considerable difficulty has been met with in trying to prepare the arsenious chloride from *p*-phenylaminophenylarsinic acid. Attempts at reduction analogous to those of the corresponding acetyl derivative using the crude acid were unsuccessful owing to the persistence of the green matter. An attempt at reduction in the absence of hydrochloric acid to produce the oxide, caused elimination of the arsenic and diphenylamine was obtained, identified by its melting point and the melting point of its hydrochloride. The pure acid on reduction in the presence of hydrochloric acid gave a crystalline product which was mainly diphenylamine hydrochloride. The crystals did contain a small amount of a substance containing arsenic, but not in sufficient quantity for identification.

Action of Arsenious Chloride on Aniline.—Aniline (51 g.) was added carefully to arsenious chloride (18 g.), and the mixture boiled gently for 72 hours. During the heating a sublimate of aniline hydrochloride and ammonium chloride formed. The product was made alkaline with sodium hydroxide solution and steam-distilled until the distillate was free from aniline and ammonia. By continued steam distillation, diphenylamine, identified by its melting point and the melting point of its hydrochloride, was obtained.

The insoluble residue in the flask was filtered, washed with water, dried at 100°, and weighed (39% of theory). The crude oxy-compound was converted into 10-chloro-5 : 10-dihydrophenarsazine by hydrochloric acid and acetone, and subsequent evaporation of the solution to dryness. The crude chloro-compound on crystallisation from carbon tetrachloride melted at 186—187°.

Action of Arsenious Chloride on β-Naphthylamine.—A mixture of β-naphthylamine (21·5 g.), arsenious chloride (30 g.), and *o*-dichlorobenzene (60 c.c.) was boiled under reflux for 18 hours. On mixing, a colourless, crystalline compound separated, which on warming dissolved. Hydrogen chloride was evolved and a white solid (ammonium chloride) collected in the condenser. The solution, on cooling, deposited a dark orange, crystalline mass. This was purified by three crystallisations from nitrobenzene and was thus obtained in yellow needles, m. p. 355° (decomp.) (Found : As, 19·3; N, 3·9. $C_{20}H_{13}NClAs$ requires As, 19·85; N, 3·7%).

14-*Chloro*-14 : 7-*dihydrodibenzophenarsazine* (XIV).—Di-β-naphthylamine (13·5 g.), arsenious chloride (10 g.), and *s*-tetrachloroethane (70 c.c.) were boiled under reflux for 90 minutes. After the first 30 minutes the yellow product began to separate from the boiling solution. The compound was filtered off and crystallised from nitrobenzene, separating in yellow needles, m. p. 355° (decomp.). The yield was 55% of the theoretical (Found : As, 19·6; N, 3·9. $C_{20}H_{13}NClAs$ requires As, 19·85; N, 3·7%).

7-*Chloro*-7 : 14-*dihydrodibenzophenarsazine* (XV).—Di-α-naphthylamine (13·5 g.; 1 mol.) and 10 g. of arsenious chloride (1·1 mols.) were boiled in 20 c.c. of *s*-tetrachloroethane for 7 hours. Hydrogen chloride escaped rather more slowly than in the previous preparations. The product separated, on cooling, as a brown powder (11·4 g., or 60·3%).

7-Chloro-7 : 14-dihydrodibenzophenarsazine crystallises from hot nitrobenzene in minute, yellowish-brown needles, m. p. 278—279° (decomp.) (Found : As, 19·6. $C_{20}H_{13}NClAs$ requires As, 19·85%).

10 : 10′-*Oxy*-5 : 10-*dihydrophenarsazine.*—A mixture of diphenylamine (15 g.), arsenious oxide (2·9 g.), and phosphorus pentoxide (3·2 g.) is heated with vigorous mechanical stirring at 160—170° for 1 hour. On cooling, a hard, black cake is obtained which is treated with sodium carbonate solution, and steam-distilled, diphenylamine (10·7 g.) passing over. The remaining oxy-compound (5 g.) is filtered off, and converted into 10-chloro-5 : 10-dihydrophenarsazine by dissolving it in acetone by addition of sufficient hydrochloric acid and evaporating the resulting solution to dryness. Crystallisation from carbon tetrachloride gives the pure product.

A mixture of 10 : 10′-oxy-5 : 10-dihydrophenarsazine (10 g.),

acetyl chloride (3·2 g.) and dry benzene (100 c.c.) is boiled under reflux for 6 hours, solution occurring after a few minutes' heating; on cooling, crystalline matter separates. This is filtered off and on washing with cold acetone yields crude 10-chloro-5-acetyl-5 : 10-dihydrophenarsazine (3·5 g.), m. p. 221—224°. By crystallisation from benzene, the pure product is readily obtained (compare Burton and Gibson, *loc. cit.*).

If 10 : 10′-oxy-5 : 10-dihydrophenarsazine (19·1 g.) is treated with benzoyl chloride (10·7 g.; 2 mols.) under similar conditions, no 10-chloro-5-benzoyl-5 : 10-dihydrophenarsazine is produced, but 10-chloro-5 : 10-dihydrophenarsazine (20·5 g.; theory, 21·2 g.), m. p. 190—191°, and benzoic anhydride (7·9 g.; theory, 8·6 g.), m. p. 41°, are obtained.

Molecular Compounds of 10-*Chloro*-5 : 10-*dihydrophenarsazine.*—When 10-chloro-5 : 10-dihydrophenarsazine is crystallised from the following solvents, crystals are obtained containing solvent of crystallisation. These crystals effloresce slowly in air, but heating at 110° causes rapid dissociation, leaving pure 10-chloro-5 : 10-dihydrophenarsazine in each case.

(*a*) Acetic acid	$A,C_2H_4O_2$	(Loss, 18·5;	calc., 17·8%)
(*b*) *s*-Tetrachloroethane	$2A,C_2H_2Cl_4$	(,, 23·7;	,, 23·2)
(*c*) Chlorobenzene	$2A,C_6H_5Cl$	(,, 17·0;	,, 16·8)
(*d*) *o*-Dichlorobenzene	$2A,C_6H_4Cl_2$	(,, 21·0;	,, 20·9)
(*e*) Acetone	$2A,C_3H_6O$	(,, 9·3;	,, 9·5)
(*f*) Carbon tetrachloride	A,CCl_4	(,, 35·6;	,, 35·7)

(A denotes $NH<^{C_6H_4}_{C_6H_4}>AsCl$).

10-Chloro-5 : 10-dihydrophenarsazine is extremely soluble in arsenious chloride, giving a dark green solution. A hot, concentrated solution, on cooling, deposits magnificent, scarlet scales of the compound $A,AsCl_3$ (loss, 39·3; calc., 39·7%). This is sufficiently stable to allow of filtration, but on exposure to air or washing with solvents yields the original chloro-compound.

10-*Bromo*-5 : 10-*dihydrophenarsazine.*—(*a*) A mixture of diphenylamine (8·5 g.), arsenious bromide (17·3 g.), and *o*-dichlorobenzene (20 c.c.) is boiled under reflux for 18 hours. Hydrogen bromide is liberated steadily. The crude bromo-compound (9·6 g.) that separates on cooling crystallises from toluene in greenish-yellow prisms, m. p. 217—218°.

(*b*) 10-Acetyl-5 : 10-dihydrophenarsazine (15 g.) dissolved in boiling glacial acetic acid (200 c.c.) is treated with hydrobromic acid (10 c.c.; 30%) in glacial acetic acid (25 c.c.). On cooling, 10-bromo-5 : 10-dihydrophenarsazine (13·3 g.) separates (Found : As, 23·3; Br, 24·8%).

10-*Iodo*-5 : 10-*dihydrophenarsazine.*—On treating a hot solution

of 10-acetyl-5 : 10-dihydrophenarsazine (4·5 g.) in glacial acetic acid (70 c.c.) with hydriodic acid (2·5 c.c.; 50%) diluted with acetic acid (10 c.c.) the pure iodo-compound (5·6 g.) separates in brownish-orange needles, m. p. 217—221° (decomp.) (Found : As, 20·1%).

10-n-*Butoxy*-5 : 10-*dihydrophenarsazine*, $NH(C_6H_4)_2As{\cdot}O{\cdot}C_4H_9$.—A solution of 10 : 10′-oxy-5 : 10-dihydrophenarsazine (5 g.) in *n*-butyl alcohol (50 c.c.), on cooling deposited a mass of pale yellow needles, m. p. 158—160° (Found : As, 23·7. $C_{16}H_{18}ONAs$ requires As, 23·8%).

A boiling solution of 10 : 10′-oxy-5 : 10-dihydrophenarsazine (15 g.) in *n*-butyl alcohol (180 c.c.) is saturated with dry hydrogen sulphide for 2 hours. The compound crystallises during the reaction and after collection is recrystallised from toluene. 10 : 10′-Sulpho-5 : 10-dihydrophenarsazine crystallises in yellow needles, m. p. 256—264° (decomp.). Yield 67% of theory (Found : As, 29·1%).

10-*Benzyloxy*-5 : 10-*dihydrophenarsazine*,

$$NH(C_6H_4)_2AsO{\cdot}CH_2{\cdot}C_6H_5,$$

prepared in an analogous manner to the corresponding *n*-butyl compound, crystallises in colourless needles, m. p. 173—175° (Found : As, 21·1. $C_{19}H_{16}ONAs$ requires As, 21·5%).

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