CVIII.—10-*Chloro*-5 : 10-*dihydrophenarsazine and its Derivatives. Part VII. The Synthesis of the* 1-*Methyl and* 3-*Methyl Homologues.*

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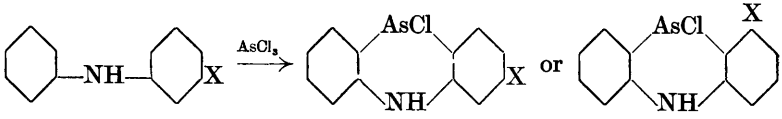
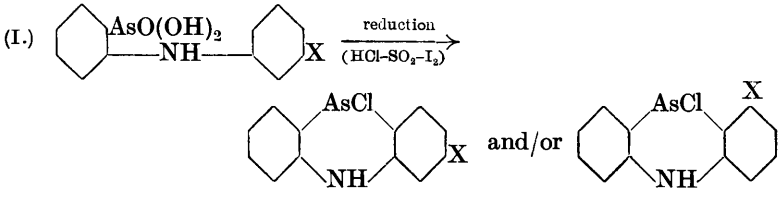
IN the preceding parts of this series, three methods have been described for the preparation of derivatives of 10-chloro-5 : 10-dihydrophenarsazine, *viz.*, (*a*) the condensation of substituted diphenylamines with arsenious chloride (or bromide) in the presence of a suitable solvent, (*b*) the preparation of *o*-bromo-*o'*-amino-diphenylarsinic acid, followed by the elimination of hydrogen bromide under the conditions described in Part I (J., 1926, 452), yielding phenarsazinic acid, and (*c*) the preparation of substituted diphenylamine-*o*-arsinic acids on the one hand by the condensation of *o*-bromophenylarsinic acid with substituted anilines, and, on the other hand, by the condensation of *o*-aminophenylarsinic acid with

substituted bromobenzenes, followed in each case by ring closure under prescribed conditions. Some of the conditions limiting the usefulness of method (*a*) have already been mentioned (J., 1926, 2243), and method (*b*), which has not been investigated so thoroughly, is obviously limited by the practical difficulties attending the preparation of the substituted diphenylarsinic acids. Further, in method (*a*) it is obvious that, in the condensations of *m*-substituted diphenylamines with arsenious chloride, the product (if homogeneous) may have one or other of two structural formulæ :



The condensations of arsenious chloride with *m*-aminodiphenylamine (J., 1926, 2244), *m*-chlorodiphenylamine (*ibid.*, p. 2246), phenyl-β-naphthylamine (*ibid.*, p. 2243), *p*-tolyl-β-naphthylamine (*ibid.*, p. 2244), di-β-naphthylamine (*ibid.*, p. 462), and *NN'*-diphenyl-*m*-phenylenediamine (J., 1928, 2212) are instances where there is this possibility. In all these cases the condensation product appeared to be homogeneous, and, as far as this reaction is concerned, there is at present no evidence for the production of more than one product in any particular case.

In Parts IV, V, and VI of this series, the third method (*c*) of preparation of derivatives of 10-chloro-5 : 10-dihydrophenarsazine was shown to be of general applicability. In this case also, there is the possibility that in substituted diphenylamine-*o*-arsinic acids of type (I), ring closure may lead to one or other, or both, of two isomerides :

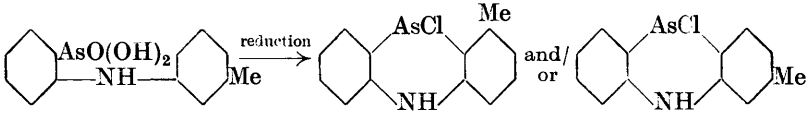


Several derivatives of 10-chloro-5 : 10-dihydrophenarsazine have already been prepared from diphenylamine-*o*-arsinic acids of type (I) by this method, and of those previously described may be mentioned the 1- or 3-carboxy- (J., 1927, 249) and the 1- or 3-nitro- (J., 1928, 2514) derivatives.

The orientation of the group X in the phenarsazine nucleus finds

its parallel in the work of Roberts and Turner (J., 1925, **127**, 2005) on the formation of 5 : 8-dichlorophenoxarsine from 2-*m*-chlorophenoxyphenyldichloroarsine. In this particular case, the ring compound was synthesised by a method which leaves no doubt as to its constitution, and it was found to be identical with the product derived from 2-*m*-chlorophenoxyphenyldichloroarsine.

With a view to determine the direction of ring closure when substances of type (I) are reduced, it seemed desirable to investigate the simple case where X = CH_3. 3-Methyldiphenylamine-6'-arsinic acid (II) can on ring closure by reduction yield 10-chloro-1-methyl-5 : 10-dihydrophenarsazine (III) and/or 10-chloro-3-methyl-5 : 10-dihydrophenarsazine (IV).

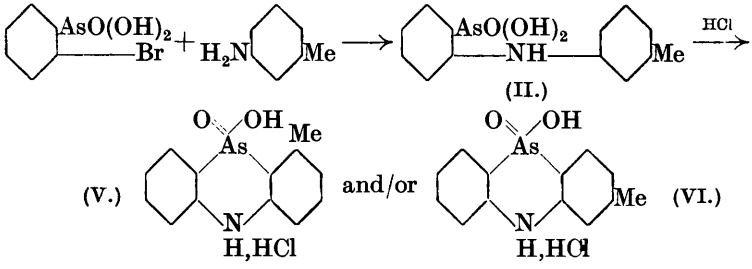


(II.) (III.) (IV.)

The isomeric 2-methyl and 4-methyl homologues (J., 1927, 2508, 2510) of 10-chloro-5 : 10-dihydrophenarsazine have already been synthesised by this method, and in these cases there is no possibility of producing more than one compound in each reaction. In the reaction now under discussion there is no *a priori* reason why either (III) or (IV) should be produced to the complete exclusion of the other, since, whatever the directing influence of the substituted phenylamino-group may be, it is certain to be identical in value for the two ortho-positions in the right hand benzene nucleus of (II), and the effect of the methyl group will be to produce ortho-para-substitution to itself. Presumably the para-directing influence of the methyl group should be stronger than the ortho-, and it seems reasonable to believe that the favoured direction of ring closure will be that leading to the production of 10-chloro-3-methyl-5 : 10-dihydrophenarsazine (IV). Another circumstance which should favour the formation of (IV) by suppressing the formation of (III) is the steric factor, since, as is pointed out in the experimental portion, the difficulty of reducing 3-bromo-*o*-tolylarsinic acid (XII) and the comparative ease with which dearsenication of 3-amino-*o*-tolylarsinic acid (XI) occurs, are separate examples of the protecting action of the adjacent methyl group and bromine atom on the one hand and the reluctance of the arsinic acid group to remain between methyl and amino-groups on the other.

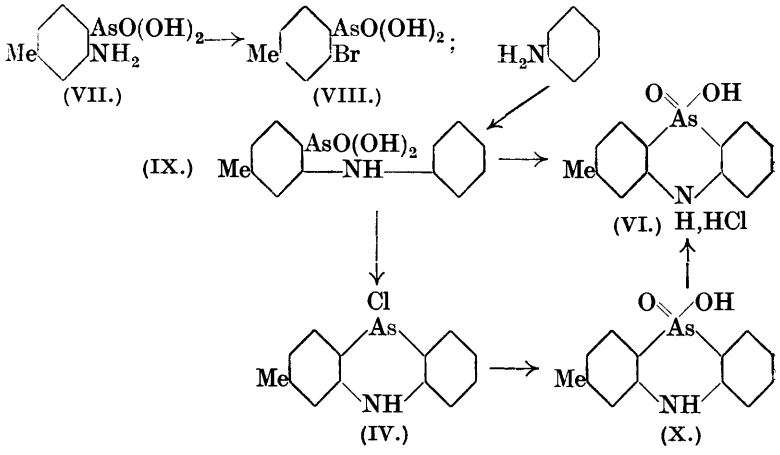
3-*Methyldiphenylamine*-6'-*arsinic acid* (II) was readily prepared by condensing *o*-bromophenylarsinic acid with *m*-toluidine under

the conditions described in the experimental portion, the crude product being purified through its sodium salt. Ring closure was effected in different ways. On boiling the acid with concentrated hydrochloric acid for a few minutes, the hydrochloride of a methylphenarsazinic acid was produced (compare the hydrochlorides of the 2- and 4-methylphenarsazinic acids, J., 1927, 2508, 2510). The product appeared homogeneous when crystallised from a mixture of ethyl alcohol and concentrated hydrochloric acid, yielding colourless needles, m. p. 232—233° (vigorous decomp.). It may, however, have consisted of the 1-methyl- or the 3-methyl-phenarsazinic acid hydrochloride, or of a mixture of these, formed according to the scheme :



Reduction of 3-methyldiphenylamine-6′-arsinic acid by the alcohol–hydrochloric acid–iodine–sulphur dioxide method gave a yellow product, but although a search for the presence of two substances was carefully carried out, the melting point of the last traces of the crude reduction product separating from the mother-liquor was but slightly lower than that of the main bulk of substance. After repeated recrystallisation from benzene, care being taken to examine all mother-liquors for fractions of differing melting points, the product was obtained in long yellow needles of constant melting point, 216—216·5° : this is a melting point, there being no decomposition as is so often the case with substances of the phenarsazine type. On oxidation with hydrogen peroxide or with chloramine-T, the corresponding methylphenarsazinic acid was obtained in fine colourless needles, decomposing slightly at 316°. Its sodium salt is insoluble in cold concentrated sodium hydroxide solution, and the hydrochloride is indistinguishable from that obtained by boiling 3-methyldiphenylamine-6′-arsinic acid with concentrated hydrochloric acid. On reduction of the methylphenarsazinic acid in hydrobromic acid–alcohol solution, the corresponding methyl-10-bromo-5 : 10-dihydrophenarsazine (m. p. 206—208°) was obtained.

In order to compare the ring compounds derived from 3-methyldiphenylamine-6′-arsinic acid with substances of known constitution, the synthesis of 10-chloro-3-methyl-5 : 10-dihydrophenarsazine (IV) and of 10-chloro-1-methyl-5 : 10-dihydrophenarsazine (III) was accomplished in the following manner.

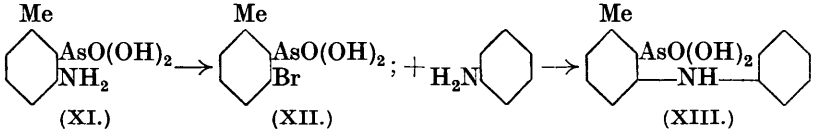


3-Amino-*p*-tolylarsinic acid (VII) (Jacobs, Heidelberger, and Rolf, *J. Amer. Chem. Soc.*, 1918, **40**, 1585) is readily converted into 3-bromo-*p*-tolylarsinic acid (VIII) or the corresponding chloro-compound by the Sandmeyer reaction. These acids may be converted into the corresponding dichloroarsines by reduction, and from these the corresponding arsenious oxides may be obtained. The acids may also be oxidised to the corresponding 2-bromo-(chloro)-4-carboxyphenylarsinic acids by means of an alkaline solution of potassium permanganate. 3-Bromo-*p*-tolylarsinic acid (VIII) condensed readily with aniline. The 3-*methyldiphenylamine*-6-*arsinic acid* (IX) produced, purified through its ammonium salt, had m. p. 158—159° and was quite different, as would be expected from its mode of preparation, from the isomeric 3-methyldiphenylamine-6′-arsinic acid (II). On reduction by the alcohol–hydrochloric acid–iodine–sulphur dioxide method, this acid gave 10-chloro-3-methyl-5 : 10-dihydrophenarsazine (IV) as a homogeneous product, which crystallised from benzene in yellow needles, m. p. 216—216·5°, and did not depress the melting point of the reduction product of 3-methyldiphenylamine-6′-arsinic acid. On oxidation with hydrogen peroxide or with chloramine-T, 3-methylphenarsazinic acid (X) was obtained, the sodium salt being insoluble in

concentrated sodium hydroxide solution and the hydrochloride having m. p. 231—232° (decomp.). The same hydrochloride was produced on boiling the acid (IX) with concentrated hydrochloric acid, and did not depress the melting point (or rather the decomposition point) of the hydrochloride of the methylphenarsazinic acid formed from (II). Obviously, no stress can be laid on a negative depression of decomposition points, as this may mean anything; on the other hand, if a depression had been produced, it would certainly prove the non-identity of the two substances. 3-Methylphenarsazinic acid on reduction in hydrobromic acid–alcohol solution gave 10-bromo-3-methyl-5 : 10-dihydrophenarsazine, which again was indistinguishable from the bromo-derivative mentioned above.

The evidence thus far indicated that ring closure of (II) gave derivatives of 10-chloro-3-methyl-5 : 10-dihydrophenarsazine and not of the 1-methyl derivative. These indications were, however, found to be untrustworthy, since when the corresponding 1-methyl derivatives were prepared they were only by the very slightest differences, as shown below, distinguishable from the rationally synthesised 3-methyl derivatives.

In describing the method of synthesis of the 1-methyl derivatives, it is necessary to indicate those factors which might have an influence on the product formed when 3-methyldiphenylamine-6′-arsinic acid is subjected to the action of reagents which effect ring closure. The starting point was 3-amino-*o*-tolylarsinic acid (XI) (Jacobs, Heidelberger, and Rolf, *loc. cit.*). This substance is readily dearsenicated by the action of alkalis and acids, *m*-toluidine being formed. The amino-group is readily replaced by bromine or chlorine, yielding 3-*bromo*(*chloro*)-o-*tolylarsinic acid* (XII). The difficulty of obtaining the *dichloroarsines* by reduction of these acids has been mentioned above, but they were obtained as low-melting solids resembling the isomeric 3-bromo(chloro)-*p*-tolyldichloroarsines in most properties but were less readily attacked by water and alkalis.



(XI.) (XII.) (XIII.)

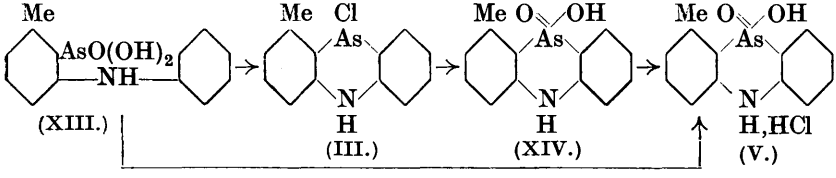
The corresponding *arsenious oxides* were obtained as white amorphous substances by the prolonged action of alkali. These oxides, however, were soluble with difficulty even in a large excess

of hot sodium hydroxide solution. Since the solubility in alkali of phenylarsenious oxides is due to the formation of alkali salts, it is clear that 3-chloro- and 3-bromo-*o*-tolylarsenious oxides have little tendency to salt formation, which is further evidence that the two groups in the two ortho-positions to the arsinic acid group protect it from chemical reaction. When 3-bromo-*o*-tolylarsinic acid was condensed with aniline, 3-*methyldiphenylamine*-2-*arsinic acid* (XIII) was obtained in good yield, in colourless needles, m. p. 170—171° (decomp.).

The three methyldiphenylamine-*o*-arsinic acids are therefore obviously distinct and different from one another. On reduction by the alcohol–hydrochloric acid–iodine–sulphur dioxide method, 3-methyldiphenylamine-2-arsinic acid was *slowly* reduced, so slowly that on one occasion the hydrochloride of the acid (V) separated in almost colourless needles from the cooling solution and, thus escaping reduction, might easily have been mistaken for the reduction product. In order to reduce (XIII) completely it is necessary to heat the liquid, saturated with sulphur dioxide, for some time. This observation bears on the mode of formation of compounds of the phenarsazine type by reduction of diphenylamine-*o*-arsinic acids. The hypothesis has been suggested (J., 1927, 2506) that formation of compounds of the phenarsazine type by reduction of diphenylamine-*o*-arsinic acids takes place through the intermediate formation of the dichloroarsine. It would appear from the results described in the present communication and from the results of investigations which have been made on dimethyl derivatives of 10-chloro-5 : 10-dihydrophenarsazine that the formation of derivatives of 10-chloro-5 : 10-dihydrophenarsazine by reduction of diphenylamine-*o*-arsinic acids may, however, be preceded by the formation of the hydrochloride of the ring-acid, followed by reduction. The previous suggestion would appear then to require some modification, but it may be pointed out that in the reduction of nitromethyldiphenylamine-*o*-arsinic acids (an account of these substances and of the dimethyl and dinitro-derivatives will shortly be submitted for publication) the ring closure must be effected through the dichloroarsine, since they do not form isolable hydrochlorides, nor is ring closure effected by simple boiling with concentrated hydrochloric acid.

The product formed by the reduction of (XIII) must be considered to be 10-*chloro*-1-*methyl*-5 : 10-*dihydrophenarsazine* (III). It crystallised in yellow needles, m. p. 216—216·5° without decomposition. It did not depress the melting point of 10-chloro-3-methyl-5 : 10-dihydrophenarsazine, nor the melting point of the reduction

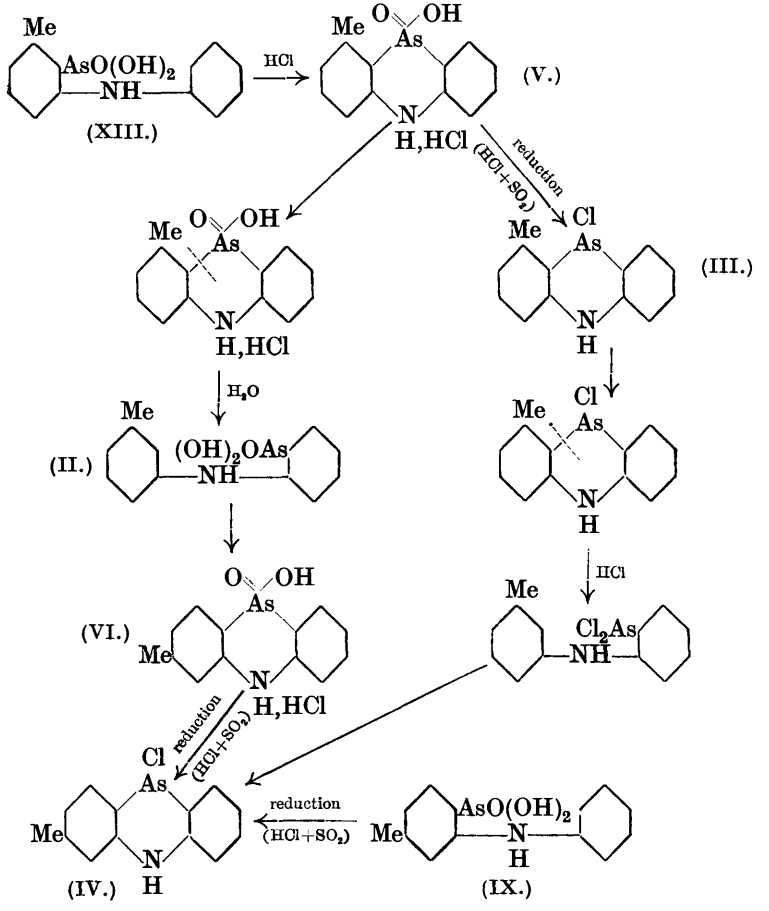
product of (II), several different mixtures being taken. On oxidation, 1-methylphenarsazinic acid (XIV) was obtained, indistinguishable from the 3-methyl isomeride; its sodium salt was insoluble in cold concentrated sodium hydroxide solution and the hydrochloride (V) had m. p. 231—232° (vigorous decomp.). The hydrochloride of 1-methylphenarsazinic acid was also formed on boiling the acid (XIII) with concentrated hydrochloric acid.



The 1- and 3-methyl derivatives appeared thus to be indistinguishable by the ordinary methods and the problem of deciding whether on ring closure compound (II) gives 1- or 3-methyl derivatives or a mixture of them in any proportions became all the more difficult. Preliminary determinations of the solubilities of methyl-10-chloro-5 : 10-dihydrophenarsazines showed that in benzene, the most suitable solvent, they were apparently equally soluble. Under the microscope they appeared to be the same. Determination of refractive indices or of densities of solutions could not be of much value, since these substances have small solubilities in the suitable solvents at the ordinary and at higher temperatures. An attempt was made to differentiate between the two substances by Sidgwick's freezing-point method (J., 1915, **107**, 672), the solvent being benzene. The solubility at the melting point of benzene was, however, very small and the maximum observed depression of the freezing point of a solution of 10-chloro-1-methyl-5 : 10-dihydrophenarsazine was 0·046° (mean of three determinations). On addition of 10-chloro-3-methyl-5 : 10-dihydrophenarsazine there was a further depression of only 0·004° (mean of two determinations). Therefore no conclusion as to a difference between these two compounds can be drawn from this experiment.

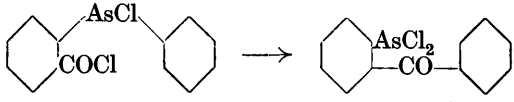
From the evidence which it has been possible to accumulate, it cannot be said that the direction of ring closure in the case of (II) has been ascertained In fact, it is not impossible that 10-chloro-1-methyl-5 : 10-dihydrophenarsazine and 10-chloro-3-methyl-5 : 10-dihydrophenarsazine are one and the same substance. Bearing in mind the ease of dearsenication of 2-amino-6-methylphenarsazinic acid, it will be seen that the formation of 10-chloro-3-methyl-5 : 10-dihydrophenarsazine by reduction of 3-methyldiphenylamine-2-

arsinic acid (XIII) is not impossible according to one of the following schemes :



One observation which would appear to exclude the mechanism indicated on the left is that the hydrochlorides of the ring acids are formed with the greatest ease from the open-chain acids, yet the complete reduction of (XIII) takes place with difficulty, whereas the reduction of (IX) is extremely facile, as indicated in the experimental portion, and the reduction of (II) takes place with intermediate ease as far as can be judged from what can only be qualitative experiments. It may be that this indicates that the reduction product is a mixture of the 1- and 3-methyl isomerides. In this connexion, a reaction of this type has been discussed by Aeschlimann

and McCleland (J., 1924, **125**, 2025), who showed that the acid chloride of *o*-carboxydiphenylchloroarsine when heated with aluminium chloride gave benzophenone-*o*-dichloroarsine, thus :



Indications have been obtained of the possibility of determining whether the above two compounds are identical with or different from each other by chemical methods. The accumulation, however, of the necessary materials for the investigation, which requires the carrying out of a very long series of preparations, is very difficult. In the meantime, by the preparation of other derivatives and particularly the examination of other physical properties, including absorption spectra, it is hoped to arrive at a solution of the problem.

EXPERIMENTAL.

If excess of water be avoided in the preparation of 3-amino-*p*-tolylarsinic acid (VII) (Jacobs, Heidelberger, and Rolf, *loc. cit.*), part of the amino-acid is obtained on acidifying the filtrate prior to treatment of the solution with barium chloride. This may be filtered off, and the filtrate treated as described by the above authors except that the concentration of the aqueous solution may be carried out at the ordinary pressure. When crystallised from alcohol, 3-amino-*p*-tolylarsinic acid has m. p. 184—185°.

3-*Chloro*-p-*tolylarsinic acid*, $C_6H_3MeCl\cdot AsO(OH)_2$.—3-Amino-*p*-tolylarsinic acid (10·0 g.), dissolved in hydrochloric acid (18·7 c.c.) and water (16·5 c.c.) by warming, was diazotised below 0° with sodium nitrite (3·33 g.) in water (6·6 c.c.). The diazo-solution was added to a solution of cuprous chloride (3·8 g.) in hydrochloric acid (12·7 c.c.) with constant stirring in the course of about 3 minutes without any cooling. Water (25 c.c.) was added and the liquid stirred for 30 minutes, the precipitated acid then being filtered off, washed with cold water until the washings were colourless, and recrystallised from hot water after treatment with decolorising charcoal. Yield, 7·0 g. (65%).

3-*Chloro*-p-*tolylarsinic acid* forms colourless, flat, truncated prisms, m. p. 189—191° (slight softening at 184°) (Found : Cl, 14·4. $C_7H_8O_3ClAs$ requires Cl, 14·2%). It is almost insoluble in cold water but dissolves fairly readily on boiling; it is readily soluble in concentrated hydrochloric acid, methyl and ethyl alcohols, and alkali hydroxides and carbonates.

3-*Chloro*-p-*tolyldichloroarsine*, $C_6H_3MeCl\cdot AsCl_2$.—The preceding compound (4·3 g.), dissolved in hot concentrated hydrochloric acid

(14 c.c.) containing a trace of iodine, was treated with a rapid stream of sulphur dioxide for about 5 minutes. After cooling, the precipitated oil was extracted with benzene, and the extract filtered from amorphous matter and dried over calcium chloride. The benzene was evaporated and the residual oil was distilled under reduced pressure. The colourless, highly refracting liquid distilled at 166—167°/17 mm. and solidified to a mass of short needles, m. p. 27—29°. The liquid has a marked tendency to supercool (Found : Cl, 39·4. $C_7H_6Cl_3As$ requires Cl, 39·2%). It is readily soluble in ligroin, ethyl alcohol and benzene, but insoluble in water, by which it is slowly hydrolysed.

3-*Chloro*-p-*tolylarsenious Oxide*, $C_6H_3MeCl{\cdot}AsO$.—3-Chloro-*p*-tolyldichloroarsine (1·0 g.) was warmed on the water-bath with ammonia solution (*d* 0·88; 5 c.c.) and water (5 c.c.). The pasty mass soon solidified to a white amorphous mass. This was heated for about 20 minutes, collected, well washed with water, dissolved in warm sodium hydroxide solution, and reprecipitated by means of carbon dioxide (distinction from 3-chloro-*p*-tolylarsinic acid). It separated as a white amorphous mass, m. p. 277°. This *oxide* is insoluble in all the usual solvents and in sodium carbonate solution (Found : Cl, 16·6. C_7H_6OClAs requires Cl, 16·4%).

3-*Bromo*-p-*tolylarsinic Acid* (VIII).—The solution prepared by diazotising 3-amino-*p*-tolylarsinic acid (30·0 g.) in hydrobromic acid (*d* 1·265; 100 c.c.) and water (50 c.c.) with sodium nitrite (10·0 g.) in water (20 c.c.) below 0°, was added in the course of about 5 minutes to a solution of cuprous bromide [prepared by mixing solutions of copper sulphate crystals (28·5 g.) in water (94 c.c.) and potassium bromide (14·1 g.) in water (33 c.c.) and saturating the mixture with sulphur dioxide] in hydrobromic acid (*d* 1·49; 51 c.c.) as described for 3-chloro-*p*-tolylarsinic acid, water (60 c.c.) being added afterwards. After 45 minutes' stirring, the orange-coloured precipitate was filtered off and well washed with water. It was recrystallised from hot water after previous treatment with decolorising charcoal and obtained in colourless, flat, truncated prisms, m. p. 208—210° (decomp.). Yield, 72% (Found : Br, 27·4. $C_7H_8O_3BrAs$ requires Br, 27·1%).

The acid is readily soluble in acetic acid, hydrochloric acid, and ethyl alcohol. It is almost insoluble in cold water, and in benzene, but is readily soluble in hot water. A dilute solution of the ammonium salt gave no precipitate with solutions of calcium chloride and barium nitrate. The mercurous salt is a white precipitate soluble in hot water, the silver salt is white and soluble in ammonia, and the mercuric salt forms a brown precipitate somewhat soluble in hot water.

3-*Bromo*-p-*tolyldichloroarsine*, $C_6H_3MeBr{\cdot}AsCl_2$.—A hot solution of the preceding compound (8·3 g.) in hydrochloric acid (25 c.c.) containing a trace of iodine was reduced with sulphur dioxide. The oily product was worked up as described for 3-chloro-*p*-tolyldichloroarsine. 3-*Bromo*-p-*tolyldichloroarsine* was thus obtained in 60% yield as a colourless, highly refracting liquid, b. p. 176—177°/14 mm., which solidified to a mass of radiating needles, m. p. 47—49° (Found: 0·3059 g. gave 0·4632 g. of mixed silver halides. $C_7H_6Cl_2BrAs$ requires 0·4596 g.). It is soluble in ligroin and benzene and only slowly attacked by water, in which it is insoluble.

3-*Bromo*-p-*tolylarsenious oxide*, $C_6H_3MeBr{\cdot}AsO$, was obtained by treating the preceding compound (2·94 g.) with ammonia (10 c.c.) and water (10 c.c.) as described for the chloro-compound. It was obtained as a white amorphous mass, m. p. 266—268°, insoluble in the ordinary organic solvents but soluble in caustic alkalis, from which solutions it was precipitated by carbon dioxide (Found: Br, 30·9. C_7H_6OBrAs requires Br, 30·7%).

2-*Chloro*-4-*carboxyphenylarsinic Acid*, $CO_2H{\cdot}C_6H_3Cl{\cdot}AsO(OH)_2$.—A warm solution of 3-chloro-*p*-tolylarsinic acid (5·0 g.) in sodium carbonate (decahydrate, 5·7 g., in water, 20 c.c.) was added to potassium permanganate (12·6 g.) in water (312 c.c.) and boiled during 8 hours. A current of carbon dioxide was continually passed through the mixture in order to minimise the replacement of the chlorine by hydroxyl by means of the potassium hydroxide formed during the oxidation. The resulting solution was filtered whilst hot, and the manganese dioxide extracted with boiling water. The aqueous solutions were mixed and concentrated to about 250 c.c., cooled, and acidified with concentrated hydrochloric acid. 2-*Chloro*-4-*carboxyphenylarsinic acid* was slowly precipitated as colourless needles or long flat plates, unmelted at 310° (Found: Cl, 12·6. $C_7H_6O_5ClAs$ requires Cl, 12·65%). The alkali salts are readily soluble in water; the barium salt forms rhomb-shaped plates, the calcium salt tufts of colourless needles; the silver, mercurous and mercuric salts are white precipitates, the first being soluble in ammonia. The magnesium salt appears to be soluble in water and not precipitated under ordinary conditions.

2-*Bromo*-4-*carboxyphenylarsinic Acid*, $CO_2H{\cdot}C_6H_3Br{\cdot}AsO(OH)_2$.—The oxidation of 3-bromo-*p*-tolylarsinic acid (9·45 g.) in sodium carbonate (decahydrate, 9·15 g., in water, 30 c.c.) with potassium permanganate (20·24 g.) in water (500 c.c.) was carried out as for the preceding substance. The product (yield, 65%) formed colourless needles, unmelted at 317°, slightly soluble in boiling water, almost insoluble in the cold (Found: Br, 24·8. $C_7H_6O_5BrAs$ requires Br, 24·6%).

3-*Methyldiphenylamine*-6-*arsinic Acid* (IX).—A mixture of 3-bromo-*p*-tolylarsinic acid (11·8 g.), aniline (3·75 g.), anhydrous potassium carbonate (8·8 g.), amyl alcohol (35 c.c.), and a trace of copper powder was boiled for 5 hours. Volatile substances were removed from the product by steam distillation and the filtered aqueous solution after treatment with decolorising charcoal was carefully acidified with dilute hydrochloric acid. A discoloured pasty mass (7·55 g., 63%) was precipitated. It was filtered off, well washed with water, and dried in a desiccator. The acid so obtained is sufficiently pure for most of the preparations described below, but the crude acid, which cannot be conveniently crystallised, was purified as follows. It was thoroughly mixed with a little concentrated solution of ammonia in the cold, and the mixture cautiously warmed to bring about solution; concentrated ammonia solution was then added and, if care had been taken to avoid loss of ammonia by excessive heating, the solution on cooling and stirring deposited the ammonium salt in clusters of colourless needles. The ammonium salt was filtered off and dissolved in water, and the solution acidified with dilute hydrochloric acid. The precipitated acid was dissolved in boiling 50% acetic acid and water added until the solution became slightly turbid; the liquid was heated to boiling, treated with decolorising charcoal and filtered; the filtrate on cooling deposited 3-*methyldiphenylamine*-6-*arsinic acid* in colourless needles, m. p. 158—159° (turning slightly brown) (Found: As, 24·5. $C_{13}H_{14}O_3NAs$ requires As, 24·4%). The acid is readily soluble in acetic acid, methyl and ethyl alcohols and acetone. Its solubility in water is very small. The sodium, potassium and ammonium salts are readily soluble in water, the silver, lead and mercuric salts form white flocculent precipitates insoluble in cold and hot water; the silver salt is soluble in ammonia. The mercurous, calcium, and barium salts are white precipitates insoluble in cold but soluble in hot water. The magnesium salt is formed only when a solution of the ammonium salt is boiled with magnesia mixture.

10-*Chloro*-3-*methyl*-5 : 10-*dihydrophenarsazine* (IV).—3-Methyldiphenylamine-6-arsinic acid (crude or pure, 3·45 g.), dissolved in a hot mixture of hydrochloric acid (15 c.c.) and alcohol (15 c.c.) containing a trace of iodine, was reduced by passing sulphur dioxide for a few minutes. Reduction and ring closure took place immediately, solid matter separating as soon as sulphur dioxide passed through the liquid. After cooling, the precipitated solid (2·2 g.) was filtered off, washed with a little alcohol, and dried at 100°. It was recrystallised from benzene and obtained in slender yellow needles, m. p. 216—216·5° (Found: Cl, 12·2. $C_{13}H_{11}NClAs$

requires Cl, 12·1%). It is sparingly soluble in benzene at the ordinary temperature but more soluble in the hot solvent; it is somewhat readily soluble in acetone.

3-*Methylphenarsazinic Acid* (X).—(*a*) 10-Chloro-3-methyl-5 : 10-dihydrophenarsazine (2·0 g.), dissolved in cold acetone (70 c.c.), was treated with a cold solution of chloramine-T (4·5 g.) in water (63 c.c.). The yellow colour of the chloro-compound immediately disappeared and in a few minutes colourless crystalline material (1·6 g., 81%) began to separate. After 30 minutes, this was filtered off, well washed with water, and crystallised from glacial acetic acid, in which it was moderately easily soluble on boiling. The compound was obtained in clusters of fine colourless needles which retained a molecule of acetic acid of crystallisation even after drying over potassium hydroxide (Found : $C_2H_4O_2$, 17·2; As, in "dry" material, 25·55. $C_{13}H_{12}O_2NAs,C_2H_4O_2$ requires $C_2H_4O_2$, 17·2%. $C_{13}H_{12}O_2NAs$ requires As, 25·95%). The compound decomposes slightly at 316°.

(*b*) 10-Chloro-3-methyl-5 : 10-dihydrophenarsazine (2·0 g.) was boiled in acetic acid suspension (20 c.c.) with hydrogen peroxide (20 vols., 4·0 c.c.). The yellow chloro-compound was rapidly replaced by a white solid. After a few minutes' boiling, the liquid was cooled, water (80 c.c.) added, and the solid material filtered off and well washed with water. It was dissolved in hot dilute sodium hydroxide solution and treated with decolorising charcoal, and to the hot filtrate 25% sodium hydroxide solution was added in excess. On cooling, the sodium salt crystallised in fine colourless needles. This was filtered off and dissolved in warm water, and the acid (1·6 g., 79%) precipitated with concentrated hydrochloric acid. The acid, after drying at 150°, appeared to be identical with the product obtained by the previous method.

The *hydrochloride* (VI) of 3-methylphenarsazinic acid was prepared in two ways. (*a*) A solution of 3-methylphenarsazinic acid (1·6 g.) in a hot mixture of alcohol (47 c.c.) and hydrochloric acid (14 c.c.) was allowed to cool. The hydrochloride was deposited in fine colourless needles or elongated plates, m. p. 232—233° (decomp., turning emerald-green) (Found : Cl, 11·2. $C_{13}H_{12}O_2NAs,HCl$ requires Cl, 10·9%). What appeared to be the same hydrochloride was obtained whether the 3-methylphenarsazinic acid had been prepared by method (*a*) or (*b*) described above.

(*b*) 3-Methyldiphenylamine-6-arsinic acid was boiled with an excess of concentrated hydrochloric acid; it liquefied, emitting the characteristic odour which has been mentioned previously (J., 1927, 2503), and within half a minute crystalline material began to separate. After cooling, this was filtered off and recrystallised from

a mixture of alcohol and hydrochloric acid. It appeared to be identical with the product obtained by method (*a*).

10-*Bromo*-3-*methyl*-5 : 10-*dihydrophenarsazine* (formula as IV).—3-Methylphenarsazinic acid (0·82 g.) was dissolved in a boiling mixture of hydrobromic acid (*d* 1·49; 12 c.c.) and alcohol (12 c.c.) containing a trace of iodine and reduced by passage of sulphur dioxide for a few minutes. After cooling, the precipitated *bromo*-compound (0·77 g.) was filtered off, washed with alcohol, and dried at 150°. It was recrystallised from benzene and obtained in orange rectangular plates or slender needles, m. p. 206—208° (Found : Br, 24·1. $C_{13}H_{11}NBrAs$ requires Br, 23·8%).

3-*Nitro*-p-*tolyldichloroarsine*, $NO_2 \cdot C_6H_3Me \cdot AsCl_2$.—3-Nitro-*p*-tolylarsinic acid (2·85 g.), dissolved in boiling hydrochloric acid (20 c.c.) containing a little hydriodic acid, was saturated with sulphur dioxide. The precipitated oil soon solidified and after drying on porous porcelain it was crystallised from ligroin (b. p. 60—80°). The compound obtained formed pale yellow, flat prisms, m. p. 113° (Found : Cl, 25·0. $C_7H_6O_2NCl_2As$ requires Cl, 25·2%).

3-Nitro-*o*-toluidine (Gabriel and Thieme, *Ber.*, 1919, **52**, 1079) was converted into 3-nitro-*o*-tolylarsinic acid by the method of Jacobs, Heidelberger, and Rolf (*loc. cit.*). After coupling of the diazo-solution as described with alkaline sodium arsenite solution, precipitation of feebly acidic substances with acetic acid, and treatment with charcoal, the cooled filtrate on acidification with hydrochloric acid should yield the nitro-arsinic acid, m. p. 223—230° (decomp.). It was found that if an excess of acetic acid was added to the "coupled" solution in the first place, the cooled filtrate deposited colourless needles before the addition of hydrochloric acid. The precipitated substance could be recrystallised from water, was soluble in sodium carbonate, sodium hydroxide or ammonia solution, and was reprecipitated on addition of acetic acid. The air-dried material melted at 97°, resolidified at 125—130°, and then remained unmelted at 300°. When the substance in sodium hydroxide solution was acidified with hydrochloric, hydrobromic or sulphuric acid, the nitro-arsinic acid, m. p. 228—230°, was obtained. This, dissolved in sodium hydroxide solution, gave the substance, m. p. 97° (etc.), on acidification with acetic acid. This substance proved to be the *sodium hydrogen* salt of 3-nitro-*o*-tolylarsinic acid and it is formed whenever a solution of the acid in sodium hydroxide is acidified with acetic acid, whereas mineral acids precipitate the nitro-acid itself [Found in air-dried material : As, 19·3; N, 3·8; Na, 5·9; H_2O (over phosphoric oxide), 26·9 (by heating, slight decomposition), 29·5. $C_7H_7O_5NAsNa,6H_2O$ requires As, 19·2; N, 3·6; Na, 5·9; H_2O, 27·6%]. 3-Nitro-*o*-tolylarsinic acid is colourless.

3-*Nitro*-o-*tolyldichloroarsine*, $NO_2 \cdot C_6H_3Me \cdot AsCl_2$.—A boiling solution of 3-nitro-*o*-tolylarsinic acid (12 g.) in hydrochloric acid (60 c.c.) containing a trace of iodine was reduced by passage of sulphur dioxide for a few minutes. An oil was precipitated which solidified on cooling; it was filtered off, washed with concentrated hydrochloric acid, pressed on porous porcelain, and crystallised from ligroin (b. p. 60—80°, decolorising charcoal being used). The *compound* (7·0 g.) separated in pale yellow needles, m. p. 93° (Found: Cl, 24·9. $C_7H_6O_2NCl_2As$ requires Cl, 25·2%). It is readily soluble in acetone and benzene and somewhat less soluble in ligroin. Like other dichloroarsines, it is hydrolysed by water.

3-*Nitro*-o-*tolyldibromoarsine*, $NO_2 \cdot C_6H_3Me \cdot AsBr_2$.—On boiling 3-nitro-*o*-tolylarsinic acid (12·2 g.) with hydrobromic acid (*d* 1·49; 100 c.c.) containing a trace of iodine, bromine was evolved and an oil separated, the hydrobromic acid apparently acting as a reducing agent. Reduction was completed by saturating the solution with sulphur dioxide, and the product worked up as in the previous preparation. Recrystallised from benzene–ligroin (b. p. 60—80°), the *dibromoarsine* (16 g., 92%) was obtained in pale yellow, flat plates, m. p. 116·5—117·5° (Found: Br, 42·8. $C_7H_6O_2NBr_2As$ requires Br, 43·1%).

3-Amino-*o*-tolylarsinic acid (XI) was prepared according to the method of Jacobs, Heidelberger, and Rolf (*loc. cit.*). Contrary to the case of 3-amino-*p*-tolylarsinic acid (p. 776), the evaporation of the aqueous solution of the sodium salt must be carried out under reduced pressure, otherwise considerable dearsenication occurs and the yield is very small. Even when the evaporation was carried out under reduced pressure the aqueous distillate contained *m*-toluidine (formed by dearsenication), which was identified by conversion into 2:4:6-tribromo-*m*-toluidine (m. p. 97°). After the solution had been concentrated it was cautiously acidified and the amino-acid, mixed with a little salt, was filtered off, roughly dried, and boiled with alcohol to separate the amino-acid from the salt. The alcoholic filtrate on concentration deposited the pure amino-acid. The alcoholic mother-liquor on further evaporation left a dark-coloured oil, which solidified on the addition of water. This product was recrystallised from hot water (decolorising charcoal) and was then obtained in pale pink needles, m. p. 117°, unchanged on further recrystallisation. On treatment with dilute sodium hydroxide solution, this substance gave an oil which was identified as *m*-toluidine (benzoyl derivative, m. p. 125°). The properties of the substance indicated that it was a salt of *m*-toluidine and it was therefore compared with the *arsenate* of *m*-toluidine. This was prepared by adding *m*-toluidine (10 g.) to a hot solution of arsenic

acid (14 g.) in water (56 c.c.), treating it with decolorising charcoal, and filtering and cooling it. *m*-Toluidine arsenate crystallised in colourless leaflets, softening at 93° and melting at 141—144° (Found : N, 5·8; As, 30·4. C_7H_9N,H_3AsO_4 requires N, 5·6; As, 30·2%). The substance obtained as a by-product in the above preparation was not identical with *m*-toluidine arsenate, and its nature is for the present unknown.

3-*Chloro*-o-*tolylarsinic Acid*, $C_6H_3MeCl{\cdot}AsO(OH)_2$.—3-Amino-*o*-tolylarsinic acid (12·0 g.) was dissolved in a mixture of hydrochloric acid (22·4 c.c.) and water (20 c.c.) and diazotised below 5° with a solution of sodium nitrite (4·0 g.) in water (8·0 c.c.). Towards the end of the diazotisation the diazo-compound separated in pale yellow needles; separation of the diazo-compound also took place during the preparation of the corresponding bromo-compound (below). The suspension was added at the ordinary temperature with constant stirring to a solution of cuprous chloride (4·55 g.) in hydrochloric acid (15·3 c.c.), ether being used to control excessive frothing. The mixture was heated on the water-bath to complete the reaction, water added, and the *chloro-acid* (9·85 g., 76%) filtered off, well washed with water, and crystallised from alcohol. It was obtained in colourless prisms or prismatic needles, m. p. 236—239° (decomp.) after slight softening at 232° (Found: Cl, 13·9. $C_7H_8O_3ClAs$ requires Cl, 14·2%). It is readily soluble in ethyl alcohol and in acetic acid, but almost insoluble in water. The silver and mercurous salts are characteristic : the former is precipitated in clusters of colourless needles and the latter in fine colourless needles.

3-*Chloro*-o-*tolyldichloroarsine*, $C_6H_3MeCl{\cdot}AsCl_2$.—The preceding compound (7·5 g.) was dissolved in boiling hydrochloric acid (20 c.c.) containing a little hydriodic acid, and the solution saturated with sulphur dioxide. Reduction was very slow, it being necessary to boil the solution several times during the reduction to prevent the precipitation of the acid. This retardation of reduction clearly indicates steric hindrance and was even more marked in the case of the reduction of 3-bromo-*o*-tolylarsinic acid (see below). The crude product was a thick oil, which was worked up as described for the isomeric 3-chloro-*p*-tolyldichloroarsine. It distilled at 156°/11 mm. as a colourless oil, rapidly assuming a pink colour. It has m. p. 37·5° and forms colourless stout prisms (yield, 78%) (Found : Cl, 39·4. $C_7H_6Cl_3As$ requires Cl, 39·2%). It has a phenolic odour and is readily soluble in the ordinary organic solvents. It is slowly hydrolysed by water, forming the oxide.

3-*Chloro*-o-*tolylarsenious Oxide*, $C_6H_3MeCl{\cdot}AsO$.—The preceding substance (1·75 g.) was heated with water (10 c.c.) and ammonia

(10 c.c.) on the water-bath. The conversion of the dichloroarsine into the arsenious oxide was hindered by the latter forming an insoluble protecting coating over the former; benzene was therefore added and the mixture well shaken at intervals during the heating (1 hour) on the water-bath. The colourless *3-chloro-o-tolylarsenious oxide*, being insoluble in water and all the usual organic solvents, was filtered off and thoroughly washed. It is insoluble in alkali carbonate and hydroxide solutions. At 234—237° it forms a milky liquid, clearing at 254° (Found: Cl, 16·15. C_7H_6OClAs requires Cl, 16·4%).

3-Bromo-o-tolylarsinic Acid (XII).—This substance was obtained in 75% yield in a manner similar to that used for the isomeric compound (p. 777), except that the evolution of nitrogen after mixture of the diazo-solution with the copper solution was completed by heating on the water-bath for 30 minutes instead of by stirring the liquid for 45 minutes. The product crystallised from aqueous alcohol in colourless thin needles. At 200°, it shrank somewhat; at 245°, it appeared to be converted into a white powder which remained unmelted at 306°. When the melting-point tube was introduced into the preheated apparatus at 260°, the substance melted to a clear liquid, effervesced, and then solidified to a white powder which remained unmelted at 306°. It is suggested that these phenomena indicate the formation of an anhydride which remains unmelted at 306° (Found: Br, 27·2. $C_7H_8O_3BrAs$ requires Br, 27·1%). The *acid* resembles the corresponding chloro-acid in general properties. The alkali and mercuric salts appear to be readily soluble in water; the silver, lead, and mercurous salts are white curdy precipitates; the magnesium salt is formed as a white amorphous precipitate only on boiling a strong solution of the ammonium salt with magnesia mixture; the calcium salt forms colourless needles, and the barium salt colourless plates, only when a strong solution of the ammonium salt is boiled with solutions of the appropriate metallic salts.

3-Bromo-o-tolyldichloroarsine, $C_6H_3MeBr\cdot AsCl_2$.—A boiling solution of 3-bromo-*o*-tolylarsinic acid (10·0 g.) in a mixture of hydrochloric acid (16·0 c.c.) and alcohol (10 c.c.) containing a little hydriodic acid was reduced, and the product worked up as described for 3-chloro-*o*-tolyldichloroarsine. It distilled as an almost colourless oil, b. p. 170—171°/13 mm., which solidified in a freezing mixture to a mass of stout prisms, m. p. 25—27° (Found: 0·6464 g. gave 0·9693 g. of mixed silver halides. $C_7H_6Cl_2BrAs$ requires 0·9712 g.) (yield, 6·8 g.). The compound had a faint, not unpleasant odour; it was soluble in all the usual organic solvents and was slowly hydrolysed by water.

3-*Bromo*-o-*tolylarsenious Oxide*, $C_6H_3MeBr{\cdot}AsO$.—The preceding substance (1·25 g.) was heated with water (5 c.c.) and ammonia (5 c.c.) on the water-bath, the conversion into the colourless *oxide* being very slow. The product was insoluble in the usual organic solvents and in alkali carbonates, but it dissolved slightly in a large volume of sodium hydroxide solution, from which it was reprecipitated in an amorphous condition by passage of carbon dioxide. It had an indefinite melting point, 214—219° (Found: Br, 30·7. C_7H_6OBrAs requires Br, 30·7%).

3-*Methyldiphenylamine*-2-*arsinic Acid* (XIII).—A mixture of 3-bromo-*o*-tolylarsinic acid (11·8 g.), aniline (3·75 g.), anhydrous potassium carbonate (8·8 g.), amyl alcohol (35 c.c.), and a trace of copper powder was boiled for 5 hours. Volatile substances were removed by steam distillation and the aqueous solution was treated with decolorising charcoal, cooled, and carefully acidified with dilute hydrochloric acid. The precipitated *acid* (8·2 g., 67%) was almost colourless. It was recrystallised from dilute acetic acid (50%) and obtained in colourless needles, m. p. 170—171° (decomp.) (Found: As, 24·3. $C_{13}H_{14}O_3NAs$ requires As, 24·4%). The acid is soluble in alcohol and acetic acid and almost insoluble in water. The sodium salt is precipitated on cooling its solution in 20% sodium hydroxide solution; the silver, lead, mercurous, and mercuric salts are white amorphous precipitates; the ammonium, calcium and magnesium salts appear to be readily soluble in water; the barium salt crystallises from hot water in colourless plates.

10-*Chloro*-1-*methyl*-5 : 10-*dihydrophenarsazine* (III).—The preceding acid (5·5 g.), dissolved in a boiling mixture of alcohol (40 c.c.) and hydrochloric acid (40 c.c.) containing a trace of iodine, was reduced by passing a current of sulphur dioxide for some time. Reduction does not take place so readily as with the two isomeric acids (II) and (IX), it being necessary to boil the solution repeatedly during the reduction and to heat it on the water-bath for 30 minutes afterwards to complete the reaction. (The hydrochloride of the ring-acid tends to separate if the solution cools during the reduction and this is not very readily attacked.) The crystalline product was dried in a desiccator over potassium hydroxide and recrystallised from glacial acetic acid (the crystals retaining some green colouring matter) and then twice from benzene. It was obtained in slender, prismatic, yellow needles, m. p. 216—216·5° (Found: Cl, 11·8. $C_{13}H_{11}NClAs$ requires Cl, 12·1%). It dissolves fairly readily in acetone.

1-*Methylphenarsazinic Acid* (XIV).—The oxidation of the preceding compound was carried out as described for the 3-methyl isomeride (p. 780). The product crystallised from acetic acid

in colourless needles, m. p. 316° (decomp.) (Found : As, 25·7. $C_{13}H_{12}O_2NAs$ requires As, 25·95%). The most characteristic salt is the sodium salt, which crystallises from a 20% sodium hydroxide solution in fine colourless needles.

1-*Methylphenarsazinic acid hydrochloride* (V) was prepared in two ways :

(*a*) 3-Methyldiphenylamine-2-arsinic acid (1·1 g.) was boiled for a few minutes with concentrated hydrochloric acid (8 c.c.) and when the oil first formed had been replaced by a crystalline precipitate (about 1 minute), alcohol (8 c.c.) was added, the solution then being quite clear while boiling. On cooling, the *hydrochloride* separated in fine needles, m. p. 231—232° (decomp., turning emerald-green) (Found : Cl, 10·8. $C_{13}H_{12}O_2NAs,HCl$ requires Cl, 10·9%).

(*b*) A solution of 1-methylphenarsazinic acid (1·0 g.) in a boiling mixture of alcohol (25 c.c.) and hydrochloric acid (8 c.c.) was allowed to cool. The product appeared to be identical with that prepared by method (*a*).

3-*Methyldiphenylamine-6'-arsinic Acid* (II).—A mixture of *o*-bromophenylarsinic acid (21·0 g.), *m*-toluidine (8·0 g.), amyl alcohol (65 c.c.), anhydrous potassium carbonate (16·3 g.), and a trace of copper powder was boiled for 5 hours, and the product worked up in the manner already described for the isomeric compounds. It was purified through the sodium salt. The crude acid (14 g., 61%) was dissolved in hot 10% sodium hydroxide solution and to the boiling filtered solution, 25% sodium hydroxide solution was added until the crystalline sodium salt began to separate. After cooling, this was filtered off and worked up in the manner described for the ammonium salt of 3-methyldiphenylamine-6-arsinic acid The *acid* was obtained from its solution in dilute acetic acid in clusters of prismatic needles or elongated hexagonal prisms, m. p. 141—142° after slight softening (Found : As, 24·6. $C_{13}H_{14}O_3NAs$ requires As, 24·4%). It is readily soluble in acetic acid and in ethyl alcohol, but insoluble in water.

Reduction of 3-*Methyldiphenylamine-6'-arsinic Acid.*—The preceding compound (crude or pure, 14·0 g.), dissolved in a hot mixture of hydrochloric acid (80 c.c.) and alcohol (80 c.c.) containing a trace of iodine, was reduced and the product worked up as described for 10-chloro-3-methyl-5 : 10-dihydrophenarsazine. The main portion of the crude product had m. p. 210—213° and the last portion separating from the mother-liquor had m. p. 209—210°. After one recrystallisation from benzene, the product (A) had m. p. 216—217° and this was unchanged by further recrystallisation (Found : Cl, 12·3. $C_{13}H_{11}NClAs$ requires Cl, 12·1%).

Oxidation of the 1- *and/or* 3-*Methyl*-10-*chloro*-5 : 10-*dihydrophenarsazine.*—The preceding substance was oxidised by both methods described for the preparation of 3-methylphenarsazinic acid, the product being indistinguishable from the rationally synthesised 1-methyl- and 3-methyl-phenarsazinic acids. The sodium salt, colourless needles, was also insoluble in a cold concentrated solution of sodium hydroxide.

Effects of Acids on 3-*Methyldiphenylamine*-6′-*arsinic Acid.*—On boiling 3-methyldiphenylamine-6′-arsinic acid with concentrated hydrochloric acid the same phenomena as were observed in the case of 3-methyldiphenylamine-6-arsinic acid and 3-methyldiphenylamine-2-arsinic acid were noticed. The hydrochloride isolated crystallised from alcohol–hydrochloric acid in fine colourless needles having m. p. 232—233° (vigorous decomp., turning emerald-green), indistinguishable from the hydrochloride of either 1-methyl- or 3-methylphenarsazinic acid. On boiling 3-methyldiphenylamine-6′-arsinic acid with 50% sulphuric acid for a few minutes and cooling and diluting the solution, what appeared to be 3-methylphenarsazinic acid was precipitated.

1- *and/or* 3-*Methyl*-10-*bromo*-5 : 10-*dihydrophenarsazine.*—The reduction of 1- and/or 3-methylphenarsazinic acid to give 1- and/or 3-methyl-10-bromo-5 : 10-dihydrophenarsazine was carried out as described for the 3-methyl compound. The products appeared to be identical when compared under the microscope and no depression of melting point of the mixed substances was observed.

Comparison of the Reduction Product (*A*) *of* 3-*Methyldiphenylamine*-6′-*arsinic Acid with the Rationally Synthesised* 10-*Chloro*-1-*methyl- and* -3-*methyl*-5 : 10-*dihydrophenarsazines.*—Mixed melting-point determinations on mixtures of 10-chloro-1- and -3-methyl-5 : 10-dihydrophenarsazines, which both melt at 216—217°, failed to show any depression. As a natural consequence of this remarkable fact, it was observed that mixtures of product (A) and these two substances separately also showed no depression of the melting point. From this it followed that product (A) could be the pure 1-methyl compound, the pure 3-methyl compound, or any possible mixture of 10-chloro-1-methyl- and -3-methyl-5 : 10-dihydrophenarsazines.

The solubilities of 10-chloro-1-methyl- and -3-methyl-5 : 10-dihydrophenarsazines in benzene were found to be approximately the same, *viz.*, about 0·3% at the ordinary temperature and about 3% at the boiling point.

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