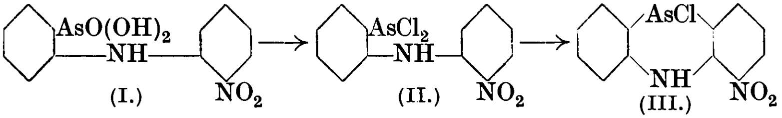
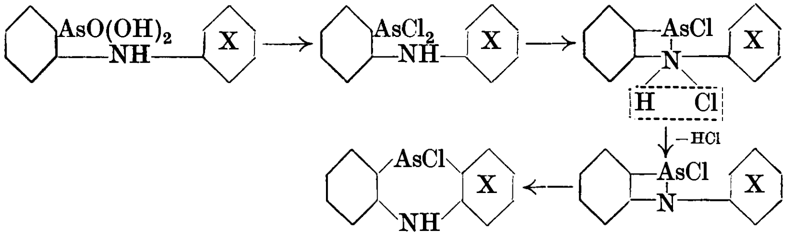
CLXIII.—10-*Chloro*-5 : 10-*dihydrophenarsazine and its Derivatives. Part IX. The Synthesis of Nitromethyldiphenylamine*-6′-*arsinic Acids and their Conversion into Nitromethyl Derivatives of* 10-*Chloro*-5 : 10-*dihydrophenarsazine. Constitution of* 10-*Chloro*-5 : 10-*dihydrophenarsazine.*

By CHARLES STANLEY GIBSON and JOHN DOBNEY ANDREW JOHNSON.

FROM the experiments on the synthesis of 2-nitro-, 1(or 3)-nitro- and 4-nitro-10-chloro-5 : 10-dihydrophenarsazines from the corresponding 4-nitro-, 3-nitro-, and 2-nitro-diphenylamine-6′-arsinic acids (Part V, J., 1927, 2504) the following facts were noted : (*a*) The reduction of 4-nitro- and 3-nitro-diphenylamine-6′-arsinic acids in the presence of hydrochloric acid yielded nitro-derivatives of 10-chloro-5 : 10-dihydrophenarsazine directly, and 2-nitrodiphenylamine-6′-arsinic acid (I) under the same conditions gave the intermediate dichloroarsine (II), which was converted into 10-chloro-4-nitro-5 : 10-dihydrophenarsazine (III) by boiling in acetic acid solution; and (*b*) the 1(or 3)-nitro- and 4-nitro-10-chloro-5 : 10-dihydrophenarsazines are deep red, whereas the 2-nitro-compound is yellow.



Of the many substituted diphenylamine-6′-arsinic acids which have been described in this series of communications, compound (I) is unique in yielding an isolable dichloroarsine on reduction, and 1(or 3)-nitro- and 4-nitro-10-chloro-5 : 10-dihydrophenarsazines are remarkable in possessing a deep red colour, whereas all the other derivatives of the parent substance are either yellow or colourless. At that time the following scheme of formation of derivatives of 10-chloro-5 : 10-dihydrophenarsazine from substituted diphenylamine-6′-arsinic acids, in which the dichloroarsine is always an intermediate product, was suggested :



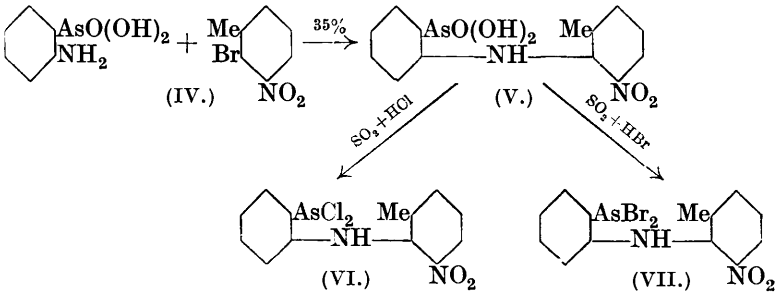
When the substituent group (X) is a nitro-group, nitrogen-arsenic ring formation would not take place so readily because of the diminished basicity of the nitrogen atom, and this would be especially marked in the case where the nitro-group is adjacent to the nitrogen atom.

One of the objects of the present work was to study the cyclisation of diphenylamine-6′-arsinic acids in greater detail, since, if the ring-formation process follows the course suggested above, all substituted diphenylamine-6′-arsinic acids having a nitro- or other strongly electronegative group in the ortho-position to the :NH group should yield isolable dichloroarsines on reduction in the presence of hydrochloric acid. Secondly, although deductions concerning the constitutions of substances based upon visible colour are subject to criticism, in this further work evidence has been obtained which enables us to state with some certainty the constitution of the reduction product of 3-nitrodiphenylamine-6′-arsinic acid. The particular case of the direction of ring closure of 3-methyldiphenylamine-6′-arsinic acid, which may yield 10-chloro-1(or 3)-methyl-5 : 10-dihydrophenarsazine, has already been discussed (Part VII, this vol., p. 767), and the cyclisation of 3-nitrodiphenylamine-6′-arsinic acid is a subject of the same nature. Finally, the properties of a large number of new substances which have been prepared afford some indication of the constitution of the parent substance and of its derivatives.

By studying the preparation of various nitromethyldiphenylamine-6′-arsinic acids and their ring closure it has been possible to investigate the above three problems. The nitromethyldiphenylamine-6′-arsinic acids were chosen partly because they were for the most part moderately easily accessible and the introduction of two different groups increases the number of possible isomerides, enabling conclusions to be drawn from a large number of cases, and partly because the nitro-group could be forced into a specified position by blocking with the methyl group one of the available ortho-positions to the :NH group.

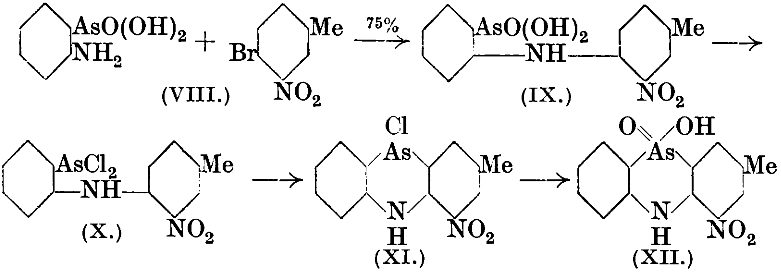
The nitromethyldiphenylamine-6′-arsinic acids were prepared on the one hand by condensing bromonitrotoluenes with *o*-aminophenylarsinic acid and, on the other hand, by condensing bromonitrobenzenes with aminotolylarsinic acids under the previously described conditions (Part V, *loc. cit.*). Twelve of the possible thirty-four acids are described in the present communication.

Using 2-*bromo*-3-*nitrotoluene* (IV), the following series of reactions was carried out, the relatively low yield of 2-nitro-6-methyldiphenylamine-6′-arsinic acid (V) being undoubtedly due to steric hindrance :



Compound (V) is highly crystalline and yellow and markedly volatile under reduced pressure at the ordinary temperature. The *dichloro-* and *dibromo-arsines* (VI and VII) cannot be converted into tricyclic compounds.

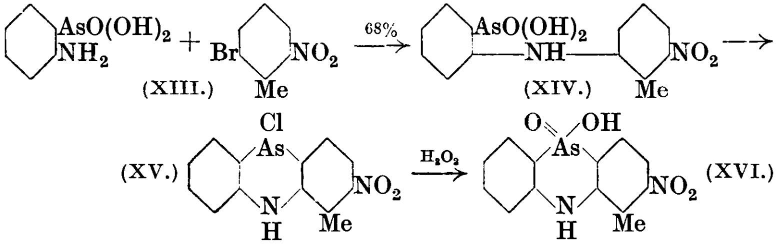
Starting with 4-bromo-3-nitrotoluene (VIII), the following series of reactions was accomplished :



(VIII.) (IX.) (X.) (XI.) (XII.)

Compound (IX) again was golden-yellow and somewhat volatile under reduced pressure. On reduction, as was expected, the corresponding *dichloroarsine* (X) was formed and was obtained as an orange-yellow crystalline substance. It was distinguished from derivatives of 10-chloro-5 : 10-dihydrophenarsazine by its high solubility in the usual organic solvents and its low melting point (91—93°). On boiling with acetic acid, hydrogen chloride was evolved and 10-*chloro*-4-*nitro*-2-*methyl*-5 : 10-*dihydrophenarsazine* (XI) was produced. This was crimson, had m. p. 187—188°, and was less soluble in organic solvents than the dichloroarsine but more soluble than those derivatives of 10-chloro-5 : 10-dihydrophenarsazine having the nitro-group in the 2-position. Reduction of (IX) in the presence of hydrobromic acid gave an oil mixed with solid material. The latter was shown to be the *bromo*-derivative corresponding to (XI); the former, although it could not be purified, had all the properties of the open-chain *dibromoarsine* corresponding to (X). In this case, it appears that partial ring closure takes place in the presence of hydrobromic acid.

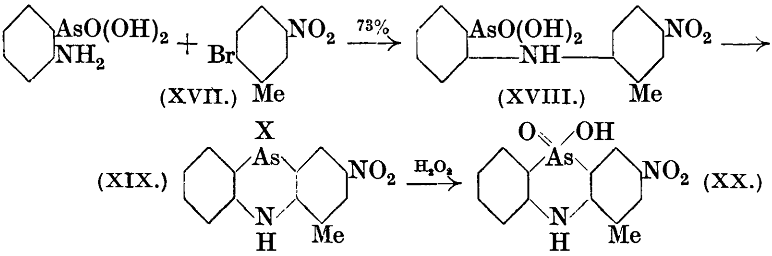
The next series of reactions investigated was the following :



(XIII.) (XIV.) (XV.) (XVI.)

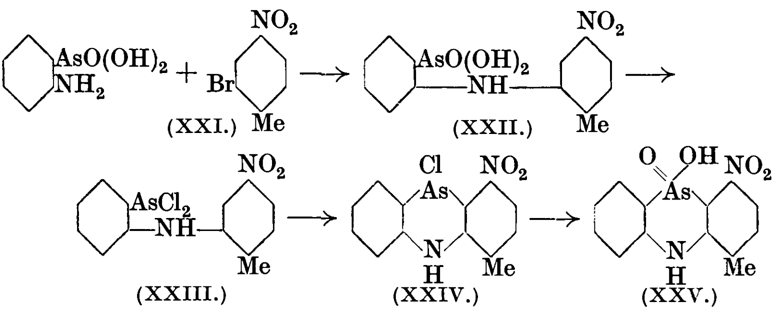
The compound (XIV) is pale yellow and yields the cyclic compound (XV) directly on reduction. In the preparation of the corresponding *bromo*-compound, the primary formation of an oil was observed, but it rapidly solidified and when crystallised from benzene (a medium which does not appear to favour cyclisation) only 10-*bromo*-3-*nitro*-4-*methyl*-5 : 10-*dihydrophenarsazine* was isolated. The reduction of (XIV) to the chloro-compound (XV) is one of the cases where the nitro-group is forced into a definite position owing to the blocking effect of the methyl group.

The next series of reactions was the following :


(XVII.) (XVIII.) (XIX.) (XX.)

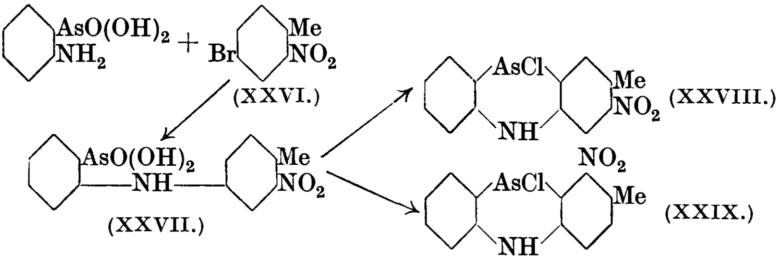
Compound (XVIII) is pale yellow and decomposes at a high temperature. It yields compound (XIX) (X = Cl or Br) on reduction, no indication of the formation of a dichloro- (or dibromo-) arsine being observed. The sodium and potassium salts of 2-*nitro*-4-*methylphenarsazinic acid* (XX) show remarkable colour changes on dilution and addition of alkali; these colour changes appear to be characteristic of the 2-nitrophenarsazinic acids.

The most unexpected result in this part of the present investigation was the observation that 5-*nitro*-2-*methyldiphenylamine*-6′-*arsinic acid* (XXII), prepared as indicated, gave a *dichloroarsine* (XXIII) on reduction :


(XXI.) (XXII.) (XXIII.) (XXIV.) (XXV.)

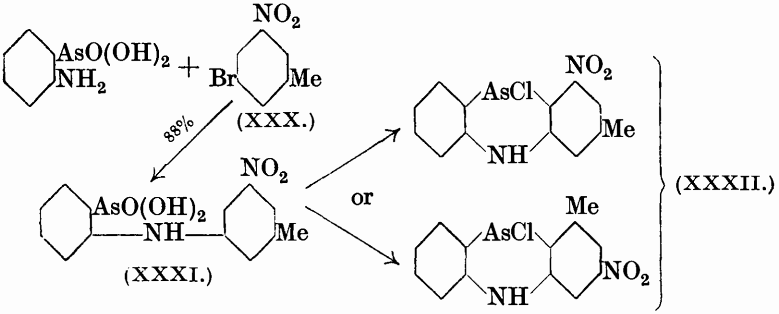
This was bright yellow and, for a dichloroarsine, had the unusually high m. p. of 173°. On boiling in acetic acid solution for 2 hours, ring closure was effected and 10-*chloro*-1-*nitro*-4-*methyl*-5 : 10-*dihydrophenarsazine* (XXIV) was produced. This is another case where the nitro-group is forced into a definite position because of the presence of the methyl group. The substance (XXIV) was deep red, not very soluble in the usual organic solvents, and had a high m. p. (258—260°). When compound (XXII) was reduced in the presence of hydrobromic acid, a mixture of yellow *dibromoarsine*, m. p. 164°, and deep red 10-*bromo*-1-*nitro*-4-*methyl*-5 : 10-*dihydrophenarsazine*, decomp. 272°, was obtained. The *phenarsazinic acid* (XXV) obtained by oxidising compound (XXIV) underwent complex reactions when heated with alkalis, yielding amorphous, discoloured, acidic products presumably of the Mikado-brown type.

The three other bromonitrotoluenes on condensation with *o*-aminophenylarsinic acid furnished nitromethyldiphenylamine-6′-arsinic acids which could theoretically give rise to two cyclic products in each case on reduction. In only one case were two isomeric cyclic compounds isolated, namely, when 3-*nitro*-4-*methyldiphenylamine*-6′-*arsinic acid* (XXVII) was reduced in the presence of hydrochloric acid. The following was the series of reactions investigated :


(XXVI.)
(XXVII.)
(XXVIII.)
(XXIX.)

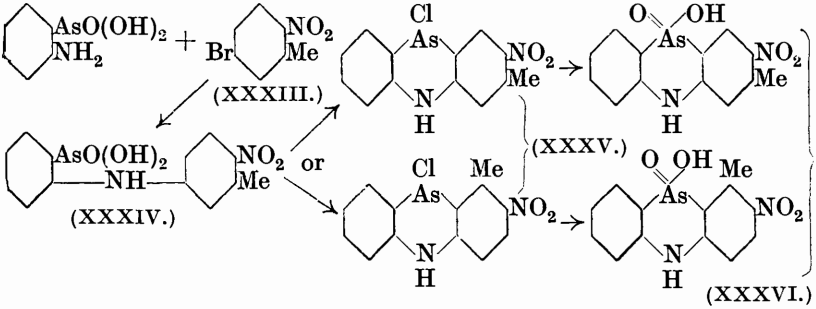
The acid (XXVII), purified through its *barium* salt, when reduced in the usual manner gave an orange-yellow precipitate, and the filtrate from this gave a red product on further treatment with sulphur dioxide. The former was only slightly soluble in benzene, and the latter crystallised in bright red needles, decomp. 225—226°. The orange-yellow material crystallised from acetic acid in orange-yellow prisms, decomp. 257—258°. Since the two substances could be crystallised side by side from benzene, it cannot be a case of dimorphism, and analysis showed that the products can only be the two substances (XXVIII) and (XXIX). The oxidation products of these two substances, the corresponding phenarsazinic acids, could not be distinguished from each other by the methods at our disposal.

The next series of reactions investigated was the following :

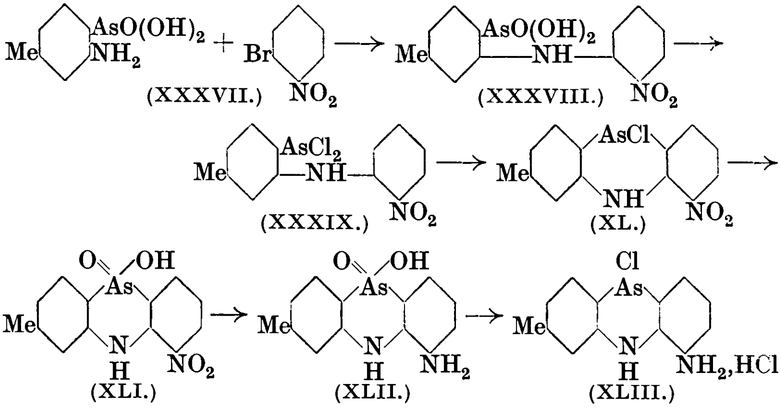


The orange-yellow product (XXXII) had m. p. 225—228° and since it was insoluble in the ordinary organic solvents the probability of its being a derivative of 10-chloro-5 : 10-dihydrophenarsazine and not a dichloroarsine was indicated. On crystallisation from butyric acid, the best solvent, it formed orange-coloured needles, decomp. 245—247°. The substance appeared to be homogeneous. The *bromo*-compound, prepared similarly, was deep red and also appeared to be homogeneous, although its melting point was somewhat indefinite.

After some difficulty 4-*nitro*-3-*methyldiphenylamine*-6′-*arsinic acid* (XXXIV) from the condensation of 3-bromo-6-nitrotoluene (XXXIII) with *o*-aminophenylarsinic acid was obtained in pale yellow needles. The reduction product (XXXV) when crude had m. p. 220—228° (decomp.) and this was only raised to 236—238° after crystallisation from acetic acid. This indicated that cyclisation had taken place along with the reduction, and the product, orange-yellow needles, appeared to be homogeneous. The corresponding phenarsazinic acid (XXXVI) obtained from this by oxidation showed the remarkable colour changes with alkalis already noted in the case of compound (XX).



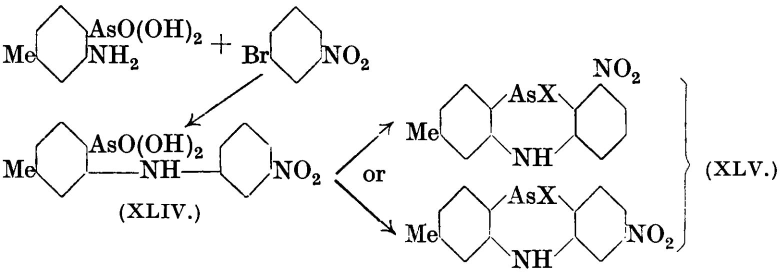
Several methylnitrodiphenylamine-6′-arsinic acids in which the methyl and nitro-groups were in different rings were next studied. The first of this series of reactions investigated was :



(XXXVII.) (XXXVIII.) (XXXIX.) (XL.) (XLI.) (XLII.) (XLIII.)

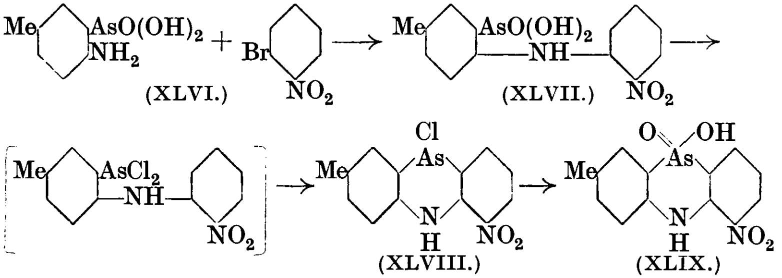
Compound (XXXVIII) is golden-yellow, and volatile under reduced pressure at the ordinary temperature; compound (XL) also is appreciably volatile under the same conditions.

The condensation products from *m*- and *p*-bromonitrobenzenes and 3-amino-*p*-tolylarsinic acid (XXXVII) were difficult to purify and work on that produced from *p*-bromonitrobenzene was especially restricted. The following illustrates the reactions carried out with *m*-bromonitrobenzene, the cyclic *chloro-* and *bromo-*compounds (XLV) (X = Cl or Br) being obtained as deep red substances difficult to purify.



(XLIV.) (XLV.)

Finally, 4-amino-*m*-tolylarsinic acid (XLVI) was condensed with *o*-bromonitrobenzene : the product, 2-*nitro*-4′-*methyldiphenylamine*-6′-*arsinic acid* (XLVII), had properties similar to those of the acid (XXXVIII). On reduction an uncrystallisable oil was obtained. Its ready solubility and the fact that hydrogen chloride was evolved on boiling it in acetic acid solution indicated that it was the dichloroarsine; the product obtained on boiling with acetic acid was the cyclic compound 10-*chloro*-4-*nitro*-8-*methyl*-5 : 10-*dihydrophenarsazine* (XLVIII), which on oxidation with hydrogen peroxide gave the phenarsazinic acid (XLIX).


(XLVI.) (XLVII.) (XLVIII.) (XLIX.)

The following summarises the more important observations arising from the experiments :

(1) All substituted nitrodiphenylamine-6′-arsinic acids in which the nitro-group is in the ortho-position to the :NH group, on reduction in the presence of hydrochloric acid, yield dichloroarsines (compounds I, V, IX, XXXVIII, XLVII).

(2) All substituted nitrodiphenylamine-6′-arsinic acids in which the nitro-group is in the para-position to the :NH group, on reduction in presence of hydrochloric acid, yield the corresponding cyclic chloro-compound, *e.g.*, 4-nitrodiphenylamine-6′-arsinic acid (J., 1927, 2504) (compounds XVIII and XXXIV).

(3) With the exception of 5-nitro-2-methyldiphenylamine-6′-arsinic acid (XXII), all substituted nitrodiphenylamine-6′-arsinic acids in which the nitro-group is in the meta-position to the :NH group, on reduction in presence of hydrochloric acid, yield the corresponding cyclic chloro-compound, *e.g.*, 3-nitrodiphenylamine-6′-arsinic acid (J., 1927, *loc. cit.*) (compounds XIV, XXVII, XXXI, and XLIV).

(4) All substituted 10-chloro-4-nitro-5 : 10-dihydrophenarsazines are crimson, have lower melting points than the other nitro-10-chloro-5 : 10-dihydrophenarsazines, are generally more soluble in organic solvents, and are volatile under diminished pressure at the ordinary temperature.

(5) All substituted 10-chloro-2-nitro-5 : 10-dihydrophenarsazines are yellow, are soluble with difficulty in the usual solvents, and generally have very high melting points. The exceptionally low melting point of 10-chloro-2-nitro-1(or 3)-methyl-5 : 10-dihydrophenarsazine (XXXV, 236—238°) will be discussed later.

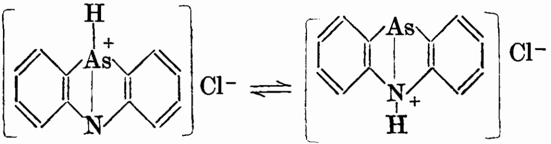
(6) One derivative of 10-chloro-5 : 10-dihydrophenarsazine, in which the nitro-group is definitely in the 3-position, *viz.*, 10-chloro-

3-nitro-4-methyl-5 : 10-dihydrophenarsazine (XV), is yellow and has m. p. 216·5°.

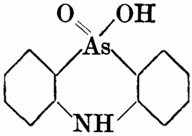
(7) One derivative, in which the nitro-group is definitely in the 1-position, 10-chloro-1-nitro-4-methyl-5 : 10-dihydrophenarsazine (XXIV), is deep red, has m. p. 258—260°, but is not generally so soluble in organic solvents as the 4-nitro-compounds.

(8) The 2-nitrophenarsazinic acids give the characteristic colour changes with alkalis which have been noted above.

The following explanation of the results is suggested. All the simple derivatives of 10-chloro-5 : 10-dihydrophenarsazine in which the arsenic atom is in the tervalent condition are yellow unless the hydrogen of the :NH group has been replaced by an acyl group, in which case the compounds are practically colourless. Wieland and Rheinheimer (*Annalen*, 1921, **423**, 1) suggested that the yellow colour of 10-chloro-5 : 10-dihydrophenarsazine was due to an atomic interaction between the arsenic and nitrogen atoms which involves their possessing a quinonoid-like structure. Sufficient experimental evidence has now been provided to ascribe to this parent compound the constitution (L) or (LI), which may be in equilibrium.



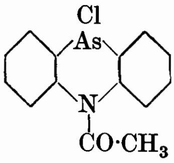
(L.) (LI.)

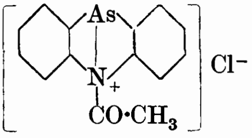


(LII.)

Since visible colour is absent in the case of phenarsazinic acid (LII), where a transannular N—As bond is precluded, it would appear that the yellow colour of 10-chloro-5 : 10-dihydrophenarsazine is due to the presence of the transannular structure indicated above. The colourless nature of 5-acetyl-10-chloro-5 : 10-dihydrophenarsazine (LIII) is readily explained, since the presence of a transannular bond as in (LIV) would necessitate the nitrogen atom carrying a

(LIII.)



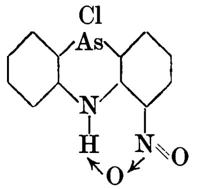


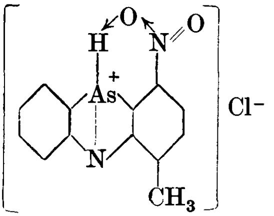
(LIV.)

positive charge although it has the negative acetyl group attached to it.

The physical properties of the 4-nitro-derivatives are those usually associated with chelate compounds and since these properties are generally absent in the case of the 2-nitro-compounds it is reasonable to assume that the chelate ring formation is a consequence of the proximity of the nitro- and :NH groups as indicated in formula (LV).

(LV.)





(LVI.)

The deep red colour of the 4-nitro-compounds must then be associated with the presence of the chelate ring and consequently those substances in which the presence of the chelate ring of the type above mentioned is precluded should not possess a deep red colour. This is actually the case, compound (XV) and all the 2-nitro-derivatives being yellow or orange-yellow. On the other hand, 10-chloro-1-nitro-4-methyl-5 : 10-dihydrophenarsazine (XXIV) is deep red, and this suggests a structure similar to (LV). This can readily be assigned to the substance if the transannular bond is also present, the constitution then being that indicated by (LVI). The difference between (LV) and (LVI) is that the latter is a salt whereas the former has simply co-valencies. The high melting point of (LVI) (258—260°) compared with those of the 4-nitro-derivatives of type (LV) [187—188° (XII), 201—202° (XL), 206° (XLVIII)] and its lower solubility in organic solvents are in agreement with this view.*

Following from this argument, provisional constitutions may be assigned to those compounds which may be 1(or 3)-nitro-derivatives of 10-chloro-5 : 10-dihydrophenarsazine. The reduction product of 3-nitro-3′-methyldiphenylamine-6′-arsinic acid (XLIV) may be 10-chloro-1(or 3)-nitro-7-methyl-5 : 10-dihydrophenarsazine. It is deep red in colour and has m. p. 253—255°, indicating the 1-nitro-structure. Similarly, the deep red reduction product of 3-nitro-diphenylamine-6′-arsinic acid (J., 1927, 2504) has most probably the 1-nitro-structure. On the other hand, the reduction product of 5-nitro-3-methyldiphenylamine-6′-arsinic acid (XXXI) is orange-yellow and has m. p. 245—247°, suggesting the 3-nitro-structure.

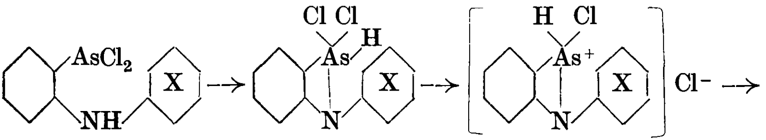
---

* Through the kind co-operation of Sir Robert Robertson, Dr. J. J. Fox, and Mr. E. S. Hiscocks the absorption spectra in the visible and ultra-violet regions of the most typical of these compounds are being examined and it is hoped to describe the results in a future communication. The differences in the visible colour, however, are so marked that the authors feel justified in basing conclusions upon them. Preliminary work shows that the accurate determination of the absorption spectra of these highly complicated substances confirms the conclusions now drawn.

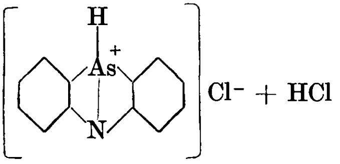
The most convincing evidence is probably that furnished by the reduction products of 3-nitro-4-methyldiphenylamine-6′-arsinic acid (XXVII). These must be 3-nitro-2-methyl- and 1-nitro-2-methyl-10-chloro-5 : 10-dihydrophenarsazines respectively. The more soluble, lower-melting isomeride is deep red; the less soluble, higher-melting compound is orange-yellow. To the former, the 1-nitro-structure (XXIX) is assigned, whereas the latter is presumed to be the 3-nitro-compound (XXVIII).

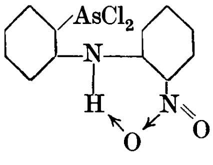
It is clear that the proximity of the methyl and nitro-groups may have some effect on the melting point, and this is especially marked in the case of the 10-chloro-2-nitro-1(or 3)-methyl-5 : 10-dihydrophenarsazine (XXXV), where the nitro- and methyl groups are in the ortho-position with respect to each other. Chelate ring formation is possible, mutual saturation follows, and less residual affinity remains to bind molecule to molecule, resulting in a lower melting point (236—238°) than is usual with 2-nitro-derivatives.

Since there is the probable presence of a chelate ring in the substituted 10-chloro-4-nitro-5 : 10-dihydrophenarsazines, the presence of a similar structure in the corresponding open-chain acids and dichloroarsines is also probable. This is in accord with the observations that the former are volatile under reduced pressure at the ordinary temperature and more easily soluble than the 3- and 4-nitrodiphenylamine-6′-arsinic acids, and that the dichloroarsines are low-melting solids of high solubility. In view of this a more detailed explanation of the mechanism of, and factors underlying, ring closure is now possible. In the simple general case, the dichloroarsine will be formed first; the $-AsCl_2$ group will react with the :NH group, hydrogen chloride will be eliminated, and the ring chloro-compound formed. The following mechanism seems to fit the facts better than that previously put forward (p. 1230).



(LVII.) (LVIII.)



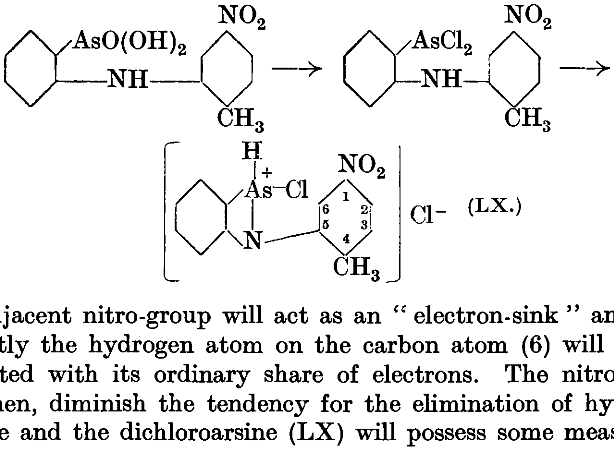


(LIX.)

The presence of any group in the dichloroarsine (LVII) which prevents or inhibits the movement of the hydrogen atom of the

:NH group will prevent or inhibit the subsequent formation of the substance represented by (LVIII) and consequently the dichloroarsine will be stable. A nitro-group in the 2-position in (LVII) would, owing to the presence of a chelate ring as in (LIX), restrict the movement of the hydrogen atom; consequently all 2-nitrodiphenylamine-6′-arsinic acids should yield stable dichloroarsines. In solution in a substance of high dielectric constant, this chelate ring would be weakened and conversion of the dichloroarsine into the ring chloro-compound would not be impeded to such an extent as before. Acetic acid, having a dielectric constant of about 9, is such a solvent and hence ring closure is effected on boiling in acetic acid solution but not in benzene.

3-Nitro- and 4-nitro-diphenylamine-6′-arsinic acids would not show this peculiarity unless some other factor played a part. The one case where a dichloroarsine was isolated although the nitro-group was not in the ortho-position to the :NH group is such an exception. The dichloroarsine isolated on reducing 5-nitro-2-methyldiphenylamine-6′-arsinic acid (XXII) was bright yellow and had m. p. 173°, which is unusually high for a dichloroarsine. The latter property suggests a salt-like structure, and the former suggests a constitution resembling the transannular bond structure postulated for 10-chloro-5 : 10-dihydrophenarsazine. The structure represented by (LX) is in agreement with these views. The positive character now acquired by the arsenic atom will be in part transmitted to the attached chlorine atom; the ease with which hydrogen chloride is eliminated will depend upon the extent to which the hydrogen atom attached to carbon atom (6)—which will be eliminated as hydrogen chloride—will be able to make up the electron deficiency associated with the chlorine atom.

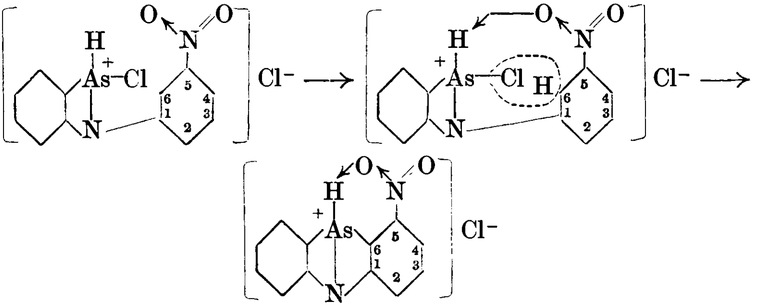


(LX.)

The adjacent nitro-group will act as an " electron-sink " and consequently the hydrogen atom on the carbon atom (6) will not be associated with its ordinary share of electrons. The nitro-group will, then, diminish the tendency for the elimination of hydrogen chloride and the dichloroarsine (LX) will possess some measure of stability. Solution of the dichloroarsine in a substance of high dielectric constant (such as acetic acid) would diminish electrostatic forces in the molecule and the elimination of hydrogen chloride would be assisted.

We have yet to consider the course of the reactions which lead to the formation sometimes of 1-nitro- and sometimes of 3-nitro-derivatives of 10-chloro-5 : 10-dihydrophenarsazine. In two cases, cyclisation appeared to yield only the 1-nitro-compound; in these cases no methyl group was present in the same ring as the nitro-group. In one case, cyclisation yielded apparently only the 3-nitro-derivative, and in another case, a mixture of the 1- and the 3-nitro-derivative was produced. In the latter cases, a methyl group was present in the same ring as the nitro-group. The factors which influence the *direction* of ring closure are the steric factor, the polar factor, and that due to the restricted rotation of the right-hand nucleus, due partly to the steric factor and partly to the polar factor.

Considering the cases where only the 1-nitro-compound was formed, it will be seen that the steric factor would favour the formation of the 3-nitro-derivative. Secondly, because of the proximity of the nitro-group, the hydrogen atom on carbon atom (6) would have less association with electrons than that on carbon atom (2). This also would favour the formation of the 3-nitro-derivative. But since there is evidence of the presence of a chelate ring in the 1-nitro-compounds, it is probable that this exists prior to the final ring closure. Free rotation is thus prevented and ring closure takes place on the carbon atom (6).



When a methyl group is present in the 3-position, the steric factor will still favour ring closure to give the 3-nitro-compound. The polar factor would now have the predominant effect, for the hydrogen atom on the carbon atom (2) would have a large electron surplus compared with that on carbon atom (6) because of the proximity of the electron source (the methyl group) at position (3) and the remoteness of the " electron sink " (the nitro-group). The polar factor is now able to outweigh the combined effects of the steric factor and that due to restricted rotation, and the 3-nitro-compound results.

Finally, the intermediate case where both the 1- and the 3-nitro-compound are formed can be explained in similar fashion. The " electron source " is now at position (4), its effect is diminished at (2) and increased slightly at (6). An intermediate effect is obtained and both isomerides are produced.

This explanation of the mechanism of ring closure, while admittedly imperfect, is considered the most likely and further work in this field will probably produce more evidence in its favour.

The present work has shown that there is a greater tendency for ring closure in the case of the bromo-compounds than in the case of the chloro-compounds. This also is in keeping with the above suggestions, since one would expect that the less electronegative bromine atom would be more satisfied with a hydrogen atom not too richly associated with electrons than a chlorine atom would; hence the conversion of the bromine analogue of (LX) into the ring compound should be more facile than that of the chloro-compound and this agrees with the experimental result.

EXPERIMENTAL.

Of the ten theoretically possible bromonitrotoluenes, only seven have been described. An eighth—*2-bromo-3-nitrotoluene*—has now been prepared and the methods of preparation of some of those already known have been modified and improved. Improved methods of preparation of some of the intermediate compounds have also been developed.

Aceto-*o*-toluidide has the following boiling points : 176°/14 mm., 184°/21 mm., 194°/32 mm.

2-Bromo-3-nitrotoluene (IV).—A suspension of finely divided 2-amino-3-nitrotoluene (50 g.) in a mixture of hydrobromic acid (36%, 35 c.c.) and water (90 c.c.) was diazotised below 0° with a solution of sodium nitrite (23·5 g.) in water (40 c.c.). The filtered diazonium solution was run fairly rapidly with constant stirring into a solution of cuprous bromide [prepared by saturating with sulphur dioxide a mixture of copper sulphate solution (crystals 60 g., in water 200 c.c.) and potassium bromide solution (30 g., in water 70 c.c.)] in hydrobromic acid (*d* 1·49, 110 c.c.) without external cooling. After being stirred for a few minutes, the mixture was heated on the water-bath for about 30 minutes, and the 2-bromo-3-nitrotoluene isolated by steam distillation. The distillate was extracted with ether; the extract was washed with dilute sodium hydroxide solution and with water, dried with calcium chloride and evaporated, and the residue distilled under reduced pressure. 2-*Bromo*-3-*nitrotoluene* was obtained in 67% yield as a yellow solid, m. p. 41—42°, b. p. 135—136°/8 mm. and 157°/22 mm. (Found : Br, 36·7. $C_7H_6O_2NBr$ requires Br, 37·0%). It is readily soluble in alcohol and almost insoluble in water. If the molten substance is allowed to cool slowly, it forms long thick six-sided prisms.

2-Bromo-5-nitrotoluene (XVII) was prepared in a similar way (66% yield) from 2-amino-5-nitrotoluene (30 g.) in a mixture of hydrochloric acid (40 c.c.) and water (55 c.c.), the quantities of the other materials being proportionate. Instead of being isolated by steam distillation, the product, after being heated on the water-bath, was cooled, diluted, and filtered, and the 2-bromo-5-nitrotoluene crystallised from a little alcohol (charcoal); m. p. 75—76° (compare Nevile and Winther, *Ber.*, 1880, **13**, 969).

The following experimental details for the preparation of 2-amino-4-nitrotoluene supplement those supplied by Anschütz and Heusler (*Ber.*, 1886, **19**, 2161). A hot solution of 2 : 4-dinitrotoluene (91 g.) in alcohol (95%, 1 litre) was rapidly cooled in order to obtain the compound in a fine state of division. Dry hydrogen chloride was passed into a mixture of stannous chloride (crystals, 339 g.) and alcohol (95%, 680 c.c.) until a clear solution resulted. The latter solution was then added in small portions with cooling and shaking to the suspension of the dinitro-compound. A clear yellow solution resulted. After 30 minutes, the alcohol was distilled off on the water-bath, water added to the residue and then sodium hydroxide until the bulk of the tin precipitate had redissolved. The liquid was extracted twice with ether; the ethereal extract was washed twice with water, dried with calcium chloride, and evaporated to dryness. A tarry mass remained which partly solidified. This was allowed to drain on porous porcelain and the solid 2-amino-4-nitrotoluene remaining was pure after one crystallisation from benzene–ligroin (b. p. 60—80°). The yield was poor—20 g.; m. p. 107°.

2-Bromo-4-nitrotoluene (XXI) was prepared in 86% yield from 2-amino-4-nitrotoluene exactly as described for 2-bromo-3-nitrotoluene. After removal of the ether, it was obtained pure and had m. p. 76° (compare Scheufelin, *Annalen*, 1885, **231**, 171; Wallach, *ibid.*, 1886, **235**, 248; Nevile and Winther, *Ber.*, 1881, **14**, 418).

2 : 6-Dinitrotoluene was obtained in poor yield by deamination of 2 : 6-dinitro-4-aminotoluene (compare Hollemann and Böeseken, *Rec. trav. chim.*, 1897, **16**, 427).

2-Amino-6-nitrotoluene (compare Cunerth, *Annalen*, 1874, **172**,

223) was obtained in 49% yield from 2 : 6-dinitrotoluene by the following method. The dinitro-compound (43 g.) was dissolved in hot alcohol (95%, 107 c.c.) and obtained in a finely divided state by rapid cooling. Ammonium sulphide (about 86 c.c.), prepared by saturating ammonia (20%) with hydrogen sulphide, was added in small portions to this suspension with thorough shaking but without cooling. The mixture became hot, a deep red solution resulted, and crystalline material began to separate. After 1 hour, the product was evaporated to dryness, and the residue extracted with boiling hydrochloric acid (*d* 1·075) until the extracts no longer gave a precipitate on basification with sodium hydroxide. The whole extract was basified with sodium hydroxide and cooled, and the precipitated nitro-amine crystallised from benzene–ligroin (b. p. 60—80°).

2-Bromo-6-nitrotoluene (XIII) (Noelting, *Ber.*, 1904, **37**, 1021) was obtained in 93% yield from the preceding compound by the method described for 2-bromo-3-nitrotoluene; b. p. 143°/22 mm., m. p. 42°.

3-Amino-6-nitrotoluene was prepared by nitrating *m*-toluidine according to the method of Noelting and Stoecklin (*Ber.*, 1891, **24**, 564). 3-Bromo-6-nitrotoluene (XXXIII) was prepared in 81% yield from the corresponding amino-compound by the method used for the preparation of 2-bromo-3-nitrotoluene; m. p. 56°. (Compare Wroblewski, *Annalen*, 1873, **168**, 170; Grete, *ibid.*, 1875, **177**, 246, who prepared this substance by nitrating *m*-bromotoluene. The constitution of the nitration product is thus established.)

3-Bromo-2-amino-5-nitrotoluene (compare Nevile and Winther, *Ber.*, 1880, **13**, 964) was prepared by adding bromine (23·3 c.c.) drop by drop to a solution of 2-amino-5-nitrotoluene (70 g.) in acetic acid (700 c.c.). (It was necessary to warm the acetic acid to dissolve the nitro-amine, but by rapid cooling a supersaturated solution was obtained to which the bromine was added.) A pale yellow crystalline mass was precipitated; on pouring the product into water, a bulky yellow precipitate was obtained and this was filtered off and extracted with water. The dry substance (99 g.) had m. p. 176° and was sufficiently pure for the following preparation.

3-*Bromo*-5-*nitrotoluene* (XXX) (Nevile and Winther, *loc. cit.*, p. 969).—Finely divided 3-bromo-2-amino-5-nitrotoluene (65 g.) was mixed with alcohol (300 c.c.), and sulphuric acid (72 c.c.) slowly added with constant stirring. The mixture was treated slowly at the ordinary temperature with a solution of sodium nitrite (20·8 g.) in water (45 c.c.), and the product heated on the water-bath until the evolution of nitrogen and acetaldehyde was completed. The resulting mixture was submitted to steam distillation. The distillate was extracted with ether, and the ethereal extract worked up in the usual manner. On removal of the ether, the 3-bromo-5-nitrotoluene was obtained pure (m. p. 83°) without crystallisation. The average yield in four experiments was 40%.

3-Bromo-5-aminotoluene was prepared by adding a hot solution of 3-bromo-5-nitrotoluene (64·3 g.) in alcohol (514 c.c.) in small quantities at a time to a solution of stannous chloride (crystals, 258 g.) in hydrochloric acid (386 c.c.) previously heated to 60° in a 3-litre flask fitted with a reflux condenser; a vigorous reaction took place. After heating for 30 minutes on the water-bath, some of the alcohol was evaporated and the residue treated with sodium hydroxide until the tin precipitate just dissolved. The 3-bromo-5-aminotoluene was isolated by steam distillation and extraction with ether in the ordinary way. It was distilled twice under reduced pressure. The pure, colourless material was obtained in 84% yield and had b. p. 151°/23·5 mm., 157·5°/28 mm., m. p. 37—38°. Attempts to nitrate its acetyl derivative were unsuccessful or led to dinitro-compounds. Further attempts to prepare 3-bromo-2-nitrotoluene will be described later.

4-Bromo-2-nitrotoluene (XXVI) was prepared from 4-amino-2-nitrotoluene, and 4-bromo-3-nitrotoluene (VIII) from 4-amino-3-nitrotoluene, as described for 2-bromo-3-nitrotoluene.

In the following description of new organic arsenicals, attention has been paid to a complete description of the salts of acids where these are characteristic. The melting points of many of the acids lie close together and the salts described may serve for purpose of identification.

2-*Nitro*-3′-*methyldiphenylamine*-6′-*arsinic Acid* (XXXVIII).—A mixture of 3-amino-*p*-tolylarsinic acid (23·1 g.), *o*-bromonitrobenzene (20·2 g.), anhydrous potassium carbonate (17·3 g.), amyl alcohol (100 c.c.), and a trace of copper powder was boiled for 5 hours. After removal of the amyl alcohol by steam distillation, the hot aqueous solution was filtered, cooled, and carefully acidified with concentrated hydrochloric acid. The precipitated acid (23·1 g., 66%), recrystallised from dilute acetic acid (charcoal), was obtained in clusters of well-defined, golden-yellow, prismatic needles, m. p. 215—217° (decomp.) after slight softening (Found: As, 21·6. $C_{13}H_{13}O_5N_2As$ requires As, 21·3%).

This nitro-acid is somewhat volatile, as is also 10-chloro-4-nitro-7-methyl-5 : 10-dihydrophenarsazine (XL). When either of these pure substances is left over potassium hydroxide under reduced pressure, a deep red crust is rapidly formed on the surface of the drying agent. The amphoteric nature of the above acid is shown by its solubility in a mixture of alcohol and hydrochloric acid and in aqueous alkali. It is scarcely soluble in cold or hot alcohol and is only moderately easily soluble in acetone. The alkali salts give deep red solutions; the magnesium salt is formed only on boiling with magnesia mixture.

2-*Nitro*-3′-*methyldiphenylamine*-6′-*dichloroarsine* (XXXIX).—A boiling solution of the preceding substance (1·0 g.) in a mixture of alcohol (6·0 c.c.) and hydrochloric acid (8·0 c.c.) containing a trace of iodine was reduced by passing a rapid stream of sulphur dioxide for 5 minutes. A dark-coloured oil separated which became semi-solid on cooling; it was extracted with benzene (about 100 c.c.), and the benzene solution dried over calcium chloride and concentrated to about 15 c.c. on the water-bath. On cooling, the *dichloroarsine* was slowly deposited in bright yellow, rhomb-shaped plates. After recrystallisation from benzene it had m. p. 129·5—130° (Found: Cl, 19·3. $C_{13}H_{11}O_2N_2Cl_2As$ requires Cl, 19·0%). It is readily soluble in hot benzene, moderately easily soluble in acetic acid, and almost insoluble in ligroin.

10-*Chloro*-4-*nitro*-7-*methyl*-5 : 10-*dihydrophenarsazine* (XL).—2-Nitro-3′-methyldiphenylamine-6′-arsinic acid (10·75 g.) was reduced as just described, the crude dichloroarsine remaining after evaporation of the benzene being boiled in acetic acid solution (140 c.c.) for 1½ hours. Hydrogen chloride was freely evolved and red crystalline material, ultimately filling the liquid, gradually separated. After cooling, the precipitate was filtered off and recrystallised from acetic acid (1 g. in 25 c.c. when boiling). The *compound* (7·4 g., 72% yield) crystallised in sheaves of deep red, doubly refracting needles, m. p. 201—202° (without decomp. but with previous slight softening) (Found: Cl, 10·3. $C_{13}H_{10}O_2N_2ClAs$ requires Cl, 10·5%). It is readily soluble in hot acetone or benzene, slightly soluble in these cold solvents, and insoluble in ligroin (b. p. 80—100°). When an aqueous solution of chloramine-T was warmed with an acetone solution of the compound, a bright yellow acid was precipitated, but the method was not suitable for the preparation of the nitrophenarsazinic acid.

4-*Nitro*-7-*methylphenarsazinic Acid* (XLI).—A suspension of finely divided 10-chloro-4-nitro-7-methyl-5:10-dihydrophenarsazine (5·5 g.) in acetic acid (55 c.c.) was mixed with hydrogen peroxide (20 vols., 36 c.c.) and gently heated to boiling. The deep red colour of the chloro-compound was rapidly replaced by the yellow-orange colour of the nitrophenarsazinic acid. Oxidation was completed by heating for 15 minutes on the water-bath. After cooling, water (110 c.c.) was added and the solid material filtered off, well washed with water, and dissolved in a hot dilute aqueous solution of sodium hydroxide. The hot liquid was filtered from non-acidic substances, and the filtrate cooled; the orange-coloured sodium salt then separated in rhomb-shaped plates. This was dissolved in hot water, the solution acidified with hydrochloric acid, and the precipitated *nitro-acid* (4·0 g.) filtered off, well washed with water, dried at 140°, and recrystallised from dilute acetic acid, giving yellow needles, m. p. 300—303° (decomp.) (Found : As, 22·2. $C_{13}H_{11}O_4N_2As$ requires As, 22·45%).

This nitro-acid is not very soluble in cold aqueous alkaline solutions, but dissolves in hot dilute aqueous sodium hydroxide to a deep red solution. If this solution is treated with an excess of a strong aqueous solution of sodium hydroxide, a deep reddish-brown solution is produced, which, however, deposits the orange-coloured sodium salt on cooling. The acid dissolves in a mixture of alcohol and hydrochloric acid, is soluble in hot glacial acetic acid, slightly soluble in alcohol and acetone, and insoluble in water.

4-*Amino*-7-*methylphenarsazinic Acid* (XLII).—A hot solution of the preceding nitro-acid (3·2 g.) in dilute aqueous sodium hydroxide (0·5 g. in 60 c.c.) was added to a suspension of ferrous hydroxide prepared by mixing a solution of ferrous sulphate (crystals, 21 g.) in water (63 c.c.) with aqueous sodium hydroxide (25%, 20 c.c.) contained in a wide-mouth flask, more water (15 c.c.) being used to wash in the sodium salt of the acid. The suspension was shaken for 10 minutes and filtered. The colourless filtrate rapidly acquired an amethyst colour due to atmospheric oxidation. The residue on the filter was thoroughly washed with warm water, and the filtrate mixed with the main volume of liquid. The filtrate was cooled and carefully acidified with dilute hydrochloric acid, a slightly discoloured and somewhat gelatinous *acid* being precipitated. This was filtered off, well washed with water, and recrystallised from dilute acetic acid, short colourless needles being obtained, which remained unmelted at 310° (Found : As, 24·5. $C_{13}H_{13}O_2N_2As$ requires As, 24·7%). The acid is somewhat soluble in concentrated hydrochloric acid, easily soluble in acetic acid, and insoluble in ethyl alcohol and in water. The sodium salt is precipitated as colourless needles when a strong aqueous solution of sodium hydroxide is added to a warm aqueous solution of the sodium salt and the mixture allowed to cool. The acid is readily soluble in a mixture of alcohol and hydrochloric acid.

10-*Chloro*-4-*amino*-7-*methyl*-5 : 10-*dihydrophenarsazine Hydrochloride* (XLIII).—The preceding compound (1·0 g.), dissolved in a hot mixture of alcohol (3·0 c.c.) and hydrochloric acid (3 c.c.) containing a trace of iodine, was reduced with sulphur dioxide. A greyish-yellow crystalline solid was precipitated together with some tarry matter. After cooling, the product was filtered off, dissolved in a hot mixture of equal volumes of ethyl alcohol and hydrochloric acid, and boiled with decolorising charcoal. To the filtrate, concentrated hydrochloric acid was added until crystalline material began to separate. 10-*Chloro*-4-*amino*-7-*methyl*-5 : 10-*dihydrophenarsazine hydrochloride* crystallises in clusters of greyish-yellow needles, m. p. 216—220° (decomp.) (Found : Cl, 20·9. $C_{13}H_{12}N_2ClAs,HCl$ requires Cl, 20·7%). It is slightly soluble in cold alcohol and readily soluble in the hot solvent.

3-*Nitro*-3′-*methyldiphenylamine*-6′-*arsinic Acid* (XLIV).—The condensation of 3-amino-*p*-tolylarsinic acid (23·1 g.) with *m*-bromonitrobenzene (20·2 g.) in boiling amyl alcohol (100 c.c.) in the presence of anhydrous potassium carbonate (17·3 g.) and a trace of copper powder gave a 73% yield of crude 3-*nitro*-3′-*methyldiphenylamine*-6′-*arsinic acid.* It was recrystallised three times from glacial acetic acid and obtained in long yellow needles, m. p. 191—192° (Found : As, 21·6. $C_{13}H_{13}O_5N_2As$ requires As, 21·3%). It is very soluble in hot glacial acetic acid but only slightly soluble in the cold; it is soluble in a mixture of alcohol and concentrated hydrochloric acid.

10-*Chloro*-1(or 3)-*nitro*-7-*methyl*-5 : 10-*dihydrophenarsazine* (XLV).—The preceding substance (15·0 g.), dissolved in a boiling mixture of alcohol (90 c.c.) and hydrochloric acid (120 c.c.) containing a trace of iodine, was reduced in the usual manner with sulphur dioxide. The precipitated *chloro*-compound after drying was recrystallised with difficulty from nitrobenzene and thoroughly washed with benzene (Found : Cl, 10·9. $C_{13}H_{10}O_2N_2ClAs$ requires Cl, 10·5%). It forms deep red, small plates, m. p. 253—255° (decomp.) after slight shrinking and darkening; it is almost insoluble in benzene, acetic acid, formic acid, alcohol, and acetone, slightly soluble in chloroform, and somewhat readily soluble in *o*-dichlorobenzene and nitrobenzene.

10-*Bromo*-1(or 3)-*nitro*-7-*methyl*-5 : 10-*dihydrophenarsazine*.—A boiling solution of 3-nitro-3′-methyldiphenylamine-6′-arsinic acid (3 g.) in alcohol (18 c.c.) and hydrobromic acid (35%, 24 c.c.) containing a trace of iodine, on reduction, yielded a deep red product, which was recrystallised with difficulty from *o*-dichlorobenzene and obtained in small, deep red plates, decomp. 248—250° after previous softening (Found : Br, 21·4. $C_{13}H_{10}O_2N_2BrAs$ requires Br, 21·0%). Its solubility is similar to that of the corresponding chloro-compound; it is also soluble in *s*-tetrachloroethane.

4-*Nitro*-3′-*methyldiphenylamine*-6′-*arsinic Acid.*—A mixture of 3-amino-*p*-tolylarsinic acid (23·1 g.), *p*-bromonitrobenzene (20·2 g.), anhydrous potassium carbonate (17·3 g.), amyl alcohol (100 c.c.), and a trace of copper powder was boiled for 5 hours. The product (89% yield), worked up as described for similar condensations, crystallised with extreme difficulty from glacial acetic acid in minute yellow prisms, m. p. 276° (vigorous decomp.) (Found : As, 21·3. $C_{13}H_{13}O_5N_2As$ requires As, 21·3%).

4-Amino-*m*-tolylarsinic acid (XLVI) was obtained in poor yield by the Béchamp reaction on *p*-toluidine (Benda, *Ber.*, 1909, **42**, 3621).

2-*Nitro*-4′-*methyldiphenylamine*-6′-*arsinic Acid* (XLVII).—A 65% yield of this compound (crude) was obtained on boiling a mixture of 4-amino-*m*-tolylarsinic acid (13·45 g.), *o*-bromonitrobenzene (11·75 g.), anhydrous potassium carbonate (10·1 g.), amyl alcohol (58 c.c.), and a trace of copper powder for 5 hours and working up the product as in similar condensations. It was readily purified by crystallisation from dilute acetic acid (about 50%) and was obtained in deep bronze-yellow, prismatic needles somewhat soluble in acetic acid. It was somewhat volatile and on standing over potassium hydroxide under reduced pressure a deep red incrustation of the potassium salt formed on the surface of the drying agent. It had m. p. 226—227° and decomposed at 234° (Found : As, 20·85. $C_{13}H_{13}O_5N_2As$ requires As, 21·3%). The acid is slightly soluble in acetone. Apart from the alkali salts, which give deep red solutions, the salts are not characteristic.

Reduction of 2-*Nitro*-4′-*methyldiphenylamine*-6′-*arsinic Acid.*—A boiling solution of the preceding acid (5·25 g.) in a mixture of alcohol (30 c.c.) and hydrochloric acid (30 c.c.) containing a trace of iodine was treated with sulphur dioxide. A deeply coloured oil was precipitated. The cold supernatant liquid was decanted and the residue dissolved in benzene. The benzene solution was dried with calcium chloride and evaporated to dryness. The oily residue was taken up in benzene and cautiously treated with ligroin (b. p. 60—80°) in order to precipitate amorphous matter. Further addition of ligroin to the filtered liquid gave an oil which could not be induced to solidify. Its ready solubility in the usual organic solvents indicated that it was the dichloroarsine in an impure form. When the oil was boiled with acetic acid (30 c.c.), hydrogen chloride was evolved and at the end of 1 hour it was necessary to add more acetic acid (15 c.c.) because of the red crystalline material which had separated filling the liquid. Boiling was continued for 1 hour. 10-*Chloro*-4-*nitro*-8-*methyl*-5 : 10-*dihydrophenarsazine* (XLVIII) formed minute prismatic needles, m. p. 206°. It was recrystallised from acetic acid (Found : Cl, 10·6. $C_{13}H_{10}O_2N_2ClAs$ requires Cl, 10·5%). It was distinctly soluble in benzene, insoluble in ligroin (b. p. 60—80°), soluble in acetone, and somewhat readily volatile under reduced pressure at the ordinary temperature.

4-*Nitro*-8-*methylphenarsazinic Acid* (XLIX).—The preceding compound (2·25 g.), suspended in cold acetic acid (23 c.c.), was treated with hydrogen peroxide (11 c.c.), and the mixture gently warmed on the water-bath. Oxidation was readily effected, the colour changing from crimson to orange-yellow. After 15 minutes, water (50 c.c.) was added, and the cold liquid filtered from the acid, which was washed with water, dissolved in cold dilute sodium hydroxide solution, and the filtered liquid acidified. The precipitated *acid* crystallised with difficulty from slightly diluted acetic acid in small, orange-yellow needles, decomp. 297—300° (Found : As, 22·45. $C_{13}H_{11}O_4N_2As$ requires As, 22·45%). It is insoluble in alcohol or acetone but dissolves in a mixture of alcohol and hydrochloric acid. The salts are very characteristic. The sodium salt (*aci*-salt of the ψ-nitro-acid ?) forms bronze-yellow, hair-like needles when concentrated aqueous sodium hydroxide is added to a solution of the sodium salt. The ammonium salt is deposited from solution in hot concentrated aqueous ammonia, on cooling, in thin, deep red needles; when its aqueous solution is boiled, ammonia is evolved and the acid is precipitated. The barium salt is precipitated in clusters of reddish-yellow needles from dilute solutions; the calcium salt is slowly precipitated from dilute solutions in clusters of orange-yellow needles; the magnesium salt, obtained only on boiling the ammonium salt with magnesia mixture, forms glistening, orange-coloured, rhomb-shaped plates. The salts of the heavy metals are amorphous.

3-*Nitro*-2-*methyldiphenylamine*-6'-*arsinic Acid* (XIV).—A mixture of 2-bromo-6-nitrotoluene (XIII) (18·3 g.), *o*-aminophenylarsinic acid (18·3 g.), potassium carbonate (14·7 g.), amyl alcohol (85 c.c.), and a trace of copper powder, on boiling for 5 hours, gave a 68% yield of crude 3-*nitro*-2-*methyldiphenylamine*-6'-*arsinic acid*. After two crystallisations from dilute acetic acid (charcoal), it was obtained in very pale yellow, glistening plates, m. p. 223—224° (decomp.) after slight softening (Found : As, 21·2. $C_{13}H_{13}O_5N_2As$ requires As, 21·3%). The acid is readily soluble in hot alcohol. The sodium salt, precipitated on addition of 25% aqueous sodium hydroxide to a strong aqueous solution, forms pale yellow, glistening needles; the ammonium salt separates from its solution in hot concentrated aqueous ammonia, on cooling, in yellow needles. The barium salt is obtained, on cooling a hot solution containing a little ammonia, in pale, truncated, flat prisms soluble in hot water. The calcium salt, similarly prepared, crystallises in clusters of pale yellow needles.

10-*Chloro*-3-*nitro*-4-*methyl*-5 : 10-*dihydrophenarsazine* (XV).—The preceding acid (8 g.), dissolved in a mixture of alcohol (45 c.c.) and hydrochloric acid (30 c.c.) containing a trace of iodine, on reduction with sulphur dioxide, gave a yellow product, m. p. 214—215°.

When recrystallised from benzene, in which it was somewhat soluble, it formed thick yellow prisms, m. p. 216·5° (Found : Cl, 10·85. $C_{13}H_{10}O_2N_2ClAs$ requires Cl, 10·5%). It is somewhat more soluble in the usual organic solvents than might have been anticipated.

10-*Bromo*-3-*nitro*-4-*methyl*-5 : 10-*dihydrophenarsazine* was obtained in a similar way by reducing the arsinic acid (2·2 g.) in solution in a mixture of alcohol (12 c.c.) and hydrobromic acid (36%, 12 c.c.). The oil which was first precipitated quickly solidified and then crystallised from benzene in orange-yellow prisms, m. p. 216·5° (Found : Br, 21·2. $C_{13}H_{10}O_2N_2BrAs$ requires Br, 21·0%).

3-*Nitro*-4-*methylphenarsazinic Acid* (XVI).—It was necessary to heat a mixture of the chloro-compound (XV) (1·2 g.), acetic acid (12 c.c.), and hydrogen peroxide (20 vols., 6 c.c.) for 1½ hours on the water-bath to effect complete oxidation. Water (20 c.c.) was added, the precipitated acid was dissolved in warm dilute sodium hydroxide solution to separate it from non-acidic substances, the filtered liquid treated with decolorising charcoal, and concentrated sodium hydroxide solution added to the hot filtrate. On cooling, the sodium salt was precipitated in orange-yellow, thin needles. The *acid*, which was precipitated in good yield in a gelatinous form on acidification of the sodium salt, crystallised from a mixture of acetic acid and dilute hydrochloric acid in clusters of pale yellow needles. It remained unmelted at 306° (Found : As, 22·2. $C_{13}H_{11}O_4N_2As$ requires As, 22·45%). A solution of the sodium salt is pale orange-yellow.

4-*Nitro*-2-*methyldiphenylamine*-6′-*arsinic Acid* (XVIII).—2-Bromo-5-nitrotoluene (XVII) (25·2 g.), *o*-aminophenylarsinic acid (25·2 g.), potassium carbonate (20·2 g.), amyl alcohol (117 c.c.), and a trace of copper powder, boiled for 5 hours, gave a 73% yield of the crude condensation product. The only satisfactory method of purification was to dissolve the crude material in a boiling mixture of alcohol and concentrated hydrochloric acid and add an excess of warm water to the filtered solution. The *acid* was thus obtained in thin, pale yellow needles, decomposing vigorously at 277° (Found : As, 21·4. $C_{13}H_{13}O_5N_2As$ requires As, 21·3%). It is insoluble in water, alcohol, and acetic acid; it dissolves in concentrated sulphuric acid, yielding an orange-coloured solution which rapidly changes to bluish-green and then, on addition of nitric acid, to olive-green and finally to orange. The salts of this acid are particularly well defined. The sodium salt is precipitated from concentrated solutions by the addition of concentrated sodium hydroxide solution in golden-yellow flat needles which dissolve in cold water, giving an orange-red solution. Addition of concentrated aqueous sodium hydroxide to this solution does not produce a purple colour (compare

2-nitro-4-methylphenarsazinic acid, below). The ammonium salt (precipitated only when 0·880 ammonia solution is used) forms orange-yellow needles which yield a deep red aqueous solution. The barium salt, prepared only in the presence of a slight excess of ammonia, forms thick yellow plates when crystallised from hot water, in which it is only slightly soluble. The calcium salt, prepared in a similar manner, forms orange-yellow plates insoluble in cold and in hot water. The magnesium salt is an orange amorphous precipitate produced when the acid is boiled with magnesia mixture. The mercurous and mercuric salts, the former soluble in ammonia, crystallise in tufts of yellow needles; the silver and lead salts are flocculent yellow precipitates, the former soluble in ammonia.

10-*Chloro*-2-*nitro*-4-*methyl*-5 : 10-*dihydrophenarsazine* (XIX).—The preceding acid (10 g.) was reduced by saturating with sulphur dioxide a boiling solution in alcohol (160 c.c.) and hydrochloric acid (50 c.c.) containing a trace of iodine. The yellow precipitate was washed with alcohol and, after drying at 110°, recrystallised from *o*-dichlorobenzene, giving deep yellow needles, m. p. 303—305° (decomp.) (Found : Cl, 10·85. $C_{13}H_{10}O_2N_2ClAs$ requires Cl, 10·5%). It is insoluble in benzene, acetic acid, alcohol, and ether, but slightly soluble in acetone. The same substance is produced when 2-nitro-4-methylphenarsazinic acid (see below) is reduced with sulphur dioxide under similar conditions to the above.

10-*Bromo*-2-*nitro*-4-*methyl*-5 : 10-*dihydrophenarsazine* was obtained by reducing 4-nitro-2-methyldiphenylamine-6′-arsinic acid with sulphur dioxide in the presence of hydrobromic acid under the usual conditions. The product was finally recrystallised from *o*-dichlorobenzene and obtained in orange-yellow plates with a metallic sheen; m. p. 301—302° (decomp.) (Found : Br, 21·4. $C_{13}H_{10}O_2N_2BrAs$ requires Br, 21·0%). It is insoluble in benzene and ether and slightly soluble in alcohol, acetone, and acetic acid (see below).

2-*Nitro*-4-*methylphenarsazinic Acid* (XX).—Either of the two preceding compounds (3·85 g.) was boiled with acetic acid (50 c.c.); most of it dissolved. The liquid was cooled rapidly to obtain fine crystals, and hydrogen peroxide (20 vols., 25 c.c.) added. When the mixture was gently warmed and finally boiled for 5 minutes, a pale yellow solid separated; water was added after the mixture had cooled. The acid was dissolved in dilute sodium hydroxide solution, heated to boiling, and decolorised with charcoal, and the filtrate acidified with dilute hydrochloric acid. The *phenarsazinic acid* was precipitated as a pale yellow, gelatinous mass which, recrystallised from much glacial acetic acid, formed clusters of pale yellow needles, unmelted at 306° (Found : As, 22·5. $C_{13}H_{11}O_4N_2As$

requires As, 22·4%). The ammonium salt is precipitated in fine yellow needles by the addition of an excess of concentrated aqueous ammonia to a solution of the acid in dilute ammonia solution. On boiling a solution of the ammonium salt, ammonia is evolved and the acid is precipitated. The barium salt forms clusters of pale yellow needles insoluble in cold and in hot water. The calcium salt forms short orange-yellow prisms. The silver salt is an amorphous yellow precipitate soluble in ammonia solution; the magnesium salt, formed only on boiling, crystallises in thin yellow prisms. The mercurous and mercuric salts are pale yellow amorphous precipitates; the lead salt is similar but deep yellow. The potassium salt is precipitated from solutions in hot 25% potassium hydroxide solution on cooling, in thin golden-yellow prisms. These dissolve in water to an orange-red solution (concentrated) or pale yellow solution (dilute). Addition of 25% potassium hydroxide solution to either solution causes it to become deep purple (formation of the dipotassium salt of the ψ-acid?); on dilution, this solution becomes pale yellow, and will then again go through the same changes. The sodium salt crystallises in tufts of orange-yellow needles and its solutions behave similarly.

5-*Nitro*-2-*methyldiphenylamine*-6′-*arsinic Acid* (XXII).—A mixture of 2-bromo-4-nitrotoluene (XXI) (22·4 g.), *o*-aminophenylarsinic acid (22·4 g.), potassium carbonate (18 g.), amyl alcohol (104 c.c.), and a trace of copper powder was submitted to the usual treatment. The crude product was recrystallised from 50% acetic acid and obtained in 56% yield in clusters of light yellow needles, m. p. 224—226° (slight decomp.) (Found: As, 21·3. $C_{13}H_{13}O_5N_2As$ requires As, 21·3%). The *acid* is insoluble in water, slightly soluble in cold alcohol, and somewhat readily soluble in hot alcohol. It dissolves readily in a mixture of alcohol and concentrated hydrochloric acid. The alkali salts dissolve readily in water, forming deep red solutions. The barium salt crystallises in yellow plates and the calcium salt in bright yellow needles. The lead, silver and mercurous salts are yellow gelatinous precipitates, the mercuric salt crystallises in thin yellow needles, and the magnesium salt, formed only on boiling the acid with magnesia mixture, separates in tufts of colourless needles.

5-*Nitro*-2-*methyldiphenylamine*-6′-*dichloroarsine* (XXIII).—A boiling solution of the preceding acid (10 g.) in a mixture of alcohol (60 c.c.) and hydrochloric acid (40 c.c.) containing a trace of iodine was reduced with sulphur dioxide. After cooling, the precipitated orange-yellow crystalline solid was separated and recrystallised from benzene and obtained in bright yellow, rhomb-shaped plates, m. p. 173° (Found: Cl, 18·5. $C_{13}H_{11}O_2N_2Cl_2As$ requires Cl, 19·0%).

10-*Chloro*-1-*nitro*-4-*methyl*-5 : 10-*dihydrophenarsazine* (XXIV).—The crude reduction product from compound (XXII) (10 g.) was added to acetic acid (40 c.c.), and the mixture boiled for 2 hours. The acetic acid solution was evaporated to one-third of its volume, and, on cooling, the product separated in thick, deep red prisms which, after recrystallisation from glacial acetic acid, had m. p. 258—260° (Found : Cl, 10·9. $C_{13}H_{10}O_2N_2ClAs$ requires Cl, 10·5%). The compound is slightly soluble in hot acetic acid, sparingly soluble in acetone, alcohol, and benzene, and insoluble in ligroin, but readily soluble in boiling *o*-dichlorobenzene.

5-*Nitro*-2-*methyldiphenylamine*-6′-*dibromoarsine and* 10-*Bromo*-1-*nitro*-4-*methyl*-5 : 10-*dihydrophenarsazine*.—A boiling solution of compound (XXII) (4·7 g.) in alcohol (60 c.c.) and hydrobromic acid (*d* 1·324, 60 c.c.) containing a trace of iodine was reduced with sulphur dioxide. The crystalline reduction product appeared to be a mixture of yellow and orange substances. After filtration and drying on porous porcelain, it was extracted twice with boiling benzene. The insoluble deep red substance was recrystallised from *o*-dichlorobenzene and obtained in stout, deep red prisms, decomposing vigorously at 272°. The benzene extract was evaporated to dryness and the residue recrystallised from benzene (charcoal). The yellow flat plates obtained had m. p. 164°. The substance became deep red at its melting point, partly solidified as the temperature was raised, and decomposed vigorously at 230°.

The deep red product was only slightly soluble in the usual solvents and proved to be 10-*bromo*-1-*nitro*-4-*methyl*-5 : 10-*dihydrophenarsazine* (Found : Br, 21·2. $C_{13}H_{10}O_2N_2BrAs$ requires Br, 21·0%). The yellow substance was readily soluble in acetone, hot benzene, and hot glacial acetic acid; it proved to be 5-*nitro*-2-*methyldiphenylamine*-6′-*dibromoarsine* (Found : Br, 34·2. $C_{13}H_{11}O_2N_2Br_2As$ requires Br, 34·6%).

1-*Nitro*-4-*methylphenarsazinic Acid* (XXV).—Compound (XXIV) (0·75 g.), mixed with acetic acid (7·5 c.c.) and hydrogen peroxide (20 vols., 3·7 c.c.), was slowly oxidised by heating on the water-bath for 30 minutes. The acid precipitated by the addition of water was dissolved in warm dilute aqueous sodium hydroxide (charcoal), and the filtered solution immediately acidified. The orange-yellow *acid* obtained could not be recrystallised directly; it darkened at about 295° but remained unmelted at 305° (Found : As, 22·1. $C_{13}H_{11}O_4N_2As$ requires As, 22·45%). On boiling with moderately concentrated sodium hydroxide solution for a short time, a brown amorphous acid was precipitated. This presumably was a mixture of dinitroso-, azoxy-, and azo-stilbenearsinic acid derivatives, analogous to that obtained when a simple arsinic acid having a methyl group in the para-position to a nitro-group is treated with hot concentrated sodium hydroxide solution (compare Benda and Schultz, *Ber.*, 1886, **19**, 3234).

2-*Nitro*-6-*methyldiphenylamine*-6′-*arsinic Acid* (V).—A mixture of *o*-aminophenylarsinic acid (12·55 g.), 2-bromo-3-nitrotoluene (12·55 g.), potassium carbonate (10·1 g.), amyl alcohol (58 c.c.), and a trace of copper powder was boiled for 5 hours. The crude product (7·15 g., 35%) was obtained pure after one recrystallisation from dilute acetic acid (charcoal). The *compound* crystallises in golden-yellow plates, m. p. 195—197° (Found : As, 21·2. $C_{13}H_{13}O_5N_2As$ requires As, 21·3%). It is readily soluble in boiling glacial acetic acid, but not very soluble in the cold solvent. Dilute acetic acid is the best medium for recrystallisation. The arsinic acid is very sparingly soluble in alcohol and in water, but dissolves readily in a mixture of alcohol and concentrated hydrochloric acid. It is remarkably volatile, especially under reduced pressure. The ammonium salt is a yellow microcrystalline powder insoluble in excess of ammonia solution; the sodium salt is precipitated in yellow needles from a solution in concentrated aqueous sodium hydroxide; the barium salt, somewhat soluble in hot water, crystallises in orange-yellow plates and is the most characteristic salt of the acid.

2-*Nitro*-6-*methyldiphenylamine*-6′-*dichloroarsine* (VI).—A boiling solution of the preceding compound (2 g.) in alcohol (15 c.c.) and hydrochloric acid (15 c.c.) containing a little iodine, on reduction with sulphur dioxide, gave a deeply coloured, heavy oil, which was separated by decantation and dissolved in benzene; the benzene solution was washed with concentrated hydrochloric acid and dried with calcium chloride, and the benzene evaporated. The residue was again dissolved in benzene, and the amorphous material separated by the careful addition of ligroin. The filtrate was again evaporated to dryness, and the somewhat resinous residue recrystallised from a small quantity of glacial acetic acid. The *dichloroarsine* was thus obtained in small, orange-yellow prisms, m. p. 104—105° (Found : Cl, 18·5. $C_{13}H_{11}O_2N_2Cl_2As$ requires Cl, 19·0%). It is easily soluble in benzene, acetone, chloroform, and hot acetic acid. It is also slightly soluble in ligroin (b. p. 60—80°).

2-*Nitro*-6-*methyldiphenylamine*-6′-*dibromoarsine* (VII) was prepared and isolated in a similar manner to the preceding compound, hydrobromic acid (36%, 15 c.c.) being used for similar quantities. It crystallised in slender, bronze-orange prisms, m. p. 97—98° after slight softening. Its solubility is generally very similar to that of the corresponding chloro-compound (Found : Br, 34·2. $C_{13}H_{11}O_2N_2Br_2As$ requires Br, 34·6%).

2-*Nitro*-4-*methyldiphenylamine*-6′-*arsinic Acid* (IX).—A mixture of *o*-aminophenylarsinic acid (11·2 g.), 4-bromo-3-nitrotoluene (VIII) (11·2 g.), potassium carbonate (9·0 g.), amyl alcohol (52 c.c.), and a trace of copper powder was boiled for 5 hours. The crude condensation product, isolated as in other cases, crystallised from dilute acetic acid in golden-yellow needles, m. p. 227—229° (decomp.) (Found : As, 21·3. $C_{13}H_{13}O_5N_2As$ requires As, 21·3%). It is insoluble in water, but readily soluble in hot glacial acetic acid. Solutions of the alkali salts are deep red; the magnesium salt is formed only on boiling with magnesia mixture.

2-*Nitro*-4-*methyldiphenylamine*-6′-*dichloroarsine* (X).—The preceding substance (10·3 g.), dissolved in a boiling mixture of alcohol (30 c.c.) and hydrochloric acid (33 c.c.) containing a trace of iodine, was reduced in the usual manner. A heavy oil separated; this was decanted and dissolved in benzene, and the filtered solution dried with calcium chloride. Approximately two-thirds of the solution was reserved for the preparation of the succeeding compound (XI), the remaining portion being concentrated to small bulk. Cautious addition of ligroin (b. p. 60—80°) caused the precipitation of amorphous matter, which was filtered off, and the further addition of ligroin precipitated an oil which was finally obtained crystalline. It was recrystallised from benzene–ligroin, and the *dichloroarsine* thus obtained in short orange-yellow prisms, m. p. 91—93°. It is readily soluble in benzene and acetone and somewhat readily soluble in hot ligroin (Found : Cl, 18·55. $C_{13}H_{11}O_2N_2Cl_2As$ requires Cl, 19·0%).

10-*Chloro*-4-*nitro*-2-*methyl*-5 : 10-*dihydrophenarsazine* (XI).—The benzene extract reserved in the previous preparation was evaporated to dryness, and the residual oil (approx. 6 g.) boiled in acetic acid solution (65 c.c.) for 3 hours. Hydrogen chloride was evolved, but no solid separated until the solution was cooled. The substance was recrystallised from glacial acetic acid and obtained in deep red needles, m. p. 187—188° after slight softening (Found : Cl, 10·35. $C_{13}H_{10}O_2N_2ClAs$ requires Cl, 10·5%). It is readily soluble in acetone, benzene, and hot glacial acetic acid and only sparingly soluble in ligroin.

10-*Bromo*-4-*nitro*-2-*methyl*-5 : 10-*dihydrophenarsazine*.—A hot solution of compound (IX) (6 g.) in a mixture of alcohol (30 c.c.) and hydrobromic acid (*d* 1·265, 30 c.c.) containing a trace of iodine was reduced with sulphur dioxide. An oil and a deep red solid were precipitated. The two were separated by decantation; the red solid had m. p. 180—186°. The oil was readily soluble in benzene, but application of the methods successfully applied to dichloroarsines similarly prepared did not lead to the isolation of the dibromoarsine in a state of purity. The oil was therefore boiled with acetic acid (45 c.c.) for 3 hours, hydrogen bromide being evolved. On cooling, deep red needles were deposited and on recrystallisation from glacial acetic acid the product was obtained in deep crimson needles, m. p. 186—188° (Found: Br, 21·5. $C_{13}H_{10}O_2N_2BrAs$ requires Br, 21·0%). The red solid precipitated with the oil was shown to be the same substance. Reduction of 2-nitro-4-methyldiphenylamine-6′-arsinic acid leads therefore to the formation of the dibromoarsine and the ring bromo-compound.

10-*Bromo*-4-*nitro*-2-*methyl*-5 : 10-*dihydrophenarsazine* is more soluble in the usual solvents than the corresponding chloro-compound.

4-*Nitro*-2-*methylphenarsazinic Acid* (XII).—A suspension of the chloro-compound (XI) (2 g.) in acetic acid (20 c.c.) was treated with hydrogen peroxide (20 vols., 13 c.c.) as described in similar oxidations. The crude product readily dissolved in cold dilute sodium hydroxide solution; after being boiled with decolorising charcoal, filtered, acidified, and cooled, the deep red solution yielded the *phenarsazinic acid* as a voluminous yellow precipitate. This crystallised from dilute acetic acid (about 80%) in clusters of fine needles (Found: As, 22·5. $C_{13}H_{11}O_4N_2As$ requires As, 22·45%). It decomposes violently at 305°, is insoluble in cold alcohol, slightly soluble in hot alcohol, and apparently insoluble in cold or hot water. Its amphoteric character is demonstrated by the ease with which it dissolves in acetic acid and in a mixture of alcohol and hydrochloric acid. The ammonium salt loses ammonia when its aqueous solution is boiled, the acid being precipitated. When a 20% solution of sodium hydroxide is added to a solution of the acid in dilute aqueous sodium hydroxide, a sodium salt is precipitated in short yellow plates; the hot solution, however, yields a deep brown (*aci*?) crystalline salt, which changes to the former on cooling. The silver salt is an orange-yellow amorphous substance soluble in ammonia; the barium salt forms small, deep yellow, flat needles, the calcium salt long plates arranged in clusters. The last two salts are very well defined and characteristic.

5-*Nitro*-3-*methyldiphenylamine*-6′-*arsinic Acid* (XXXI).—3-Bromo-5-nitrotoluene (XXX) (22·4 g.), condensed under the usual conditions with *o*-aminophenylarsinic acid (22·4 g.), gave an 88% yield of the crude acid. The somewhat tarry product solidified on standing and was then recrystallised from 50% acetic acid (charcoal). After a further recrystallisation, the pure *acid* was obtained in long, pale yellow needles, m. p. 228—230° (decomp.) (Found: As, 21·5. $C_{13}H_{13}O_5N_2As$ requires As, 21·3%). The ammonium salt is sparingly soluble in an excess of concentrated ammonia solution and its solution in water is deep red. The calcium salt crystallises in clusters of yellow needles; the barium salt is easily crystallised from hot water and is obtained in glistening yellow plates; the silver, mercurous, mercuric and lead salts are yellow amorphous precipitates; the sodium salt is deep reddish-brown and sparingly soluble in a concentrated solution of sodium hydroxide. The magnesium salt, unlike those of most arsinic acids, is formed in the cold solution in clusters of yellow needles.

10-*Chloro*-1(or 3)-*nitro*-3(or 1)-*methyl*-5 : 10-*dihydrophenarsazine* (XXXII).—A boiling solution of the preceding acid (10 g.) in alcohol (50 c.c.) and hydrochloric acid (40 c.c.) containing a little iodine, on reduction in the usual manner with sulphur dioxide, gave a good yield of homogeneous material and the mother-liquor gave no further precipitate when resaturated with sulphur dioxide and kept. The melting point of the crude material was 225—228° and this indicated that ring closure had taken place; moreover the material was insoluble in the usual organic solvents and also in *o*-dichlorobenzene and in *s*-tetrachloroethane. It was sparingly soluble in nitrobenzene. It crystallised from butyric acid (the best solvent for purification) in clusters of orange-coloured needles, decomp. 245—247° (Found : Cl, 10·5. $C_{13}H_{10}O_2N_2ClAs$ requires Cl, 10·5%).

10-*Bromo*-1(or 3)-*nitro*-3(or 1)-*methyl*-5 : 10-*dihydrophenarsazine*.—A boiling solution of the acid (XXXI) (5·3 g.) in alcohol (40 c.c.) and hydrobromic acid (36%, 30 c.c.) containing a little iodine, on reduction in the usual manner, gave a homogeneous deep red product. It was recrystallised from a large volume of acetic acid and obtained in thick red prisms having an indefinite melting point (237—242°), the last portions to separate from the mother-liquor having also the same indefinite melting point (Found : Br, 21·2. $C_{13}H_{10}O_2N_2BrAs$ requires Br, 21·0%).

1(or 3)-*Nitro*-3(or 1)-*methylphenarsazinic Acid*.—The chloro-compound (XXXII) (0·9 g.), suspended in acetic acid (10 c.c.), was gently warmed with hydrogen peroxide (20 vols., 5·0 c.c.), its colour changing to yellow. The mixture was boiled for a few minutes, water (20 c.c.) added, and the yellow solid which separated on cooling was filtered off and dissolved in the minimum quantity of dilute sodium hydroxide solution. After treatment with decolorising charcoal, the filtrate was acidified with the minimum quantity of dilute hydrochloric acid, the *phenarsazinic acid* being precipitated as a gelatinous yellow solid. It crystallised from dilute acetic acid in clusters of short yellow needles, which remained unmelted at 300° (Found : As, 22·05. $C_{13}H_{11}O_4N_2As$ requires As, 22·45%). The sodium salt is obtained in soft needles sparingly soluble in dilute sodium hydroxide solution.

3-*Nitro-4-methyldiphenylamine-6′-arsinic Acid* (XXVII).—4-Bromo-2-nitrotoluene (XXVI) (16·8 g.), condensed with *o*-aminophenylarsinic acid (16·8 g.) in the presence of potassium carbonate (13·5 g.), amyl alcohol (78 c.c.) and a trace of copper powder, gave a tarry product which could not be crystallised directly. It was therefore treated in boiling dilute ammonia solution with barium nitrate (the boiling solution must contain free ammonia); the *barium* salt (28·4 g.) then crystallised in golden-yellow, rhomb-shaped plates containing $6H_2O$ (Found: H_2O, 17·3, 17·9. $C_{13}H_{11}O_5N_2AsBa,6H_2O$ requires H_2O, 18·1%). The anhydrous salt is chocolate-brown (Found: Ba, 23·0. $C_{13}H_{11}O_5N_2AsBa$ requires Ba, 23·0%) and readily reverts to the yellow hydrate on warming with water. The free acid was obtained by suspending the barium salt in boiling water, acidifying it with dilute hydrochloric acid, and adding acetic acid to the boiling solution until the latter was homogeneous. After treatment with decolorising charcoal, the filtrate deposited the *arsinic acid* in bright yellow needles, m. p. 165—166° (Found: As, 21·0. $C_{13}H_{13}O_5N_2As$ requires As, 21·3%). It is insoluble in water and readily soluble in boiling acetic acid.

Reduction of 3-*Nitro-4-methyldiphenylamine-6′-arsinic Acid*.—The preceding substance (4·2 g.), dissolved in a boiling mixture of alcohol (30 c.c.) and hydrochloric acid (20 c.c.) containing a trace of iodine, was reduced with sulphur dioxide. A quantity of orange-yellow material (*A*) separated. This was filtered off and the filtrate was boiled and again saturated with sulphur dioxide. A quantity of red material (*B*) was precipitated. *A* and *B* were separately washed with alcohol and dried on porous porcelain. *A*, almost insoluble in benzene, crystallised from acetic acid in orange-yellow prisms, m. p. 257—258° (decomp.). *B*, readily soluble in hot benzene, crystallised from this solvent in bright red needles, m. p. 225—226° (decomp.). The decomposition point of the mixture was 225—226°. The substances are different not only in colour and crystalline form but also in solubility, *B* being generally much more soluble than *A*. When a mixture of *A* and *B* was dissolved in hot benzene, the two substances crystallised out side by side and could be separated mechanically. From the results of analysis the two substances must be the two isomeric ring condensation compounds [Found: for *A* (probably XXVIII), Cl, 10·2; for *B* (probably XXIX), Cl, 10·15. $C_{13}H_{10}O_2N_2ClAs$ requires Cl, 10·5%].

1- *and* 3-*Nitro-2-methylphenarsazinic Acids*.—*Oxidation of substance* A. The chloro-compound (3·3 g.) was heated with acetic acid (33 c.c.) and hydrogen peroxide (20 vols., 15 c.c.). A clear solution resulted while boiling and yellow needles soon began to separate. After 10 minutes' boiling, water (60 c.c.) was added:

the precipitated *acid* crystallised from a large volume of dilute acetic acid in minute yellow needles, unmelted at 297° (Found: As, 22·3. $C_{13}H_{11}O_4N_2As$ requires As, 22·45%). The barium salt formed orange-coloured needles; the sodium salt, obtained from a solution in concentrated aqueous sodium hydroxide, formed thin, pale yellow needles.

Oxidation of substance B. This was oxidised in the same way as the above, the two acids and salts being superficially indistinguishable (Found: As, 22·2. $C_{13}H_{11}O_4N_2As$ requires As, 22·45%). The acid was unmelted at 297°.

4-*Nitro*-3-*methyldiphenylamine*-6′-*arsinic Acid* (XXXIV).—The condensation of 3-bromo-6-nitrotoluene (XXXIII) (19·4 g.) with *o*-aminophenylarsinic acid (19·4 g.) in presence of amyl alcohol (90 c.c.), potassium carbonate (15·6 g.), and a trace of copper powder gave a product which was purified as follows. The crude acid (86% yield) was dissolved in hot 20% sodium hydroxide solution and allowed to cool. The sodium salt was filtered off, recrystallised from 20% aqueous sodium hydroxide, and obtained in golden-yellow needles. It was dissolved in hot water and treated with glacial acetic acid until a faint turbidity was produced in the boiling solution; this was then boiled with decolorising charcoal, filtered, and allowed to cool. The *acid* was precipitated usually in pale yellow needles, but occasionally as a gum which solidified on cooling. In the latter case, a little of the acid was used for seeding the solution after it had been reheated and allowed to cool. The acid was finally recrystallised from dilute acetic acid and obtained in pale yellow needles with no definite melting point, ultimately decomposing vigorously at 200° (Found: As, 21·2. $C_{13}H_{13}O_5N_2As$ requires As, 21·3%). All the salts appear to be amorphous except the sodium and ammonium salts.

10-*Chloro*-2-*nitro*-1(or 3)-*methyl*-5 : 10-*dihydrophenarsazine* (XXXV).—On reduction of the preceding acid (6 g.), dissolved in a mixture of alcohol (20 c.c.) and hydrochloric acid (20 c.c.), in the usual way, an oil and solid matter were precipitated. The oil solidified on cooling, and the dry solid mass had m. p. 220—228° (decomp.). It was sparingly soluble in benzene and was recrystallised from acetic acid (charcoal), forming orange-yellow prisms, m. p. 236—238° (decomp.) (Found: Cl, 10·7. $C_{13}H_{10}O_2N_2ClAs$ requires Cl, 10·5%). It is moderately easily soluble in acetone, slightly soluble in alcohol and *s*-tetrachloroethane, but insoluble in carbon tetrachloride.

2-*Nitro*-1(or 3)-*methylphenarsazinic Acid* (XXXVI).—The oxidation of the preceding substance (2·6 g.), suspended in acetic acid (26 c.c.), with hydrogen peroxide (13 c.c.) proceeded slowly even in the boiling solution on account of the sparing solubility of the chloro-compound. After boiling for 5 minutes, it was heated on the water-bath for 30 minutes, water (52 c.c.) added, and the precipitated acid separated from non-acidic substances by solution in alkali. The filtered deep red solution on acidification gave a yellow gelatinous precipitate of the *acid*, which was crystallised from a mixture of acetic acid and dilute hydrochloric acid, forming yellow needles, unmelted at 308°. It was insoluble in water and only slightly soluble in acetic acid (Found : As, 22·45. $C_{13}H_{11}O_4N_2As$ requires As, 22·45%). The calcium and barium salts form pale yellow needles. The salts of the heavy metals are amorphous. The sodium salt gives in water a deep red solution which becomes yellow on dilution; on addition of concentrated sodium hydroxide solution, the red colour is again produced, which again changes to yellow on dilution (compare 2-nitro-4-methylphenarsazinic acid XX). The sodium salt is precipitated in crimson needles when its hot solution in moderately concentrated aqueous sodium hydroxide is cooled.

GUY'S HOSPITAL MEDICAL SCHOOL (UNIVERSITY OF LONDON),
LONDON, S.E. 1.

[*Received, April* 17*th,* 1929.]