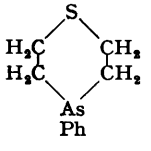
198. *The Synthetic Application of Phenylarsinebis(magnesium Bromide). Part III. The Preparation and Properties of 4-Substituted Tetrahydro-1 : 4-oxarsines and of 1 : 4-Disubstituted Hexahydro-1 : 4-azarsines.**

By M. H. Beeby and Frederick G. Mann.

The above Grignard reagent reacts with di-(2-bromoethyl) ether to give tetrahydro-4-phenyloxarsine (II) and with bis-2-bromoethylaniline to give hexahydro-1 : 4-diphenylazarsine (VI). The properties of these novel heterocyclic compounds have been studied in some detail. It is noteworthy that the azarsine (VI) forms only monoquaternary salts, and evidence is adduced that this quaternisation occurs on the tertiary arsine group.

It has been shown by Job, Reich, and Vergnaud (*Bull. Soc. chim.*, 1924, **35**, 1404) that phenylarsinebis(magnesium bromide) reacted with 2 : 2′-dichlorodiethyl sulphide to give a resinous material, which on extraction with light petroleum furnished a 7% yield of the compound (I), which they termed phenylthiarsine (this would be termed tetrahydro-4-phenylthiarsine on the nomenclature system adopted in this paper). It formed crystals, m. p. 38°, b. p. 134°/14 mm. We find that the above Grignard reagent reacts with di-(2-bromoethyl) ether also to give a resinous product, which was largely unaffected by extraction with light petroleum: when,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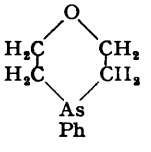
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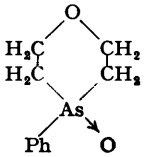
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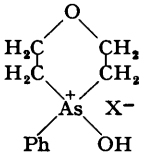
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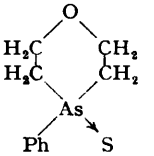

(V.)

however, this product was destructively distilled under reduced pressure, a series of three rather indefinite fractions was obtained; from the middle fraction tetrahydro-4-phenyloxarsine (II) was ultimately isolated. These results indicate that in both the oxygen and the sulphur series the initial reaction forms a complex product, probably owing to linear condensation of the dihalogeno-compound with the Grignard reagent, and that it is this product which on thermal decomposition gives the simple monocyclic derivative such as (II).

It is noteworthy that the first of the above fractions contained diethylphenylarsine. It is probable therefore that the secondary reaction (A) occurred (cf. Beeby, Cookson, and Mann, *J.*, 1950, 1917), and that the phenyldibromoarsine so formed then reacted with the ethyl-

$$2O(CH_2{\cdot}CH_2Br)_2 + AsPh(MgBr)_2 \longrightarrow 2Br{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}MgBr + AsPhBr_2 \quad (A)$$

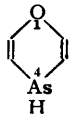
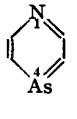
magnesium bromide—which was present in excess in the formation of the phenylarsinebis-(magnesium bromide)—to give diethylphenylarsine. In these circumstances the magnesium derivative $Br{\cdot}[CH_2]_2{\cdot}O{\cdot}[CH_2]_2{\cdot}MgBr$ would decompose and ultimately yield ethylene and

$$AsPh(MgBr)_2 + AsPhBr_2 \longrightarrow PhAs{:}AsPh + 2MgBr_2 \quad . \quad . \quad . \quad . \quad . \quad (B)$$

2-bromoethyl alcohol (cf. Tallman, *J. Amer. Chem. Soc.*, 1934, **56**, 126). In earlier experiments in which the excess of ethylmagnesium bromide was not used, the diethylphenylarsine was largely replaced as a by-product by arsenobenzene. It is reasonably certain that the latter is formed by the interaction of the phenylarsinebis(magnesium bromide) with the phenyldibromoarsine (reaction B), but that the latter compound reacts preferentially with ethylmagnesium bromide, when this is present in excess, to form diethylphenylarsine.

To isolate the pure tetrahydro-4-phenyloxarsine (II), the crude distilled product was oxidised

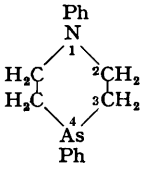
* These two novel heterocyclic systems are regarded as hydrogenated derivatives of the fundamental ring systems. 1 : 4-oxarsine (A) and 1 : 4-azarsine (B). respectively.

(A.)   (B.)

in acetone solution by hydrogen peroxide to the oxide (III), which was then precipitated as the crystalline hydroxy-picrate (IV; X = $C_6H_2O_7N_3$) since the latter could be readily purified by recrystallisation. This salt was then converted by hydrochloric acid into the hydroxy-chloride (IV; X = Cl), which on reduction gave the pure tetrahydro-4-phenyloxarsine (II), a colourless liquid having b. p. 149—151°/18 mm. It was characterised as its methiodide, systematically named tetrahydro-4-methyl-4-phenyl-1 : 4-oxarsinium iodide and as its palladochloride derivative, namely dichlorobis(tetrahydro-4-phenyloxarsine)palladium, $[(C_{10}H_{13}OAs)_2PdCl_2]$.

To obtain decisive evidence that the compound (II) had the simple six-membered ring, instead of possibly a twelve-membered ring, the oxide (III) was converted by hydrogen sulphide into tetrahydro-4-phenyloxarsine sulphide (V), a stable highly crystalline derivative the molecular weight of which in alcoholic solution confirmed the structure (V).

Di-(2-bromoethyl)aniline, $NPh(CH_2{\cdot}CH_2Br)_2$, reacts with phenylarsinebis(magnesium bromide) also to give a mixture of a crystalline and a resinous solid, the latter possibly also being the result of extensive linear reaction. Extraction of this mixture with hot light petroleum leaves the resin almost unaffected, but the extract yields the crystalline hexahydro-1 : 4-diphenyl-1 : 4-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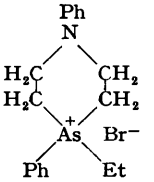
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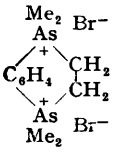
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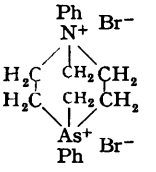
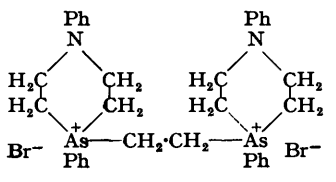

(IX.)

azarsine (VI), m. p. 97—97·5°, in 50% yield. This compound readily formed a monomethiodide, and when heated with an excess of ethyl bromide in a sealed tube at 100° formed only a monoethobromide (VII), the structure of which is discussed below: even with *p*-chlorophenacyl bromide (a very vigorous quaternising agent) only the monoquaternary salt was obtained.

It is known, however, that although *o*-phenylenebisdimethylarsine, $C_6H_4(AsMe_2)_2$, will form only a monomethobromide and methiodide (unpublished work), it will readily combine with ethylene dibromide to form the cyclic di(arsonium bromide) (VIII) (Glauert and Mann, *J.*, 1950, 682). Attempts were therefore made to combine the compound (VI) with one equivalent of ethylene dibromide to form the tricyclic diquaternary bromide (IX); again, however, each unit of (VI) underwent solely monoquaternisation, and the product was therefore *s*-ethylenebis(hexahydro-1 : 4-diphenylazarsinium) dibromide (X).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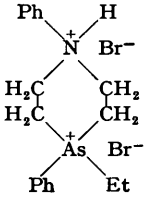
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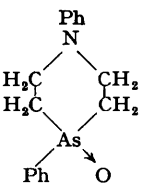
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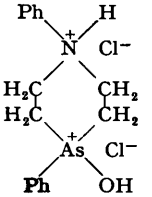

(XIII.)

The formulation of these various quaternary salts as arsinium salts instead of the isomeric ammonium salts rests on the following evidence.

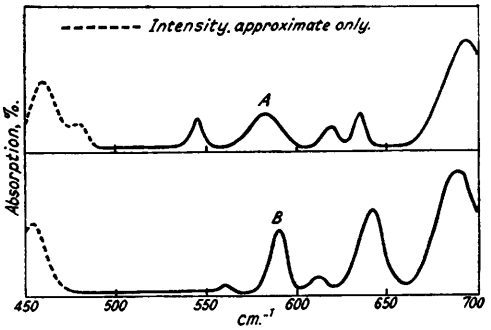
(i) It is common experience that a tertiary arsine will react with an alkyl halide much more readily than will the analogous tertiary amine, and this has been confirmed by careful measurement of the velocity of these quaternisations (Davis and Lewis, *J.*, 1934, 1599; Davis and Addis, *J.*, 1937, 1622).

(ii) The monoethobromide (VII) will form a monohydrobromide (XI). Clearly, had the initial quaternisation occurred on the nitrogen atom, the tertiary arsine group would have been neutral and therefore could not have formed a salt.

(iii) The azarsine when treated in acetone solution with very dilute hydrogen peroxide gave the oxide (XII). The structure of this compound is shown by the following facts: (*a*) the same compound was obtained by oxidation of the azarsine with chloramine-T, a reagent which readily oxidises tertiary arsines but leaves tertiary amines unaffected (Mann, *J.*, 1932, 958); (*b*) the oxide (XII) gave only a monopicrate, but gave a stable dihydrochloride (XIII) which

could be recrystallised from alcohol. It is clear that this strong acid gives a normal hydrochloride with the tertiary amine group and a hydroxy-chloride with the arsine oxide group. If the oxide had, however, been formed by oxidation of the tertiary amine group, the amine oxide would have given a hydroxy-chloride, but the tertiary arsine group would have been unaffected by the hydrochloric acid. This greater reactivity of the tertiary arsine group than of the tertiary amine towards oxidising agents would almost certainly be shown also towards quaternising agents.

(iv) The above chemical evidence, particularly (ii), places the constitution of these quaternary salts beyond doubt. Some confirmatory evidence from the infra-red absorption spectra has kindly been obtained by Dr. N. Sheppard, to whom we are indebted for the following report. " It was hoped to obtain infra-red spectroscopic evidence to help determine whether, in the crystalline methiodide of (VI), quaternisation had occurred on the amine or the arsine group. For this purpose, spectra were obtained in the potassium bromide region from 700 to 500 cm.$^{-1}$ for the above methiodide and also (for comparison) for phenyltrimethylarsonium iodide [$PhMe_3As$]I. The C–As linkages might be expected to have their stretching vibration frequencies in this region of the spectrum, as they occur at 572 and 584 cm.$^{-1}$ in trimethylarsine (Rosenbaum, Rubin, and Sandberg, *J. Chem. Physics*, 1940, **8**, 366). Should quaternisation have occurred at the arsenic atom of the compound (VI), it might be expected that the spectra of the two compounds would have some similarity in the region of the above stretching frequencies. The two spectra are shown in the annexed figure. The strong absorption bands above 650 cm.$^{-1}$



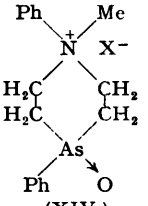
A. Methiodide of hexahydro-1 : 4-diphenyl-1 : 4-azarsine.
B. Phenyltrimethylarsonium iodide.

are probably caused by the phenyl group, but it appears likely that one or more of the other absorption bands in each spectrum can be associated with the vibration of C–As linkages. Although the two spectra are not sufficiently similar to decide unequivocally whether or not a quaternary arsenic atom is present in the methiodide of the arsine (VI), the general similarity would appear to be consistent with the presence of such a structure."

It is clear, therefore, that when the valency of the arsenic atom in the azarsine (VI) is increased to four, the tertiary nitrogen atom has its normal activity very considerably reduced. This effect appears (as would be expected) to be more marked when the tertiary arsine group is converted into a quaternary arsonium group than when it is converted into a tertiary arsine oxide. Further evidence on this point is provided by the arsine oxide (XII) which, when heated with an excess of methyl toluene-*p*-sulphonate at 100°, gave ultimately the quaternary salt (XIV; X = $C_7H_7{\cdot}SO_3$), which was characterised by conversion into the crystalline hydroxy-dipicrate. It is clear that the arsine oxide group under these vigorous conditions could not prevent quaternisation of the tertiary nitrogen group, yet no example was found of a similar quaternisation of the tertiary amine group when the tertiary arsine group had already been converted into a quaternary salt.

Furthermore, when the azarsine (VI) was oxidised with concentrated hydrogen peroxide it formed the dioxide (XV), which was undoubtedly formed by the further oxidation of the intermediate arsine oxide (XII) : here, again, the tertiary amine group is not entirely inactivated by arsine oxide formation. It is noteworthy that the dioxide (XV) formed only a monopicrate. It is probable that in this salt it is the oxygen joined to the arsenic, and not that joined to the nitrogen, which has formed the hydroxy-group on combination with the picric acid, although there is no decisive evidence on this point : the significant fact is that both the oxide groups cannot simultaneously combine with a weak acid such as picric acid.

The general explanation of these results is probably closely parallel to that given by Mann and Watson (*J. Org. Chem.*, 1948, **13**, 502), who pointed out that, for example, pyrazine forms only a monohydrochloride and a monomethiodide, whereas 1 : 4-dimethylpiperazine forms both a dihydrochloride and a dimethiodide. It was suggested that the electronic attraction exerted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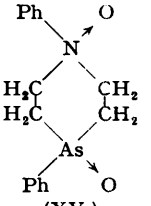
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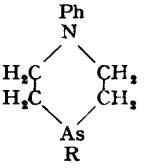
(XVI.)

by the strong positive pole on the first nitrogen atom of the pyrazine salts could be relayed readily by the mesomeric effect through the pyrazine ring to the second nitrogen atom, which was thus inactivated. When the dimethylpiperazine formed a monohydrochloride or a methiodide, this electronic attraction could be exerted only by the much weaker inductive effect through the saturated ring system, and the effect on the second nitrogen atom was too weak to cause inactivation. Many intermediate examples were given in tertiary amines, phosphines, and arsines of a positive pole on one of these atoms causing only a partial deactivation of a neighbouring and similar group, which therefore would, for example, give a stable hydrochloride but not a stable picrate.

In the case of 1 : 4-diphenylpiperazine, *i.e.*, the nitrogen analogue of our azarsine (VI), the two phenyl groups would in any case reduce the normal reactivity of the two nitrogen atoms compared with that of those in 1 : 4-dimethylpiperazine, and the diphenylpiperazine consequently forms only a monomethiodide (Dunlop and Jones, *J.*, 1909, **95**, 419). Precisely the same factors apply to our azarsine (VI) : the normal reactivity of the nitrogen atom would be reduced by the phenyl group, and the formation of a positive pole on the arsenic atom—by quaternisation or oxidation—would still further reduce this activity, a fact which is amply illustrated by the above examples.

One further point deserves comment. It has already been shown that the action of boiling hydriodic acid on a wide variety of heterocyclic tertiary arsines having an aryl group joined to the arsenic atom is to replace the aryl group by an iodine atom, the heterocyclic ring remaining unaffected (cf. Lyon, Mann, and Cookson, *J.*, 1947, 662; Beeby, Cookson, and Mann, *loc. cit.*; Beeby, Mann, and Turner, *J.*, 1950, 1923). The azarsine (VI) behaved similarly, with the formation of the cream-coloured crystalline hydriodide of the 4-iodo-1-phenyl derivative (XVI: R = I), which could be readily hydrolysed to the colourless 4-hydroxy-1-phenyl derivative (XVI; R = OH). When, however, the azarsine (VI) was boiled with hydriodic acid containing free iodine, the chocolate-brown crystalline hydriodide of the 4-tri-iodo-1-phenyl derivative (XVI; R = I_3) was formed : this was a stable compound which could be readily recrystallised, but when shaken with an aqueous solution of sulphur dioxide it was rapidly reduced to the above hydriodide of the monoiodo-derivative.

Experimental.

Tetrahydro-4-phenyl-1 : 4-oxarsine (II).—A solution of phenylarsinebis(magnesium bromide) was prepared by the action of a solution of phenylarsine (40 g.) in benzene (200 c.c.) on a Grignard reagent prepared from ethyl bromide (80 g., 2·8 mols.), ether (250 c.c.), and magnesium (18·8 g.) (cf. Beeby, Cookson, and Mann, *loc. cit.*). A solution of di-(2-bromoethyl) ether (57 g., 0·95 mol.) in benzene (100 c.c.) was added dropwise to the arsine Grignard reagent which was chilled and stirred for 2 hours. The product was then boiled under reflux for 2 hours, cooled, and hydrolysed with ammonium chloride solution, and the ethereal layer then separated, dried, and evaporated. The viscous residue was completely soluble in alcohol and hence contained very little (if any) arsenobenzene. Distillation at 0·1 mm. gave a small fraction at *ca.* 80° without decomposition, but the bulk of the distillate was obtained by slowly increasing the temperature of the bath to 250—300°, whereat contamination of the distillate with dark products of the decomposition became marked. Redistillation of this crude product at 20 mm. gave the fractions : (*a*) b. p. 110—130°, 10 g.; (*b*) b. p. 150—165°, 19 g.; (*c*) b. p. 165—190°, 4 g.

Fraction (*b*), which contained the major portion of the oxarsine, was dissolved in acetone, and the solution filtered to remove free arsenic and then oxidised with an excess of hydrogen peroxide (20-vol.). The solution, after concentration under reduced pressure, was treated with picric acid, the *tetrahydro-oxarsine hydroxy-picrate* (IV; X = $C_6H_2O_7N_3$) being precipitated; from alcohol this formed yellow crystals, m. p. 123° (Found : C, 40·9; H, 3·3; N, 9·2. $C_{16}H_{16}O_9N_3As$ requires C, 40·9; H, 3·4; N, 9·0%) (20·8 g., 18% based on the dibromo-ether).

The picrate in aqueous suspension was decomposed with hydrochloric acid, the picric acid extracted with ether, and the aqueous solution of the hydroxy-chloride (IV: X = Cl) divided into two portions:

(i) The major portion was reduced by a stream of sulphur dioxide in the presence of chloroform and a trace of potassium iodide. The liberated arsine dissolved in the chloroform which, when separated, dried, and distilled, gave *tetrahydro-4-phenyl-1 : 4-oxarsine* (II) as a colourless liquid, b. p. 149—151°/18 mm. (Found: C, 52·4; H, 5·9. $C_{10}H_{13}OAs$ requires C, 53·6; H, 5·85%) (the low carbon value was apparently due to oxidation). The arsine readily gave a *methiodide*, colourless crystals (from alcohol), m. p. 162—162·5° (Found: C, 35·9; H, 4·3. $C_{11}H_{16}OIAs$ requires C, 36·1; H, 4·4%), and also *dichlorobis(tetrahydro-4-phenyloxarsine)palladium*, which, after crystallisation first from ethanolic dioxan and then from dioxan, separated as orange crystals, m. p. 182°, containing 1 mol. of dioxan (Found: C, 40·0; H, 4·6. $C_{20}H_{26}O_2Cl_2As_2Pd.C_4H_8O_2$ requires C, 40·35; H, 4·8%).

(ii) The minor portion of the hydroxy-chloride solution was made alkaline with ammonia, evaporated to dryness, and extracted with chloroform. The extract was saturated with hydrogen sulphide, dried, and evaporated: the residue after crystallisation from alcohol furnished colourless crystals of *tetrahydro-4-phenyloxarsine sulphide* (V), m. p. 101·5—102° (Found: C, 47·0; H, 5·3%; *M*, ebullioscopic in 0·924% alcoholic solution, 253. $C_{10}H_{13}OSAs$ requires C, 46·9; H, 5·1%; *M*, 256).

Fraction (*a*) when treated with methyl iodide gave an impure methiodide, which could not be readily recrystallised; its solution in alcohol was therefore treated with sodium picrate, and the crude precipitated picrate, thrice recrystallised from alcohol, gave yellow crystals of *diethylmethylphenylarsonium picrate*, m. p. 81—81·5° (Found: C, 44·85; H, 4·2; N, 9·3. $C_{17}H_{20}O_7N_3As$ requires C, 45·0; H, 4·45; N, 9·3%). A sample of pure diethylphenylarsine was converted into the methopicrate, which when similarly recrystallised had m. p. 85—86°; a mixture of the two samples had m. p. 82—85·5°.

Fraction (*c*) when treated with methyl iodide, gave the methiodide of the oxarsine, m. p. 162° after three recrystallisations from alcohol (Found: C, 36·2; H, 4·54%). The difficulty in assessing the amount of arsine in fraction (*c*) prevented an accurate determination of the total yield.

Di-(2-bromoethyl)aniline.—Aniline was converted by ethylene chlorohydrin into di-(2-hydroxyethyl)-aniline, and the latter by phosphorus tribromide into di-(2-bromoethyl)aniline by Ross's method (*J.*, 1949, 183): the bromo-compound had m. p. 51—53° after recrystallisation from alcohol.

Hexahydro-1 : 4-diphenyl-1 : 4-azarsine (VI).—A solution of di-(2-bromoethyl)aniline (46·2 g.) in benzene (150 c.c.) was added slowly to a cooled, well-stirred solution of phenylarsinebis(magnesium bromide), prepared from phenylarsine (24·3 g., 1·05 mols.) and ethylmagnesium bromide. The mixture was stirred in the cold for 3 hours and then whilst boiling for 1·5 hours. After cooling and hydrolysis with aqueous ammonium chloride, the ethereal layer was collected, dried, and evaporated. The residue was thrice extracted with boiling light petroleum (b. p. 60—80°), and the united extracts were filtered and evaporated. The residue so obtained, when recrystallised from alcohol, gave the colourless *azarsine* (VI), m. p. 96—97·5° (Found: C, 64·4; H, 6·2; N, 5·05%; *M*, ebullioscopic in 1·181% alcohol solution, 272. $C_{16}H_{18}NAs$ requires C, 64·2; H, 6·1; N, 4·7%; *M*, 299); 22·8 g., 50% yield. The azarsine readily gave a *picrate*, yellow crystals (from alcohol), m. p. 172—173° (preliminary softening) (Found: C, 50·0; H, 4·3; N, 10·5. $C_{16}H_{18}NAs,C_6H_3O_7N_3$ requires C, 50·0; H, 4·0; N, 10·6%).

A solution of this azarsine in cold methyl iodide rapidly deposited the *monomethiodide*, colourless crystals (from alcohol), m. p. 181—182° (preliminary softening and darkening) (Found: C, 46·2; H, 4·55; N, 3·3. $C_{17}H_{21}NIAs$ requires C, 46·3; H, 4·8; N, 3·2%). The use of boiling methyl iodide gave the same product.

A mixture of the arsine and an excess of ethyl bromide was heated in a sealed tube at 100° for 6 hours. Evaporation gave a residue consisting solely of the *monoethobromide* (VII), colourless crystals, m. p. 179—179·5°, from ethyl acetate–alcohol (Found: C, 53·3; H, 6·0; N, 3·6. $C_{18}H_{23}NBrAs$ requires C, 52·9; H, 5·7; N, 3·5%). The addition of concentrated hydrobromic acid to a concentrated aqueous solution of this salt precipitated the *ethobromide hydrobromide* (XI), which after recrystallisation from alcohol formed colourless crystals, m. p. 207—208° (decomp.) (Found: C, 44·3; H, 5·3. $C_{18}H_{23}NBrAs.HBr$ requires C, 44·2; H, 4·95%). These slowly acquired a faint blue tint when stored.

A solution of the arsine (0·5 g.) and *p*-chlorophenacyl bromide (0·7 g., 2 mols.) in benzene (45 c.c.) was boiled for 4 hours. On cooling, a portion of the unchanged bromide was recovered. Evaporation of the solvent gave a syrup which could not be crystallised, but readily gave the p-*chlorophenacyl azarsinium picrate*, hygroscopic yellow crystals (from alcohol), m. p. 93—94° (Found: C, 52·8; H, 4·0; N, 8·0. $C_{30}H_{26}O_8N_4ClAs$ requires C, 52·9; H, 3·85; N, 8·2%).

A mixture of the azarsine (1·03 g.) and ethylene dibromide (0·65 g., 1 mol.) under nitrogen was heated at 115—120° for 5 hours. The product, thrice recrystallised from alcohol, gave the *diethanolate* of *s-ethylenebis(hexahydro-1 : 4-diphenyl-1 : 4-azarsinium) dibromide* (X), colourless crystals, m. p. 226—227° (decomp.) (Found: C, 51·8; H, 6·0; N, 3·6. $C_{34}H_{40}N_2Br_2As_2.2C_2H_6O$ requires C, 51·9; H, 6·0; N, 3·2%). This compound readily formed the corresponding unsolvated *dipicrate*, yellow crystals (from alcohol), m. p. 166—167° (preliminary decomp.) (Found: C, 51·2; H, 4·1; N, 10·8. $C_{46}H_{44}O_{14}N_8As_2$ requires C, 51·0; H, 4·1; N, 10·35%).

A similar reaction with trimethylene dibromide gave a viscous syrup which did not crystallise or give a crystalline picrate.

Oxidation of the Azarsine (VI).—(i) *With dilute hydrogen peroxide.* The addition of 0·6% hydrogen peroxide (30 c.c.) to a cold solution of the azarsine (1 g.) in acetone (30 c.c.) reprecipitated the arsine, which, however, slowly redissolved. Next day the solution was evaporated to dryness, and the colourless crystalline residue, when recrystallised from water, afforded the slightly hygroscopic *dihydrate* of the *azarsine oxide* (XII), m. p. 123—124° (Found: C, 54·2; H, 6·2. $C_{16}H_{18}ONAs.2H_2O$ requires C, 54·7; H, 6·3%). The dihydrate underwent considerable dehydration during storage in a vacuum over phosphoric anhydride for 5 days, but the product rapidly re-formed the dihydrate on exposure to damp air.

The oxide, treated in alcoholic solution with picric acid, gave the *azarsine hydroxy-picrate*, orange-red crystals (from alcohol), m. p. 188—189° (preliminary darkening) (Found : C, 48·2; H, 3·8: N, 10·4. $C_{22}H_{21}O_8N_4As$ requires C, 48·5: H, 3·9: N, 10·3%).

A solution of the oxide in an excess of hydrochloric acid was evaporated in a vacuum-desiccator, and the residue, once recrystallised from alcohol, gave colourless crystals of the *dihydrochloride* (XIII), m. p. 156—156·5° (Found : C, 49·3: H, 5·3: N, 3·9. $C_{16}H_{18}ONAs.2HCl$ requires C, 49·5: H, 5·2: N, 3·6%).

(ii) *With chloramine-T.* A solution of the azarsine (VI) (0·53 g.) and hydrated chloramine-T (0·5 g., 1 mol.) in alcohol (50 c.c.) was boiled under reflux for 1 hour, concentrated, cooled, and filtered to remove precipitated sodium chloride. The addition of alcoholic picric acid to the filtrate precipitated the above azarsine hydroxy-picrate, which after one recrystallisation from alcohol had m. p. 187·5—188·5°, unchanged by admixture with the previous sample.

(iii) *With concentrated hydrogen peroxide.* When an acetone solution of the azarsine (VI) was treated with an excess of 30% hydrogen peroxide and then kept at 50° for 3 hours, the dioxide (XV) was obtained as a syrup. When alcoholic solutions of this syrup and of picric acid were mixed, the *dioxide monopicrate* was precipitated, and after recrystallisation from alcohol was obtained as yellow crystals, m. p. 179° (preliminary decomp.) (Found : C, 47·1: H, 3·9: N, 10·2. $C_{16}H_{18}O_2NAs.C_6H_3O_7N_3$ requires C, 47·1: H, 3·8: N, 10·0%).

A mixture of the azarsine monoxide (XII) (0·2 g.) and methyl toluene-*p*-sulphonate (0·6 g., *ca.* 6 mols.) was heated in a sealed tube at 100° for 3 hours. Addition of ether to a concentrated alcoholic solution of the product precipitated an oil which slowly solidified. This solid, when recrystallised from alcohol–acetone, gave colourless crystals of the sulphonate (XIV; X = $C_7H_7{\cdot}SO_3$). For characterisation, these crystals in alcoholic solution were treated with picric acid, and the precipitate, when once recrystallised from alcohol, gave *hexahydro-4-hydroxy-1-methyl-1 : 4-diphenyl-1 : 4-azarsinium dipicrate* as yellow crystals, m. p. 182—183° (preliminary darkening) (Found : C, 44·9; H, 3·4; N, 12·4. $C_{29}H_{26}O_{15}N_7As$ requires C, 44·2: H, 3·3: N, 12·5%).

Action of Hydriodic Acid on the Azarsine (VI).—(i) A mixture of the azarsine (1 g.) and pure constant-boiling hydriodic acid (50 c.c.) was boiled under reflux in a carbon dioxide atmosphere for 2 hours, and the volume of acid then reduced by distillation under reduced pressure. The product was cooled, and the orange-coloured powder which had separated, when collected and recrystallised from methyl alcohol, furnished cream-coloured crystals of the *hydriodide*, m. p. 173—174° (decomp.), of *hexahydro-4-iodo-1-phenyl-1 : 4-azarsine* (XVI; R = I) (Found : C, 25·4; H, 3·2; N, 2·9. $C_{10}H_{13}NIAs,HI$ requires C, 25·2: H, 3·0: N, 2·9%). When this compound was shaken with a mixture of aqueous sodium hydrogen carbonate solution and chloroform, rapid decolorisation and dissolution occurred. The chloroform solution on evaporation gave a colourless crystalline residue, which after recrystallisation from *cyclo*hexane furnished the *hexahydro-4-hydroxy-azarsine* (XVI; R = OH), m. p. 116—116·5° (Found : C, 50·7: H, 5·9: N, 5·9. $C_{10}H_{14}ONAs$ requires C, 50·2; H, 5·9; N, 5·9%).

(ii) The above experiment was repeated with an old sample of hydriodic acid which was black with free iodine. Concentration of the acid solution now gave a dark deposit, which when collected, dried, and recrystallised from benzene furnished chocolate-brown crystals of the *hydriodide*, m. p. 136—138° (decomp.), of *hexahydro-4-tri-iodo-1-phenyl-1 : 4-azarsine* (XVI; R = I_3) (Found : C, 16·9: H, 2·2: N, 2·1. $C_{10}H_{13}NI_3As,HI$ requires C, 16·4; H, 1·9: N, 1·9%). These crystals, when treated in aqueous suspension with sulphur dioxide water, were rapidly converted into cream-coloured crystals of the above hydriodide of the 4-iodo-compound, which, after recrystallisation from methyl alcohol, had m. p. 173—175°, unchanged by admixture with the above compound. This process could be readily reversed : when hot benzene solutions of the hydriodide of the 4-iodo-compound and of iodine were mixed and cooled, the chocolate-brown crystals of the hydriodide, m. p. 134—138°, of the 4-tri-iodo-compound, rapidly separated.

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