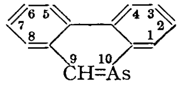
610. *The Synthesis of* 10-*Substituted* 9 : 10-*Dihydroarsanthridines.*

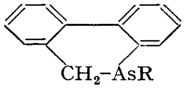
By Gerald H. Cookson and Frederick G. Mann.

Two synthetic routes have been developed for the preparation of alkyl(or aryl)-*o*-phenylbenzylchloroarsines, which under the influence of aluminium chloride undergo ready cyclisation to the corresponding 10-alkyl(or aryl)-9 : 10-dihydroarsanthridines (II), of which a number of derivatives has been prepared. Evidence is adduced that in this novel heterocylic system the two benzene rings are not coplanar, and the stereochemistry of these compounds and their quaternary arsonium salts is discussed.

It is extremely rare for a 3-covalent arsenic atom, which is a member of a ring system, to be bound to neighbouring carbon atoms by one single and one double bond; in fact, decisive evidence is still lacking for the constitution of phenarsazine and arsanthren, the only two compounds in which the presence of such a grouping has been claimed (Wieland and Reinheimer, *Annalen*, 1921, **423**, 16; Kalb, *ibid.*, p. 66). Consequently the arsenic analogue of phenanthridine, which we have termed " arsanthridine " (I), assuming it is capable of existence, is probably highly unstable. We have therefore investigated the synthesis of the hitherto unknown 9 : 10-dihydroarsanthridine ring system (II), which could reasonably be expected to possess a greater stability than the parent compound (I).

(I.)



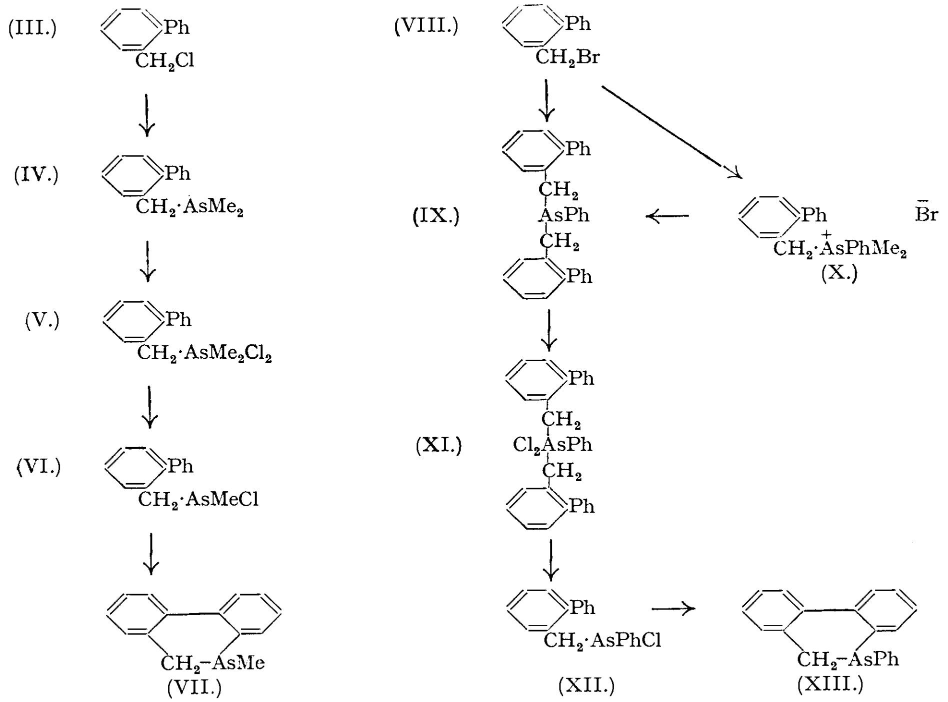


(II.)

Compounds of type (II), in which R may be an alkyl or aryl group, are of interest for several reasons. Clearly they contain the same type of ring system as that in both the 1 : 2 : 3 : 4-tetrahydroarsinolines of Burrows and Turner (*J.*, 1921, **119**, 430) and the 1 : 2 : 3 : 4-tetrahydro*iso*arsinolines of Holliman and Mann (*J.*, 1943, 547); they can be regarded as benz-derivatives of the dihydro-form of either of these systems. Furthermore there is considerable evidence that the tricyclic ring system in (II) cannot be planar, and the stereochemistry of such compounds consequently presents very interesting features, which are discussed later. On the therapeutic side, the fact that many phenanthridine derivatives, *e.g.*, 2 : 7-diamino-9-phenyl-10-methylphenanthridinium chloride (Walls, *J.*, 1945, 294), possess marked trypanocidal activity indicates that the possible therapeutic properties of analogous arsanthridine compounds should not be ignored.

In our earlier attempts to synthesise compounds of type (II), we experienced considerable (and expected) difficulties because many of the intermediate compounds possessed a substituted benzyl group directly attached to an arsenic atom, and such groups are notoriously labile. We have however successfully developed two synthetic routes (leading essentially to the same penultimate stage), and in the second of these routes the labile character of the benzyl group has been advantageously employed.

In the first method, *o*-phenylbenzyl chloride (III) was converted into a Grignard reagent which, when treated with dimethyliodoarsine, gave *o*-phenylbenzyldimethylarsine (IV), a liquid characterised by a *methiodide* and a *dichloropalladium* derivative. The tertiary arsine (IV) in carbon tetrachloride solution was then treated with chlorine to form the arsine dichloride (V). Distillation of the solvent caused the dichloride (V) to lose methyl chloride with the production of *o*-phenylbenzylmethylchloroarsine (VI). This crude product without purification was cyclised in carbon disulphide solution in the presence of aluminium chloride, and 10-methyl-9 : 10-dihydroarsanthridine (VII) thus obtained; since this arsine did not crystallise, it was characterised by conversion into its crystalline methiodide, *i.e.*, as 10 : 10-*dimethyl*-9 : 10-*dihydroarsanthridinium iodide*.



In our second method we have utilised phenylarsinebis(magnesium bromide), Ph•As(MgBr)$_2$, prepared by the interaction of phenylmagnesium bromide and phenylarsine (cf. Job, Reich, and Vergnaud, *Bull. Soc. chim.*, 1924, **35**, 1404; Blicke and Oneto, *J. Amer. Chem. Soc.*, 1935, **57**, 749). When two molecular proportions of *o*-phenylbenzyl bromide (VIII) were treated with one of this di-Grignard reagent, the crystalline *phenylbis*-o-*phenylbenzylarsine* (IX) was obtained. Alternatively, the bromo-compound (VIII) was combined with phenyldimethylarsine to give phenyl-*o*-phenylbenzyldimethylarsonium bromide (X) which on heating dissociated to give both the required tertiary arsine (IX) and *s*-bis-2-diphenylylethane. This reaction illustrates the ready migration of the *o*-phenylbenzyl group. Since other reactions also occurred, this method is far less satisfactory than that using the above di-Grignard reagent.

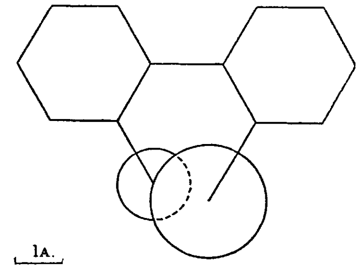
The arsine (IX) was next converted into the arsine dichloride (XI), which when heated readily lost one of the benzyl groups to give phenyl-*o*-phenylbenzylchloroarsine (XII). This crude product when cyclised in carbon disulphide solution with aluminium chloride gave 10-phenyl-9 : 10-dihydroarsanthridine (XIII), characterised as its crystalline *methiodide*, *methopicrate*, and *dichloropalladium* and *dibromopalladium* derivatives $(C_{19}H_{15}As)_2PdX_2$.

A scale diagram of the 9 : 10-dihydroarsanthridine ring system is shown in Fig. 1, in which the two aromatic rings have been drawn in the plane of the paper, using bond-lengths in the benzene rings intermediate between those in benzene and in diphenyl, and circles have been drawn around the centres of the methylene carbon atom and the arsenic atom with radii appropriate for a single C–As bond. These overlap to a considerable extent, and consequently the $-CH_2\cdot As-$ bridge can be accommodated only if the two aromatic rings are twisted relatively to one another about the central diphenyl bond. The angle thus subtended between these two rings, calculated on the basis of the distances used in constructing Fig. 1, is 34°.

It will be seen therefore that a 10-substituted 9 : 10-dihydroarsanthridine (II) must possess molecular dis-symmetry, and a quaternary salt (XIV), having two unlike groups joined to the arsenic atom, would in addition have an asymmetric arsenic atom. Such a compound should therefore be capable of existing in two racemic forms. It would be stereochemically similar to phenyldihydrothebaine, which Robinson (*Nature*, 1947, **160**, 815) has shown to contain twisted diphenyl rings linked through the 2 : 2′-positions by a third ring containing one asymmetric carbon atom.

FIG. 1.

Scale diagram of the 9 : 10-*dihydroarsanthridine ring system.*

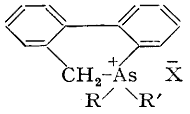


Bond lengths (A) *used.*	
C–C *in rings*	1·4
C–C *between rings*	1·5
Ring C–As	1·95
Ring C–CH_2	1·54
Radius of As	1·21
Radius of CH_2	0·77

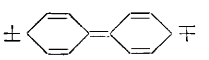
Observed bond lengths.	
C–C *in benzene*	1·39
C–C *in rings in diphenyl*	1·42
C–C *between rings in diphenyl*	1·48
C–Me *in* C_6Me_6	1·53
C–C *in* C_2H_6	1·55
C–As *in* $AsMe_3$	1·98
C–As *in* $AsPh_4I$	1·94

(*The observed bond lengths are taken from Wheland,* " The Theory of Resonance," 1944, *pp.* 286—296.)

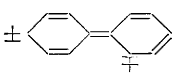
In view of these results, the ultra-violet absorption spectra of certain of the above arsanthridinium salts have been determined. Diphenyl has a characteristic absorption band at 252 mμ. ($\varepsilon_{max.}$ 17,000), which is considered to be due to the excited states arising from the 10 different ionic structures such as (XV*a*) and (XV*b*), in all of which the central double bond requires the two benzene rings to be co-planar. If the presence of substituents caused these rings to be permanently twisted (*i.e.*, non-coplanar), this band should therefore disappear. If however, the nature of these substituents, while causing a general twisting of the rings, allowed also a certain amount of oscillation of the rings about the coplanar position, this band should be still present but with considerably reduced intensity. Rodebush *et al.* (*J. Amer. Chem. Soc.*, 1940, **62**, 2906; 1941, **63**, 3018) consider that the absence of this band is a much more sensitive test for restricted rotation in diphenyl derivatives than is optical resolution. For example, a scale diagram of 2 : 2′-dimethyldiphenyl shows that when the rings are coplanar the van der Waals radii of the methyl groups and the 6 : 6′-hydrogen atoms overlap, and Rodebush *et al.* have shown that this compound does not possess the diphenyl absorption band. On the other hand, 9 : 10-dihydrophenanthrene, in which the covalently-bound methylene carbon atoms can approach one another more closely, shows an absorption band of the same intensity as that of diphenyl but displaced to 265 mμ.



(XIV.)



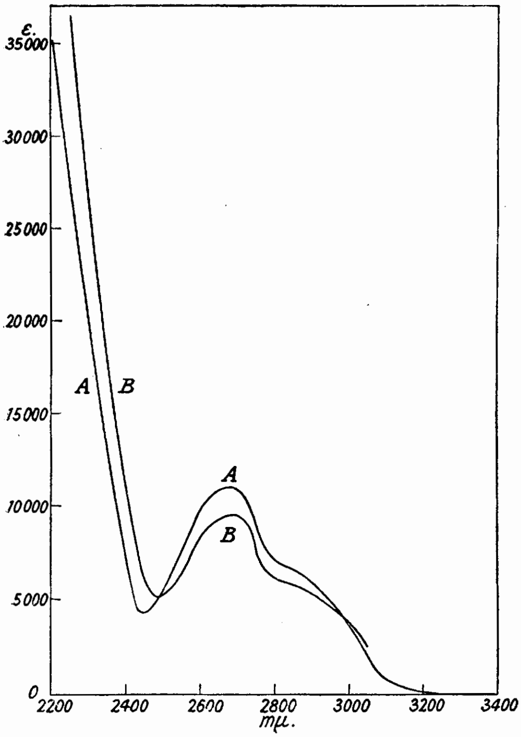
(XV*a*.)



(XV*b*.)

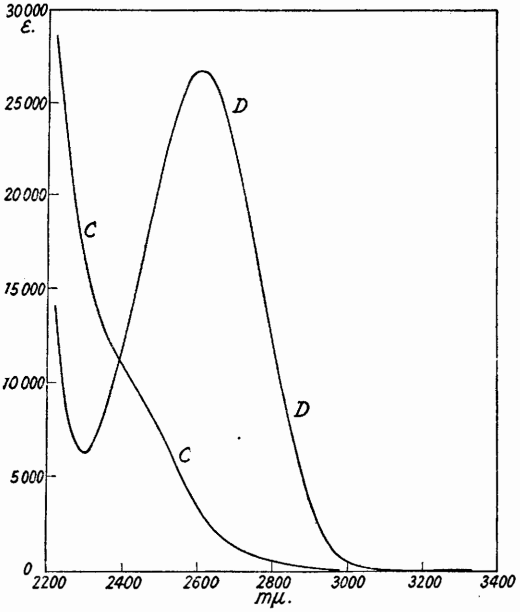
In Fig. 2 are shown the absorption bands of 10 : 10-dimethyl-9 : 10-dihydroarsanthridinium iodide (A) and of the 10-phenyl-10-methyl analogue (B). The two spectra are closely similar, the former having a marked band at 268 mμ., $\varepsilon_{max.}$ 11,100, and the latter at 269 mμ., $\varepsilon_{max.}$ 9,600. In contrast to these compounds, the spectra of two other arsonium salts having a diphenyl group without the third heterocyclic ring have been determined. In Fig. 3 are shown the spectra of *o*-phenylbenzyltrimethylarsonium iodide (C) and of *phenyl*-p-*phenylbenzyldimethylarsonium bromide* (D). The spectrum of the former of these two compounds shows no indication of the diphenyl band, and it would follow that in this compound restricted rotation is complete, *i.e.*, the benzene rings are never coplanar. In compound (D) however, where restricted rotation cannot occur, a marked band occurs at 261 mμ., $\varepsilon_{max.}$ 26,700; this is closely similar to that of diphenyl, but far more intense. A stricter comparison could have been obtained by using phenyl-*o*-phenylbenzyldimethylarsonium bromide in place of the compound (C), but this bromide and the corresponding iodide proved too deliquescent for accurate work.

FIG. 2.



(*A*) 10 : 10-*Dimethyl*-9 : 10-*dihydroarsanthridinium iodide.*
(*B*) 10-*Phenyl*-10-*methyl*-9 : 10-*dihydroarsanthridinium iodide.*

FIG. 3.



(*C*) o-*Phenylbenzyltrimethylarsonium iodide.*
(*D*) *Phenyl*-p-*phenylbenzyldimethylarsonium bromide.*

The significance of the absorption bands of the arsanthridinium salts (A) and (B) is uncertain. The bands at 268 and 269 mμ. may be diphenyl absorption bands slightly displaced and reduced in intensity; if so, they indicate that the twisted rings of the diphenyl portion of the molecule do undergo some oscillation about the coplanar position. On the other hand, both 2-phenyl-2-*p*-chlorophenacyl-1 : 2 : 3 : 4-tetrahydro*iso*arsinolinium bromide and *As-spiro*-bis-1 : 2 : 3 : 4-tetrahydro*iso*arsinolinium iodide show absorption bands at 263 mμ., $\varepsilon_{max.}$ 10,500, and 263 mμ., $\varepsilon_{max.}$ 810, respectively (Holliman and Mann, *J.*, 1943, 552; 1945, 46). These bands were ascribed to the presence of the *o*-phenylene groups in these compounds. In view of the almost identical position of these bands in the two sets of compounds, the structural significance of these spectra must at present remain uncertain. The absorption spectra of other heterocyclic arsonium salts are being investigated to obtain further evidence on this subject.

The stereochemical features and therapeutic properties of the 9 : 10-dihydroarsanthridine derivatives are being investigated.

EXPERIMENTAL.

2-Nitrodiphenyl was prepared by the nitration of diphenyl (Morgan and Walls, *J. Soc. Chem. Ind.*, 1930, **49**, 15T) and by the Gomberg reaction between diazotised *o*-nitroaniline and benzene (Elks, Haworth, and Hey, *J.*, 1940, 1284). Although the yields were 25% and 40% respectively, the former method proved by far the more convenient. Morgan and Walls (*loc. cit.*) reduced this compound to 2-aminodiphenyl with iron and hydrochloric acid. We have reduced the nitro-compound in batches of 150 g. in ethanol solution by hydrogen at 75 atmospheres in the presence of Raney nickel. The reaction began at *ca.* 80°, and if necessary stirring was temporarily stopped to prevent the temperature rising above 100°. The amine had b. p. 166—168°/16 mm., m. p. 47—48°; yield, 90%. It was then converted into 2-iododiphenyl by Cook's method (*J.*, 1930, 1090).

o-*Phenylbenzyl* (2-*Diphenylylmethyl*) *Alcohol.*—The middle neck of a 3-necked flask of 1-l. capacity was fitted with a mercury-sealed stirrer and a reflux condenser; one of the outer necks was fitted with a dropping-funnel and the other closed during the formation of a Grignard reagent prepared by the action of 2-iododiphenyl (127 g.) in ether (210 c.c.) on magnesium (12·2 g.) under ether (40 c.c.). The reaction was started by a crystal of iodine and, after all the iododiphenyl solution had been slowly added through the funnel, was completed by heating the mixture under reflux for 30 minutes. Benzene (100 c.c.) was then added.

The third neck of the flask was next fitted with a glass tube of *ca.* 12 mm. internal diameter which reached to 2 cm. above the surface of the liquid. The other end of the tube was connected to a flask containing paraformaldehyde (30 g.), previously thoroughly dried (cf. Gilman and Catlin, *Org. Synth.*, Coll. Vol. I, p. 188). The paraformaldehyde was heated in a bath at 200°, and the depolymerised formaldehyde swept by a slow stream of nitrogen into the flask containing the Grignard solution which was cooled in ice and vigorously stirred. This was continued until Gilman's test for a Grignard reagent (formation of a dye with Michler's ketone) was negative, a period of *ca.* 30 minutes being required. The stream of formaldehyde was then stopped, and the mixture boiled under reflux for 15 minutes, cooled, and hydrolysed with dilute sulphuric acid. The organic layer when dried (Na_2SO_4) and distilled gave two fractions, (*a*) diphenyl, b. p. 90—100°/0·6 mm. (11 g.), and (*b*) *o*-phenylbenzyl alcohol, b. p. 136—138°/0·5 mm. (55 g., 66%). The alcohol had m. p. 45—49°, increased to 50—51° by recrystallisation from *cyclo*hexane. Von Braun and Manz (*Annalen*, 1929, **468**, 258) obtained this alcohol as an oil, b. p. 174°/13 mm., by the action of nitrous acid on *o*-phenylbenzylamine.

The residue from the fractionation consisted chiefly of the acetal, $(Ph{\cdot}C_6H_4{\cdot}CH_2{\cdot}O)_2CH_2$, b. p. 230—240°/0·4 mm. If too much formaldehyde was used, the yield of the acetal increased; but, since the acetal was readily decomposed by hydrobromic acid, the total yield of bromide (VIII) (see below) was almost unaffected.

o-Phenylbenzyl bromide (VIII) was obtained by heating the alcohol for 4 hours under reflux with hydrobromic acid of constant b. p. It had b. p. 129—130°/0·4 mm., 179—181°/20 mm.; yield, 77% (cf. von Braun and Manz, *loc. cit.*). The acetal, similarly treated, gave a further 8·4 g. of the bromide, the over-all yield of which from the 2-iododiphenyl was 58%.

The chloride (III), and the iodide, were similarly prepared from the alcohol.

Small amounts of by-products were obtained when the bromide was purified. One was apparently 1 : 2-*dibromo*-1 : 2-*di*-2′-*diphenylylethane*, m. p. 101—101·5° (depressed to 50—57° by admixture with *p*-phenylbenzyl bromide of m. p. 82°) (Found: C, 63·6; H, 4·3. $C_{26}H_{20}Br_2$ requires C, 63·4; H, 4·1%). On one occasion treatment of the acetal with hydrobromic acid also gave a small quantity of 1 : 2-di-2′-diphenylylethane.

The *o*-phenylbenzyl bromide (VIII) was characterised by warming it with pyridine: the colourless crystals of o-*phenylbenzylpyridinium bromide* which separated were collected and recrystallised from ethanolic *cyclo*hexane and had m. p. 181—183° (Found: C, 66·9; H, 5·0. $C_{18}H_{16}NBr$ requires C, 66·3; H, 4·9%). The *iodide*, similarly prepared and recrystallised from ethanol, had m. p. 181—185° (decomp.) (Found: C, 57·55; H, 4·1; N, 3·7. $C_{18}H_{16}NI$ requires C, 57·9; H, 4·3; N, 3·75%). The *picrate*, prepared from the bromide in aqueous solution with sodium picrate, formed golden needles (from ethanol), m. p. 114—115° (Found: C, 61·2; H, 4·0; N, 12·1. $C_{24}H_{18}O_7N_4$ requires C, 60·7; H, 3·8; N, 11·8%).

The possible formation of a Grignard reagent by the interaction of magnesium with *o*-phenylbenzyl chloride (III) and bromide (VIII) under standard conditions was carefully investigated, the ethereal solution after complete reaction being treated with a considerable excess of solid carbon dioxide in order to estimate the Grignard reagent as 2-diphenylylacetic acid. It was found that the chloride (III) gave this acid in 48% yield as colourless crystals, m. p. 114° (Found: C, 79·0; H, 5·7. Calc. for $C_{14}H_{12}O_2$: C, 79·2; H, 5·7%), and also 1 : 2-di-2′-diphenylylethane in 7% yield. The bromide (VIII) however gave the acid in negligible yield (*ca.* 0·5%), but gave the above ethane in 95% yield as colourless needles, m. p. 116—117° (Found: C, 93·4; H, 6·5. Calc. for $C_{26}H_{22}$: C, 93·4; H, 6·6%). von Braun and Manz (*loc. cit.*) prepared this hydrocarbon by the action of sodium on an ethereal solution of the bromide, and describe it as an oil, b. p. 260°/12 mm. It is clear that the bromide (VIII) cannot be used for the preparation of a Grignard reagent under normal conditions.

o-*Phenylbenzyldimethylarsine* (IV).—A Grignard reagent was prepared under a nitrogen atmosphere by adding a solution of the chloride (III) (19 g., 1 mol.) in ether (60 c.c.) to magnesium (4·4 g., 1·9 atoms) under ether (10 c.c.), the reaction being initiated by methyl iodide, and the chloride solution then added at such a rate that the mixture remained hot but did not boil (*ca.* 50 minutes). The complete mixture was then boiled under reflux for 15 minutes, and chilled while a solution of dimethyliodoarsine (13·9 g., 0·64 mol.) in benzene (25 c.c.) was added during 10 minutes. The mixture was heated under reflux for 1 hour, cooled, and hydrolysed with aqueous ammonium chloride, the organic layer being then collected, dried, and filtered under carbon dioxide. After removal of the solvent, distillation at 0·4 mm. gave 4 indefinite liquid fractions: (*a*) b. p. 84—90° (0·43 g.), (*b*) b. p. 90—103° (3·1 g.), (*c*) b. p. 115—124° (2·6 g.), and (*d*) b. p. 124—126° (9·8 g.). Only a very small non-volatile residue remained. Fraction (*d*) was the required arsine (IV), and the yield is 60% based on the iodoarsine used.

This arsine (IV) had an unpleasant smell and rapidly became turbid on exposure to the air. It was therefore characterised by combination with methyl iodide (which occurred readily at room temperature) to give o-*phenylbenzyltrimethylarsonium iodide*, colourless crystals, m. p. 232—235°, from ethanol (Found: C, 46·3; H, 5·1. $C_{16}H_{20}IAs$ requires C, 46·4; H, 4·8%), and by reaction with ammonium palladochloride to give *dichlorobis*(o-*phenylbenzyldimethylarsine*)*palladium*, which separated as the pale orange crystalline *monohydrate*, m. p. 150°, from aqueous acetone (Found : C, 48·7; H, 5·3. $C_{30}H_{34}Cl_2As_2Pd,H_2O$ requires C, 48·65; H, 4·9%).

Methiodide of 10-*Methyl*-9 : 10-*dihydroarsanthridine* (9-*Methyl*-9 : 10-*dihydro*-9-*arsaphenanthrene* *) (VII).—A solution of the arsine (IV) (9·2 g.) in carbon tetrachloride (15 c.c.) was cooled in ice and stirred under an atmosphere of carbon dioxide while a solution of chlorine (2·4 g., 1 mol.) in carbon tetrachloride (40 c.c.) was added during 30 minutes. The solution deposited stout colourless crystals, undoubtedly of the arsine dichloride (V), but no attempt to isolate them was made. The solvent was then removed under very slightly reduced pressure, much foaming occurring initially presumably owing to the evolution of methyl chloride. The residue was finally heated to 150°/30 mm. for a short time.

The distillate of carbon tetrachloride undoubtedly contained some dimethylchloroarsine. Some of this evil-smelling oil which remained in the side-arm of the distilling flask was shaken with an aqueous solution of potassium palladochloride, whereby a yellow precipitate of *dichlorobis*(*dimethylarsinous acid*)*palladium*, $[(Me_2As{\cdot}OH)_2PdCl_2]$, was obtained. This compound separated from ethanol as pale lemon-coloured crystals, which when heated became orange at *ca.* 130° and ultimately black, decomposing at *ca.* 250° with the deposition of a mirror of palladium (Found : C, 11·7; H, 3·1; Pd, 25·3. $C_4H_{14}O_2Cl_2As_2Pd$ requires C, 11·4; H, 3·3; Pd, 25·3%).

The above residue, which contained the crude chloroarsine (VI), was dissolved in carbon disulphide (30 c.c.), cooled to 0°, and treated with freshly sublimed aluminium chloride (6 g.). The containing flask was then fitted with a reflux condenser closed by a calcium chloride tube, and removed from the ice-bath. The mixture became warm spontaneously and evolved hydrogen chloride. It was heated under reflux for 5 hours and then cooled, and the carbon disulphide decanted from the lower deep-violet layer. The disulphide on evaporation left only diphenyl (0·6 g.).

The violet layer was poured on crushed ice, which converted it into a yellow oil. This was extracted with chloroform, dried, and distilled in carbon dioxide at 0·1 mm., giving the fractions : (*a*) b. p. 80—110° (0·22 g.), diphenyl, (*b*) b. p. 121—128° (0·5 g.), a yellow oil, and (*c*) b. p. 145—200° (0·25 g.), a yellow oil. Fractions (*b*) and (*c*) consisted of unchanged arsine (IV) and the required methylarsanthridine (VII), the latter being present in larger proportion in fraction (*c*). The arsines were separated (in both fractions) by dissolution in warm methyl iodide, whereupon the methiodide of the arsine (IV) rapidly crystallised and was collected after a few minutes. The filtrate when set aside overnight deposited the methiodide of the arsine (VII), *i.e.*, 10 : 10-*dimethyl*-9 : 10-*dihydroarsanthridinium iodide* [Fraction (*c*) thus yielded 0·11 g. of the former and 0·3 g. of the latter methiodide]. The colourless arsanthridinium iodide crystallised from ethanol as the *hemihydrate*, m. p. 210—215° (effervescence) depressed by admixture with the former iodide (Found : C, 44·2; H, 4·1. $C_{15}H_{16}IAs,\frac{1}{2}H_2O$ requires C, 44·25; H, 4·2%). This hydrate when placed in a vacuum over phosphoric anhydride gave the pure iodide, m. p. 212—215° (slight effervescence) (Found : C, 45·2; H, 4·0. $C_{15}H_{16}IAs$ requires C, 45·25; H, 4·0%).

Phenylbis-o-*phenylbenzylarsine* (IX).—(*A*) A Grignard reagent was prepared under nitrogen from bromobenzene (29·6 g., 2·1 mols.) and magnesium (4·7 g.) in ether (100 c.c.). This solution was cooled and stirred while a solution of phenylarsine (13·8 g., 1 mol.) in benzene (40 c.c.) was added. The dark brown solution was heated under reflux for 30 minutes and then cooled, and a solution of *o*-phenylbenzyl bromide (VIII) (42·5 g., 1·9 mols.) in benzene (70 c.c.) was added during 20 minutes. The pale yellow mixture was boiled under reflux for 1 hour, cooled, and hydrolysed with aqueous ammonium chloride. The organic layer was separated, dried, and filtered in a carbon dioxide atmosphere. The solvents were removed and the residue heated at 0·1 mm. until a distillate (3·7 g.), consisting mainly of unchanged bromide (VIII) had collected. The pale yellow residue of the crude arsine (IX) (39·3 g., 94% calculated on the bromide taken) slowly crystallised on cooling.

The crude *arsine* (IX) could be distilled at *ca.* 225°/5 × 10^{-4} mm. but partial decomposition to give arsenic occurred. Repeated recrystallisation from ethanol, before or after distillation, gave large well-formed colourless crystals, m. p. 70—77°, unaffected by the use of charcoal or by recrystallisation under carbon dioxide (Found : C, 79·0; H, 6·1. $C_{32}H_{27}As$ requires C, 79·0; H, 5·6%). This material contained a trace of phenylarsine oxide, since when boiled with an ethanolic solution of piperidine *N*-pentamethylenedithiocarbamate it gave a small yield of phenylarsinobis-(*N*-pentamethylenedithiourethane), m. p. 173°, unchanged by admixture with an authentic sample. The arsine (IX) recovered from this mother-liquor and recrystallised had m. p. 80—83° (Found : C, 78·9; H, 5·85%) and was clearly purer.

An acetone solution of this arsine when treated with aqueous potassium palladochloride gave *dichlorobis*(*phenylbis*-o-*phenylbenzylarsine*)*palladium*, which separated from aqueous dioxan as orange needles which had 2·5 mols. of water of crystallisation and m. p. 188—190° (decomp.) (Found : C, 64·3; H, 5·3. $C_{64}H_{54}Cl_2As_2Pd,2{\cdot}5H_2O$ requires C, 64·3; H, 4·9%). These crystals, when heated at 137°/0·05 mm., gave the anhydrous compound of unchanged m. p. (Found : C, 67·1; H, 4·6. $C_{64}H_{54}Cl_2As_2Pd$ requires C, 66·8; H, 4·7%).

The arsine, when treated with 15% ethanolic mercuric chloride, gave the *mercurichloride*, which after crystallisation from ethanol gave white crystals, which decomposed at 172—173° to a clear liquid and a white solid, presumably mercuric chloride (Found : C, 51·0; H, 3·8. $C_{64}H_{54}Cl_4As_2Hg_2$ requires C, 50·7; H, 3·6%). The empirical formula of this compound is doubled in accordance with the structural evidence of Evans, Mann, Peiser, and Purdie (*J.*, 1940, 1209) for compounds of this class.

The oxide, methiodide, and methopicrate of the arsine could not be obtained crystalline.

(*B*) When a mixture of *o*-phenylbenzyl bromide (VIII) (0·68 g.) and phenyldimethylarsine (0·5 g., 1 mol.) was prepared in a flask containing carbon dioxide and then gently warmed, it rapidly became cloudy and finally formed a glass. The latter was ground with ether, but owing to its highly deliquescent nature it was characterised by treatment in aqueous solution with sodium picrate, whereby *phenyl* o-*phenylbenzyldimethylarsonium picrate* was obtained as yellow crystals (1·1 g., 70%), m. p. 102°

* The systematic name for use if the trivial name based on arsanthridine is not ultimately accepted.

after crystallisation from ethanol (Found : C, 56·4; H, 4·2; N, 7·7. $C_{27}H_{24}O_7N_3As$ requires C, 56·1; H, 4·2; N, 7·3%). The iodide, similarly prepared, was also deliquescent.

On a larger scale, a mixture of the bromide (VIII) (5·56 g.) and phenyldimethylarsine (4·1 g., 1 mol.) was heated under carbon dioxide at 14 mm. pressure at 200° for 1 hour, gas being steadily evolved. The partly crystalline residue, on distillation, gave fractions: (*a*) b. p. 92—134°/15 mm. (2·75 g.), (*b*) b. p. 80—100°/0·1 mm. (0·3 g.), and (*c*) b. p. 250—260°/0·05 mm. (2·7 g.) Fraction (*a*) was identified as phenyldimethylarsine. Fraction (*c*), a viscous oil containing free arsenic, was dissolved in acetone, filtered, and redistilled at 0·01 mm., giving fractions: (*c*i) b. p. 80—150° (0·2 g.), (*c*ii) b. p. 150—200° (0·2 g.), and (*c*iii) b. p. 200—250° (1·75 g.). The last fraction consisted mainly of the arsine (IX) contaminated with a trace of arsenic. It gave the above dichloropalladium derivative, m. p. 186—188° (mixed and alone), and also the above-mentioned mercurichloride (Found : C, 50·9; H, 3·9%). This fraction when dissolved in ethanol deposited a small quantity of 1 : 2-di-2′-diphenylylethane, m. p. 115—116° (alone and mixed) and later the arsine (IX), m. p. 70—77°; this sample was not purified. Fractions (*b*) and (*c*ii) also slowly deposited the above hydrocarbon, m. p. 114—116°.

10-*Phenyl*-9 : 10-*dihydroarsanthridine* (9-*Phenyl*-9 : 10-*dihydro*-9-*arsaphenanthrene*) (XIII).—Solutions of the arsine (IX) (7·75 g.) and of chlorine (1 mol.), each in carbon tetrachloride (15 c.c.), were mixed at 0° during 15 minutes, with shaking, under an atmosphere of carbon dioxide. The solvent was removed under reduced pressure, and the residue of the crude arsine dichloride (XI) heated to 150° at 0·2 mm. for a short time. A fraction, b. p. 97—105° (2·9 g.), was collected and identified as *o*-phenylbenzyl chloride. The oily residue (7·7 g.), which preliminary experiments had shown to consist largely of the chlorarsine (XII), was dissolved in carbon disulphide (15 c.c.), mixed with aluminium chloride (3 g.), and then heated under reflux for 3 hours. The carbon disulphide was decanted from the cold mixture, and the residue hydrolysed with dilute hydrochloric acid and then repeatedly extracted with chloroform. The dried extract after evaporation of the solvent gave fractions : (*a*) b. p. 76—90°/0·2 mm. diphenyl (0·9 g.), (*b*) b. p. 118—150°/0·005 mm., a yellow oil (0·15 g.), (*c*) b. p. 150—200°/0·001 mm., a cloudy yellow oil (0·75 g.), and (*d*) b. p. 200—240°/0·001 mm., a cloudy yellow oil (0·07 g.) containing free arsenic. Fraction (*c*) which contained the 10-phenyl-9 : 10-dihydroarsanthridine, represented a 15% yield based on the arsine (IX). It was identified by the following derivatives. *Dichlorobis*-(10-*phenyl*-9 : 10-*dihydroarsanthridine*)*palladium*, slender pale yellow needles, m. p. 244—245° (decomp.; with darkening at *ca.* 220°), from dioxan (Found : C, 55·9; H, 4·0; Pd, 13·2. $C_{38}H_{30}Cl_2As_2Pd$ requires C, 56·1; H, 3·7; Pd, 13·1%). The corresponding *dibromo*-derivative, prepared from an acetone solution of the arsine and recrystallised from a mixture of benzene and diethyl ketone, formed yellow crystals, m. p. 244—245° (decomp.; with softening at *ca.* 240°) (Found : C, 50·7; H, 3·4. $C_{38}H_{30}Br_2As_2Pd$ requires C, 50·55; H, 3·3%). 10-*Phenyl*-10-*methyl*-9 : 10-*dihydroarsanthridinium iodide* crystallised from a solution of the arsine in methyl iodide when set aside overnight. The first preparation separated as large yellow sparkling blades, which on being touched with a spatula became opaque as they changed to another crystalline form which was obtained on all subsequent occasions. Recrystallisation from ethanol gave faintly cream-coloured compact crystals, m. p. 195° (effervescence, with slight preliminary softening) in a preheated bath (Found : C, 52·2; H, 3·8. $C_{20}H_{18}IAs$ requires C, 52·2; H, 3·9%). This gave the corresponding *picrate*, yellow crystals (from ethanol), m. p. 150—151° after slight shrinking at 140° (Found : C, 55·8; H, 3·6; N, 7·8. $C_{26}H_{20}O_7N_3As$ requires C, 55·65; H, 3·6; N, 7·5%).

In earlier attempts to synthesise this arsine, an effort was made to purify the intermediate chloroarsine (XII) by vacuum-distillation before carrying out the ring closure, but considerable decomposition occurred during the distillation, the chloroarsine (XII) undergoing dismutation to the original arsine (IX) and phenyldichloroarsine. Although the arsine (XIII) was obtained on one occasion by this method, it became clear that only the above direct cyclisation of the crude undistilled chloroarsine (XII) is practicable.

Phenyl-p-*phenylbenzyldimethylarsonium Bromide.*—This was prepared by the direct union of *p*-phenylbenzyl bromide and phenyldimethylarsine (1 mol.) in carbon tetrachloride solution. The solvent was distilled off and the residual *arsonium bromide*, when crystallised from ethanol, formed colourless crystals, m. p. 192—193° (Found : C, 58·9; H, 5·2. $C_{21}H_{22}BrAs$ requires C, 58·8; H, 5·1%).

Phenyl-o-*phenylbenzylarsonous Acid*, (o-Ph·C_6H_4·CH_2)AsPhO·OH.—This acid was prepared in order to investigate whether cyclisation would give 10-phenyl-9 : 10-dihydroarsanthridine oxide. *o*-Phenylbenzyl bromide (5·4 g.) was added to a chilled mixture of phenyldichloroarsine (4·9 g., 1 mol.) and 40% aqueous sodium hydroxide solution (8·8 c.c.). The mixture became warm and viscous as most of the bromide dissolved; after 30 minutes' shaking, it was heated under reflux for 45 minutes. The cooled solution was diluted with water, extracted with ether, made just acid to phenolphthalein, filtered, and then made acid to Congo-red. The *arsonous acid* (7·2 g., 93%) separated as a white gum which soon solidified and after crystallisation from benzene had m. p. 138—140° (Found: C, 64·8; H, 5·2. $C_{19}H_{17}O_2As$ requires C, 64·8; H, 4·8%). Hot aqueous solutions of the sodium salt of this acid and of *S*-*p*-chlorobenzylthiuronium chloride when mixed gave a precipitate of the *thiuronium* salt, white needles (from dioxan), m. p. 136—137° (Found : C, 58·3; H, 5·0; N, 4·8. $C_{27}H_{26}O_2N_2ClSAs$ requires C, 58·6; H, 4·7; N, 5·1%). All attempts to cyclise the arsonous acid by the action of hydrogen fluoride, thionyl chloride, or phosphoric oxide failed, rupture of the C–As link apparently always occurring.

p-*Chlorophenyl*-o-*phenylbenzylarsonous Acid.*—This acid was obtained in 90% yield by the method described above; it could not be induced to crystallise, however, and was therefore characterised as its S-p-*chlorobenzylthiuronium* salt, white needles (from dioxan), m. p. 135° (Found : C, 55·0; H, 5·0; N, 5·0. $C_{27}H_{25}O_2N_2Cl_2SAs$ requires C, 55·2; H, 4·3; N, 4·8%). All attempts to cyclise the arsonous acid failed.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, July* 13*th*, 1949.]