391. *The Synthetic Application of Phenylarsinebis(magnesium Bromide). Part I. The Synthesis of* iso*Arsindolines, Tetrahydro*iso*arsinolines, and 2-Arsaperinaphthanes.*

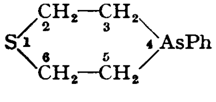
By M. H. Beeby, Gerald H. Cookson, and Frederick G. Mann.

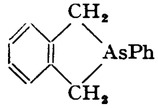
It is shown that the above Grignard reagent, $Ph{\cdot}As(MgBr)_2$, reacts with *o*-xylylene dibromide and dichloride to give 2-phenyl*iso*arsindoline and with *o*-(2-bromoethyl)benzyl bromide to give 2-phenyl-1 : 2 : 3 : 4-tetrahydro*iso*arsinoline. The high yield of each compound makes this method of preparation superior to previous methods. The reagent also reacts with 1 : 8-bisbromomethylnaphthalene to give 2-phenylarsaperinaphthane, which represents a new type of heterocyclic arsenic compound. The probable mechanism of the formation of these compounds is briefly discussed.

Phenylarsinebis(magnesium bromide), $Ph{\cdot}As(MgBr)_2$, was first prepared by Job and Reich (*Compt. rend.*, 1923, **177**, 56) by the interaction of phenylarsine, $Ph{\cdot}AsH_2$, and ethylmagnesium bromide in ethereal solution. Later, Job, Reich, and Vergnaud (*Bull. Soc. chim.*, 1924, **35**, 1404) showed that this reagent reacted with 2 : 2′-dichlorodiethyl sulphide to form 4-phenylthiarsine (I) in 7% yield. Blicke and Oneto (*J. Amer. Chem. Soc.*, 1935, **57**, 749) have similarly prepared diphenylarsinemagnesium bromide, $Ph_2As{\cdot}MgBr$, using however phenylmagnesium bromide advantageously in place of ethylmagnesium bromide.

Phenylarsinebis(magnesium bromide), prepared by Blicke and Oneto's modified method, *i.e.*, by the interaction of phenylarsine and phenylmagnesium bromide, has recently been used by Cookson and Mann (*J.*, 1949, 2888) for converting *o*-phenylbenzyl bromide, $Ph{\cdot}C_6H_4{\cdot}CH_2Br$, into phenylbis-*o*-phenylbenzylarsine, $Ph{\cdot}As(CH_2{\cdot}C_6H_4Ph)_2$, in almost theoretical yield. We have now investigated its use for the preparation of various heterocyclic derivatives of arsenic on the lines of Job, Reich, and Vergnaud's earlier work.

It has been shown by Lyon and Mann (*J.*, 1945, 30) and by Lyon, Mann, and Cookson (*J.*, 1947, 662) that 2-phenyl*iso*arsindoline (II) can be prepared either by the action of *o*-xylylene dibromide, $C_6H_4(CH_2Br)_2$, on phenyldichloroarsine in the presence of sodium, or by the thermal decomposition of the quaternary salt which the dibromide forms with phenyldimethylarsine.


(I.)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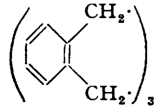
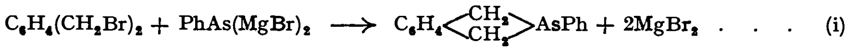

(III.)

These methods furnish the crude *iso*arsindoline (II) in 19% and 60% yield respectively. We now find that a third synthetic route is available, for *o*-xylylene dibromide reacts with a cold solution of phenylarsinebis(magnesium bromide) to give the crude *iso*arsindoline in 80% yield. This method is therefore the most efficacious of the three.

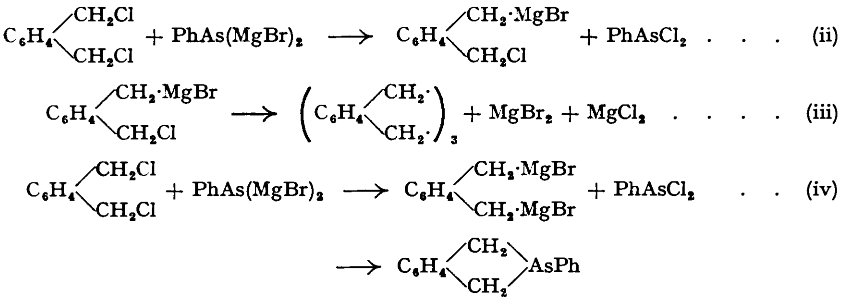
It would appear from this result that the reaction is of the simple character :



$$C_6H_4(CH_2Br)_2 + PhAs(MgBr)_2 \longrightarrow C_6H_4{<}\substack{CH_2\\CH_2}{>}AsPh + 2MgBr_2 \quad . \; . \; . \quad (i)$$

When however this reaction was carried out with *o*-xylylene dichloride instead of the dibromide, the *iso*arsindoline (II) was obtained in 40% yield, the other products isolated being phenyldichloroarsine (*ca.* 15%) and also a small quantity of *s*-tribenz*cyclo*dodecatriene (III), the hydrocarbon that Baker, Banks, Lyon, and Mann (*J.*, 1945, 27) had obtained by the action of sodium on *o*-xylylene dibromide.

The origin of the phenyldichloroarsine is uncertain, but the following mechanism for the formation of these by-products is suggested. In addition to the main reaction (i), it is possible that one (or both) of the chlorine atoms of the *o*-xylylene dichloride directly displaces the magnesium bromide portion of the Grignard reagent, with the formation of phenyldichloroarsine (reaction ii). A portion of the *o*-xylylene magnesium derivative undergoes direct decomposition to give the hydrocarbon (reaction iii). If both the chlorine atoms in the *o*-xylylene dichloride undergo replacement by magnesium bromide (reaction iv), the two products may undergo further interaction to form the *iso*arsindoline. It should be emphasised however that there is at present no evidence that the *iso*arsindoline is formed by reaction (iv) rather than by the more simple direct reaction (i); indeed this appears improbable, since Blicke and Oneto (*loc. cit.*) state that the di-Grignard reagent, $o\text{-}C_6H_4(CH_2{\cdot}MgBr)_2$, does not react with diphenylbromoarsine, Ph_2AsBr, whereas *o*-xylylene dibromide reacts readily with diphenylarsinemagnesium bromide, $Ph_2As{\cdot}MgBr$, to give the diarsine, $o\text{-}C_6H_4(CH_2{\cdot}AsPh_2)_2$.



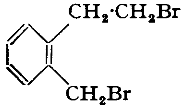
$$C_6H_4{<}\substack{CH_2Cl\\CH_2Cl} + PhAs(MgBr)_2 \longrightarrow C_6H_4{<}\substack{CH_2{\cdot}MgBr\\CH_2Cl} + PhAsCl_2 \quad . \; . \; . \quad (ii)$$

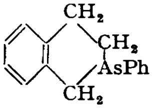
$$C_6H_4{<}\substack{CH_2{\cdot}MgBr\\CH_2Cl} \longrightarrow \left(C_6H_4{<}\substack{CH_2{\cdot}\\CH_2{\cdot}}\right)_3 + MgBr_2 + MgCl_2 \quad . \; . \; . \; . \quad (iii)$$

$$C_6H_4{<}\substack{CH_2Cl\\CH_2Cl} + PhAs(MgBr)_2 \longrightarrow C_6H_4{<}\substack{CH_2{\cdot}MgBr\\CH_2{\cdot}MgBr} + PhAsCl_2 \quad . \; . \quad (iv)$$

$$\longrightarrow C_6H_4{<}\substack{CH_2\\CH_2}{>}AsPh$$

Evidence for the formation of compounds of the type shown in reaction (ii) is provided by the interaction of *o*-(2-bromoethyl)benzyl bromide (IV) and the Grignard reagent. Holliman and Mann (*J.*, 1943, 547) have shown that the dibromide (IV) reacts with phenyldichloroarsine and sodium to give pure 2-phenyl-1 : 2 : 3 : 4-tetrahydro*iso*arsinoline (V) in 31% yield based on the dibromide used. We find furthermore that the dibromide reacts smoothly with cold phenylarsinebis(magnesium bromide) to give the crude *iso*arsinoline (V) in 70% yield. In addition to the *iso*arsinoline (V), however, *o*-(2-bromoethyl)toluene (VI) is formed in moderate quantity, and phenyldibromoarsine, $PhAsBr_2$, is also undoubtedly formed although its isolation


(IV.)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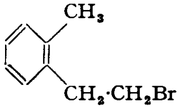
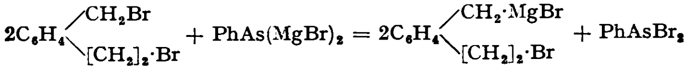

(VI.)

in the pure state is difficult. It is highly probable that the compound (VI) arises by initial reaction of the bromomethyl group in the dibromide (IV) with the Grignard reagent thus :



$$2C_6H_4\begin{cases}CH_2Br\\ [CH_2]_2\cdot Br\end{cases} + PhAs(MgBr)_2 = 2C_6H_4\begin{cases}CH_2\cdot MgBr\\ [CH_2]_2\cdot Br\end{cases} + PhAsBr_2$$

(VII.)

This is of course analogous to reaction (ii). The compound (VII), if it underwent no further immediate reaction, would on subsequent hydrolysis give the monobromo-compound (VI). It is clear that the greater reactivity of the bromomethyl group compared with that of the bromoethyl group in the dibromide (IV) would favour the formation of the monomagnesium bromide (VII) : if however a further reaction occurred to a small extent, and both groups were to give this same reaction, the traces of *o*-ethyltoluene which would be formed on hydrolysis would probably escape detection in the subsequent isolation of the products.

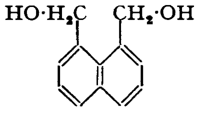
It is noteworthy that, although Job, Reich, and Vergnaud (*loc. cit.*) found that phenylarsinebis(magnesium bromide) reacted with both carbonyl chloride and ethylene dibromide with the formation of arsenobenzene, we find that the above reaction with cold *o*-xylylene dibromide produces no detectable amount of arsenobenzene, and that the cold dibromide (IV)

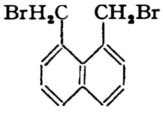
$$PhAsBr_2 + PhAs(MgBr)_2 \longrightarrow PhAs{:}AsPh + 2MgBr_2 \quad . \; . \; . \; . \; . \; . \; . \quad (v)$$

gives only a very small quantity. When however the dibromide (IV) was added to a benzene solution of the Grignard reagent at 70°, the yield of the crude *iso*arsinoline fell to 38%, and arsenobenzene was formed in 20% yield. It is probable that at this higher temperature the phenyldibromoarsine as fast as it was formed reacted competitively with unchanged phenylarsinebis(magnesium bromide) to form the arsenobenzene (reaction v) : we have some evidence, at present incomplete, that the interaction of these two compounds at room temperature is slow.

Apart from the mechanism of the reactions involved, however, the synthetic value of the Grignard reagent for the production of these cyclic arsines is now manifest. It is noteworthy that when the dibromide (IV) was heated with phenyldimethylarsine, the *iso*arsinoline (V) was formed in only 8% yield, and, for the synthesis of this ring system in particular, the arsine–Grignard method is far superior to the other available methods.

To illustrate further the application of the arsine–Grignard reagent for the synthesis of heterocyclic arsenic systems, we have reduced methyl naphthalate by lithium aluminium


(VII.)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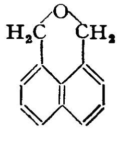
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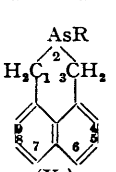
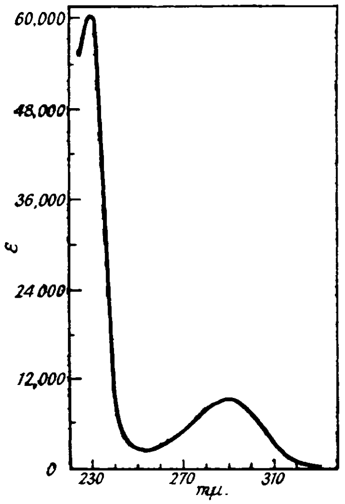

(X.)

hydride to 1 : 8-bishydroxymethylnaphthalene (VII), and converted this into 1 : 8-bisbromomethylnaphthalene (VIII), a process which, in spite of a wide variation in conditions employed, always gave also the highly stable 2-oxaperinaphthane (alternatively named 1 : 3-naphtho-[1 : 8-*cd*]pyran) (IX). When the dibromo-compound (VIII) was treated under the usual conditions with phenylarsinebis(magnesium bromide), 2-phenylarsaperinaphthane (X; R = Ph) was obtained as an oil which could not be crystallised, nor could it be distilled without decomposition even in a high vacuum. It was characterised as its crystalline methiodide, 2-phenyl-2-methylarsoniaperinaphthane iodide, and as its palladochloride derivative, dichlorodi(2-phenylarsaperinaphthane)palladium, $[(C_{18}H_{15}As)_2PdCl_2]$.

The heterocyclic ring in the 2-phenyl compound (X; R = Ph) possesses considerable stability, because, when this compound is heated with hydriodic acid, the phenyl group is evicted with the formation of 2-iodoarsaperinaphthane (X; R = I). This reaction is precisely analogous to the conversion of 2-phenyl*iso*arsindoline into 2-iodo*iso*arsindoline (Lyon, Mann, and Cookson, *loc. cit.*) and of 2-phenyl*iso*arsinoline into 2-iodo*iso*arsinoline (see later), and it is of considerable synthetic value, as the iodo-group could clearly now be replaced by any desired alkyl or aryl group by the application of the appropriate Grignard reagent.

Methiodide of 2-phenylarsaperinaphthane.



The absorption spectrum of the methiodide of 2-phenylarsaperinaphthane is shown in the adjoining Figure. This spectrum proved almost completely identical with that of 2-iodoarsaperinaphthane, which in consequence is not depicted. The fact that these spectra should be virtually identical indicates clearly that the absorption is only very slightly affected by the nature of the groups joined to the arsenic, and by the valency state of the arsenic itself. This is further confirmed by the fact that the two marked absorption bands in the spectrum of the methiodide are almost certainly the two typical bands of naphthalene, but displaced to wavelengths longer by 10—12 mμ. This point is of considerable importance, because it provides indirect confirmation for Cookson and Mann's suggestion (*loc. cit.*) that the marked absorption band shown by the methiodide of 10-phenyl-9 : 10-dihydroarsanthridine is probably the characteristic diphenyl band similarly shifted by *ca.* 16 mμ. but (in this case) reduced in intensity. As a corollary, this would provide stronger evidence that the two *o*-phenylene groups in the 9 : 10-dihydroarsanthridine ring system undergo some oscillation about the coplanar position.

Considerable further work is required before the complete mechanism of the reaction of phenylarsinebis(magnesium bromide) with organic halides, and also the limitations attending its use, are fully understood. It is noteworthy that we find that, when the arsine–Grignard reagent reacted with either bromoacetonitrile or with bromoacetone diethyl ketal, the only products isolated were arsenobenzene and phenyldibromoarsine. Ethyl bromoacetate gave the same products, but in addition a 5% yield of the required tertiary arsine, phenylbiscarbethoxymethylarsine,

$$PhAs(CH_2{\cdot}CO_2Et)_2;$$

however, since this compound was a liquid it was identified solely as its crystalline palladobromide derivative, dibromodi(phenylbiscarbethoxymethylarsine)palladium, $[(C_{14}H_{19}O_4As)_2PdBr_2]$. Ethylene oxide appeared to react with the Grignard reagent, but no definite products could be isolated.

EXPERIMENTAL.

Phenylarsinebis(magnesium Bromide).—In view of the very ready oxidation of phenylarsine it was always weighed first and the amounts of the other reagents then accordingly adjusted. The technique involved, with typical weights of reagents employed, is described now and applies to all subsequent experiments. A stoppered nitrogen-filled dropping-funnel was weighed, and the phenylarsine (11·1 g.), which had been stored under carbon dioxide, was transferred to the funnel which was again weighed. The transference was most conveniently performed by forcing the arsine by nitrogen pressure up into a vertical nitrogen-filled pipette, the tip of which was then inserted deeply into the funnel before the arsine was released. Under these conditions very little oxidation occurred. For large-scale work, however, the arsine was syphoned directly from the storage vessel to the funnel by nitrogen pressure. Dry benzene (70 c.c.) was then added. Meanwhile a Grignard reagent was prepared by the action of bromobenzene (24·8 g., 2·2 mols.) in ether (45 c.c.) on magnesium (4 g., 2·3 atoms) under ether (7 c.c.). The Grignard reagent was boiled under reflux for 15 minutes and then cooled, and the air displaced by nitrogen. The reagent was then chilled in ice-water and gently stirred whilst the arsine–benzene mixture was added during 10—15 minutes, heat being evolved during the reaction. The formation of the arsine–Grignard reagent was completed by 30 minutes' boiling under reflux and then cooling, nitrogen being passed over the mixture throughout. The solution, which was very sensitive to moisture and air, was quite clear but dark in colour. The second reagent was added at this stage. The use of bromobenzene in the formation of the arsine–Grignard reagent always produced a small quantity of diphenyl. If the latter proved difficult to separate from any of the final products, ethyl bromide was used in place of the bromobenzene.

2-*Phenyl*iso*arsindoline* (II).—(i) A solution of *o*-xylylene dibromide (23·6 g., 1 mol.) in benzene (100 c.c.) was added to the stirred solution of the arsine-Grignard reagent, prepared from phenylarsine (15·3 g., 1 mol.), at such a rate that no appreciable rise in temperature occurred. The complete mixture was then boiled under reflux for 90 minutes, during which fine white crystals separated, and was then cooled in ice-water, whereupon much of the crystalline material redissolved. The solution was then hydrolysed by saturated aqueous ammonium chloride solution, and the pale yellow organic layer was collected, dried, filtered, and distilled under a carbon dioxide atmosphere throughout. The following fractions were collected at 0·15 mm.: (*a*) b. p. 60—110°, unchanged dibromide (1·8 g.); (*b*) b. p. 110—150°, crude *iso*arsindoline (11·5 g.); (*c*) b. p. 150—175°, also crude *iso*arsindoline (6·3 g.). For characterisation and purification, fractions (*b*) and (*c*) were oxidised to the hydroxynitrate, which was then recrystallised from alcohol (cf. Lyon and Mann, *loc. cit.*) and its identity confirmed by analysis and mixed m.p.s. The yields of the pure salt from (*b*) and (*c*) were 11·4 and 3·9 g., respectively. With allowance for the recovered bromide, the yield of crude *iso*arsindoline is therefore 84% and that of the pure hydroxynitrate is 55·5%.

(ii) The previous experiment was repeated, using however the Grignard reagent from phenylarsine (5·35 g., 1 mol.), and *o*-xylylene dichloride (6 g., 1 mol.). The organic layer was again collected, dried, and filtered, and the solvent then removed. The cold residue consisted of a viscous oil containing a small quantity of crystals. These were collected by hand, washed with alcohol, and recrystallised from alcohol; they had m. p. 181—182°, changed to 181—185° when mixed with an authentic sample of the hydrocarbon (III) of m. p. 188°. Lack of material prevented further recrystallisation. The viscous liquid, when distilled at 0·1 mm., gave the fractions: (*a*) b. p. 70—110° (mainly 75—80°), 1·15 g.; (*b*) b. p. 110—133° (mainly 129—133°), 3·45 g.; (*c*) b. p. 133—145°, 1·15 g. The b. p. and halogen content of fraction (*a*) indicated that it was phenyldichloroarsine. This was confirmed by boiling a sample with an alcoholic solution of piperidine *N*-pentamethylenedithiocarbamate, whereby phenylarsinebis-(*N*-pentamethylenedithiourethane) was deposited, m. p. (after purification) 175—176°, unchanged by admixture with an authentic sample. Fraction (*a*) represents 15% of the phenylarsine taken. Fraction (*b*) was almost pure phenyl*iso*arsindoline (40% yield), whilst (*c*) was less pure material. The two fractions when united and oxidised gave the pure hydroxynitrate, m. p. 148° (alone and mixed) (2·35 g., 20%).

2-*Phenyl*-1 : 2 : 3 : 4-*tetrahydro*iso*arsinoline* (V).—(i) A solution of the dibromide (IV) (8·13 g., 1 mol.) in benzene (40 c.c.) was added to the Grignard reagent prepared from phenylarsine (4·5 g., 1 mol.) and initially at 10°. Heat was evolved during the addition, and the complete mixture was boiled under reflux for 90 minutes, and then cooled and hydrolysed as usual. The organic layer, when distilled at 0·3 mm., gave two main fractions: (*a*) b. p. 73—77° (1·5 g.); (*b*) 140—145° (4·7 g.). Fraction (*a*) contained bromine and was identified as the bromohydrocarbon (VI) by treatment with hot alcoholic piperidine *N*-pentamethylenedithiocarbamate, which gave S-2-o-*tolylethyl*-N-*pentamethylenedithiourethane* as colourless crystals, m. p. 99·5—101°, from alcohol (Found: C, 64·5; H, 7·2; N, 4·8. $C_{15}H_{21}NS_2$ requires C, 64·45; H, 7·6; N, 5·0%). An authentic sample of *o*-2-bromoethyltoluene, prepared by the method of Kipping and Wild (*J.*, 1940, 1239) gave the dithiourethane, m. p. 99—100°, unchanged by admixture with the previous sample. Fraction (*b*) consisted of the crude *iso*arsinoline (60%), and was identified by oxidation to the corresponding hydroxynitrate, which after purification had m. p. 146—147° (mixed and unmixed) (Found: C, 51·4; H, 4·4. Calc. for $C_{15}H_{16}O_4NAs$: C, 51·6; H, 4·6%) (3·8 g., 38%).

Repetition of this experiment using an excess of phenylarsine, *i.e.*, the dibromide (14·6 g.) and phenylarsine (9 g., 1·1 mol.), gave arsenobenzene (1·4 g.). The organic layer again furnished fractions (*a*) (2·6 g.) containing the bromohydrocarbon (VI) and (*b*) containing the crude *iso*arsinoline, b. p. 140—150/0·2 mm. (10·2 g., 72%). On redistillation, (*b*) gave the almost pure *iso*arsinoline, b. p. 127—132°/0·1 mm. (7·7 g., 54%).

(ii) A solution of the dibromide (7·05 g.) in benzene (30 c.c.) was added rapidly to a solution of the Grignard reagent prepared from phenylarsine (3·9 g., 1 mol.) and maintained at 70°. Arsenobenzene (0·75 g.) was obtained, and the *iso*arsinoline gave the purified hydroxynitrate (1·7 g., 25%).

(iii) *By decomposition of the arsonium salt.* A mixture of the dibromide (IV) (6·8 g., 1 mol.) and phenyldimethylarsine (4·45 g., 1 mol.), on gentle heating, rapidly formed a glassy mass of the arsonium salt, which was then slowly heated under reflux to 180—200°/17 mm. during 5½ hours. At the higher temperatures, a liquid refluxed in the condenser and a solid separated in the flask. The total product was then distilled at 0·2 mm. and three fractions were collected arbitrarily since no sharp separation was possible: (*a*) b. p. 90—100°, (*b*) b. p. 100—135°, (*c*) b. p. 135—150°. A portion of fraction (*a*) which contained bromine, when oxidised with nitric acid, furnished phenylmethylarsine dihydroxynitrate, $PhMeAs(OH)_2\cdot NO_3$, which after crystallisation from alcohol and then from dilute nitric acid gave colourless crystals, m. p. 146° (Found: C, 32·6; H, 3·4; N, 5·4. Calc. for $C_7H_{10}O_5NAs$: C, 31·9; H, 3·8; N, 5·3%). Burrows (*J. Proc. Roy. Soc. New South Wales*, 1935, **68**, 72) gives m. p. 151°. There is little doubt therefore that fraction (*a*) contained crude phenylmethylbromoarsine, although there was insufficient hydroxynitrate for complete purification.

The addition of ether (or benzene) to the remainder of fraction (*a*) and to fractions (*b*) and (*c*) after exposure to damp air precipitated phenyldimethylarsine hydroxybromide, $PhMe_2As(OH)Br$, which when collected and purified by careful precipitation from alcoholic solution by ethyl acetate formed colourless crystals, m. p. 152—153° (Found: C, 34·8; H, 4·4. Calc. for $C_8H_{12}OBrAs$: C, 34·4; H, 4·3%). This compound was converted into the corresponding hydroxypicrate, m. p. 130—131° after recrystallisation from alcohol (Found: C, 39·6; H, 3·7; N, 9·85. Calc. for $C_{14}H_{14}O_8N_3As$: C, 39·3; H, 3·3; N, 9·8%). Steinkopf and Schwen (*Ber.*, 1021, **54**, 2791) give m. p. 162° and 132° respectively for these compounds.

The ether-soluble portions of fractions (*b*) and (*c*) were concentrated and oxidised, 2-phenyl-1 : 2 : 3 : 4-tetrahydro*iso*arsinoline hydroxynitrate, m. p. 140—141°, being obtained after recrystallisation from alcohol and dilute nitric acid. Its identity was confirmed by mixed m. p., but the yield was very low.

Repetition of this experiment gave an 8% yield of the hydroxynitrate, and it is obvious that the arsonium salt decomposition method, which is so valuable in the *iso*arsindoline series, is not a practicable preparative method in the *iso*arsinoline series.

2-*Iodo*-1 : 2 : 3 : 4-*tetrahydro*iso*arsinoline*.—A mixture of the 2-phenylarsine (V) (1·65 g.) and hydriodic acid of constant b. p. (85 c.c.) was boiled under reflux in a carbon dioxide atmosphere for 2 hours. The cold product was diluted with water and extracted with ether. Removal of the solvent left the 2-iodo-arsine as a red oil which did not solidify. In view of the small quantity available, it was identified by reaction with piperidine *N*-pentamethylenedithiocarbamate in hot alcohol; the solid derivative, when thrice recrystallised from alcohol and once from *cyclo*hexane, gave N-*pentamethylene*-S-2-(1 : 2 : 3 : 4-*tetrahydro*iso*arsinoline*)*dithiourethane* as colourless crystals, m. p. 121·5—122° (Found : C, 51·55; H, 5·5; N, 4·0. $C_{15}H_{20}NS_2As$ requires C, 51·0; H, 5·7; N, 4·0%).

1 : 8-*Bishydroxymethylnaphthalene* (VII).—Lithium aluminium hydride (9 g., 2·7 equivs.) and ether (280 c.c.) were stirred together in a dry apparatus for several hours to obtain complete dissolution. Powdered methyl naphthalate (21·8 g., 1 equiv.) was placed in an extraction thimble below a reflux condenser fitted to the reaction flask, and the ether boiled gently so that the ester was transferred to the solution during *ca.* 75 minutes. The mixture was cooled to 0°, hydrolysed with 10% sulphuric acid, and filtered. The *diol* (VII), being almost insoluble in ether, was thus collected, and recrystallised from methyl alcohol, forming colourless crystals, m. p. 152—154° (Found : C, 76·5; H, 6·3. $C_{12}H_{12}O_2$ requires C, 76·5; H, 6·4%) (12·1 g., 72%). The above large excess of the hydride was found to be essential in order to avoid contamination of the diol with unchanged ester.

1 : 8-*Bisbromomethylnaphthalene* (VIII).—A mixture of the powdered diol (VII) (13·6 g.) and hot hydrobromic acid of constant b.p. (50 c.c.) was shaken for 45 minutes and then cooled. The solid material which separated was collected and recrystallised from benzene, the *dibromo*-compound (VIII) being thus obtained as large colourless crystals, m. p. 128—129·5° (Found : C, 46·1; H, 3·4. $C_{12}H_{10}Br_2$ requires C, 45·9; H, 3·2%) (5·6 g., 25%).

The benzene mother-liquor was evaporated and the residue, when recrystallised from light petroleum (b. p. 60—80°), furnished well-formed compact crystals of 2-oxaperinaphthane (IX), m. p. 80—81° (Found : C, 84·7; H, 5·8. Calc. for $C_{12}H_{20}O$: C, 84·7; H, 5·9%) (2·8 g., 23%). No ready method for the conversion of this ether into the dibromide (VIII) was found, and the original conversion of the diol (VII) into the dibromide was less satisfactory when acetic acid was used as a solvent.

2-*Phenylarsaperinaphthane* (X; R = Ph).—A solution of the dibromide (VIII) (6 g.) in warm benzene (35 c.c.) was added to an agitated solution of the Grignard reagent prepared as before from phenylarsine (3·1 g.) and maintained at 0°. The complete mixture was boiled under reflux for 1 hour, cooled, and hydrolysed with 10% sulphuric acid. The organic layer was separated from a small quantity of arsenobenzene and dried (Na_2SO_4), and the solvent removed. The pale brown residual gum (3·5 g., 60%) did not boil below 180°/0·1 mm. and could not be obtained crystalline.

When a portion was dissolved in warm methyl iodide, the *methiodide* rapidly crystallised. It was recrystallised from alcohol containing a small proportion of acetone, and separated as a *mono-alcoholate*, m. p. 196—199° in a pre-heated bath (Found : C, 52·95; H, 4·75. $C_{19}H_{18}IAs,C_2H_6O$ requires C, 52·7; H, 5·0%). When this substance was heated at 100°/0·4 mm. for 10 hours, the solvent-free salt, of unchanged m. p., was obtained (Found : C, 51·15; H, 4·0. $C_{19}H_{18}IAs$ requires C, 50·95; H, 4·0%).

An acetone solution of the arsine, when treated with an aqueous-alcoholic solution of potassium palladochloride, readily furnished *dichlorodi-(2-phenylarsaperinaphthane)palladium* as an orange powder insoluble in all common solvents. It was washed with water, acetone, and hot benzene in turn, and was unaffected by being heated to 240° (Found : C, 54·4; H, 4·1. $C_{36}H_{30}Cl_2As_2Pd$ requires C, 54·7; H, 3·8%).

2-*Iodoarsaperinaphthane* (X; R = I).—A mixture of the 2-phenyl derivative and hydriodic acid of constant b. p. was heated at 125° for 90 minutes in a carbon dioxide atmosphere. The cold partly-solid product was washed with water, and then extracted with boiling alcohol, which on cooling deposited pale yellow crystals of the 2-*iodo-arsine*, m. p. 117—119° (preliminary softening) (Found : C, 40·45; H, 3·1. $C_{12}H_{10}IAs$ requires C, 40·5; H, 2·8%).

Reaction with Bromoacetonitrile.—A solution of bromoacetonitrile (16·5 g., 1·9 mols.) in benzene (45 c.c.) was added in the usual way to an ice-cold solution of the Grignard reagent prepared from phenylarsine (11·1 g.), much heat being initially evolved. The complete mixture was boiled under reflux for 3 hours, a reddish-brown gummy material being precipitated. Hydrolysis of the cold product, performed as usual with 10% sulphuric acid, did not redissolve the precipitate. The organic layer was worked up as usual, and after removal of the solvent the residue was extracted with acetone, leaving a residue of arsenobenzene, m. p. 213—216° (1·45 g., 13%). The acetone solution, when carefully distilled at 0·5 mm., gave a number of indefinite fractions, all of which were liquid, contained bromine, and did not crystallise or apparently form a methiodide. The presence of phenyldibromoarsine in some of the fractions was proved by conversion into the bisdithiourethane, m. p. 173—174° (mixed and unmixed).

Reaction with Bromoacetone Diethyl Ketal.—This experiment was performed as the previous one, using the ketal (29·8 g., 2 mols.) and phenylarsine (10·9 g.). The acetone extraction afforded arsenobenzene, m. p. 214—215° (6·3 g., 59%). Distillation of the organic liquid again afforded indefinite fractions, one of which was crude phenyldibromoarsine (6·3 g., 28·5%). The latter was identified (*a*) by cautious treatment with a small proportion of piperidine *N*-pentamethylenedithiocarbamate, whereby *phenylbromoarsine*-N-*pentamethylenedithiourethane*, colourless crystals, m. p. 125—127°, from ethyl acetate (Found : C, 37·25; H, 4·05; N, 3·6. $C_{12}H_{15}NBrS_2As$ requires C, 36·75; H, 3·8; N, 3·6%), was obtained, (*b*) by treatment with a larger proportion of the reagent, whereby the usual bisdithiourethane, m. p. 173—174°, was obtained. The relation between the two products was confirmed by the ready conversion of the first into the second on treatment with the dithiocarbamate.

Reaction with Ethyl Bromoacetate.—The usual method was employed, using ethyl bromoacetate (19·7 g., 2 mols.) and phenylarsine (9·55 g.). Arsenobenzene (3·1 g., 33%) was isolated, and distillation of the liquid organic residue gave the crude arsine contaminated with phenyldibromoarsine, which could not be readily separated by distillation. The crude redistilled arsine, b. p. 137—144°/0·5 mm., when suitably treated with potassium palladobromide, gave *dibromodiphenyl(biscarbethoxymethylarsine)palladium*, orange crystals, m. p. 110—111°, from methyl alcohol (Found : C, 36·85; H, 4·2; Pd, 11·9. $C_{28}H_{38}O_8Br_2As_2Pd$ requires C, 36·6; H, 4·1; Pd, 11·6%). The phenyldibromoarsine was identified in the usual way.

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