783. *The Preparation and Quaternisation of* o-*Dimethylaminophenyldiethylphosphine and an Analogous Arsine.*

By FREDERICK G. MANN and H. R. WATSON.

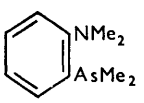
The preparation of this amine-phosphine, which was required for a study of its co-ordinated metallic derivatives, is described.

The tertiary phosphine group can be readily quaternised with alkyl halides, but this process deactivates the tertiary amine group. Consequently alkylene dibromides, such as ethylene, trimethylene, and *o*-xylylene dibromide, react by quaternisation with two molecules of the amine-phosphine.

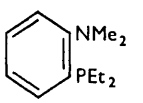
The analogous *o*-dimethylaminophenyldimethylarsine behaves similarly. It reacts also with methanolic *o*-xylylene dibromide under more vigorous conditions to give *o*-dimethylaminophenyl-2-methoxymethylbenzyldimethylarsonium bromide.

PREPARATION of *o*-dimethylaminophenyldimethylarsine (I) has recently been recorded by Mann and Stewart.[1] The analogous *o*-dimethylaminophenyldiethylphosphine (II) was also required for a study of the co-ordination properties of the amine-phosphine with metallic salts, and particularly the ability of the tertiary amine group to co-operate with the phosphine group to form a chelated ring (see following paper [2]).

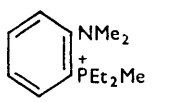
The amine-phosphine (II) is readily prepared by the action of chlorodiethylphosphine, Et_2PCl, on the Grignard reagent prepared from *o*-bromo-*NN*-dimethylaniline. The quaternary salts obtained from this amine-phosphine, and from the amine-arsine (I), warrant brief discussion.



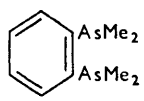
(I)



(II)



(III)



(IV)

The amine-phosphine (II) reacts readily with methanolic methyl iodide to give the methylphosphonium iodide (III; X = I), and even under forcing conditions quaternisation of the tertiary amine group was not achieved. This was not unexpected, for the positive pole on the phosphorus atom would tend largely to deactivate the amine group. This deactivation is clearly shown by the fact that the ethanolic solution of the iodide when added to an ethanolic solution either of sodium picrate or of sodium picrate and picric acid deposited the phosphonium picrate (III; X = O·$C_6H_2O_6N_3$), the free amine group being unaffected by the picric acid.

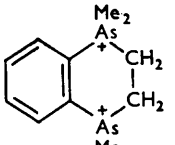
This deactivation recalls the behaviour of the analogous *o*-phenylenebis(dimethylarsine) [3] (IV), which normally forms only a monometho-bromide and -iodide, and vigorous forcing conditions are required to form the dimetho-bromide and -iodide. In contrast to this behaviour, the diarsine (IV), when heated with ethylene dibromide, readily undergoes diquaternisation with cyclisation to form the ethylenetetramethyl-*o*-phenylenediarsonium dibromide (V), and with trimethylene dibromide forms the homologous dibromide.

When however the amine-phosphine (II) was similarly heated with one equivalent of ethylene dibromide, under a variety of conditions, the sole product isolated was *s*-ethylenebis-(*o*-dimethylaminophenyldiethylphosphonium) dibromide (VI; R = ·$[CH_2]_2$·). The deactivation of the amine groups in this compound also was demonstrated by addition of the aqueous dibromide to an aqueous solution of sodium picrate and picric acid, whereby

[1] Mann and Stewart, *J.*, 1955, 1269.
[2] Mann and Watson, *J.*, 1957, following paper.
[3] Mann and Baker, *J.*, 1952, 4142.

only the dipicrate (as VI) was precipitated. The amine-phosphine reacted similarly with trimethylene dibromide and with *o*-xylylene dibromide to form the dibromides (VI; R = $\cdot[CH_2]_3\cdot$ and $\cdot CH_2\cdot C_6H_4\cdot CH_2\cdot$, respectively).

This reaction of the amine-phosphine (II) with ethylene dibromide is analogous to that shown by hexahydro-1 : 4-diphenyl-1 : 4-azaphosphine [4] and by hexahydro-1 : 4-diphenyl-1 : 4-azarsine,[5] which by quaternisation with the dibromide become linked solely through two phosphorus and two arsenic atoms respectively.



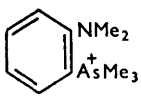
(V)

$[Me_2N\cdot C_6H_4\cdot \overset{+}{P}Et_2-R-\overset{+}{P}Et_2\cdot C_6H_4\cdot NMe_2]\,2Br^-$

(VI)

There is no doubt that, in all these monoquaternary salts of di-tertiary amine-phosphines and amine-arsines, the quaternisation has occurred on the phosphine or arsine group and not upon the amine group, for Davies and Lewis [6] have adduced both qualitative and quantitative evidence that, under comparable conditions, the rate of reaction of a tertiary phosphine with an alkyl halide is greater than that of the corresponding arsine, which in turn is greater than that of the corresponding amine.

The amine-arsine (I) behaves similarly to the amine-phosphine (II). Mann and Stewart [1] prepared the methiodide (VII; X = I) and the methopicrate (VII; X = $C_6H_2O_7N_3$). We find that forcing conditions do not give a dimethiodide, and that ethylene, trimethylene, and *o*-xylylene dibromide react readily to give the crystalline dibromides (VIII; R = $\cdot[CH_2]_2\cdot$, $\cdot[CH_2]_3\cdot$, and $\cdot CH_2\cdot C_6H_4\cdot CH_2\cdot$ respectively).



(VII)

$[Me_2N\cdot C_6H_4\cdot \overset{+}{As}Me_2-R-\overset{+}{As}Me_2\cdot C_6H_4\cdot NMe_2]\,2Br$

(VIII)

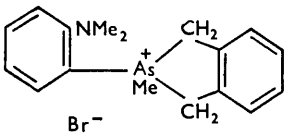
The reaction with *o*-xylylene dibromide is of particular interest. The dibromide (VIII; R = $\cdot CH_2\cdot C_6H_4\cdot CH_2\cdot$) was best obtained by boiling a methanolic solution of *o*-xylylene dibromide and the amine-arsine (two molecular equivalents) under reflux for 30 min. The dibromide, when heated in a vacuum, underwent decomposition with the regeneration of the amine-arsine in high yield. When however an equimolecular mixture of *o*-xylylene dibromide and the amine-arsine in anhydrous methanol was heated at 100° for 3 hr., methyl bromide was liberated, with the formation of a highly crystalline quaternary bromide, m. p. 162—163°. The dibromide (VIII; R = $\cdot CH_2\cdot C_6H_4\cdot CH_2\cdot$), when heated with the amine-arsine (one molecular equivalent) under the same conditions, was unaffected, hence the bromide was almost certainly formed by an independent reaction and not as a secondary reaction following the initial formation of the dibromide.

The carbon and nitrogen content of the bromide, m. p. 162—163°, supported by that of the corresponding picrate, perchlorate, and chloroplatinate, indicated initially that it might be 2-*o*-dimethylaminophenyl-2-methyl*iso*arsindolinium bromide (IX). This was not improbable, for the *iso*arsindoline ring is known to be readily formed by the thermal decomposition of quaternary *o*-xylylenearsonium bromides. For example, *o*-xylylenebis-(dimethylphenylarsonium bromide) (X) when heated gives 2-phenyl*iso*arsindoline,[7] and

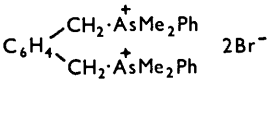
[4] Mann and Millar, *J.*, 1952, 3039.
[5] Beeby and Mann, *J.*, 1951, 886.
[6] Davies and Lewis, *J.*, 1934, 1599.
[7] Lyon, Mann, and G. H. Cookson, *J.*, 1947, 662.

AsAs'-dimethyl-*o*-phenylene-*o*-xylylenediarsine dimethobromide (XI) gives *o*-phenylenebis-(2-*iso*arsindoline).[8]

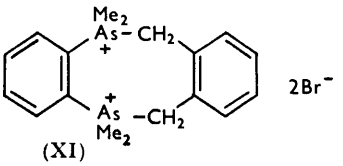
2-Iodo*iso*arsindoline [7] was therefore treated with *o*-dimethylaminophenylmagnesium bromide to give the crystalline 2-*o*-dimethylaminophenyl*iso*arsindoline, which was then converted into the authentic methobromide (IX), which however was not identical with the bromide, m. p. 162—163°. The latter was finally identified as *o*-dimethylaminophenyl-



(IX)

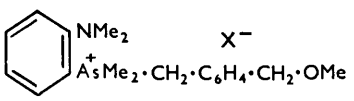


(X)

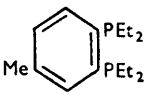


(XI)

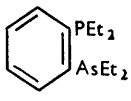
2-methoxymethylbenzyldimethylarsonium bromide (XII; X = Br) by direct comparison of its derivatives with those of the corresponding chloride (XII; X = Cl), which was synthesised unambiguously by quaternisation of the amine-arsine (I) with 2-methoxymethylbenzyl chloride.[9] It is clear therefore that the bromide (XII; X = Br) must have arisen under the vigorous conditions of the initial preparation by monoquaternisation of



(XII)



(XIII)



(XIV)

one molecule of the amine-arsine (I) with one molecule of *o*-xylylene dibromide, the remaining bromomethyl group being then converted by the methanol into a methoxymethyl group.

The synthesis of compounds analogous to (I) and (II) in the nitrogen–phosphorus–arsenic series is now complete, for 4-methyl-*o*-phenylenebis(diethylphosphine) [10] (XIII), *o*-diethylphosphinophenyldiethylarsine [11] (XIV), and *o*-phenylenebis(dimethylarsine) [12] (IV), and certain homologues of (XIV) [11] and (IV),[12,13] have been reported earlier.

Experimental

All compounds were colourless unless otherwise described.

o-*Dimethylaminophenyldiethylphosphine* (II).—A solution of *o*-bromo-*NN*-dimethylaniline (15·8 g.) in ether (55 c.c.) was slowly added to magnesium (2·1 g.) under ether (7 c.c.), in a nitrogen atmosphere. The resulting Grignard solution was boiled under reflux for 45 min., then cooled in ice whilst monochlorodiethylphosphine (9·8 g., 1 mol.) in ether (40 c.c.) was added dropwise with vigorous stirring. A vigorous reaction ensued, with deposition of a viscous yellow oil. The mixture was boiled under reflux for 2 hr., cooled as before, and hydrolysed by 10% aqueous ammonium chloride (50 c.c.). The dried ethereal layer gave the *phosphine* (II) (55%), of unpleasant odour, b. p. 132—135°/16 mm. (Found: N, 6·8. $C_{12}H_{20}NP$ requires N, 6·7%).

Addition of methyl iodide, followed by ether, to a methanolic solution of the phosphine deposited the *methiodide* (III; X = I), m. p. 128—130° after crystallisation from methanol–ether (Found: C, 44·3; H, 6·4. $C_{13}H_{23}NIP$ requires C, 44·4; H, 6·5%). The same product was obtained when a methanolic solution of the phosphine and methyl iodide was boiled under

[8] Emrys R. H. Jones and Mann, *J.*, 1955, 405.
[9] Mann and Stewart, *J.*, 1954, 2819.
[10] Hart and Mann, *J.*, 1957, preceding paper.
[11] Emrys R. H. Jones and Mann, *J.*, 1955, 4472.
[12] Chatt and Mann, *J.*, 1939, 610.
[13] Cochran, Hart, and Mann, *J.*, 1957, 2816.

reflux for 5 hr. Addition of the methiodide to an excess of sodium picrate, both in aqueous solution, gave the yellow *methopicrate* (III; X = O·$C_6H_2O_6N_3$), m. p. 111°, from water (Found: N, 12·45. $C_{19}H_{25}O_7N_4P$ requires N, 12·4%). Repetition of this experiment, with sodium picrate and picric acid, gave the same methopicrate, m. p. 110° (unrecrystallised), unchanged on admixture with the previous sample.

Quaternisation of the Amine-phosphine (II) *with Alkylene Dibromides.*—(*A*) A mixture of the amine-phosphine (0·42 g.), ethylene dibromide (0·38 g., 1 mol.), and methanol (5 c.c.) was heated in a sealed tube at 100° for 4 hr. Evaporation under reduced pressure at room temperature left a gum, which when recrystallised from acetone–methanol, gave the *dibromide* (VI; R = ·$[CH_2]_2$·), m. p. 221—224° (Found: C, 51·6; H, 7·3; N, 4·6. $C_{26}H_{44}N_2Br_2P_2$ requires C, 51·5; H, 7·3; N, 4·6%).

The dibromide in methanol when added to a methanolic solution of sodium picrate, or of sodium picrate and picric acid, gave the *dipicrate* (as VI; R = ·$[CH_2]_2$·), yellow needles, m. p. 183—184°, unchanged by crystallisation (Found: C, 50·4; H, 5·2; N, 12·5. $C_{38}H_{48}O_{14}N_8P_2$ requires C, 50·5; H, 5·3; N, 12·4%).

(*B*) A mixture of the phosphine (0·42 g.), trimethylene dibromide (0·40 g., 1 mol.), and methanol (6 c.c.), when treated as in (*A*), gave a gum which was vigorously stirred with ether, and then crystallised from acetone at −75°, but the *s*-trimethylenebis-(*o*-dimethylaminophenyldiethylphosphonium) dibromide (VI; R = ·$[CH_2]_3$·) remained extremely deliquescent even after several recrystallisations. It was therefore added to potassium iodide, each in concentrated aqueous solution, whereby the *di-iodide monohydrate* separated as needles, m. p. 186° (Found: C, 44·7; H, 6·6. $C_{27}H_{46}N_2I_2P_2,H_2O$ requires C, 44·3; H, 6·6%). The dibromide gave a *dipicrate*, yellow plates, m. p. 158—159° from methanol (Found: C, 51·4; H, 5·1; N, 12·1. $C_{39}H_{50}O_{14}N_8P_2$ requires C, 51·2; H, 5·1; N, 12·2%).

(*C*) The phosphine (0·42 g.), *o*-xylylene dibromide (0·53 g., 1 mol.), and methanol (4 c.c.), when treated as in (*A*), gave a gum which was stirred with ether and then treated with boiling acetone, in which it was only sparingly soluble. The gum was thus converted into minute hygroscopic crystals of s-o-*xylylenebis*-(o-*dimethylaminophenyldiethylphosphonium*) *dibromide* (VI; R = ·CH_2·C_6H_4·CH_2·), m. p. 223—224° (Found: C, 55·9; H, 6·9. $C_{32}H_{48}N_2Br_2P_2$ requires C, 56·3; H, 7·0%). It gave a yellow *dipicrate*, m. p. 141° (from methanol) (Found: C, 53·85; H, 5·7; N, 11·6. $C_{44}H_{52}O_{14}N_8P_2$ requires C, 54·1; H, 5·3; N, 11·45%).

Quaternisation of the Amine-arsine (I) *with Alkylene Dibromides.*—(*D*) Condensation of the arsine with ethylene dibromide, performed as in (*A*), furnished the crystalline s-*ethylenebis*-(o-*dimethylaminophenyldimethylarsonium*) *dibromide* (VIII; R = ·$[CH_2]_2$·), m. p. 191—192° (from acetone containing a trace of methanol) (Found: C, 41·3; H, 5·9; N, 4·1. $C_{22}H_{36}N_2Br_2As_2$ requires C, 41·4; H, 5·65; N, 4·4%). It gave a *dipicrate*, deep mustard-yellow needles, m. p. 150° (from ethanol) (Found: C, 43·5; H, 4·5; N, 11·9. $C_{34}H_{40}O_{14}N_8As_2$ requires C, 43·7; H, 4·3; N, 12·0%).

(*E*) The arsine, condensed with trimethylene dibromide as in (*B*), gave a gum, which was initially obtained crystalline by slow addition of ethyl acetate to a solution of the gum in acetone containing a trace of methanol. The crystals then recrystallised directly from the acetone–methanol, affording the *dibromide* (VIII; R = ·$[CH_2]_3$·), m. p. 209—210° (decomp.) (Found: C, 42·0; H, 6·2; N, 4·2. $C_{23}H_{38}N_2Br_2As_2$ requires C, 42·3; H, 5·8; N, 4·3%). It gave a *dipicrate*, m. p. 113° (decomp.) (Found: C, 44·2; H, 4·8; N, 12·0. $C_{35}H_{42}O_{14}N_8As_2$ requires C, 44·3; H, 4·4; N, 11·8%).

(*F*) (i) A solution of the amine-arsine (0·75 g.) and *o*-xylylene dibromide (0·43 g., 0·5 mol.) in methanol (10 c.c.) was boiled under reflux for 30 min., and then evaporated to dryness at 20 mm. The crystalline residue, when recrystallised from acetone–methanol, gave s-o-*xylylenebis*-(o-*dimethylaminophenyldimethylarsonium*) *dibromide* (VIII; R = ·CH_2·C_6H_4·CH_2·), m. p. 203° (decomp.) (Found: C, 46·8; H, 5·9; N, 4·0. $C_{28}H_{40}N_2Br_2As_2$ requires C, 47·1; H, 5·6; N, 3·9%). It gave a *dipicrate*, brilliant yellow needles, m. p. 166° (from ethanol) (Found: C, 47·3; H, 4·9; N, 11·0. $C_{40}H_{44}O_{14}N_8As_2$ requires C, 47·5; H, 4·4; N, 11·0%).

A mixture of this dibromide (1·0 g.), *o*-xylylene dibromide (0·37 g., 1 mol.), and methanol (2 c.c.) was heated in a sealed tube at 100° for 3 hr. The product yielded solely the unchanged arsonium dibromide.

The dibromide (1·4 g.), when heated at 14 mm., decomposed smoothly, giving a minute fraction, b. p. 87°/14 mm., and a much larger fraction, b. p. 120—142°/14 mm., having a strong odour of the amine-arsine (I). The quantity of this fraction precluded useful refractionation,

and for identification it was therefore heated with methanolic methyl bromide at 45° for 3 hr. The product was evaporated in a desiccator to a semi-solid residue, an ethanolic solution of which, when chilled and cautiously diluted with ether, deposited the crystalline *methobromide* (VII; X = Br), m. p. 260—261° (effervescence) after recrystallisation from acetone containing a trace of methanol (Found: C, 40·9; H, 5·45; N, 4·5. $C_{11}H_{19}NBrAs$ requires C, 40·8; H, 5·9; N, 4·4%). It gave the yellow methopicrate (VII; X = O·$C_6H_2O_6N_3$), m. p. 180—181° (from ethanol) (Found: N, 12·0. Calc. for $C_{17}H_{21}O_7N_4As$: N, 12·0%). Mann and Stewart [1] give m. p. 179—181°.

(ii) A mixture of the arsine (I) (0·45 g.), *o*-xylylene dibromide (0·53 g., 1 mol.), and anhydrous methanol (6 c.c.) was heated in a sealed tube at 100° for 3 hr. The cold product when gently warmed evolved methyl bromide. It was then evaporated to dryness at 20 mm. and the crystalline residue, when recrystallised from acetone–methanol, afforded o-*dimethylaminophenyl*-2-*methoxymethylbenzyldimethylarsonium bromide* (XII; X = Br), m. p. 162—163° (Found: C, 51·6; H, 6·6; N, 3·1; Br, 18·55. $C_{19}H_{27}ONBrAs$ requires C, 51·8; H, 6·1; N, 3·2; Br, 18·2%).

The bromide in aqueous solution gave a yellow *picrate* (XII; X = O·$C_6H_2O_6N_3$), m. p. 104° (from methanol–ether) (Found: C, 51·3; H, 5·1; N, 9·65. $C_{25}H_{27}O_8N_4As$ requires C, 51·0; N, 4·9; N, 9·5%). The bromide solution, when added to an excess of 30% aqueous perchloric acid, deposited the *perchlorate hemihydrate* (XII; X = ClO_4), needles, m. p. 159—160°, unchanged by crystallisation from 5% perchloric acid (Found: C, 48·9; H, 6·0. $C_{19}H_{27}O_5NClAs,\frac{1}{2}H_2O$ requires C, 48·7; H, 6·0%). The aqueous bromide, when added to an excess of chloroplatinic acid, gave the crystalline *chloroplatinate monohydrate*, m. p. 192—193° (decomp.) (Found: C, 39·7; H, 4·95. $C_{38}H_{54}O_2N_2Cl_6As_2Pt,H_2O$ requires C, 39·8; H, 4·9%).

Direct Synthesis of the Chloride (XII; X = Cl).—A solution of the amine-arsine (I) (0·251 g.) and 2-methoxymethylbenzyl chloride (0·190 g., 1 mol.) in methanol (7 c.c.) was heated under reflux for 2 hr., and the solvent evaporated. The residue, when triturated with ether, gave the crystalline hygroscopic *chloride*, m. p. 140—142° after crystallisation from acetone–ether (Found: C, 57·4; H, 7·1. $C_{19}H_{27}ONClAs$ requires C, 57·65; H, 6·8%).

The chloride, when added to an excess of sodium picrate, both in aqueous solution, deposited the oily picrate which slowly solidified when the mixture was shaken: recrystallisation from ethanol gave the pure picrate, m. p. 103—104°. The perchlorate, also prepared from the chloride, formed colourless crystals, m. p. 159—160°, from water (Found: C, 49·5; H, 5·7. $C_{19}H_{27}O_5NClAs$ requires C, 49·6; H, 5·7%). The m. p.s of the picrate and perchlorate were unaffected by admixture with the corresponding salts prepared by the *o*-xylylene dibromide method described above.

2-o-*Dimethylaminophenyl*iso*arsindoline*.—2-Iodo*iso*arsindoline (3·4 g.) in benzene (30 c.c.) was added with stirring to a Grignard reagent prepared from *o*-bromodimethylaniline (2·8 g.) and magnesium (0·34 g.) in ether (7 c.c.) under nitrogen. The ether was distilled from the mixture, which was then boiled under reflux for 3 hr., a copious deposit separating. After hydrolysis of the cold mixture with aqueous ammonium chloride, the organic layer was separated, washed with water, dried (Na_2SO_4), and distilled, affording the iso*arsindoline* (2·25 g., 68%), b. p. 151—154°/0·5 mm., m. p. 75° (from methanol) (Found: C, 63·9; H, 6·0; N, 4·8. $C_{16}H_{18}NAs$ requires C, 64·2; H, 6·0; N, 4·7%).

A mixture of the *iso*arsindoline (0·5 g.), methyl bromide (1 g.), and methanol (4 c.c.) was heated in a sealed tube at 75° for 3 hr. The solution was evaporated, and the residual gum, on trituration with ether, gave the crystalline *methobromide hemihydrate* (IX), m. p. 189—190° (effervescence) (Found: C, 50·35; H, 5·85. $C_{17}H_{21}NBrAs,\frac{1}{2}H_2O$ requires C, 50·6; H, 5·35%). An aqueous solution of the bromide, when added to 5% aqueous perchloric acid, deposited the *perchlorate* (as IX), colourless needles, m. p. 156° (from water) (Found: C, 49·1; H, 5·5. $C_{17}H_{21}O_4NClAs$ requires C, 49·3; 5·1%). A mixture of this salt and of (XII; X = ClO_4) had m. p. 137—140°.

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