Organometallic Cyclisation Reactions. Part 3.[1] Synthesis of Substituted Arsetans and Arsolans

By **Murray Mickiewicz** and **Stanley Bruce Wild,*** Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, W.A. 6009, Australia

The reductive cyclisation of 3-chloropropyliodo(methyl)arsine and 3-chloropropyliodo(phenyl)arsine with sodium in tetrahydrofuran affords the four-membered alicyclic tertiary arsines 1-methylarsetan and 1-phenylarsetan respectively. The five-membered homologues 1-methyl- and 1-phenyl-arsolan may be prepared similarly from the corresponding 4-chlorobutyliodo-methylarsine and -phenylarsine.

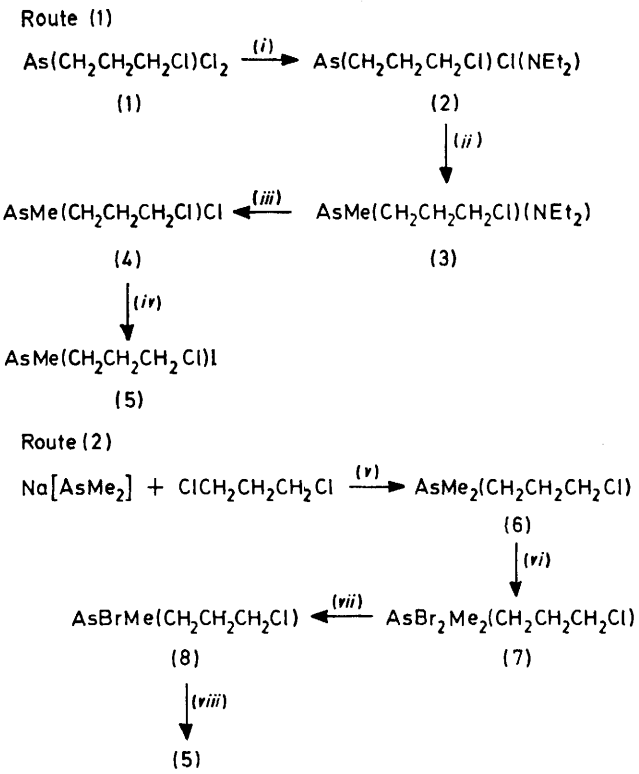
THE reductive-cyclisation reaction is a convenient method of obtaining five- and six-membered organometallic rings containing tertiary arsines and transition-metal atoms.[1] The method is of general application to the formation of metal–carbon bonds when suitably substituted metal complexes form nucleophilic organometallate ions. We report here an extension of this work which has led to the synthesis of four-membered arsenic heterocycles for the first time.

[1] Part 2, M. Mickiewicz, K. P. Wainwright, and S. B. Wild, *J.C.S. Dalton*, 1976, 262.

RESULTS AND DISCUSSION

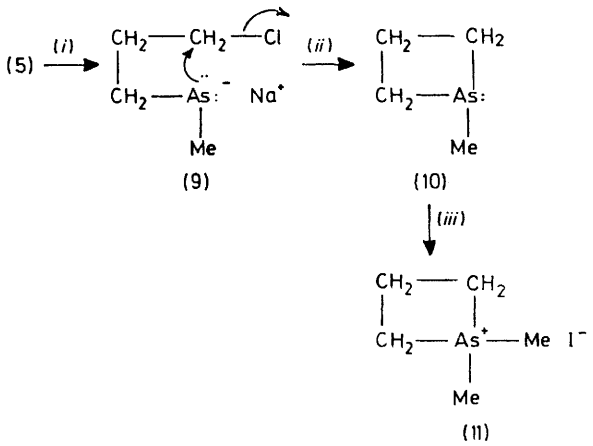
Preparation of 1-*Methylarsetan*, (10), *and* 1-*Phenylarsetan*, (16).—There are two alternative routes to the precursor of (10), 3-chloropropyliodo(methyl)arsine(V),

and these are summarised in Scheme 1. In the second procedure the need for $As[(CH_2)_3Cl]Cl_2$ is eliminated



SCHEME 1 (*i*) $2NEt_2H$, $-[NEt_2H_2]Cl$; (*ii*) MgMeI; (*iii*) HCl(g), $-[NEt_2H_2]Cl$; (*iv*) NaI, $-$NaCl; (*v*) tetrahydrofuran (thf), $-$NaCl; (*vi*) Br_2 in CCl_4; (*vii*) heat, $-$MeBr; (*viii*) NaI, $-$NaBr

and this considerably shortens the time required for the synthesis. The iodoarsine (5) was obtained as a yellow oil, b.p. 40—41 °C (1 mmHg),* which was readily reduced by sodium to the deep yellow anion (9) at room



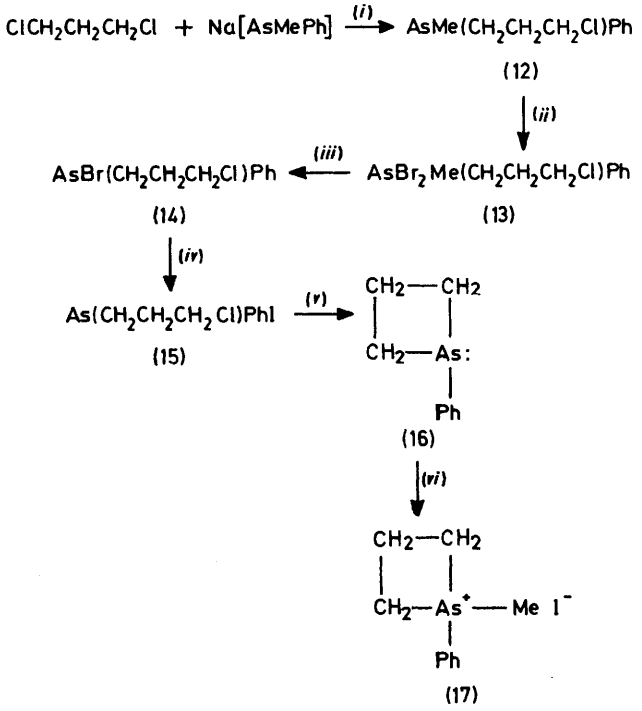
SCHEME 2 (*i*) 2Na in thf, $-$NaI; (*ii*) $-$NaCl; (*iii*) MeI

temperature. However, it was necessary to heat the reaction mixture under reflux for 48 h to obtain a reasonable yield of the cyclisation product (Scheme 2).

* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

1-Methylarsetan is a pale yellow air-sensitive liquid, b.p. 58—64 °C (20 mmHg), which forms 1,1-dimethylarsetanium iodide (11), m.p. 220—222 °C, when dissolved in iodomethane. The ^1H n.m.r. spectrum of (10) consisted of a broad multiplet centred at δ 2.25 p.p.m. (6 H) for the methylenic protons and a sharp singlet at δ 0.90 p.p.m. (3 H) for the $As-CH_3$ resonance. The mass spectrum of (10) showed the presence of a molecular ion at *m/e* 132 which is 20% of the intensity of the base peak at *m/e* 43 ($C_3H_7^+$). A 15% yield of (10) was also obtained from the reaction between Na_2[AsMe] and 1,3-dichloropropane.

The analogue 1-phenylarsetan (16) was obtained similarly from the reductive cyclisation of 3-chloropropyliodo(phenyl)arsine (15) as outlined in Scheme 3



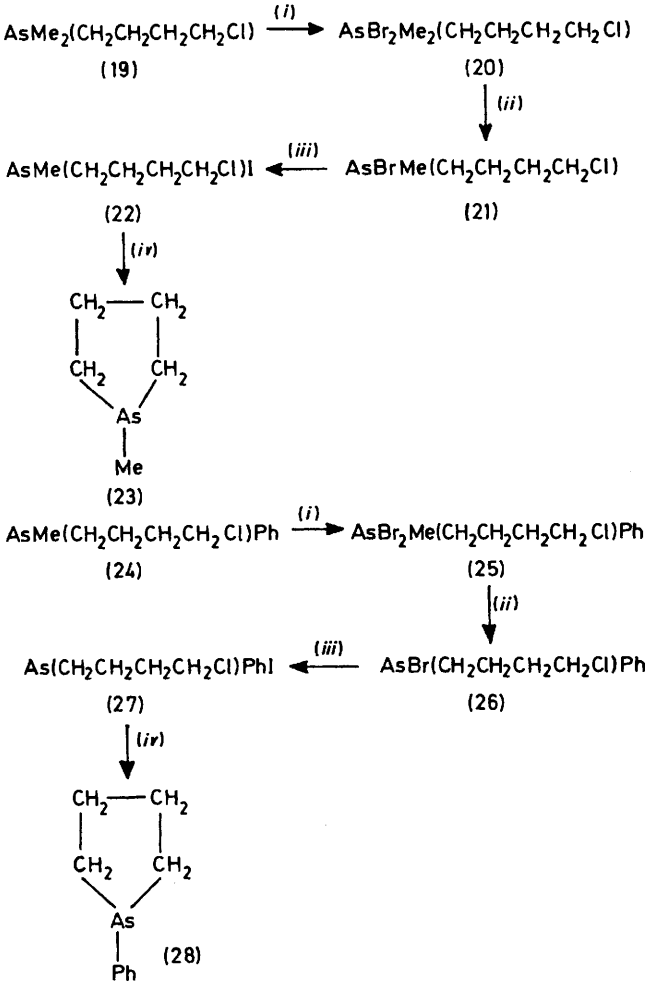
SCHEME 3 (*i*) $-$NaCl; (*ii*) Br_2 in CCl_4; (*iii*) heat, $-$MeBr; (*iv*) NaI in acetone, $-$NaCl; (*v*) 2Na in thf, $-$NaCl,NaI; (*vi*) MeI

Again, even though the anion formed readily, cyclisation was slow and a reaction time of 60 h was required to obtain a 42% yield of the product. The heterocycle (16) distilled as a yellow oil, b.p. 80—82 °C (1 mmHg). The ^1H n.m.r. spectrum of (16) is consistent with cyclisation and the structure proposed. Quaternisation with iodomethane afforded 1-methyl-1-phenylarsetanium iodide (17), m.p. 258—260 °C (decomp.). The mass spectrum of (16) showed the presence of a weak molecular ion at *m/e* 194 (7%) and the base peak occurred at *m/e* 152 (C_6H_5As).

A small quantity (12%) of the ditertiary diarsine 1,3-bis(methylphenylarsino)propane (18), b.p. 140—146 °C (0.5 mmHg), was formed as a side product in the reaction between sodium methylphenylarsenide and

1,3-dichloropropane, although only 1 equivalent of the anion was added. At 90 MHz the ^{1}H n.m.r. spectrum of (18) revealed the presence of its epimeric *meso* and *racemic* diastereoisomers. The two peaks at δ 1.0 and 1.01 p.p.m. (90 MHz) have been assigned to the As–CH_3 resonances of *rac*- and *meso*-(18), respectively, on the basis of our previous work.[2]

1-Methylarsolan, (23), *and 1-Phenylarsolan,* (28).—Five-membered heterocyclic rings containing arsenic are well known.[3] The Grignard reagent obtained from



SCHEME 4 (*i*) Br_2 in CCl_4; (*ii*) heat, −MeBr; (*iii*) NaI in acetone, −NaBr; (*iv*) 2Na in thf, −NaI, NaCl

1,4-dibromobutane, $(BrMgCH_2CH_2)_2$, reacts with dichlorophenylarsine to give (28).[4] The methyl analogue (23) is obtained in a similar reaction with dichloromethylarsine although the product was not isolated.[5] We isolated (23), and re-prepared (28), with considerably improved yields by the reductive cyclisation of 4-chlorobutyliodo(methyl)arsine (22) and 4-chlorobutyliodo(phenyl)arsine (27), respectively (Scheme 4).

[2] B. Bosnich and S. B. Wild, *J. Amer. Chem. Soc.*, 1970, **92**, 459.

[3] F. G. Mann, ' The Heterocyclic Derivatives of Phosphorus, Arsenic, Antimony, and Bismuth,' 2nd edn., Wiley, New York, 1970, pp. 357—389.

EXPERIMENTAL

All the reactions were carried out in an atmosphere of pure nitrogen using the Schlenk technique. Solvents were dried in the usual way and degassed by distillation through a stream of pure nitrogen. Microanalyses were by the Australian Micro-analytical Service, Melbourne. Hydrogen-1 n.m.r. spectra were usually recorded at 60 MHz using a Varian A-60 spectrometer, but also where indicated at 90 MHz using a Bruker HX-90 spectrometer; chemical shifts are quoted relative to tetramethylsilane as internal standard.

Preparation of 1-*Methylarsetan,* (10).—The following alternative procedures gave a satisfactory yield of 3-chloropropyliodo(methyl)arsine, (5).

Route (1): *chloro(3-chloropropyl)(diethylamino)arsine,* (2). A solution of diethylamine (13.07 g) in diethyl ether was slowly added to a stirred solution of dichloro(3-chloropropyl)arsine, (1) (20 g), in the same solvent (100 cm^3) at 0 °C. After the addition the reaction mixture was filtered (to remove the diethylammonium chloride) and the filtrate was evaporated to dryness. Fractional distillation of the residue afforded the product as a yellow oil, b.p. 98—99 °C (1.5 mmHg), 15.8 g (76%) (Found: C, 32.0; H, 6.2. $C_7H_{16}AsCl_2N$ requires C, 32.3; H, 6.2%). Hydrogen-1 n.m.r. spectrum in $CDCl_3$: δ 1.19 [6 H, br t, *J* 7, $N(CH_2CH_3)_2$], 2.24 (4 H, m, $AsCH_2CH_2$), 3.27 [4 H, br q, *J* 7 Hz, $N(CH_2CH_3)_2$], and 3.75 p.p.m. (2 H, m, CH_2Cl).

3-Chloropropyl(diethylamino)methylarsine, (3).—Methylmagnesium iodide [from Mg (1.45 g) and MeI (8.48 g) in diethyl ether (50 cm^3)] was carefully added to a solution of (2) in diethyl ether (100 cm^3). The mixture was stirred at room temperature for 1 h and then cooled to 0 °C, hydrolysed with aqueous $[NH_4]Cl$, and the product extracted into diethyl ether (3 × 100 cm^3). The extract was dried ($Mg[SO_4]$) and the solvent was removed to leave an oil which on distillation gave (3), b.p. 60—62 °C (1 mmHg), 9.2 g (73%) (Found: C, 40.3; H, 7.9. $C_8H_{19}AsClN$ requires C, 40.1; H, 7.9%). Hydrogen-1 n.m.r. spectrum in $CDCl_3$: δ 0.98 (3 H, s, $AsCH_3$), 1.31 [12 H, br m, $AsCH_2CH_2$ and $N(CH_2CH_3)_2$], and 3.32 p.p.m. (6 H, m, CH_2Cl and $N(CH_2CH_3)_2$].

Chloro(3-chloropropyl)methylarsine, (4). Dry HCl gas was bubbled through a solution of (3) (9.2 g) in diethyl ether for 0.5 h. The $[NEt_2H_2]Cl$ which precipitated was filtered off and the colourless filtrate was evaporated to dryness. The residue on distillation gave pure (4), b.p. 85—86 °C (20 mmHg), 6.2 g (70%) (Found: C, 24.1; H, 4.6. C_4H_9AsCl requires C, 23.6; H, 4.5%). Hydrogen-1 n.m.r. spectrum in $CDCl_3$: δ 1.57 (3 H, s, $AsCH_3$), 2.23 (4 H, m, $AsCH_2CH_2$), and 3.62 p.p.m. (2 H, br t, *J* 7 Hz, CH_2Cl).

3-Chloropropyliodo(methyl)arsine, (5).—A solution of (4) (6.2 g) in acetone (50 cm^3) was treated with an excess of NaI in the same solvent. After 0.5 h the solvent was removed and the residue was extracted into CH_2Cl_2 (100 cm^3). Removal of the CH_2Cl_2 left a yellow oil which on distillation gave the pure product, b.p. 40—41 °C (1 mmHg), 7.9 g (86%) (Found: C, 16.6; H, 3.2. C_4H_9AsClI requires C, 16.3; H, 3.0%). Hydrogen-1 n.m.r. in $CDCl_3$: δ 2.0 (3 H, s, $AsCH_3$), 2.25 (4 H, m, $AsCH_2CH_2$), and 3.66 p.p.m. (2 H, br t, *J* 7 Hz, CH_2Cl).

Route (2): *3-Chloropropyldimethylarsine,* (6). The

[4] G. Grüttner and E. Krause, *Chem. Ber.*, 1916, **49**, 437.

[5] W. Steinkopf, I. Schubart, and J. Roch, *Chem. Ber.*, 1932, **65**, 409.

[6] G. A. Barclay, R. S. Nyholm, and R. V. Parish, *J. Chem. Soc.*, 1961, 4439.

tertiary arsine (6) is usually prepared by the method of Barclay *et al.*[6] However, the following procedure provides a quicker route. A solution of $AsMe_2I$ (23.2 g) in thf (100 cm^3) was slowly added to sodium pieces (4.6 g) in the same solvent (200 cm^3) to produce an olive-green solution of $Na[AsMe_2]$ containing solid NaI. The reaction mixture was heated under reflux for 1 h, cooled, and then filtered to remove the NaI and unchanged Na. This solution was then slowly added to a well stirred solution of 1,3-dichloropropane (11.3 g) in thf (100 cm^3) at 0 °C. Stirring was continued for 0.5 h after the completion of the addition and the reaction mixture was then allowed to warm to room temperature. The solvent was distilled off and the residue was extracted into diethyl ether and transferred to a distillation apparatus. Distillation under reduced pressure gave two fractions.

Fraction (*i*). The desired product (6) as a colourless oil, b.p. 70—72 °C (20 mmHg), 4 g (33%). Hydrogen-1 n.m.r. spectrum in $CDCl_3$: δ 0.93 (6 H, s, $AsCH_3$), 1.65 (4 H, br m, $AsCH_2CH_2$), and 3.57 p.p.m. (2 H, t, *J* 7 Hz, CH_2Cl). A sample of (6) prepared from dichloro(3-chloropropyl)-arsine and MgMeI gave an identical ^1H n.m.r. spectrum.

Fraction (*ii*). A pale yellow liquid, b.p. 96—98 °C (20 mmHg), 2.3 g (9%), 1,3-bis(dimethylarsino)propane (Found: C, 33.2; H, 7.0. $C_7H_{18}As_2$ requires C, 33.4; H, 7.2%). Hydrogen-1 n.m.r. spectrum in $CDCl_3$: δ 0.91 (12 H, s, $AsCH_3$) and 1.55 p.p.m. (6 H, br s, $AsCH_2CH_2CH_2As$).

Bromo(3-chloropropyl)methylarsine, (8). A solution of (6) (4 g) in CCl_4 (30 cm^3) was cooled to 0 °C and a solution of Br_2 (3.52 g) in the same solvent (30 cm^3) was slowly added. A pale yellow granular precipitate of the air- and moisture-sensitive arsenic(V) species (7) separated which was filtered off and dried. On heating *in vacuo* [*ca.* 100 °C (20 mmHg)] (7) decomposed to leave crude (8) as a red liquid. Distillation gave first a small quantity of *bromodimethylarsine* as a colourless liquid, b.p. 30—40 °C (20 mmHg), and then pure (8) as a pale yellow liquid, b.p. 106—108 °C (20 mmHg), 3.2 g (60%) (Found: C, 19.8; H, 3.9. $C_4H_9AsBrCl$ requires C, 19.4; H, 3.7%). Hydrogen-1 n.m.r. spectrum in $CDCl_3$: δ 1.78 (3 H, s, $AsCH_3$), 2.20 (4 H, m, $AsCH_2CH_2$), and 3.63 p.p.m. (2 H, br t, *J* 7 Hz, CH_2Cl). Metathesis of (8) with NaI in acetone in the usual way gave a good yield of (5) (80%).

1-*Methylarsetan*, (10). The addition of (5) (4.8 g, 0.02 mol) to sodium pieces (1.2 g, 0.05 mol) in thf (150 cm^3) led to the rapid formation of the anion (9). The yellow-green solution of the anion was heated under reflux for 48 h during which time it became colourless and precipitated the sodium halides. The thf was removed and the residue was extracted with diethyl ether and the sodium salts dissolved in water. The organic layer was separated, dried ($Mg[SO_4]$), and distilled to yield (10) as an air-sensitive oil, b.p. 58—64 °C (20 mmHg), 0.66 g (25%) (Found: C, 36.3; H, 6.7. C_4H_9As requires C, 36.4; H, 6.8%). Hydrogen-1 n.m.r. spectrum in $CDCl_3$: δ 0.90 (3 H, s, $AsCH_3$) and 1.70 p.p.m. (6 H, br m, $CH_2CH_2CH_2$). Mass spectrum: *m/e* 132 (20%) (C_4H_9As). A small portion of (10) on dissolution in iodomethane rapidly precipitated the white crystalline *methiodide* (11), m.p. 220—222 °C (90%) (Found: C, 21.8; H, 4.4. $C_5H_{12}AsI$ requires C, 21.9; H, 4.4%). Hydrogen-1 n.m.r. spectrum in $CDCl_3$: δ 1.61 (6 H, s, $\overset{+}{A}sCH_3$) and 1.91 p.p.m. (6 H, br m, $CH_2CH_2CH_2$).

A 15% yield of (10) was also obtained from the reaction between $Na_2[AsMe]$ and 1,3-dichloropropane in thf.

Preparation of 1-*Phenylarsetan*, (16).—*3-Chloropropyl(methyl)phenylarsine*, (12). The addition of an equivalent amount of Na[AsMePh] [from AsMePhI (29.4 g) and Na (4.1 g)] to 1,3-dichloropropane (11.3 g) and work-up as described for (6) gave the colourless product, b.p. 104—108 °C (0.5 mmHg), 10.2 g (42%) (Found: C, 49.2; H, 5.8. $C_{10}H_{14}AsCl$ requires C, 49.1; H, 5.8%). Hydrogen-1 n.m.r. spectrum in $CDCl_3$: δ 1.06 (3 H, s, $AsCH_3$), 1.86 (4 H, m, $AsCH_2CH_2$), 3.36 (2 H, br t, CH_2Cl), and 7.43 p.p.m. (5 H, m, aromatics). A quantity of 1,3-bis(methylphenylarsino)propane (18) also distilled, b.p. 140—146 °C (0.5 mmHg), 5.8 g (12%) (Found: C, 43.0; H, 4.8. $C_{17}H_{22}As_2$ requires C, 42.9; H, 4.7%). Hydrogen-1 n.m.r. spectrum in $CDCl_3$: δ 1.01 (6 H, s, $AsCH_3$), 1.67 (6 H, br s, $CH_2CH_2CH_2$), and 7.25 p.p.m. (10 H, m, aromatics). The ^1H n.m.r. spectrum of (18) in $CDCl_3$ at 90 MHz showed the presence of the two diastereoisomers *rac-* and *meso-*(18): δ 1.11 (3 H, s, $AsCH_3$), 1.22 (3 H, s, $AsCH_3$), 1.65 (6 H, br m, $CH_2CH_2CH_2$), and 7.32 p.p.m. (10 H, m, aromatics).

Bromo(3-chloropropyl)phenylarsine, (14). The addition of bromine to (12) (8.56 g) and thermal decomposition of the adduct (13) gave (14) as a yellow oil, b.p. 120—122 °C (1 mmHg), 7.8 g (72%) (Found: C, 35.1; H, 3.7. $C_9H_{11}AsBrCl$ requires C, 34.9; H, 3.6%). Hydrogen-1 n.m.r. spectrum in $CDCl_3$: 2.27 (4 H, m, $AsCH_2CH_2$), 3.56 (2 H, m, CH_2Cl), and 7.58 p.p.m. (5 H, m, aromatics).

3-Chloropropyliodo(phenyl)arsine, (15). The usual exchange reaction with NaI gave an 80% yield of (15) as a yellow oil, b.p. 151—153 °C (1 mmHg) (Found: C, 30.7; H, 3.3. $C_9H_{11}AsClI$ requires C, 30.3; H, 3.1%). Hydrogen-1 n.m.r. spectrum in $CDCl_3$: δ 2.22 (4 H, m, $AsCH_2CH_2$), 3.46 (2 H, m, CH_2Cl), and 7.50 p.p.m. (5 H, m, aromatics).

1-*Phenylarsetan*, (16). A 42% yield of (16) was obtained after refluxing a solution of (15) (3 g) in thf (50 cm^3) containing sodium (0.4 g) for 60 h. The *heterocycle* distilled at 80—82 °C (1 mmHg) (Found: C, 55.7; H, 5.7. $C_9H_{11}As$ requires C, 55.7; H, 5.7%). Hydrogen-1 n.m.r. spectrum in $CDCl_3$: δ 1.78 (6 H, br m, $CH_2CH_2CH_2$) and 7.31 p.p.m. (5 H, m, aromatics). Mass spectrum: *m/e* 194 (7%) ($C_9H_{11}As$). A solution of (12) in iodomethane gave the *methiodide* (17) in 90% yield, m.p. 258—260 °C (decomp.) (Found: C, 35.9; H, 4.5. $C_9H_{14}AsI$ requires C, 35.7; H, 4.4%). Hydrogen-1 n.m.r. spectrum in $CDCl_3$: δ 1.56 (3 H, s, $\overset{+}{A}sCH_3$), 1.94 (6 H, br m, $CH_2CH_2CH_2$), and 7.31 p.p.m. (5 H, m, aromatics).

Preparation of 1-*Methylarsolan*, (23).—*4-Chlorobutyldimethylarsine*, (19). The reaction of $Na[AsMe_2]$ [from $AsMe_2I$ (23.2 g) and Na (4.60 g) in thf (90 cm^3)] with $Cl[CH_2]_4Cl$ (12.7 g) gave, following the usual procedure, two tertiary arsines: (*i*) (19), b.p. 40—42 °C (0.1 mmHg), 9.7 g (49%) (Found: C, 36.9; H, 7.3. $C_6H_{14}AsCl$ requires C, 36.7; H, 7.2%), ^1H n.m.r. spectrum in $CDCl_3$ δ 0.89 (6 H, s, $AsCH_3$), 1.62 (6 H, br m, $AsCH_2CH_2CH_2$), and 3.50 p.p.m. (2 H, t, *J* 6.5 Hz, CH_2Cl); and (*ii*) 1,4-*bis(dimethylarsino)butane*, b.p. 54—57 °C (0.15 mmHg), 3.2 g (12%) (Found: C, 36.4; H, 7.8. $C_8H_{20}As_2$ requires C, 36.1; H, 7.6%), ^1H n.m.r. spectrum in $CDCl_3$, δ 0.90 (12 H, s, $AsCH_3$) and 1.49 p.p.m. (8 H, br s, $As[CH_2]_4As$).

Bromo(4-chlorobutyl)methylarsine, (21). Bromine oxidation of (19) (3.2 g) gave (20) which after decomposition afforded the *product* as a yellow oil, b.p. 60 °C (0.05 mmHg), 3.8 g (89%) (Found: C, 23.3; H, 4.4. $C_5H_{11}AsBrCl$ requires C, 23.0; H, 4.2%). Hydrogen-1 n.m.r. spectrum

in $CDCl_3$: δ 1.80 ($AsCH_3$), 1.97 (6 H, br m, $AsCH_2CH_2CH_2$), and 3.50 p.p.m. (2 H, m, CH_2Cl).

4-Chlorobutyliodo(methyl)arsine, (22). This was prepared in 85% yield from (21) in the usual way as a pale yellow oil, b.p. 91 °C (0.05 mmHg) (Found: C, 19.7; H, 3.7. $C_5H_{11}AsClI$ requires C, 19.5; H, 3.6%). Hydrogen-1 n.m.r. spectrum in $CDCl_3$: δ 2.0 (3 H, s, $AsCH_3$), 2.10 (6 H, br m, $AsCH_2CH_2CH_2$), and 3.50 p.p.m. (2 H, m, CH_2Cl).

1-Methylarsolan, (23).—The reaction of (22) with 2 equivalents of sodium under reflux conditions for 2 h gave (23) as a colourless liquid, b.p. 65—66 °C (15 mmHg) (52%) (Found: C, 40.7; H, 7.4. $C_5H_{11}As$ requires C, 41.1; H, 7.5%). Hydrogen-1 n.m.r. spectrum in $CDCl_3$: δ 0.83 (3 H, $AsCH_3$) and 1.50 p.p.m. (8 H, br m, $[CH_2]_4$). Mass spectrum: *m/e* 146 (30%) ($C_5H_{11}As$).

Preparation of 1-Phenylarsolan, (28).—*4-Chlorobutyl(methyl)phenylarsine*, (24). The reaction of Na[AsMePh] [from AsMePhI (29.4 g) and Na (4.6 g) in thf (100 cm^3)] and $Cl[CH_2]_4Cl$ (12.7 g) in thf gave (24), b.p. 114—116 °C (0.02 mmHg), 8 g (31%) (Found: C, 51.3; H, 6.2. $C_{11}H_{16}AsCl$ requires C, 51.0; H, 6.2%). Hydrogen-1 n.m.r. spectrum in $CDCl_3$: δ 1.17 (3 H, s, $AsCH_3$), 1.85 (6 H, m, $AsCH_2CH_2CH_2CH_2$), 3.46 (2 H, br t, *J* 7 Hz, CH_2Cl), and 7.25 p.p.m. (5 H, m, aromatics). A higher-boiling fraction containing *1,4-bis(methylphenylarsino)butane* was also obtained, b.p. 136—138 °C (0.2 mmHg) (Found: C, 55.5; H, 6.2. $C_{18}H_{24}As_2$ requires C, 55.4; H, 6.2%). Hydrogen-1 n.m.r. spectrum in $CDCl_3$: δ 1.14 (6 H, s, $AsCH_3$), 1.53 (8 H, br s, $As[CH_2]_4As$), and 7.24 p.p.m. (10 H, m, aromatics).

Bromo(4-chlorobutyl)phenylarsine, (26). Oxidation of (24) (3.3 g) with bromine (2.0 g) and decomposition of the adduct (25) in the usual way afforded (26), b.p. 110—114 °C (0.1 mmHg), 3.5 g (85%) (Found: C, 37.4; H, 4.2. $C_{10}H_{13}AsBrCl$ requires C, 37.1; H, 4.0%). Hydrogen-1 n.m.r. spectrum in $CDCl_3$: δ 2.05 (6 H, m, $AsCH_2CH_2CH_2$), 3.48 (2 H, m, CH_2Cl), and 7.40 p.p.m. (5 H, m, aromatics).

4-Chlorobutyliodo(phenyl)arsine, (27). An exchange reaction between (26) and NaI produced the *iodoarsine* as a yellow oil, b.p. 147—150 °C (0.1 mmHg) (62%) (Found: C, 32.5; H, 3.5. $C_{10}H_{13}AsClI$ requires C, 32.4; H, 3.5%). Hydrogen-1 n.m.r. spectrum in $CDCl_3$: δ 2.12 (6 H, m, $AsCH_2CH_2CH_2$), 3.39 (2 H, m, CH_2Cl), and 7.45 p.p.m. (5 H, m, aromatics).

1-Phenylarsolan, (28). The reduction of (27) with sodium in thf followed by refluxing of the solution for 2 h gave a 58% yield of (28), b.p. 130—134 °C (20 mmHg) [lit.,[4] 110—127 °C (10 mmHg)] (Found: 57.6; H, 6.2. $C_{10}H_{13}As$ requires C, 57.7; H, 6.3%). Hydrogen-1 n.m.r. spectrum in $CDCl_3$: δ 1.68 (8 H, br m, $[CH_2]_4$) and 7.33 p.p.m. (5 H, m, aromatics). Mass spectrum: *m/e* 208 (45%) ($C_{10}H_{13}As$).

One of us (M. M.) thanks the University of Western Australia for a Research Studentship.

[6/1830 *Received*, 29*th September*, 1976]