

## THE REACTIONS OF ARSENIC HALIDES WITH SOME ORGANOSILICO- COMPOUNDS OF NITROGEN AND SULPHUR

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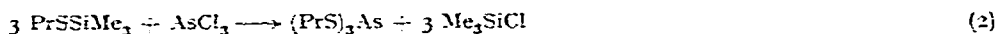
The reactions of silicon-nitrogen and silicon-sulphur compounds with a variety of covalent halides, notably phosphorus<sup>1,2</sup>, have shown the method to be most useful for the preparation of nitrogen and sulphur derivatives of many elements. Reactions of arsenic chloride with aminosilanes, already reported<sup>1</sup>, have shown that the third chlorine does not appear to be replaceable by this method.

Direct interaction of both methyl- and phenyl-hexamethyldisilazanes with arsenic trichloride according to eqn. (1) causes the elimination of chlorotrimethylsilane and formation of the corresponding arsazanes.



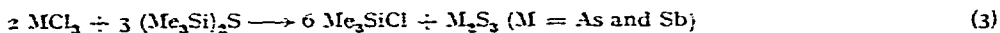
Although the arsazanes produced in this way analyse well for their empirical formulae, they appear to be completely insoluble in any solvents. In the light of this we suspect that they are either linear or large ring polymers, in contrast to the six-membered ring arsazanes previously reported.

Arsenic trichloride reacts with (*n*-propylthio)trimethylsilane according to eqn. (2) to produce tri-*n*-propyltrithioarsenite.



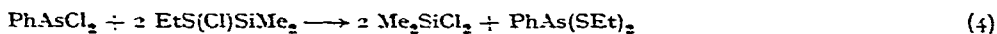
Efforts were made to prepare di-*n*-propyl dithiochloroarsenite and *n*-propyl thiodichloroarsenite by varying the proportions of the reagents in eqn. (2). In each case, however, although the requisite quantity of chlorotrimethylsilane was produced, the only other products isolated were tri-*n*-propyl trithioarsenite and arsenic trichloride. It would appear, therefore, that if the chloroesters were produced in these reactions they underwent disproportionation completely to the trithioarsenite and arsenic trichloride.

Both arsenic and antimony trichlorides removed sulphur completely from hexamethyldisilthiane (eqn. 3), in common with the corresponding reactions of bis(trimethyltin) sulphide<sup>3</sup>.

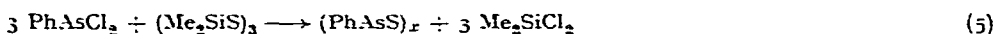


We have observed no cleavage of aminosilanes or disilazanes by phenylarsenic dichloride. This is in contrast to the behaviour of phenylphosphorus dichloride, but is in line with the lower reactivity of arsenic trichloride towards aminosilanes compared

with phosphorus trichloride. Phenylarsenic dichloride does, however, cause fission of alkylthiosilanes to give the di-*n*-alkyl dithiophenylarsonite as illustrated for example in eqn. 4.



Phenylarsenic dichloride further reacts with hexamethylcyclotrisilthiane to give phenylarsenic sulphide (eqn. 5).



When the corresponding phosphorus compound was made in an analogous manner, it was found to be trimeric, and a six-membered phosphorus-sulphur ring system was proposed for a structure<sup>2</sup>. We find that the phenylarsenic sulphide prepared as above, is tetrameric, and the melting point of 175–176° agrees with a previous report<sup>1a</sup>. It is, however, different from a trimeric phenylarsenic sulphide reported<sup>1b</sup>.

It has already been noted that the size of the organosilicon ring system used as starting material, in no way controls the ring size of the end product<sup>5</sup>.

We think it likely that (PhAsS)<sub>4</sub> has an eight membered ring structure of alternate arsenic and sulphur atoms.

#### EXPERIMENTAL

The chlorosilanes isolated from each experiment were characterised by boiling point and refractive index. The silicon-nitrogen and silicon-sulphur compounds used were all prepared by reported methods, viz. (Me<sub>3</sub>Si)<sub>2</sub>NMe<sup>6</sup>, (Me<sub>3</sub>Si)<sub>2</sub>NPh<sup>7</sup>, Me<sub>2</sub>ClSiEt<sup>8</sup>, Me<sub>3</sub>SiSPr<sup>9</sup>, (Me<sub>2</sub>SiS)<sub>3</sub><sup>10</sup>, (Me<sub>3</sub>Si)<sub>2</sub>S<sup>11</sup>, as was phenylarsenic dichloride<sup>12</sup>.

#### *Reaction of arsenic trichloride with N-methylhexamethyldisilazane*

The disilazane (10.7 g, 1 mol.) was carefully added to arsenic trichloride (11.1 g, 1 mol.) in toluene. A precipitate was formed which disappeared on warming. Subsequent distillation yielded chlorotrimethylsilane (94%), and removal of the solvent yielded *N*-methylchloroarsazane (80%), m.p. 90–110° (Found C, 9.0; H, 2.4; N, 9.5. CH<sub>3</sub>AsClN calcd.: C, 8.6; H, 2.2; N, 10.1%) as an insoluble cream powder. It was too insoluble at room temperature for a molecular weight determination.

#### *Reaction of arsenic trichloride with N-phenylhexamethyldisilazane*

The disilazane (15.5 g, 1 mol.) was slowly added to arsenic trichloride (11.9 g, 1 mol.) in toluene. A reaction occurred on warming with subsequent elimination of chlorotrimethylsilane (88%). Recrystallisation from boiling toluene yielded *N*-phenylchloroarsazane (11.5 g, 87%), m.p. 157–170° (Found: C, 36.2; H, 2.8; N, 7.2. C<sub>6</sub>H<sub>5</sub>AsClN calcd.: C, 35.8; H, 2.5; N, 7.0%), as a yellow powder, too insoluble in common solvents at room temperature for a molecular weight determination.

#### *Reaction of (n-propylthio)trimethylsilane with arsenic trichloride*

*In mole ratio 3:1.* Arsenic trichloride (2.7 g, 1 mol) was slowly added to *n*-propylthiotrimethylsilane (6.6 g, 3 mol.). A vigorous reaction occurred and subsequent fractionation gave chlorotrimethylsilane (81%) and tri-*n*-propyltrithioarsenite (3.2 g,

74%), b.p.  $106^{\circ}/0.001$  mm  $n_D^{25}$  1.5836 (Found: C, 36.4; M, 7.3.  $C_9H_{21}S_3As$  requires C, 35.8; H, 7.0%) as an air sensitive liquid.

*In mole ratio 2:1.* (*n*-Propylthio)trimethylsilane (13.9 g, 2 mol.) was carefully added to arsenic trichloride (8.5 g, 1 mol.) with cooling. An exothermic reaction occurred and after leaving standing for 1 h, volatile material was pumped off and trapped to give chlorotrimethylsilane (97%). The residue (12.3 g,  $n_D^{25}$  1.5898) was vacuum-distilled to give arsenic trichloride, which was trapped and redistilled (2.1 g, 74%) b.p.  $130^{\circ}$ , together with tri-*n*-propyl trithioarsenite (93 g, 98%), b.p.  $116^{\circ}/0.05$  mm,  $n_D^{25}$  1.5827.

*In mole ratio 1:1.* (*n*-Propylthio)trimethylsilane (8.7 g, 1 mol.) was carefully added to arsenic trichloride (10.7 g, 1 mol.) with cooling. After leaving 1 h, the volatile material was pumped off and distilled to give chlorotrimethylsilane (95%). The residual liquid (11.3 g,  $n_D^{25}$  1.5965) was vacuum-distilled to give arsenic trichloride, which was trapped and redistilled (4.8 g, 78%), b.p.  $130^{\circ}$ , together with tri-*n*-propyl trithioarsenite (4.5 g, 88%), b.p.  $116^{\circ}/0.05$  mm,  $n_D^{25}$  1.5822.

#### *Reaction of arsenic trichloride with hexamethyldisilthiane*

Hexamethyldisilthiane (9.6 g, 3 mol.) was carefully added to arsenic trichloride (6.52 g, 2 mol.) with cooling. A vigorous reaction occurred, with precipitation of a yellow solid. Subsequent fractionation gave chlorotrimethylsilane (91%), while washing the precipitate with ether and pumping dry yielded arsenic trisulphide (4.5 g, 99%), as a yellow, alkali-soluble powder.

#### *Reaction of antimony trichloride with hexamethyldisilthiane*

Hexamethyldisilthiane (4.1 g, 3 mol.) was carefully added to antimony trichloride (3.5 g, 2 mol.) at room temperature. A reaction occurred and on warming, chlorotrimethylsilane (68%) was evolved. The residue was washed with ether and pumped dry to give antimony trisulphide (2.0 g, 77%) as a red, alkali-soluble powder.

#### *Reaction of phenylarsenic dichloride with (ethylthio)dimethylchlorosilane*

Phenylarsenic dichloride (4.3 g, 1 mol.) was added to the thiosilane (5.95 g, 2 mol.) at room temperature. On warming, dichlorodimethylsilane (81%) was evolved and vacuum distillation of the residue yielded di-*n*-propyl dithiophenylarsonite (3.9 g, 74%), b.p.  $88^{\circ}/0.01$  mm,  $n_D^{25}$  1.6290 (Found: C, 43.7; H, 5.5.  $C_{10}H_{15}AsS_2$  calcd.: C, 43.7; H, 5.5%) as a colourless liquid.

#### *Reaction of hexamethylcyclotrisilthiane with phenylarsenic dichloride*

The dichloride (16.8 g, 3 mol.) was added to the cyclosilthiane (6.79 g, 1 mol.) in toluene (10 ml) and dichlorodimethylsilane (74%) was eliminated on heating. On cooling the remaining liquid, crystals separated which were filtered and recrystallised twice from toluene to give tetraphenylcyclotetraarsthiane,  $(PhAsS)_4$ , m.p.  $175-6^{\circ}$ . (Found: C, 39.4; H, 3.0; mol. wt. osmometric in benzene, 734.  $C_6H_5AsS$  calcd.: C, 39.1; H, 2.7%; mol. wt., 736.)

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## SUMMARY

Arsenic trichloride reacts with silicon-nitrogen and silicon-sulphur compounds to give the chlorosilane and corresponding arsenic-nitrogen or arsenic-sulphur compound. Phenylarsenic dichloride reacts in a similar way with silicon-sulphur compounds but not with silicon-nitrogen derivatives.

## REFERENCES

- E. W. ABEL, D. A. ARMITAGE AND G. R. WILLEY, *J. Chem. Soc.*, (1965) 57.  
E. W. ABEL, D. A. ARMITAGE AND R. P. BUSH, *J. Chem. Soc.*, (1964) 5584.  
H. H. ANDERSON, *J. Org. Chem.*, 19 (1954) 1766.  
(a) A. E. KRETOV AND A. YA. BERLIN, *Zh. Obshch. Khim.*, 1 (1931) 411; *Chem. Abstr.*, 26 (1932) 2415.  
(b) L. ANSCHUTZ AND H. WIRTH, *Chem. Ber.*, 89 (1956) 1530; *Naturwissenschaften*, 43 (1956) 590.  
E. W. ABEL, D. A. ARMITAGE AND R. P. BUSH, *J. Chem. Soc.*, (1965) 3045.  
R. C. OSTHOFF AND S. W. KANTOR, *Inorg. Syn.*, 5 (1957) 56.  
E. W. ABEL AND G. R. WILLEY, *J. Chem. Soc.*, (1964) 1528.  
E. W. ABEL AND D. A. ARMITAGE, *J. Chem. Soc.*, (1964) 5975.  
S. H. LANGER, S. CONNELL AND I. WENDER, *J. Org. Chem.*, 23 (1958) 50.  
T. NOMURA, M. YOKOI AND K. YAMASAKI, *Proc. Japan Acad.*, 29 (1953) 342; *Chem. Abstr.*, 49 (1955) 12274g.  
G. CHAMPETIER, Y. ETIENNE AND R. KULLMAN, *Compt. Rend.*, 234 (1952) 1985.  
I. L. KNUNYANTS, V. YA. PIL'SKAYA, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, (1955) 472; *Chem. Abstr.*, 50 (1956) 6298.

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