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11. *Reactions of Aminosilanes and Disilazanes with Halogeno-compounds of Phosphorus and Arsenic.*

By E. W. ABEL, D. A. ARMITAGE, and G. R. WILLEY.

Phosphorus trichloride, phosphorus tribromide, phosphoryl chloride, phenylphosphorus dichloride, diphenylphosphorus chloride, and arsenic trichloride react with compounds containing silicon–nitrogen bonds to produce a variety of linear and cyclic nitrogen derivatives of phosphorus and arsenic.

THE use of aminosilanes and disilazanes as intermediates in the preparation of amino-derivatives of certain elements has recently been reported. In particular, boron–nitrogen [1] and sulphur–nitrogen [2] bonds are formed very conveniently.

Phosphorus trichloride has been reported [3] to yield the polymeric material $(R_3SiNPCl)_n$ upon treatment with the sodium salt of the disilazane $NaN(SiR_3)_2$, and hexamethyldisilazane reacts with esters of chlorophosphonic acid and phosphoryl chloride to give products involving the cleavage of only one silicon–nitrogen bond.[4,5] With *N*-methylaminotrimethylsilane, however, these chloro-esters of phosphorus are reported to react with the N–H bond and to leave the Si–N bond intact.[5]

In the reactions reported below, aminosilanes and disilazanes react with different proportions of halogeno-phosphorus and -arsenic compounds, causing cleavage of the Si–N bond only. In all cases yields of halogenotrimethylsilane evolved were good; most reactions were vigorous at room temperature and were cooled to −80°.

Equimolar proportions of phosphorus trichloride and diethylaminotrimethylsilane react

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[1] Jenne and Niedenzu, *Inorg. Chem.*, 1964, **3**, 68; Nöth, *Z. Naturforsch.*, 1961, **16**b, 618; Lappert and Srivastava, *Proc. Chem. Soc.*, 1964, 120.

[2] Abel and Armitage, *J.*, 1964, 3122.

[3] Wannagat, *Angew. Chem., Internat. Edn.*, 1963, **2**, 161.

[4] Becke-Goehring and Wunsch, *Annalen*, 1958, **618**, 43.

[5] Becke-Goehring and Wunsch, *Chem. Ber.*, 1960, **93**, 326.

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to give dichlorodiethylaminophosphine in good yield after removal of chlorotrimethylsilane by-product. Similarly, phosphorus tribromide gives dibromodi-n-propylaminophosphine.

$$R_2N{\cdot}SiMe_3 + PX_3 \longrightarrow R_2N{\cdot}PX_2 + Me_3SiX \ (X = Cl \text{ or } Br) \qquad (1)$$

Similar reactions involving phosphorus trichloride with two and three molar proportions of diethylaminotrimethylsilane resulted in formation of chlorobisdiethylaminophosphine and trisdiethylaminophosphine, respectively.

$$2Et_2N{\cdot}SiMe_3 + PCl_3 \longrightarrow (EtN)_2PCl + 2Me_3SiCl \qquad (2)$$

$$3Et_2N{\cdot}SiMe_3 + PCl_3 \longrightarrow (Et_2N)_3P + 3Me_3SiCl \qquad (3)$$

Phenylphosphorus dichloride and diphenylphosphorus chloride were converted in very high yield into bisdiethylamino(phenyl)phosphine and diethylaminodiphenylphosphine, respectively, on reaction with the requisite proportion of diethylaminotrimethylsilane.

$$PhPCl_2 + 2Et_2N{\cdot}SiMe_3 \longrightarrow PhP(NEt_2)_2 + 2Me_3SiCl \qquad (4)$$

$$Ph_2PCl + Et_2N{\cdot}SiMe_3 \longrightarrow Ph_2P{\cdot}NEt_2 + Me_3SiCl \qquad (5)$$

Phosphoryl chloride and dimethylaminotrimethylsilane in equimolar proportions reacted vigorously to produce mainly dimethylaminophosphoryl dichloride (eqn. 6), but a small quantity of bisdimethylaminophosphoryl chloride was also isolated. Bisdialkylaminophosphoryl chloride was obtained in high yield when phosphoryl chloride reacted with diethylaminotrimethylsilane in 1 : 3 molar proportions (eqn. 7).

$$Me_2N{\cdot}SiMe_3 + POCl_3 \longrightarrow Me_2N{\cdot}POCl_2 + Me_3SiCl \qquad (6)$$

$$2Et_2N{\cdot}SiMe_3 + POCl_3 \longrightarrow (Et_2N)_2POCl + 2Me_3SiCl \qquad (7)$$

However, the reaction of three moles of diethylaminotrimethylsilane with phosphoryl halide did not produce any trisdialkylaminophosphine oxide, and, even after prolonged heating together, bisdiethylaminophosphoryl chloride and diethylaminotrimethylsilane were recovered unchanged. It therefore appears that the third chlorine atom in phosphoryl chloride cannot be replaced by this method, in contrast to phosphorus trichloride in which all three are easily replaced on reaction with excess of aminosilane.

Arsenic trichloride and diethylaminotrimethylsilane react in equimolar proportions to give dichlorodiethylaminoarsine in good yield (eqn. 8). Similarly, 1 : 2 molar proportions of the reactants produce chlorobisdiethylaminoarsine (eqn. 9). Further replacement of chlorine by nitrogen on arsenic has not proved possible by this method, and, even after prolonged heating together, dimethylaminotrimethylsilane and chlorobisdiethylaminoarsine were recovered unchanged.

$$Et_2N{\cdot}SiMe_3 + AsCl_3 \longrightarrow Et_2N{\cdot}AsCl_2 + Me_3SiCl \qquad (8)$$

$$2Et_2N{\cdot}SiMe_3 + AsCl_3 \longrightarrow (Et_2N)_2AsCl + 2Me_3SiCl \qquad (9)$$

Interaction of arsenic trichloride and ethylaminotrimethylsilane did not produce the expected dichloroethylaminoarsine, $EtNH{\cdot}AsCl_2$. The requisite amount of chlorotrimethylsilane was evolved, but hydrogen chloride was also formed, to produce $(EtNAsCl)_n$ (eqn. 10). The compound of this formula previously reported[6] appears to be identical with our product, and it seems likely that $n = 3$, but other values of n are known depending upon the groups attached to arsenic and nitrogen.[6,7]

$$EtNH{\cdot}SiMe_3 + AsCl_3 \longrightarrow (EtNAsCl)_n + Me_3SiCl + HCl \qquad (10)$$

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[6] Olah and Oswald, *Canad. J. Chem.*, 1960, **38**, 1428.
[7] Ipatiev, Rosuwaiew, and Stromski, *Ber.*, 1929, **62**, 598.

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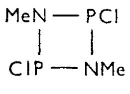
N-Methylhexamethyldisilazane reacted with an equimolar quantity of phosphorus trichloride to give mainly 1,3-dimethyl-2,4-dichlorocyclodiphosph(III)azane (I) (eqn. 11). The analogous reaction between equimolar quantities of *N*-ethylhexamethyldisilazane and phosphorus trichloride gave 1,3,5-triethyl-2,4,6-trichlorocyclotriphosph(III)azane (II) and what appears to be 1,3,5,7-tetraethyl-2,4,6,8-tetrachlorocyclotetraphosph(III)azane (III) (eqn. 12).

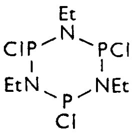
$$2\mathrm{MeN(SiMe_3)_2} + 2\mathrm{PCl_3} \longrightarrow \mathrm{(MeN{\cdot}PCl)_2} + 4\mathrm{Me_3SiCl} \qquad (11)$$

$$\mathrm{EtN(SiMe_3)_2} + \mathrm{PCl_3} \longrightarrow \frac{1}{n}\,\mathrm{(EtNPCl)}_n + 2\mathrm{Me_3SiCl} \quad (n = 3 \text{ and } 4) \qquad (12)$$

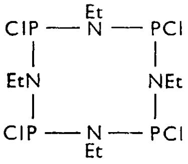
The four-membered ring system (I) has been reported [8] from direct interaction of aniline and phosphorus trichloride, but, apart from a preliminary communication of this work, the ring systems in (II) and (III) are new. A comparison between the six-membered system (II) and the isomeric derivatives of the better known phosphonitrilic compounds has been made.[9]



(I)



(II)



(III)

Each of these three ring compounds could be distilled at reduced pressure; the four-membered and six-membered remained mobile liquids at room temperature, but the eight-membered is a crystalline solid. All three are very sensitive to air, in which the liquids occasionally catch fire, and the solid crystals of (III) may be observed under a microscope to decompose very rapidly after the evaporation of a protective layer of light petroleum, thus rendering analysis of the compounds difficult.

N-Methylhexamethyldisilazane reacts with phosphoryl chloride to evolve the requisite quantity of trimethylchlorosilane, but the product, $\mathrm{(MeNPOCl)}_n$, appears to be completely polymeric.

EXPERIMENTAL

All reactions were conducted under perfectly dry conditions because of the ease of hydrolysis of all reactants and products. Where necessary, reactions and distillations were also carried out in an atmosphere of nitrogen to avoid oxidation of the products. Analyses and molecular-weight measurements are by the Microanalytical Laboratories of Imperial College, London.

Interaction of Diethylaminotrimethylsilane and Phosphorus Trichloride (*eqn.* 1).—Diethylaminotrimethylsilane (16·2 g., 1 mol.) was added dropwise to phosphorus trichloride (17·0 g., 1 mol.) at 0°. A vigorous reaction occurred with the formation of a yellow mass. After refluxing for 1 hr., distillation gave chlorotrimethylsilane, and dichlorodiethylaminophosphine, a clear liquid (11·5 g., 72%), b. p. 189—190°, n_D^{20} 1·4975 (Found: C, 27·4; H, 5·8; N, 8·0. Calc. for $\mathrm{C_4H_{10}Cl_2NP}$: C, 27·6; H, 5·8; N, 8·0%).

Interaction of Di-n-propylaminotrimethylsilane and Phosphorus Tribromide (*eqn.* 1).—Di-n-propylaminotrimethylsilane (18·3 g., 1 mol.) was added dropwise to an ice-cooled solution of phosphorus tribromide (28·7 g., 1 mol.) in dry benzene (20 ml.). Warming to room temperature caused an exothermic reaction with formation of a yellow precipitate. Removal of bromotrimethylsilane and benzene (b. p. 79—82°) left a deep red liquid which afforded *dibromodi-n-propylaminophosphine* (13·8 g., 76%), b. p. 99—100°/3 mm., n_D^{20} 1·5133 (Found: C, 25·0; H, 4·9; N, 4·8. $\mathrm{C_6H_{14}Br_2NP}$ requires C, 24·8; H, 4·8; N, 4·5%).

Interaction of Diethylaminotrimethylsilane and Phosphorus Trichloride (*eqn.* 2).—Diethylaminotrimethylsilane (39·5 g., 2 mol.) was added to phosphorus trichloride (18·7 g., 1 mol.).

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[8] Michaelis and Schroeter, *Ber.*, 1894, **27**, 490.

[9] Abel and Willey, *Proc. Chem. Soc.*, 1962, 308.

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Fractional distillation gave chlorotrimethylsilane, and chloro-bisdiethylaminophosphine, a clear liquid (20·1 g., 70%), b. p. 55—57°/0·2 mm., n_D^{20} 1·4686 (Found: C, 45·1; H, 9·5; N, 13·0. Calc. for $C_8H_{20}ClN_2P$: C, 45·6; H, 9·6; N, 13·5%).

Interaction of Diethylaminotrimethylsilane and Phosphorus Trichloride (*eqn.* 3).—Diethylaminotrimethylsilane (49·8 g., 3 mol.) was added to phosphorus trichloride (15·8 g., 1 mol.). Distillation yielded chlorotrimethylsilane, and trisdiethylaminophosphine, a clear liquid (19·2 g., 68%), b. p. 71—72°/0·1 mm., n_D^{20} 1·4756 (Found: C, 57·8; H, 12·1; N, 16·8. Calc. for $C_{12}H_{30}N_3P$: C, 58·3; H, 12·2; N, 17·0%).

Interaction of Phenyldichlorophosphine with Diethylaminotrimethylsilane (*eqn.* 4).—Diethylaminotrimethylsilane (14·0 g., 2 mol.) was slowly added to phenyldichlorophosphine (8·66 g., 1 mol.) at −78°. A vigorous reaction occurred and, on fractionation, chlorotrimethylsilane (72%) was obtained. Vacuum distillation of the residue gave bisdiethylamino(phenyl)phosphine[10] as a colourless liquid (9·70 g., 84%), b. p. 80°/0·005 mm., n_D^{20} 1·5339 (Found: C, 65·5; H, 10·0; N, 11·8. Calc. for $C_{14}H_{25}N_2P$: C, 66·6; H, 10·0; N, 11·1%).

Interaction of Chlorodiphenylphosphine and Diethylaminotrimethylsilane (*eqn.* 5).—Diethylaminotrimethylsilane (3·24 g., 1 mol.) was added dropwise to chlorodiphenylphosphine (4·93 g., 1 mol.) at room temperature. Slight warming occurred, and after 12 hr. distillation gave chlorotrimethylsilane (79%). Vacuum distillation of the residue gave diethylaminodiphenylphosphine[10] as a colourless liquid (4·2 g., 73%), b. p. 114°/0·002 mm., n_D^{20} 1·5920 (Found: C, 74·3; H, 8·6; N, 5·65. Calc. for $C_{16}H_{20}NP$: C, 74·6; H, 7·8; N, 5·45%).

Interaction of Phosphoryl Chloride and Dimethylaminotrimethylsilane (*eqn.* 6).—Dimethylaminotrimethylsilane (15·22 g., 1 mol.) was added dropwise to phosphoryl chloride (19·96 g., 1 mol.) at −80°. After the vigorous reaction, fractionation gave chlorotrimethylsilane (90%). Vacuum distillation of the residue gave dimethylaminophosphoryl dichloride (11·20 g., 53%), b. p. 76°/10 mm., n_D^{20} 1·4650 (Found: C, 15·0; H, 3·75; N, 9·35. Calc. for $C_2H_6Cl_2NOP$: C, 14·75; H, 3·7; N, 8·6%), and crude bisdimethylaminophosphoryl chloride (5·30 g., 24·9% based on the aminosilane), b. p. 108°/10 mm., n_D^{20} 1·4677 (Found: C, 26·2; H, 6·6; N, 16·75. Calc. for $C_4H_{12}ClN_2OP$: C, 28·2; H, 7·05; N, 16·35%).

Interaction of Diethylaminotrimethylsilane and Phosphoryl Chloride (*eqn.* 7).—Diethylaminotrimethylsilane (11·66 g., 3 mol.) was slowly added to phosphoryl chloride (4·12 g., 1 mol.) at room temperature. Slight warming occurred on standing, and after 24 hr. distillation gave chlorotrimethylsilane (60%), and bisdiethylaminophosphoryl chloride (4·2 g., 68%), b. p. 79°/0·03 mm., n_D^{20} 1·4655 (Found: C, 42·0; H, 8·7. Calc. for $C_8H_{20}ClN_2OP$: C, 42·4; H, 8·9%).

Attempted Interaction of Diethylaminotrimethylsilane and Bisdiethylaminophosphoryl Chloride.—Diethylaminotrimethylsilane (7·09 g., excess) was added to bisdiethylaminophosphoryl chloride (3·59 g.) and the mixture refluxed for 24 hr. Fractionation gave diethylaminotrimethylsilane (5·60 g., 79%), b. p. 124—125°, n_D^{20} 1·4100, and bisdiethylaminophosphoryl chloride (3·0 g., 80%), b. p. 80°/0·03 mm., n_D^{20} 1·4659, but no chlorotrimethylsilane.

Interaction of Diethylaminotrimethylsilane and Arsenic Trichloride.—(*a*) 1 : 1 (*Eqn.* 8). Diethylaminotrimethylsilane (16·3 g., 1 mol.) was added dropwise to arsenic trichloride (20·3 g., 1 mol.) at 0° during 1 hr. An exothermic reaction occurred and copious white fumes were evolved. The resulting brown solution was refluxed for 1 hr., and then chlorotrimethylsilane (88%) was slowly collected. Careful fractionation of the residue gave dichlorodiethylaminoarsine as a clear liquid (19·3 g., 79%), b. p. 36–37°/0·1 mm., n_D^{20} 1·5341 (Found: C, 21·9; H, 4·4; N, 6·4. Calc. for $C_4H_{10}AsCl_2N$: C, 22·0; H, 4·6; N, 6·4%). A brown residue (1·0 g.) remained after distillation.

(*b*) 2 : 1 (*Eqn.* 9). Diethylaminotrimethylsilane (29·2 g., 2 mol.) was added to arsenic trichloride (18·2 g., 1 mol.). Distillation gave chlorotrimethylsilane, and chlorobisdiethylaminoarsine as a colourless liquid (19·7 g., 77%), b. p. 45—46°/0·08 mm., n_D^{20} 1·5094 (Found: C, 37·8; H, 8·0; N, 10·7. Calc. for $C_8H_{20}AsClN_2$: C, 37·8; H, 7·9; N, 11·0%).

(*c*) 3 : 1. Addition of diethylaminotrimethylsilane (44·0 g., 3 mol.) to arsenic trichloride (18·3 g., 1 mol.) gave chlorotrimethylsilane, and chlorobisdiethylaminoarsine (31·2 g., 81%) as a colourless liquid, b. p. 48—49°/0·1 mm., n_D^{20} 1·5096 (Found: C, 37·8; H, 7·8; N, 10·9%).

Attempted Interaction of Dimethylaminotrimethylsilane and Chlorobisdiethylaminoarsine.—Addition of dimethylaminotrimethylsilane (10·8 g., 1 mol.) to chlorobisdiethylaminoarsine (23·5 g., 1 mol.) in the usual manner gave, after refluxing for 6 hr., dimethylaminotrimethylsilane

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[10] Ewart, Payne, Porte, and Lane, *J.*, 1962, 3984.

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(6·6 g., 61%), b. p. 84—85°, n_D^{20} 1·3956, and chlorobisdiethylaminoarsine (17·0 g., 72%), b. p. 47—48°/0·1 mm., n_D^{20} 1·5088.

Interaction of Ethylaminotrimethylsilane and Arsenic Trichloride (*eqn.* 10).—Ethylaminotrimethylsilane (12·8 g., 1 mol.) was added to arsenic trichloride (19·8 g., 1 mol.) at 0°. After 2 hr., distillation gave chlorotrimethylsilane (77%) and a white residual mass. Extraction with dry ether (2 × 20 ml.) and recrystallisation from benzene–toluene gave what was initially thought to be dichloroethylaminoarsine, a white solid (12·7 g., 61%), m. p. 92—95° (Found: C, 15·8; H, 3·4; N, 9·4. Calc. for $C_2H_6AsCl_2N$: C, 12·7; H, 3·2; N, 7·4%). But the analysis figures and m. p. correspond to the compound [6] formed by the elimination of hydrogen chloride (Calc. for C_2H_5AsClN: C, 15·7; H, 3·3; N, 9·1%) (lit.,[6] b. p. 155°/10 mm., m. p. 90—95°), which appears to be identical with our compound. The previous workers [6] report a molecular weight of 507, which appears to indicate a six-membered ring system analogous to (II).

Interaction of N-*Methylhexamethyldisilazane and Phosphorus Trichloride* (*eqn.* 11)—Phosphorus trichloride (37·5 g., 1 mol.) was added slowly to *N*-methylhexamethyldisilazane (47·6 g., 1 mol.) in light petroleum (b. p. 80—100°) (40 g.) at room temperature. A solid was slowly precipitated, and after 18 hr. the mixture was heated. The solid decomposed, and chlorotrimethylsilane (95%) was evolved, followed by the solvent. Vacuum distillation of the residue gave 1,3-*dimethyl*-2,4-*dichlorocyclodiphosph*(III)*azane* (8·0 g., 33%), b. p. 34°/0·5 mm., n_D^{20} 1·5770 [Found: N, 14·3; P, 30·3%; *M* (ebullioscopic in benzene) 190. $(CH_3ClNP)_2$ requires N, 14·8; P, 32·4%; *M*, 191], and small amounts of higher-boiling material. Much decomposition product remained. This material was very sensitive to air and satisfactory analyses for carbon and hydrogen were not obtained. Various values were obtained from the same homogeneous liquid product, and samples gained weight during the weighing. With rapid weighing, good analyses for phosphorus, nitrogen, and molecular weight were obtained.

Interaction of N-*Ethylhexamethyldisilazane and Phosphorus Trichloride* (*eqn.* 12).—Phosphorus trichloride (29·5 g., 1 mol.) was added slowly to *N*-ethylhexamethyldisilazane (40·6 g., 1 mol.) in toluene (75 g.) at room temperature. On standing overnight, a pale yellow solid was precipitated which decomposed on refluxing. Chlorotrimethylsilane (96%) was distilled out, together with the solvent toluene. Vacuum distillation of the residual liquor yielded 1,3,5-triethyl-2,4,6-trichlorocyclotriphosph(III)azane (11.2 g., 48%), b. p. 110°/0·001 mm., n_D^{20} 1·5645 [Found: C, 22·0; H, 4·3; N, 12·5; P, 31·4%; *M*, 329. Calc. for $(C_2H_5ClNP)_3$: C, 22·0; H, 4·6; N, 12·8; P, 28·3%; *M*, 329], together with 1,3,5,7-*tetraethyl*-2,4,6,8-*tetrachlorocyclotetraphosph*(III)*azane* (3·3 g., 14%), b. p. 142°/0·001 mm. [Found: C, 23·4; H, 6·5; N, 13·5%; *M* (ebullioscopic in benzene), 461. $(C_2H_5ClNP)_4$ requires C, 22·0; H, 4·6; N, 12·8%; *M*, 438], which crystallised from benzene–light petroleum and was oxidised and hydrolysed rapidly when exposed to moist air.

Interaction of Phosphoryl Chloride and N-*Methylhexamethyldisilazane*.—Phosphoryl chloride (11·12 ml., 1 mol.) was slowly added to *N*-methylhexamethyldisilazane (21·03 g., 1 mol.) in xylene (25 ml.) at −78°. A steady reaction occurred, and after 24 hr. fractionation gave chlorotrimethylsilane (94%). Pumping off of the solvent left a brittle *solid* which was insoluble in common solvents and had an approximately correct analysis for polymeric $(MeN\cdot POCl)_n$, m. p. $\nless$ 314° [Found: C, 9·25; H, 3·2. $(CH_3ClNOP)_n$ requires C, 10·8; H, 2·7%].

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