

1069. The Formation of Phosphorus-Sulphur Compounds from Phosphorus Halides and Alkylthiosilanes and Silthianes.

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Phosphorus halides and organophosphorus halides react with alkylthiotrimethylsilanes, hexamethyldisilthiane, hexamethylcyclotrisilthiane, and tetramethylcyclodisilthiane to produce a variety of thio-esters of phosphorus, organophosphorus sulphides, phosphorus sulphides, and phosphorus oxy-sulphide. In each case the corresponding organosilicon halide is produced as a volatile by-product.

THE use of silicon-nitrogen compounds as synthetic intermediates in reactions with covalent halides has proved very useful and is now well documented.¹ The corresponding reactions between covalent halides and compounds containing silicon-sulphur bonds are also proving of interest.² Herein, we report the action of various halides of phosphorus upon alkylthiosilanes and silthianes.

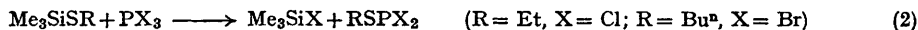
Reactions of compounds containing silicon-sulphur bonds with phosphorus halides were not, in general, as vigorous as those with the aminosilanes and silazanes.^{1b} Usually upon heating, however, evolution of halogenosilane was virtually quantitative, though yields of the residual organophosphorus compounds, after work-up and purification, were not invariably high.

Phosphorus tribromide and trichloride react with alkylthiotrimethylsilanes in the ratio 1:3 to give the trialkyl phosphorotrithioites, P(SR)₃ (reaction 1).

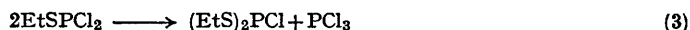


The corresponding reaction between phenylthiotrimethyltin and phosphorus tribromide produced³ trimethyltin bromide and the phenyl phosphorotrithioite.

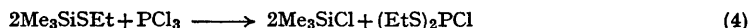
In equimolar proportions the phosphorus trihalides and alkylthiotrimethylsilanes yield the alkyl phosphorodihalogenothioites, RSPX₂ (reaction 2).



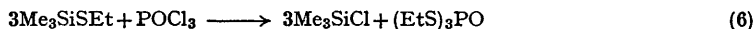
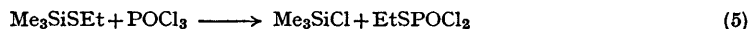
Yields of these dichloro-esters were low after purification by distillation, owing to disproportionation (reaction 3).



The monochloro-ester formed in reaction 3 was also made directly by the interaction of phosphorus trichloride and ethylthiotrimethylsilane in the molar proportion 1:2 (reaction 4).



Phosphoryl chloride and ethylthiotrimethylsilane reacted in the proportions 1:1 and 1:3 (reactions 5 and 6) to give ethyl phosphorodichloridothiolate and triethyl phosphorotrithiolate, respectively.



In reaction 5 it was difficult to separate the dichloro-ester from less-chlorinated products. Only a low yield of the trialkyl ester (reaction 6) was obtained under the conditions used, probably owing to the low reactivity of the last chlorine atom towards replacement. This

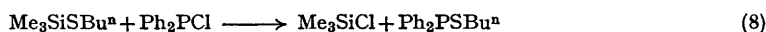
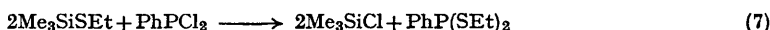
¹ (a) E. W. Abel and D. A. Armitage, *J.*, 1964, 3122; (b) E. W. Abel, D. A. Armitage, and G. R. Willey, *J.*, 1965, 57; (c) E. W. Abel, D. A. Armitage, R. P. Bush, and G. R. Willey, *J.*, 1965, 62; (d) H. Nöth, *Z. Naturforsch.*, 1962, 16b, 618; (e) M. Becke-Goehring and H. Krill, *Chem. Ber.*, 1961, 94, 1059; (f) H. Jenne and K. Niedenzu, *Inorg. Chem.*, 1964, 3, 68.

² E. W. Abel, D. A. Armitage, and R. P. Bush, *J.*, 1964, 2455.

³ E. W. Abel and D. B. Brady, *J.*, 1965, 1192.

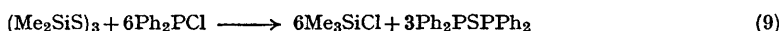
last chlorine was not replaced at all in the corresponding reaction with the dialkylamino-trimethylsilanes.^{1b}

Both chlorine atoms were replaced by alkylthio-groups during the reaction of phenylphosphorus dichloride with ethylthiotrimethylsilane, to give di-S-ethyl phenylphosphonodithioite, $\text{PhP}(\text{SEt})_2$ (reaction 7).



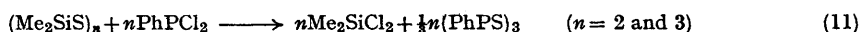
Similarly, diphenylphosphorus chloride can be converted into S-n-butyl diphenylphosphinothioite (Ph_2PSBu^n) by the action of n-butylthiotrimethylsilane (reaction 8).

Diphenylphosphorus chloride reacted with hexamethylcyclotrisilthiane (equation 9).



We believe the product to be bisdiphenylphosphino sulphide, from its mode of formation and properties known to date; it is being fully investigated.

Hexamethyldisilthiane, tetramethylcyclodisilthiane, and hexamethylcyclotrisilthiane all react with phenylphosphorus dichloride to give the same product (reactions 10 and 11).



The same sulphur compound was produced in both cases. It is trimeric, despite the use of a linear and two different ring-size silicon–sulphur compounds as starting materials. The structure is under investigation, and the six-membered ring of alternate phosphorus and sulphur atoms is tentatively proposed.

Phosphorus trichloride and hexamethyldisilthiane react in the ratio 2:3, to evolve trimethylchlorosilane, and form a yellow solid (reaction 12.)



From the stoicheiometry shown, the product should be $(\text{P}_2\text{S}_3)_n$, but no such sulphide of phosphorus is known. After washing and drying the residue, a phosphorus analysis was closer to P_4S_7 than P_4S_6 . Subsequently an X-ray powder photograph, upon comparison with the A.S.T.M. index⁴ showed that predominantly crystalline P_4S_7 was present, with some other faint lines possibly due to lower sulphides. These lower sulphides may have been partly removed upon washing, thus explaining the analysis deviation from P_4S_6 towards P_4S_7 .

Phosphoryl chloride and hexamethyldisilthiane react to produce the pale yellow crystalline oxysulphide $\text{P}_4\text{O}_4\text{S}_6$. This melts sharply and possibly has a structure analogous to P_4O_{10} but with the six bridging oxygen atoms of the cage replaced by sulphur atoms. This would make it also analogous to $\text{P}_4\text{S}_4\text{O}_6$, except that oxygen and sulphur atoms would all be interchanged.⁵



EXPERIMENTAL

In all reactions described, an organosilicon halide was evolved, and was collected and characterised in each case by boiling point, refractive index, and infrared spectrum. In all cases yields of the organosilicon halide were high. Yields of the pure phosphorus compounds varied, depending upon the method of work-up and purification.

Interaction of Phosphorus Trichloride and n-Butylthiotrimethylsilane (reaction 1).—The trichloride (4.21 g.) was added to n-butylthiotrimethylsilane (14.85 g.) at room temperature, and the mixture was heated. During 15 hr. trimethylchlorosilane (78%) was collected, and vacuum-distillation of the residue yielded tri-n-butyl phosphorotrithioite⁶ (4.05 g., 44%), b. p. 114–115°/0.001 mm., n_D^{20} 1.5467 (Found: C, 47.8; H, 8.8. Calc. for $\text{C}_{12}\text{H}_{27}\text{PS}_3$: C, 48.3; H, 9.1%).

⁴ American Society for Testing Materials. X-Ray powder data file. Card No. (10-336) (P_4S_7).

⁵ A. F. Wells, "Structural Inorganic Chemistry," 3rd edn., Oxford University Press, London, 1962, p. 646.

⁶ A. L. Lippert and E. E. Reid, *J. Amer. Chem. Soc.*, 1938, **60**, 2370.

Interaction of Phosphorus Tribromide and Ethylthiotrimethylsilane (reaction 1).—The tribromide (5.26 g.) was added to ethylthiotrimethylsilane (7.81 g.). No heating was noted upon mixing, but, on heating, a steady stream of trimethylbromosilane (92.5%) was evolved. Distillation of the residual oil gave triethyl phosphorotrithioite⁶ (1.66 g., 40%), b. p. 113°/0.6 mm., n_D^{20} 1.5881 (Found: C, 33.9; H, 7.2. Calc. for $C_6H_{15}PS_3$: C, 33.7; H, 7.0).

Interaction of Phosphorus Trichloride and Ethylthiotrimethylsilane (reaction 2).—The trichloride (14.9 g.) and ethylthiotrimethylsilane (14.55 g.) were heated together, and trimethylchlorosilane (92%) was slowly removed. Distillation of the residue gave ethyl phosphorodichlorodithioite⁷ (4.0 g., 23%), b. p. 55–57°/10 mm., n_D^{20} 1.5550 (Found: C, 14.5; H, 3.2. Calc. for $C_2H_5Cl_2PS$: C, 14.2; H, 3.1%), as the expected product, together with diethyl phosphorochlorodithioite,⁷ $(EtS)_2PCl$ (6.0 g., 77% based on reaction 3), b. p. 68°/1 mm., n_D^{20} 1.5871, infrared spectrum identical with that of an authentic sample. During the vacuum-distillation, phosphorus trichloride (4.5 g.) was collected in a liquid-air trap.

Interaction of Phosphorus Tribromide and n-Butylthiotrimethylsilane (reaction 2).—The tribromide (5.43 ml.) and n-butylthiotrimethylsilane (9.26 g.), when warmed, evolved trimethylbromosilane (87%) during $\frac{1}{2}$ hr. Distillation of the residue gave n-butyl phosphorodibromothioite (7.0 g., 47%), b. p. 67°/0.001 mm., n_D^{21} 1.6103 (Found: C, 16.2; H, 3.2. Calc. for $C_4H_9Br_2PS$: C, 17.2; H, 3.2%), and higher-boiling fractions which could not be cleanly separated.

Interaction of Ethylthiotrimethylsilane and Phosphorus Trichloride (reaction 4).—The trichloride (9.30 g.) and ethylthiotrimethylsilane (18.40 g.) were heated together for 14 hr. during which time trimethylchlorosilane (93%) was evolved. Distillation of the residual oil gave a small fore-run and then diethyl phosphorochlorodithioite (5.40 g., 42%), b. p. 78°/1.5 mm., n_D^{20} 1.5881 (Found: C, 31.4; H, 6.5. Calc. for $C_4H_{10}ClPS$: C, 30.6; H, 6.4%).

Interaction of Phosphoryl Chloride and Ethylthiotrimethylsilane (reaction 5).—Phosphoryl chloride (4.06 ml.) and ethylthiotrimethylsilane (5.9 g.), when heated together for 2 hr., evolved trimethylchlorosilane (88%). Distillation of the residual liquid gave mainly ethyl phosphorodichlorodithiolate (4.0 g., 51%) as a colourless oil, b. p. 32°/0.1 mm., n_D^{23} 1.5145 (Found: C, 14.5; H, 2.5. Calc. for $C_2H_5Cl_2OPS$: C, 13.35; H, 2.8%). Considerable difficulty was experienced in the fractionation, owing to the formation of $(EtS)_2POCl$ and $(EtS)_3PO$ which were difficult to remove completely from the main product, thus accounting for the slightly high values in the carbon and hydrogen analyses.

Interaction of Phosphoryl Chloride and Ethylthiotrimethylsilane (reaction 6).—Phosphoryl chloride (12.23 g.) and ethylthiotrimethylsilane (32.00 g.) were heated together, to yield trimethylchlorosilane (95%). Fractionation of the resulting oil gave a large fore-run (7.1 g., b. p. 88–107°/0.001 mm.) and triethyl phosphorotrithiolate⁶ (5.6 g., 32%), b. p. 107°/0.001 mm., n_D^{22} 1.6068 (Found: C, 31.1; H, 6.3. Calc. for $C_6H_{15}OPS_3$: C, 31.3; H, 6.6%).

Interaction of n-Butylthiotrimethylsilane and Diphenylphosphorus Chloride (reaction 8).—The chloride (4.85 g.) and the n-butylthiotrimethylsilane (3.56 g.) evolved trimethylchlorosilane (83%) during heating for 1 hr. Distillation of the residue gave S-n-butyl diphenylphosphinothioite (2.1 g., 43%), b. p. 150°/0.005 mm., n_D^{20} 1.6191 (Found: C, 70.3; H, 6.8. $C_{16}H_{19}PS$ requires C, 70.0; H, 6.9%).

Interaction of Ethylthiotrimethylsilane and Phenylphosphorus Dichloride (reaction 7).—The phenyldichlorophosphine (5.47 g.) was heated with ethylthiotrimethylsilane (8.17 g.) for 2 hr., during which time trimethylchlorosilane (88%) was evolved. Distillation of the residue gave di-S-ethyl phenylphosphonodithioite⁸ (6.0 g., 85%), b. p. 92°/0.001 mm., n_D^{20} 1.6175 (Found: C, 52.3; H, 6.4. Calc. for $C_{10}H_{15}PS_2$: C, 52.1; H, 6.55%).

Interaction of Hexamethylcyclotrisilthiane and Diphenylphosphorus Chloride (reaction 9).—The trisilthiane (5.74 g.) and the chloride (28.15 g.), when heated together, yielded dimethyl-dichlorosilane (73%). A viscous liquid remained which was taken up in benzene; after filtration, addition of light petroleum produced a crystalline white precipitate of crude bisdiphenylphosphino sulphide (10 g., 39%), m. p. 130° (from benzene–light petroleum) (Found: C, 71.3; H, 5.35. $C_{12}H_{10}P_2S$ requires C, 71.6; H, 5.0%), v_{max} . (CS_2) 3140vw, 3076m, 3060vs, 3004w, 1250vs, 1212s, 1189vs, 1160w, 1135s, 1112s, 1099s, 1070m, 1031m, 1002m, 950vs, 919s, 850vw, 750vs, 745vs, 735s, 720s, 699vs, 680sh, 652m, v_{max} . ($CHCl_3$) 1990m, 1970m, 1918m, 1900m, 1820m, 1780w, 1725w, 1672m, 1618w, 1596vs, 1579m, 1480m, 1440m, 1431m, 1415m, 1380m, 1333s, 1312s.

Interaction of Tetramethylcyclodisilthiane with Phenylphosphorus Dichloride (reaction 11,

⁷ A. F. Divinskii, M. I. Kabachnik, and V. V. Sidorenko, *Doklady Akad. Nauk S.S.S.R.*, 1948, **60**, 999.

⁸ A. E. Arbuzof and G. Kh. Kamai, *J. Russ. Phys. Chem. Soc.*, 1929, **61**, 619.

$n = 2$).—The tetramethylcyclodisilthiane (4.85 g.) and phenylphosphorus dichloride (9.63 g.) were heated together to produce dimethyldichlorosilane (93%). Upon cooling, the residue solidified to a crystalline mass which was recrystallized from benzene to give white crystals of *trimeric phenylphosphorus sulphide* (4.0 g., 53%), m. p. 148° [Found: C, 51.2; H, 3.7; P, 21.3; S, 23.1%; M (ebullioscopic in benzene) 419. $(C_6H_5PS)_3$ requires C, 51.4; H, 3.6; P, 22.1; S, 22.9%; M , 420].

Interaction of Hexamethylcyclotrisilthiane and Phenylphosphorus Dichloride (reaction 11, $n = 3$).—The disilthiane (16.75 g.) and the dichloride (33.4 g.) were heated together to evolve dimethyldichlorosilane (91%). Upon cooling, a waxy solid remained, which was recrystallised from benzene to yield trimeric phenylphosphorus sulphide (11 g., 50%), m. p. 145–148° (Found: C, 51.65; H, 4.6%). This was identical with the product obtained in the last experiment (mixed m. p. and infrared spectroscopy).

Interaction of Hexamethyldisilthiane and Phenylphosphorus Dichloride (reaction 10).—Heating together the dichloride (7.84 g.) and disilthiane (7.79 g.) caused evolution of trimethylchlorosilane (90%). Upon cooling, the residual oily crystalline mass was recrystallized twice from benzene, to give trimeric phenylphosphorus sulphide (5.0 g., 82%), m. p. 148–150°, identical with the products from the last two experiments (mixed m. p. and infrared spectra).

Interaction of Hexamethyldisilthiane with Phosphorus Trichloride (reaction 12).—The chloride (4.09 g.) and the disilthiane (7.94 g.) were heated together for 14 hr., to evolve trimethylchlorosilane (6.92 g., 72%), leaving a yellow crystalline mass. This was copiously washed with diethyl ether and then dried under a vacuum (Found: P, 37.0. Calc. for P_2S_3 : P, 39.25%). From an X-ray diffraction powder photograph of this material the values of the corresponding interplanar spacings ("d" values) have been calculated. All of the strongest lines reported for tetraphosphorus heptasulphide P_4S_7 (P = 35.6%) in the A.S.T.M. index are present in our photograph. Other very faint lines appeared to be possibly assignable to lower sulphides such as P_4S_3 and P_4S_5 , but were too faint to record with confidence.

Interaction of Phosphoryl Chloride and Hexamethyldisilthiane (reaction 13).—The chloride (3.39 g.) and the disilthiane (5.90 g.) were heated together, to evolve trimethylchlorosilane (70%), leaving a pale yellow crystalline residue. This was washed copiously with dry diethyl ether. Subsequent pumping (3 hr./0.001 mm.) left pale yellow crystals, m. p. 290–295° (Found: S, 50.1. $P_4O_4S_6$ requires S, 50.6%).

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