Synthesis of a Perfluoro Compound of Phosphorus and Silicon. Tris(trifluorosilyl)phosphine

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Summary Tris(trifluorosilyl)phosphine, the first perfluoro compound of phosphorus and silicon, has been synthesized in high yield from the mercury-sensitized photolysis of Si_2F_6 with PF_3.

COMPOUNDS comprised solely of the elements phosphorus, silicon, and fluorine have not been reported previously; indeed, despite the well developed chemistry of fluoroalkyl-phosphines[1,2] and -phosphoranes,[2] molecules containing the trifluorosilyl group bonded to phosphorus also appear to be unknown.

Our recent discovery[3] that trifluorosilyl radicals can be readily generated *via* mercury-sensitized photolysis of Si_2F_6 has led us to investigate the interaction of these radicals with PF_3. We report here the synthesis and characterization of the compound tris(trifluorosilyl)phosphine obtained from the mercury-sensitized cophotolysis of Si_2F_6 with PF_3.

In a typical reaction, 30 Torr of Si_2F_6, 80 Torr of PF_3, and a small amount of mercury vapour in a 400 ml quartz vessel were irradiated for 90 min at 35 °C with a bank of low-pressure mercury discharge lamps (predominant output at 2537 Å). A small amount of pale yellow translucent film was deposited on the walls of the reaction vessel during the reaction. Volatile products were passed through two traps, the first cooled to -130 and the second to -196 °C, on a glass high vacuum system. The fraction which passed -130 °C and was collected at -196 °C was determined by i.r. analysis to consist solely of SiF_4 and unchanged PF_3. The fraction held at -130 °C was subjected to n.m.r.

analyses, and was found to contain unchanged Si_2F_6, $P(SiF_3)_3$, and very small amounts of $(SiF_3)_2PH$ and Si_2OF_6. 68% of the hexafluorodisilane had reacted; conversion of Si_2F_6 into $P(SiF_3)_3$ was 84%.†

Tris(trifluorosilyl)phosphine is a colourless, air-sensitive liquid at room temperature with a strong, acrid odour. Definitive characterization of the molecule is possible on the basis of fluorine and phosphorus n.m.r. spectra, which include both $P(^{28}SiF_3)_3$ and $F_3{}^{29}SiP(^{28}SiF_3)_2$ species. Coupling constants, chemical shifts, satellite intensities and multiplicities, and heteronuclear decoupling data are all fully consistent with the assigned structure [$P(^{28}SiF_3)_3$: ^{19}F n.m.r. δ 113·7 p.p.m. {d, ^2J(P–F) 1·8 Hz} (upfield from external $CFCl_3$), ^{31}P n.m.r. δ 324·9 p.p.m. {decet, ^2J(P–F) 1·7 Hz} (upfield from external 85% H_3PO_4); $F_3{}^{29}SiP(^{28}SiF_3)_2$: ^{19}F n.m.r. {d of d of septets, ^1J(Si–F) 308·0, ^3J(F–F) 2·6 Hz}, ^{31}P n.m.r. {^1J(Si–P) 22·5 Hz}]. Further characterization of the molecule is afforded by its i.r. and mass spectra. A mass spectrum taken at a low (*ca.* 12 eV) ionizing voltage contained only the molecular ion at *m/e* 286 and a fragment ion at *m/e* 182 corresponding to loss of the very stable neutral SiF_4 from the molecular ion. Similar behaviour has been observed for other polyfluoropolysilanes.[4] The i.r. spectrum of the molecule contains characteristic SiF_3 stretching modes at 1001 and 839 cm^{-1}.

$P(SiF_3)_3$ is hydrolysed by stoicheiometric amounts of water vapour to PH_3, Si_2OF_6, and SiF_4; however, presence of smaller quantities of water leads to production of the species $(SiF_3)_2PH$‡ and SiF_3PH_2.§ Excess of bromine readily cleaves the Si–P bonds at room temperature to give PBr_5 and SiF_3Br. The corresponding reaction with anhydrous hydrogen bromide is rather more complex as SiF_4 is liberated along with SiF_3Br.

Complete separation of $P(SiF_3)_3$ from Si_2F_6 is difficult on a vacuum line. The most convenient route to the pure compound is an extended (3—4 h) photolysis of PF_3 with Si_2F_6, since attack of excited mercury atoms on Si_2F_6 is apparently faster than on the Si–P bonds in the product.

When Si_2F_6–PF_3 mixtures are photolysed for much shorter periods (10 min), the predominant product is still $P(SiF_3)_3$. No clear evidence for the presumed intermediate compounds SiF_3PF_2 and $(SiF_3)_2PF$ has yet been obtained in any of the above systems.

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† Based on the equation: $3Si_2F_6 + PF_3 \rightarrow 3SiF_4 + P(SiF_3)_3$.

‡ Characterized by n.m.r. and mass spectra.

§ Characterized by mass spectra.

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