Tristrifluoromethylbis(trimethylsiloxy)phosphorane, $(CF_3)_3P[OSi(CH_3)_3]_2$, and Bistrifluoromethyltrimethylsiloxyphosphine Oxide, $(CF_3)_2P(O)OSi(CH_3)_3$

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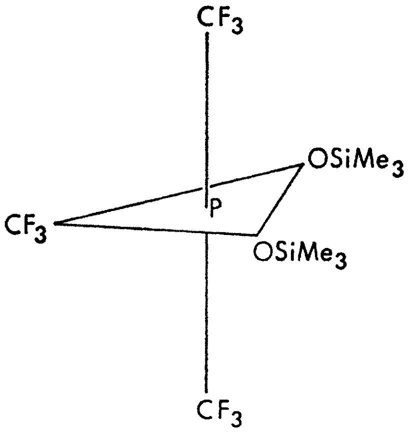
Summary Direct combination of $(CF_3)_3PO$ with hexamethyldisiloxane yields the new phosphorane $(CF_3)_3P(OSiMe_3)_2$ which thermally decomposes to $(CF_3)_2P(O)OSiMe_3$; the latter new compound can also be obtained by reaction of $(CF_3)_2P(O)Cl$ with hexamethyldisiloxane.

THE reaction of tristrifluoromethylphosphine oxide[1] (in excess) with hexamethyldisiloxane in a sealed glass tube at room temperatures for several days gave a nearly quantitative yield of the addition compound tristrifluoromethylbis(trimethylsiloxy)phosphorane which was separated by means of a vacuum reflux distillation column.[2] The i.r. spectrum of the low volatile liquid in both liquid and gas phases was completely clear in the 1300—2000 cm^{-1} region indicating the absence of a P=O stretching band. A strong band at 1070 cm^{-1} can be assigned to the P–O–Si structure. The room temperature ^{19}F n.m.r. spectrum shows a doublet (ϕ 69·7 p.p.m. *vs.* CCl_3F; $^2J_{PF}$ 108·5 Hz) and the ^1H n.m.r. spectrum shows a moderately broad singlet (τ 9·52) due to equivalent $OSiMe_3$ groups which do not show observable coupling with phosphorus. The room temperature ^{31}P n.m.r. spectrum shows an eight line pattern ($^2J_{PF}$ 108 Hz) centred at +205 p.p.m. *vs.* P_4O_6 with an intensity distribution in good agreement with that expected for the central eight lines of a ten line pattern arising from nine equivalent fluorine atoms thus confirming the presence of three CF_3 groups on phosphorus. All observed peaks are distinctly separated from those arising from the starting materials with the most definitive evidence for the phosphorane being provided by the very high field ^{31}P chemical shift value.[3,4] Chemical confirmation of the formula was provided by the reaction of three moles of dimethylamine with one of the phosphorane according to equation (1)

$$(CF_3)_3P(OSiMe_3)_2 + 3Me_2NH \rightarrow CF_3H + 2Me_2NSiMe_3 + Me_2NH_2{}^+O_2P(CF_3)_2{}^- \quad (1)$$

for which a satisfactory mass balance was obtained. All of the products were identified by a combination of mass, i.r., and n.m.r. spectroscopy.[5]

Apart from the known substituted phosphorus pentahalides, few five-co-ordinate phosphorus compounds are known which contain only organic or organometallic substituents. The present case is related to the cyclic oxyphosphoranes[6] and $(EtO)_5P$[7] but it appears to be the first pentaphosphorane to be synthesised directly from the phosphine oxide. It is surprising, in view of the high bond energy of the P=O bond, that this structural unit is sacrificed in favour of the formation of P–O–Si bridges, but this must be a more favourable bonding situation, possibly as a result of strong π-bonding between oxygen and both phosphorus and silicon.



FIGURE

The doublet pattern observed in the ^{19}F n.m.r. spectrum of the phosphorane at room temperature collapses completely at 0° and provides two broad chemically shifted regions which appear to resolve at distinctly different temperatures between −40° and −100°. At −70° the low-field component is clearly resolved into a doublet of septets (ϕ 63·7 p.p.m. *vs.* CCl_3F, $^2J_{FF}$ 115·5, $^4J_{FF}$ 13·5 Hz) arising from coupling between non-equivalent CF_3 groups.

The high-field component centred about 72 p.p.m. is complex and resolves only partially even at −100° into a doublet (*J ca.* 108 Hz) of apparent quartets plus additional peaks spread over a region of several hundred cycles, suggesting that this part of the spectrum is second order. These spectral features become much sharper at −140° and, in addition, the low-field doublet of septets shows additional splitting. A complete analysis of the spectrum is in progress. It is clear, however, that CF_3 groups exist in two different environments at low temperatures thus excluding from three alternative trigonal-bipyramidal structures the structure in which all CF_3 groups occupy the equatorial plane of the trigonal bipyramid. Because the ^1H n.m.r. spectrum of the $OSiMe_3$ groups is unchanged from room temperatures to −140°, the second alternative structure involving one axial and one equatorial $OSiMe_3$ group can be excluded leaving as the most probable structure the one shown in the Figure.

Thermal decomposition of the phosphorane yields principally $(CF_3)_2P(O)OSiMe_3$ which is also obtained from reaction (2). The ^{19}F n.m.r. spectrum of $(CF_3)_2P(O)OSiMe_3$ at room temperatures is a doublet (ϕ 73·1 p.p.m. *vs.* CCl_3F, $^2J_{PF}$ 122 Hz), the ^1H n.m.r. spectrum a singlet (τ 9·47), and the ^{31}P n.m.r. spectrum shows a septet (δ +143·4 p.p.m. *vs.* P_4O_6, $^2J_{PF}$ 122 Hz). I.r. and mass spectra further confirm the identification.

$$(CF_3)_2P(O)Cl + Me_3Si{\cdot}O{\cdot}SiMe_3 \rightarrow (CF_3)_2P(O)OSiMe_3 + Me_3SiCl \qquad (2)$$

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