Cleavage of the Silicon–Carbon Bond by a Phosphorus Fluoride: Methylene(bis)tetrafluorophosphorane

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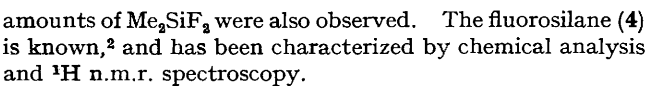
Summary Methylene(bis)tetrafluorophosphorane has been prepared by cleavage of the Si–C bond of 1,1,3,3-tetramethyl-1,3-disilacyclobutane with phosphorus pentafluoride; it has been characterized by chemical means and by n.m.r. and mass spectroscopy.

The cleavage reactions of element–trimethylsilyl linkages, E-SiMe$_3$ (E = N, P, O, S) with phosphorus pentafluoride and its derivatives, $\mathrm{R}_n\mathrm{PF}_{5-n}$ (n = 0—3; R = hydrocarbon group) have been applied extensively to the synthesis of derivatives of PF$_5$ with substituents containing these heteroatoms.[1] We now report the first case of cleavage of a silicon–carbon bond by a phosphorus fluoride, which gives rise to a novel type of tetrafluorophosphorane, methylene(bis)tetrafluorophosphorane (3), in addition to (4), small amounts of Me$_2$SiF$_2$ were also observed. The fluorosilane (4) is known,[2] and has been characterized by chemical analysis and ^{1}H n.m.r. spectroscopy.



$$\begin{matrix}\mathrm{Me_2Si{-}CH_2}\\ |\quad\;\; |\\ \mathrm{CH_2{-}SiMe_2}\end{matrix} + 2\mathrm{PF_5} \rightarrow \mathrm{F_4PCH_2PF_4} + \mathrm{FMe_2SiCH_2CH_2SiMe_2F}$$

(1) (2) (3) (4)

The bis-tetrafluorophosphorane (3) is a volatile, highly reactive liquid, b.p. *ca.* 68 °C (estimated from its vapour pressure curve), and it was characterized by n.m.r. spectroscopy. From ^{19}F and ^{31}P n.m.r. spectra between +30 and −100 °C it is evident that fast positional exchange of ligands at phosphorus occurs throughout the temperature range accessible. Such exchange is typical of PF$_5$ and many of its substitution products.[1]

The ^{1}H n.m.r. spectrum shows a 1:2:1 triplet; each component of the triplet is split into 9 lines (equal coupling between ^{1}H and 8 ^{19}F nuclei of the two PF$_4$ groups); δ_{H} + 3·27 (int. Me$_4$Si); $^2J_{\mathrm{PH}}$ 25·9Hz; $^3J_{\mathrm{HF}}$ 6 Hz. The ^{19}F n.m.r. spectrum is a second-order spectrum of type X$_4$AA′X′$_4$ with δ_{F} − 40·2 p.p.m. (int. CCl$_3$F) separation of the main peaks $|^1J_{\mathrm{PF}} + {}^3J_{\mathrm{PF}}|$ 965·3 Hz. The ^{31}P n.m.r. spectrum shows −22·6 p.p.m. (ext. H$_3$PO$_4$).

The mass spectrum of (3) exhibited a minor parent peak at *m/e* 228 [CH$_2$(PF$_4$)$_2^+$] of relative intensity 0·4; the strongest fragment was PF$_4^+$ at *m/e* 107, as for other alkyltetrafluorophosphoranes.[5]

Two carbon–phosphorus bonds were formed in (3) during the cleavage reaction of (1) with (2); stepwise hydrolysis of (3) gave rise to the bis-phosphonic difluoride (5) and methylene (bis)phosphonic acid, respectively. Compound

$$\underset{(\mathbf{3})}{CH_2(PF_4)_2} \xrightarrow{H_2O} \underset{(\mathbf{5})}{CH_2[P(:O)F_2]_2} \xrightarrow{H_2O} \underset{(\mathbf{6})}{CH_2[P(:O)(OH)_2]_2}$$

(**5**) was identified by its ^{19}F n.m.r. spectrum which was identical to that of the authentic compound, synthesized by an independent route[3] [δ_F − 58·5 p.p.m. (int. CCl_3F); J_{PF} 1130 Hz]. The bisphosphonic acid (**6**) is also known.[4] We identified our hydrolysis product as (**6**) by ^{31}P n.m.r. spectroscopy; J_{PH} 20 Hz; δ_P + 17·6 p.p.m. (from ext. H_3PO_4); lit.[4b] + 17·8 p.p.m.

We thank Professor G. Greber and Dr. W. R. Bamford (I.C.I.) for samples of the disilacyclobutane. W. A. and H.K. acknowledge support through Verband der Chemischen Industrie and Deutsche Forschungsgemeinschaft.

(*Received*, 27*th January* 1975; *Com.* 094.)

[1] See, for example: R. Schmutzler, in 'Halogen Chemistry,' Vol. 2, ed. V. Gutmann, Academic Press, London and New York, 1967, pp. 31 ff.

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