The Synthesis of a Trifluorophosphorane and a Diazadiphosphetidine Containing the Perfluoropinacolyl Ring System

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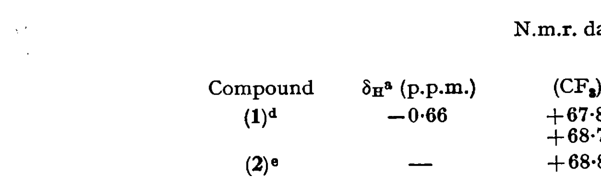
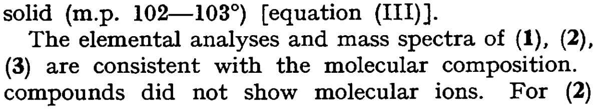
Summary Perfluoropinacolyltrifluorophosphorane is prepared by reaction of PF_5 with perfluoropinacolyl-bis-(trimethylsilyl)aminodifluorophosphorane (**1**); (**1**) yields a diazadiphosphetidine on pyrolysis.

Perfluoropinacol can form chelate ring systems of high stability for a number of heteroatoms.[1] Oxidation reactions of P^{III} compounds with hexafluoroacetone yield phosphoranes containing the pinacolyl ring system.[2] Mono- and difluorophosphoranes have also been prepared in this way.[3] We now report the synthesis of the parent compound of these fluorophosphoranes and the preparation of the first diazadiphosphetidine involving the perfluoropinacolyl unit, from an organosilicon aminodifluorophosphorane precursor (**1**). (**1**) was prepared by the reaction of bis-(trimethylsilyl)aminodifluorophosphine[4] with hexafluoroacetone [equation (I)].



(I)

Attempts at the oxidation of PF_3 with hexafluoroacetone have not been successful. The reaction of (**1**) with PF_5, however, produced perfluoropinacolyltrifluorophosphorane (**2**) in 70% yield [equation (II)]. No evidence was found for a $F_3P{=}N$-group linked to phosphorus. (**2**) is a liquid (b.p. 55°, m.p. −10°) which fumes strongly in air, and is one of the few examples of a dioxytrifluorophosphorane.[5]



(II)

(**1**) was also found to eliminate Me_3SiF above 150° to give quantitatively a phosphetidine (**3**) which was a stable white solid (m.p. 102—103°) [equation (III)].

The elemental analyses and mass spectra of (**1**), (**2**), and (**3**) are consistent with the molecular composition. The compounds did not show molecular ions. For (**2**) the

Table

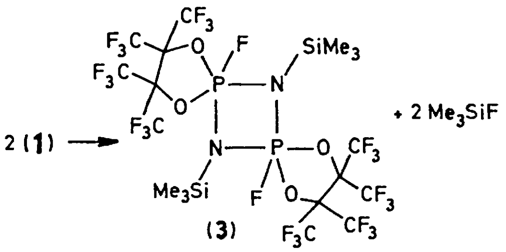
N.m.r. data of (**1**), (**2**), and (**3**)

Compound	δ_H[a] (p.p.m.)	δ_F[b] (p.p.m.)		δ_P[c] (p.p.m.)	J_{PF} (Hz)
		(CF_3)	(PF)		
(**1**)[d]	−0·66	+67·8 +68·7	+38·6	+40·5	876
(**2**)[e]	—	+68·8	+65·2	+54·5	935[f]
(**3**)[g]	−0·25	+67·1 +70·3	+69·5	+47·5	994[h]

[a] Measured at 60 MHz relative to internal Me_4Si reference. [b] Measured at 56·4 MHz relative to internal CCl_3F reference. [c] Measured at 24·3 MHz relative to external 85% H_3PO_4 reference. [d] 50% solution in CH_2Cl_2. [e] Neat liquid. [f] ${}^4J_{PF}$ 0·8 Hz; ${}^5J_{FF}$ 2·1 Hz. [g] 15% solution in CCl_4. [h] $|{}^1J_{PF} + {}^3J_{PF}|$.

highest mass peak was $(M - \mathrm{F})^+$ (low abundance of M^+ is common for fluorophosphoranes[6]) while for (**1**) and (**3**) peaks due to $(M - \mathrm{Me})^+$ were observed (typical for $\mathrm{Me_3Si}$ containing substances[7]). The base peak in the fragmentation patterns of (**1**), (**2**), and (**3**) was the ion $\mathrm{CF_3}^+$ and the characteristic breakdown of the remaining pinacolyl unit was also found. The presence of this unit was indicated by absorptions[1] in the i.r. spectra. The ambient temperature n.m.r. data are listed in the Table.

The fluxional character of these compounds is of considerable interest, *e.g.* the temperature-dependent non-equivalence of sets of $\mathrm{CF_3}$ groups in (**1**) and (**3**). Hyperfine coupling constants were observed consistent with the structures shown. Similar effects have been found by other workers[8] and the relevant spectra are at present under investigation.



(III)

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