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THE CHEMISTRY OF A PHOSPHORANIDE ANION, STABILIZED BY THE PERFLUOROPINACOLYL GROUPING

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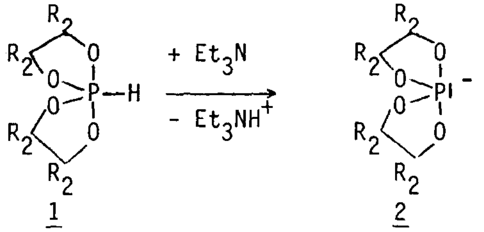
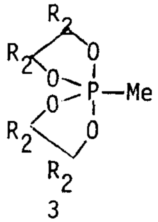
The hydrophosphorane 1 and triethylamine gives the phosphoranide anion 2.



(R= CF_3)

Compound 1 is obtained easily from the chlorophosphite $ClP[OC(CF_3)_2C(CF_3)_2O]$ and triethylammonium perfluoropinacolate. The x-rax structure analysis exhibits a rather unusual, distorted trigonal bipyramidal geometry. The difference in length of the axial P-O bonds is remarkable (0.25 Å). Species 2 can be considered a model of a stable intermediate in a $S_N2(P)$ reaction. The 31-P nmr spectrum shows that 2 is in solution in an equilibrium with a monocyclic λ^3P phosphite alkoxide. Methyliodide reacts with the title compound to yield the methyl spirophosphorane 3, whereas the analogous reaction with trimethylsilyl iodide furnishes the λ^3P derivative 4.



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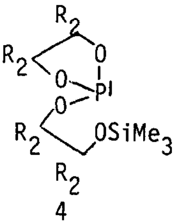

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(R= CF_3)

The phosphoranide anion 2 attacks benzyl bromide and acetyl chloride as a nucleophile, a benzyl and a acetyl spirophosphorane are obtained. The hydrolysis of 2 gives phosphorous acid and perfluoropinacole. Reactions with halogens yield halogenospirophosphoranes which react with water to form a stable hydroxyphosphorane.