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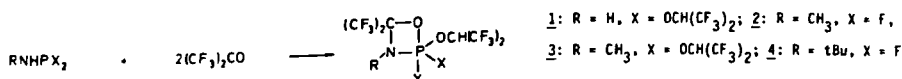
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# Reaction of Hexafluoroacetone with Aminophosphites Containing the 2,2,2-Trifluoro-1-(trifluoromethyl)ethyl Grouping

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The reactions of dihaloaminophosphines  $\text{RNHPF}_2$  ( $\text{R}=\text{H}$ , Me, tBu) and  $\text{R}_2\text{NPCl}_2$  ( $\text{R}=\text{Me}$ , Et, SiMe<sub>3</sub>;  $\text{R}_2=\text{CH}_2(\text{CH}_2\text{CMe}_2)_2$  with  $\text{LiOCH}(\text{CF}_3)_2$  yield the corresponding aminophosphites  $\text{R}_2\text{NP}[\text{OCH}(\text{CF}_3)_2]_2$ . Hexafluoroacetone reacts with  $\text{RNH}[\text{OCH}(\text{CF}_3)_2]_2$  as well as  $\text{MeNHPF}_2$  and  $\text{tBuNHPF}_2$  in good yields to the 1,3,5 $\lambda^5$ -oxazaphosphoranes 1 - 4, which show rapid pseudorotation at room temperature.



The X-ray structure of 1 exhibits a distorted trigonal bipyramid.

With dialkylaminophosphites hexafluoroacetone gives the monocyclic phosphoranes 5 and 6, whereas with aminophosphites containing bulky alkylgroups no reaction occurs. A replacement of the  $(\text{CF}_3)_2\text{CHO}$ -groups by smaller substituents results in easier addition of hexafluoroacetone. Therefore the aminophosphines  $\text{tBuP}(\text{X})\text{NEt}_2$  ( $\text{X}=\text{F}$ , Cl,  $\text{OCH}(\text{CF}_3)_2$ ) react with hexafluoroacetone in high yields to the 1,3,2 $\lambda^5$ -dioxaphospholanes 7 - 9. The phosphoranes 5 - 9 show no ligand exchange process at room temperature.

