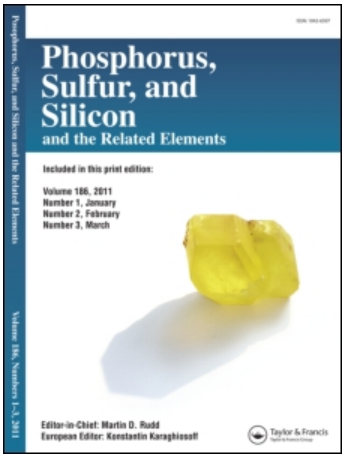


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

The Reactivity of Hexafluorothioacetone and Hexafluoroacetone versus Phosphites

Joachim Heine[a]; Gerd-Volker Röschenthaler[a]
[a] Fachbereich 2 (Biologie/Chemie) der Universität, Bremen, Federal Republic of Germany

To cite this Article Heine, Joachim and Röschenthaler, Gerd-Volker(1987) 'The Reactivity of Hexafluorothioacetone and Hexafluoroacetone versus Phosphites', Phosphorus, Sulfur, and Silicon and the Related Elements, 30: 3, 722
To link to this Article: DOI: 10.1080/03086648708079216
URL: http://dx.doi.org/10.1080/03086648708079216

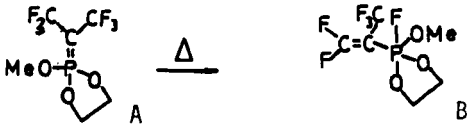
The Reactivity of Hexafluorothioacetone and Hexafluoroacetone versus Phosphites

Joachim Heine and Gerd-Volker Röschenthaler *

Fachbereich 2 (Biologie/Chemie) der Universität,

D-28 Bremen 33, Federal Republic of Germany

The dimer of hexafluorothioacetone reacted with various phosphites to form thiophosphates and bis(trifluoromethyl)methylenphosphoranes, being unstable in the case of $(Me_3SiO)_nP(OMe)_{3-n}$ (n = 1-3), where phosphonates $(Me_3SiO)_{n-1}(MeO)_{3-n}P(O)\left[C(CF_3)=CF_2\right]$ (n = 1-3) and Me_3SiF were observed. In general, cyclic phosphites behaved similar to acyclic ones. The resulting bis(trifluoromethyl)methylenphosphoranes were thermally stable except compound A, because of a new intramolecular fluorine transfer to phosphorus forming fluorophosphorane B.



A B

Hexafluoroacetone, however, reacted with the silylphosphites mentioned above to furnish phosphonates $(MeO)_{3-n}(Me_3SiO)_{n-1}P(O)C(CF_3)_2OSiMe_3$ (n = 1-3), which on heating rearranged loosing Me_3SiF to give phosphoric acid esters $(MeO)_{3-n}(Me_3SiO)_{n-1}P(O)\left[OC(CF_3)=CF_2\right]$, precursors for $HOC(CF_3)=CF_2$. Cyclic phosphites gave 1:2 adducts, spirocyclic 1,3,2λ^5- and 1,3,4λ^5-dioxaphospholanes, in their reactions with hexafluoroacetone. A 2 D homocorrelated ^{19}F-NMR spectrum proved a long range F-F-coupling through a non-bond mechanism in a 1,3,4λ^5-dioxaphospholane.