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The Reactivity of Hexafluorothioacetone and Hexafluoroacetone versus Phosphites

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The dimer of hexafluorothioacetone reacted with various phosphites to form thiophosphates and bis(trifluoromethyl)methylenphosphoranes, being unstable in the case of $(\text{Me}_3\text{SiO})_n\text{P}(\text{OMe})_{3-n}$ ($n = 1-3$), where phosphonates $(\text{Me}_3\text{SiO})_{n-1}(\text{MeO})_{3-n}\text{P}(\text{O})[\text{C}(\text{CF}_3)=\text{CF}_2]$ ($n = 1-3$) 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.



Hexafluoroacetone, however, reacted with the silylphosphites mentioned above to furnish phosphonates $(\text{MeO})_{3-n}(\text{Me}_3\text{SiO})_{n-1}\text{P}(\text{O})\text{C}(\text{CF}_3)_2\text{OSiMe}_3$ ($n = 1-3$), which on heating rearranged losing Me_3SiF to give phosphoric acid esters $(\text{MeO})_{3-n}(\text{Me}_3\text{SiO})_{n-1}\text{P}(\text{O})[\text{OC}(\text{CF}_3)=\text{CF}_2]$, precursors for $\text{HOC}(\text{CF}_3)=\text{CF}_2$. Cyclic phosphites gave 1:2 adducts, spirocyclic $1,3,2\lambda^5$ - and $1,3,4\lambda^5$ -dioxaphospholanes, in their reactions with hexafluoroacetone. A 2 D homo-correlated ^{19}F -NMR spectrum proved a long range F-F-coupling through a non-bond mechanism in a $1,3,4\lambda^5$ -dioxaphospholane.