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REACTIONS OF HEXAFLUOROACETONE WITH PHOSPHORUS(III) COMPOUNDS

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Hexafluoroacetone reacts with PH3 and MePH2 under insertion into the P-H bond yielding either H₂PC(CF₃)₂OH and HP[C(CF₃)₂OH]₂ or Me(H)PC(CF₃)₂OH and $MeP[C(CF_3)_2OH]_2$ whereas Me_2PH gives a mixture of $Me_2P(F)[OCH(CF_3)_2]_2$, Me_2PPMe_2 , and $Me_2P(0)OCH(CF_3)_2$. Me_3P forms a dialkoxyphosphorane if there is a 1 : 2 ratio (Me₃P : (CF₃)₂CO). H₂PC(CF₃)₂OH and HP[C(CF₃)₂OH]₂ are easily O-silylated to give H_PC(CF3)_OSiMe3 and HP[C(CF3)_OSiMe3]2. The monosilylated compound is oxidized by chlorine(bromine) under cleavage of the P-C bond furnishing $PCl_3(PBr_3)$, $(CF_3)_2CO$, and $Me_3SiCl(Me_3SiBr)$. The P-C bond stays intact using N-chloro(bromo)succinimide where H(X)PC(CF₃)₂OSiMe₃ (X = C1, Br) is obtained. $H(F)PC(CF_3)_2OSiMe_3$ is available from the bromo precursor by fluorination with SbF_3 . Similar procedures are applied for the synthesis of $X_2PC(CF_3)_2OSiMe_3$ and $XP[C(CF_3)_2OSiMe_3]_2$ (X = F, C1, Br). The corresponding iodo derivatives are thermally unstable. H(Br)PC(CF3)20SiMe3 can be converted by Me_3N to $[Me_3Si0(CF_3)_2CP]_n$ (n = 2, 3). Me_3P and $(CF_3)_2CO$ in the ratio 1 : 1 gives a fluorophosphetane besides other products. The pyrolysis of this four membered ring system leads to $Me_2P(0)F$ and $(CF_3)_2C=CH_2$, the hydrolysis to the phosphine oxide Me₂P(0)CH₂(CF₃)₂OH.