

C(CF₃)₂OH → OCH(CF₃)₂ ISOMERISM IN SOME SULFUR AND PHOSPHORUS COMPOUNDS

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The insertion of (CF₃)₂CO into the P-H bond of Me_nH_{3-n}P yields Me_nH_{2-n}PC(CF₃)₂OH and Me_nH_{1-n}P[C(CF₃)₂OH]₂ (n=0,1), respectively [1]. MeP[C(CF₃)₂OH]₂ rearranges giving the diphosphine [MePOCH(CF₃)₂]₂ and the phosphorane MeP[OCH(CF₃)₂]₄. Me₂PH reacts with (CF₃)₂CO forming several products, e.g. MePF[OCH(CF₃)₂]₂ and Me₂PPMe₂ [1]. The phosphines tBu(R)PH(R=Me, tBu), however, add (CF₃)₂CO giving rise to the phosphinites tBu(R)POCH(CF₃)₂, which furnish stable phosphonium salts upon treating with MeI. (CF₃)₂CO inserts into the S-H bond of RSH to yield RSC(CF₃)₂OH (R=H, Me, Ph), which were reacted with MeI, too. Reacting SCl₂ with LiOCH(CF₃)₂ gives S[OCH(CF₃)₂]₂ which is oxidised by chlorine to the sulfurane ClS[OCH(CF₃)₂]₃ [2]. The sulfurane is able to transfer (CF₃)₂CHO groups to phosphorus(III) compounds, e.g. P[OCH(CF₃)₂]₃ and Me₃P yielding P[OCH(CF₃)₂]₅ and [Me₃POCH(CF₃)₂]⁺Cl⁻. ClS[OCH(CF₃)₂]₃ gives a stable salt upon reaction with SbCl₅, like ClP[OCH(CF₃)₂]₄. The mechanisms for these reactions are discussed.

1 G.-V. Röschenenthaler, Z. Naturforsch. 33b, 311 (1978).

2 G.-V. Röschenenthaler, Angew. Chem. 89, 900 (1977).

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