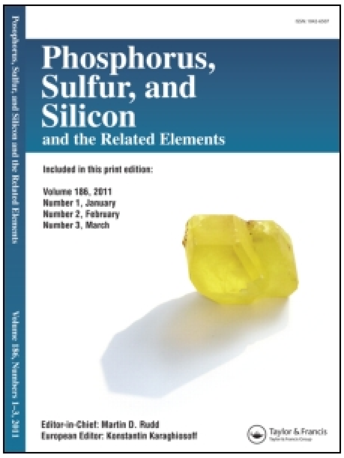

Phosphorus, Sulfur, and Silicon and the Related Elements

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Halogenotropy in Phosphorus-Carbon Diad

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HALOGENOTROPY IN PHOSPHORUS-CARBON DIAD

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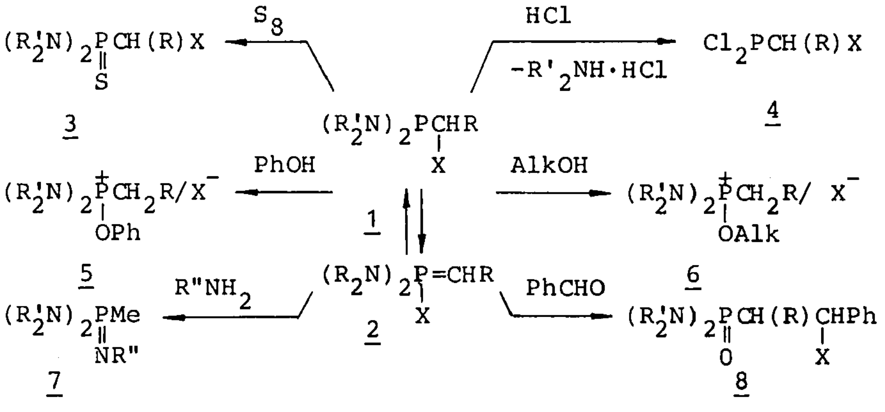
NMR and chemical studies have shown that α-halogenoalkylphosphines 1 and P-halogenoylids 2 exist as halogenotropic tautomeric systems. The position of the equilibrium depends on the used solvent, temperatures and substituents at the α-carbon atom. For example, the equilibrium 1 2 shifts towards the phosphine from 1 if the substituents at the α-carbon atom are electron-donating (R = H, Me, Pr, i-Pr). These compounds, existing preferably in the phosphine form, undergo typical reactions both for tervalent phosphorus compounds and P-halogenoylids. Tervalent phosphorus compounds, α-halogenoalkylphosphines 1 add sulfur and react with anhydrous HCl to convert into the dichlorophosphines 4. Like the P-halogenoylids, they add alcohols and phenols forming the phosphonium salts 5, 6, react with primary amines and aniline to yield the iminophosphonates 7. They also form the 2-halogenoalkylphosphonates 8 in the reaction with aldehydes



The products 5-8 are formed via the reactions of alcohols, phenols, amines, and benzaldehyde with the ylid halogenotropic form 2 which exists in the tautomeric equilibrium with the phosphine form 1.