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Element-Substituted Acylphosphines

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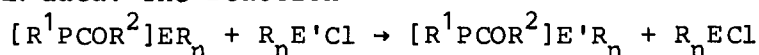
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ELEMENT-SUBSTITUTED ACYLPHOSPHINES

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Element-substituted acylphosphines are stable in form $R^1P(ER_n)COR^2$ (A), when $E=Ge, Sn, Sb, P, Tl$ and in form $R^1P=C(OER_n)R^2$ (B), when $E=Si$. The structures are confirmed by NMR data. The reaction



was investigated. The unstable compounds (A), which were formed in petroleum ether ($E=Li, E'=B, Si, R^2=i-Pr$), rearranged to O-E-isomers. On the other hand O-Z-isomers were kinetically controlled products in dimethoxyethane as a solvent (E,Z-equilibria, catalyzed by R_nEX^1 followed). When $E=Tl$ and $E'=Ge, P$ ($R=i-Pr$), kinetically controlled reaction gave isomers (B), which rearranged slowly into (A). Only thermodynamically stable isomers were identified under more strict conditions for other substituents. The conversion of E into E' was irreversible (except Sn and Ge) in the series $Tl \rightarrow Sn \rightleftharpoons Ge \rightarrow Si \rightarrow B \rightarrow P$.

The irreversible prototropic rearrangement of compounds (B) ($E=B, Si, R^2=i-Pr$) to vinylphosphines $R^1P(H)C(OER_n)=CMe_2$, taking place under the action of nucleophilic or electrofilic catalysts², was found.

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