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## Dialkylaminoethylation of Trimethylsilyl Esters of Trivalent Phosphorus Acids

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DIALKYLAMINOETHYLATION OF TRIMETHYLSILYL ESTERS OF TRIVALENT PHOSPHORUS ACIDS

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Dialkylaminomethylation of trimethylsilyl esters of trivalent phosphorus acids using bis(dialkylamino)methanes was carried out for the first time. This reaction is a convenient method for preparation of quaternary coordinated phosphorus compounds, including dialkylaminomethyl and functional groups. Thus trimethylsilylphosphites and -phosphonites of various structures react with bis(dialkylamino)-methanes according to Arbuzov reaction in the presence of zinc chloride as a catalyst, when heated to 120°C, resulting in formation of phosphonates and phosphinates (I).

$$\begin{array}{c}
\text{RO} \\
\text{X} & \text{POSiMe}_{3} + (R_{2}^{N})_{2}^{CH_{2}} \xrightarrow{\text{ZnCl}_{2}} & \text{RO} \\
& & \text{RO}_{2}^{NSiMe}_{3} & \text{X} & \text{PCH}_{2}^{NR_{2}}
\end{array}$$

 $R = Alk, X = AlkO, (AlkO)_2CH, Me_3SiOCH_2$ 

Trimethylsilylhypophosphites, including two highly reactive fragments (PH and POSi), react with the excess of bis(dialkylamino)methane via double dialkylaminomethylation to give bis(dialkylaminomethyl)phosphinates (II).

$$\begin{array}{c} \text{RO} \\ \text{PH} + 2 \left( \text{R}_2^{\text{I}} \text{N} \right)_2 \text{CH}_2 \end{array} \xrightarrow{\begin{array}{c} \text{ZnCl}_2 \\ -\text{R}_2^{\text{I}} \text{NH}, \text{ R}_2^{\text{I}} \text{NSiMe}_3 \end{array}} \begin{array}{c} \text{ROP} \left( \text{CH}_2 \text{NR}_2^{\text{I}} \right)_2 \end{array} \qquad \text{II}$$

 $R = Alk, Me_3Si; R' = Alk$ 

Under similar conditions the reaction between dialkyl(tri-methylsilyl)phosphites and dimethylformamide dimethylacetal proceeds with trimethyl(methoxy)silane splitting off and tetraalkyl(dimethylaminomethylene)diphosphonates formation.