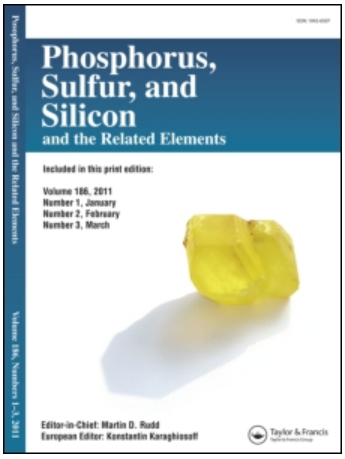

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New Directions in the Reactions of Heterosubstituted Carbcations with Phosphites

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NEW DIRECTIONS IN THE REACTIONS OF HETEROSUBSTITUTED CARBCATIONS WITH PHOSPHITES

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A restriction of the Arbuzov reaction for the interaction of alkylchlorides with trialkylphosphites was found. A different way of reaction leading to realkylation was observed for some amidonium compounds of chloroderivatives of ternary amides and lactams capable to self O-alkylation. The way is preferably realized for phosphites with increased electrophility of α-carbon ethers (1).

$$RCl + (R'O)_3P \longrightarrow ROP(OR')_2 + R'Cl$$

R = $(CH_2)n$ N<(C=O) ; n = 2, 3; $(CH_2)_4C(=O)NR''_2$; R',R" = Alk

A new reaction was also observed for di- and trialkylphosphites reacting with phosphorylsubstituted carbonic cations obtained from α-heterosubstituted phosphonates. The reaction proceeds with disruption of respective phosphonates and results in the replacement of the phosphoryl and alcoxygroups by a phosphoryl group (2).

$$(RO)_2P(=O)-\underset{OR'}{\overset{X}{C}}NMe_2 + (R''O)_2PHO \longrightarrow (RO)_2P(=O)OR' + (R''O)_2P(=O)\overset{X}{C}HNMe_2$$

R, R',R" = Alk; X = NMe_2, OEt

$$\begin{matrix} EtO \\ R \end{matrix}\!\!>\!P(=O)-\underset{OEt}{CH}NMe_2 + (EtO)_3P \longrightarrow RP(=O)(OEt)_2 + (EtO)_2P(=O)CH_2NMe_2 + C_2H_4$$

R = EtO, Ph

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(2) V.V.Moskva, V.U.Mavrin, Zn. Obshch. Khim. 58, 1667-1670, (1988).