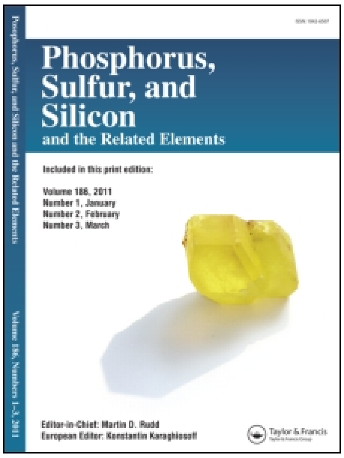

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Mechanism of the Reaction of Nucleophiles >P-O$^-$ with the C-Br Bond. Bromophosphate as an Intermediate

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MECHANISM OF THE REACTION OF NUCLEOPHILES >P-O$^-$ WITH THE C-Br BOND. BROMOPHOSPHATE AS AN INTERMEDIATE.

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Abstract The reaction of the ions >P-O$^-$ and >P-S$^-$ with α-bromocarboxylic esters proceeds through the nucleophilic displacement on bromine which results in the release of an enol anion as a nucleofuge.

The anions of the type >P-O$^-$ and >P-S$^-$ in reaction with α-bromocarboxylates yield debrominated products. ^{31}P NMR spectra of the products of the reductive debromination reaction as well as the reaction of bromophosphate with the phosphite anion present the same picture. Methyl 1-bromo-2,2-diphenylcyclopropanecarboxylate with dibenzylphosphine oxide at the presence of sodium methanolate also yields the debrominated product and methyl dibenzylphosphinate. On the other hand, bromophosphate is captured by an enolate of α-bromoamide to form N-phosphorylated amide. The debromination of methyl 1-bromo-2,2-diphenylcyclopropanecarboxylate with 2-mercapto-5,5-dimethyl-1,3,2-dioxaphosphorinan sodium salt yields 2-bromo-2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinan. These suggest that the X-philic substitution operates in the reaction in focus.