

有机磷化合物的研究 X:五价磷(磷)酸酯与卤代烷在卤化钠存在下的酯烷基交换反应

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摘要

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Studies on organophosphorous compounds X: The ester alkyl exchange reaction of quinque-valent phosphorus esters with alkyl halide in the presence of sodium halide

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Abstract A detailed study on the ester alkyl exchange reaction of various types of quinque-valent phosphorus esters with alkyl halide in the presence of sodium bromides was reported. This ester alkyl exchange reaction was evidently influenced by the structure of phosphorus esters and alkyl halides as well as by the nature of the halides of metal ions. In contrast with the reaction without sodium halide, the alkyl phosphinmate is more reactive than phosphonate and phosphate by treatment with alkyl halide in the presence of sodium halide. This is consistent with the high nucleophilicity of $>P(CO)O^-$ as leaving group. The reactivity of butyl halides was decreased in the following order: $n\text{-BuBr} > i\text{-BuBr} > s\text{-BuBr} > t\text{-BuBr}$. Alkyl iodide was proved to be more reactive than the corresponding bromide and chloride. However, the use of iodide is limited by the formation of alkene resulted from the elimination of HI. These structural effects show the general characteristics of a nucleophilic substitution reaction. A reaction mechanism involving the formation of sodium salt intermediate was proposed based on the concept of HSAB principle. This reaction may, however, be used as a convenient method for the preparation of mixed esters of quinque-valent phosphorus acids.

Key words [SODIUM COMPOUNDS](#) [REACTION MECHANISM](#) [HALIDE](#) [ORGANO PHOSPHORUS COMPOUNDS](#) [HALOHYDROCARBON](#) [PHOSPHORIC ACID ESTER](#) [PENTAVALENCE](#) [TRANSESTERIFICATION](#)

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