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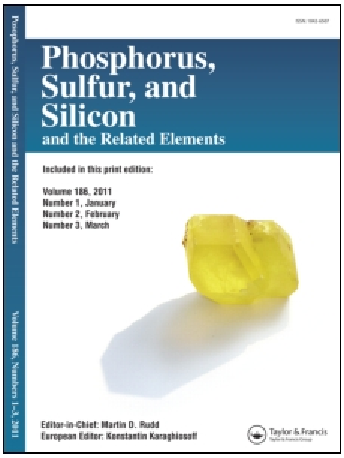

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Synthesis and Solvolysis of [(ω-(Dimethylphenoxysilyl)alkyl]-diphenylphosphines, Phosphine Oxides and Phosphine Sulfides

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Synthesis and Solvolysis of [ω-(Dimethylphenoxysilyl)alkyl]-diphenylphosphines,Phosphine Oxides and Phosphine Sulfides

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Kinetics of base catalysed solvolytic cleavage of phenoxy group from compounds of general structure

$X(CH_2)_nSiMe_2OPh$, where n=1,2,3 and X=Me,Ph_2P, $Ph_2P(O)$, $Ph_2P(S)$

has been investigated. The main purpose was to study the effect of phosphorus groups on the reactivity in substitution reaction at silicon. We wanted to answer the question whether there is any direct interaction of the phosphorus groups with silicon moiety, modifying this reactivity. Complementary NMR studies have also been performed for this purpose.

Compounds of similar structure are often used for immobilising transition metal catalysts on supports. Since anchoring takes place as a result of the substitution of an organyloxy group at silicon atom, the reaction studied here could be considered as a model of this process.

^{29}Si NMR, useful probe for coordination at silicon, does not give the answer to the question of phosphoryl group to silicon coordination. Kinetic studies of methanolysis in the presence of Me_3N-$Me_3N{\cdot}HCl$ buffer show that phosphorus groups facilitate the nucleophile substitution at Si atom. However, this effect, which increases in the direction P:<P(S)<P(O), is not very large. The direct coordination effect is thus of minor importance in this system.