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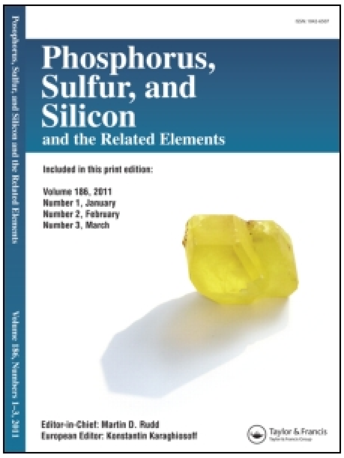

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Sulfenylation Reaction of Some α-Phosphoryl Sulfoxides

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SULFENYLATION REACTION OF SOME α-PHOSPHORYL SULFOXIDES.

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Abstracts Some α-methylsulfanyl phosphorylsulfoxides were obtained by sulfenylation reaction in homogeneous phase.

Key words S-methyl methanethiolsulfonate, α-phosphorylsulfoxides, Horner-Wittig.

In the course of our studies of sulfenylation of sulfoxides and sulfones[1,2] we became interested in investigating the sulfenylation reaction of α-phosphorylsulfoxides. Previous reports on the alkylation,[3] Horner-Wittig reactions[4] and chlorination[5] of the latter compounds indicated high reactivity of the corresponding carbanions with eletrophiles and, therefore, a successful sulfenylation reaction was expected to occur. In fact, when some α-phosphoryl sulfoxides 1a-c were treated with BuLi/THF, followed by addition of S-methyl methanethiolsulfonate, the corresponding α-sulfenylated derivatives 2a-c were obtained in 50-75% yields.

$$\underset{1}{(MeO)_2PO\text{-}CH_2SOR} \xrightarrow[MeSSO_2Me]{BuLi/THF,\ -78^0} \underset{2}{(MeO)_2PO\text{-}CH(SMe)SOR}$$

R = Me (a); C_6H_5 (b); p-Me-C_6H_4

Preliminary attempts using NaH/DMSO/$MeSSO_2Me$ or K_2CO_3/$MeSSO_2Me$ under PTC were unsuccessful.

When sulfenylation was performed with the optically active α-dimethylphosphoryl methyl p-tolyl sulfoxide (-)S the optically active α-sulfenylated derivative, containing two chiral centres, was obtained. The latter compound is of interest as it would lead, through the Horner-Wittig reaction with carbonyl compounds, to the optically active ketene dithioacetal S-oxides, useful reagents for asymmetric Michael additions[6] and Diels-Alder reactions[7].

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