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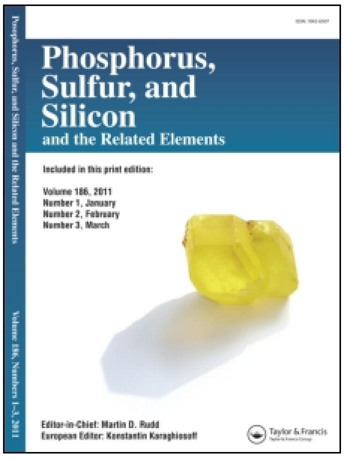

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ALKYLATION OF HYDROTHIOPHOSPHORYL COMPOUNDS UNDER PHASE TRANSFER CATALYSIS CONDITIONS

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Abstract The PTC method was applied to Michaelis - Becker alkylation of hydrothiophosphoryl compounds, affording products in high yields. The side products were studied and the formation mechanisms of major and side products were suggested.

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INTRODUCTION

In the past 15 years, radical improvements have been introduced into the Michaelis-Becker reaction as applied to oxygen-containing hydrophosphoryl compounds. Procedures for carring out this reaction under phase transfer catalysis (PTC) conditions have been developed.[1] The pioneering work of using this technique for the synthesis of PO-anions was that by Makosza et al.[2] published in 1978. In 1981, several publications of american[3] and soviet[4,5] authors have appeared simultaneously. As to the alkylation of hydrothiophosphoryl compounds, the PTC technique has not been used for this purpose.

THE CONDITIONS OF PHASE TRANSFER REACTION

We have studied the use of the PTC technique as applied to hydrothiophosphoryl compounds in three systems: organic phase/aqueous NaOH (50%), organic phase/K_2CO_3 (dry powder), and organic phase/KOH (dry powder). Benzene, methylene chloride, acetonitrile, THF and DMSO were used as organic phase. The hydrothiophosphoryl compounds introduced into the reaction as substrates included R′R″P(S)H with R′ = R″ = EtO, BuO, Bu and Ph and also R′ = Me, R″ = BuO and i - BuO.

Reactions were carried out with alkylating agents which significantly differed in electrophilicity: MeI, EtBr, EtI, BuBr, $PhCH_2Cl$, $ClCH_2COOEt$, $ClCH_2CONH_2$, $ClCH_2CONEt_2$. Of catalysts, tetraalkylammonium salts and crown esters were applied in the ammounts of 0.5 mol%. In these reactions, the alkylation products were obtained in rather high yields (85% and above).

$$R'R''P(S)H + RX \xrightarrow{CH_2Cl_2/KOH\ (dry)} R'R''P(S)R + KX$$

Experiments on alkylation with MeI of different hydrothiophosphoryl compounds in the three systems have revealed that the stronger the hydrothiophosphoryl compound as a PH-acid is, the easier is its alkylation under PTC conditions. On alkylation of $Ph_2P(S)H$ with varying alkylating agents, it has been established that the alkylation rate is directly correlated with electrophilicity of the reagent.

Experiments with the organic phase/solid state systems have revealed in some cases the advantages over the organic phase/aqueous NaOH systems. Alkylation with KOH is so vigorous in some cases that application of a catalyst is not necessary.

Effect of the organic phase is not unambigous and it depends on the substrate, the base applied and conditions of the reaction; C_6H_6, CH_2Cl_2 and MeCN afford the best results. The data obtained give evidence that each system should be optimized towards the substrate and alkylating agent.

THE SIDE PRODUCTS AND MECHANISM

In some cases a small amount of side products was formed. They were isolated and identified. Thus along with the major product, $R_2P(S)R'$ (a) (Scheme), the following compounds are formed: monothioester $R_2P(O)SR'$ (b), dithioester $R_2P(S)SR'$ (c), phosphonium salt $R_2R_2'P^+X^-$ (d) and phosphoryl compound $R_2P(O)R'$ (e). The yields ratio for side

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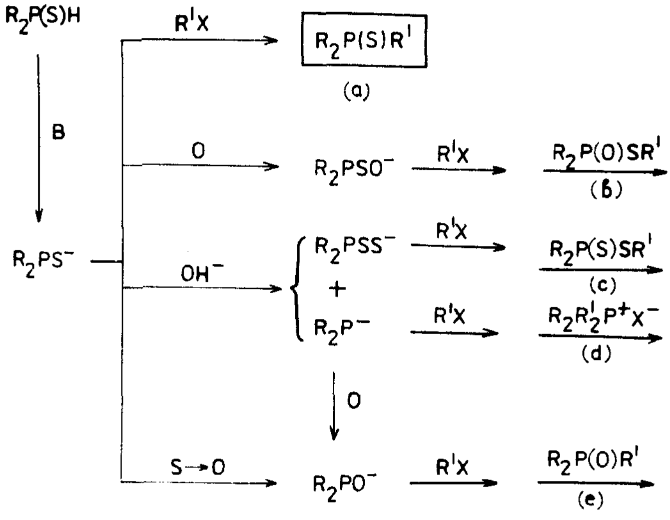
products depends on the relative rates of the oxidation, disproportionation and alkylation reactions of intermediates.



Scheme

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In this case, a significant dependence on the character of the organic phase and the base is observed. The highest amount of side products is obtained on employing K_2CO_3 in DMSO.

Consideration of the mechanism of phase transfer alkylation of hydrothiophosphoryl compounds may rely on the scheme suggested by Kem et al.[3] for the oxygen analogs. Certian corrections should, however, be introduced into this scheme to account for differences in the properties of hydrothiophosphoryl compounds and their oxygen analogs. Hydrothiophosphoryl compounds are more lipophilic, less soluble in water, and have higher acidities than the oxygen analogs. Consequently, they are easier deprotonated in contact with a basic phase, and the appearing ion-pairs easier pass into the organic phase. Therefore, in our case, the phase transfer alkylation may by represented as follows: first stage - reaction of hydrothiophosphoryl compounds occuring on the interface to form ion-pair $R_2PS^-Na^+$. Second stage - the ion-pair is attacked by catalyst, for example Q^+X^-, formation of a new ion-pair $R_2PS^-Q^+$, which is more lipophilic and, at the third stage, easily passes into the organic phase, and at the fourth stage, it is easily alkylated with the regeneration of the catalyst. But hydrothiophosphoryl compounds in some cases are easily alkylated without catalyst. It is probably brought about by the high lipophilicity, when the ion-pair $R_2PS^-K^+$, formed in the first stage at the interface can go into the organic phase where it is alkylated. However, it can not be excluded, that interface alkylation occurs.

No doubt, the Michaelis-Becker reaction, carried out under the phase transfer conditions, represents a wonderful path for synthesis of different thiophosphoryl compounds.

The present work has been done with participation of senior researchers I.M. Aladzheva and I.L. Odinets. The author wishes to express her sincere thanks to them.

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