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## Phosphorus, Sulfur, and Silicon and the Related Elements

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Interaction of Tertiary Phosphines with Acetylenic Compouxds. Alkyl Migration Accompanied by C-P Bond Cleavage and Fragmentation During the Interaction of Trialkyphosphines with Phenylacetylene in the Presence of Proton Donors

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INTERACTION OF TERTIARY PHOSPHINES WITH ACETYLENIC COMPOUNDS. ALKYL MIGRATION ACCOMPANIED BY C-P BOND CLEAVAGE AND FRAGMENTATION DURING THE INTERACTION OF TRIALKYPHOSPHINES WITH PHENYLACETYLENE IN THE PRESENCE OF PROTON DONORS

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We have recently described phosphobetaines with negative charge on  $\beta$ -carbon atom of vinyl group or on  $\delta$ -carbon atom of 1,3-butadienyl group prepared by interaction of trial-kylphosphines with acetylenic and vinylacetylenic compounds, respectively. In the course of developing these investigations an extra route of phosphobetaine formation has been found representing the deprotonation of corresponding phosphonium salts. It has been found that the reaction of trialkylphosphines with phenylacetylene in the presence of proton donors leads to the formation of an intermediate compound containing pentacovalent phosphorus linked with negatively charged oxygen atom. The intermediate undergoes a migration of alkyl group followed either by protonation of  $\beta$ -carbon atom or by unusual cleavage of P-C bond as a result of the electrons back transition:

$$R_3P + PhC = CH \xrightarrow{HOX} R_3 \stackrel{P}{\xrightarrow{c}} CH = CHPh \longrightarrow R_2 \stackrel{R}{\xrightarrow{c}} CH = CHPh \longrightarrow R_2 \stackrel{Q}{\xrightarrow{c}} CH = CHP$$

X = H,  $C_2H_5$ ,  $C(CH_3) = CHCOOC_2H_5$   $R_2P(O)H + RCH = CHPh$ 

The experimental data obtained during the investigation of the reaction of trialkylphosphines with phenylacetylene in aqueous media is in favour of C-C fragmentation in intermediate O-phosphobetaine.