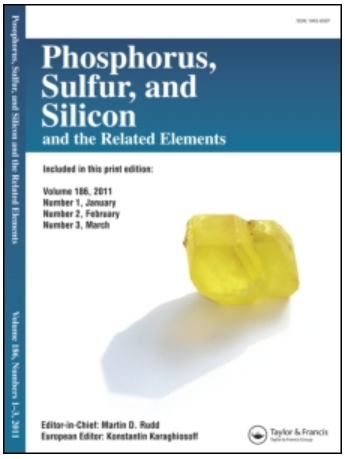

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Reaction of Red Phosphorus with Electrophilic Reagents in Superbasic Systems

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REACTION OF RED PHOSPHORUS WITH ELECTROPHILIC REAGENTS IN SUPERBASIC SYSTEMS

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A new method for generating highly nucleophilic ions from red phosphorus in superbasic systems, such as alkali metal hydroxide - dipolar aprotic solvent (HMPA, DMSO) or solvent of moderate polarity (toluene) with or without a phase-transfer catalyst, has been developed and shown to cover non-standard convenient routes to triorganylphosphines, -phosphine oxides and their derivatives. This is illustrated by the following examples:

$$P_n + {}^{-}OH \longrightarrow P_kOH + P_m^{-}$$

$$P_m^{-} + PhC{\equiv}CH \longrightarrow \underset{55\%}{(PhCH{=}CH)_3P} + \underset{3\%}{(PhCH{=}CH)_3P{=}O}$$

$$P_m^{-} + CH_2{=}CHCH_2Hal \longrightarrow \underset{30\%}{(CH_2{=}CHCH_2)_3P{=}O} + \underset{35\%}{(MeCH{=}CH)_3P{=}O}$$

$$P_m^{-} + RHal \longrightarrow \underset{60\text{-}70\%}{R_3P{=}O}$$

R = Et, Pr, Bu, Bz; Hal = Cl, Br, I

Tris(Z-styryl)phosphine reacts readily with aqueous solution of hydrogen peroxide, elemental sulfur and selenium to form corresponding tris(Z-styryl)phosphine chalcogenides $(PhCH{=}CH)_3P{=}X$ (X = O, S, Se) in yield 90%, 68% and 50%, respectively.