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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:

$$P_{n} + OH \longrightarrow P_{k}OH + P_{m}$$

$$P_{m}^{-} + PhC = CH \longrightarrow (PhCH = CH)_{3}P + (PhCH = CH)_{3}P = 0$$

$$55\% \qquad 3\%$$

$$P_{m}^{-} + CH_{2} = CHCH_{2}Hal \longrightarrow (CH_{2} = CHCH_{2})_{3}P = 0 + (MeCH = CH)_{3}P = 0$$

$$30\% \qquad 35\%$$

$$P_{m}^{-} + RHal \longrightarrow R_{3}P = 0$$

$$60 - 70\%$$

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

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) $_3$ P=X (X = O, S, Se) in yield 90%, 68% and 50%, respectively.