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GENERATION OF PHOSPHIDE ANIONS FROM PHOSPHORUS RED AND PHOSPHINE IN STRONGLY BASIC SYSTEMS TO FORM ORGANYLPHOSPHINES AND -OXIDES

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Abstract Generation of phosphide anions from phosphorus red or phosphine under the action of strong bases followed by their reactions with organyl halides, electrophilic alkenes and alkynes proves to be the most straightforward and well-controlled route to mono-, di- or triorganylphosphines or phosphine oxides of diverse structure.

Key words: phosphorus, phosphine, electrophiles, super bases.

INTRODUCTION

Simple phosphorus-centred nucleophiles like phosphide and phosphinite anions generated from elemental phosphorus or phosphine under the action of strong bases are valuable intermediates for the synthesis of various organyl phosphines and -phosphine oxides, although until recently this opportunity to easily create carbon-phosphorus bond remained almost neglected.

A decade ago we started a systematical study of the red phosphorus P-P bond cleavage in super base media, which has led to a series of facile methods for the preparation of diverse organic phosphines and phosphine oxides [1, 2].

Here we present new data and overview the results together with rationalizations basically dealing with the formation of the P-C bond from elemental phosphorus and/or phosphine in super base media.

Systems P(red)/KOH/Polar Nonhydroxylic Solvent

The essence of the reactions proceeding in the super base systems of type P(red)/KOH/polar nonhydroxylic solvent (DMSO or HMPA)/electrophile is a competition between the hydroxide anion and phosphorus nucleophiles for the electrophile. Therefore, the key question is, how well do the phosphorus nucleophiles match the electrophile in a sense of the frontier orbitals interaction or the HSAB concept?

In fact, in the system P(red)/KOH/DMSO/H_2O, benzyl chloride reacts mostly with the phosphorus nucleophiles to afford tribenzylphosphine oxide in 65% yield [2], whereas the phenyl bromide and iodide as well as allyl chloride give no expected phosphine oxides at all. But, with acetals of bromoacetaldehyde, in the same system, they again are formed in 11-18% yield.

Unexpectedly, an excellent electrophile - nucleophile correspondence was discovered for phosphorus nucleophiles generated from red phosphorus in the above systems and weakly electrophilic olefines like styrene and vinylpyridines. The 40-60% yield of substituted triethylphosphine oxides has been achieved in the DMSO - tailored systems with styrene [2], 4-vinyl- and 2-methyl-5-vinylpyridines [3] at 80-110°C.

$$\text{P/KOH/DMSO} \xrightarrow{\text{RCH=CH}_2} (\text{RCH}_2\text{CH}_2)_3\text{P=O}$$

R = Ph, 4-pyridyl, 2-methyl-5-pyridyl

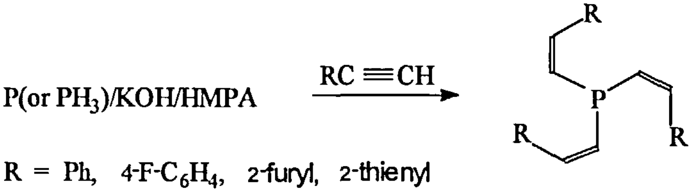
The steric requirements prove to be important in this reaction as it is demonstrated with α-methylstyrene. No tri(2-phenylpropyl)phosphine oxide at all has been detected in this case.

Vinylarenes and vinylhetarenes proved to be also the active traps of the phosphide anions, generated from phosphine in the KOH/DMSO system. We have succeeded in finding the conditions (60-65°C, atmospheric pressure) allowing selective synthesis of secondary phosphines in 60-80% yields [4]. Phosphine was obtained from phosphorus red and potassium hydroxide in water-dioxane media.

$$\text{PH}_3 + \text{R(R')C=CH}_2 \xrightarrow{\text{KOH/DMSO}} [\text{R(R')CHCH}_2]_2\text{PH}$$

R = H, R' = Ph, 4-F-C_6H_4, 2-furyl, 4-pyridyl, 2-thienyl; R = Me, R' = Ph

Arylacetylenes are another group of electrophiles for which the phosphorus nucleophiles generated from phosphorus red or phosphine in KOH/HMPA suspension proved to be capable of winning the competition over hydroxide ion to give chemo-, regio- and stereoselectively Z,Z,Z-isomers of substituted trivinylphosphines in a yield up to 80% [2, 5, 6].



Phase-transfer Conditions

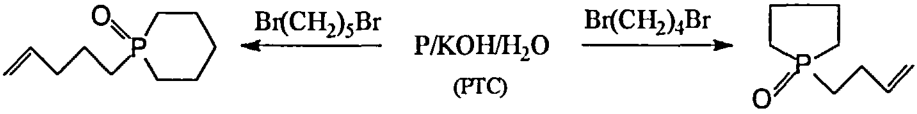
The phase-transfer catalysis with strongly basic aqueous solutions is commonly considered as producing super bases [7]. We have found that under phase-transfer conditions (PTC), the suspensions consisting of red phosphorus, KOH, dioxane, water, and phase-transfer catalyst (benzyl triethyl ammonium chloride) react readily with organyl halides to form tri(organyl)phosphine oxides [1, 2]:

$R_3P{=}O$, R = *n*-Alk (60-65%), Bz (75%), $EtSCH_2$ (10%).

Under similar conditions allyl halides are also capable of phosphorylating to afford tri(allyl)phosphine oxide and its isomer, tri(E-1-propenyl)phosphine oxide [2]:

$(CH_2{=}CHCH_2)_3P{=}O$ (30%), $(E\text{-}CH_3CH{=}CH)_3P{=}O$ (35%).

1,4- And 1,5-Dibromoalkanes react with phosphorus nucleophiles produced in the above-mentioned phase-transfer system to furnish alkenyl phospholane- and phoshorinane oxides in moderate yield (12 and 25%, respectively) due to side elimination processes manifested themselves by the presence of alkenyl group at the phosphorus atom.



The feasibility of the ring closure falls from the six- to five-membered ring with the four membered ring being not capable to form at all. Instead, in the case of 1,3-dibromopropane, a mixture of tri(allyl)- and tri(E-1-propenyl)phosphine oxides has been isolated.

Systems P/Li/NH_3/*t*-AlkOH

Petrov *et al.* reported on the reaction of red phosphorus with sodium in liquid ammonia and subsequent alkylation, affording tetraalkyldiphosphines, dialkylphosphines and trialkylphosphines (isolated as phosphine sulfides) in 17-34% yields [8].

We have developed a new method of selective generation of mono- or diphosphide anions from red phosphorus by the system Li/NH_3 liq in the presence of *t*-BuOH which as a mild proton donor drastically assists the fission of P-P bonds in the phosphorus molecule. As a result of alkylation the primary or secondary phosphines have been prepared in 65-85% yield [9, 10].

$$P + 3Li + 2t\text{-}BuOH \xrightarrow{NH_3\ liq} LiPH_2/2t\text{-}BuOLi \xrightarrow{RX} RPH_2$$

$$P + 3Li + t\text{-}BuOH \xrightarrow{NH_3\ liq} Li_2PH/t\text{-}BuOLi \xrightarrow{2RX} R_2PH$$

R = alkyl, cycloalkyl, benzyl; X = Cl, Br

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