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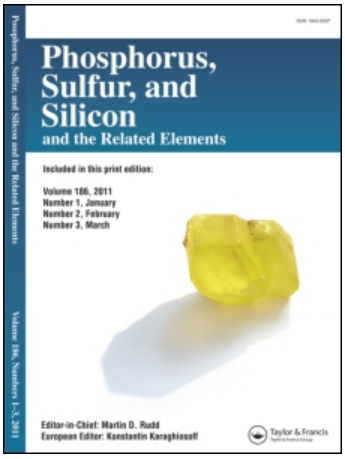

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
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SUPERBASE-INDUCED GENERATION OF PHOSPHIDE AND PHOSPHINITE IONS AS APPLIED IN ORGANIC SYNTHESIS

B. A. Trofimov[a]; N. K. Gusarova[a]; S. F. Malysheva[a]; T. N. Rakhmatulina[a]; M. G. Voronkov[a]; V. I. Dmitriev[b]; S. I. Shaikhudinova[b]
[a] Siberian Division, Irkutsk Institute of Organic Chemistry, Irkutsk, USSR [b] Irkutsk University, Irkutsk, USSR

To cite this Article Trofimov, B. A. , Gusarova, N. K. , Malysheva, S. F. , Rakhmatulina, T. N. , Voronkov, M. G. , Dmitriev, V. I. and Shaikhudinova, S. I.(1991) 'SUPERBASE-INDUCED GENERATION OF PHOSPHIDE AND PHOSPHINITE IONS AS APPLIED IN ORGANIC SYNTHESIS', Phosphorus, Sulfur, and Silicon and the Related Elements, 55: 1, 271 — 274
To link to this Article: DOI: 10.1080/10426509108045950
URL: http://dx.doi.org/10.1080/10426509108045950

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Phosphorus, Sulfur, and Silicon, 1991, Vol. 55, pp. 271–274
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Printed in the United Kingdom

SUPERBASE-INDUCED GENERATION OF PHOSPHIDE AND PHOSPHINITE IONS AS APPLIED IN ORGANIC SYNTHESIS

B. A. TROFIMOV, N. K. GUSAROVA, S. F. MALYSHEVA,
T. N. RAKHMATULINA and M. G. VORONKOV
Irkutsk Institute of Organic Chemistry, Siberian Division, Ac. Sci. USSR, Irkutsk 664033, USSR

and

V. I. DMITRIEV and S. I. SHAIKHUDINOVA
Irkutsk University, Irkutsk 664033, USSR

(Received January 4, 1990; in final form March 9, 1990)

A series of new direct reactions of red phosphorus (or white) with organyl halides, alkenes and acetylenes have been developed. Reactions occur in superbasic systems, such as alkali metal hydroxide-dipolar aprotic complexing solvent (DMSO, HMPA) or under phase-transfer conditions to afford earlier inaccessible triorganylphosphines and -phosphine oxides including unsaturated ones in good yields.

Key words: phosphorus, electrophiles, superbase, triorganylphosphines, triorganylphosphine oxides.

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INTRODUCTION

About a decade ago we launched a general approach to the synthesis of vinylic sulfur, selenium and tellurium compounds by straight-forward reactions of these elements with acetylenes in superbase media.[1] The key step of these syntheses is the capture by triple bond of highly nucleophilic polyelement anionic species generated by cleavage of the element-element bond with the activated (super-basic) OH anion.

Now, we wish to report our results on expansion of the aforementioned approach to elemental phosphorus.

It is known,[2] that white phosphorus reacts with *N*-hydroxymethyl-dialkylamines to give tris(dialkylaminomethyl)phosphine oxides, bis(dialkylaminomethyl) phosphinic acids, and dialkylaminomethyl phosphonic acids. Red phosphorus does not react with *N*-hydroxymethyl-dialkylamines under the conditions used in this reaction.

RESULTS AND DISCUSSION

Initially, as a logic development of our approach to chalcogenation, we have discovered a new general method for the phosphide and phosphinite ions generation

from red phosphorus (and white) under the action of strong bases. It allows the earlier unknown direct phosphorylation of organohalides, alkenes and acetylenes to be brought about.

Under phase-transfer conditions (PTC) the synthesis of trialkylphosphine oxides (*1*) from red phosphorus and alkyl halides were realized.[3] The interaction proceeds in a multiphase system (elemental phosphorus-50% aqueous solution of KOH-THF) in the presence of phase-transfer catalyst at 60–65°C. In the reaction mixture, small amounts of corresponding dialkylphosphinous acid (*2*) are commonly present.

$$RX + P \xrightarrow{KOH/H_2O} \underset{1}{R_3P{=}O} + \underset{2}{R_2P(O)H} \qquad (1)$$

$$R = Et,\ n\text{-Pr},\ n\text{-Bu},\ n\text{-Am},\ n\text{-}C_8H_{17}; \qquad X = Cl,\ Br,\ I$$

The yield of trialkylphosphine oxides exceeds 40%.

It should be emphasized that trialkylphosphines are not observed among the reaction products obtained even under the argon blanket. Apparently, the interaction of the triade P/KOH/H_2O with alkyl halides proceeds through polyphosphinite anions, resulting from a cleavage of the P—P bond by the hydroxide ion.

$$P_n + {}^-OH \longrightarrow P_m^- + P_l{-}OH \qquad (2)$$

$$P_l{-}OH + {}^-OH \xrightarrow[-H_2O]{} O{=}P_l^- \xrightarrow{RX} O{=}P_lR$$

$$\xrightarrow[-P_gOH]{{}^-OH} R(O)P_f^- \xrightarrow{RX} R_2P_f{=}O \quad \text{etc.}$$

Upon heating (70–80°C) in the suspension KOH/DMSO (or HMPA) red phosphorus interacts with benzyl chloride to form mainly tribenzylphosphine oxide (*3*) in 65% yield and small amounts of tribenzylphosphine (*4*) and tetrabenzylphosphonium chloride (*5*).[3,4]

$$PhCH_2Cl + P \xrightarrow{KOH/DMSO} \underset{3}{(PhCH_2)_3P{=}O}$$

$$+ \underset{4}{(PhCH_2)_3P} + \underset{5}{[(PhCH_2)_4P^+]Cl^-}$$

Since in the reaction mixture the phosphonium salt *5* and toluene are identified, an alternative pathway of the phosphine oxide *3* formation could be the known decomposition of the quaternary phosphonium hydroxide.

$$P_m^- + 3\ PhCH_2Cl \longrightarrow (PhCH_2)_3P_m \xrightarrow[-P_{m-1}]{} 4$$

$$\xrightarrow{PhCH_2Cl} 5 \xrightarrow{KOH} [(PhCH_2)_4P^+]OH^- \xrightarrow[-PhMe]{} 3$$

From allyl halides and red phosphorus under PTC, the earlier unkown tris(E-propen-1-yl)phosphine oxide (*6*) together with the expected tris(propen-2-yl)-phosphine oxide (*7*) have been obtained in 35 and 30% yields, respectively.[3,5,6]

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$$P + CH_2{=}CHCH_2Br \xrightarrow{KOH/H_2O} \underset{6}{(CH_2^1CH^2{=}CH^3)_3P{=}O} + \underset{7}{(CH_2^1{=}CH^2CH_2^3)_3P{=}O} \quad (3)$$

In superbase suspensions KOH – HMPA (or DMSO) – H_2O, styrene behaves as an electrophile towards the phosphide ions generated from red or white phosphorus upon heating (70–80°C) to form tris(2-phenylethyl)phosphine oxide (*8*) in 60% yield and bis(2-phenylethyl)phosphinous acid (*9*) as a minor product.[7]

$$P \text{ (or } P_4) + PhCH{=}CH_2 \xrightarrow{KOH/H_2O} \underset{8}{(PhCH_2CH_2)_3P{=}O} + \underset{9}{(PhCH_2CH_2)_2P(O)H}$$

The hydroxide ion generated under PTC is not active enough to bring about this reaction. Initiators or inhibitors of radical processes do not influence the reaction.

In this new phosphorylation, acetylenes can be also successfully employed as electrophiles. For examples, phenylacetylene, when treated with phosphorylating systems such as red phosphorus—alkali metal hydroxide—highly polar nonhydroxylic solvent or under PTC, affords stereospecifically tris(*Z*-styryl)phosphine (*10*) as the main product in a yield of 55% and a minor product, the corresponding phosphine oxide *11*.[3,6,8]

$$P + PhC{\equiv}CH \xrightarrow{KOH/H_2O} \underset{10}{P(CH^1{=}CH^2C_6H_5^3)_3} + \underset{11}{O{=}P(CH^1{=}CH^2C_6H_5^3)_3} \quad (4)$$

The reaction (4) proceeds upon heating (70–85°C) for 5 hr.

The triple bond seems to be attacked by the initially formed polyphosphide anions (see Equation 2), since phosphine is a weak nucleophile.

$$P_m^- + PhC{\equiv}CH \longrightarrow P_mCH{=}\bar{C}Ph \xrightarrow{H_2O} P_mCH{=}CHPh$$

$$+ {}^-OH \xrightarrow[-P_kOH]{} PhCH{=}CHP_j^- \xrightarrow[H_2O]{PhC{\equiv}CH} (PhCH{=}CH)_2P_j \quad \text{etc.}$$

According to NMR (^1H and ^{31}P) data all styryl moieties have *Z*-configuration showing that of four possible stereoisomers only *Z,Z,Z*-isomer is formed which is in keeping with the key stage being a trans-nucleophilic addition.

Under ultrasonic activation the phosphorylation of phenylacetylene proceeds about 5 times faster and without external heating.

EXPERIMENTAL

^1H and ^{31}P NMR spectra were recorded on a Bruker WP-200 SY and Varian XL-100/12 spectrometers, respectively. Mass spectra were obtained on a MAT-212 spectrometer.

The given yields in every case are based on the corresponding electrophile used.

Trialkylphosphine oxides (*general procedure, Equation 1*). To a mixture of red phosphorus (3.1 g, 0.1 mol), alkyl bromide (0.13 mol), benzyltriethylammonium chloride (1.1 g, 5 mmol) and 40 ml of

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THF a solution of KOH (25 g, 0.45 mol) in H_2O (25 ml) was added dropwise at room temperature. The reaction mixture was stirred at 60–65°C for 6 hr. The organic layer was separated and THF was distilled off, the residue was fractionated in vacuum to give the corresponding trialkylphosphine oxide.

Tris(E-propen-1-yl)phosphine oxide (*6*) and *tris(propen-2-yl)phosphine oxide* (*7*) were synthesized in a similar way from red phosphorus and allyl bromide (Equation 3). Phosphine oxides *6* and *7* were isolated in the pure form by preparative GLC (chromatograph PAHV-07, column: 1200 × 10 mm with 15% Carbowax 6000 on Chromaton N-AW-DMCS). For *6*: yield 35%, m.p. 72°C, $M^{+\cdot}$ 170 m/e. NMR, ppm (^1H; ^{31}P): 6.58 m (H^2), 5.84 *dd* (H^3), 1.91 m (H^1); 13.00 (*P*); J_H2_H3 17.6, $J_{PH}2$ 17.0, $J_{PH}3$ 23.2 Hz. For *7*: yield 30%, b.p.$_5$ 130–133°C, $M^{+\cdot}$ 170 m/e. NMR, ppm (^1H; ^{31}P): 5.90–5.60 m (H^2), 5.20 *dd* (H^1), 2.60 *dd* (H^3); 20.00 (*P*); $J_{PH}3$ 16.4 Hz.

Tris(Z-styryl)phosphine (*10*) and *tris(Z-styryl)phosphine oxide* (*11*). To a mixture of red phosphorus (3.1 g, 0.1 mol), phenylacetylene (7.6 g, 0.075 mol) and 70 ml of HMPA a solution of KOH (10 g, 0.18 mol) in water (4 ml) was added dropwise at room temperature. The reaction mixture was stirred at 83–85°C for 5 hr, diluted with water, extracted with Et_2O. The organic layer was washed with water, dried over K_2CO_3 and solvent was removed by distillation. The residue was washed with ethanol and dried under reduced pressure to give 4.7 g (55%) of *10*. The evaporation of ethanol from the washing leaves 0.12 g (2%) phosphine oxide *11*. For *10*: viscous oil, n_D^{20} 1.6761, $M^{+\cdot}$ 340 m/e. NMR, ppm (^1H; ^{31}P): 7.30 m (H^3), 7.11 *dd* (H^2), 6.26 *dd* (H^1); −63.83 (*P*); J_H1_H2 12.68, $J_{PH}1$ 1.22, $J_{PH}2$ 24.40 Hz. For *11*: m.p. 93–94°C (ether), $M^{+\cdot}$ 356 m/e. NMR, ppm (^1H; ^{31}P): 7.30 m (H^3), 6.89 *dd* (H^2), 5.83 *dd* (H^1); 10.00 (*P*); J_H1_H2 14.08, $J_{PH}1$ 18.10, $J_{PH}2$ 41.00 Hz.

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