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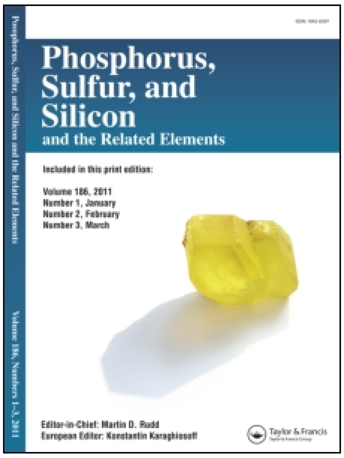

Phosphorus, Sulfur, and Silicon and the Related Elements

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Phosphorylation of Allyl Halides with White Phosphorus

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PHOSPHORYLATION OF ALLYL HALIDES WITH WHITE PHOSPHORUS

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White phosphorus reacts with allyl bromide in the system KOH-dioxane-H_2O at room temperature to form tris(propen-2-yl), bis(propen-2-yl)(E-propen-1-yl), and bis(E-propen-1-yl)(propen-2-yl)phosphine oxides in a total quantitative yield, their molar ratio being 1:0.5:0.1.

Keywords: Allyl halides; phosphorylation; propenylphosphine oxides; white phosphorus

INTRODUCTION

Phosphorylation of electrophiles with elemental phosphorus in the presence of strong bases represents one of the most convenient methods for C—P bond formation and synthesis of phosphines and phosphine oxides,[1–6] key compounds in organophosphorus synthesis, efficient ligands for design of metal complex catalysts of new generation,[7–10] extract agents and sorbents of rare earth uranium and transuranium metal,[11] and halogen-free flame retardants.[12] A special position among these compounds is held by unsaturated phosphines and phosphine oxides, highly reactive building blocks for organic synthesis, monomers and co-monomers used, for example, for the preparation of new nonflammable polymers. At the same time the synthesis of unsaturated organophosphorus compounds is associated with certain difficulties because, as a rule, it involves the use of hazardous phosphorus halides and organometallic reagents. Previously we reported[2,13] on the

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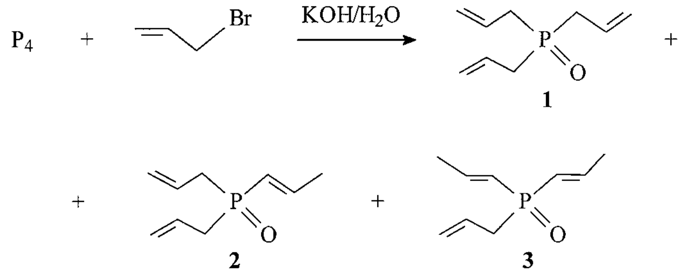
reaction of allyl halides with red phosphorus which proceeds in the phase-transfer system KOH-dioxane-H_2O-benzyl triethyl ammonium chloride at 90–95°C to give a mixture of tertiary propenyl phosphines oxides, from which bis(*E*-propen-1-yl)(propen-2-yl) and tris(*E*-propen-1-yl)phosphine oxides were isolated in moderate yield. The former was erroneously attributed as tris(propen-2-yl)phosphine oxide.

With the aim of development of an efficient method for the preparation of unsaturated phosphine oxides, in the present work we have investigated the reaction of white phosphorus with readily available allyl halides.

RESULTS AND DISCUSSION

White phosphorus has been found to react easily with allyl bromide in the superbase system consisting of 60% aqueous KOH and dioxane at room temperature to afford the expected tris(propen-2-yl)phosphine oxide **1** as a main product, as well as products of its prototropic isomerisation: bis(propen-2-yl)(*E*-propen-1-yl)phosphine oxide **2** and bis(*E*-propen-1-yl)(propen-2-yl)phosphine oxide **3**, in a total yield of 96% (Scheme 1).



SCHEME 1

The molar ratio of the above phosphine oxides **1–3** is 1:0.5:0.1 respectively. Individual phosphine oxides **1–3** were isolated by means of preparative GLC and characterized by NMR (^1H, ^{13}C, ^{31}P) and IR methods (Table I). Their composition was proven by the data of elemental analysis.

Under comparable conditions, the reactivity of red phosphorus was found to be much lower: the total yield of phosphine oxides **1–3** was only about 2%.

Allyl chloride reacts with white phosphorus in the system KOH-H_2O-dioxane at room temperature to form (propen-2-yl)phosphine in 13%

TABLE I Spectral Data[a] of Phosphine Oxides **1–3**

Phosphine Oxide, number, structural formula	NMR, δ, ppm; J, Hz ($CDCl_3$)		
	^1H NMR	^{13}C NMR	^{31}P NMR
1, $(C^1H_2{=}C^2HC^3H_2)_3P{=}O$	2.55 dd (6H C^3-H, $^3J_{HH}$ 7.6 , $^2J_{PH}$ 14.8), 5.15 dd (3H, C^1-H, $^2J_{HH}$ 1.0, $^3J_{PH}$ 15.2), 5.19 dd (3H, C^1-H,$^3J_{HH}$10.5), 5.76 sx (3H, C^2-H)	33.10 d ($C^{3,1}J_{PC}$ 62.7), 120.62 d ($C^{1,3}J_{PC}$ 11.2), 127.35 d ($C^{2,2}J_{PC}$ 7.2)	41.70
2, $(C^1H_2{=}C^2HC^3H_2)_2$-$(C^4H_3C^5H{=}C^6H)P{=}O$	1.88–1.92 d (3H, C^4-H,$^3J_{HH}$ 6.4), 2.59 dd (4H, C^3-H, $^3J_{HH}$ 7.6, $^2J_{PH}$ 14.8), 5.17 m (2H, C^1-H, $^2J_{HH}$ 1.0, $^3J_{PH}$ 15.2), 5.25 m (2H, C^1-H, $^3J_{HH}$ 10.4), 5.74–5.82 m (3H, $C^{2,6}$-H), 6.67–6.77 tq (1H, C^5-H,$^3J_{HMe}$ 6.8, $^3J_{HH}$17.2, $^3J_{PH}$ 23.6)	20.20 d ($C^{4,3}$ J_{PC} 17.3), 35.00 d ($C^{3,1}$ J_{PC} 66.7), 120.34 d ($C^{1,3}$ J_{PC} 11.5), 121.62 d ($C^{6,1}$ J_{PC} 94.9), 127.53 d ($C^{2,2}$ J_{PC} 8.7), 148.05 s ($C^{5,2}$ J_{PC} 0)	31.57
3, $(C^1H_2{=}C^2HC^3H_2)$-$(C^4H_3C^5H{=}C^6H)_2P{=}O$	1.92 m (6H, C^4-H,$^3J_{HH}$ 6.8), 2.65 dd (2H, C^3-H, $^3J_{HH}$ 7.4, $^2J_{PH}$ 14.8), 5.14–5.21 m (2H, C^1-H), 5.74–5.87 m (3H, $C^{2,6}$-H), 6.54–6.68 m (2H C^5-H)	20.10 d ($C^{4,3}J_{PC}$ 17.6), 37.90 d ($C^{3,1}J_{PC}$ 70.1), 120.00 d ($C^{1,3}J_{PC}$ 11.6), 123.76 d ($C^{6,1}J_{PC}$ 99.0), 127.78 d ($C^{2,2}J_{PC}$ 8.3), 148.11 s ($C^{5,2}J_{PC}$ 0)	22.80

[a] IR spectra for phosphine oxides, ν, cm^{-1}: 1150 (P=O), 1640 ($CH_2{=}CH$).

yield (data of ^{1}H, ^{31}P, NMR). The latter was isolated from the reaction mixture along with unreacted initial allyl chloride.

Therefore, reaction of allyl halides with white phosphorus easily effected under mild conditions represents a new convenient route to the valuable unsaturated organophosphorus compounds.

EXPERIMENTAL

^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker DPX 400 (400, 100, and 161.98 MHz respectively) spectrometer. IR spectra were taken on a Specord IR-75 instrument. PGLC (PAKHV-07 chromatograph, 1000 × 10 mm column, stationary phase: Chezasorb (0.25–0.36 mm), mobile phase: polyphenylmethylsiloxane (15%), carrier gas: helium). All experiments were carried out under argon atmosphere.

Phosphorylation of Allyl Bromide with White Phosphorus

To a mixture 0.50 g (16.1 mmol) of white phosphorus in 10 mL of dioxane, 4.8 g (85.7 mmol) of KOH and 3.2 mL of H_2O were added consequently. The temperature of the reaction mixture elevated exothermically to 40°C causing white phosphorus to melt and disperse. The suspension was cooled to room temperature and 1.54 g (12.7 mmol) of allyl bromide was added. The mixture was stirred for an additional 5 h at 20–22°C; the dioxane layer was separated and dried (K_2CO_3). The solvent was removed in vacuum to produce 0.69 g (96%) of a residue, composed of a mixture of phosphine oxides **1–3**. According to ^{31}P NMR data, the mixture contained 62% of **1**, 31% of **2**, and 7% of **3**.

Phosphorylation of Allyl Chloride with White Phosphorus

To a mixture 0.50 g (16.1 mmol) of white phosphorus in 10 mL of dioxane, 4.8 g (85.7 mmol) of KOH and 3.2 mL of H_2O were added consequently. The temperature of the reaction mixture elevated exothermically to 40°C causing white phosphorus to melt and disperse. The suspension was cooled to room temperature and 0.95 g (12.4 mmol) of allyl chloride was added. The mixture was stirred for additional 4 h at 20–22°C. From the reaction flask, a mixture of primary phosphine and unreacted allyl chloride was condensed under reduced pressure into a trap, cooled to -70°C. A total of 0.45 g of a fraction, containing 0.09 g (13% yield) of (propen-2-yl)phosphine (according to ^{1}H NMR data), was obtained. ^{31}P NMR ($CDCl_3$), δ, ppm: 133.47, $^1J_{\text{P-H}}$ 193 Hz; lit[14] for (propen-2-yl)phosphine: $^1J_{\text{P-H}}$ 193 Hz.

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