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## LETTERS TO THE EDITOR

# Nucleophilic Addition of Phosphine to Vinyl Sulfoxides

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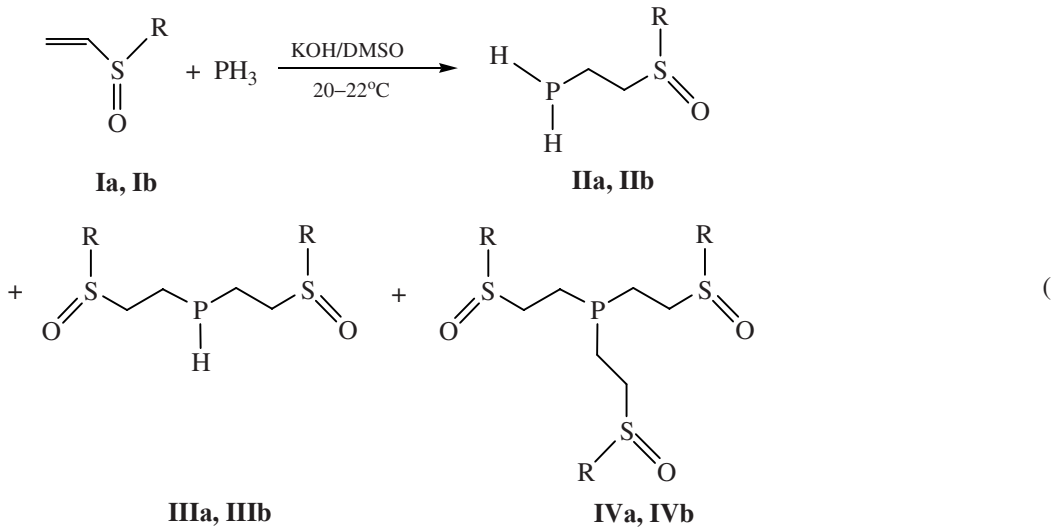
Reaction of addition of phosphine to multiple bonds represents an obvious alternative to the synthesis of organophosphorus compounds by the use of phosphorus halogenides, opening the route to atom-sparing design of various phosphines and their derivatives. In spite of its attractiveness up to now this alternative has not been systematically developed although the addition of phosphine to some alkenes and acetylenes is described in a number of publications [1, 2]. So far nothing is known about the addition of phosphine to vinyl sulfoxides. At the same time, this reaction opens a direct one-step route to difficultly accessible phosphines with sulfoxide groups, promising semilabile chelating ligands [3, 4] and intermediates for preparation of, e.g., radioactive diagnosticums [5–7].

Our attempts to perform this reaction under radical conditions (butyl vinyl sulfoxide, DINIZ, 65°C, 5 h) failed.

At the same time, nucleophilic addition of phosphine to vinyl sulfoxides **Ia, Ib** in superbasic system KOH–DMSO [8] was possible. The reaction proceeded at room temperature (phosphine was passed into the suspension consisting of vinyl sulfoxide, KOH, DMSO). The formation of all possible phosphines was observed ($^{31}$P NMR): primary **IIa, IIb**, secondary **IIIa, IIIb** and tertiary **IVa, IVb**.

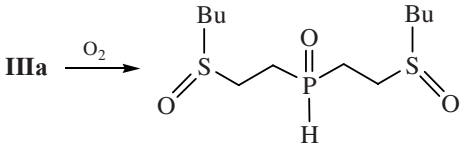



(1)

R = Bu (**a**), Ph (**b**).

Note that a less basic catalytic system KOH–dioxane turned out to be ineffective.

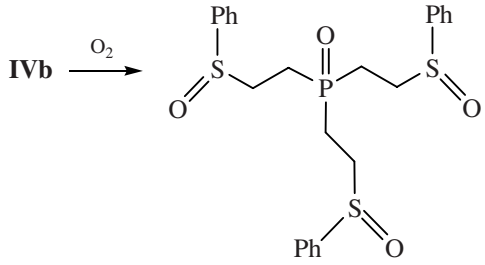
By controlling the conditions of reaction (1) it was possible to selectively obtain the secondary phosphine **IIIa** isolated as the corresponding phosphine oxide **V** (nonoptimized preparative yield of pure product was 35%).



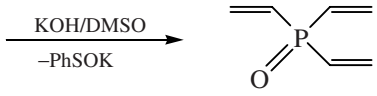

(2)

**V**

In the case of vinyl phenyl sulfoxide **Ib** during treatment of the reaction mixture it was possible to identify by comparison with authentic sample [9] ($^1$H, $^{31}$P NMR) trivinyl phosphine oxide **VI**, the product of elimination of three molecules of phenylsulfenic acid from tertiary phosphine oxide **VII** (formed by air oxidation of the corresponding phosphine **IVb**).




**VII**




(3)

**VI**

Therefore, nucleophilic addition of phosphine to vinyl sulfoxides, an important class of functional alkenes, was performed for the first time. It provides a simple and convenient approach to the synthesis of new demanded phosphines and phosphine oxides with sulfoxide groups.

Phosphine was generated in a separate flask from red phosphorus and KOH in water-toluene medium [10].

**Bis[2-(butylsulfinyl)ethyl]phosphine oxide (V).** To a mixture of 1.80 g of powdered KOH, 16 ml of DMSO, and 1 ml of $H_2O$ after flushing with argon and saturating with phosphine, 0.60 g of butyl vinyl sulfoxide **Ia** in 10 ml of DMSO was added dropwise during 1 h at room temperature with simultaneous passing of phosphine; passing of phosphine continued for another 2 h, then it was stopped, the reaction mixture was flushed with argon. In the $^{31}$P NMR spectrum ($\delta_P$, ppm) of the reaction mixture the following signals were present: –135.0 t ($^1J_{PH}$ 194 Hz), –67.8 d ($^1J_{PH}$ 198 Hz), and –26.2 in a 2:37:1 ratio, belonging to primary **IIa**, secondary **IIIa**, and tertiary **IVa** phosphines, respectively. The reaction mixture was diluted with equal volume of water, extracted successively with ether and chloroform, ethereal extracts were dried with potassium carbonate, ether was removed, the residue was dried in a vacuum. 0.10 g of the mixture of primary **IIa** and secondary **IIIa** phosphines was obtained in the ratio 1 : 4 ($^{31}$P NMR). Chloroform extracts were dried with potassium carbonate, chloroform removed under reduced pressure to 3/4 of the initial volume. After 7 days the precipitate formed was filtered off, washed with ether, and dried in a vacuum to give 0.25 g (35%) of bis[2-(butylsulfinyl)ethyl]phosphine oxide (**V**) as a white powder, mp 166–168°C (ether). $^1$H NMR ($CDCl_3$), δ, ppm: 0.98 t (6H, Me, $^3J_{HH}$ 7.3 Hz), 1.50 m (4H, $CH_2Me$), 1.76 m (4H, $CH_2Et$), 2.37 m (4H, $CH_2P$), 2.70 m, 2.78 m, 2.88 m, 3.08 m (8H, $CH_2SO$). $^{31}$P NMR ($CDCl_3$), $\delta_P$, ppm: 30.6 d ($^1J_{PH}$ 474 Hz). IR spectrum (KBr, $cm^{-1}$): 1009 (S=O), 1163 (P=O), 2368 (P–H). Found, %: C 45.57; H 8.88; P 9.88; S 19.90. $C_{12}H_{27}O_3PS_2$. Calculated, %: C 45.84; H 8.65; P 9.85; S 20.40.

**Trivinyl phosphine oxide (VI).** To a mixture of 1.80 g of powdered KOH, 16 ml of DMSO, and 1 ml of $H_2O$ after flushing with argon and saturating with phosphine 0.91 g of vinyl phenyl sulfoxide **Ib** in 10 ml of DMSO was added dropwise during 2 h at room temperature with simultaneous passing of phosphine. Phosphine was bubbled for another 2 h, then it was stopped, the reaction mixture was flushed with argon and analyzed by $^{31}$P NMR. The following signals were present in the spectrum ($\delta_P$, ppm): –134.8 t ($^1J_{PH}$ 196 Hz), –68.2 d ($^1J_{PH}$ 200 Hz), –26.7 and 25.9 in the ratio 2 : 8 : 1 : 2, belonging to primary **IIb**, secondary **IIIb**, tertiary **IVb** phosphines, and tertiary phosphine oxide **VII**, respectively. To the reaction mixture 0.64 g of vinyl phenyl sulfoxide **Ib** in 12 ml of DMSO was added, the mixture was stirred for another 5 h, diluted with equal amount of water, extracted with chloroform, dried with potassium carbonate, solvent was removed, the residue was dried in a vacuum. 0.25 g

of the product was obtained containing, according to the $^{31}P$ NMR spectrum ($\delta_P$, $CDCl_3$) trivinyl phosphine oxide **VI** (18.2 ppm) and phosphine oxide **VII** (25.6 ppm) in the ~2:1 ratio (yield 18 and 10%, respectively). $^{1}H$ and $^{31}P$ NMR spectra of individual trivinyl phosphine oxide (isolated by sublimation) are identical to those of an authentic sample [9].

$^{1}H$ and $^{31}P$ NMR spectra were registered on a Bruker DPX-400 spectrometer (400.13 and 161.98 MHz, respectively), internal standard HMDS, external standard 85% $H_3PO_4$. IR spectra were taken on a Bruker-IFS 25 instrument in KBr pellets.

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