β-HYDROXY- AND β-ETHOXYETHYLDIPHENYLPHOSPHINE OXIDES AS EQUIVALENTS OF VINYLDIPHENYLPHOSPHINE OXIDE IN ADDITION REACTIONS

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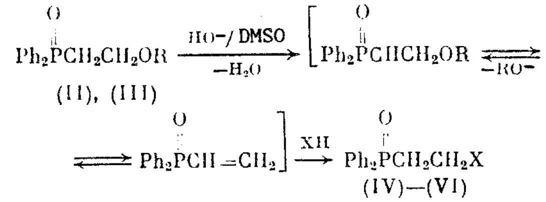
Vinyldiphenylphosphine oxide (I) is commonly used in the synthesis of functionally substituted phosphine oxides due to its capacity readily to add nucleophilic reagents [1,2]. We have found that the same products may be obtained by the action of nucleophilic reagents in DMSO in the presence of aqueous alkali on β-hydroxyethyldiphenylphosphine (II), that is, on the starting compound for the synthesis of vinyl oxide (I) [3]. β-Ethoxyethyldiphenylphosphine oxide (III) may be used for the same purposes.



$$\underset{\text{(II), (III)}}{\mathrm{Ph_2\overset{O}{\overset{\|}{P}}CH_2CH_2OR}} \xrightarrow[-\mathrm{H_2O}]{\mathrm{HO^-/DMSO}} \left[\mathrm{Ph_2\overset{O}{\overset{\|}{P}}\bar{C}HCH_2OR} \underset{-\mathrm{RO^-}}{\rightleftarrows} \mathrm{Ph_2\overset{O}{\overset{\|}{P}}CH{=}CH_2}\right] \xrightarrow{\mathrm{XH}} \underset{\text{(IV)—(VI)}}{\mathrm{Ph_2\overset{O}{\overset{\|}{P}}CH_2CH_2X}}$$

R = H (II), Et (III), X = Ph_2P (IV), $N(CH_2)_5$ (V), $Ph_2P(O)$ (VI).

Tetraphenylethylenediphosphine Monooxide (IV). A mixture of 1.5 g (8 mmoles) Ph_2PH, 2.0 g (8 mmoles) oxide (II) [3], and 50% aqueous solution of 0.2 g (4 mmoles) KOH in 5 ml DMSO was heated with stirring in an argon stream for 45 min at 85-90°C and then diluted with 50 ml water. The precipitate was filtered off and recrystallized from ethanol to give 3.0 g (91%) (IV), mp 193-194°C. Found: C, 75.1; H, 5.9; P, 14.7%. Calculated for $C_{26}H_{24}OP_2$: C, 75.4; H, 5.8; P, 14.9%. ^{31}P NMR spectrum in $CHCl_3$ (δ, ppm): −11.9 (Ph_2P), 31.6 ($Ph_2P{=}O$), J_{PP} = 51.2 Hz.

β-Piperidinoethyldiphenylphosphine oxide (V) was obtained from 5.0 g (20 mmoles) oxide (II) [3], 0.6 g (10 mmoles) KOH, and 2.6 g (30 mmoles) piperidine in 15 ml DMSO upon heating for 3 h at 80°C. The yield of (V) was 4.9 g (78%), mp 112-113°C (from ethyl acetate-hexane) [2]. ^{31}P NMR spectrum in $CHCl_3$: 30.9 ppm. Oxide (V) was also obtained from oxide (III) [1] under analogous conditions in 85% yield.

Tetraphenylethylenediphosphine dioxide (VI) was obtained from 1.0 g (3.7 mmoles) oxide (III) [1], 0.1 g (1.8 mmoles) KOH, and 1.1 g (5.6 mmoles) Ph_2PHO in 3.5 ml DMSO upon heating at 60°C for 1.5 h. The yield of (VI) was 0.8 g (50%), mp 269-270°C [1,4]. $Ph_2P(O)OH$, which is the product of the oxidation of Ph_2PHO by alkali, was isolated from the aqueous layer [4].

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