

SHORT
COMMUNICATIONS

Synthesis of Tertiary Bisphosphine Oxides from Methylacetylene and Secondary Phosphine Oxides

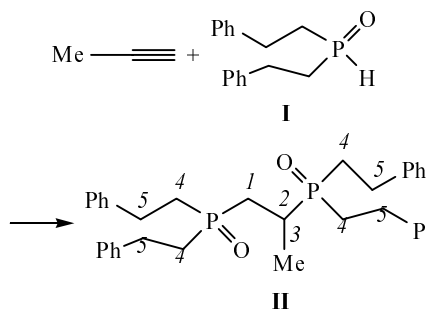
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Bisphosphine oxides are promising polydentate ligands for metal complex catalysts, as well as fire retardants and efficient extractants for isolation of rare and transuranium elements. Of specific importance are bisphosphine oxides possessing chiral centers, which are intermediate products in the synthesis of optically active bisphosphine oxides; their reduction leads to the corresponding optically active bisphosphines which are widely used in catalytic stereoselective syntheses [1]. However, synthetic procedures for the preparation of such chiral bisphosphine oxides are as a rule multistep and laborious.

With the use of bis(2-phenylethyl)phosphine oxide (**I**), which is readily available from red phosphorus and styrene [2–4], we were the first to demonstrate that accessible methylacetylene (the chemistry of this reagent is extensively developing [5–7]) reacts with secondary phosphine oxide in a superbasic medium (KOH–DMSO) [8] to afford *P,P,P',P'*-tetrakis(2-phenylethyl)-1,2-propanedioldi(phosphine oxide) (**II**) in high yield.



Thus double nucleophilic addition of secondary phosphine oxides to methylacetylene can be regarded as a new method of synthesis of bisphosphine oxides possessing an asymmetric carbon atom.

Reaction of bis(2-phenylethyl)phosphine oxide (I**) with methylacetylene.** A suspension of 3.5 g (62.5 mmol) of KOH in 10 ml of DMSO was saturated with methylacetylene at 60°C, and a solution of 1 g (3.9 mmol) of phosphine oxide **I** in 4 ml of DMSO was added dropwise over a period of 30 min while continuously bubbling methylacetylene. The mixture was then stirred for 1.5 h at 60°C while continuously bubbling methylacetylene, cooled, diluted with water, and extracted with benzene. The extracts were washed with water, dried over potassium carbonate, and evaporated, and the residue was dried under reduced pressure. Bisphosphine oxide **II** was isolated as colorless transparent crystals with mp 96°C (from hexane). Yield 1.1 g (93%). IR spectrum (KBr): $\nu(\text{P}=\text{O})$ 1175 cm^{-1} . $^1\text{H}-\{^3\text{P}\}$ NMR spectrum (CDCl_3), δ , ppm (J , Hz): 1.36 d or d.d in the spectrum recorded without decoupling from phosphorus (3H, CH_3 , $^3J_{2,3} = 7.0$, $^3J_{3,\text{P}} = 16.6$), 1.52 d.d (1H, 1'-H, $^2J_{1',1''} = 15.0$, $^3J_{1',2} = 11.2$), 1.88 m (1H, 4-H), 2.03 m (6H, 4-H), 2.15 m (1H, 4-H), 2.27 d (1H, 1''-H, $^3J_{1'',2}$ was not determined), 2.34 d.q (1H, 2-H), 2.93 m (8H, 5-H), 7.08–7.30 m (20H, Ph). ^{31}P NMR spectrum (CDCl_3), δ_{P} , ppm: 46.13 d and 50.29 d ($^3J_{\text{PP}} = 40.2$). The ^1H NMR signals were assigned using $^1\text{H}-^1\text{H}$ COSY two-dimensional homonuclear technique with decoupling from ^{31}P . Protons of the $\text{CH}_2\text{P}=\text{O}$ fragments are nonequivalent due to their diastereotopicity. Found, %: C 75.45; H 7.17; P 10.88. $\text{C}_{35}\text{H}_{42}\text{O}_2\text{P}_2$. Calculated, %: C 75.54; H 7.55; P 11.15.

The ^1H and ^{31}P NMR spectra were recorded on a Bruker DPX-400 instrument at 400 and 161.98 MHz, respectively.

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