ISSN 1070-4280, Russian Journal of Organic Chemistry, 2008, Vol. 44, No. 8, pp. 1245–1246. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © M.Yu. Dvorko, T.E. Glotova, I.A. Ushakov, N.K. Gusarova, B.A. Trofimov, 2008, published in Zhurnal Organicheskoi Khimii, 2008, Vol. 44, No. 8, pp. 1256–1257.

SHORT COMMUNICATIONS

Chemoselective Addition of Secondary Phosphine Oxides to Alkyl Phenylethynyl Ketones

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Received February 28, 2008

DOI: 10.1134/S1070428008080265

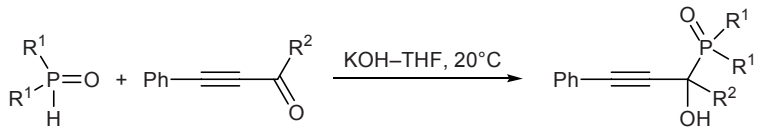
Tertiary phosphine oxides are widely used as ligands for metal complex catalysts [1, 2], special solvents for stabilization of nanosystems in the synthesis of semiconductors [3], and extractants for noble, rare-earth, and transuranium elements [4, 5]. Of particular importance are polyfunctionalized tertiary phosphine oxides; however, their synthesis involves known difficulties. A convenient atom economy approach to such compounds is based on reactions of PH addends with functionalized alkenes, alkynes [6, 7], aldehydes, and ketones [7, 8].

In the present work we examined reactions of accessible secondary phosphine oxides [9] with dielectrophilic alkyl phenylethynyl ketones with a view to synthesize new polyfunctionalized tertiary phosphine oxides. It seemed that the reaction may be nonselective. It is known that nucleophilic addition of secondary phosphine oxides to phenyl ethynyl ketone occurs chemo- and regioselectively at the triple bond [10] and that their reactions with 3-trialkylsilyl(or germyl)prop-2-ynals involves the aldehyde group in the latter [11].

We have found that secondary phosphine oxides **Ia** and **Ib** react with alkyl phenylethynyl ketones **IIa** and **IIb** in the system KOH–THF at room temperature in chemoselective fashion, yielding 63–71% of the corresponding 1-alkyl-1-phosphoryl-3-phenylprop-2-yn-1-ols **IIIa**–**IIIc**. Thus the addition of secondary phosphine oxides to alkyl phenylethynyl ketones provide a convenient method for the synthesis of previously unknown polyfunctionalized chiral tertiary phosphine oxides having a hydroxy group and an acetylenic fragment. The products attract interest as highly reactive building blocks for organic synthesis, synthetic intermediates, and precursors of optically active amphiphilic ligands for enantioselective processes.

Phosphine oxides IIIa–IIIc (*general procedure***).** A mixture of 0.5 mmol of secondary phosphine oxide **Ia** or **Ib**, 0.5 mmol of acetylenic ketone **IIa** or **IIb**, and 0.1 mmol of potassium hydroxide in 4 ml of THF was stirred for 35 h at room temperature; in the synthesis of phosphine oxide **IIIa**, 0.05 mmol of KOH was used, and the mixture was stirred for 4 h. The suspension was passed through a thin layer of aluminum oxide, the solvent was distilled off under reduced pressure, the residue was ground with 5 ml of diethyl ether, and the precipitate was filtered off and dried under reduced pressure.

2-(Diphenylphosphoryl)-4-phenylbut-3-yn-2-ol (IIIa). Yield 0.123 g (71%), mp 140–142°C. IR spectrum, ν, cm^{-1}: 3141 (OH), 2234 w (C≡C), 1175 (P=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.80 d (3H, Me, $^3J_{PH}$ = 13.2 Hz), 4.00 br.s (1H, OH), 7.21–7.40 m (5H,



Ia, **Ib** **IIa**, **IIb** **IIIa–IIIc**

I, R^1 = Ph (**a**), $PhCH_2CH_2$ (**b**); **II**, R^2 = Me (**a**), Pr (**b**); **III**, R^1 = Ph, R^2 = Me (**a**), R^1 = $PhCH_2CH_2$, R^2 = Me (**b**), R^1 = $PhCH_2CH_2$, R^2 = Pr (**c**).

PhC≡), 7.45–7.65 m (6H, *p*-H, *m*-H in PhP), 8.00–8.20 m (4H, *o*-H in PhP). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 25.85 d (Me, $^2J_{PC}$ = 3.7 Hz), 69.86 d (C^2, $^1J_{PC}$ = 87.0 Hz), 89.09 d (Ph**C**, $^3J_{PC}$ = 7.7 Hz), 88.90 d (PhC≡**C**, $^2J_{PC}$ = 2.2 Hz), 122.83 (C^i in Ph); 129.1–129.6, 130.7–132.2 (C_{arom}). ^{31}P NMR spectrum ($CDCl_3$): δ_P 34.32 ppm. Found, %: C 76.56; H 5.87; P 9.09. $C_{22}H_{19}O_2P$. Calculated, %: C 76.29; H 5.53; P 8.94.

2-[Bis(2-phenylethyl)phosphoryl]-4-phenylbut-3-yn-2-ol (IIIb). Yield 0.134 g (67%), mp 103–105°C. IR spectrum, ν, cm^{-1}: 3131 (OH), 2225 w (C≡C), 1158 (P=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.90 d (3H, Me, $^3J_{PH}$ = 12.4 Hz), 2.1–2.6 m (4H, CH_2P), 2.9–3.2 m (4H, C**H**$_2$Ph), 5.63 br.s (1H, OH), 7.2–7.4 m (15H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 24.69 d (Me, $^2J_{PC}$ = 3.6 Hz), 26.90 d (CH_2P, $^1J_{PC}$ = 60.8 Hz), 27.65 d (CH_2P, $^1J_{PC}$ = 57.2 Hz), 28.19 d (**C**H$_2$Ph, $^2J_{PC}$ = 3.6 Hz), 28.26 d (**C**H$_2$Ph, $^2J_{PC}$ = 2.8 Hz), 67.96 d (C^2, $^1J_{PC}$ = 80.0 Hz), 87.75 d (Ph**C**≡, $^3J_{PC}$ = 7.2 Hz), 88.33 d (PhC≡**C**, $^2J_{PC}$ = 2.0 Hz), 121.97 (C^i in PhC≡), 126.46 m (C^o in CH_2Ph), 128.15–128.95 (C^m, C^p in CH_2Ph, PhC≡), 131.70 (C^o in PhC≡), 141.15–141.28 (C^i in CH_2Ph). ^{31}P NMR spectrum ($CDCl_3$): δ_P 51.49 ppm. Found, %: C 77.86; H 6.89; P 7.99. $C_{26}H_{27}O_2P$. Calculated, %: C 77.59; H 6.76; P 7.70.

3-[Bis(2-phenylethyl)phosphoryl]-1-phenylhex-1-yn-3-ol (IIIc). Yield 0.135 g (63%), mp 117–119°C. IR spectrum, ν, cm^{-1}: 3083 (OH), 2221 w (C≡C), 1145 (P=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.05 t (3H, Me, $^3J_{HH}$ = 7.0 Hz), 1.87 m (2H, 5-H), 2.1–2.6 m (6H, CH_2P, 4-H), 2.9–3.2 m (4H, C**H**$_2$Ph), 4.32 br.s (1H, OH), 7.2–7.4 m (15H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.30 s (Me), 16.91 d (C^5, $^3J_{PC}$ = 7.9 Hz), 27.11 d (PCH_2, $^1J_{PC}$ = 60.0 Hz), 27.60 d (PCH_2, $^1J_{PC}$ = 58.0 Hz), 28.23 s (Ph**C**H$_2$), 38.33 d (C^4, $^2J_{PC}$ = 2.4 Hz), 71.40 d (C^3, $^1J_{PC}$ = 79.5 Hz), 87.15 d (C^2, $^2J_{PC}$ = 1.9 Hz), 88.72 d (C^1, $^3J_{PC}$ = 7.6 Hz), 122.01 (C^i in PhC≡), 126.39 m (C^o in CH_2Ph), 128.14–128.88 (C^m, C^p in CH_2Ph, PhC≡), 131.73 (C^o in PhC≡), 141.21–141.65 (C^i in CH_2Ph). ^{31}P NMR spectrum ($CDCl_3$): δ_P 51.45 ppm. Found, %: C 78.38; H 7.49; P 7.31. $C_{28}H_{31}O_2P$. Calculated, %: C 78.12; H 7.26; P 7.19.

The ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker DPX-400 spectrometer at 400.13, 101.61, and 161.98 MHz, respectively; the chemical shifts were measured relative to hexamethyldisiloxane (^{1}H, ^{13}C) or 85% H_3PO_4 (^{31}P). The IR spectra were obtained in KBr on a Bruker IFS-25 instrument.

This study was performed under financial support by the Russian Foundation for Basic Research (project no. 07-03-00562).

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