Selective Mono reduction of bis-phosphine oxides under mild conditions

Maria J. Petersson,^a Wendy A. Loughlin^b and Ian D. Jenkins,*^a

^a Eskitis Institute, Griffith University, Nathan, Brisbane, QLD, 4111, Australia. E-mail:

I.Jenkins@griffith.edu.au;

^b Eskitis Institute and School of Biomolecular and Physical Sciences, Griffith University, Nathan, Brisbane, QLD, 4111, Australia.

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1. Oxidation of bis-phosphines

Representative example: **1,2-Bis(diphenylphosphinyl)ethane (1):** 1,2-Bis-(diphenyl phosphino)ethane (5.0 g, 12.6 mmol) was dissolved in DCM (500 mL) and the solution shaken in a separating funnel with hydrogen peroxide (50 mL, 30% wt-% solution in water). The completion of the reaction (approx. 5 min) was determined by TLC (100% DCM). The DCM layer was washed with water (2 x 500 mL), dried (anhydrous MgSO₄), and filtered. The solvent was removed to afford a white solid. Recrystallisation (methanol/ethyl acetate) of the solid gave 1,2-bis(diphenylphosphinyl)ethane **1** as an amorphous white solid (5.35 g, 99%). Mp 273-276 °C (lit.,¹ mp 276-278 °C). δ_{H} (400 MHz, CDCl₃) 2.55 (4H, br d, $J = 2.4$ Hz), 7.45 (8H, dd, $J = 7.1, 7.1$ Hz), 7.51 (4H, dd, $J = 7.1, 7.1$ Hz), 7.69-7.74 (8H, m); δ_{P} (162 MHz, CDCl₃) 31.6 (s, 2P). MS (ESI) m/z 431.2 ([M+H]⁺, 64%), 453.2 ([M+Na]⁺, 100%).

Additional phosphine oxides were prepared.

Bis(diphenylphosphinyl)methane: (1.01g, 93%). Mp 177-180 °C (lit.,¹ mp 178-179 °C). δ_{H} (400 MHz, CDCl₃) 3.56 (2H, br t, $J = 14.6$ Hz), 7.33-7.36 (8H, m), 7.43 (4H, dd, $J = 7.4, 7.4$ Hz), 7.72-7.77 (8H, m); δ_{P} (162 MHz, CDCl₃) δ 26.4 (s, 2P). MS (ESI) m/z 417.2 ([M+H]⁺, 85%), 439.2 ([M+Na]⁺, 100%).

1,3-Bis(diphenylphosphinyl)propane: (1.04 g, 97%). Mp 139-140 °C (lit.,¹ mp 142-144 °C). δ_{H} (400 MHz, CDCl₃) 1.96-2.08 (2H, m), 2.47-2.53 (4H, m), 7.40-7.45 (8H, m), 7.47-7.51 (4H, m), 7.67-7.72 (8H, m); δ_{P} (162 MHz, CDCl₃) δ 32.6 (s, 2P). MS (ESI) m/z 445.2 ([M+H]⁺, 37%), 467.2 ([M+Na]⁺, 100%).

1,4-Bis(diphenylphosphinyl)butane: (1.02g, 95%). Mp 267-269 °C (lit.,¹ mp 264-266 °C). δ_{H} (400 MHz, CDCl₃) 1.72-1.74 (4H, m), 2.23-2.29 (4H, m), 7.43-7.48 (8H, m), 7.50-7.53 (4H, m), 7.67-7.72 (8H, m); δ_{P} (162 MHz, CDCl₃) δ 34.1 (s, 2P). MS (ESI) m/z 459.2 ([M+H]⁺, 86%), 481.2 ([M+Na]⁺, 100%).

***rac*-2,2'-Bis(diphenylphosphinyl)-1,1'-binaphthyl:** (2.06 g, 98%). Mp 299-301 °C (lit.,² mp 304-306 °C). δ_{H} (400 MHz, CDCl₃) 6.78-6.84 (4H, m), 7.20-7.31 (10H, m), 7.34-7.47 (10H, m), 7.71 (4H, br dd, $J = 7.9, 12.3$ Hz), 7.82 (2H, br d, $J = 7.9$ Hz), 7.86 (2H, dd, $J = 2.4, 7.9$ Hz); δ_{P} (162 MHz, CDCl₃) 30.6 (s, 2P). MS (ESI) m/z 655.3 ([M+H]⁺, 100%), 677.3 ([M+Na]⁺, 26%).

(S)-2,2'-Bis(di-p-tolylphosphinyl)-1,1'-binaphthyl: (299 mg, 97%). Mp 303-304 °C (lit.,² mp 310-315 °C). δ_{H} (400 MHz, CDCl_3) 2.31 (12H, d, $J = 15.6$ Hz), 6.86-6.92 (4H, m), 6.98-7.04 (8H, m), 7.29-7.32 (4H, m), 7.36-7.54 (8H, m), 7.80-7.84 (4H, m); δ_{P} (162 MHz, CDCl_3) 30.6 (s, 2P). MS (ESI) m/z 711.3 ($[\text{M}+\text{H}]^+$, 100%), 733.3 ($[\text{M}+\text{Na}]^+$, 24%), 717.4 ($[\text{M}+\text{Li}]^+$, 100%). HRMS calcd for $\text{C}_{48}\text{H}_{39}\text{O}_2\text{P}_2$ $[\text{M}-\text{H}]^-$: 709.2425. Found: 709.2409.

References:

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- 2 H. Takaya, K. Mashima, K. Koyano, M. Yagi, H. Kumobayashi, T. Taketomi, S. Akutagawa, R. Noyori, *Journal of Organic Chemistry* 1986, **51**, 629-35.

2. ^1H NMR and ^{31}P NMR spectra

^1H NMR at 400MHz in CDCl_3

^{31}P NMR at 162MHz in CDCl_3

^1H NMR at 400MHz in CDCl_3

^{31}P NMR at 162MHz in CDCl_3

^1H NMR at 400MHz in CDCl_3

^{31}P NMR at 162MHz in CDCl_3

^1H NMR at 400MHz in CDCl_3

^{31}P NMR at 162MHz in CDCl_3

^1H NMR at 400MHz in CDCl_3

^{31}P NMR at 162MHz in CDCl_3

^1H NMR at 400MHz in CDCl_3

^{31}P NMR at 162MHz in CDCl_3

^{13}C NMR at 100MHz in CDCl_3

3. Mass Spectral and ^1H NMR data for

Bis(diphenylphosphino)methane monoxide

δ_{H} (400 MHz, CDCl_3) 3.11 (2H, br d, $J = 12.8$ Hz), 7.24-7.29 (6H, m), 7.36-7.41 (8H, m), 7.44-7.49 (2H, m), 7.70-7.76 (4H, m). MS (ESI) m/z 401.1 ($[\text{M}+\text{H}]^+$, 100%).

1,2-Bis(diphenylphosphino)ethane monoxide (2)

δ_{H} (400 MHz, CDCl_3) 2.30 (4H, br s), 7.30-7.39 (10H, m), 7.41-7.46 (4H, m), 7.49-7.53 (2H, m), 7.61-7.66 (4H, m). MS (ESI) m/z 415.2 ($[\text{M}+\text{H}]^+$, 100%), 421.2 ($[\text{M}+\text{Li}]^+$, 100%).

1,3-Bis(diphenylphosphino)propane monoxide

δ_{H} (400 MHz, CDCl_3) 1.74-1.86 (2H, m), 2.17 (2H, br t, $J = 7.6$ Hz), 2.39-2.46 (2H, m), 7.24-7.28 (6H, m), 7.30-7.35 (4H, m), 7.38-7.42 (4H, m), 7.44-7.49 (2H, m), 7.65-7.70 (4H, m). MS (ESI) m/z 429.2 ($[\text{M}+\text{H}]^+$, 100%).

1,4-Bis(diphenylphosphino)butane monoxide

δ_{H} (400 MHz, CDCl_3) 1.49-1.58 (2H, m), 1.70-1.80 (2H, m), 2.01-2.05 (2H, m), 2.21-2.28 (2H, m), 7.30-7.33 (6H, m), 7.36-7.40 (4H, m), 7.43-7.53 (6H, m), 7.69-7.74 (4H, m). MS (ESI) m/z 443.2 ($[\text{M}+\text{H}]^+$, 100%).

2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl monooxide

δ_{H} (400 MHz, CDCl_3) 6.65 (1H, br d, $J = 8.4$ Hz), 6.71-6.75 (1H, m), 6.82 (1H, br d, $J = 8.4$ Hz), 6.87-7.39 (21H, series of m), 7.42 (1H, dd, $J = 3.2, 8.4$ Hz), 7.61 (3H, dd, $J = 8.6, 11.8$ Hz), 7.70 (1H, d, $J = 8.0$ Hz), 7.75 (1H, d, $J = 8.6$ Hz), 7.82 (1H, d, $J = 8.0$ Hz), 7.91 (1H, br dd, $J = 2.4, 8.6$ Hz). MS (ESI) m/z 639.3 ($[\text{M}+\text{H}]^+$, 100%).

2,2'-Bis(ditolylphosphino)-1,1'-binaphthyl monooxide

δ_{H} (400 MHz, CDCl_3) 2.25 (6H, br s), 2.29 (6H, br d, $J = 12$ Hz), 6.64 (1H, br d, $J = 8.4$ Hz), 6.75 (1H, br dd, $J = 7.6, 7.6$ Hz), 6.84-7.04 (12H, series of m), 7.20 (2H, dd, $J = 7.6, 7.6$ Hz), 7.25-7.37 (4H, m), 7.41-7.48 (3H, m), 7.71 (3H, br dd, $J = 8.5, 13.6$ Hz), 7.82 (1H, br d, $J = 8.5$ Hz), 7.93 (1H, br dd, $J = 8.6, 8.8$ Hz). MS (ESI) m/z 695.3 ($[\text{M}+\text{H}]^+$, 100%). Anal. Calcd for $\text{C}_{48}\text{H}_{40}\text{OP}_2$: C, 82.98; H, 5.80. Found: C, 82.65; H, 6.01.