Electronic Supplementary Information

Hydrophosphinylation of Unactivated Alkenes with Secondary Phosphine Oxides Under Visible-Light Photocatalysis

Woo-Jin Yoo, and Shū Kobayashi

Department of Chemistry, School of Science, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo, 113-0033, Japan

Contents

Part I: Substrate Scope for the Hydrophosphinylation of SPOs to Unactivated Alkenes Using Rhodamine B as a Catalyst..................................................................................................................S-2

Part II: NMR Spectra of 3a-j............................................................................................................................................S-6

Part III: References..................................................................................................................................................S-37
General Information: $^1$H and $^{13}$C NMR spectra were recorded on a JEOL ECX-500 in CDCl$_3$. Chemical shifts were reported in parts per million (ppm) from tetramethylsilane using the solvent resonance as the internal standard (chloroform: $\delta$ 7.26 ppm) for $^1$H NMR and (deuterochloroform: $\delta$ 77.0 ppm) for $^{13}$C NMR. $^{31}$P NMR spectra were referenced to external H$_3$PO$_4$ ($\delta$ 0 ppm). IR spectra were measured on a JASCO FT/IR-610 spectrometer. High-resolution mass spectrometry was carried out using a JEOL JMS-T100TD (DART). Preparative thin-layer chromatography (PTLC) was carried out using Wakogel B-5F from Wako Pure Chemical Industries, Ltd.

Reagents: Unless stated otherwise, commercial reagents were used as received. Secondary phosphine oxides 1b-1f used in this study were prepared according to known literature procedure.$^1$

Part I: Substrate Scope for the Hydrophosphinylation of SPOs to Unactivated Alkenes Using Rhodamine B as a Catalyst

In a 2 mL screw-cap vial was added rhodamine B (0.0012 g, 0.0025 mmol, 0.5 mol%), SPO 1a (0.1011 g, 0.5000 mmol), alkene 2a (100 µL, 0.497 mmol), and i-PrOH (0.2 mL). The vial was quickly flushed with argon and then was stirred for 6 h in a water bath (30 °C) under a white LED lamp (Toshiba E-CORE LDA7N/2). Then, the reaction mixture was passed through a plug of silica gel, concentrated under reduced pressure, and the resulting residue was purified by preparative TLC (EtOAc) to afford the addition product 3a (0.1526 g, 0.4456 mmol, 89%) as a white solid.

Decydiphenylphosphine oxide (3a) (Table 3, entry 1). $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 7.71-7.68 (m, 4H), 7.49-7.40 (m, 6H), 2.24-2.19 (m, 2H), 1.60-1.55 (m, 2H), 1.37-1.32 (m, 2H), 1.25-1.18 (m, 12H), 0.83 (t, 3H, $J$ = 6.9 Hz); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 133.4 (d, $J_{C,P}$ = 98.0 Hz), 131.8, 130.9 (d, $J_{C,P}$ = 9.6 Hz), 128.8 (d, $J_{C,P}$ = 10.6 Hz), 32.0, 31.1 (d, $J_{C,P}$ = 15.0 Hz), 29.9 (d, $J_{C,P}$ = 72.0 Hz), 29.6 (d, $J_{C,P}$ = 19.2 Hz), 29.4, 29.2, 22.8, 21.6, 21.5, 14.3; $^{31}$P NMR (CDCl$_3$, 200 MHz) $\delta$ 33.1. This is a known compound and the spectral data are identical to those reported in the literature.$^2$

Diphenyl(4-phenylbutyl)phosphine oxide (3b) (Table 3, entry 2). Following the above general procedure with 2b (75 µL, 0.499 mmol) for 12 h. The crude reaction mixture was purified by preparative TLC (EtOAc) to provide 3b (0.0979 g, 0.293 mmol, 59%) as a white solid. $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 7.76-7.71 (m, 4H), 7.54-7.45 (m, 6H), 7.28-7.24 (m, 2H), 7.19-7.11 (m, 3H), 2.60 (t, 2H, $J$ = 7.4 Hz), 2.32-2.27 (m, 2H), 1.78-1.66 (m, 4H); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 142.1, 133.3 (d, $J_{C,P}$ = 98.0 Hz), 131.8, 131.0 (d, $J_{C,P}$ = 8.8 Hz), 128.8 (d, $J_{C,P}$ = 11.4 Hz), 128.5, 126.0, 35.5, 32.9 (d, $J_{C,P}$ = 14.4 Hz), 29.8 (d, $J_{C,P}$ = 71.6 Hz), 21.4; $^{31}$P NMR (CDCl$_3$, 200 MHz) $\delta$ 32.9. This is a known compound and the spectral data are identical to those reported in the literature.$^3$
(3-Phenoxypropyl)diphenylphosphine oxide (3c) (Table 3, entry 3). Following the above general procedure with 2c (69 µL, 0.503 mmol) for 12 h. The crude reaction mixture was purified by preparative TLC (EtOAc) to provide 3c (0.1514 g, 0.450 mmol, 90%) as a white solid. $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 7.76-7.71 (m, 4H), 7.51-7.41 (m, 6H), 7.25-7.21 (m, 2H), 6.92-6.89 (m, 1H), 6.83-6.81 (m, 2H), 3.98 (t, $J$ = 5.9 Hz), 2.49-2.44 (m, 2H), 2.14-2.06 (m, 1H); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 158.8, 133.1 (d, $J_{C-P}$ = 9.0 Hz), 128.7 (d, $J_{C-P}$ = 98.4 Hz), 132.0, 131.0 (d, $J_{C-P}$ = 10.8 Hz), 129.6, 128.9 (d, $J_{C-P}$ = 12.0 Hz), 121.0, 114.6, 67.6 (d, $J_{C-P}$ = 14.4 Hz), 26.6 (d, $J_{C-P}$ = 73.2 Hz), 22.0; $^{31}$P NMR (CDCl$_3$, 200 MHz) $\delta$ 33.0. This is a known compound and the spectral data are identical to those reported in the literature.$^3$

(3-Hydroxypropyl)diphenylphosphine oxide (3d) (Table 3, entry 4). Following the above general procedure with 2d (34 µL, 0.500 mmol) for 12 h. The crude reaction mixture was purified by preparative TLC (MeOH:DCM = 5:95) to provide 3d (0.1145 g, 0.440 mmol, 88%) as a white solid. $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 7.75-7.68 (m, 4H), 7.52-7.41 (m, 6H), 4.16 (bs, 1H), 3.66 (t, $J$ = 5.6 Hz), 2.38 (m, 2H), 1.88-1.80 (m, 2H); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 132.5 (d, $J_{C-P}$ = 99.0 Hz), 132.0, 131.0 (d, $J_{C-P}$ = 10.0 Hz), 128.9 (d, $J_{C-P}$ = 11.4 Hz), 62.6 (d, $J_{C-P}$ = 10.2 Hz), 27.6 (d, $J_{C-P}$ = 72.0 Hz), 25.5; $^{31}$P NMR (CDCl$_3$, 200 MHz) $\delta$ 35.3. This is a known compound and the spectral data are identical to those reported in the literature.$^4$

Cyclohexyldiphenylphosphine oxide (3e) (Table 3, entry 5). Following the above general procedure with 2e (100 µL, 0.987 mmol) for 12 h. The crude reaction mixture was purified by preparative TLC (EtOAc) to provide 3e (0.0916 g, 0.322 mmol, 64%) as a white solid. $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 7.76-7.72 (m, 4H), 7.47-7.39 (m, 6H), 2.23-2.16 (m, 1H), 1.77-1.66 (m, 5H), 1.54-1.45 (m, 2H), 1.26-1.16 (m, 3H); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 132.2 (d, $J_{C-P}$ = 94.0 Hz), 131.6, 131.2 (d, $J_{C-P}$ = 9.0 Hz), 128.7 (d, $J_{C-P}$ = 10.8 Hz), 37.3 (d, $J_{C-P}$ = 74.0 Hz), 26.5 (d, $J_{C-P}$ = 13.0 Hz), 25.9, 24.9; $^{31}$P NMR (CDCl$_3$, 200 MHz) $\delta$ 34.9. This is a known compound and the spectral data are identical to those reported in the literature.$^3$
Diphenyl(tetrahydro-2H-pyran-3-yl)phosphine oxide (3f) (Table 3, entry 6). Following the above general procedure with 2f (91 µL, 1.00 mmol) for 12 h. The crude reaction mixture was purified by preparative TLC (MeOH:DCM = 1:9) to provide 3f (0.0830 g, 0.290 mmol, 58%) as a white solid. $^1$H NMR (CDCl$_3$, 500 MHz) δ 7.79-7.70 (m, 4H), 7.51-7.43 (m, 6H), 3.91-3.89 (m, 2H), 3.66-3.61 (m, 1H), 3.36 (td, 1H, J = 10.9, 3.9 Hz), 2.62-2.55 (m, 1H), 1.91-1.62 (m, 4H); $^{13}$C NMR (CDCl$_3$, 125 MHz) δ 132.1, 132.0, 131.9, 131.8, 131.1 (d, $J_{C-P}$ = 6.4 Hz), 131.0 (d, $J_{C-P}$ = 6.6 Hz), 129.0 (d, $J_{C-P}$ = 8.2 Hz), 128.9 (d, $J_{C-P}$ = 8.2 Hz), 68.2, 67.0, 36.7 (d, $J_{C-P}$ = 70.4 Hz), 25.9 (d, $J_{C-P}$ = 11.4 Hz), 22.3; $^{31}$P NMR (CDCl$_3$, 200 MHz) δ 30.8. This is a known compound and the spectral data are identical to those reported in the literature.3

Bicyclo[2.2.1]heptan-2-ylidiphenylphosphine oxide (3g) (Table 3, entry 7). Following the above general procedure with 2g (0.0942, 1.00 mmol) for 12 h. The crude reaction mixture was purified by preparative TLC (EtOAc) to provide 3g (0.1262 g, 0.426 mmol, 85%) as a white solid. $^1$H NMR (CDCl$_3$, 500 MHz) δ 7.81-7.70 (m, 4H), 7.49-7.39 (m, 6H), 2.48 (bd, 1H, $J$ = 7.9 Hz), 2.34 (bs, 1H), 2.27 (t, 1H, $J$ = 7.9 Hz), 1.96-1.83 (m, 2H), 1.59-1.51 (m, 2H), 1.42-1.13 (m, 2H); $^{13}$C NMR (CDCl$_3$, 125 MHz) δ 133.9 (d, $J_{C-P}$ = 95.4 Hz), 133.6 (d, $J_{C-P}$ = 95.4 Hz), 131.54, 131.48, 131.14 (d, $J_{C-P}$ = 8.4 Hz), 131.08 (d, $J_{C-P}$ = 9.6 Hz), 128.7 (d, $J_{C-P}$ = 12.0 Hz), 128.6 (d, $J_{C-P}$ = 12.0 Hz), 40.1 (d, $J_{C-P}$ = 72.8 Hz), 38.3, 37.5, 36.6, 32.3 (d, $J_{C-P}$ = 15.0 Hz), 31.6 (d, $J_{C-P}$ = 4.2 Hz), 28.8; $^{31}$P NMR (CDCl$_3$, 200 MHz) δ 34.5. This is a known compound and the spectral data are identical to those reported in the literature.5

Decylidip-tolylphosphine oxide (3h) (Table 3, entry 8). Following the above general procedure with 1b (0.1151, 0.500 mmol) for 12 h. The crude reaction mixture was purified by preparative TLC (EtOAc) to provide 3h (0.1167 g, 0.315 mmol, 63%) as a white solid (m.p. = 45-46 ºC). $^1$H NMR (CDCl$_3$, 500 MHz) δ 7.57 (4H, dd, $J$ = 11.3, 7.7 Hz), 7.23-7.21 (m, 4H), 2.34 (s, 6H), 2.20-2.14 (m, 2H), 1.56-1.53 (m, 2H), 1.34-1.11 (m, 14H), 0.82 (t, 3H, $J$ = 7.0 Hz); $^{13}$C NMR (CDCl$_3$, 125 MHz) δ 142.0, 130.9 (d, $J_{C-P}$ = 9.6 Hz), 130.3 (d, $J_{C-P}$ = 100.2 Hz), 129.4 (d, $J_{C-P}$ = 12.0 Hz), 32.0, 31.1 (d, $J_{C-P}$ = 14.4 Hz), 30.1 (d, $J_{C-P}$ = 72.0 Hz), 29.6, 29.5, 29.4, 29.2, 22.8, 21.7, 21.6 (d, $J_{C-P}$ = 3.6 Hz), 14.2; $^{31}$P NMR (CDCl$_3$, 200 MHz) δ 33.3; IR (KBr) cm$^{-1}$ 3043 (s), 3021 (s), 2849 (w), 1926 (s), 1659 (w), 1604 (s), 1501 (m), 1467 (s), 1401 (s), 1380 (m), 1174 (s), 1116 (s), 1099 (s); DART-HRMS (m/z) calcd. for C$_{22}$H$_{36}$O$_2$P$_1$ [(M+H)$^+$]: 371.25038, found: 371.25003.
Decylbis(4-methoxyphenyl)phosphine oxide (3i) (Table 3, entry 9). Following the above general procedure with 1c (0.1311, 0.500 mmol) and i-PrOH (0.4 mL) for 18 h at 50 °C. The crude reaction mixture was purified by preparative TLC (EtOAc) to provide 3i (0.0547 g, 0.136 mmol, 27%) as a white solid (m.p. = 47-48 °C). 1H NMR (CDCl3, 500 MHz) δ 7.60 (dd, 4H, J = 10.9, 8.3 Hz), 6.93-6.91 (m, 4H), 3.79 (s, 6H), 2.17-2.11 (m, 2H), 1.58-1.50 (m, 2H), 0.83 (t, 3H, J = 6.9 Hz); 13C NMR (CDCl3, 125 MHz) δ 162.3, 132.7 (d, J_{C-P} = 10.6 Hz), 124.9 (d, J_{C-P} = 12.5 Hz), 114.3 (d, J_{C-P} = 12.5 Hz), 55.5, 32.0, 31.2 (d, J_{C-P} = 14.6 Hz), 30.4 (d, J_{C-P} = 72.7 Hz), 29.7, 29.5, 29.4, 29.3, 22.8, 21.7, 14.3; 31P NMR (CDCl3, 200 MHz) δ 33.1; IR (KBr) cm⁻¹ 2955 (m), 2921 (s), 2851 (s), 2050 (w), 1908 (w), 1599 (s), 1571 (m), 1501 (s), 1462 (m), 1295 (s), 1255 (s), 1174 (s); DART-HRMS (m/z) calcd. for C24H36O3P1 [(M+H)⁺]: 403.24021, found: 403.24110.

Bis(4-chlorophenyl)(decyl)phosphine oxide (3j) (Table 3, entry 10). Following the above general procedure with 1d (0.1311, 0.500 mmol) and i-PrOH (0.4 mL) for 18 h at 50 °C. The crude reaction mixture was purified by preparative TLC (EtOAc) to provide 3j (0.1295 g, 0.315 mmol, 63%) as a white solid (m.p. = 51-52 °C). 1H NMR (CDCl3, 500 MHz) δ 7.63-7.59 (m, 4H), 7.43-7.39 (m, 4H), 2.21-2.15 (m, 2H), 1.57-1.51 (m, 2H), 1.36-1.31 (m, 2H), 1.25-1.00 (m, 12H), 0.82 (t, 3H, J = 7.0); 13C NMR (CDCl3, 125 MHz) δ 138.6, 132.3 (d, J_{C-P} = 10.0 Hz), 131.5 (d, J_{C-P} = 99.0 Hz), 129.3 (d, J_{C-P} = 12.0 Hz), 32.0, 31.1 (d, J_{C-P} = 14.6 Hz), 30.1, 29.6, 29.5, 29.4, 29.2, 22.8, 21.4, 14.3; 31P NMR (CDCl3, 200 MHz) δ 32.0; IR (KBr) cm⁻¹ 3052 (2), 2953 (s), 2850 (s), 1921 (w), 1718 (w), 1584 (m), 1483 (m), 1390 (m), 1184 (s), 1088 (s); DART-HRMS (m/z) calcd. for C24H30Cl2O3P1 [(M+H)⁺]: 411.14113, found: 411.14016.
Part III: NMR Spectra of 3a-j
Electronic Supplementary Material (ESI) for Green Chemistry
This journal is © The Royal Society of Chemistry 2013
Part III: References