Phosphorylation of alcohols with N-phosphoryl oxazolidinones employing copper (II) triflate catalysis

Simon Jones and Chaiwat Smanmoo

Department of Chemistry, University of Sheffield, Dainton Building, Brook Hill,
Sheffield S3 7HF, UK

E-mail: Simon.Jones@Sheffield.ac.uk

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General Experimental Procedures.

All solvents used were freshly dried over sodium (except dichloromethane which was dried over calcium hydride). Glassware was flame dried and cooled under vacuum before use. All reactions were carried out under the nitrogen atmosphere. TLC was carried out using aluminium backed tlc sheets (silica gel 60 F₂₅₄) and visualization of the plates performed using a U.V. lamp or by dipping in KMnO₄ then exposure by heating. For nmr experiments, residual proton signals from the deuteriated solvents were used as references [(chloroform (1H 7.25 ppm, 13C 77 ppm)]. Ligands **2** and **6** were purchased from commercial sources, while ligands **1**, **3**, **4**, and **5** were prepared by existing literature methods.¹

N-(5,5-Diphenyl oxazolidinyl) diethyl phosphate **7**²

n-BuLi (1.68 mL, 4.20 mmol, 2.5 M solution in hexanes) was added to a stirred suspension of 5,5-diphenyl-oxazolidin-2-one³ (1.00g, 4.20 mmol) at -78 °C in THF (15 mL), and left to stir at RT for 1h. The solution was re-cooled to -78 °C, diethylchlorophosphate (0.60 mL, 4.20 mmol) added dropwise and the solution left to stir at RT for 2h. Saturated NH₄Cl solution (10 mL) was added and the mixture extracted with EtOAc (3 $\times$ 15 mL). The combined organic extracts were washed with

sat. NaHCO₃ solution (10 mL) and brine (10 mL) and dried with MgSO₄. Filtration, evaporation of solvent and purification by chromatography on silica gel (EtOAc: petroleum ether; 1:9) afforded the title compound as an oil (0.98 g, 63 %); mpt. 70 – 72 °C; *R_f* 0.37 (EtOAc: petroleum ether; 1:9); *R_f* 0.37 (EtOAc: petroleum ether; 15:85); IR (KBr) 2923, 2853, 1783 (*C=O*), 1452; ¹H NMR (250 MHz, CDCl₃) δ 1.26 (6H, t, *J* 6.5, CH₂CH₃), 4.07 (4H, m, CH₂CH₃), 4.50 (2H, s, CH₂), 7.25–7.48 (10H, m, ArCH); ¹³C NMR (63 MHz, CDCl₃) δ 15.9 (d, *J*_{C-P} 6.8, CH₂CH₃), 57.1 (d, *J*_{C-P} 3.7, CH₂NH), 64.6 (d, *J*_{C-P} 5.9, CPh), 85.8 (d, *J*_{C-P} 8.1, CH₂O), 124.5 (ArCH), 128.5 (ArCH), 128.8 (ArCH), 141.2 (ArC), 154.1 (d, *J*_{C-P} 7.7, C=O); ³¹P NMR (101 MHz, CDCl₃) δ -4.51; MS (EI) *m/z* 375 (8%, M⁺), 331 (M⁺-CO₂, 58), 319 (35), 298 (M⁺-Ph, 24), 183 (70), 178 (79), 165 (98), 138 (100), 105 (71); Anal. Calcd. for C₁₉H₂₂NO₅P: C, 60.80; H 5.91; N 3.73. Found: C, 60.0; H, 5.72; N, 3.54.

***N*-(5,5-Diphenyl oxazolidinyl) diphenyl phosphate 8²**

n-BuLi (1.68 mL, 4.20 mmol, 2.5 M solution in hexanes) was added to a stirred suspension of 5,5-diphenyl-oxazolidin-2-one³ (1.00 g, 4.20 mmol) at -78°C in THF (15 mL), and left to stir at RT for 1h. The solution was re-cooled to -78 °C, diphenylchlorophosphate (0.37 mL, 4.20 mmol) added dropwise and the solution left to stir at RT for 2h. Saturated NH₄Cl solution (10 mL) was added and the mixture extracted with EtOAc (3 × 15 mL). The combined organic extracts were washed with sat. NaHCO₃ solution (10 mL) and brine (10 mL) and dried with MgSO₄. Filtration, evaporation of solvent and purification by chromatography on silica gel (EtOAc: petroleum ether; 15:85) afforded the title compound as an oil (1.16 g, 74 %); *R_f* 0.42 (EtOAc: petroleum ether; 15:85); IR (KBr) 2925, 1775 (*C=O*), 1589, 1490, 1458; ¹H NMR (300 MHz, CDCl₃) δ 4.46 (2H, s, CH₂), 6.95–7.38 (20H, m, ArCH); ¹³C NMR (126 MHz, CDCl₃) δ 57.3 (d, *J*_{C-P} 3.6, CH₂N), 86.1 (d, *J*_{C-P} 8.9, CPh), 120.4 (d, *J*_{C-P} 4.7, ArCH), 125.3 (ArCH), 125.9 (ArCH), 128.5 (ArCH), 128.7 (ArCH), 129.8 (ArCH), 140.7 (ArC), 149.5 (d, *J*_{C-P} 6.7, ArC), 153.4 (d, *J*_{C-P} 7.5, C=O); ³¹P NMR (101 MHz, CDCl₃) δ -12.79; MS (TOF ES) *m/z* 471 (100%, M⁺); Anal. Calcd. for C₁₇H₁₈NO₅P: C, 68.79; H, 4.70; N, 2.97. Found: C, 69.34; H, 5.10; N, 2.72.

Optimized procedure for phosphoryl transfer

Alcohol (1.0 mmol) was added to a stirred solution of copper (II) triflate (0.2 mmol) and *N,N'*-ethylenebis(benzaldimine) (BEN) (0.2 mmol) in CH₂Cl₂ (10 mL) at RT under a nitrogen atmosphere. The solution was left stirring at RT for 5 min before Et₃N (1 mmol) and dialkyl *N*-phosphoryl oxazolidinone (1 mmol) were added sequentially. The reaction mixture was left to stir at RT for 48 h before adding NH₄Cl_(aq) (10 mL), and extracting with EtOAc (3 × 30 mL). The combined organic layers were washed with NaHCO₃ (50 mL) and brine (50 mL) and dried over MgSO₄. The suspension was filtered and the solvent was removed under reduced pressure. The phosphate product was obtained after purification by appropriate silica gel column chromatography (ethyl acetate / petroleum ether).

Benzyl Diethyl Phosphate 9⁴

Obtained in 86% yield as clear oil; ¹H NMR (250 MHz, CDCl₃) δ 1.18 (6H, t, *J* 6.8, CH₃CH₂), 3.88 (4H, app pent, *J*_{P-H} 6.8 and *J* 6.8, CH₂CH₃), 4.87 (2H, d, *J*_{P-H} 8.5, CH₂O), 7.10–7.22 (5H, m, ArCH); ³¹P NMR (101 MHz, CDCl₃) δ -0.58.

Allyl Diethyl Phosphate 10⁵

Obtained in 84% yield as a colorless oil; ¹H NMR (250 MHz, CDCl₃) δ 1.29 (6H, td, *J* 7.1 and *J*_{P-H} 1.1, CH₃CH₂), 4.06 (4H, app pent, *J*_{P-H} 7.1 and *J* 7.1, CH₂CH₃), 4.47 (2H, m, CH₂OP), 5.19 (1H, dq, *J* 17.1 and 1.3, CH=CH₂), 5.31 (1H, dq, *J* 10.4 and 1.3, CH=CH₂), 5.89 (1H, m, CH=CH₂); ³¹P (101 MHz, CDCl₃) δ -0.57.

(Pro-2-ynyl) Diethyl Phosphate 11⁶

Obtained in 75% yield as a colorless oil; ¹H NMR (250 MHz, CDCl₃) δ 1.39 (6H, td, *J* 7.0 and *J*_{P-H} 1.2, CH₂CH₃), 2.50 (1H, t, *J* 2.5, C≡CH), 4.06 (2H, d, *J* 2.5, OCH₂), 4.21 (4H, m, CH₂CH₃); ³¹P NMR (101 MHz, CDCl₃) δ -0.69.

Cyclohexyl Diethyl Phosphate 12⁷

Obtained in 80 % yield as clear oil; ¹H NMR (300 MHz, CDCl₃) δ 1.16–1.27 (3H, m, CH₂), 1.25 (6H, td, *J* 7.1, and *J*_{P-H} 1.0, CH₃CH₂), 1.32–1.49 (3H, m, CH₂), 1.58–1.69 (2H, m, CH₂), 1.76–1.88 (2H, m, CH₂), 3.96 (4H, app pent, *J*_{P-H} 7.1 and *J* 7.1, CH₂CH₃), 4.24 (1H, m, CHOP); ³¹P NMR (101 MHz, CDCl₃) δ -1.67.

Isopropyl Diethyl Phosphate 13⁸

Obtained in 80% yield as a clear oil; ¹H NMR (250 MHz, CDCl₃) δ 1.25 – 1.31 (12H, m, CH₃CH₂ and CH₃CH), 4.03 (4H, app pent, *J*_{P-H} 7.3 and *J* 7.3, CH₂CH₃), 4.55 (1H, m, CHOP); ³¹P (101 MHz, CDCl₃) δ -1.48.

2-Butyl Diethyl Phosphate 14⁹

Obtained in 77% yield as a clear oil; ¹H NMR (250 MHz, CDCl₃) δ 0.80 (3H, t, *J* 7.5, CH₃CH₂), 1.21 (6H, td, *J* 7.2 and *J*_{P-H} 0.8, CH₂CH₃), 1.41 – 1.62 (3H, m, CH₂CH), 3.95 (4H, m, CH₂CH₃), 4.29 (1H, app hept, *J*_{P-H} 6.3 and *J* 6.3, CHOP); ³¹P (101 MHz, CDCl₃) δ -1.35.

(2-Methyl-2-Propyl) Diethyl Phosphate 15¹⁰

Obtained in 55% yield as a clear oil; ¹H NMR (250 MHz, CDCl₃) δ 1.03 (6H, td, *J* 6.5 and *J*_{P-H} 0.9, CH₂CH₃), 1.18 (9H, s, CH₃C), 3.74 (4H, app pent, *J*_{P-H} 6.5 and *J* 6.5, CH₂CH₃); ³¹P NMR (101 MHz, CDCl₃) δ -6.98.

(±)- α -Terpineol Diethyl Phosphate 16²

Obtained in 55% yield as a clear oil; IR / cm^{-1} (ATR) 2966, 2922, 2889, 1438, 1376, 1384, 1154; ^1H NMR (250 MHz, CDCl_3) δ 1.16 (3H, s, CH_3), 1.20 (3H, s, CH_3), 1.21–1.56 (2H, m), 1.40 (6H, td, J 6.9 and $J_{\text{P-H}}$ 1.2, CH_3CH_2), 1.63 (3H, s, CH_3), 1.70–2.13 (5H, m), 4.28 (4H, app pent, J 6.9 and $J_{\text{P-H}}$ 6.9, CH_2CH_3), 5.34 (1H, s, $\text{CH}=\text{C}$); ^{13}C NMR (75 MHz, CDCl_3) δ 15.6 (d, $J_{\text{C-P}}$ 7.8, CH_3), 23.3 (CH_3), 23.9 (CH_2), 26.2 (CH_3), 26.9 (CH_2), 27.4 (CH_3), 31.0 (CH_2), 44.9 (CH), 65.7 (d, $J_{\text{C-P}}$ 6.8, CH_2O), 72.7 [$(\text{CH}_3)_2\text{CO}$], 120.5 ($\text{CH}=\text{C}$), 133.9 ($\text{CH}=\text{C}$); ^{31}P NMR (101 MHz, CDCl_3) δ -5.16; m/z (EI) 291 (58%, MH^+), 263 (52), 235 (47), 207 (42), 179 (62), 161 (100), 99 (83), 68 (70); Anal. Calcd for $\text{C}_{14}\text{H}_{27}\text{O}_4\text{P}$: C, 57.92; H 9.37. Found: C, 58.20; H, 9.44.

(4-Bromophenyl) Diethyl Phosphate 17¹¹

Obtained in 54% yield as a white solid; ^1H NMR (250 MHz, CDCl_3) δ 1.27 (6H, td, J 6.9 and $J_{\text{P-H}}$ 1.1, CH_2CH_3), 4.15 (4H, app pent, $J_{\text{P-H}}$ 6.9 and J 6.9, CH_2CH_3), 6.98 (2H, d, J 8.7, ArCH), 7.31 (2H, d, J 8.7, ArCH); ^{31}P NMR (101 MHz, CDCl_3) δ -6.16.

(4-Nitrophenyl) Diethyl Phosphate 18¹²

Obtained in 51% yield as a clear oil; ^1H NMR (250 MHz, CDCl_3) δ 1.26 (6H, t, J 7.2, CH_2CH_3), 4.15 (4H, app pent, $J_{\text{P-H}}$ 7.2 and J 7.2, CH_2CH_3), 7.29 (2H, d, J 9.2, ArCH), 8.15 (2H, d, J 9.2, ArCH); ^{31}P NMR (101 MHz, CDCl_3) δ -7.36.

(4-Methoxyphenyl) Diethyl Phosphate 19¹³

Obtained in 31% yield as a clear oil; ^1H NMR (250 MHz, CDCl_3) δ 1.23 (6H, td, J 6.2 and $J_{\text{P-H}}$ 0.9, CH_2CH_3), 3.65 (3H, d, $J_{\text{P-H}}$ 0.9, OCH_3), 4.10 (4H, app pent, $J_{\text{P-H}}$ 6.4 and J 6.4, CH_2CH_3), 6.72 (2H, dd, J 9.7 and $J_{\text{P-H}}$ 1.5, ArCH), 7.03 (2H, dd, J 9.7 and $J_{\text{P-H}}$ 1.5, ArCH); ^{31}P NMR (101 MHz, CDCl_3) δ -5.54.

Benzyl Diphenyl Phosphate 20⁷

Obtained in 85% yield as white solid; δ_{H} (250 MHz; CDCl_3) 5.27 (2H, d, J 8.5, CH_2OP), 7.14–7.21 (6H, m, ArCH), 7.30–7.38 (9H, m, ArCH); δ_{P} (101 MHz; CDCl_3) -11.31.

Allyl Diphenyl Phosphate 21⁷

Obtained in 88% yield colorless oil; δ_{H} (250 MHz; CDCl_3) 4.66 (2H, ddt, $J_{\text{P-H}}$ 8.6, J 5.7 and 1.4, CH_2O), 5.17 (1H, dd, J 10.4 and 1.2, $\text{CH}=\text{CH}_2$), 5.28 (1H, dq, J 17.0 and 1.2, $\text{CH}=\text{CH}_2$), 5.86 (1H, m, $\text{CH}=\text{CH}_2$), 6.83–7.31 (10H, m, ArCH); δ_{P} (101 MHz; CDCl_3) -11.60.

(Pro-2-ynyl) Diphenyl Phosphate 22⁷

Obtained in 84% yield as red-brown oil; δ_{H} (250 MHz; CDCl_3) 2.51 (1H, t, J 2.6, CH), 4.06 (2H, d, J 2.6, CH_2O), 7.25–7.45 (10H, m, ArCH); δ_{P} (101 MHz; CDCl_3) -11.5.

Cyclohexyl Diphenyl Phosphate 23⁷

Obtained in 82% yield as clear oil; δ_{H} (250 MHz; CDCl_3) 1.21–1.40 (3H, m, CH_2), 1.42–1.81 (5H, m, CH_2), 1.85–2.00 (2H, m, CH_2), 4.62 (1H, m, CHO), 7.15–7.39 (10H, m, ArCH); δ_{P} (101 MHz; CDCl_3) -12.28.

Isopropyl Diphenyl Phosphate 24⁷

Obtained in 85% yield as clear oil; δ_{H} (250 MHz; CDCl_3) 1.23 (6H, d, J 6.3, CH_3CH), 4.77 (1H, app hex J 6.3 and $J_{\text{P-H}}$ 6.3, CHO), 7.20–7.24 (10H, m, ArCH); δ_{P} (101 MHz; CDCl_3) -12.43.

2-Butyl Diphenyl Phosphate 25¹⁴

Obtained in 75% yield as clear oil; δ_{H} (250 MHz; CDCl_3) 0.76 (3H, t, J 6.0, CH_3CH_2), 1.19 (3H, d, J 6.1, CH_3CH), 1.40–1.59 (2H, m, CH_2CH_3), 4.57 (1H, app hept J 6.1 and $J_{\text{P-H}}$ 6.1, CHO), 6.95–7.21 (10H, m, ArCH); δ_{P} (101 MHz; CDCl_3) -12.50.

(2-Methyl-2-Propyl) Diphenyl Phosphate 26¹⁴

Obtained in 61% yield as clear oil; δ_{H} (250 MHz; CDCl_3) 1.52 (9H, s, CH_3C), 7.01–7.33 (10H, m, ArCH); δ_{P} (101 MHz; CDCl_3) -10.26.

($\pm$)- α -Terpineol Diphenyl Phosphate 27

Obtained in 67% yield as clear oil; IR (KBr) 1488; δ_{H} (250 MHz; CDCl_3) 1.14 (3H, s, CH_3), 1.18 (3H, s, CH_3), 1.20–1.35 (1H, m), 1.37 (1H, m), 1.50 (1H, m), 1.65 (3H, m, CH_3), 1.70–2.13 (4H, m), 5.39 (1H, m, $\text{C}=\text{CH}$), 7.25–7.46 (10H, m, ArCH); δ_{C} (63 MHz; CDCl_3) 23.4 (CH_3), 24.0 (CH_2), 26.2 (CH_3), 26.9 (CH_2), 27.4 (CH_3), 31.0 (CH_2), 45.0 (CH), 72.8 [$(\text{CH}_3)_2\text{CO}$], 120.4 (d, $J_{\text{C-P}}$ 5.1, ArCH), 120.6 ($\text{CH}=\text{C}$), 126.5 (ArCH), 130.1 (d, $J_{\text{C-P}}$ 6.8, ArCH), 134.0 ($\text{CH}=\text{C}$), 149.7 (d, $J_{\text{C-P}}$ 9.1, ArC); δ_{P} (101 MHz; CDCl_3) -10.37; m/z (EI) 386 (75%, M^+), 216 (50), 118 (55), 103 (100), 77 (40), 69 (30), 91 (28), 51 (25); Anal. Calcd. for $\text{C}_{22}\text{H}_{24}\text{O}_7\text{P}$: C, 68.38; H, 7.04. Found: C, 68.44; H, 7.34.

(4-Bromophenyl) Diphenyl Phosphate 28¹⁵

Obtained in 49% yield as clear oil; δ_{H} (250 MHz; CDCl_3) 7.14 (2H, d, J 8.7, ArCH), 7.17–7.25 (6H, m, ArCH), 7.30–7.40 (4H, m, ArCH), 7.46 (2H, d, J 8.7, ArCH); δ_{P} (101 MHz; CDCl_3) -16.73.

(4-Nitrophenyl) Diphenyl Phosphate 29⁷

Obtained in 56% yield as clear oil; δ_{H} (250 MHz; CDCl_3) 7.15–7.42 (12H, m, ArCH), 8.20 (2H, d, J 8.9, ArCH); δ_{P} (101 MHz; CDCl_3) -18.07.

(4-Methoxyphenyl) Diphenyl Phosphate 30¹⁶

Obtained in 46% yield as clear oil; δ_{H} (250 MHz; CDCl_3) 3.78 (3H, s, OCH_3), 6.85 (2H, d, J 8.6, ArCH), 7.13–7.38 (12H, m, ArCH); δ_{P} (101 MHz; CDCl_3) -11.49.

Geraniol Diphenyl Phosphate 31⁷

Obtained in 92% yield as clear oil; δ_{H} (250 MHz; CDCl_3) 1.50 (3H, s, CH_3), 1.56 (6H, s, $2 \times \text{CH}_3$), 1.82–2.02 (4H, m, $2 \times \text{CH}_2$), 4.63 (1H, dd, $J_{\text{P-H}}$ 9.0 and J 7.5, CH_2O), 4.96 (1H, m, $\text{C}=\text{CH}$), 5.27 (1H, td, J 7.2 and 1.2, $\text{C}=\text{CH}$), 6.95–7.26 (10H, m, ArCH); δ_{P} (101 MHz; CDCl_3) -11.06.

Adenosine 5' Phenyl Phosphate 32¹⁷

Obtained in 49% yield as white solid; mpt. 242 °C; $[\alpha]_{\text{D}}$ -49.5 (c 2, H_2O); δ_{H} (250 MHz; D_2O) 3.92–4.10 (2H, m), 4.23 (1H, m), 4.36 (1H, t, J 5.0), 4.50 (1H, t, J 5.0), 5.83 (1H, d, J 5.0, $\text{H1}'$), 6.60 (3H, m, ArCH), 7.04 (2H, dd, J 8.2 and 7.6, ArCH), 7.80 (1H, s, ArCH), 8.23 (1H, s, ArCH); δ_{C} (63 MHz; D_2O) 64.2 (CH), 70.1 (CH), 74.4 (CH), 83.6 (d, $J_{\text{C-P}}$ 8.7, CH_2O), 87.2 (CH), 115.0 (ArCH), 117.9 (ArC), 120.3

(ArCH), 129.6 (ArCH), 139.9 (ArCH), 148.1 (ArC), 150.7 (ArCH), 153.7 (ArC), 155.1 (ArC); δ_P (101 MHz; D₂O) 2.48; m/z (TOF ES) 423 (M⁺).

Guanosine 5' Phenyl Phosphate 33

Obtained in 54% yield as white solid; mpt. 256–257 °C; $[\alpha]_D$ -86.4 (*c* 2, H₂O); $\nu_{\max}$ / cm⁻¹ (KBr) 2467, 2362, 1570, 1540, 1200; δ_H (250 MHz; D₂O) 3.91–3.99 (2H, m), 4.25 (1H, m), 4.40 (1H, app t *J* 5.0), 4.62 (1H, t, *J* 5.5), 5.82 (1H, d, *J* 5.5, H1'), 6.59–6.65 (4H, m, ArCH), 7.08 (2H, app t, *J* 7.6, ArCH), 8.05 (1H, s, ArCH); δ_C (63 MHz; D₂O) 63.4 (CH), 70.5 (CH), 74.0 (CH), 83.6 (d, *J*_{C-P} 8.6, CH₂O), 86.4 (CH), 116.5 (ArCH), 116.7 (ArC), 118.1 (ArCH), 129.7 (ArCH), 136.3 (ArCH), 151.4 (ArC), 157.9 (ArC), 159.3 (ArC), 164.0 (ArC); δ_P (101 MHz; D₂O) 6.82; m/z (TOF ES) 440 (100%, MH⁺), 456 (35); Anal. Calcd. for C₁₆H₁₈N₅O₈P: C, 43.74; H 4.13; N 15.94. Found: C, 43.8; H, 4.2; N, 16.0.

17β-Hydroxy-5α-Androstan-3-one Diphenyl Phosphate 34⁷

Obtained in 76% yield as a white solid; δ_H (250 MHz; CDCl₃) 0.45–1.92 (16H, m), 0.81 (3H, s), 1.00 (3H, s), 1.94 – 2.42 (6H, m), 4.45 (1H, app q, *J*, 7.9, CHO), 7.15 – 7.35 (10H, m, ArCH); δ_P (101 MHz; CDCl₃) -11.92.

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