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Supporting Information for

Stereoselective Reactions of Acyclic Allylic Phosphates with Organocopper Reagents

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(*E*)-2-Octen-4-ol, 1a.[1] Butylmagnesium bromide was prepared from Mg turnings (12.6 g, 0.52 mol) and *n*-butyl bromide (50 mL, 0.47 mol) in ether (225 mL). The Grignard solution was cooled in an ice bath and crotonaldehyde (32 mL, 0.39 mol) in ether (60 mL) was added dropwise. The reaction mixture was allowed to stand at room temperature for 1 hour. The reaction was quenched by dropwise addition of saturated NH_4Cl (95 mL) with vigorous stirring and ice-cooling. The reaction mixture was allowed to stand for 1 hour, after which the ether layer was decanted from the white precipitate. The precipitate was further washed twice with ether (2 × 70 mL). The ether was removed by rotary evaporation to give a slightly yellow, viscous oil. The residue was distilled under aspirator pressure through a Vigreux column to afford a clear, colorless oil (33.4 g, 67% yield) with a boiling point of 72-74°C (24 torr). IR (neat) 3368 (br), 1674 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ5.61 (1H, dq, J = 15.3, 5.9 Hz), 5.48 (1H, dd, J = 15.3, 6.6 Hz), 4.03 (1H, dt, J = 6.6, 6.6 Hz), 1.70 (3H, d, J = 5.9 Hz), 1.45 (1H br. s), 1.56-1.26 (6H, m), 0.90 (3H, t, J = 6.6 Hz); ^{13}C NMR (63 MHz, $CDCl_3$), δ134.4, 126.3, 72.9, 36.9, 27.5, 22.5, 17.5, 13.9.

(*E*)-2-Methyl-4-hexen-3-ol, 1b.[2] A similar procedure to the one outlined for **1a** was followed, using isopropylmagnesium chloride purchased from Aldrich. The alcohol was synthesized (66% yield) and used without further purification. IR (neat) 3410 (br), 1672 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ5.65 (1H, dq, J = 15.3, 6.0 Hz), 5.50 (1H, dd, J = 15.3, 7.3 Hz), 3.77 (1H, dd, J = 7.3, 6.7 Hz), 1.73 (3H, d, J = 5.7 Hz), 1.70 (1H, m), 1.56 (1H, br. s), 0.94 (3H, d, J = 6.7 Hz), 0.89 (3H, d, J = 6.8 Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ132.1, 126.6, 77.5, 33.3, 17.6 (2C), 17.0.

(*E*)-1-Cyclohexyl-2-buten-1-ol, 1c.[2] A similar procedure to the one outlined for **1a** was followed, replacing the *n*-butyl bromide with cyclohexyl chloride. The residue was distilled under high vacuum through a Vigreux column to afford a clear, colorless oil (79% yield) with a boiling point of 59-61°C (0.1 torr). IR (neat) 3401 (br), 1710 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$)

δ5.62 (1H, dq, J = 15.8, 6.5 Hz), 5.47 (1H, dd, J = 15.8, 6.9 Hz), 3.76 (1H, dd, J = 6.9, 6.9 Hz), 1.71 (3H, d, J = 6.5 Hz), 1.88-1.64 (5H, m), 1.50 (1H, br. s), 1.42-0.86 (6H, m); ^{13}C NMR (63 Hz, $CDCl_3$) δ132.8, 127.3, 77.5, 43.6, 28.7, 28.6, 26.5, 26.1, 26.0, 17.6.

(*E*)-2-Heptenal. Formylmethyltriphenylphosphorane was prepared as described by Trippett and Walker and was used without further purification.[3] A solution of this Wittig reagent (8.5 g, 28 mmol) and freshly distilled valeraldehyde (2.5 mL, 23 mmol) in benzene (150 mL) was refluxed for 20 hours. The solvent was removed under reduced pressure and the residue was purified by flash silica column chromatography (10% Et_2O in hexane) to give 0.90 g (34%) of a clear, yellow oil; IR (neat) 1690, 1639 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ9.52 (1H, d, J = 8.0 Hz), 6.86 (1H, dt, J = 15.4, 6.9 Hz), 6.14 (1H, ddt, J = 15.4, 8.0, 1.5 Hz), 2.36 (2H, q, J = 6.9 Hz), 1.54-1.26 (4H, m), 0.92 (3H, m); ^{13}C NMR (63 MHz, $CDCl_3$) δ194.0, 158.8, 133.0, 32.4, 29.9, 22.2, 13.7.

(*E*)-1-Cyclohexyl-2-hepten-1-ol, 1e.[4] A similar procedure to **1a** was followed, replacing the *n*-butyl bromide with cyclohexyl chloride and crotonaldehyde with (*E*)-heptenal. The residue was purified by flash silica gel column chromatography (1:4 Et_2O:hexane as solvent) to give a clear, colorless oil (69% yield). IR (neat) 3369 (br), 1670 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ5.61 (1H, dt, J = 15.4, 6.6 Hz), 5.46 (1H, ddt, J = 15.4, 7.3, 1.2 Hz), 3.75 (1H, m), 2.08-2.00 (2H, m), 1.89-1.63 (5H, m), 1.58 (1H, br. s), 1.43-1.01 (8H, m), 0.99-0.86 (5H, m); ^{13}C NMR (63 MHz, $CDCl_3$) δ132.7, 131.5, 77.5, 43.7, 31.9, 31.4, 28.8, 28.7, 26.5, 26.1, 26.0, 22.1, 13.7.

Diethyl (2*E*, 4*R*)-2-octen-4-yl phosphate, 2a. The reaction was run using 2.01 g (15.7 mmol) of **1a** to give 2.48 g (60%) of a clear, slightly yellow oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ5.75 (1H, dq, J = 15.3, 6.5 Hz), 5.49 (1H, ddq, J = 15.3, 8.0, 1.5 Hz), 4.69 (1H, ddt, J = 8.0, 7.0, 7.0 Hz), 4.14-4.00 (4H, 2 × AB of ABX_3, m), 1.72 (3H, dd, J = 6.5, 1.5 Hz), 1.62-1.57 (2H, m), 1.41-1.28 (4H, m, 6H, 2 × X_3 of ABX_3, m), 0.90 (3H, t, J = 6.6 Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ130.2, 129.1, 79.9, 63.2 (2C, d, J_{C-P} = 5.3 Hz), 35.6, 26.8, 22.1, 17.3, 15.9 (2C, d, J_{C-P} = 6.5 Hz), 13.7.

Diethyl (2*E*, 4*S*)-5-methyl-2-hexen-4-yl phosphate, 2b. The reaction was run using 1.00 g (8.8 mmol) of **1b** to give 0.88 g (40%) of a clear, slightly yellow oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ5.75 (1H, dq, J = 15.4, 6.6 Hz), 5.48 (1H, dd, J = 15.4, 8.0 Hz), 4.49 (1H, ddd, J = 8.0, 7.1, 7.1 Hz), 4.17-3.99 (4H, 2 × AB of ABX_3, m), 1.89 (1H, m), 1.74 (3H, d, J = 6.6 Hz), 1.45-1.20 (6H,

2 × X_3 of ABX_3, m), 1.17-0.86 (6H, m); ^{13}C NMR (63 MHz, $CDCl_3$) δ130.3, 128.0, 84.7 (d, J_{C-P} = 5.8 Hz), 63.2 (2C, d, J_{C-P} = 5.8 Hz), 33.1 (d, J_{C-P} = 6.7 Hz), 17.8, 17.4 (2C), 15.9 (2C, d, J_{C-P} = 7.1 Hz).

(1*S*, 2*E*)-1-Cyclohexyl-2-buten-1-yl diethyl phosphate, 2c. The reaction was run using 1.50 g (9.7 mmol) of **1c** to give 2.01 g (71%) of a clear, slightly yellow oil; ^1H NMR (250 MHz, $CDCl_3$) δ5.75 (1H, dq, J = 15.3, 6.4 Hz), 5.48 (1H, ddd, J = 15.3, 8.3, 1.5 Hz), 4.47 (1H, ddd, J = 8.3, 7.4, 7.4 Hz), 4.15 – 3.99 (4H, 2 × AB of ABX_3, m), 1.85-1.48 (5H, m), 1.72 (3H, dd, J = 6.4, 1.5 Hz), 1.34-1.27 (6H, 2 × X_3 of ABX_3, m), 1.27-0.89 (6H, m); ^{13}C NMR (63 MHz, $CDCl_3$) δ130.1, 128.6, 84.2 (d, J_{C-P} = 6.0 Hz), 63.2 (2C, d, J_{C-P} = 5.7 Hz), 42.8 (d, J_{C-P} = 6.0 Hz), 28.4, 28.1, 26.2, 25.8, 25.7, 17.4, 15.8 (2C).

Diethyl (2*E*, 4*S*)-5-ethyl-2-hepten-4-yl phosphate, 2d. The reaction was run using 0.51 g (3.6 mmol) of **1d** to give 0.53 g (53%) of a clear, slightly yellow oil; ^1H NMR (250 MHz, $CDCl_3$) δ5.76 (1H, dq, J = 15.3, 6.4 Hz), 5.49 (1H, dd, J = 15.3, 6.3 Hz), 4.71 (1H, m), 4.11-3.99 (4H, 2 × AB of ABX_3, m), 1.74 (3H, d, J = 6.4 Hz), 1.61-1.18 (5H, m, 6H, 2 × X_3 of ABX_3, m), 1.15-0.79 (6H, m); ^{13}C NMR (63 MHz, $CDCl_3$) δ130.0, 128.4, 82.0 (d, J_{C-P} = 7.6 Hz), 63.3 (2C, d, J_{C-P} = 5.7 Hz), 46.5 (d, J_{C-P} = 5.7 Hz), 21.7, 21.4, 17.7, 16.1 (2C, d, J_{C-P} = 7.6 Hz), 11.5, 11.3.

(1*S*, 2*E*)-1-Cyclohexyl-2-hepten-1-yl diethyl phosphate, 2e. The reaction was run using 0.43 g (2.2 mmol) of **1e** to give 0.45 g (71%) of a clear, slightly yellow oil; ^1H NMR (250 MHz, $CDCl_3$) δ5.75 (1H, dt, J = 15.4, 6.6 Hz), 5.48 (1H, dd, J = 15.4, 7.7 Hz), 4.48 (1H, ddd, J = 7.7, 7.5, 7.5 Hz), 4.12-3.99 (4H, 2 × AB of ABX_3, m), 2.07-2.02 (2H, m), 1.85-1.54 (5H, m), 1.41-0.90 (10H, m, 6H, 2 × X_3 of ABX_3, m), 0.89 (3H, t, J = 7.1 Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 135.3, 126.9, 84.1, 63.0 (2C), 42.6 (d, J_{C-P} = 7.6 Hz), 31.5, 30.8, 28.2, 27.9, 26.0, 25.5 (2C), 21.8, 15.6 (2C), 13.4.

(*R*)-3-Hexanoxyl-4-benzyl-2-oxazolidinone, 7. (*R*)-4-(Phenylmethyl)-2-oxazolidinone (prepared from *D*-phenylalanine and diethyl carbonate)[5] (1.00 g, 5.7 mmol) was dissolved in dry THF (20 mL) and cooled to 0°C at which time *n*-BuLi (1.02 M, 5.6 mL, 5.7 mmol) was added dropwise. The resulting solution was stirred at 0°C for 40 minutes and then cooled to -78°C. Hexanoyl chloride (1.0 mL, 7.2 mmol) was added dropwise via syringe. The completion of the reaction was determined by TLC. The resulting reaction mixture was quenched with saturated NH_4Cl at -78°C and was allowed to warm to room temperature. The resulting oil was purified

by column chromatography (4:1 hexane:Et_2O as solvent) to provide 1.3 g (80%) of a clear, slightly yellow oil; $[\alpha]_D$ = -93.2 (c = 1.03, EtOH) [literature value for (*S*)-isomer: $[\alpha]_D$ = +97.5 (c = 1.03, EtOH)][6]; IR (neat) 3063, 1783, 1700, 746, 703 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ7.37-7.19 (5H, m), 4.68 (1H, X of ABX, m), 4.24-4.13 (2H, m), 3.34 (1H, A of ABX, dd, J_{obs} = 13.3, 3.3 Hz), 3.01-2.82 (2H, m), 2.81-2.72 (1H, B of ABX, dd, J_{obs} = 13.3, 9.6 Hz), 1.76-1.57 (2H, m), 1.41-1.27 (4H, m), 0.91 (3H, t, J = 7.0 Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ173.3, 153.3, 135.3, 129.3 (2C), 128.8 (2C), 127.2, 66.1, 55.0, 37.9, 35.4, 31.2, 23.9, 22.3, 13.8.

(*2'R,4R*)-3-(2-Methylhexanoyl)-4-benzyl-2-oxazolidinone. A procedure similar to the one outlined by Evans *et al.* was followed.[7] A solution of **7** in THF (5 mL) was added to sodium bis(trimethylsilyl)amide (1.0 M, 3.6 mL, 3.6 mmol) in THF (15 mL) at -78°C. After 1 h, methyl iodide (1.0 mL, 16 mmol) was added and the reaction mixture was stirred at -78°C until the reaction appeared complete by TLC. The reaction was quenched with saturated NH_4Cl solution and allowed to warm to room temperature. The reaction mixture was diluted with Et_2O, washed with water, saturated $NaHCO_3$ and brine and then dried over $MgSO_4$. The organic layer was filtered and rotovapped to give a residue that was purified by silica column chromatography (4:1 hexane:Et_2O as solvent) to afford 0.78 g (82%) of a clear, pale yellow oil; $[\alpha]_D$ = -118.9 (c = 0.53, MeOH) [literature value for opposite enantiomer: $[\alpha]_D$ = +104.4 (c = 0.47, MeOH)[8], >95% de]; IR (neat) 3064, 1781, 1698, 1208 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ7.31-7.14 (5H, m), 4.62 (1H, X of ABX, m), 4.18-4.07 (2H, m), 3.66 (1H, tq, J = 6.8, 6.8Hz), 3.23 (1H, A of ABX, dd, J_{obs} = 13.3, 3.3 Hz), 2.71 (1H, B of ABX, dd, J_{obs} = 13.3, 9.6 Hz), 1.68 (1H, m), 1.51-1.10 (5H, m), 1.17 (3H, d, J = 6.9 Hz), 0.83 (3H, t, J = 6.9 Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ177.0, 152.8, 135.2, 129.2 (2C), 128.5 (2C), 126.9, 65.7, 55.0, 37.5, 37.3, 32.8, 29.1, 22.4, 17.0, 13.6.

(*R*)-2-Methylhexanoic acid, *R*-6. H_2O_2 (30%, 630 μL) and LiOH (0.11 g, 4.51 mmol) dissolved in water (2 mL) was added to (2'*R*,4*R*)-3-(2-Methylhexanoyl)-4-benzyl-2-oxazolidinone (0.44 g, 1.53 mmol) dissolved in a 4:1 mixture of THF and water (8 mL and 2 mL, respectively) at 0°C. After 0.5 h, Na_2SO_3 (0.86 g, 6.8 mmol) in water (5 mL) was added to quench excess peroxide. The acid was isolated by extracting the reaction mixture twice with CH_2Cl_2. The organic layer was dried over $MgSO_4$, after which the solvent was removed *in vacuo* to afford 0.19 g (95%) of a clear, colorless oil; $[\alpha]_D$ = -17.5 (c = 4.72, $CHCl_3$) [literature value: $[\alpha]_D$ = -8 (c = 7.0, $CHCl_3$), 56% ee[9] or $[\alpha]_D$ = +19.00 (neat), 96% ee[10] for *S* enantiomer; IR (neat) 2960 (br), 1708 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ2.47 (1H, X of ABM_2X, tq, J_{obs} = 6.9, 6.9 Hz), 1.69 (1H, A of

ABM_2X, m), 1.41 (1H, B of ABM_2X, m), 1.36-1.26 (2H, m, 2H, M_2 of ABM_2X, m), 1.20 (3H, d, J = 6.9 Hz), 0.90 (3H, t, J = 6.9 Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ183.5, 39.4, 33.2, 29.3, 22.5, 16.7, 13.8. The α-methylbenzylamide prepared from *R*-2-methylhexanoic acid and *S*-α-methylbenzylamine (DIC, HOBT, DMAP) showed a retention time of 16.13 min by GC (30 m x 0.25 mm DB-5, 70 °C for 2 min then 10 °C/min to 250 °C) whereas the major amide derived from **3c** showed a retention time of 15.99 min. Spiking experiments confirmed that **3c** has predominantly *S* stereochemistry.

References

(1) This compound has been reported in the literature but a preparative procedure and spectral data are difficult to locate. See, for example: Corey, L. D.; Singh, S. M.; Oehlschlager, A. C. *Can. J. Chem.* **1987**, *65*, 1821-1827.

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