Supporting Information

Palladium-Catalyzed Deracemization of Allylic Carbonates in Water With Formation of Allylic Alcohols: The Hydrogen Carbonate Ion as Nucleophile in the Palladium-Catalyzed Allylic Substitution and Kinetic Resolution

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Deracemation of Carbonate *rac*-1b. A Schlenk flask was successively charged with Pd₂dba₃·CHCl₃ (52 mg, 0.05 mmol), **BPA** (138 mg, 0.20 mmol) and CH₂Cl₂ (18 mL), and the resulting orange solution was stirred at room temperature for 15 min. Then water (2 mL) and carbonate *rac*-1b (390 mg, 2.5 mmol) were added. After stirring the mixture at room temperature for 24 h, it was poured in pentane/ether, 1:1 (200 mL) and filtered through a layer of silica gel (0.040–0.063 mm) (3 cm × 2 cm). The filtrate was dried (MgSO₄) and concentrated in vacuo. Purification of the residue by chromatography on silica gel (pentane/ether, 1:1) afforded alcohol **5b** (230 mg, 94%) with 97% ee.

Kinetic Resolution of Acetate *rac*-8b with KHCO₃. A Schlenk flask was successively charged with Pd₂dba₃·CHCl₃ (52 mg, 0.05 mmol), **BPA** (138 mg, 0.20 mmol), 350 mg KHCO₃ (3.5 mmol) and CH₂Cl₂ (18 mL), and the resulting orange solution was stirred at room temperature for 15 min. Then water (2 mL) and acetate *rac*-8b (350 mg, 2.5 mmol) were added. After stirring the mixture at room temperature for 48 h, it was poured in pentane/ether, 1:1 (200 mL) and filtered through a layer of silica gel (0.040–0.063 mm) (3 cm × 2 cm). The filtrate was dried (MgSO₄) and concentrated in vacuo. Purification of the residue by chromatography on silica gel (pentane/ether, 1:1) afforded alcohol **5b** (113 mg, 46%) with 94% ee and acetate **8b** (168 mg, 48%) with 72% ee.

Determination of ee-Values and Absolute Configurations

Determination of ee-values was done by GC on chiral stationary phase containing columns with coinjection of the reace mates.

Alcohol **5a**. Absolute configuration (*S*), 88% ee, CP-Chirasil-Dex-CB, t_R ((*S*)-**5a**) = 6.73 min, t_R ((*R*)-**5a**) = 7.10 min), [α]_D²⁰ -118.7 (*c* 1.00, CH₂Cl₂); ≥ 99% ee, [α]_D²⁰ -137.9 (*c* 1.1, CH₂Cl₃).¹

Alcohol **5b**. Absolute configuration (*S*), 97% ee, CP-Chirasil-Dex-CB, t_R ((*S*)-**5b**) = 14.14 min, t_R ((*R*)-**5b**) = 14.72 min), $[\alpha]_D^{20}$ -109.5 (*c* 1.03, CH₂Cl₂); 90% ee, $[\alpha]_D^{18}$ -100.8 (*c* 0.65, CH₂Cl₃).²

Alcohol **5c**. Absolute configuration (*S*), $\geq 99\%$ ee, Lipodex-E, t_R ((*S*)-**5c**) = 50.31 min, t_R ((*R*)-**5c**) = 50.98 min), $[\alpha]_D^{20}$ -28.7 (*c* 1.00, CH₂Cl₂); 92% ee, $[\alpha]_D^{20}$ -32.0 (*c* 0.20, CH₂Cl₂).³

Alcohol **7a**. Absolute configuration (*R*), 89% ee, Lipodex- γ , t_R ((*S*)-**7a**) = 7.39 min, t_R ((*R*)-**7a**) = 7.73 min), $[\alpha]_D^{20}$ +14.4 (*c* 1.02, CH₂Cl₂); 96% ee, $[\alpha]_D^{20}$ +17.6 (*c* 0.20, CH₂Cl₃).⁴

Alcohol **7b**. Absolute configuration (*R*), $\geq 99\%$ ee, Hydrodex- β -6-TBDM, t_R ((*R*)-**7b**) = 21.65 min, t_R ((*S*)-**7b**) = 23.41 min), $[\alpha]_D^{20}$ -3.9 (*c* 0.99, CH₂Cl₂).⁵

Acetate **8b**. Absolute configuration (*R*), 72% ee, CP-Chirasil-Dex-CB, t_R ((*S*)-**8b**) = 15.05 min, t_R ((*R*)-**8b**) = 14.61 min), $[\alpha]_D^{20}$ +147.7 (*c* 1.04, CH₂Cl₂); $\geq 99\%$ ee, $[\alpha]_D^{20}$ +199.0 (*c* 2.4, CH₂Cl₃).⁶

Acetate **8c**. Absolute configuration (*R*), 67% ee, Lipodex-E, t_R ((*S*)-**8c**) = 33.71 min, t_R ((*R*)-**8c**) = 30.22 min), $[\alpha]_D^{20}$ +25.0 (*c* 1.01, CH₂Cl₂); 25 % ee, $[\alpha]_D^{20}$ +7.9 (CH₂Cl₃).⁷

Columns With Chiral Stationary Phases and Conditions Used

Permethy- β -cyclodextrin (CP-Chirasil-Dex-CB): 1 bar H₂, 50 °C, 10 min, 10 K/min 80 °C, 5 min, 10 K/min 120 °C.

Octakis-(2,6-di-*O*-pentyl-3-*O*-butyryl)- γ -cyclodextrin (Lipodex-E): 1 bar H₂, 50 °C, 15 min, 10 K/min 80 °C, 5 min, 10 K/min 120 °C.

2,3-*O*-Dipentyl-6-*O*-methyl- γ -cyclodextrin (Lipodex- γ): 1 bar H₂, 50 °C, 15 min, 10 K/min 80 °C, 5 min, 10 K/min 120 °C.

Heptakis-(2,3-di-*O*-methyl-6-*O*-*t*-butyldimethylsilyl)- β -cyclodextrin (Hydrodex- β -6-TBDM): 1 bar H₂, 50 °C, 15 min, 2 K/min 80 °C, 5 min, 2 K/min 120 °C, 2 K/min 200 °C.

References

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