Synthetic Scope of Ru(OH)$_3$/Al$_2$O$_3$-Catalyzed Hydrogen-Transfer Reactions: An Application to Reduction of Allylic Alcohols via a Sequential Process of Isomerization/Meerwein-Ponndorf-Verley-Type Reduction

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Procedures for the Ru(OH)$_x$/Al$_2$O$_3$-catalyzed reduction: All operations for the reactions were carried in a glove box under Ar. Into a Pyrex-glass vial were successively placed Ru(OH)$_x$/Al$_2$O$_3$ (Ru: 2-5 mol%), allylic alcohol (1 mmol), and 2-propanol (3 mL). A Teflon-coated magnetic stir bar was added, and the reaction mixture was vigorously stirred (800 rpm) at 363 K (bath temp.) under 1 atm of Ar. The conversion and yield(s) were periodically determined by GC analysis. After the reaction was finished, the Ru(OH)$_x$/Al$_2$O$_3$ catalyst was separated by filtration and the crude products (containing small amounts of saturated ketones) were recovered by evaporation of solvent. All products are known compounds and have been identified by comparison of their GC retention time, mass, and $^1$H and $^{13}$C NMR spectra with the authentic data.$^{[S1]}$

3-Octanol (94% yield, entry 1, CAS Registry No. 589-98-0):

$^1$H NMR (270 MHz, CDCl$_3$, 298 K, TMS): $\delta$ = 0.90 (t, $^3$J(H,H) = 6.43 Hz, 3H), 0.94 (t, $^3$J(H,H) = 7.58 Hz, 3H), 1.25-1.53 (m, 10H), 1.57 (brs, 1H), 3.43-3.54 (m, 1H).

$^{13}$C{$^1$H} NMR (67.8 MHz, CDCl$_3$, 298 K, TMS): $\delta$ = 9.8, 14.0, 22.6, 25.3, 30.1, 31.9, 36.9, 73.2.

3-Hexanol (94% yield, entry 5, CAS Registry No. 623-37-0):

$^1$H NMR (270 MHz, CDCl$_3$, 298 K, TMS): $\delta$ = 0.91 (t, $^3$J(H,H) = 6.43 Hz, 3H), 0.94 (t, $^3$J(H,H) = 7.62 Hz, 3H), 1.11-1.67 (m, 6H), 1.64 (brs, 1H), 3.44-3.54 (m, 1H).

$^{13}$C{$^1$H} NMR (67.8 MHz, CDCl$_3$, 298 K, TMS): $\delta$ = 9.9, 14.2, 18.9, 30.2, 39.3, 73.1.

3-Pentanol (96% yield, entry 6, CAS Registry No. 584-02-1):

$^1$H NMR (270 MHz, CDCl$_3$, 298 K, TMS): $\delta$ = 0.90 (t, $^3$J(H,H) = 7.25 Hz, 6H), 1.29-1.44 (m, 4H), 2.09 (brs, 1H), 3.69-3.75 (m, 1H).

$^{13}$C{$^1$H} NMR (67.8 MHz, CDCl$_3$, 298 K, TMS): $\delta$ = 14.1, 30.8, 70.1

2-Butanol (97% yield, entry 7, CAS Registry No. 78-92-2):

$^1$H NMR (270 MHz, CDCl$_3$, 298 K, TMS): $\delta$ = 0.85 (t, $^3$J(H,H) = 7.58 Hz, 3H), 1.10 (d, $^3$J(H,H) = 6.10 Hz, 3H), 1.30-1.44 (m, 2H), 2.13 (brs, 1H), 3.63 (6, $^3$J(H,H) = 6.10 Hz, 3H).

$^{13}$C{$^1$H} NMR (67.8 MHz, CDCl$_3$, 298 K, TMS): $\delta$ = 9.8, 22.7, 31.9, 69.2.

1-Cyclohexyl-1-propanol (90% yield, entry 8, CAS Registry No. 17264-02-7):

$\delta$ = 0.81-1.97 (m, 13H), 0.89 (t, $^3$J(H,H) = 7.58 Hz, 3H), 3.76-3.89 (m, 1H).

$^{13}$C{$^1$H} NMR (67.8 MHz, CDCl$_3$, 298 K, TMS): $\delta$ = 10.3, 26.1, 27.3, 28.0, 29.5, 43.1, 77.3.

1-Phenyl-3-pentanol (82% yield, entry 9, CAS Registry No. 1992-50-3):

$\delta$ = 0.91 (t, $^3$J(H,H) = 7.28 Hz, 3H), 1.11-1.92 (m, 6H), 2.02 (brs, 1H), 3.61-3.75 (m, 1H), 7.04-7.39 (m,
$\text{13C}\{^1\text{H}\}$ NMR (67.8 MHz, CDCl$_3$, 298 K, TMS): $\delta = 10.0, 30.3, 31.3, 38.1, 73.3, 126.1, 127.9, 128.1, 140.7$.

1-Phenyl-1-propanol (85% yield, entry 10, CAS Registry No. 93-54-9): $\delta = 0.89$ (t, $^3J$(H,H) = 7.45 Hz, 3H), 1.64-1.73 (m, 2H), 2.16 (brs, 1H), 4.58 (t, $^3J$(H,H) = 6.58 Hz, 1H), 7.22-7.36 (m, 5H). $^1\text{H}$ NMR (270 MHz, CDCl$_3$, 298 K, TMS): $\delta = 0.89$ (t, $^3J$(H,H) = 7.45 Hz, 3H), 1.64-1.73 (m, 2H), 2.16 (brs, 1H), 4.58 (t, $^3J$(H,H) = 6.58 Hz, 1H), 7.22-7.36 (m, 5H). $^1\text{H}$ NMR (270 MHz, CDCl$_3$, 298 K, TMS): $\delta = 0.89$ (t, $^3J$(H,H) = 7.45 Hz, 3H), 1.64-1.73 (m, 2H), 2.16 (brs, 1H), 4.58 (t, $^3J$(H,H) = 6.58 Hz, 1H), 7.22-7.36 (m, 5H).

1-(4-Methylphenyl)-1-propanol (83% yield, entry 11, CAS Registry No. 25574-04-3): $\delta = 0.89$ (t, $^3J$(H,H) = 7.45 Hz, 3H), 1.64-1.73 (m, 2H), 2.16 (brs, 1H), 4.58 (t, $^3J$(H,H) = 6.58 Hz, 1H), 7.22-7.36 (m, 5H). $^1\text{H}$ NMR (270 MHz, CDCl$_3$, 298 K, TMS): $\delta = 0.89$ (t, $^3J$(H,H) = 7.45 Hz, 3H), 1.64-1.73 (m, 2H), 2.16 (brs, 1H), 4.58 (t, $^3J$(H,H) = 6.58 Hz, 1H), 7.22-7.36 (m, 5H).

2-Octanol (94% yield, entry 12, CAS Registry No. 123-96-6): $\delta = 0.89$ (t, $^3J$(H,H) = 6.43 Hz, 3H), 1.19 (d, $^3J$(H,H) = 6.20 Hz, 3H), 1.18-1.51 (m, 10H), 1.72 (brs, 1H), 3.71-3.86 (m, 1H). $^1\text{H}$ NMR (270 MHz, CDCl$_3$, 298 K, TMS): $\delta = 0.89$ (t, $^3J$(H,H) = 6.43 Hz, 3H), 1.19 (d, $^3J$(H,H) = 6.20 Hz, 3H), 1.18-1.51 (m, 10H), 1.72 (brs, 1H), 3.71-3.86 (m, 1H). $^1\text{H}$ NMR (270 MHz, CDCl$_3$, 298 K, TMS): $\delta = 0.89$ (t, $^3J$(H,H) = 6.43 Hz, 3H), 1.19 (d, $^3J$(H,H) = 6.20 Hz, 3H), 1.18-1.51 (m, 10H), 1.72 (brs, 1H), 3.71-3.86 (m, 1H).

4-Heptanol (93% yield, entry 13, CAS Registry No. 589-55-9): $\delta = 0.93$ (t, $^3J$(H,H) = 6.43 Hz, 6H), 1.02-1.71 (m, 8H), 1.74 (brs, 1H), 3.58-3.65 (m, 1H). $^1\text{H}$ NMR (270 MHz, CDCl$_3$, 298 K, TMS): $\delta = 0.93$ (t, $^3J$(H,H) = 6.43 Hz, 6H), 1.02-1.71 (m, 8H), 1.74 (brs, 1H), 3.58-3.65 (m, 1H).

2-Pentanol (95% yield, entry 14, CAS Registry No. 6032-29-7): $\delta = 0.93$ (t, $^3J$(H,H) = 6.43 Hz, 3H), 1.18 (d, $^3J$(H,H) = 6.24 Hz, 3H), 1.29-1.52 (m, 4H), 1.99 (brs, 1H), 3.69-3.82 (m, 1H). $^1\text{H}$ NMR (270 MHz, CDCl$_3$, 298 K, TMS): $\delta = 0.93$ (t, $^3J$(H,H) = 6.43 Hz, 3H), 1.18 (d, $^3J$(H,H) = 6.24 Hz, 3H), 1.29-1.52 (m, 4H), 1.99 (brs, 1H), 3.69-3.82 (m, 1H). $^1\text{H}$ NMR (270 MHz, CDCl$_3$, 298 K, TMS): $\delta = 0.93$ (t, $^3J$(H,H) = 6.43 Hz, 3H), 1.18 (d, $^3J$(H,H) = 6.24 Hz, 3H), 1.29-1.52 (m, 4H), 1.99 (brs, 1H), 3.69-3.82 (m, 1H).

Cyclohexanol (98% yield, entry 15, CAS Registry No. 108-93-0): $\delta = 1.15-1.88$ (m, 10H), 2.94 (brs, 1H), 3.54-3.64 (m, 1H). $^1\text{H}$ NMR (270 MHz, CDCl$_3$, 298 K, TMS): $\delta = 1.15-1.88$ (m, 10H), 2.94 (brs, 1H), 3.54-3.64 (m, 1H). $^1\text{H}$ NMR (270 MHz, CDCl$_3$, 298 K, TMS): $\delta = 1.15-1.88$ (m, 10H), 2.94 (brs, 1H), 3.54-3.64 (m, 1H).

5,9-Dimethy-8-decen-3-ol (91% yield, entry 16, mixture of diastereomer (ca. 1:1), CAS Registry No. 19550-54-0): $\delta = 0.859, 0.861$ (d x 2, $^3J$(H,H) = 6.48 Hz, 3H), 0.90 (t, $^3J$(H,H) = 7.56 Hz, 3H), 1.11-1.59 (m, 7H), 1.54 (s, 3H), 1.60 (s, 3H), 1.80-1.91 (m, 3H), 3.89-3.98 (m, 1H), 4.87-5.01 (m, 1H). $^1\text{H}$ NMR (67.8 MHz, CDCl$_3$, 298 K, TMS): $\delta = 10.5, 11.0, 17.7, 19.1, 19.7, 25.2, 25.3 25.7, 28.7, 28.9, 32.2, 32.6, 37.1, 37.4, 44.2, 44.3, 71.0, 71.8, 124.7, 130.0.
Synthesis of allylic alcohols (5a-8a, and 13a): Compounds 5a-8a, and 13a were synthesized by the Grignard reaction of the corresponding aldehydes with vinylmagnesium bromide.\[^{[52]}\] A typical example for the synthesis of allylic alcohols is as follows (synthesis of 6a): To a cooled (273 K) THF solution of vinylmagnesium bromide (40 mL, 1.0 M) was added 3-phenylpropanal (3.4 g, 25.3 mmol) dropwise over 15 min and the solution was kept at 273 K for 45 min. Then, the solution was allowed to warm to room temperature (ca. 293 K) and kept at room temperature for 1 h. The reaction was quenched by the addition of ice until effervescence ceased. The resulting suspension was treated with aqueous H$_2$SO$_4$ (1.0 M) until the suspension became homogeneous. The solution was diluted with dichloromethane (50 mL), and the aqueous layer was separated and washed with dichloromethane (20 mL x 3). The combined organic layers were dried over calcium chloride and distilled to give 2.1 g of 6a as a colorless oil (51% yield based on 3-phenylpropanal). Allylic alcohols 5a-8a, and 13a were synthesized by the same procedures. Data of allylic alcohols are listed as follows.

5a (53% yield based on cyclohexane carboxaldehyde, CAS Registry No. 4352-44-7): $^1$H NMR (270 MHz, CDCl$_3$, 298 K, TMS): $\delta = 0.82-1.96$ (m, 11H), 3.78 (t, $^3$J(H,H) = 6.42 Hz, 1H), 5.04-5.18 (m, 2H), 5.80 (ddd, $^3$J(H,H) = 18.1, 9.73, 6.42 Hz, 1H). $^{13}$C{$^1$H} NMR (67.8 MHz, CDCl$_3$, 298 K, TMS): $\delta = 26.0, 26.1, 26.4, 28.3, 28.6, 43.3, 77.6, 115.3, 139.8$. MS (70 eV, EI): m/z (%): 140 (0.4) [$M^+$], 96 (14), 83 (57), 82 (21), 81 (13), 67 (24), 58 (57), 57 (32), 55 (100), 41 (35).

6a (51% yield based on 3-phenylpropanal, CAS Registry No. 37904-38-4): $^1$H NMR (270 MHz, CDCl$_3$, 298 K, TMS): $\delta = 1.83-1.92$ (m, 2H), 2.25 (brs, 1H), 2.70-2.78 (m, 2H), 4.14 (q, $^3$J(H,H) = 6.43 Hz, 1H), 5.15 (d, $^3$J(H,H) = 10.4 Hz, 1H), 5.26 (d, $^3$J(H,H) = 17.1 Hz, 1H), 5.91 (ddd, $^3$J(H,H) = 17.1, 10.4, 6.43 Hz), 7.21-7.33 (m, 5H). $^{13}$C{$^1$H} NMR (67.8 MHz, CDCl$_3$, 298 K, TMS): $\delta = 31.2, 38.1, 72.0, 114.5, 125.4, 127.9, 128.0, 140.6, 141.5$. MS (70 eV, EI): m/z (%): 162 (22) [$M^+$], 144 (28), 129 (61), 105 (40), 92 (51), 91 (100), 57 (39).

7a (60% yield based on benzaldehyde, CAS Registry No. 4393-06-0): $^1$H NMR (270 MHz, CDCl$_3$, 298 K, TMS): $\delta = 2.65$ (brs, 1H), 5.08-5.29 (m, 3H), 7.21-7.32 (m, 5H). $^{13}$C{$^1$H} NMR (67.8 MHz, CDCl$_3$, 298 K, TMS): $\delta = 75.1, 114.9, 126.2, 127.5, 128.4, 140.2, 142.5$. MS (70 eV, EI): m/z (%): 134 (53) [$M^+$], 133 (100), 116 (15), 115 (40), 107 (18), 105 (84), 103 (13), 92 (72), 91 (40), 79 (86), 78 (46), 77 (99), 63 (11), 56 (11), 55 (42), 51 (44), 50
(14).

8a (63% yield based on 4-methylbenzaldehyde, CAS Registry No. 58824-48-9): $^1$H NMR (270 MHz, CDCl$_3$, 298 K, TMS): $\delta = 2.33$ (s, 1H), 2.66 (brs, 1H), 5.12-5.35 (m, 3H), 7.13-7.26 (m, 4H). $^{13}$C{$^1$H} NMR (67.8 MHz, CDCl$_3$, 298 K, TMS): $\delta = 21.1, 75.1, 114.8, 126.3, 129.2, 137.4, 139.7, 140.3$. MS (70 eV, EI): m/z (%): 148 (65) [M$^+$], 147 (17), 133 (100), 129 (11), 121 (17), 119 (48), 115 (25), 106 (26), 105 (37), 93 (48), 92 (36), 91 (93), 77 (41), 65 (27), 63 (11), 55 (55), 51 (13).

13a (60% yield based on (R)-(+-)-citroneral, mixture of diastereomer (ca. 1:1), CAS Registry No. 5208-90-2): $^1$H NMR (270 MHz, CDCl$_3$, 298 K, TMS): $\delta = 0.84, 0.85$ (d × 2, $^3$J(H,H) = 6.43 Hz, 3H), 1.02-1.50 (m, 5H), 1.53 (s, 3H), 1.60 (s, 3H), 1.87-1.97 (m, 3H), 4.04-4.14 (m, 1H), 4.97-5.16 (m, 3H), 5.70-5.84 (m, 1H). $^{13}$C{$^1$H} NMR (67.8 MHz, CDCl$_3$, 298 K, TMS): $\delta = 17.52, 17.53, 19.17, 19.83, 25.25, 25.32, 25.59, 28.69, 28.98, 36.93, 37.46, 44.29, 44.38, 70.86, 71.48, 113.90, 114.48, 124.67, 121.03, 141.43, 141.87. MS (70 eV, EI): m/z (%): 182 (0.6) [M$^+$], 149 (20), 139 (11), 126 (10), 122 (12), 121 (33), 110 (23), 109 (54), 108 (18), 107 (34), 97 (54), 95 (70), 94 (15), 93 (56), 83 (16), 45 (45), 81 (35), 79 (32), 70 (22), 69 (100), 68 (14), 67 (59), 57 (56), 56 (19), 55 (63), 53 (16), 43 (25), 41 (99).

Synthesis of (S)-1-deuterio-1-phenylethanol (15a, CAS Registry No. 71886-64-1): First, racemic 1-deuterio-1-phenylethanol was synthesized by the reduction of acetophenone using lithium aluminum deuteride by modification of the procedure reported for the synthesis of deuterium labeled toluene.$^{[S3]}$ A solution of acetophenone (4.6 g, 38.4 mmol) in dry ether (10 mL) was added dropwise to a solution of lithium aluminum deuteride (1.0 g, 23.8 mmol) in dry ether (20 mL) at 273 K and then the resulting mixture was allowed to warm to room temperature (ca. 293 K). The mixture was stirred vigorously under Ar atmosphere at room temperature. After 3 h, the mixture was cooled to 273 K, and water (5 + 15 mL) and 15% aqueous solution of NaOH (5 mL) were added to the mixture. The resulting white solid was removed by filtration and washed with dichloromethane (50 mL), and the filtrate was extracted with dichloromethane (30 mL × 5). The combined extract was dried with calcium chloride and distilled to give 4.3 g of racemic 1-deuterio-1-phenylethanol as a colorless oil (91% yield based on acetophenone). Racemic 1-deuterio-1-phenylethanol (3.1 g, 25.2 mmol) was dissolved in vinyl acetate (15 mL). The temperature of the mixture was raised to 305 K and supported lipase (PS-C
Amano II, 1 g) was added to the mixture. After 2 h, the supported lipase was removed by filtration and the solution was concentrated by the evaporation. The two products, 15a and (R)-acetate, were separated by silica gel column chromatography (Silica Gel 60N, spherical, neutral, 63–210 µm, Kanto, Cat. No. 37565-79, eluent: initial; n-hexane only, after (R)-acetate was eluted; n-hexane/ether = 3/1 v/v), giving 0.97 g of 15a as a colorless oil (31% yield based on 1-deuterio-1-phenylethanol, 97% purity containing (R)-alcohol (ca.3%)). The deuterium content at the α-position was estimated to be >98% with the mass, 1H NMR, and 2H NMR spectra. 1H NMR (270 MHz, CDCl3, 298 K, TMS): δ = 1.41 (s, 3H), 2.62 (brs, 1H), 7.18-7.31 (m, 5H). 2H NMR (41.25 MHz, benzene, 298 K, C6D6): δ = 4.57 (s, 1D). 13C{1H} NMR (67.8 MHz, CDCl3, 298 K, TMS): δ = 25.3, 70.2 (t, 3J(C,D) = 21.8 Hz), 125.8, 127.7, 128.8, 146.2. MS (70 eV, EI): m/z (%): 123 (36) [M+], 108 (100), 80 (91), 78 (33), 77 (24). GC (Rt β-CDEXM chiral capillary column, internal diameter = 0.25 mm, length = 30 m): carrier gas pressure (N2, 35 kPa), total flow (80 mL·min⁻¹), column flow (1.1 mL·min⁻¹), initial column temperature (308 K), final column temperature (473 K), progress rate (5 K/min), injection temperature (493 K), detection temperature (493 K), retention time (22.2 min).

Synthesis of 3-deuterio-1-octen-3-ol (14a, CAS Registry No. 873292-59-2): Compound 14a was synthesized by the oxidation of 1a,[84] followed by the reduction with lithium aluminum deuteride.[83] Iodobenzene diacetate (19.3 g, 60 mmol) was added to a solution of 1a (5.1 g, 40 mmol) and TEMPO (0.9 g, 6 mmol) in dichloromethane (40 mL). The mixture was stirred at room temperature (ca. 293 K) for 2 h. Then, the mixture was diluted with dichloromethane (200 mL), and then washed with a saturated Na2S2O3 (200 mL) and water (200 mL). The aqueous layer was separated and washed with dichloromethane (200 mL × 2). The combined organic layers were dried over calcium chloride and purified by silica gel column chromatography (Silica Gel 60N, spherical, neutral, 63–210 µm, Kanto, Cat. No. 37565-79, eluent: n-hexane/ether = 4/1 v/v), giving 3.5 g of pure 1-octen-3-one as a pale yellow oil (70% yield based on 1a). Compound 14a was synthesized by the reduction of 1-octen-3-one using lithium aluminum deuteride by the same procedures as that for the synthesis of 1-deuterio-1-phenylethanol (63% yield based on 1-octen-3-one, 98% purity containing saturated alcohol (ca.2%)). The deuterium content at the α-position was estimated to be >98% with the mass, 1H NMR, and 2H NMR spectra. 1H NMR (270 MHz, CDCl3, 298 K, TMS): δ = 0.89 (t, 3J(H,H) = 6.76...
Hz, 3H), 1.30-1.55 (m, 8H), 2.03 (brs, 1H), 5.01 (d, $^3J($H,H) = 10.4 Hz, 1H), 5.13 (d, $^3J($H,H) = 17.1 Hz, 1H), 5.49 (dd, $^3J($H,H) = 17.1, 10.4 Hz, 1H). $^2$H NMR (41.25 MHz, benzene, 298 K, C$_6$D$_6$): $\delta = 3.97$ (s, 1D). $^{13}$C{$^1$H} NMR (67.8 MHz, CDCl$_3$, 298 K, TMS): $\delta = 13.9, 22.5, 24.9, 31.8, 36.8, 72.6$ (t, $^1J($C,D) = 21.2 Hz), 114.3, 141.2. MS (70 eV, EI): m/z (%): 129 (0.1) [M$^+$], 99 (4), 86 (8), 73 (14), 58 (100), 43 (20).

References


Scheme S1. Reduction of 5,9-dimethyl-1,8-decadien-3-ol (13a) with metal catalysts in the presence of molecular hydrogen. Reaction conditions: 13a (1 mmol), catalyst (metal: 1 mol%), MeOH (3 mL), room temp. (ca. 295 K), 2 h in 4 atm of H$_2$. 
Table S1. Reduction of 3-octen-2-ol (9a) with metal catalysts in the presence of molecular hydrogen\textsuperscript{[a]}

\begin{equation}
\text{catalyst, } \text{H}_2 \text{ (1 atm)} \quad \text{MeOH (3 mL), 4 h, rt}
\end{equation}

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\textsuperscript{[a]} Reaction conditions: 9a (5 mmol), catalyst (metal: 1 mol%), MeOH (3 mL), room temp. (ca. 295 K), 4 h, under 1 atm of H\textsubscript{2}. Under the conditions, the reduction of 1-octene and cyclohexene quantitatively proceeded to give the corresponding alkanes within 2–3 hours. \textsuperscript{[b]} Determined by GC analyses using an internal standard technique. \textsuperscript{[c]} For 2 h in 4 atm of H\textsubscript{2}. 