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Hydroboration of Olefins with Catecholborane at Room Temperature in the Presence of *N,N*-Dimethylacetamide

Supporting Information

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GENERAL

^1H, and ^{13}C nuclear magnetic resonance spectra were recorded on Varian XL-300 or Unity-300 NMR spectrometers at ambient temperature. ^1H data are reported as follows: chemical shift in parts per million downfield from tetramethylsilane (δ scale), multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), integration, and coupling constant (Hz). ^{13}C chemical shifts are reported in ppm downfield from tetramethylsilane (δ scale). All ^{13}C spectra were determined with complete proton decoupling. ^{11}B chemical shifts are reported in ppm downfield from an external BF_3-Et_2O standard (δ scale).

Analytical thin layer chromatography was accomplished using EM Reagents 0.25 mm silica gel 60 plates. Flash chromatography was performed on EM Reagents silica gel 60 (230-400 mesh).

Gas chromatography (GC) analyses were performed on a Hewlett-Packard 5890 Series 2 Plus gas chromatograph with a flame ionization detector and a Model 3392A integrator using a 50 m capillary column with DB1701 or DB1 as the stationary phase (J & W Scientific).

Unless otherwise noted, all reactions were carried out in oven-dried glassware with magnetic stirring under an atmosphere of nitrogen or argon using standard Schlenk and/or glove box techniques.

PURIFICATION OF MATERIALS

N,N-Dimethylacetamide (Aldrich and Anachemia), *N*-methylacetamide (Eastman), triethylamine (Aldrich), 1-dodecene (Fluka), styrene (Aldrich), 2-hexyl-1-octene (Wiley), 1,2-dimethylcyclohexene (Wiley), and catecholborane (Aldrich, Fluka, and Eastman Fine Chemicals) were purified by distillation.

trans- 7-Tetradecene (Aldrich), 3-ethyl-3-octene (Wiley), and 1-dodecyne (Aldrich) were purified by column chromatography.

2-Methylcyclohexanone (Aldrich), 2,3-dimethyl-2,3-butanediol (Aldrich), BH_3-THF (Fluka), and methyllithium (Aldrich) were used as received. $LiBH_4$ (Aldrich) and 9-BBN dimer (Aldrich) were stored under an inert atmosphere and used without further purification.

Tetrahydrofuran, Et_2O, and pentane were dried and deoxygenated by refluxing over and distilling from sodium/benzophenone under a nitrogen atmosphere. Dichloromethane was stored over CaH_2 and distilled before use. $CDCl_3$ was dried over Na_2CO_3, d_8-THF was vacuum transferred, and CD_2Cl_2 was used as received (all were obtained from Cambridge Isotope Laboratories).

PREPARATION OF AUTHENTIC PRODUCTS

***cis*- 1,2-Dimethylcyclohexanol:** BH_3-THF (1 M in THF, 0.19 mL, 0.19 mmol) was added by syringe to a flask containing 1,2-dimethylcyclohexene (22.7 mg, 0.206 mmol) in a -45 °C bath. The resulting solution was stirred with slow warming to room temperature for 1.25 hours. The reaction mixture was then cooled to 0 °C, and 0.4 mL of THF : EtOH (1 : 1) was added, followed by 0.4 mL of 2N NaOH and then 0.4 mL 30% H_2O_2. The solution was allowed to warm to room temperature and stirred for two hours. An aliquot was removed for comparison by GC with the products of the following reaction.

***cis*- and *trans*-1,2-Dimethylcyclohexanol:** 2-Methylcyclohexanone (1.10 mL, 9.06 mmol) in Et_2O (10 mL) was added dropwise over 30 minutes to a -78 °C solution of methyllithium (9.5 mL, 13.3 mmol; 1.4 M in Et_2O). Upon completion of the addition, the solution was warmed to room temperature and stirred for one hour. It was then cooled to 0 °C, and an aqueous solution of saturated ammonium chloride (20 mL) was slowly added. The solution was then diluted with ether, and the ether layer was separated, extracted once with water and once with brine, then dried over $MgSO_4$, filtered, and concentrated. Column chromatography (20% Et_2O/pentane) afforded *cis*- and *trans*- 1,2-dimethylcyclohexanol. Proof of stereochemistry is based on comparison of the GC retention time of each of the products with the product from the BH_3-THF hydroboration of 1,2-dimethylcyclohexene. ***cis*- 1,2-Dimethylcyclohexanol:** ^1H NMR (300 MHz, $CDCl_3$) δ 0.87 (d, J = 7, 3H), 1.04 (s, 3H), 1.2-1.6 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.4, 20.9, 24.2, 25.4, 32.1, 41.4, 42.4, 73.2; TLC (20% Et_2O/pentane, *p*-anisaldehyde) R_f = 0.38. ***trans*- 1,2-Dimethylcyclohexanol:** ^1H NMR (300 MHz, $CDCl_3$) δ 0.86 (d, J = 6, 3H), 1.13 (s, 3H), 1.1-1.6 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.1, 22.1, 26.0, 28.6, 30.7, 40.0, 40.3, 70.9; TLC (20% Et_2O/pentane, *p*-anisaldehyde) R_f = 0.50.

***B*-Dodecylcatecholborane:** A mixture of 1-dodecene (1.50 mL, 6.76 mmol) and catecholborane (2.20 mL, 20.6 mmol) was heated to 100 °C for 21 h. After cooling to

room temperature, the residual catecholborane and 1-dodecene were removed in vacuo. The resulting cloudy white solution was diluted with pentane and filtered to remove insoluble solids. The solvent was removed from the resulting solution, and the process was repeated until no solids remained after dilution of the oil with pentane. The reaction product was contaminated with a small amount of $B_2(O_2C_6H_4)_3$. ^{1}H NMR (300 MHz, d_8-THF) δ 0.89 (t, J = 6, 3H), 1.20-1.50 (m, 20H), 1.62 (q, J = 8, 2H), 7.02 (m, 2H), 7.18 (m, 2H); ^{1}H NMR (300 MHz, CD_2Cl_2) δ 0.94 (t, J = 7, 3H), 1.18 (t, J = 7, 2H), 1.20-1.60 (m, 20H), 6.82 (m, 2H), 7.07 (m, 2H); ^{13}C NMR (75 MHz, d_8-THF) δ 14.6, 23.7, 24.9, 30.5, 30.6, 30.7, 30.8, 33.0, 33.4, 112.9, 123.3, 149.6; ^{13}C NMR (75 MHz, CD_2Cl_2) δ 14.7, 23.5, 24.5, 30.2, 30.4, 30.5, 32.7, 33.1, 112.8, 123.1, 149.1; ^{11}B NMR (96.2 MHz, THF) δ 35.6 (s); ^{11}B NMR (96.2 MHz, $CDCl_3$) δ 35.3 (s).

***B*-Dodecylpinacolborane:** A solution of pinacol (267 mg, 2.26 mmol) in THF (1.50 mL) was added to *B*-dodecylcatecholborane (212 mg, 0.74 mmol), and the resulting solution was stirred at room temperature for 18 h. The solvents were removed, and the product was chromatographed (2% EtOAc/hexane), providing 0.20 g (93%) of a very pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.85 (t, J = 7, 3H), 1.10-1.40 (m, 34H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 22.8, 24.1, 24.9, 29.4, 29.5, 29.7, 29.8, 32.0, 32.5, 82.8; ^{11}B NMR (96.2 MHz, $CDCl_3$) δ 34.0 (s); TLC (10% EtOAc/hexane, phosphomolybdic acid) R_f = 0.33.

Tridodecylborane: At room temperature, 1-dodecene (1.0 mL, 4.5 mmol) was added to a Schlenk flask, followed by BH_3-THF (1.5 mL, 1.0 M in THF, 1.5 mmol), resulting in bubbling. After 12 hours at room temperature, the volatiles were removed, resulting in a thick oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.86 (t, J = 7, 9 H), 1.16 (q, J = 8, 6H), 1.2-1.5 (m, 60H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 22.9, 24.7, 28.5, 29.6, 29.9, 32.2, 33.3, 33.4; ^{11}B NMR (96.2 MHz, $CDCl_3$) δ 86 (broad).

BH_3-*N,N*-Dimethylacetamide: In a glove box, BH_3-THF (0.60 mL, 1 M in THF, 0.60 mmol) was added to *N,N*-dimethylacetamide (100 μL, 1.08 mmol), resulting in bubbling. The reaction was followed by ^{11}B NMR for 38 minutes, during which time

no change was noted. The major resonance at δ -9.4 (q, J = 94) was assigned to BH_3-*N*,*N*-dimethylacetamide. Minor signals at δ 16.8 (br s), 1.6 (m) were also present. No BH_3-THF (δ -0.5 in THF) was evident.

AMIDE-PROMOTED HYDROBORATION REACTIONS

The yields and selectivities that are reported in Table 1 represent an average of two runs using two independently purified sets of *N,N*-dimethylacetamide and catecholborane.

Representative experimental for Table 1: Dodecene (228 μL, 1.03 mmol), *N,N*-dimethylacetamide (9.4 μL, 0.10 mmol), and CH_2Cl_2 (0.68 mL) were added sequentially to a reaction vessel. The resulting solution was cooled to 0 °C, and catecholborane (220 μL, 2.06 mmol) was added dropwise (bubbling observed). Following completion of the addition of catecholborane, the reaction mixture was allowed to warm to room temperature and stirred for 3 hours. It was then cooled to 0 °C, and 1 : 1 THF : EtOH (2 mL), 2 N NaOH (2 mL), and 30% H_2O_2 (2 mL) were added. The reaction mixture was allowed to warm to room temperature and stirred for 2 hours. It was then extracted (Et_2O/1 N NaOH), the organic layer was dried, and the solvent was removed in vacuo. Flash chromatography afforded 0.184 g (96%) of 1- and 2-dodecanol in a 94 : 6 ratio (GC).

Hydroboration of 1-dodecene (Table 1, Entry 1): The reaction products were identical by ^1H and ^{13}C NMR with commercially available 1-dodecanol (Aldrich) and 2-dodecanol (Aldrich).

Hydroboration of styrene (Table 1, Entry 2): GC analysis of the unpurified reaction mixture revealed an 85 : 15 ratio of primary : secondary alcohol. The purified reaction products were identical by ^1H and ^{13}C NMR with commercially available 1-phenylethanol (Aldrich) and 2-phenylethanol (Aldrich).

Hydroboration of 2-hexyl-1-octene (Table 1, Entry 3): GC analysis of the unpurified reaction mixture indicated >99% regioselectivity for the hydroboration. The reaction product was identical by ^1H and ^{13}C NMR with commercially available 2-hexyl-1-octanol (Wiley).

Hydroboration of 7-tetradecene (Table 1, Entry 4): The reaction product was identical by ^1H and ^{13}C NMR with commercially available 7-tetradecanol (Wiley).

Hydroboration of 3-ethyl-3-octene (Table 1, Entry 5): The reaction product was identical by ^{1}H and ^{13}C NMR with commercially available 3-ethyl-4-octanol (Wiley).

Hydroboration of 1,2-dimethylcyclohexene (Table 1, Entry 6): The reaction product was identical by ^{1}H and ^{13}C NMR with *cis*-1,2-dimethylcyclohexanol prepared by hydroboration of 1,2-dimethylcyclohexene with BH_3-THF (vide supra).

Synthesis of *B*-dodecylpinacolborane (eq 2): Catecholborane (85 μL, 0.80 mmol) was added to a -45 °C solution of dodecene (90 μL, 0.41 mmol), *N,N*- dimethylacetamide (4 μL, 0.04 mmol), and CH_2Cl_2 (0.26 mL). The reaction mixture was stirred with slow warming to room temperature for 3 hours. The solvents were removed, and then a solution of pinacol (145 mg, 1.23 mmol) in 1 mL of THF was added to the remaining oil. The reaction mixture was stirred at room temperature for 19 hours. The solvents were then removed, and the resulting material was purified by column chromatography (2% EtOAc/hexane), providing 58 mg (48%) of a very pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.85 (t, J = 8), 1.10-1.40 (m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 22.8, 24.1, 24.9, 29.4, 29.5, 29.7, 29.8, 32.0, 32.5, 82.9; ^{11}B NMR (96.2 MHz, $CDCl_3$) δ 33.8 (s); TLC (10% EtOAc/hexane, phosphomolybdic acid) R_f = 0.33. This material was identical spectroscopically with material prepared independently (vide supra).

Hydroboration of 1-dodecene: characterization of the intermediates, *B*-dodecylcatecholborane and tridodecylborane (eq 2): *N,N*-Dimethylacetamide (9.5 μL, 0.10 mmol), 1-dodecene (230 μL, 1.04 mmol), and CD_2Cl_2 (0.70 mL) were added sequentially to a reaction vessel. The resulting solution was cooled to -45 °C, and catecholborane (225 μL, 2.11 mmol) was added. The clear, colorless solution was warmed to room temperature and transferred to a J. Young NMR tube. After ^{1}H NMR indicated that 1-dodecene had been consumed (2 hours), the solution was analyzed by ^{11}B NMR (96.2 MHz, CD_2Cl_2): δ 21 (s, $B_2(O_2C_6H_4)_3$), 28 (d, J = 180, catecholborane), 35 (s, *B*-dodecylcatecholborane), 85 (broad, tridodecylborane). The identity of the peak at δ 21 was confirmed by doping the sample with independently prepared $B_2(O_2C_6H_4)_3$ (Männig, D.; Nöth, H. *J. Chem. Soc., Dalton Trans.* **1985**, 1689-1692). The reaction

mixture was subjected to the standard oxidative workup conditions (vide supra). GC analysis of the unpurified product confirmed that 1-dodecene had been completely consumed and indicated a 94 : 6 ratio of 1-dodecanol : 2-dodecanol.

In a separate experiment under identical conditions, a ^{13}C NMR spectrum (CD_2Cl_2, 75 MHz) was obtained of the reaction mixture prior to oxidation. The presence of *B*-dodecylcatecholborane and tridodecylborane was confirmed by comparison with the ^{13}C NMR spectra of authentic materials prepared independently (vide supra).

Synthesis of *B*-alkylpinacolborane (eq 3): Catecholborane (85 μL, 0.80 mmol) was added to a -45 °C solution of 1,2-dimethylcyclohexene (45.4 mg, 0.41 mmol), *N,N*-dimethylacetamide (8 μL, 0.09 mmol), and CH_2Cl_2 (0.27 mL). The solution was stirred with slow warming to room temperature for 3 hours, and then the reaction mixture was concentrated and a solution of pinacol (140 mg, 1.19 mmol) in THF (1 mL) was added. The resulting solution was stirred at room temperature for 62 h. The solvent was then removed, and the resulting material was chromatographed (2% EtOAc/hexane), providing 73.2 mg (75%) of a very pale yellow oil. ^1H NMR (300 MHz, $CDCl_3$) δ 0.76 (d, J = 7, 3H), 0.83 (s, 3H), 1.19 (s, 12H), 1.2-1.8 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.2, 18.1, 21.3, 24.7, 24.8, 25.2, 29.9, 33.7, 34.8, 82.8; ^{11}B NMR (96.2 MHz, $CDCl_3$) δ 34.8 (s); TLC (10% EtOAc/hexane, phosphomolybdic acid) R_f = 0.34.

Hydroboration of 1-dodecyne (eq 4): The reaction product was identical by ^1H and ^{13}C NMR with commercially available dodecanal (Aldrich).

Hydroboration of 1-dodecyne: characterization of the intermediate *B*-alkenylcatecholborane (eq 4): Catecholborane (220 μL, 2.06 mmol) was added to a 0 °C solution of 1-dodecyne (210 μL, 0.982 mmol), *N,N*-dimethylacetamide (9.0 μL, 0.097 mmol), and CD_2Cl_2 (0.67 mL). The resulting solution was transferred to a J. Young NMR tube, and the reaction was monitored by ^1H NMR, which showed complete consumption of 1-dodecyne in one hour. Comparison of the ^1H and ^{13}C NMR spectra of the reaction mixture with those of authentic *B*-alkenylcatecholborane, prepared through thermal reaction of 1-dodecyne with catecholborane, confirmed the identity of

the product as the *B*-alkenylcatecholborane.

Reaction of catecholborane with 0.05 equivalents of *N,N*-dimethylacetamide: Catecholborane (220 μL, 2.06 mmol) was added to a -45 °C solution of *N,N*-dimethylacetamide (9.5 μL, 0.10 mmol) in CD_2Cl_2 (0.70 mL). The resulting clear, colorless solution was warmed to room temperature and transferred to a J. Young NMR tube. ^{11}B NMR (96.2 MHz, CD_2Cl_2) (t = 30 min) δ -10.2 (q, J = 94; *N,N*-dimethylacetamide-BH_3), 18.9 (s), 21.0 (s; $B_2(O_2C_6H_4)_3$), 28.3 (d, J = 195; catecholborane). The identity of the peak at δ 21.0 was confirmed by doping the sample with independently prepared $B_2(O_2C_6H_4)_3$ (Männig, D.; Nöth, H. *J. Chem. Soc., Dalton Trans.* **1985**, 1689-1692). In a separate experiment, identical ^{11}B NMR results were obtained when the spectrum was taken three minutes after addition of catecholborane to the reaction mixture.

Reaction of tridodecylborane with catecholborane (eq 5): Catecholborane (210 μL, 1.97 mmol) was added dropwise to tridodecylborane (288 mg, 0.56 mmol) in CH_2Cl_2 (0.65 mL) in an NMR tube. The reaction was monitored by ^{11}B NMR (96.2 MHz; tridodecylborane at δ 87 (broad), *B*-dodecylcatecholborane at δ 36 (s), and catecholborane at δ 28 (d, J = 195)). After 3 hours, 28% conversion to *B*-dodecylcatecholborane was observed; after 18 hours, 48% conversion. The formation of diborane (δ 17.7, tt, J = 44, 139) was also evident. The presence of *B*-dodecylcatecholborane was confirmed by ^{13}C NMR.

In a separate experiment, it was observed that this reaction proceeded at essentially the same rate in the presence of *N,N*-dimethylacetamide.

$LiBH_4$-PROMOTED HYDROBORATION

Hydroboration of 1-dodecene with catecholborane in the presence of $LiBH_4$ (footnote 6): Catecholborane (110 μL, 1.03 mmol) was added to a mixture of lithium borohydride (2.7 mg, 0.12 mmol) in d_8-THF (0.7 mL). The solution was transferred to a J. Young NMR tube and examined by ^{11}B NMR (96.2 MHz) five minutes after mixing: BH_3-THF (δ -0.6, q, J = 102), $B(O_2C_6H_4)_2^-$ (δ 14.7, s), and catecholborane (δ 23.7, d, J = 187) were present, but not $LiBH_4$ (δ -41.7, quintet, J = 94) (cf. Männig, D.; Nöth, H. *J. Chem. Soc., Dalton Trans.* **1985**, 1689-1692).

1-Dodecene (230 μL, 1.04 mmol) was then added. After 1 hour, ^1H NMR indicated complete consumption of 1-dodecene, and ^{11}B NMR (96.2 MHz) showed mostly tridodecylborane (δ 84, broad), along with a very small amount of *B*-dodecylcatecholborane (δ 35, s). The reaction mixture was then subjected to an oxidative workup, and the unpurified products were analyzed by GC, which showed a 95 : 5 ratio of 1-dodecanol : 2-dodecanol.