Preparation of alcohols from alkenes via the homologation of boronates with (trimethylsilyl)diazomethane

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Supporting information

General: THF was freshly distilled from sodium benzophenone ketyl. Reactions were performed under an argon atmosphere. TLC: Silica Gel $60F_{254}$ plates (Merck), with detection by UV light and with an ethanol solution of phosphomolybdic acid. Column chromatography: 15-40 μm Merck Silica Gel. IR: Perkin-Elmer 2000. Melting points (uncorrected): Büchi 535. NMR: Bruker AM 300 (300.13 and 75.47 MHz for ^{1}H and ^{13}C, respectively). $CDCl_3$ as solvent. MS: Finnegan-Mat 4600 (70 eV).

Representative preparation of silanols 5: Catecholborane (1.17 mL, 11 mmol) and styrene (1.15 mL, 10 mmol) were heated under argon at 100°C for 10 hours. After cooling to room temperature, excess catecholborane was evacuated under vacuo. Dry, degassed THF (20 mL) was then added. (Trimethylsilyl)diazomethane (15 mL, 2.5 M in hexanes) was slowly introduced via syringe in the solution, which was then refluxed for 12 hours. After cooling to room temperature, 30% H_2O_2 (10 mL) and 15% NaOH (10 mL) were added cautiously. After 5 h stirring at room temperature, ether (50 mL) was added. The phases were separated, the organic layer was successively washed with 1 N HCl (2×10 mL) and water (20 mL), dried over $MgSO_4$. After filtration and concentration in vacuo, chromatography on silica gel (90:10 pentane/ether) afforded 1.25g (60%) of 3-phenyl-1-(trimethylsilyl)propan-1-ol (**5a**).

3-Phenyl-1-(trimethylsilyl)propan-1-ol (5a). ^{1}H NMR: δ = 0.09 (s, 9H), 1.26 (s, 1H), 1.85 (m, 2H), 2.65 (m, 1H), 2.95 (m, 1H), 3.35 (dd, *J* = 4.9, 9.2 Hz, 1H), 7.28 (m, 5H); ^{13}C NMR: δ = -3.9, 33.4, 35.4, 65.6, 125.8, 128.4, 128.5, 142.5; IR (film) ν = 3404, 1247 cm^{-1}.

3-(4-Methoxyphenyl)-1-(trimethylsilyl)propan-1-ol (5b). ^{1}H NMR: δ = 0.07 (s, 9H), 1.27 (s, 1H), 1.80 (m, 2H), 2.60 (m, 1H), 2.85 (m, 1H), 3.35 (dd, *J* = 4.9, 9.2 Hz, 1H), 3.78 (s, 3H), 6.82 (d, *J* = 8.5 Hz, 2H), 7.11 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR: δ = 4.0, 32.3, 35.5, 55.2, 65.4, 113.8, 129.3, 134.2, 157.8; IR (film) ν = 3430, 2836, 1512, 1247, 838 cm^{-1}.

1-(Trimethylsilyl)undecan-1-ol (5c). ^{1}H NMR: δ = 0.01 (s, 9H), 0.92 (t, *J* = 6.8 Hz, 3H), 1.2-1.4 (m, 19 H), 3.27 (m, 1H); IR (film) ν = 3372, 1466, 1247, 838 cm^{-1}.

3,3-Diphenyl-1-(trimethylsilyl)propan-1-ol (5d). ^{1}H NMR: δ = 0.09 (s, 9H), 1.32 (s, 1H), 2.12 (m, 2H), 3.25 (dd, *J* = 3.1, 11.0 Hz, 1H), 4.36 (dd, *J* = 5.5, 10.5 Hz, 1H), 7.29 (m, 10H); ^{13}C NMR: δ = -4.3, 38.9, 47.7, 63.6, 115.2, 120.2, 126.0, 126.2, 127.6, 128.5, 145.4; IR (film) ν = 3428, 1599, 1493, 1450, 1247, 837 cm^{-1}.

***exo*-2-Norbornanyl(trimethylsilyl)methanol (5e).** Obtained as a 40:60 mixture of diastereomers. ^{1}H NMR. Minor isomer: δ = 0.02 (s, 9H), 0.8-1.6 (m, 10H), 1.94 (broad s, 1H), 2.21 (broad s, 1H), 3.02 (d, *J* = 8.6 Hz, 1H); Major isomer: δ = 0.00 (s, 9H), 0.8-1.6 (m, 10H), 2.14 (broad s, 1H), 2.35 (broad s, 1H), 2.84 (d, *J* = 11.6 Hz, 1H); ^{13}C NMR: δ = 2.9, 28.6 (minor), 28.9 (major), 30.0 (major), 30.7 (minor), 34.7, (major), 34.9 (minor), 35.4, 36.5, 36.6, 36.7, 37.3, 40.3, 45.8 (major), 46.3 (minor), 68.6 (major), 70.0 (minor).

Preparation of alcohol 6b from 2-[2-(4-methoxyphenyl)-ethyl]-benzo[1,3,2]dioxaborole: 2-[2-(4-Methoxyphenyl)ethyl]-benzo[1,3,2]dioxaborole was prepared from catecholborane and 4-vinylanisole, as described above, and recrystallized from pentane / ether.

To a refluxing solution of 2-[2-(4-methoxyphenyl)ethyl]-benzo[1,3,2]dioxaborole (508 mg, 2 mmol) in THF (12 mL) was added dropwise (trimethylsilyl)diazomethane (2 mL, 2 M in hexanes, 4 mmol). The solution was then refluxed for 15 h. After cooling to room temperature, 30% H_2O_2 (10 mL) and 15% NaOH (10 mL) were added cautiously. After 3 h stirring at room temperature, ether (50 mL) was added. The phases were separated, the organic layer was successively washed with water (10 mL), 1 N HCl (2×10 mL) and water (10 mL), dried over $MgSO_4$. After filtration and concentration in vacuo, chromatography on silica gel (8:1 pentane/ether) afforded 301 mg (63%) of 3-(4-methoxyphenyl)-1-(trimethylsilyl)propan-1-ol (**5b**) and 81 mg (27%) of 2-(4-methoxyphenyl)ethanol.

2-[2-(4-Methoxyphenyl)ethyl]-benzo[1,3,2]dioxaborole. Mp: 65-66°C; ^{1}H NMR: δ = 1.66 (t, *J* = 8.0 Hz, 2H), 2.95 (t, *J* = 8.0 Hz, 2H), 3.81 (s, 3H), 6.85 (m, 2H), 7.10 (m, 2H), 7.15-7.25 (m, 4H).

Representative preparation of alcohols 6: To a solution of compound **5a** (50 mg, 0.24 mmol) in THF (1 mL) was added tetrabutylammonium fluoride (0.24 mL, 1 M in moist THF). After stirring for 10 h at room temperature, one equivalent of tetrabutylammonium fluoride was added and after several minutes, THF was evacuated under vacuo. Ether (10 mL) was added, the organic phase was washed with water (3×3 mL) and dried over $MgSO_4$. After filtration, concentration under vacuo afforded 32.3 mg (quantitative) of pure 3-phenylpropan-1-ol (**6a**).

3-Phenylpropan-1-ol (6a). ^{1}H NMR: δ = 1.47 (s, 1H), 1.87 (m, 2H), 2.70 (t, *J* = 7.4 Hz, 2H), 3.65 (t, *J* = 6.1 Hz, 2H), 7.25 (m, 5H).

3-(4-Methoxyphenyl)propan-1-ol (6b). ^{1}H NMR: δ = 1.39 (s, 1H), 1.85 (m, 2H), 2.65 (t, *J* = 7.6 Hz, 2H), 3.65 (t, *J* = 6.4 Hz, 2H), 3.78 (s, 3H), 6.81 (d, *J* = 8.5 Hz, 2H), 7.12 (d, *J* = 8.5 Hz, 2H).

Undecan-1-ol (6c). ^{1}H NMR: δ = 0.85 (t, *J* = 6.7 Hz, 3H), 1.25 (m, 19H), 3.61 (t, *J* = 6.7 Hz, 2H).

3,3-Diphenylpropan-1-ol (6d). ^{1}H NMR: δ = 1.43 (s, 1H), 2.31 (m, 2H), 3.61 (t, *J* = 6.7 Hz, 2H), 4.14 (t, *J* = 7.9 Hz, 1H), 7.21 (m, 10H).

***exo*-2-Norbornanemethanol (6e).** ^{1}H NMR: δ = 0.80-1.65 (m, 9H), 2.05-2.20 (m, 3H), 3.20-3.40 (m, 2H); ^{13}C NMR: δ = 29.0, 29.9, 34.1, 35.2, 36.2, 38.2, 44.9, 66.8.

Preparation of ethyl 3-(trimethylsilyl)heptanoate 8: To a solution of (trimethylsilyl)diazomethane (1.8 mL, 2 M in hexanes, 3.6 mmol) in THF (10 mL) was added a solution of tributylborane (1 mL, 1M in THF). After stirring for 24 h at room temperature, ethyl diazoacetate (0.38 mL, 3.6 mmol) was added, and the solution was refluxed for 12 h. Then propionic acid (5 mL) was added and the solution was refluxed for 24 h. After cooling to room temperature, the mixture was concentrated under vacuo. Ether (40 mL) was added, the organic phase was washed with 10% aqueous $NaHCO_3$ (3×10 mL) and water (20 mL), then dried over $MgSO_4$. After filtration and concentration in vacuo, chromatography on silica gel (98:2 pentane/ether) afforded 218 mg (33%) of ethyl 3-(trimethylsilyl)heptanoate.

Ethyl 3-(trimethylsilyl)heptanoate 8: ^{1}H NMR: δ = 0.01 (s, 9H), 0.05 (m, 1H), 0.80 (t, *J* = 6.9 Hz, 3H), 1.25 (m, 9H), 2.30 (m, 2H), 4.20 (q, *J* = 7.3 Hz, 2H); MS (CI, NH_3): *m/z* = 248 [$M^+ + NH_4$].