A Mild Radical Procedure for the Reduction of *B*-Alkylcatecholboranes to Alkanes.

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Supporting Information

General Techniques. Catecholborane was distilled under reduced pressure (50 °C, 50 mm Hg). Other reagents were obtained from commercial sources and used as received. All glassware was oven-dried at 130 °C, assembled hot and allowed to cool under vacuum. Column chromatography and filtrations were carried out using SDS silica gel (40-63 μ m) and AcOEt, Et₂O, cyclohexane, pentane and *t*-BuOMe as eluents. Thin layer chromatography (TLC) was performed using Merck silica gel 60 F254 analytical plates; detection via UV or dipping in a solution of KMnO₄ (3 g), K₂CO₃ (20 g), NaOH 5 % (5 ml) in H₂O (300 ml). NMR spectroscopy was carried out on a Bruker AC 300 (1H = 300 MHz, 13C = 75.5 MHz), chemical shifts in ppm relative to CHCl₃ (δ = 7.26 ppm) and CDCl₃ for 13C (δ = 77 ppm). GC analysis were carried out on a CE instruments MEGA Series HRGC fitted with an Optima delta-3 (Macherey-Nagel) capillary column (30 m and 10 m). GC/MS analysis were carried out on a Finnigan Trace GC/MS fitted with an Optima delta-3 (30 m).

Procedure A: O₂ initiation

Catecholborane (0.4 ml, 3 mmol) was added dropwise at 0 °C to a solution of the alkene (1.5 mmol) and *N,N*-dimethylacetamide (14 μ l, 0.15 mmol) in CH₂Cl₂ (2.0 ml) under N₂. The reaction mixture was heated under reflux for 5 h. After cooling down to 0 °C, MeOH (0.24 ml, 6 mmol) was added. The solution was heated under reflux and air (60 ml, 0.5 mmol O₂) was introduced over 1.5 h with a syringe (needle placed just below the surface of the reaction mixture). GC yield was determined using phenylcyclohexane as internal standard.

Procedure B: *t*-BuOO*t*-Bu initiation

Catecholborane (0.4 ml, 3 mmol) was added dropwise at 0 °C to a solution of the alkene (1.5 mmol) and *N,N*-dimethylacetamide (14 μ l, 0.15 mmol) in CH₂Cl₂ (2.0 ml) under N₂. The reaction mixture was heated under reflux for 5 h. After cooling down to 0 °C, MeOH (0.24 ml, 6 mmol) was added and the solution was further stirred for 15 min at rt. N₂ was blown across the surface of the solution until all the CH₂Cl₂ had been removed and then the organoborane was redissolved in 1,2-dichlorobenzene (2 ml). The solution was transferred to a microwave reaction vessel containing *t*-BuOO*t*-Bu (10 mol %) in 1,2-dichlorobenzene (2 ml). The reaction mixture was then heated under microwave irradiation for 15 min at 140 °C (300 W). GC yield was determined using phenylcyclohexane as internal standard.

cis-Pinane (cis-3)

From (+)- α -pinene **1** (0.240 ml, 1.5 mmol) according to procedure A. GC yield: 80%.

From (+)- α -pinene **1** (0.240 ml, 1.5 mmol) according to procedure B. GC yield: 74%. The retention time (t_r =2.57 min, 60 °C-280 °C, rate: 6 °C/min, 45 KPa, helium, l=10 m) and CG/MS

analysis of the reduced product were found to be identical with commercially available (1R)-(+)-*cis*-pinane.

From β -pinene **4** (0.240 ml, 1.5 mmol) according to procedure A. GC yield: 96%, dr 9:1. The retention time (t_r =2.57 min, t_r = 2.36 min, 60°C-280 °C, rate: 6°C/min, 45 KPa helium, l=10 m) and CG/MS analysis of the reduced product was found to be identical with commercially available (1R)-(+)-*cis*-pinane.

Octane (6)

From 1-octene **5** (0.170 ml, 1.0 mmol) according to procedure A. GC yield: 90%. The retention time (t_r =1.26 min, 50°C 2 min, 50°C-280°C, rate 8°C/min, 45 KPa, helium, l=10 m) and CG/MS analysis of the reduced product were found to be identical with commercially available octane.

1-Methylene-4-phenylcyclohexane (7)

KOt-Bu was added to a solution of CH₃PPh₃Br (5.36 g, 15 mmol) in Et₂O (40 ml) at rt under N₂ atmosphere. The resulting yellow suspension was stirred for 30 min at rt. Then a solution of phenylcyclohexanone (1.74 g, 10 mmol) in Et₂O (20 ml) was added dropwise to the reaction mixture. The suspension was stirred under reflux for 1.5 h, cooled to rt and further stirred for 20 h. The reaction mixture was then washed with brine (2 × 20 ml) and dried over MgSO₄. The solvent was removed under reduced pressure. The residue was dissolved in EtOAc and triphenylphosphine oxide precipitated upon slow addition of hexane. The mixture was filtered through a short pad of silica gel and the solvent removed under reduced pressure. FC (cyclohexane/EtOAc 9.9 :0.1) gave **7** (1.25 g, 73 %). Colourless oil. ¹H NMR (300 MHz, CDCl₃): 7.36-7.20 (m, 5H), 4.73 (s, 2H), 2.71 (tt, J=3.4, 12.2 Hz, 1H), 2.51-2.43 (m, 2H), 2.30-2.18 (m, 2H), 2.10-2.00 (m, 2H), 1.60 (qd, J=3.4, 12.7 Hz, 2H). ¹³CNMR (75.5 MHz, CDCl₃): 148.8, 146.8, 128.3, 126.8, 126.0, 107.3, 44.1, 35.5, 35.1. IR (film): 2928, 1650, 1492, 1442, 887, 697 cm⁻¹. EI-MS m/z (%): 173 (15, M⁺+1), 172 (100, M⁺), 157 (25), 143 (45), 130 (35), 115 (35), 104 (100), 91 (60), 79 (50). HRMS calcd. for C₁₃H₁₆ : 172.12520, found: 172.12521.

1-Methyl-4-phenylcyclohexane (8)

From **7** (0.258 g, 1.5 mmol) according to procedure A. FC (pentane) afforded **8** (0.130 g, 50%, *cis*:*trans* 1:1). Colourless oil. ¹H NMR (300 MHz, CDCl₃): 7.32-7.15 (m, 10H, 2 dias.), 2.58-2.40 (m, 2H, 2 dias.), 1.98-1.40 (m, 16H, 2 dias.), 1.01 (m, 2H, 2 dias.), 0.95 (d, J=7.1 Hz, 3H, 1 dias.), 0.86 (d, J=6.5 Hz, 3H, 1 dias.). ¹³C NMR (75.5 MHz, CDCl₃): 147.9, 147.7, 128.3, 127.0, 126.9, 125.8, 125.7, 44.3, 43.7, 35.7, 34.4, 32.5, 28.7, 27.6, 22.7, 18.3. IR (film): 2919, 1447, 751, 696 cm⁻¹. EI-MS m/z (%): 175 (10, M⁺+1), 174 (70, M⁺), 117 (75), 104 (100), 91 (45). HRMS calcd. for C₁₃H₁₈: 174.14085, found: 174.14082.

Cyclohexane (10)

From cyclohexene **9** (0.152 ml, 1.5 mmol). GC yield: 94%. The retention time (t_r =4.26 min, 40°C 3 min, 40°C-300°C, rate: 6°C/min, 80 KPa, helium, l=30 m) and CG/MS analysis of the reduced product were found to be identical with commercially available cyclohexane.

O-(*p*-Methoxybenzyl)- β -sitosterol (11).

To a solution of commercially available β -sitosterol (1.66 g, 4 mmol) in THF (15 mL) was added KOt-Bu (0.58 g, 5.2 mmol) in THF (15 mL). The solution was stirred at rt for 30 min then *p*-methoxybenzyl chloride (PMBCl 0.63 g, 4 mmol) was added dropwise. After stirring at rt for 48 h, the reaction mixture was diluted with Et₂O, washed with NH₄Cl and extracted with Et₂O. The

organic phase was dried with MgSO_4 and filtered. After evaporation of the solvent the crude product was purified by FC (pentane/ Et_2O 9.5:0.5) to give **11** (1.38 g, 65 %). White solid. ^1H NMR (300 MHz, CDCl_3): 7.28-7.26 (m, 4H), 6.87 (d, $J=8.3$ Hz, 2H), 5.34 (m, 1H), 4.49 (s, 2H), 3.80 (s, 3H), 3.26 (m, 1H), 2.44-2.37 (m, 2H), 2.03-1.78 (m, 4H), 1.70-0.80 (m, 37 H), 0.68 (s, 3H). ^{13}C NMR (75.5 MHz, CDCl_3): 159.0, 141.1, 131.2, 129.1, 121.5, 113.8, 78.3, 69.6, 56.8, 56.1, 55.3, 50.2, 45.9, 42.3, 39.8, 39.2, 37.3, 36.9, 36.1, 34.0, 32.0, 31.9, 29.2, 28.5, 28.2, 26.1, 24.3, 23.1, 21.1, 19.8, 19.4, 19.0, 18.8, 12.0, 11.9. IR (film): 2933, 2857, 1515, 1464, 1253, 1089, 823 cm^{-1} . EI-MS m/z (%): 536 (7, $\text{M}^+ + 2$), 535 (7, $\text{M}^+ + 1$), 534 (10, M^+), 414 (10), 398 (50), 228 (25), 172 (90), 143 (50), 104 (100), 91 (70), 79 (55). HRMS calcd. for $\text{C}_{37}\text{H}_{58}\text{O}_2$: 534.4437, found: 534.4435.

Reduced *O*-(*p*-methoxybenzyl)- β -sitosterol (**12**)

Starting from **11** (0.267 g, 0.5 mmol) according to procedure A. FC (pentane/ Et_2O 95:5) afforded **12** (0.165 g, 61 %) as a white solid. ^1H NMR (300 MHz, CDCl_3): 7.28-7.25 (d, $J=8.8$, 2H), 6.87 (d, $J=8.8$ Hz, 2H), 4.48 (s, 2H), 3.80 (s, 3H), 3.36-3.26 (m, 1H), 2.00-0.76 (m, 47 H), 0.65 (s, 3H). ^{13}C NMR (75.5 MHz, CDCl_3): 159.0, 131.4, 129.1, 113.8, 69.4, 56.6, 56.2, 55.3, 54.5, 45.9, 44.9, 42.6, 40.1, 37.1, 36.2, 35.8, 35.5, 34.9, 33.9, 32.2, 29.2, 28.9, 28.4, 28.3, 26.1, 24.2, 23.0, 21.2, 19.8, 19.1, 18.7, 12.3, 12.1, 12.0. IR (film): 2930, 2846, 1515, 1463, 1252, 1092, 1036, 816 cm^{-1} . EI-MS m/z (%): 536 (10, M^+), 270 (15), 149 (15), 122 (60), 121 (100), 91 (15), 43 (30). HRMS calcd. for $\text{C}_{37}\text{H}_{60}\text{O}_2$: 536.45933, found: 536.45935.

(4-Isopropylidenecyclohexyl)benzene (**13**).

Isopropyl-triphenylphosphonium iodide ^[1] (8.53 g, 20 mmol) was added to a solution of NaH (0.58 g, 24 mmol) in DMSO (15 ml) at rt. The solution was stirred for 30 min at rt and then for 1 h at 50 °C. The 4-phenylcyclohexanone (3.49 g, 20 mmol) in DMSO (15 ml) was added to the solution and heated at 50 °C for 18 h. The solution was treated with water (50 ml), extracted with ethyl acetate and dried over anhydrous MgSO_4 . The solvent was removed under reduced pressure and the residue was purified by FC (cyclohexane/ Et_2O 99:1) to afford **13** (1.44 g, 36%). Colourless oil. ^1H NMR (300 MHz, CDCl_3): 7.35-7.19 (m, 5H), 2.85 (d, $J=13.4$ Hz, 2H), 2.72 (tt, $J=3.4$, 12.2 Hz, 1H), 2.00-1.85 (m, 4H), 1.75 (s, 6H), 1.5 (m, 2H). ^{13}C NMR (75.5 MHz, CDCl_3): 147.3, 130.8, 128.3, 126.9, 125.8, 121.0, 44.9, 35.3, 30.1, 20.0. IR (film): 2924, 2854, 1491, 1437, 1217, 746, 696 cm^{-1} . EI-MS m/z (%): 201 (7, $\text{M}^+ + 1$), 200 (45), 172 (50), 157 (35), 143 (45), 130 (40), 104 (100), 91 (55). HRMS calcd. for $\text{C}_{15}\text{H}_{20}$: 200.15650, found: 200.15637.

1-Isopropyl-4-phenylcyclohexane (**14**)

According to procedure A. Starting from **13** (0.200 g, 1 mmol). FC (pentane) afforded **14** (0.145 g, 71%, cis/trans 1:1). Colourless oil. ^1H NMR (300 MHz, CDCl_3): 7.31-7.14 (m, 10H, 2 dias.), 2.65 (m, 1H, 1 dias.), 2.45 (tt, $J=3.4$, 12.2 Hz, 1H, 1 dias.), 1.95-1.68 (m, 10 H, 2 dias.), 1.56-1.38 (m, 6H, 2 dias.), 1.26-1.06 (m, 4H, 2 dias.), 0.91 (d, $J=6.6$ Hz, 6H, 1 dias.), 0.90 (d, $J=6.7$ Hz, 6H, 1 dias.). ^{13}C NMR (75.5 MHz, CDCl_3): 147.9, 147.3, 128.2, 127.0, 126.8, 125.8, 125.6, 44.7, 43.7, 42.9, 40.9, 34.5, 33.0, 30.1, 29.2, 27.8, 27.2, 21.0, 19.8. IR (film): 2921, 2853, 1447, 754, 697 cm^{-1} . EI-MS m/z (%): 203 (10, $\text{M}^+ + 1$), 202 (50, M^+), 160 (25), 117 (45), 104 (100), 91 (75). HRMS calcd. for $\text{C}_{15}\text{H}_{22}$: 202.17215, found: 202.17227.

cis-*p*-Menth-2-ene (**16**)

Starting from (+)-2-carene **15** (0.204 g, 1.5 mmol) according to procedure A. FC (pentane) afforded **16** (0.116 g, 56%) as a colourless oil. GC/MS analysis revealed a purity of 90% (Figure

1). ^1H - and ^{13}C -NMR spectra are in good accordance with literature data.^[2] ^1H NMR (300 MHz, CDCl_3): 5.51 (m, 2H), 2.01 (m, 1H), 1.84-1.73 (m, 1H), 1.72-1.09 (m, 5H), 0.92-0.78 (m, 9H). ^{13}C NMR (75.5 MHz, CDCl_3): 133.5, 129.9, 41.5, 32.2, 29.4, 28.9, 22.0, 21.2, 20.0, 19.8. EI-MS m/z (%): 139 (10, M^++1), 138 (10, M^+), 137 (70), 136 (30), 121 (30), 95 (50), 93 (65), 81 (100), 67 (55), 55 (65), 41 (75). HRMS calcd. for $\text{C}_{10}\text{H}_{18}$: 138.14085, found: 138.14098.

Figure 1. GC/MS analysis of the crude product of the reaction with (+)-2-carene **15** (Optima delta-3 Macherey-Nagel capillary column, 30 m, 40 °C (2 min) to 280 °C (5 °C/min). Top: GC trace, bottom, MS of the peak at 8.15 min.

Deuteration experiment with (+)- α -pinene (**1**).

According to procedure B. Starting from α -pinene **1** (0.159 ml, 1 mmol) and methanol- d_4 (CD_3OD), -d_3 (CD_3OH) and -d_1 (CH_3OD). Methanol- d_4 and -d_1 afforded (+)-*cis*-**3** in 14% and in 17% yield respectively. GC/EI-MS analysis revealed an isotopic purity $\geq 60\%$ with methanol- d_4 and -d_1 . EI-MS m/z (%): 139 (5, M^++1), 138 (5, M^+), 124 (7), 123 (12), 110 (5), 109 (6), 96 (40), 95 (70), 83 (55), 82 (55), 67 (70), 55 (100), 41 (95).

Methanol- d_3 afforded the non-deuterated *cis*-**3** in 42% yield.

Figure 2: MS spectra for non-deuterated *cis*-3 (left) and deuterated (+)-*cis*-3 (right).

FURTHER EVIDENCE FOR THE RADICAL MECHANISM:

In order to probe further the radical nature of the reaction, a second radical probe, 2-phenylmethylenecyclopropane, was used. Reaction of 2-phenylmethylenecyclopropane according to procedure A afforded traces of the ring-opened but-3-enylbenzene. The major product identified is a dimer resulting from the dimerization of the intermediate ring-opened radical. This demonstrates further the radical nature of the process and indicates that the reducing species does not efficiently reduce benzylic radicals.

A deuteration experiment with methanol- d_1 afforded (but-3-en-1-yl)benzene- d_1 together with the dimer. However, the amount of reduced product decreased relative to the dimer. This is in accordance with the expected kinetic isotopic effect.

Reduction of 1-methylene-2-phenylcyclopropane

According to procedure A. Starting from 1-methylene-2-phenylcyclopropane (0.137 ml, 1 mmol). GC/EI-MS analysis revealed the formation of three different products in a 1:2:1 ratio. The retention time of the first product (t_r = 12.05 min, 40°C 1 min, 40°C-280°C, rate: 6°C/min, 45 KPa helium, l=30 m) was found to be identical with the pure 4-phenyl-1-butene. The second product (t_r = 16.43 min, 40°C 1 min, 40°C-280°C, rate: 6°C/min, 45 KPa helium, l=30 m) was not identified and the third (t_r = 29.13 min, 40 °C 1 min, 40°C-280°C, rate: 6°C/min, 45 KPa

helium, $l=30$ m) was found to be the dimer 1-(1-allyl-2-phenyl-4-pentenyl)-benzene (mixture of diastereomers). The dimer was isolated by FC (cyclohexane/*t*-BuOMe 98:2). Spectroscopic data of 4-phenyl-1-butene were in accordance to the literature^[3]. Spectroscopic data of 1-(1-allyl-2-phenyl-4-pentenyl)-benzene: ^1H NMR (300 MHz, CDCl_3): 7.35-7.09 (m, 20 H, 2 dias.), 5.92-5.35 (m, 4H, 2 dias.), 5.06-4.67 (m, 8H, 2 dias.), 3.05-2.97 (m, 2H, 2 dias.), 2.87-2.78 (m, 2H, 2 dias.), 2.69-2.52 (m, 2H, 2 dias.), 2.44-2.30 (m, 2H, 2 dias.), 2.17-2.11 (m, 4H, 2 dias.). ^{13}C NMR (75.5 MHz, CDCl_3): 137.2, 136.9, 129.3, 129.0, 128.3, 127.5, 126.3, 126.0, 116.1, 115.6, 51.9, 50.1, 38.7, 37.5. EI-MS m/z (%): 264 (40, $\text{M}^+ + 2$), 262 (40, M^+), 221 (50), 131 (100), 130 (50), 117 (25), 91 (80). HRMS calcd. for $\text{C}_{20}\text{H}_{22}$: 262.17215, found: 262.17236.

Deuteration experiment with 1-methylene-2-phenylcyclopropane

According to procedure A. Starting from 1-methylene-2-phenylcyclopropane (0.137 ml, 1 mmol) and methanol- d_1 . GC/EI-MS analysis revealed the formation of (but-3-en-1-yl)benzene- d_1 (isotopic purity $\geq 90\%$) with methanol- d_1 (Figure 2). EI-MS m/z (%): 133 (25, $\text{M}^+ + 1$), 132 (25, M^+), 118 (100), 117 (60), 92 (30), 91 (60), 77 (40), 63 (35), 51 (50), 39 (50).

No deuterium incorporation was observed when methanol- d_3 was used.

Figure 3: MS spectra of 4-deutero-4-phenyl-1-butene (left) and 4-phenyl-1-butene (right).

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Reduced *O*-(*p*-methoxybenzyl)- β -sitosterol (**12**): ^1H NMR

Reduced *O*-(*p*-methoxybenzyl)- β -sitosterol (**12**): ^{13}C NMR