14. The Adamantane Rearrangement of Tricyclo[4.2.2.$0^{1,5}$]decane to Tricyclo[5.3.0.$0^{4,8}$]decane

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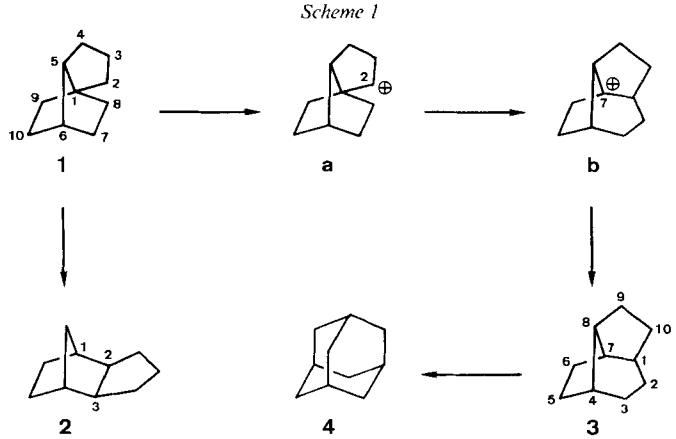
Regioselective generation of the C(2)-carbocation **a** of tricyclo[4.2.2.$0^{1,5}$]decane (**1**) by treatment of both corresponding epimeric alcohols **5** and **6** with BF_3 and trapping the rearranged tricyclo[5.3.0.$0^{4,8}$]decan-7-yl carbocation **b** with Et_3SiH as hydride-ion donor (ionic hydrogenation) gives the corresponding hydrocarbon **3** as sole product in almost quantitative yield. The latter is a known intermediate in the *Lewis*-acid-catalyzed rearrangement of **1** to adamantane (**4**).

1. Introduction and Results. – Tricyclo[4.2.2.$0^{1,5}$]decane (**1**)[1]), first synthesized in our group [1] and independently by a different route by *Skattebøl* and *Holm* [2], holds an extraordinary position among the 19 $C_{10}H_{16}$ isomers of the adamantaneland [3]. *Schleyer et al.* [2], who described **1** as an 'energetic bottle neck [4]', studied the $AlBr_3$-catalyzed isomerization of **1** (calc. $\Delta H_f^0 = -10.88$ kcal/mol [5]) and observed that it behaves as a 'continental divide', rearraging both 'backwards' to 2-*exo*,3-*exo*-trimethylene-8,9,10-tri-

Scheme 1



[1]) The compounds **1–3** are also called as follows: **1**: 1,7-trimethylene-8,9,10-trinorbornane, 8,9-methanediyl-10-norbornane, hexahydro-1*H*-1,3a-ethanopentalene (*CA*, 9th Collect. Index); **2**: *exo*-tricyclo[5.2.1.$0^{2,5}$]decane, *exo*-3,4,8,9-tetrahydrodicyclopentadiene, octahydro-(3aα,4β,7β,7aα)-4,7-methano-1*H*-indene (*CA*, 9th Collect. Index); hexahydro-*exo*-4,7-methanoindene (*CA*, 8th Collect. Index); **3**: 2-homobrexane, octahydro-1,4-ethanopentalene (*CA*, 8th and 9th Collect. Index).

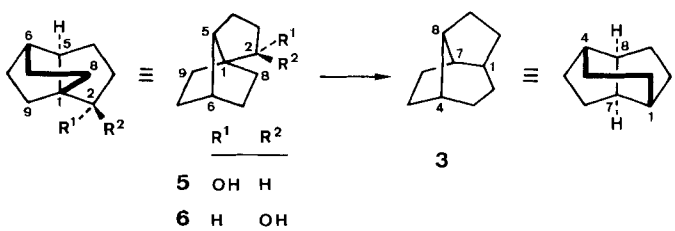
norbornane (**2**)[1]); 60%; calc. $\Delta H_f^0 = -16.77$ kcal/mol [5]) as well as 'forwards' to adamantane (**4**; 40%). Among the three intermediates formed at shorter reaction times in amounts never exceeding 3–5%, tricyclo[5.3.0.$0^{4,8}$]decane (**3**)[1]) [2] [6–8]; calc. $\Delta H_f^0 = -18.68$ kcal/mol [5]) was recognized as an intermediate in an entirely new pathway from **1** to adamantane (**4**), this in contrast to the predictions based on the graphical analysis of the adamantane rearrangement [9] and the calculated heats of formation of the isomeric hydrocarbons and their corresponding carbocations [4] [5]. *Schleyer et al.* [2] comment on this unexpected result as follows: 'Our earlier analysis [4] discounted possible rearrangements through **3** on the grounds that the necessary intermediate, **b**, was a relatively unstable bridgehead carbenium ion. However, as we have emphasized, the relative energies of competing rearrangement transition states really determine the course of reaction. These transition states may not be approximated well by the energies of the starting and of the final carbocations. Rearrangement of **a** to **b** involves a strain-relieving norbornane ring expansion for which there is ample precedent [10]'.

Tobe et al. [8] confirmed **3** as an intermediate. In their experiments with $AlCl_3$ in CH_2Cl_2, **3** could be accumulated up to 33% within 3 min at 15° (in addition to 2.8% of **1**, 38.1% of **2**, and 26.2% of **4**). After 10 min at 15°, **2** (39.6%) and **4** (60.4%) were obtained as the sole products in a combined yield of 79%.

Our experiments [11] with $AlBr_3$ in CS_2 gave a qualitatively similar result. At 0°, the composition was 22% of **1**, 41% of **2**, 11% of **3**, and 26% of **4** after 30 min, and 55% of **2** and 45% of **4** after 60 min.

Continuing our systematic studies on the rearrangement of adamantane isomers by regioselective generation and trapping of the primarily formed and/or the rearranged carbocations [12] by the method of 'ionic hydrogenation' [13], we synthesized the two epimeric C(2)-alcohols **5** ($OH^{C(9)}$)[2]) and **6** ($OH^{C(8)}$)[2]) and treated both of them with BF_3(gas)/Et_3SiH in CH_2Cl_2 in order to study the behaviour of the C(2)-carbocation **a**. Indeed, tricyclo[5.3.0.$0^{4,8}$]decane (**3**) was obtained almost quantitatively as the only hydrocarbon (*ca.* 75% conversion after 10 min and 100% after 30 min, resp., at r.t.). These selective experiments confirm the interesting rearrangement **a**→**b** and fully support the route of the above discussed *Lewis*-acid-catalyzed rearrangement of **1** to adamantane (**4**) *via* **3**.

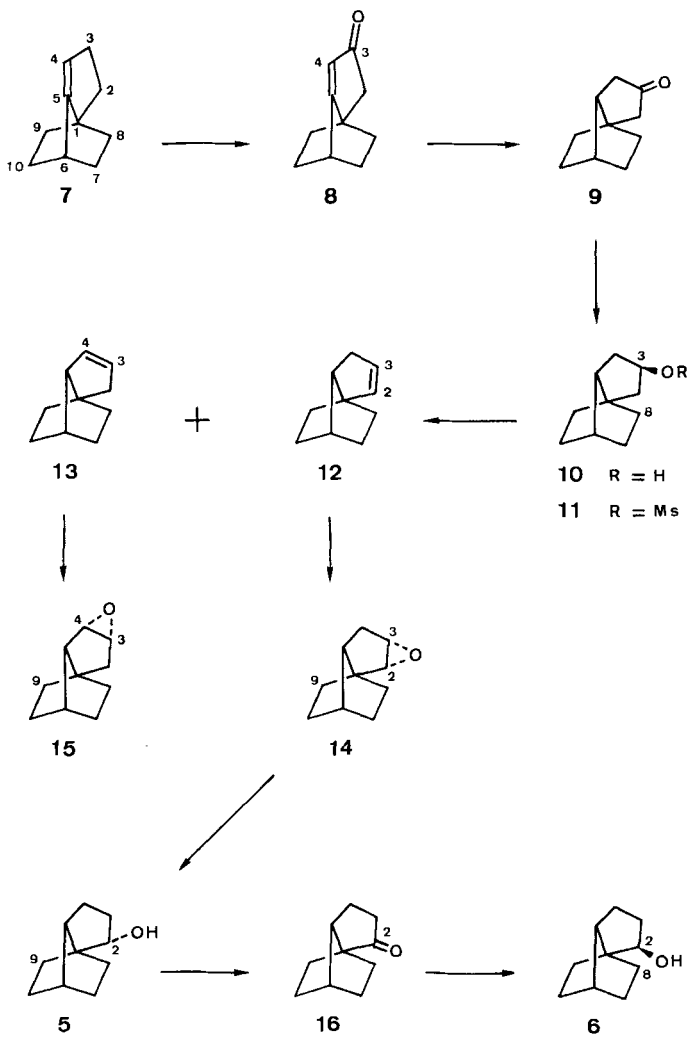
Scheme 2



2. Synthesis of the Alcohols 5 and 6. – The known tricyclo[4.2.2.$0^{1,5}$]dec-4-ene (**7**) [14] [15] was oxidized in the allylic position to the α,β-unsaturated ketone **8**, which subse-

[2]) The superscripts indicate toward which C-atom a substituent or H-atom is orientated.

Scheme 3



quently was catalytically (H_2, Pd/C) reduced to the corresponding saturated ketone **9**. The latter, on treatment with $LiAlH_4$, stereoselectively led to the $OH^{C(8)}$-alcohol **10**. Its methanesulfonate **11**, upon base-catalyzed (*t*-BuOK) elimination, gave a 6:1 mixture of the C(2),C(3)- and the C(3),C(4)-olefins **12**/**13**, which was transformed to the corresponding epoxides **14** and **15** (separated by CC). On both olefins, the attack of the peracid proceeded stereoselectively from the less hindered side orientated towards C(9). Regioselective ring opening in **14** with $LiAlH_4$ gave the $OH^{C(9)}$-alcohol **5**. Its oxidation to the corresponding ketone **16** and subsequent $LiAlH_4$-reduction with high stereoselectivity yielded the epimeric $OH^{C(8)}$-alcohol **6** (ratio **6**/**5** *ca.* 25:1).

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Experimental Part

General. See [16].

Tricyclo[4.2.2.0^{1,5}]dec-4-en-3-one (**8**). To a stirred suspension of 26.98 g (270 mmol) of CrO_3 in 250 ml of CH_2Cl_2 under Ar at $< -20°$, 25.72 g (268 mmol) of 3,5-dimethylpyrazole were added, and 20 min later, 3.615 g (27 mmol) of tricyclo[4.2.2.0^{1,5}]dec-4-ene (**7**) [15] [16] in 25 ml of CH_2Cl_2 were added dropwise over 10 min. Stirring was continued for 10 h at $< -20°$ and then for 13 h by warming up to 10°. The mixture was cooled to 0°, treated with 150 ml of 5N aq. NaOH and stirred for 1 h. Workup (800 ml of Et_2O, washing with H_2O, 6N HCl, and $NaHCO_3$ sol.) followed by CC with pentane/Et_2O 4:1 gave 2.011 g (50.5%) of **8**, which was distilled (120°/12 Torr). IR: 3410*w*, 1715*s*, 1655*s*, 1453*m*, 1411*m*, 1290*w*, 1242*m*, 1174*w*, 1151*m*, 1143*w*, 1113*w*, 955*w*, 904*w*, 877*w*, 850*w*. ^{1}H-NMR: 1.3–1.45 (*m*, H_{endo}–C(7), H_{endo}–C(10)); 1.7–1.85 (*m*, 2 H–C(8), 2 H–C(9)); 1.9–2.1 (*m*, H_{exo}–C(7), H_{exo}–C(10)); 2.28 (*s*, 2 H–C(2)); 2.90 (*t*, $J(6,7exo) = J(6,10exo) = 4$, H–C(6)); 5.62 (*s*, H–C(4)). MS: 148 (48, $M^{+\cdot}$), 133 (5.5), 120 (100), 119 (19), 105 (14), 92 (36), 91 (57), 79 (10), 78 (6), 77 (8), 65 (11), 63 (6), 53 (7), 52 (6), 51 (11), 50 (5), 41 (7), 39 (21), 28 (12).

Tricyclo[4.2.2.0^{1,5}]decan-3-one (**9**). A mixture of 2.007 g (13.6 mmol) of **8** and 450 mg of 10% Pd/C in 50 ml of EtOH was stirred under H_2 for 3½ h. Filtration through *Celite*, solvent removal, and CC with pentane/Et_2O 3:1 yielded 1.792 g (88%) of **9**. M.p. 72°. IR: 1740*s*, 1475*w*, 1455*w*, 1412*m*, 1324*w*, 1295*w*, 1238*w*, 1211*w*, 1181*m*, 1155*w*, 1119*w*, 1100*m*, 1042*w*, 963*w*, 910*w*. ^{1}H-NMR: 1.15–1.35 (*m*, 1 H); 1.35–1.65 (*m*, 5 H); 1.7–2.0 (*m*, 4 H); 2.15, 2.31 (2 *d*, $J_{gem} = 17.5$, 2 H–C(2)); 2.1–2.25 (*m*, 2 H). MS: 150 (32, $M^{+\cdot}$), 123 (7.5), 122 (80), 121 (4), 108 (12), 107 (43), 95 (9), 94 (40), 93 (100), 92 (6.5), 91 (17), 81 (17), 80 (64), 79 (78), 78 (9), 77 (19), 68 (18), 67 (22), 66 (9), 65 (5), 55 (11), 54 (9), 53 (14), 41 (18), 39 (9).

Tricyclo[4.2.2.0^{1,5}]decan-3$^{C(8)}$-ol[2]) (**10**). At 0° under Ar, a soln. of 1.763 g (11.8 mmol) of **9** in 15 ml of Et_2O was added dropwise over 30 min to a stirred suspension of 500 mg (13.2 mmol) of $LiAlH_4$ in 50 ml of Et_2O. After further 2 h at r.t., workup (0.5 ml of H_2O, 0.5 ml of 15% NaOH, 1.5 ml of H_2O, extraction with Et_2O) gave 1.620 g (90.5%) of **10**. M.p. 65–67°. IR: 3610*m*, 3550–3100*w*, 1480*w*, 1458*m*, 1443*w*, 1306*w*, 1258*w*, 1228*w*, 1160*w*, 1098*w*, 1023*m*, 1000*w*, 966*w*, 928*w*. ^{1}H-NMR: 1.15–1.45 (*m*, 4 H); 1.15–1.35 (*m*, among others $J_{gem} = 12$, $J(3^{C(9)}, 4) = 7$, H–C(4)); 1.5–1.8 (*m*, 3 H); 1.52 (*dd*, $J_{gem} = 13.5$, $J(2^{C(8)}, 3^{C(9)}) = 2.5$, $H^{C(8)}$–C(2)); 1.60 (*s*, $HO^{C(8)}$–C(3)); 1.8–2.05 (*m*, 3 H); 1.89 (*dd*, $J_{gem} = 13.5$, $J(2^{C(9)}, 3^{C(9)}) = 9$, $H^{C(9)}$–C(2)); 1.95–2.05 (*m*, among others $J_{gem} = 12$, $J(3^{C(9)}, 4') = 7$, $J(4', 5) = 7$, H–C(4')); 4.77 (*dtd*, $J(2^{C(9)}, 3^{C(9)}) = 9$, $J(3^{C(9)}, 4) = J(3^{C(9)}, 4') = 7$, $J(2^{C(8)}, 3^{C(9)}) = 2.5$, $H^{C(9)}$–C(3)). MS: 152 (14, $M^{+\cdot}$), 134 (23), 124 (15), 123 (15), 119 (12), 109 (12), 108 (58), 106 (23), 105 (16), 96 (9), 95 (26), 94 (9), 93 (42), 92 (12), 91 (17), 81 (23), 80 (100), 79 (37), 77 (11), 67 (19), 55 (12), 41 (13).

Tricyclo[4.2.2.0^{1,5}]decan-3$^{C(8)}$-yl Methanesulfonate[2]) (**11**). A soln. of 1.441 g (9.48 mmol) of **10**, 1.190 g (10.39 mmol) of CH_3SO_2Cl, and 1.140 g (11.29 mmol) of Et_3N in 20 ml of CH_2Cl_2 was stirred under Ar for 1¾ h at 0°. Workup (dilution with 100 ml of H_2O, extraction with Et_2O, washed with sat. NaCl, sat. $NaHCO_3$, and again sat. NaCl soln.) gave 2.168 g (100%) of crude **11**.

Tricyclo[4.2.2.0^{1,5}]dec-2- and -3-ene (**12** and **13**, resp.). A soln. of 2.100 g (9.13 mmol) of crude **11** in 20 ml of DMSO under Ar at r.t. was treated at once with 1.550 g (13.84 mmol) of *t*-BuOK. After 1 h, the mixture was poured on 150 ml of ice/H_2O. Extraction with pentane, washing with sat. NaCl soln., careful removal of the solvent by distillation *via* a *Vigreux* column, and CC with pentane gave 500 mg (41%) of a 6:1 mixture (determined by capillary GLC (*SE 52*)) of **12** and **13**. IR: 3130*w*, 3045*m*, 1474*w*, 1458*m*, 1440*w*, 1344*m*, 1314*w*, 1304*m*, 1262*w*, 1200*w*, 1175*w*, 972*w*, 940*w*, 914*w*, 716*m*, 700*m*, 686*w*. ^{1}H-NMR (**12**): 1.15–1.65, 1.8–2.2 (2*m*, 12 H); 5.69, 6.04 (2*m*, $w_{1/2} \approx 10$ each, H–C(2), H–C(3)). MS: 134 (9, $M^{+\cdot}$), 119 (5.5), 106 (15), 105 (100), 91 (19), 79 (15), 78 (12).

2$^{C(9)}$,3$^{C(9)}$- and 3$^{C(9)}$,4$^{C(9)}$-Epoxytricyclo[4.2.2.0^{1,5}]decane[2]) (**14** and **15**, resp.). A soln. of 620 mg (3.24 mmol) of 90% *m*-chloroperbenzoic acid in 8 ml of CH_2Cl_2 was added under Ar to a stirred soln. of 400 mg (2.985 mmol) of a 6:1 mixture **12**/**13** in 8 ml of CH_2Cl_2 at 0°[3]). After 15 h, the mixture was worked up (40 ml of 10% Na_2SO_3 soln., 90 ml of CH_2Cl_2, washed with sat. $NaHCO_3$ and sat. NaCl soln.). CC with pentane/Et_2O 4:1 yielded 58 mg (13%) of **15** and 344 mg (77%) of **14**.

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[3]) The reaction was followed by capillary GLC: **12** was already completely converted to **14** after 1 h, whereas **13** to **15** only after 15 h.

14: IR: 3020*m*, 1474*w*, 1459*m*, 1440*w*, 1376*m*, 1304*w*, 1284*w*, 1266*w*, 1244*w*, 1234*w*, 1208*m*, 974*w*, 934*w*, 916*m*, 835*m*, 680*w*, 650*w*. ^{1}H-NMR: 1.15–1.45 (*m*, 4 H); 1.4–1.65 (*m*, 3 H); 1.6–1.85 (*m*, 3 H); 1.9–2.05 (*m*, 2 H); 3.27, 3.57 (2*m*, $w_{1/2} \approx 5$ each, among others $J(2^{C(8)},3^{C(8)}) = 2.5$, $H^{C(8)}$–C(2), $H^{C(8)}$–C(3)). MS: 150 (25, M^+), 135 (13), 122 (34), 121 (82), 117 (12), 107 (42), 106 (39), 94 (100), 93 (72), 91 (58), 81 (25), 80 (30), 79 (92), 78 (26), 77 (49), 67 (42), 66 (25), 65 (23), 55 (23), 53 (31), 51 (20), 41 (53), 39 (61), 28 (64).

15: IR: 3020*m*, 1476*w*, 1462*m*, 1451*w*, 1368*m*, 1350*w*, 1321*w*, 1300*m*, 1280*w*, 1270*w*, 1240*w*, 1215*w*, 1196*w*, 1178*w*, 1050*w*, 1030*w*, 918*m*. ^{1}H-NMR: 1.15–1.65 (*m*, 6 H); 1.47 (*d*, $J_{gem} = 13.5$, $H^{C(9)}$–C(2)); 1.65–2.0 (*m*, 3 H); 1.79 (*dd*, $J_{gem} = 13.5$, $J(2^{C(8)},3^{C(8)}) = 3.5$, $H^{C(8)}$–C(2)); 2.22 (*m*, $w_{1/2} \approx 10$, among others $J(4^{C(8)},6) \approx 0.5$, H–C(6)); 3.24 (*ddd*, $J(3^{C(8)},4^{C(8)}) = 2.5$, $J(4^{C(8)},5) = 0.5$, $J(4^{C(8)},6) \approx 0.5$, $H^{C(8)}$–C(4)); 3.73 (*dd*, $J(2^{C(8)},3^{C(8)}) = 3.5$, $J(3^{C(8)},4^{C(8)}) = 2.5$, $H^{C(8)}$–C(3)). MS: 150 (6, M^+), 135 (7), 122 (27), 121 (48), 108 (14), 107 (100), 106 (36), 104 (17), 94 (56), 93 (65), 91 (50), 81 (29), 80 (22), 79 (82), 78 (37), 77 (43), 67 (28), 65 (19), 55 (18), 53 (27), 51 (16), 41 (42), 39 (53), 28 (61).

Tricyclo[4.2.2.0^{1,5}]decan-2$^{C(9)}$-ol^2) (**5**). At 0° under Ar a soln. of 178 mg (1.19 mmol) of **14** in 5 ml of Et_2O was treated wit 188 mg (4.95 mmol) of $LiAlH_4$. After 12 h of stirring, workup (H_2O, 15% NaOH) and CC with pentane/Et_2O gave 126 mg (70%) of **5**. M.p. 119°. IR: 3610*m*, 3480 (br.), 1470*w*, 1463*m*, 1436*w*, 1335*w*, 1324*w*, 1303*m*, 1260*w*, 1208*w*, 1191*w*, 1157*w*, 1068*m*, 995*m*, 954*w*, 910*w*, 872*w*. ^{1}H-NMR: 1.07 (*m*, $w_{1/2} \approx 25$, 1 H); 1.12–1.3 (*m*, among others $J_{gem} \approx 12$–15, $J(4^{C(8)},5) = 11$, $J(3^{C(8)},4^{C(8)}) = 10.5$, $J(3^{C(9)},4^{C(8)}) = 9.5$ or 7.5, $H^{C(8)}$–C(4)); 1.15–1.45 (*m*, 3 H); 1.35–1.6 (*m*, among others $J_{gem} \approx 12$–15, $J(3^{C(9)},4^{C(9)}) = 9.5$ or 7.5, $J(4^{C(9)},5) = 8$, $J(3^{C(8)},4^{C(9)}) = 2.5$, $H^{C(9)}$–C(4)); 1.45 (*m*, $HO^{C(9)}$–C(2)); 1.5–1.6 (*m*, 2 H); 1.72–1.86 (*m*, 1 H); 1.9–2.05 (*m*, among others $J_{gem} = 14.5$, $J(3^{C(9)},4^{C(8)})$ and $J(3^{C(9)},4^{C(9)}) = 9.5$ and 7.5, $J(2^{C(8)},3^{C(9)}) = 1$, $H^{C(9)}$–C(3)); 1.95–2.1 (*m*, 2 H); 2.19 (*dd*, $J(4^{C(8)},5) = 11$, $J(4^{C(9)},5) = 8$, further $J(3^{C(8)},5) \leqslant 0.5$, H–C(5)); 2.72 (*dddd*, $J_{gem} = 14.5$, $J(3^{C(8)},4^{C(8)}) = 10.5$, $J(2^{C(8)},3^{C(8)}) = 6$, $J(3^{C(8)},4^{C(9)}) = 2.5$, further $J(3^{C(8)},5) \leqslant 0.5$, $H^{C(8)}$–C(3)); 3.98 (*dd*, $J(2^{C(8)},3^{C(8)}) = 6$, $J(2^{C(8)},3^{C(9)}) = 1$, $H^{C(8)}$–C(2)). MS: 152 (42, M^+), 137 (8), 134 (35), 124 (42), 123 (34), 119 (22), 110 (24.5), 109 (100), 108 (24), 106 (38), 105 (22), 97 (40), 96 (93), 95 (64), 93 (52), 92 (19), 91 (30), 83 (50), 82 (27), 81 (46), 80 (48), 79 (50), 70 (15), 68 (20), 67 (58), 55 (30), 43 (12), 41 (20).

Tricyclo[4.2.2.0^{1,5}]decan-2-one (**16**). A soln. of 50 mg (0.329 mmol) of **5** in 3 ml of CH_2Cl_2 was treated with 25 mg (0.305 mmol) of NaOAc and 100 mg (0.464 mmol) of pyridinium chlorochromate (PCC). The mixture was stirred at r.t. for 90 min. Usual workup and filtration through silica gel in pentane/Et_2O 3:1 yielded 39 mg (79%) of **16**. IR: 1735*s*, 1480*w*, 1463*m*, 1408*m*, 1320*m*, 1308*w*, 1297*w*, 1258*m*, 1238*w*, 1190*m*, 1160*w*, 1140*m*, 890*w*. ^{1}H-NMR: 1.30 (*m*, $w_{1/2} \approx 30$, 1 H); 1.4–1.8 (*m*, 4 H, 2 H–C(3)); 1.85–2.05 (*m*, 3 H); 2.19 (*m*, $w_{1/2} \approx 10$, H–C(6)); 2.27 (*dd*, $J(4^{C(8)},5) = 11$, $J(4^{C(9)},5) = 6.5$, further $J(3^{C(9)},5) \leqslant 0.5$, H–C(5)); 2.52 (*dt*, $J_{gem} = 19$, $J(3^{C(9)},4^{C(8)}) = J(3^{C(9)},4^{C(9)}) = 8.5$, further $J(3^{C(9)},5) \leqslant 0.5$, $H^{C(9)}$–C(3)); 2.77 (*ddd*, $J_{gem} = 19$, $J(3^{C(8)},4^{C(8)}) = 8$, $J(3^{C(8)},4^{C(9)}) = 1.5$, $H^{C(8)}$–C(3)). MS: 150 (98, M^+), 135 (37), 122 (30), 121 (43), 117 (13), 109 (21), 108 (41), 107 (39), 106 (18), 96 (22), 95 (17), 94 (39), 93 (67), 91 (23), 81 (52), 80 (33), 79 (100), 77 (14), 67 (21).

Tricyclo[4.2.2.0^{1,5}]decan-2$^{C(8)}$-ol^2) (**6**). Under Ar at 0°, a soln. of 35 mg (0.233 mmol) of **16** in 2 ml of Et_2O was treated with 30 mg (0.789 mmol) of $LiAlH_4$. After 3 h of stirring, usual workup, and filtration through silica gel in pentane/Et_2O 3:1, 28 mg (79%) of **6** were obtained, which contained a small amount of **5** (ratio *ca.* 25:1). IR: 3600*m*, 3400 (br.), 1479*w*, 1453*m*, 1392*w*, 1143*w*, 1114*m*, 1065*w*, 1040*m*, 1007*w*, 968*w*, 912*w*. ^{1}H-NMR: 1.15–1.65 (*m*, 7 H and $HO^{C(8)}$–C(2)); 1.75–2.05 (*m*, 4 H); 1.95–2.1 (*m*, among others $J_{gem} = 14$, $J(2^{C(9)},3^{C(9)}) = 6$, $H^{C(9)}$–C(3)); 1.96 (*m*, $w_{1/2} \approx 10$, H–C(6)); 2.52 (*dtd*, $J_{gem} = 14$, $J(2^{C(9)},3^{C(8)}) = J(3^{C(8)},4) = 9$, $J(3^{C(8)},4') = 7$, $H^{C(8)}$–C(3)); 4.29 (*dd*, $J(2^{C(9)},3^{C(8)}) = 9$, $J(2^{C(9)},3^{C(9)}) = 6$, $H^{C(9)}$–C(2)). MS: 152 (50, M^+), 134 (40), 124 (37), 123 (33), 119 (23), 110 (23), 109 (100), 108 (23), 106 (37), 105 (23), 97 (33), 96 (75), 95 (57), 93 (47), 92 (19), 91 (29), 83 (45), 82 (24), 81 (38), 80 (40), 79 (40), 70 (13), 67 (42), 55 (21), 41 (11).

Ionic Hydrogenation of **5** *and* **6**. a) *Analytical Scale* (representative procedure). A soln. of 5.2 mg (0.034 mmol) of the alcohol, 3.2 mg (0.024 mmol) of adamantane as internal standard and 15 µl of Et_3SiH in 4 ml of CH_2Cl_2 (filtered through basic Al_2O_3) was stirred at r.t. under BF_3/Ar atmosphere (strong balloon). Samples were taken out with a syringe through a septum and quenched by addition of a 10% Na_2CO_3 soln. The probes were diluted with CH_2Cl_2, the org. soln. taken away, dried ($MgSO_4$), and analyzed by capillary GLC (*SE 30*). The reaction showed *ca.* 75% of conversion after 10 min and full conversion after 30 min.

b) *Preparative Scale*. In analogy to the above procedure with *ca.* 50 mg of alcohol, however without an internal standard. Most of the solvent was carefully distilled off through a *Vigreux* column and the hydrocarbon **1** isolated by prep. GLC (*OV 17*). ^{1}H-NMR ($CDCl_3$): 1.13 (*m*, 2 H); 1.42–1.87 (*m*, 10 H); 1.87 (*m*, $w_{1/2} \approx 13$, 2 H); 2.08 (*m*, $w_{1/2} \approx 13$, 2 H). ^{13}C-NMR ($CDCl_3$): 24.70 (*t*); 26.58 (*t*); 31.40 (*t*); 40.18 (*d*); 46.87 (*d*).

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