

# 14. The Adamantane Rearrangement of Tricyclo[4.2.2.0<sup>1,5</sup>]decane to Tricyclo[5.3.0.0<sup>4,8</sup>]decane

by Kanai L. Ghatak and Camille Ganter\*

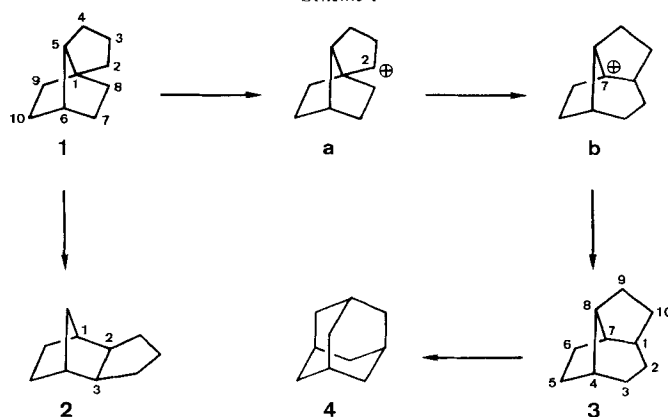
Laboratorium für Organische Chemie der Eidgenössischen Technischen Hochschule, ETH-Zentrum, Universitätstr. 16, CH-8092 Zürich

(23.XI.87)

Regioselective generation of the C(2)-carbocation **a** of tricyclo[4.2.2.0<sup>1,5</sup>]decane (**1**) by treatment of both corresponding epimeric alcohols **5** and **6** with BF<sub>3</sub> and trapping the rearranged tricyclo[5.3.0.0<sup>4,8</sup>]decan-7-yl carbocation **b** with Et<sub>3</sub>SiH 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<sup>1,5</sup>]decane (**1**)<sup>1)</sup>, 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<sub>10</sub>H<sub>16</sub> isomers of the adamantaneland [3]. Schleyer *et al.* [2], who described **1** as an ‘energetic bottle neck [4]’, studied the AlBr<sub>3</sub>-catalyzed isomerization of **1** (calc.  $\Delta H_f^0 = -10.88$  kcal/mol [5]) and observed that it behaves as a ‘continental divide’, rearranging both ‘backwards’ to 2-*exo*,3-*exo*-trimethylene-8,9,10-tri-

Scheme 1



<sup>1)</sup> 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, 9<sup>th</sup> Collect. Index); **2**: *exo*-tricyclo[5.2.1.0<sup>2,5</sup>]decane, *exo*-3,4,8,9-tetrahydrodicyclopentadiene, octahydro-(3 $\alpha$ ,4 $\beta$ ,7 $\beta$ ,7 $\alpha$ )-4,7-methano-1*H*-indene (CA, 9<sup>th</sup> Collect. Index); hexahydro-*exo*-4,7-methanoindene (CA, 8<sup>th</sup> Collect. Index); **3**: 2-homobrexane, octahydro-1,4-ethanopentalene (CA, 8<sup>th</sup> and 9<sup>th</sup> Collect. Index).

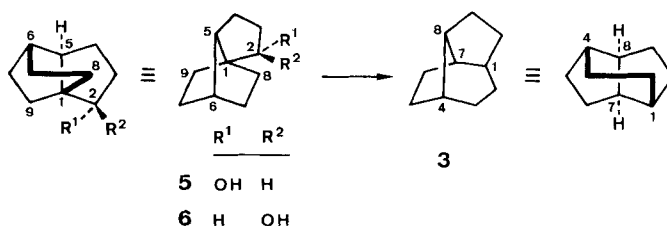
norbornane (**2**)<sup>1)</sup>; 60%; calc.  $\Delta H_f^0 = -16.77$  kcal/mol [5]) as well as ‘forwards’ to adamantane (**4**; 40%). Among the three intermediates formed at shorter reaction times in amounts never exceeding 3–5%, tricyclo[5.3.0.0<sup>4,8</sup>]decane (**3**)<sup>1)</sup> [2] [6–8]; calc.  $\Delta H_f^0 = -18.68$  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  $\text{AlCl}_3$  in  $\text{CH}_2\text{Cl}_2$ , **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  $\text{AlBr}_3$  in  $\text{CS}_2$  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** ( $\text{OH}^{\text{C}(9)}$ )<sup>2)</sup> and **6** ( $\text{OH}^{\text{C}(8)}$ )<sup>2)</sup> and treated both of them with  $\text{BF}_3(\text{gas})/\text{Et}_3\text{SiH}$  in  $\text{CH}_2\text{Cl}_2$  in order to study the behaviour of the C(2)-carbocation **a**. Indeed, tricyclo[5.3.0.0<sup>4,8</sup>]decane (**3**) was obtained almost quantitatively as the only hy-

Scheme 2

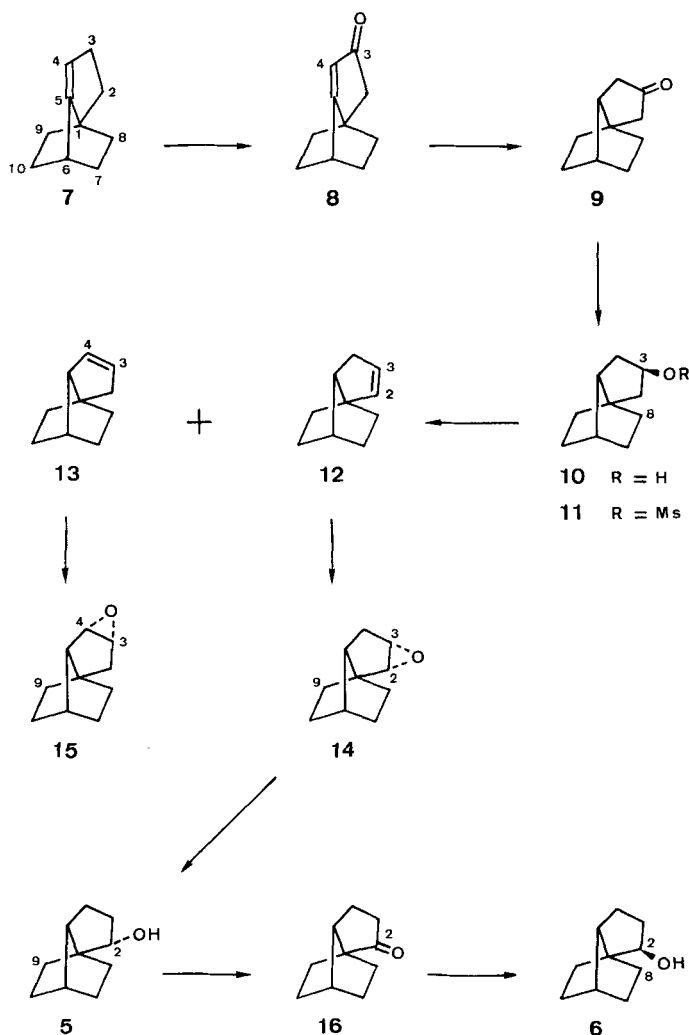


drocarbon (ca. 75% conversion after 10 min and 100% after 30 min, resp., at r.t.). These selective experiments confirm the interesting rearrangement **a** → **b** and fully support the route of the above discussed *Lewis*-acid-catalyzed rearrangement of **1** to adamantane (**4**) *via* **3**.

**2. Synthesis of the Alcohols **5** and **6**.** – The known tricyclo[4.2.2.0<sup>1,5</sup>]dec-4-ene (**7**) [14] [15] was oxidized in the allylic position to the  $\alpha,\beta$ -unsaturated ketone **8**, which subse-

<sup>2)</sup> The superscripts indicate toward which C-atom a substituent or H-atom is orientated.

Scheme 3



quently was catalytically ( $\text{H}_2$ , Pd/C) reduced to the corresponding saturated ketone **9**. The latter, on treatment with  $\text{LiAlH}_4$ , stereoselectively led to the  $\text{OH}^{\text{C}(8)}$ -alcohol **10**. Its methanesulfonate **11**, upon base-catalyzed ( $t\text{-BuOK}$ ) 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  $\text{LiAlH}_4$  gave the  $\text{OH}^{\text{C}(9)}$ -alcohol **5**. Its oxidation to the corresponding ketone **16** and subsequent  $\text{LiAlH}_4$ -reduction with high stereoselectivity yielded the epimeric  $\text{OH}^{\text{C}(8)}$ -alcohol **6** (ratio **6/5** ca. 25:1).

Financial support by the *Swiss National Science Foundation* and by *Ciba Geigy AG*, Basel, is gratefully acknowledged. We are indebted to the following persons in our analytical department for their help: Miss B. Brandenburg (NMR) and Prof. J. Seibl (MS).

### Experimental Part

General. See [16].

*Tricyclo[4.2.2.0<sup>1,5</sup>]dec-4-en-3-one (8)*. To a stirred suspension of 26.98 g (270 mmol) of  $\text{CrO}_3$  in 250 ml of  $\text{CH}_2\text{Cl}_2$  under Ar at  $< -20^\circ$ , 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<sup>1,5</sup>]dec-4-ene (7) [15] [16] in 25 ml of  $\text{CH}_2\text{Cl}_2$  were added dropwise over 10 min. Stirring was continued for 10 h at  $< -20^\circ$  and then for 13 h by warming up to  $10^\circ$ . The mixture was cooled to  $0^\circ$ , treated with 150 ml of 5*N* aq. NaOH and stirred for 1 h. Workup (800 ml of  $\text{Et}_2\text{O}$ , washing with  $\text{H}_2\text{O}$ , 6*N* HCl, and  $\text{NaHCO}_3$  sol.) followed by CC with pentane/ $\text{Et}_2\text{O}$  4:1 gave 2.011 g (50.5%) of **8**, which was distilled ( $120^\circ/12$  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*.  $^1\text{H-NMR}$ : 1.3–1.45 (*m*,  $\text{H}_{\text{endo}}\text{-C}(7)$ ,  $\text{H}_{\text{endo}}\text{-C}(10)$ ); 1.7–1.85 (*m*, 2  $\text{H-C}(8)$ , 2  $\text{H-C}(9)$ ); 1.9–2.1 (*m*,  $\text{H}_{\text{exo}}\text{-C}(7)$ ,  $\text{H}_{\text{exo}}\text{-C}(10)$ ); 2.28 (*s*, 2  $\text{H-C}(2)$ ); 2.90 (*t*,  $J(6,7_{\text{exo}}) = J(6,10_{\text{exo}}) = 4$ ,  $\text{H-C}(6)$ ); 5.62 (*s*,  $\text{H-C}(4)$ ). MS: 148 (48,  $M^{+}$ ), 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<sup>1,5</sup>]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  $\text{H}_2$  for  $3\frac{1}{2}$  h. Filtration through *Celite*, solvent removal, and CC with pentane/ $\text{Et}_2\text{O}$  3:1 yielded 1.792 g (88%) of **9**. M.p.  $72^\circ$ . 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*.  $^1\text{H-NMR}$ : 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*,  $J_{\text{gem}} = 17.5$ , 2  $\text{H-C}(2)$ ); 2.1–2.25 (*m*, 2 H). MS: 150 (32,  $M^{+}$ ), 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<sup>1,5</sup>]decan-3<sup>C(8)</sup>-ol<sup>2</sup> (10)*. At  $0^\circ$  under Ar, a soln. of 1.763 g (11.8 mmol) of **9** in 15 ml of  $\text{Et}_2\text{O}$  was added dropwise over 30 min to a stirred suspension of 500 mg (13.2 mmol) of  $\text{LiAlH}_4$  in 50 ml of  $\text{Et}_2\text{O}$ . After further 2 h at r.t., workup (0.5 ml of  $\text{H}_2\text{O}$ , 0.5 ml of 15% NaOH, 1.5 ml of  $\text{H}_2\text{O}$ , extraction with  $\text{Et}_2\text{O}$ ) 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*.  $^1\text{H-NMR}$ : 1.15–1.45 (*m*, 4 H); 1.15–1.35 (*m*, among others  $J_{\text{gem}} = 12$ ,  $J(3^{\text{C}(9)}, 4) = 7$ ,  $\text{H-C}(4)$ ); 1.5–1.8 (*m*, 3 H); 1.52 (*dd*,  $J_{\text{gem}} = 13.5$ ,  $J(2^{\text{C}(8)}, 3^{\text{C}(9)}) = 2.5$ ,  $\text{H}^{\text{C}(8)}\text{-C}(2)$ ); 1.60 (*s*,  $\text{HO}^{\text{C}(8)}\text{-C}(3)$ ); 1.8–2.05 (*m*, 3 H); 1.89 (*dd*,  $J_{\text{gem}} = 13.5$ ,  $J(2^{\text{C}(9)}, 3^{\text{C}(9)}) = 9$ ,  $\text{H}^{\text{C}(9)}\text{-C}(2)$ ); 1.95–2.05 (*m*, among others  $J_{\text{gem}} = 12$ ,  $J(3^{\text{C}(9)}, 4') = 7$ ,  $J(4', 5) = 7$ ,  $\text{H-C}(4')$ ); 4.77 (*ddd*,  $J(2^{\text{C}(9)}, 3^{\text{C}(9)}) = 9$ ,  $J(3^{\text{C}(9)}, 4) = J(3^{\text{C}(9)}, 4') = 7$ ,  $J(2^{\text{C}(8)}, 3^{\text{C}(8)}) = 2.5$ ,  $\text{H}^{\text{C}(9)}\text{-C}(3)$ ). MS: 152 (14,  $M^{+}$ ), 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<sup>1,5</sup>]decan-3<sup>C(8)</sup>-yl Methanesulfonate<sup>2</sup> (11)*. A soln. of 1.441 g (9.48 mmol) of **10**, 1.190 g (10.39 mmol) of  $\text{CH}_3\text{SO}_2\text{Cl}$ , and 1.140 g (11.29 mmol) of  $\text{Et}_3\text{N}$  in 20 ml of  $\text{CH}_2\text{Cl}_2$  was stirred under Ar for  $1\frac{1}{4}$  h at  $0^\circ$ . Workup (dilution with 100 ml of  $\text{H}_2\text{O}$ , extraction with  $\text{Et}_2\text{O}$ , washed with sat. NaCl, sat.  $\text{NaHCO}_3$ , and again sat. NaCl soln.) gave 2.168 g (100%) of crude **11**.

*Tricyclo[4.2.2.0<sup>1,5</sup>]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/ $\text{H}_2\text{O}$ . 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*.  $^1\text{H-NMR}$  (**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,  $\text{H-C}(2)$ ,  $\text{H-C}(3)$ ). MS: 134 (9,  $M^{+}$ ), 119 (5.5), 106 (15), 105 (100), 91 (19), 79 (15), 78 (12).

*2<sup>C(9)</sup>, 3<sup>C(9)</sup>- and 2<sup>C(9)</sup>, 4<sup>C(9)</sup>-Epoxyttricyclo[4.2.2.0<sup>1,5</sup>]decane<sup>2</sup> (14 and 15, resp.)*. A soln. of 620 mg (3.24 mmol) of 90% *m*-chloroperbenzoic acid in 8 ml of  $\text{CH}_2\text{Cl}_2$  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  $\text{CH}_2\text{Cl}_2$  at  $0^\circ$ . After 15 h, the mixture was worked up (40 ml of 10%  $\text{Na}_2\text{SO}_3$  soln., 90 ml of  $\text{CH}_2\text{Cl}_2$ , washed with sat.  $\text{NaHCO}_3$  and sat. NaCl soln.). CC with pentane/ $\text{Et}_2\text{O}$  4:1 yielded 58 mg (13%) of **15** and 344 mg (77%) of **14**.

<sup>3)</sup> 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 $w$ .  $^1\text{H-NMR}$ : 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  $J(2^{\text{C}(8)}, 3^{\text{C}(8)}) = 2.5$ ,  $\text{H}^{\text{C}(8)}\text{--C}(2)$ ,  $\text{H}^{\text{C}(8)}\text{--C}(3)$ ). 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 $m$ .  $^1\text{H-NMR}$ : 1.15–1.65 ( $m$ , 6 H); 1.47 ( $d$ ,  $J_{\text{gem}} = 13.5$ ,  $\text{H}^{\text{C}(9)}\text{--C}(2)$ ); 1.65–2.0 ( $m$ , 3 H); 1.79 ( $dd$ ,  $J_{\text{gem}} = 13.5$ ,  $J(2^{\text{C}(8)}, 3^{\text{C}(8)}) = 3.5$ ,  $\text{H}^{\text{C}(8)}\text{--C}(2)$ ); 2.22 ( $m$ ,  $w_{1/2} \approx 10$ , among others  $J(4^{\text{C}(8)}, 6) \approx 0.5$ ,  $\text{H--C}(6)$ ); 3.24 ( $ddd$ ,  $J(3^{\text{C}(8)}, 4^{\text{C}(8)}) = 2.5$ ,  $J(4^{\text{C}(8)}, 5) = 0.5$ ,  $J(4^{\text{C}(8)}, 6) \approx 0.5$ ,  $\text{H}^{\text{C}(8)}\text{--C}(4)$ ); 3.73 ( $dd$ ,  $J(2^{\text{C}(8)}, 3^{\text{C}(8)}) = 3.5$ ,  $J(3^{\text{C}(8)}, 4^{\text{C}(8)}) = 2.5$ ,  $\text{H}^{\text{C}(8)}\text{--C}(3)$ ). 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<sup>1,5</sup>]decan-2<sup>C(9)</sup>-ol<sup>2</sup>* (**5**). At 0° under Ar a soln. of 178 mg (1.19 mmol) of **14** in 5 ml of Et<sub>2</sub>O was treated with 188 mg (4.95 mmol) of LiAlH<sub>4</sub>. After 12 h of stirring, workup (H<sub>2</sub>O, 15% NaOH) and CC with pentane/Et<sub>2</sub>O 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 $w$ .  $^1\text{H-NMR}$ : 1.07 ( $m$ ,  $w_{1/2} \approx 25$ , 1 H); 1.12–1.3 ( $m$ , among others  $J_{\text{gem}} \approx 12\text{--}15$ ,  $J(4^{\text{C}(8)}, 5) = 11$ ,  $J(3^{\text{C}(8)}, 4^{\text{C}(8)}) = 10.5$ ,  $J(3^{\text{C}(9)}, 4^{\text{C}(8)}) = 9.5$  or  $7.5$ ,  $\text{H}^{\text{C}(8)}\text{--C}(4)$ ); 1.15–1.45 ( $m$ , 3 H); 1.35–1.6 ( $m$ , among others  $J_{\text{gem}} \approx 12\text{--}15$ ,  $J(3^{\text{C}(9)}, 4^{\text{C}(9)}) = 9.5$  or  $7.5$ ,  $J(4^{\text{C}(9)}, 5) = 8$ ,  $J(3^{\text{C}(8)}, 4^{\text{C}(9)}) = 2.5$ ,  $\text{H}^{\text{C}(9)}\text{--C}(4)$ ); 1.45 ( $m$ ,  $\text{HO}^{\text{C}(9)}\text{--C}(2)$ ); 1.5–1.6 ( $m$ , 2 H); 1.72–1.86 ( $m$ , 1 H); 1.9–2.05 ( $m$ , among others  $J_{\text{gem}} = 14.5$ ,  $J(3^{\text{C}(9)}, 4^{\text{C}(8)})$  and  $J(3^{\text{C}(9)}, 4^{\text{C}(9)}) = 9.5$  and  $7.5$ ,  $J(2^{\text{C}(8)}, 3^{\text{C}(9)}) = 1$ ,  $\text{H}^{\text{C}(9)}\text{--C}(3)$ ); 1.95–2.1 ( $m$ , 2 H); 2.19 ( $dd$ ,  $J(4^{\text{C}(8)}, 5) = 11$ ,  $J(4^{\text{C}(9)}, 5) = 8$ , further  $J(3^{\text{C}(8)}, 5) \leq 0.5$ ,  $\text{H--C}(5)$ ); 2.72 ( $dddd$ ,  $J_{\text{gem}} = 14.5$ ,  $J(3^{\text{C}(8)}, 4^{\text{C}(8)}) = 10.5$ ,  $J(2^{\text{C}(8)}, 3^{\text{C}(8)}) = 6$ ,  $J(3^{\text{C}(8)}, 4^{\text{C}(9)}) = 2.5$ , further  $J(3^{\text{C}(8)}, 5) \leq 0.5$ ,  $\text{H}^{\text{C}(8)}\text{--C}(3)$ ); 3.98 ( $dd$ ,  $J(2^{\text{C}(8)}, 3^{\text{C}(8)}) = 6$ ,  $J(2^{\text{C}(8)}, 3^{\text{C}(9)}) = 1$ ,  $\text{H}^{\text{C}(8)}\text{--C}(2)$ ). 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<sup>1,5</sup>]decan-2-one* (**16**). A soln. of 50 mg (0.329 mmol) of **5** in 3 ml of CH<sub>2</sub>Cl<sub>2</sub> 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<sub>2</sub>O 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 $w$ .  $^1\text{H-NMR}$ : 1.30 ( $m$ ,  $w_{1/2} \approx 30$ , 1 H); 1.4–1.8 ( $m$ , 4 H, 2  $\text{H--C}(3)$ ); 1.85–2.05 ( $m$ , 3 H); 2.19 ( $m$ ,  $w_{1/2} \approx 10$ ,  $\text{H--C}(6)$ ); 2.27 ( $dd$ ,  $J(4^{\text{C}(8)}, 5) = 11$ ,  $J(4^{\text{C}(9)}, 5) = 6.5$ , further  $J(3^{\text{C}(9)}, 5) \leq 0.5$ ,  $\text{H--C}(5)$ ); 2.52 ( $dt$ ,  $J_{\text{gem}} = 19$ ,  $J(3^{\text{C}(9)}, 4^{\text{C}(8)}) = J(3^{\text{C}(9)}, 4^{\text{C}(9)}) = 8.5$ , further  $J(3^{\text{C}(9)}, 5) \leq 0.5$ ,  $\text{H}^{\text{C}(9)}\text{--C}(3)$ ); 2.77 ( $ddd$ ,  $J_{\text{gem}} = 19$ ,  $J(3^{\text{C}(8)}, 4^{\text{C}(8)}) = 8$ ,  $J(3^{\text{C}(8)}, 4^{\text{C}(9)}) = 1.5$ ,  $\text{H}^{\text{C}(8)}\text{--C}(3)$ ). 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<sup>1,5</sup>]decan-2<sup>C(8)</sup>-ol<sup>2</sup>* (**6**). Under Ar at 0°, a soln. of 35 mg (0.233 mmol) of **16** in 2 ml of Et<sub>2</sub>O was treated with 30 mg (0.789 mmol) of LiAlH<sub>4</sub>. After 3 h of stirring, usual workup, and filtration through silica gel in pentane/Et<sub>2</sub>O 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 $w$ .  $^1\text{H-NMR}$ : 1.15–1.65 ( $m$ , 7 H and  $\text{HO}^{\text{C}(8)}\text{--C}(2)$ ); 1.75–2.05 ( $m$ , 4 H); 1.95–2.1 ( $m$ , among others  $J_{\text{gem}} = 14$ ,  $J(2^{\text{C}(9)}, 3^{\text{C}(9)}) = 6$ ,  $\text{H}^{\text{C}(9)}\text{--C}(3)$ ); 1.96 ( $m$ ,  $w_{1/2} \approx 10$ ,  $\text{H--C}(6)$ ); 2.52 ( $dt$ ,  $J_{\text{gem}} = 14$ ,  $J(2^{\text{C}(9)}, 3^{\text{C}(8)}) = J(3^{\text{C}(8)}, 4) = 9$ ,  $J(3^{\text{C}(8)}, 4') = 7$ ,  $\text{H}^{\text{C}(8)}\text{--C}(3)$ ); 4.29 ( $dd$ ,  $J(2^{\text{C}(9)}, 3^{\text{C}(8)}) = 9$ ,  $J(2^{\text{C}(9)}, 3^{\text{C}(9)}) = 6$ ,  $\text{H}^{\text{C}(9)}\text{--C}(2)$ ). 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  $\mu\text{l}$  of Et<sub>3</sub>SiH in 4 ml of CH<sub>2</sub>Cl<sub>2</sub> (filtered through basic Al<sub>2</sub>O<sub>3</sub>) was stirred at r.t. under BF<sub>3</sub>/Ar atmosphere (strong balloon). Samples were taken out with a syringe through a septum and quenched by addition of a 10% Na<sub>2</sub>CO<sub>3</sub> soln. The probes were diluted with CH<sub>2</sub>Cl<sub>2</sub>, the org. soln. taken away, dried (MgSO<sub>4</sub>), 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).  $^1\text{H-NMR}$  (CDCl<sub>3</sub>): 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).  $^{13}\text{C-NMR}$  (CDCl<sub>3</sub>): 24.70 ( $t$ ); 26.58 ( $t$ ); 31.40 ( $t$ ); 40.18 ( $d$ ); 46.87 ( $d$ ).

## REFERENCES

- [1] F.J. Jäggi, C. Ganter, *Helv. Chim. Acta* **1980**, *63*, 214.
- [2] P.v.R. Schleyer, P. Grubmüller, W.F. Maier, O. Vostrowsky, L. Skattebøl, K.H. Holm, *Tetrahedron Lett.* **1980**, 921.
- [3] R. C. Fort, Jr., 'Adamantane, The Chemistry of Diamond Molecules', M. Dekker, Inc., New York, 1976.
- [4] E. M. Engler, M. Farcasiu, A. Sevin, J. M. Cense, P.v.R. Schleyer, *J. Am. Chem. Soc.* **1973**, *95*, 5769.
- [5] E. M. Engler, J. D. Andose, P.v.R. Schleyer, *J. Am. Chem. Soc.* **1973**, *95*, 8005.
- [6] S. Masamune, H. Zenda, M. Wiesel, N. Nakatsuka, G. Bigam, *J. Am. Chem. Soc.* **1968**, *90*, 2727.
- [7] J. R. Wiseman, J. J. Vanderbilt, W. M. Butler, *J. Org. Chem.* **1980**, *45*, 667.
- [8] Y. Tobe, K. Terashima, Y. Sakai, Y. Odaira, *J. Am. Chem. Soc.* **1981**, *103*, 2307.
- [9] H. W. Whitlock, Jr., M. W. Siefken, *J. Am. Chem. Soc.* **1968**, *90*, 4929.
- [10] E.g., T. Irie, H. Tanida, *J. Org. Chem.* **1978**, *43*, 3274 and refs. cit. therein.
- [11] M. Brossi, K. L. Ghatak, C. Ganter, unpublished results.
- [12] A. M. Klester, C. Ganter, *Helv. Chim. Acta* **1985**, *68*, 734.
- [13] W. P. Weber, in 'Reactivity and Structure Concepts in Organic Chemistry', 'Silicon Reagents in Organic Synthesis', Springer-Verlag, Berlin, 1983, Vol. 14, p. 273.
- [14] Y. Tobe, Y. Hayauchi, Y. Sakai, Y. Odaira, *J. Org. Chem.* **1980**, *45*, 637.
- [15] P. E. Eaton, P. G. Jobe, I. D. Reingold, *J. Am. Chem. Soc.* **1984**, *106*, 6437.
- [16] H.-R. Känel, C. Ganter, *Helv. Chim. Acta* **1985**, *68*, 1226.