95. The Adamantane Rearrangement of *syn*- and *anti*-Tricyclo[4.2.1.1.$1^{2,5}$]decane

Part II[1])

Rearrangements Initiated by Regioselective Formation of Carbocations at C(3) and C(9)

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The *endo*- and *exo*-alcohols **5–12** of *syn*- (**1**) and *anti*-tricyclo[4.2.1.$1^{2,5}$]decane (**2**) were treated with BF_3/Et_3SiH (ionic hydrogenation) in order to study the behaviour of the corresponding regioselectively generated carbocations at C(3) (**a** (*syn*), **b** (*anti*)) and C(9) (**c** (*syn*), **d** (*anti*)). The *anti*-hydrocarbon **2** is practically the sole product obtained starting with the four 3-alcohols (*via* **a** → **b** from **5** and **6** (*syn*) and *via* **b** from **9** and **10** (*anti*)). The four 9-alcohols in each case yield a mixture of 2-*endo*, 3-*endo*- (**3**) and 2-*exo*,3-*exo*-trimethylene-8,9,10-trinorbornane (**4**) (*via* **c** → **e** from **7** and **8** (syn) and *via* **d** → **f** from **11** and **12** (*anti*)), but no hydrocarbon **2**, *i.e.* none of the 1,3-H shifts **c** → **a** and **d** → **b** is involved.

In the presence of $AlBr_3$ in CS_2, *syn*-tricyclo[4.2.1.$1^{2,5}$] decane[3]) (**1**) isomerizes exclusively to *anti*-tricyclo[4.2.1.$1^{2,5}$]decane[3]) (**2**), whereby hydride abstraction occurs at C(3) (→ carbocation **a**). Neither 2-*endo*,3-*endo*- (**3**) nor 2-*exo*,3-*exo*-trimethylene-8,9,10-trinorbornane (**4**) is observed. The *anti*-isomer **2** rearranges to **4**, most probably as the result of hydride abstraction at C(9) (→ carbocation **d**) [1].

In order to obtain more detailed information about the adamantane rearrangement[4]) of both **1** and **2**, we applied the ionic hydrogenation method[5]), by which we were able to generate regioselectively each of the four possible secondary carbocations at C(3) and C(9): **a** and **c** of the *syn*-isomer **1** as well as **b** and **d** of the *anti*-isomer **2**. As substrates for our studies we used **5–12**, the *endo*- and *exo*-alcohols[3]) at C(3) and C(9). The heterolyses

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[3]) The configurational prefixes *syn* and *anti* are used for compounds **1, 2, 5–12, 16–26,** and **28–31** with the two methylene bridges (CH_2(9) and CH_2(10)) on the same and opposite side, respectively, of the plane C(1)–C(2)–C(5)–C(6). In these compounds, an *exo* substituent lies in a plane parallel to the reference plane C(1)–C(2)–C(5)–C(6) and an *endo* substituent stands out from this parallel plane.

[4]) *'Adamantaneland':* a set of 19 isomeric saturated, tricyclic $C_{10}H_{16}$ hydrocarbons, which contain neither a three- nor a four-membered ring, and no alkyl group [2–4]. *'Adamantane rearrangement':* rearrangement of any one of the 18 adamantane isomers to any other member of the *adamantaneland via* carbocation intermediates, eventually resulting in the formation of the thermodynamically most stable product, the adamantane [2–4].

[5]) See the review [5] and ref. cit. therein.

of the C–O bonds were effected at room temperature by gaseous BF_3, and the primarily formed and/or the rearranged carbocations were trapped by Et_3SiH. The results are summarized in the *Table*.

Scheme 1

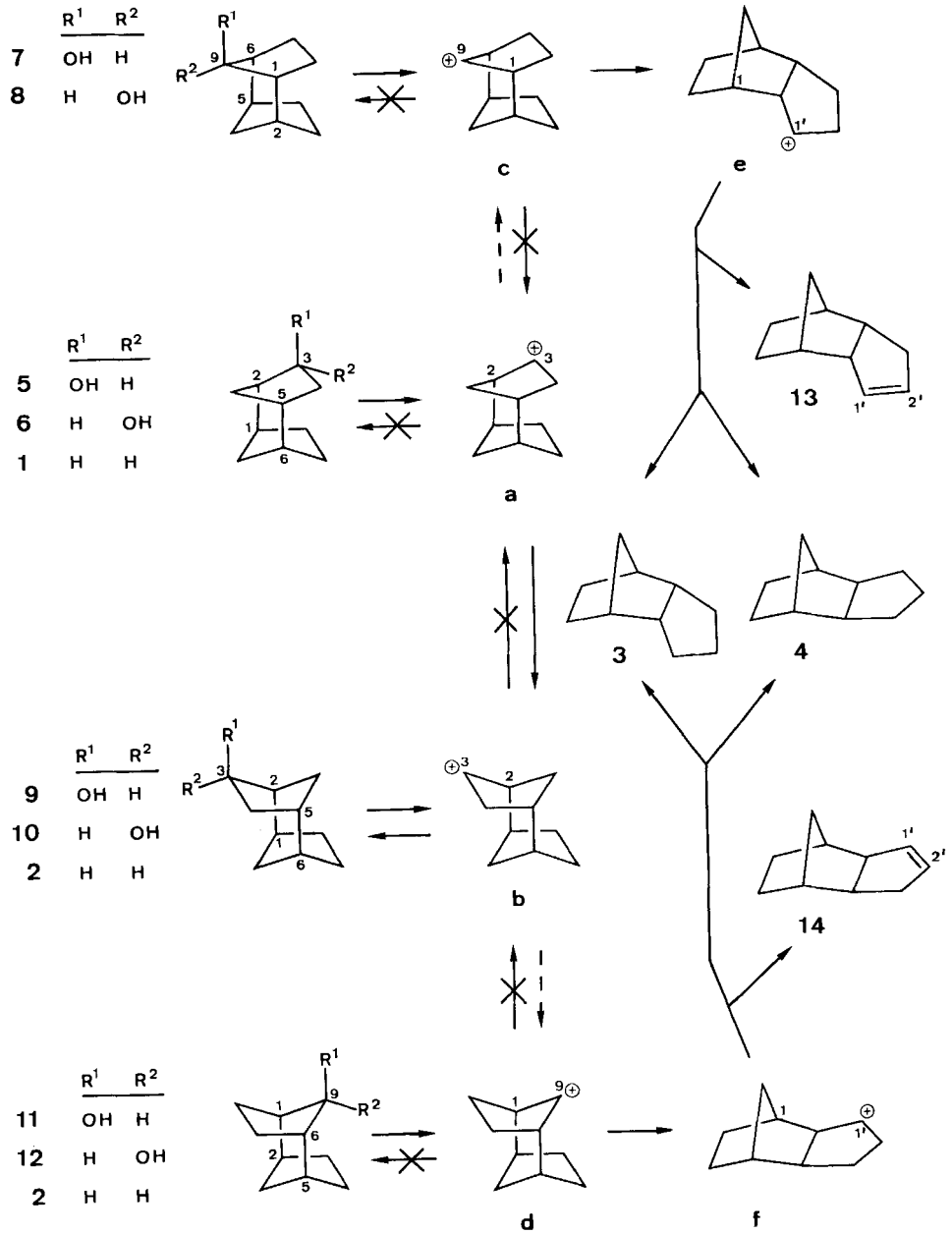


Table. *Treatment of the Alcohols* **5–12** *with* BF_3/Et_3SiH

Run	Reactant	Reaction time [min]	Composition [%][a]					
			Reactant	**2**	**3**	**13**	**4**	**14**
1	**5**	5–10	5–10	80–85	5			
2	**6**	5–10	30–35	55–60				
3	**6**	60	10	85	< 5			
4	**7**	5–10			50–55	10	30–35	
5	**8**	5–10			20–25	5	40–45	[b]
6	**9**	5–10		95	5			
7	**10**	5–10	85–90	5				
8	**10**	60	70	15	< 5			
9	**11**	5–10			40–45		40	15–20[c]
10	**12**	5–10			35–40		35–40	20–25

[a] Average of ≥ 3 experiments. Combined yield of products: ≥ 90%; the compositions were determined by cap. GLC *(SE 52)*; compounds in < 5% are not listed.

[b] In addition, 15–25% of **15**[8].

[c] In addition, 5% of unidentified products.

The following features were observed and the following conclusions could be drawn: *a*) of a given pair of diastereoisomers, especially in the case of the 3-alcohols, the '*exo*'-alcohol is remarkably more reactive than the sterically more hindered '*endo*'-alcohol (**5** > **6**, **9** > **10**). However, this difference in reactivity has no influence on the ratio of the products formed.

b) Carbocations of C(9) at the CH_2 bridges (**c** and **d**) are generated more rapidly (total conversion of the reactants is achieved already after 5–10 min, *Runs 4,5,9*, and *10*) than those of C(3) of the CH_2CH_2 bridges (**a** and **b**, *Runs 1–3* and *6–8*).

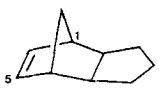
c) All four 3-alcohols (**5** and **6** (*'syn'*), **9** and **10** (*'anti'*)) yield almost exclusively the *'anti'*-hydrocarbon **2** (*Runs 1–3* and *6–8*)[6]. For **5** and **6**, this result can best be interpreted in terms of the intermediacy of the *'syn'*-carbocation **a** which rearranges to the '*anti*'-carbocation **b**; these species undergo a 1,3-H shift to **c** and **d**, respectively, only to very minor extents (≤ 5% of **3**; dotted arrows in *Scheme 1*). This result is consistent with the isomerization of **1** into **2** on treatment with $AlBr_3$ [1].

d) A completely different reaction course is followed starting from the 9-alcohols **7** and **8** (*'syn'*; *Runs 4* and *5*) as well as **11** and **12** (*'anti'; Runs 9* and *10*). No trace of *'anti'*-hydrocarbon **2** could be detected, it suggests that none of the possible 1,3-H shifts **c** → **a** and **d** → **b** is operative. In each case, a mixture of 2-*endo*,3-*endo*- (**3**) and 2-*exo*,3-*exo*-trimethylene-8,9,10-trinorbornane (**4**) is obtained[7]). In addition, depending on the C-skeleton of the reactants (*'syn'* or *'anti'*), the 1',2'-olefin **13** (2-*endo*,3-*endo*; *Runs 4* and

[6] In very small amounts (≤ 5%), 2-*endo*,3-*endo*-trimethylene-8,9,10-trinorbornane (**3**) is formed as the only further product.

[7] This result is in sharp contrast to the $AlBr_3$-catalyzed adamantane rearrangement of the *'anti'*-hydrocarbon **2**, where only **4** (calc. $\Delta H_f^\circ = -16.77$ kcal/mol [6]), thermodynamically more stable than the isomers **3** (calc. $\Delta H_f^\circ = -12.31$ kcal/mol [6]; −14.36 kcal/mol [7]; exper. $\Delta H_f^\circ = -14.38$ kcal/mol [8]), is obtained.

[8] Further experiments have to be carried out to rationalize the appearance of 15–20% of 2-*exo*,3-*exo*-trimethylene-8,9,10-trinorborn-5-ene (**15**).



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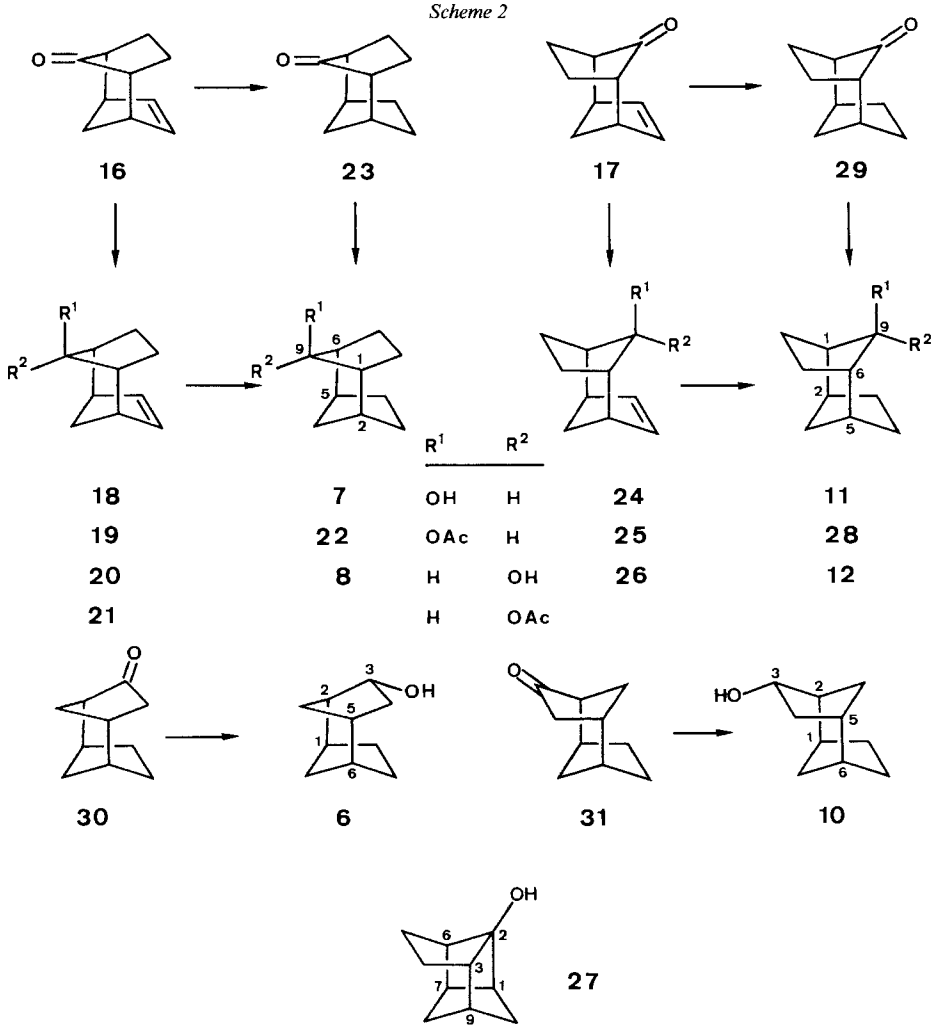
5) or **14** (2-*exo*,3-*exo*; *Runs 9* and *10*) is a by-product. They probably result from proton elimination at C(2') in the intermediate 1'-carbocations **e** and **f**, resp., which themselves originate from the 9-carbocations **c** (*'syn'*) and **d** (*'anti'*), resp., by a 1,2-alkyl shift from C(1) to C(9). Independent of the alcoholic precursor (**7, 8, 11,** and **12**), both isomeric hydrocarbons **3** and **4**, are the main products. They are formed in nearly equal ratio (*Runs 4* and *5*[8]), *9* and *10*) in all experiments. This indicates that their formation proceeds through common intermediates. Further studies, mainly with D-labelled reactants and Et_3SiD as trapping reagent are planned, hoping to gain more information about the involved reaction pathways.

Reactants and Products. – *Syntheses and Structure Assignments.* The following reactants and products have already been described earlier: **1** [9–12], **2** [9–11] [13], **3**

Scheme 2



[14–17][9]), **4** [13–17][9]), **5** [10] [11][10]), **8** [9][9]), **9** [10] [11] [13][10]), **12** [9][10]), **13** [14–17][11]), **14** [14–17][12]), **15** [14–17][13]).

The novel alcohols **6**, **7**, **10**, and **11** were synthesized according to *Scheme 2*. A separable mixture of the unsaturated ketones **16** and **17** can be prepared according to *Schmid* [25].

Cycloaddition of the allylic cation generated from 5-chloro-1-morpholinocyclopentene to cyclopentadiene followed by base-catalyzed hydrolysis of the intermediate immonium salts yielded **16/17** in the ratio of 88:12. Recently, *Zimmerman* and *Linder* [26] described a new approach to the *anti*-isomer **17**: Triethylamine-catalyzed condensation of 2-chlorocyclopentanone with cyclopentadiene in MeOH, apparently, gave **17** in 15% yield as the sole product. However, carefully applying *Zimmerman*'s procedure, we obtained again a mixture **16/17** in the same ratio[14]) as *Schmid* [25].

Starting from the *'syn'*-ketone **16**, the 9-*'exo'*-alcohol **7** was prepared by two different routes. Reduction with Na in toluene yielded 70.5% of the unsaturated *'exo'*-alcohol **18**[15]) and 17.5% of the *'endo'*-alcohol **20**[15]). The former was transformed to the desired compound **7**[15]) by catalytic hydrogenation. Na-Reduction of the saturated ketone **23** [9] gave only 44.5% of **7**; in addition, 50.5% of the *'endo'*-alcohol **8** were isolated. The latter can easily be obtained as sole product from **16** *via* **20.**

Analogous was the preparation of the *'anti'*-9-*exo*-alcohol **11**[15]). Treatment of the unsaturated ketone **17** with Na in toluene led to 54% of the *'exo'*-alcohol **24**[15]), 9% of the corresponding *'endo'*-isomer **26** [27] [28], and 26% of the tetracyclic alcohol **27**. Subsequent catalytic hydrogenation of **24** yielded **11**. Reduction of the saturated ketone **29** [9] [13] [26] with Na gave 77% of **11** and 4% of the *'endo'*-isomer **12.**

The *'syn'*-3-*'endo'*-alcohol **6** was prepared by $LiAlH_4$ reduction of the corresponding ketone **30** [10] [11] and the *'anti'*-3-*'endo'*-alcohol **10** from ketone **31** [10] [11] [13].

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Experimental Part

General. See [28] [29].

Procedures for the Ionic Hydrogenations of the Alcohols **5–12** *with* BF_3/Et_3SiH. a) *Preparative Scale.* A soln. of 100 mg (0.66 mmol) of reactant in 20 ml of CH_2Cl_2 (filtered through basic Al_2O_3) was treated with 150 µl (0.94 mmol) of Et_3SiH. Under Ar and vigorous stirring gas BF_3 was bubbled through the soln. (two-necked round bottom flask, fitted with a strong balloon and a septum) for 10 s. The reactions were quenched by adding 1 ml of sat. Na_2CO_3 soln. The mixture was stirred for 5 min, the org. layer sucked off with a syringe, dried ($MgSO_4$) and filtered. By careful bulb-to-bulb distillation the solvent was removed and the products distilled. The percentage of the compositions were determined by cap. GLC (*Carlo Erba Fractovap 4160* or *GI* using a 20 m or 50 m × 0.32 mm *SE 52* glass capillary column). Separation and isolation of the products was performed by prep. GLC (5% *SE 30* on *Chromosorb W* (80/100 mesh) AW-DMCS).

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[9]) See also *e.g.* [18].

[10]) See also *Exper. Part.*

[11]) See also *e.g.* [19–21] and *Exper. Part.*

[12]) See also *e.g.* [19] [22] [23] and *Exper. Part.*

[13]) See also *e.g.* [24].

[14]) The isolated yields were 3.5% of **16** and 23.5% of **17.**

[15]) The alcohols **7**, **11**, **18**, **20**, and **24** were also characterized as their corresponding acetates **22**, **28**, **19**, **21**, and **25.**

b) *Analytical Scale.* In analogy to the above procedure, with *ca.* 1–5 mg of reactant and the addition of adamantane or decane as internal standard.

syn-*Tricyclo[4.2.1.1^{2,5}]decan-3*-exo-*ol* (**5**). IR: 3620*m*, 3480*w* (br.), 3035*w*, 2980*m*, 2935*s*, 2890*m*, 1479*w*, 1466*w*, 1453*w*, 1318*w*, 1287*w*, 1236*w*, 1214*w*, 1058*m*, 1054*w* (sh), 1021*m*, 988*m*, 956*w*, 941*w*, 938*w*, 899*w*, 882*w*. ^{1}H-NMR: 0.54 (*dtm*, J_{gem} = 11.5, *J*(1,9-*exo*) = *J*(6,9-*exo*) = 2.5, $w_{½}$ ≈ 2, H_{exo}–C(9)); 1.03 (*ddt*, J_{gem} = 14, *J*(4-*exo*,5) = 6, *J*(3-*endo*,4-*exo*) = *J*(2,4-*exo*) = 2, *J* ≈ 0.5, H_{exo}–C(4)); 1.04 (*dt*, J_{gem} = 11.5, *J*(2,10-*exo*) = *J*(5,10-*exo*) = 3, H_{exo}–C(10)); 1.15–1.35 (*m*, H_{exo}–C(7), H_{exo}–C(8)); 1.26 (*m*, $w_{½}$ ≈ 5, *exo*-HO–C(3)); 1.6–1.75 (*m*, H_{endo}–C(7), H_{endo}–C(8)); 1.79 (*ddt*, J_{gem} = 11.5, *J*(4-*endo*, 10-*endo*) = 3, *J*(2,10-*endo*) = *J*(5,10-*endo*) = 1.5, H_{endo}–C(10)); 1.91 (*dm*, J_{gem} = 11.5, $w_{½}$ ≈ 6, H_{endo}–C(9)); 2.07 (*dm*, *J*(1,2) = 10, $w_{½}$ ≈ 6, among others *J*(2,10-*exo*) = 3, *J*(2,4-*exo*) = 2, *J*(2,3-*endo*) < 0.5, H–C(2)); 2.2–2.35 (*m*, H–C(1), H–C(5), H–C(6)); 2.3–2.4 (*m*, H_{endo}–C(4)); 4.44 (*dddd*, *J*(3-*endo*, 4-*endo*) = 6.5, *J*(3-*endo*, 4-*exo*) = 2, *J*(3-*endo*, 10-*endo*) = 1.5, *J*(2,3-*endo*) < 0.5, H_{endo}–C(3)). ^{13}C-NMR: 25.87, 26.65, 26.88, 30.34 (4*t*, C(7), C(8), C(9), C(10)); 34.45 (*t*, C(4)); 34.36, 36.17, 37.14 (3*d*, C(1), C(5), C(6)); 42.09 (*d*, C(2)); 76.41 (*d*, C(3)). MS: 152 (3, M^+, $C_{10}H_{16}O$), 134 (47), 121 (14), 119 (20), 109 (13), 108 (27), 107 (11), 106 (24), 105 (23), 95 (17), 93 (51), 92 (31), 91 (31), 83 (17), 81 (19), 80 (65), 79 (100), 78 (23), 77 (22), 70 (19), 68 (12), 67 (67), 66 (64), 65 (11), 57 (16), 55 (25), 54 (23), 53 (18), 41 (48), 39 (33), 29 (13), 27 (20).

syn-*Tricyclo[4.2.1.1^{2,5}]decan-3*-endo-*ol* (**6**). A soln. of 25 mg (0.17 mmol) of **30** in 10 ml of abs. Et_2O was treated under Ar with a small amount of $LiAlH_4$ for 2 h at r.t. Workup with sat. $(NH_4)_2SO_4$ soln., filtration through *Celite*, removal of the solvent and CC on 3 g of silica gel in pentane/Et_2O 3:1 yielded 17.5 mg (69%) of **6**. IR: 3630*m*, 3020*w*, 2980*w*, 2935*s*, 2885*m*, 1481*w*, 1462*w*, 1454*w* (sh), 1440*w*, 1348*w*, 1314*w*, 1298*w*, 1278*m*, 1204*w*, 1162*m*, 1118*s*, 1053*m*, 1038*m*, 997*w*, 925*w*. ^{1}H-NMR: 0.57 (*dt*, J_{gem} = 12, *J*(2,10-*exo*) = *J*(5,10-*exo*) = 2.5, H_{exo}–C(10)); 0.57 (*dt*, J_{gem} = 11, *J*(1,9-*exo*) = *J*(6,9-*exo*) = 2.5, H_{exo}–C(9)); 1.2–1.5 (*m*, H_{exo}–C(7), H_{exo}–C(8)); 1.53 (*ddd*, J_{gem} = 13.5, *J*(3-*exo*,4-*endo*) = 5, *J*(4-*endo*,5) = 3.5, H_{endo}–C(4)); 1.60 (*ddt*, J_{gem} = 12, *J*(4-*endo*,10-*endo*) = 3.5, *J*(2,10-*endo*) = *J*(5,10-*endo*) = 1.75, H_{endo}–C(10)); 1.65–1.8 (*m*, among others *J*(7-*endo*,8-*endo*) = 8, H_{endo}–C(7)); 1.69 (*m*, $w_{½}$ ≈ 4, *endo*-HO–C(3)); 1.75 (*dm*, J_{gem} = 11, $w_{½}$ ≈ 7 each, among others *J*(8-*endo*,9-*endo*) = 3, H_{endo}–C(9)); 1.88 (*ddd*, J_{gem} = 14, *J*(3-*exo*, 4-*exo*) = 10, *J*(4-*exo*, 5) = 7, H_{exo}–C(4)); 2.2–2.3 (*m*, among others *J*(1,2) ≈ 8, *J*(5,6) ≈ 8, *J*(4-*endo*, 5) = 3.5, *J*(2, 10-*endo*) = *J*(10-*endo*, 5) = 1.75, H–C(2), H–C(5)); 2.35–2.45 (*m*, among others *J*(1,2) ≈ 8, *J*(5,6) ≈ 8, H–C(1), H–C(6)); 2.66 (*dddd*, J_{gem} = 13, *J*(7-*endo*,8-*endo*) = 8, *J*(7-*exo*,8-*endo*) = 4.5, *J*(8-*endo*,9-*endo*) = 3, H_{endo}–C(8)); 4.18 (*dt*, *J*(3-*exo*,4-*exo*) = 10, *J*(3-*exo*,4-*endo*) = 5, *J*(2,3-*exo*) = 5, H_{exo}–C(3)). ^{13}C-NMR: 25.83, 26.56, 26.78, 30.28 (4 *t*, C(7), C(8), C(9), C(10)); 34.33 (*d*, C(6)); 34.39 (*t*, C(4)); 36.09, 37.07 (2 *d*, C(1), C(5)); 41.99 (*d*, C(2)); 76.28 (*d*, C(3)). MS: 152 (3, M^+, $C_{10}H_{16}O$), 134 (52), 121 (14), 119 (26), 109 (14), 108 (28), 107 (11), 106 (27), 105 (33), 95 (16), 93 (56), 92 (40), 91 (41), 83 (15), 81 (20), 80 (65), 79 (100), 78 (25), 77 (25), 70 (18), 69 (10), 68 (11), 67 (73), 66 (85), 65 (12), 57 (16), 55 (41), 54 (21), 53 (16), 43 (11), 41 (48), 39 (31), 29 (16), 28 (22), 27 (19).

syn-*Tricyclo[4.2.1.1^{2,5}]decan-9*-exo-*ol* (**7**). a) *From* **18**. Hydrogenation (H_2, 5% Pd/C) of 86 mg (0.57 mmol) of **18** in Et_2O and CC on 10 g of silica gel in pentane/Et_2O 2:1 gave 81 mg (93%) of **7**. M.p. 170–171°. IR: 3615*m*, 3400*w* (br.), 3000*w*, 2975*w*, 2935*s*, 1502*w*, 1483*w*, 1471*w*, 1451*w*, 1397*w* (br.), 1312*w*, 1226*w*, 1137*w*, 1077*s*, 1045*m*, 1017*w*, 982*m*, 955*w*, 914*w* (br.), 882*w*, (br.), 843*w*, 676*w*. ^{1}H-NMR: 0.52 (*dt*, J_{gem} = 11.5, *J*(2,10-*exo*) = *J*(5,10-*exo*) = 2.5, H_{exo}–C(10)); 0.99 (*m*, $w_{½}$ ≈ 5, *exo*-HO–C(9)); 1.15–1.25 (*m*, H_{exo}–C(3), H_{exo}–C(4)); 1.45–1.65 (*m*, H_{exo}–C(7), H_{exo}–C(8)); 1.7–1.8 (*m*, H_{endo}–C(7), H_{endo}–C(8)); 1.75–1.9 (*m*, H_{endo}–C(3), H_{endo}–C(4)); 1.95 (*dm*, J_{gem} = 11.5, $w_{½}$ ≈ 6 each, H_{endo}–C(10)); 2.08 (*m*, $w_{½}$ ≈ 18, among others *J*(1,2) = *J*(5,6) = 9.5, *J*(1,9-*endo*) = *J*(6,9-*endo*) = 2.5, H–C(1), H–C(6)); 2.35 (*m*, $w_{½}$ ≈ 18, among others *J*(1,2) = *J*(5,6) = 9.5, *J*(2,10-*exo*) = *J*(5,10-*exo*) = 2.5, H–C(2), H–(5)); 4.52 (*m*, $w_{½}$ ≈ 5, among others *J*(1,9-*endo*) = *J*(6,9-*endo*) = 2.5, H_{endo}–C(9)). ^{13}C-NMR: 21.94 (*t*, C(3), C(4)); 26.05 (*t*, C(7), C(8)); 28.22 (*t*, C(10)); 36.27 (*d*, C(2), C(5)); 41.16 (*d*, C(1), C(6)); 73.25 (*d*, C(9)). MS: 152 (21, M^+, $C_{10}H_{16}O$), 134 (11), 124 (11), 123 (57), 121 (26), 119 (23), 110 (19), 109 (100), 108 (13), 106 (17), 105 (19), 96 (11), 95 (34), 93 (58), 92 (32), 91 (36), 83 (16), 81 (36), 80 (31), 79 (61), 78 (14), 77 (21), 70 (18), 68 (10), 67 (52), 66 (18), 65 (11), 57 (20), 55 (25), 54 (11), 53 (15), 41 (40), 39 (29), 29 (12), 27 (18).

b) *From* **23**. A soln. of 171.5 mg (1.14 mmol) of **23** in 10 ml of i-PrOH was added under Ar dropwise and under vigorous stirring to a mixture of 500 mg (2.15 mmol) of Na (added as small pieces) and 20 ml of abs. toluene. After 4 h at reflux, workup (Et_2O, 2 × sat. $(NH_4)_2SO_4$, 2 × sat. NaCl soln.) and CC on 25 g of silica gel in pentane/CH_2Cl_2/Et_2O 3:2:1, 2.5 mg of reactant **23**, 76 mg (44%) of **7** and 87 mg (50%) of **8** (see below) were obtained.

syn-*Tricyclo[4.2.1.1^{2,5}]decan-9*-endo-*ol* (**8**). a) *From* **20**. Hydrogenation (H_2, 10% Pd/C) of 29 mg (0.19 mmol) of **20** in 20 ml of Et_2O for 3 h and CC on 5 g silica gel in pentane/Et_2O 3:1 led to 25.5 mg (87%) of **8**. IR: 3630*m*, 3000*w*, 2990*w* (sh), 2930*s*, 2880*m*, 1494*w*, 1475*m*, 1425*w*, 1315*w* (br.), 1268*w* (br.), 1215*w*, 1188*m*, 1148*m*, 1076*w*, 1023*w*, 848*w*, 716*w*, 650*w*. ^{1}H-NMR: 0.63 (*dt*, J_{gem} = 11, *J*(2,10-*exo*) = *J*(5,10-*exo*) = 3, H_{exo}–C(10));

1.2–1.3 (*m*, H_{exo}–C(7), H_{exo}–C(8)); 1.25–1.4 (*m*, H_{exo}–C(3), H_{exo}–C(4)); 1.5–1.6 (*m*, H_{endo}–C(7), H_{endo}–C(8)); 1.6–1.7 (*m*, H_{endo}–C(3), H_{endo}–C(4)); 1.77 (*m*, $w_{1/2} \approx 4$, *endo*-HO–C(9)); 2.15 (*m*, $w_{1/2} \approx 18$, among others $J(1,2) = J(5,6) = 9$, $J(1,9\text{-}exo) = J(6,9\text{-}exo) = 3$, H–C(1), H–C(6)); 2.37 (*m*, $w_{1/2} \approx 18$, among others $J(1,2) = J(5,6) = 9$, $J(2,10\text{-}exo) = J(5,10\text{-}exo) = 3$, H–C(2), H–C(5)); 2.86 (*dm*, $J_{gem} = 11$, $w_{1/2} \approx 6$ each, H_{endo}–C(10)); 3.63 (*t*, $J(1,9\text{-}exo) = J(6,9\text{-}exo) = 3$, H_{exo}–C(9)). ^{13}C-NMR: 23.08 (*t*, C(3), C(4)); 26.83 (*t*, C(7), C(8)); 30.12 (*t*, C(10)); 35.73 (*d*, C(2), C(5)); 40.25 (*d*, C(1), C(6)); 75.49 (*d*, C(9)). MS: 152 (6.3, M^+, $C_{10}H_{16}O$), 123 (15), 109 (27), 93 (17), 91 (12), 81 (10), 79 (17), 67 (18), 41 (11), 32 (26), 28 (100).

b) *From* **23**. A soln. of 21 mg (0.14 mmol) of **23** in 2 ml of Et_2O was treated under Ar with 20 mg (0.5 mmol) of $LiAlH_4$. Stirring (2 h) at r.t. and workup (sat. $(NH_4)_2SO_4$ soln., filtration through *Celite*) gave 20.5 mg (96%) of **8**. M.p. 199–204°.

anti-*Tricyclo[4.2.1.1^{2,5}]decan-3*-exo-*ol* (**9**). IR: 3620*m*, 3400*w* (br.), 2995*m*, 2950*m*, 2925*s*, 2870*m*, 1487*w*, 1476*m*, 1457*m*, 1438*w*, 1327*w*, 1307*w*, 1291*w*, 1276*w*, 1272*w*, 1237*w*, 1205*w*, 1160*w*, 1116*w*, 1079*m*, 1049*m*, 1013*s*, 998*m*, 952*w*, 910*w*, 903*w*, 896*w*, 841*w*. ^{1}H-NMR: 0.90 (*dm*, $J_{gem} = 11.5$, $w_{1/2} \approx 8$ each, H_{exo}–C(9)); 1.31 (*dm*, $J_{gem} = 11.5$; $w_{1/2} \approx 10$ each, H_{exo}–C(10)); 1.37 (*ddd*, $J_{gem} = 13.5$, $J(4\text{-}exo,5) = 5.5$, $J(3\text{-}endo,4\text{-}exo) = 2$, H_{exo}–C(4)); 1.4–1.75 (*m*, 2 H–C(7), 2 H–C(8), H_{endo}–C(9)); 1.81 (*dm*, $J_{gem} = 11.5$, $w_{1/2} \approx 7$ each, H_{endo}–C(10)); 1.83, 1.94, 2.04, 2.11 (4 *m*, $w_{1/2} \approx 8$, $w_{1/2} \approx 13$, $w_{1/2} \approx 13$, $w_{1/2} \approx 12$, H–C(1), H–C(2), H–C(5), H–C(6)); 2.20 (*ddd*, $J_{gem} = 13.5$, $J(3\text{-}endo,4\text{-}endo) = 6.5$, $J(4\text{-}endo,10\text{-}endo) = 3$, H_{endo}–C(4)); 4.26 (*ddd*, $J(3\text{-}endo,4\text{-}endo) = 6.5$, $J(3\text{-}endo,4\text{-}exo) = 2$, $J(3\text{-}endo,10\text{-}endo) = 1.5$, H_{endo}–C(3)). MS: 152 (12, M^+, $C_{10}H_{16}O$), 134 (53), 123 (11), 119 (13), 108 (37), 107 (10), 106 (14), 105 (16), 95 (10), 93 (30), 92 (18), 91 (20), 81 (23), 80 (100), 79 (66), 78 (15), 77 (16), 67 (40), 57 (10), 55 (35), 54 (13), 53 (10), 41 (30), 39 (20), 29 (11), 27 (12).

anti-*Tricyclo[4.2.1.1^{2,5}]decan-3*-endo-*ol* (**10**). A soln. of 78 mg (0.5 mmol) of **31** in 15 ml of Et_2O was treated with a small amount of $LiAlH_4$. Stirring for 1½ h at r.t., workup (sat. $(NH_4)_2SO_4$ soln., filtration through *Celite*) and twice CC on 5 g of silica gel, once in pentane/Et_2O 3:1 and once in pentane/Et_2O 10:1 yielded 55.5 mg (70%) of **10**. IR ($CDCl_3$): 3610*m*, 2995*w*, 2945*m*, 2925*s*, 1475*w*, 1455*w*, 1377*w*, 1345*w*, 1293*w*, 1240*w*, 1180*w*, 1154*w*, 1045*m*, 1029*m*, 982*m*. ^{1}H-NMR: 1.02 (*dm*, $J_{gem} = 11.5$, $w_{1/2} \approx 9$, H_{exo}–C(10)); 1.06 (*dm*, $J_{gem} = 11.5$, $w_{1/2} \approx 9$, H_{exo}–C(9)); 1.60 (*dt*, $J_{gem} = 13$, $J(3\text{-}exo,4\text{-}endo) = J(4\text{-}endo,10\text{-}endo) = 4$, H_{endo}–C(4)); 1.55–1.8 (*m*, 2 H–C(7), 2 H–C(8)); 1.77 (*m*, $w_{1/2} \approx 4$, *endo*–HO–C(3)); 1.89 (*dd*, $J_{gem} = 11.5$, $J(4\text{-}endo,10\text{-}endo) = 4$, H_{endo}–C(10)); 1.9–2.1 (*m*, H–C(1) or H–C(6), H–C(2), H_{exo}–C(4), H–C(5)); 2.15 (*m*, $w_{1/2} \approx 12$, H–C(1) or H–C(6)); 2.49 (*dm*, $J_{gem} = 11.5$, $w_{1/2} \approx 5$ each, H_{endo}–C(9)); 4.46 (*ddd*, $J(3\text{-}exo,4\text{-}exo) = 10$, $J(2,3\text{-}exo) = 5$, $J(3\text{-}exo,4\text{-}endo) = 4$, H_{exo}–C(3)). ^{13}C-NMR: 29.48, 30.25, 31.85 (3 *t*, C(7), C(8), C(10)); 34.32 (*t*, C(9)); 35.80 (*d*, C(6)); 38.00 (*t*, C(4)); 38.66, 39.32 (2 *d*, C(1), C(5)); 44.37 (*d*, C(2)); 76.64 (*d*, C(3)).

anti-*Tricyclo[4.2.1.1^{2,5}]decan-9*-exo-*ol* (**11**). a) *From* **24**. Hydrogenation (H_2, 5% Pd/C) of 102 mg (0.68 mmol) of **24** in 10 ml of Et_2O and CC on 10 g of silica gel in pentane/Et_2O 3:1 gave 96 mg (93%) of **11**. M.p. 175–177° (sublimation). IR: 3625*m*, 3460*w*, 2995*w* (sh), 2945*s* (sh), 2930*s*, 2875*m*, 1485*w*, 1467*m*, 1451*w*, 1336*w*, 1314*w*, 1292*w*, 1278*w*, 1189*w*, 1162*w*, 1133*w* (br.), 1061*s*, 1049*m*, 992*w*, 971*s*, 933*w*, 871*w*, 858*w*, 709*w*. ^{1}H-NMR: 0.82 (*dtm*, $J_{gem} = 11.5$, $w_{1/2} \approx 2$ each, H_{exo}–C(10)); 1.17 (*m*, $w_{1/2} \approx 4$, *exo*–HO–C(9)); 1.4–1.65 (*m*, 2 H–C(3), 2 H–C(4), H_{endo}–C(7), H_{endo}–C(8)); 1.65–1.75 (*m*, H_{exo}–C(7), H_{exo}–C(8)); 1.82 (*dm*, $J_{gem} = 11.5$, $w_{1/2} \approx 6$, H_{endo}–C(10)); 1.9–2.1 (*m*, H–C(1), H–C(2), H–C(5), H–C(6)); 4.18 (*m*, $w_{1/2} \approx 4$, H_{endo}–C(9)). ^{13}C-NMR: 25.95 (*t*, C(3), C(4)); 28.76 (*t*, C(7), C(8)); 30.31 (*t*, C(10)); 39.21 (*d*, C(2), C(5)); 45.68 (*d*, C(1), C(6)); 75.02 (*d*, C(9)). MS: 152 (100, M^+, $C_{10}H_{16}O$), 134 (25), 124 (15), 123 (54), 121 (41), 119 (28), 110 (21), 109 (69), 108 (20), 106 (27), 105 (25), 96 (24), 95 (47), 94 (15), 93 (71), 92 (55), 91 (42), 84 (11), 83 (27), 82 (11), 81 (39), 80 (58), 79 (76), 78 (23), 77 (25), 70 (32), 69 (14), 68 (19), 67 (79), 66 (35), 65 (14), 57 (38), 56 (10), 55 (39), 54 (20), 53 (24), 51 (10), 43 (14), 41 (63), 39 (40), 29 (19), 28 (10), 27 (25).

b) *From* **29**. A soln. of 201 mg (1.34 mmol) of **29** in 10 ml of i-PrOH was added under Ar dropwise and under vigorous stirring to a mixture of 400 mg (17 mmol) of Na (added in small pieces) and 20 ml of abs. toluene. After 4 h at reflux, workup (Et_2O, 2 × sat. $(NH_4)_2SO_4$, 2 × sat. NaCl soln.) and CC on 20 g of silica gel in pentane/Et_2O 4:1, 44.5 mg **29**, 122.5 mg (60% or 77% with respect to converted **29**) of **11** and 6 mg (3% or 4% with respect to converted **29**) of **12** were obtained.

anti-*Tricyclo[4.2.1.1^{2,5}]decan-9*-endo-*ol* (**12**). M.p. 201–203° (after sublimation at 63°/0.02 Torr). IR: 3620*m*, 3480*w* (br.), 1482*w*, 1460*m*, 1375*w*, 1345*m*, 1320*w*, 1277*m*, 1176*m*, 1168*m*, 1147*w*, 1115*w*, 1083*m*, 1072*w*. ^{1}H-NMR: 1.04 (*dm*, $J_{gem} = 11.5$, $w_{1/2} \approx 8$ each, H_{exo}–C(10)); 1.45–1.65 (*m*, H_{exo}–C(3), H_{exo}–C(4), 2 H–C(7), 2 H–C(8)); 1.75 (*m*, $w_{1/2} \approx 3$, *endo*–HO–C(9)); 1.84 (*m*, $w_{1/2} \approx 12$, H–C(1), H–C(6)); 2.05 (*m*, $w_{1/2} \approx 12$, H–C(2), H–C(5)); 2.14 (*dm*, $J_{gem} = 11.5$, $w_{1/2} \approx 6$ each, H_{endo}–C(10)); 2.3–2.4 (*m*, H_{endo}–C(3), H_{endo}–C(4)); 3.88 (*m*, $w_{1/2} \approx 9$, H_{exo}–C(9)). MS: 152 (73, M^+, $C_{10}H_{16}O$), 134 (20), 124 (12), 123 (47), 121 (32), 119 (30), 110 (18), 109 (67), 108 (18), 106 (32), 105 (26), 96 (16), 95 (34), 94 (12), 93 (72), 92 (55), 91 (52), 83 (23), 81 (37), 80 (55), 79 (77), 78 (27), 77 (24), 70 (22), 68 (18), 67 (100), 66 (48), 65 (13), 57 (33), 55 (33), 54 (15), 53 (19), 41 (54), 39 (33), 29 (17), 27 (20).

2-endo,3-endo-Trimethylene-8,9,10-trinorborn-1'-ene (**13**). To a stirred suspension of 600 mg (3.1 mmol) of potassium azodicarboxylate (PADA) in 3 ml of CH_3OH, 196 mg (1.5 mmol) of *endo*-dicyclopentadiene was added under Ar. After 30 min at r.t., 500 µl (8.75 mmol) of AcOH were added over 15 min. After further 15 min of stirring, the mixture was worked up (pentane, 1 × 2N HCl, 1 × sat. $NaHCO_3$, 1 × sat. NaCl soln.). Cap. GLC *(SE 52)* showed reactant/**13**/**3** in the ratio of 3:88:5. Prep. GLC (10% NPGS) yielded 125 mg (64%) of **13**. IR: 3040*m*, 2930*s*, 2890*w*, 2860*m*, 2840*m*, 1606*w*, 1465*m*, 1450*m*, 1443*s*, 1351*m*, 1321*m*, 1311*m*, 1290*m*, 1271*m*, 1258*w*, 1241*w*, 1209*w*, 1182*w*, 1155*w*, 1145*m*, 1071*w*, 1035*w*, 941*s*, 916*w*, 891*w*, 877*w*, 679*s*, 666*s*. ^{1}H-NMR: 1.15–1.3 (*m*, 2 H–C(5), 2 H–C(6)); 1.40 (*dt*, $J_{gem} = 9$, $J(1,7^{C(5)}) = J(4,\ 7^{C(5)}) = 1$, $H^{C(5)}$–C(7)); 1.47 (*dtt*, $J_{gem} = 9$, $J(1,7^{C(2)}) = J(4,7^{C(2)}) = 2$, J(5-*endo*,$7^{C(2)}$) = J(6-*endo*,$7^{C(2)}$) ≈ 2, $H^{C(2)}$–C(7)); 2.12 (*m*, $w_{½} \approx 10$, H–C(4)); 2.15–2.3 (*m*, 2 H–C(3')); 2.27 (*m*, $w_{½} \approx 11$, H–C(1)); 2.53 (*ddt*, J(2-*exo*,3-*exo*) = 10.5, J(3-*exo*,3'*exo*) = 8.5, J(3-*exo*,4) = J(3-*exo*,3'-*endo*) = 4.5, H_{exo}–C(3)); 3.00 (*m*, $w_{½} \approx 20$, among others J(2-*exo*,3-*exo*) = 10.5, J(1,2-*exo*) = 5, J(2-*exo*,1') = J(2-*exo*,2') = 2, H_{exo}–C(2)); 5.55 and 5.65 (2 *dq*, $J(1',2') = 5.5$, J(2-*exo*,1') = J(1',3'-*endo*) = J(1',3'-*exo*) = 2, and J(2-*exo*,2') = J(2',3'-*endo*) = J(2',3'-*exo*) = 2, H–C(1') und H–C(2')). ^{13}C-NMR: 21.98 (*t*, C(5)); 25.23 (*t*, C(6)); 32.26 (*t*, C(3')); 39.53 (*d*, C(1)); 40.95 (*d*, C(4)); 41.15 (*t*, C(7)); 42.40 (*d*, C(3)); 52.94 (*d*, C(2)); 130.36 (*d*, C(2')); 132.96 (*d*, C(1')).

2-exo,3-exo-Trimethylene-8,9,10-trinorborn-1'-ene (**14**). Hydrogenation (H_2, 10% Pd/C) of 20 mg (0.15 mmol) of *exo*-dicyclopentadiene in 5 ml of pentane for 30 min gave a mixture of **14** and **4** (ratio 87:13, determined by cap. GLC (*SE 52*)) in almost quant. yield[16]). IR ($CDCl_3$): 3040*m*, 2940*s*, 2865*m*, 2835*m*, 1610*w*, 1447*m*, 1438*m*, 1350*m*, 1317*w*, 1299*m*, 1291*w*, 1264*w*, 1190*w*, 1122*w*, 1045*w* (br.), 965*w*, 785*w*. ^{1}H-NMR: 0.95 (*dquint.*, $J_{gem} = 10$, $J(1,7^{C(5)}) = J$(2-*endo*,$7^{C(5)}$) = J(3-*endo*,$7^{C(5)}$) = $J(4,7^{C(5)}) = 1.5$, $H^{C(5)}$–C(7)); 1.1–1.28 (*m*, H_{exo}–C(5), H_{exo}–C(6)); 1.32 (*dquint.*, $J_{gem} = 10$, $J(1,7^{C(2)}) = J(4,7^{C(2)}) = J$(5-*exo*,$7^{C(2)}$) = J(6-*exo*,$7^{C(2)}$) = 2, $H^{C(2)}$–C(7)); 1.37–1.57 (*m*, H_{endo}–C(5), H_{endo}–C(6)); 1.88 (*dm*, $J_{gem} = 15$, $w_{½} \approx 10$ each, H_{exo}–C(3')); 1.92 and 1.98 (2 *m*, $w_{½} \approx 7$ each, H–C(1), H–C(4)); 2.11 (*dddd*, J(2-*endo*,3-*endo*) = 10, J(3-*endo*,3'-*endo*) = 7.5, J(3-*endo*,3'-*exo*) = 3.5, J(3-*endo*,$7^{C(5)}$) = 1.5, H_{endo}–C(3)); 2.56 (*m*, among others J(2-*endo*,3-*endo*) = 10, H_{endo}–C(2)); 2.57 (*ddm*, $J_{gem} = 15$, J(3-*endo*,3'-*endo*) = 7.5, $w_{½} \approx 6$ each, H_{endo}–C(3')); 5.47 (*ddddm*, $J(1',2') = 5.5$, 3 $J = 3$ each, H–C(1') or H–C(2')); 5.65 (*ddddm*, $J(1',2') = 5.5$, 3 $J = 2.5$ each, H–C(1') or H–C(2')). ^{13}C-NMR: 28.84, 29.17, (2 *t*, C(5), C(6)); 31.66 (*t*, C(7)); 39.78 (*t*, C(3')); 40.49 (*d*, C(1)); 43.15 (*d*, C(4)); 43,89 (*d*, C(3)); 55.80 (*d*, C(2)); 131.81, 132.63 (2 *d*, C(1'), C(2')).

syn-*Tricyclo[4.2.1.1^{2,5}]dec-3-en-9-*exo-*ol* (**18**). To a soln. of 108 mg (0.73 mmol) of **16** in 4 ml of abs. toluene under Ar, 300 mg (13 mmol) of Na in small pieces and dropwise 1 ml of i-PrOH were added. After 4 h of reflux, workup (Et_2O, 2 × sat. $(NH_4)_2SO_4$, 2 × sat. NaCl soln.) and CC on 15 g of silica gel in pentane/Et_2O/CH_2Cl_2 3:1:1 gave 8 mg of **16**, 18 mg (16.5%) of **20** (see below) and 71.5 mg (66.5% or 70.5% with respect to converted **16**) of **18**. IR: 3630*m*, 3490*w* (br.), 3060*m*, 3020*m*, 2950*s*, 2875*m*, 1655*w* (br.), 1578*w* (br.), 1497*w*, 1460*w* (br.), 1441*w*, 1348*m*, 1308*w*, 1263*w*, 1236*w*, 1096*m*, 1076*s*, 1047*s*, 1013*m*, 971*m*, 930*m*, 881*w*, 850*m*. ^{1}H-NMR: 0.99 (*dt*, $J_{gem} = 10.5$, J(2,10-*exo*) = J(5,10-*exo*) = 3, H_{exo}–C(10)); 1.22 (*m*, $w_{½} \approx 8$, *exo*–HO–C(9)); 1.3–1.65 (*m*, 2H–C(7), 2 H–C(8)); 1.97 (*dtm*, $J_{gem} = 10.5$, J(2,10-*endo*) = J(5,10-*endo*) = 1.5, J(3,10-*endo*) = J(4,10-*endo*) < 0.5, H_{endo}–C(10)); 2.25 (*m*, $w_{½} \approx 17$, among others $J(1,2) = J(5,6) = 9$, H–C(1), H–C(6)); 2.67 (*dddm*, $J(1,2) = J(5,6) = 9$, J(2,10-*exo*) = J(5,10-*exo*) = 3, J(2,10-*endo*) = J(5,10-*endo*) = 1.5, $J(2,3) = J(4,5) < 0.5$, H–C(2), H–C(5)); 4.69 (*m*, $w_{½} \approx 8$, H_{endo}–C(9)); 6.29 (*m*, $w_{½} \approx 5$, H–C(3), H–C(4)). ^{13}C-NMR: 24.14 (*t*, C(7), C(8)); 33.56 (*t*, C(10)); 40.46, 42.02 (2 *d*, C(1), C(2), C(5), C(6)); 74.58 (*d*, C(9)); 139.71 (*d*, C(3), C(4)). MS: 150 (12, M^+, $C_{10}H_{14}O$), 132 (18), 121 (11), 119 (14), 117 (31), 108 (16), 107 (10), 105 (11), 104 (48), 96 (16), 94 (15), 93 (40), 92 (20), 91 (75), 84 (66), 83 (49), 82 (26), 81 (15), 80 (29), 79 (74), 78 (27), 77 (63), 70 (13), 67 (56), 66 (100), 65 (29), 57 (25), 55 (21), 53 (18), 51 (19), 41 (33), 40 (11), 39 (52), 29 (13), 27 (24).

syn-*Tricyclo[4.2.1.1^{2,5}]dec-3-en-9-*exo-*yl Acetate* (**19**). A soln. of 15 mg (0.09 mmol) of **18** in 2 ml of Ac_2O/pyridine 1:1 was kept for 24 h at r.t. Cooling to 0°, addition of 5 ml of ice/H_2O, stirring for 30 min, workup (Et_2O, 3 × 2N HCl, 2 × 1M $NaHCO_3$, 1 × sat. NaCl soln.) and CC on 3 g of silica gel in pentane/Et_2O 3:1 yielded 18.5 mg (96%) of **19**. IR: 3055*w*, 2950*s*, 2865*w*, 1728*s*, 1457*w*, 1438*w*, 1388*w*, 1363*m*, 1336*w*, 1318*w*, 1309*w*, 1263*m*, 1259*m* (sh), 1237*s*, 1193*w*, 1096*w*, 1058*w*, 1040*m*, 1017*m*, 991*w*, 968*w*, 927*w*, 878*w*, 837*w*. ^{1}H-NMR: 1.08 (*dt*, $J_{gem} = 10.5$, J(2,10-*exo*) = J(5,10-*exo*) = 3, J_{exo}–C(10)); 1.3–1.55 (*m*, 2 H–C(7), 2 H–C(8)); 1.96 (*s*, CH_3COO–C(9)); 2.05 (*dm*, $J_{gem} = 10.5$, $w_{½} \approx 3$ each, H_{endo}–C(10)); 2.40 (*m*, $w_{½} \approx 17$, among others $J(1,2) = J(5,6) = 9$, H–C(1), H–C(6)); 2.72 (*m*, $w_{½} \approx 16$, among others $J(1,2) = J(5,6) = 9$, H–C(2), H–C(5)); 5.60 (*m*, $w_{½} \approx 4$, H_{endo}–C(9)); 6.31 (*m*, $w_{½} \approx 5$, H–C(3), H–C(4)). MS: 192 (2, M^+, $C_{12}H_{16}O_2$), 132 (16), 126 (12), 117 (12), 91 (18), 84 (16), 83 (10), 79 (12), 77 (10), 67 (55), 66 (87), 43 (56), 41 (11), 32 (24), 28 (100).

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[16]) Compound **14** can also be prepared by PADA reduction of *exo*-dicyclopentadiene.

syn-*Tricyclo[4.2.1.1^{2,5}]dec-3-en-9*-endo-*ol* (**20**). A soln. of 52 mg (0.35 mmol) of **16** in 5 ml of Et_2O were treated with 30 mg (0.8 mmol) of $LiAlH_4$ and stirred for 2 h at r.t. Workup (sat. $(NH_4)_2SO_4$ soln. filtration through *Celite*) and CC on 5 g of silica gel in pentane/Et_2O 2:1 gave 46 mg (88%) of **20**. M.p. 131–132° (sublimation). IR: 3630*m*, 3320*m* (br.), 3050*m*, 2930*s*, 2870*m*, 2795*w*, 1652*w*, 1644*w* (sh), 1577*w*, 1460*m*, 1443*m*, 1339*m*, 1318*w*, 1298*w*, 1288*m*, 1256*m*, 1177*s*, 1162*m*, 1121*w*, 1093*m*, 1076*s*, 1056*m*, 1022*w*, 994*w*, 980*w*, 921*w*, 897*w*, 883*w* (sh), 874*m*, 860*w*, 722*w*, 659*m*. ^{1}H-NMR: 1.35–1.55 (*m*, 2 H–C(7), 2 H–C(8), H_{exo}–C(10)); 1.94 (*s*, $w_{1/2} \approx 3$, *endo*–HO–C(9)); 2.24 (*ddt*, $J(1,2) = J(5,6) = 9$, $J(1,9\text{-}exo) = J(6,9\text{-}exo) = 3.5$, $J(1,8\text{-}endo) = J(1,8\text{-}exo) = J(6,7\text{-}endo) = J(6,7\text{-}exo) = 2$, H–C(1), H–C(6)); 2.64 (*dt*, $J(1,2) = J(5,6) = 9$, $J(2,10\text{-}endo) = J(5,10\text{-}endo) = 1.5$, $J(2,3) = J(4,5) = 1.5$, H–C(2), H–C(5)); 3.24 (*dtm*, $J_{gem} = 9.5$, $J(2,10\text{-}endo) = J(5,10\text{-}endo) = 1.5$, $J(3,10\text{-}endo) = J(4,10\text{-}endo) < 0.5$, H_{endo}–C(10)); 4.09 (*t*, $J(1,9\text{-}exo) = J(6,9\text{-}exo) = 3.5$, H_{exo}–C(9)); 6.47 (*tm*, $J(2,3) = J(4,5) = 1.5$, $J(3,10\text{-}endo) = J(4,10\text{-}endo) < 0.5$, H–C(3), H–C(4)). ^{13}C-NMR: 26.22 (*t*, C(7), C(8)); 36.81 (*t*, C(10)); 40.37, 40.47 (2 *d*, C(1), C(2), C(5), C(6)); 79.75 (*d*, C(9)); 143.28 (*d*, C(3), C(4)). MS: 132 (31, M^+, $C_{10}H_{14}O$), 117 (24), 93 (20), 91 (37), 84 (10), 83 (21), 80 (15), 79 (33), 78 (14), 77 (25), 67 (60), 66 (100), 65 (11), 57 (16), 55 (11), 41 (18), 39 (20), 27 (11).

syn-*Tricyclo[4.2.1.1^{2,5}]dec-3-en-9*-endo-*yl Acetate* (**21**). A soln. of 10 mg (0.07 mmol) of **20** in 2 ml of Ac_2O/pyridine 1:1 was kept for 18 h at r.t. workup (ice/H_2O, Et_2O, 3 × 2N HCl, 2 × 1N $NaHCO_3$, 1 × sat. NaCl soln.) and CC on 3 g of silica gel in pentane/Et_2O 3:1 yielded 12 mg (95%) of **21**. IR: 3045*w*, 2955*s*, 2910*m*, 2875*w*, 1737*s*, 1476*m*, 1463*m*, 1446*w*, 1422*w* (br.), 1367*s*, 1340*m*, 1332*w*, 1292*m*, 1273*w*, 1255*w* (sh), 1241*s*, 1197*m*, 1171*s*, 1159*s*, 1124*w*, 1096*m*, 1066*s*, 1046*s*, 927*m*, 898*w*, 885*w*, 875*m*, 860*w*, 684*w*, 652*w*. ^{1}H-NMR: 1.4–1.65 (*m*, 2 H–C(7), 2 H–C(8), H_{exo}–C(10)); 2.09 (*s*, *endo*–CH_3COO–C(9)); 2.45 (*m*, $w_{1/2} \approx 17$, H–C(1), H–C(6)); 2.62 (*m*, $w_{1/2} \approx 16$, H–C(2), H–C(5)); 2.76 (*dm*, $J_{gem} = 10$, $w_{1/2} \approx 3$ each, H_{endo}–C(10)); 4.73 (*t*, $J(1,9\text{-}exo) = J(6,9\text{-}exo) = 3$, H_{exo}–C(9)); 6.45 (*m*, $w_{1/2} \approx 5$, H–C(3), H–C(4)). ^{13}C-NMR: 21.78 (*q*, *endo*–CH_3COO–C(9)); 25.59 (*t*, C(7), C(8)); 37.20 (*t*, C(10)); 38.28, 40.09 (2 *d*, C(1), C(2), C(5), C(6)); 79.98 (*d*, C(9)); 142.83 (*d*, C(3), C(4)); 170.66 (*s*, *endo*–CH_3COO–C(9)). MS: 192 (0.4, M^+, $C_{12}H_{16}O_2$), 132 (21), 131 (10), 117 (20), 104 (11), 91 (21), 86 (51), 84 (79), 79 (11), 78 (20), 77 (10), 67 (31), 66 (48), 49 (12), 47 (17), 43 (31), 39 (10), 32 (23), 28 (100).

syn-*Tricyclo[4.2.1.1^{2,5}]dec-9*-exo-*yl Acetate* (**22**). a) *From* **7**. A soln. of 30 mg (0.2 mmol) of **7** in 5 ml of Ac_2O/pyridine 1:1 and a catalytical amount of 4-(*N*,*N*-dimethylamino)pyridine was kept for 18 h at r.t. Workup (ice/H_2O, Et_2O, 3 × 2N HCl, 2 × 1N $NaHCO_3$, 1 × sat. NaCl soln.) and twice CC on 3 g of silica gel in pentane/Et_2O 19:1 gave 27.5 mg (72%) of **22**. IR: 3030*w*, 2995*m*, 2930*s*, 2920*s*, 2880*w*, 2865*w*, 1752*w*, 1724*s*, 1496*w*, 1480*m*, 1467*w*, 1448*m*, 1386*w*, 1359*s*, 1318*w*, 1308*m*, 1294*w*, 1238*s*, 1192*w*, 1140*w*, 1107*w*, 1056*m*, 1031*s*, 1017*m*, 951*w*, 929*m*, 904*w*, 879*w*. ^{1}H-NMR: 0.59 (*dt*, $J_{gem} = 12$, $J(2,10\text{-}exo) = J(5,10\text{-}exo) = 3$, H_{exo}–C(10)); 1.15–1.3 (*m*, H_{exo}–C(3), H_{exo}–C(4)); 1.4–1.5 (*m*, H_{exo}–C(7), H_{exo}–C(8)); 1.7–1.8 (*m*, H_{endo}–C(7), H_{endo}–C(8)); 1.75–1.85 (*m*, H_{endo}–C(3), H_{endo}–C(4)); 1.97 (*s*, *exo*–CH_3COO–C(9)); 2.02 (*dm*, $J_{gem} = 12$, $w_{1/2} \approx 6$ each, H_{endo}–C(10)); 2.24 (*m*, $w_{1/2} \approx 18$, among others $J(1,2) = J(5,6) = 9.5$, $J(1,9\text{-}endo) = J(6,9\text{-}endo) \approx 2.5$, H–C(1), H–C(6)); 2.41 (*m*, $w_{1/2} \approx 18$, among others $J(1,2) = J(5,6) = 9.5$, $J(2,10\text{-}exo) = J(5,10\text{-}exo) = 3$, H–C(2), H–C(5)); 5.37 (*m*, $w_{1/2} \approx 5$, among others $J(1,9\text{-}endo) = J(6,9\text{-}endo) \approx 2.5$, H_{endo}–C(9)). ^{13}C-NMR: 21.44 (*q*, CH_3COO–C(9)); 22.48 (*t*, C(3), C(4)); 25.85 (*t*, C(7), C(8)); 28.47 (*t*, C(10)); 36.27 (*d*, C(2), C(5)); 38.86 (*d*, C(1), C(6)); 77.67 (*d*, C(9)); 171.16 (*s*, CH_3COO–C(9)).

b) *From* **19**. Hydrogenation (H_2, 10% Pd/C) of 11.5 mg (0.06 mmol) of **19** in Et_2O for 2 h at r.t. yielded 9.5 mg (82%) **22**.

anti-*Tricyclo[4.2.1.1^{2,5}]dec-3-en-9*-exo-*ol* (**24**). To a suspension of 100 mg (4.3 mmol) of Na (added in small pieces) in 8 ml of abs. toluene, a soln. of 103 mg (0.7 mmol) of **17** in 4 ml of i-PrOH was added dropwise under Ar. After 4 h at reflux, workup (Et_2O, 2 × sat. $(NH_4)_2SO_4$, 2 × sat. NaCl soln.) and CC on 10 g of silica gel in pentane/Et_2O/CH_2Cl_2 6:2:1 afforded 11 mg of **17**, 6,5 mg (6.5%) of **26**, 45 mg (43% or 48% with respect to converted **17**) of **24** and 18.5 mg (17.5%) of **27** (see below) as well as 8 mg (13%) of a 1:1 mixture of **24**/**27**. **24**: m.p. 149–150°. IR: 3615*m*, 3480*w* (br.), 3050*w*, 3000*m*, 2935*s*, 2890*w*, 2875*m*, 1478*w*, 1449*w*, 1332*m*, 1319*w*, 1284*w*, 1259*w*, 1226*m*, 1188*w*, 1094*m*, 1057*s*, 1041*s*, 991*m*, 962*m*, 959*m* (sh.), 913*w*, 900*w*, 887*w*, 850*m*, 709*s*. ^{1}H-NMR: 1.07 (*m*, $w_{1/2} \approx 6$, *exo*–HO–C(9)); 1.15 (*dtm*, $J_{gem} = 10.5$, $J(2,10\text{-}exo) = J(5,10\text{-}exo) = 3.5$, $w_{1/2} \approx 2$, H_{exo}–C(10)); 1.45–1.55 (*m*, H_{endo}–C(7), H_{endo}–C(8)); 1.69 (*dm*, $J_{gem} = 10.5$, $w_{1/2} \approx 3$ each, H_{endo}–C(10)); 1.75–1.9 (*m*, H_{exo}–C(7), H_{exo}–C(8)); 2.49 (*m*, $w_{1/2} \approx 11$, H–C(1), H–C(2), H–C(5), H–C(6)); 3.84 (*m*, $w_{1/2} \approx 6$, H_{endo}–C(9)); 5.82 (*m*, $w_{1/2} \approx 4$, H–C(3), H–C(4)). ^{13}C-NMR: 26.72 (*t*, C(10)); 38.05 (*t*, C(7), C(8)); 38.18 (*d*, C(1), C(6)); 43.78 (*d*, C(2), C(5)); 77.29 (*d*, C(9)); 131.83 (*d*, C(3), C(4)). MS: 150 (5, M^+, $C_{10}H_{14}O$), 95 (11), 93 (18), 91 (22), 84 (100), 83 (65), 82 (13), 80 (11), 79 (24), 77 (21), 67 (30), 66 (35), 57 (11), 55 (11), 41 (15), 39 (18), 27 (10).

anti-*Tricyclo[4.2.1.1^{2,5}]dec-3-en-9*-exo-*yl Acetate* (**25**). A soln. of 19 mg (0.12 mmol) of **24** in 4 ml of Ac_2O/pyridine 1:1 and a catalytical amount of 4-(*N*,*N*-dimethylamino)pyridine was kept for 5 h at r.t. Workup (ice/H_2O, Et_2O, 3 × 2N HCl, 2 × 1N $NaHCO_3$, 1 × sat. NaCl soln.) and CC on 2 g of silica gel in pentane/Et_2O 6:1

gave 19.5 mg (83%) of **25**. IR: 3050*w*, 3000*m*, 2950*s*, 2895*w*, 2880*m*, 1727*s*, 1479*w*, 1451*m*, 1430*w*, 1376*m*, 1362*s*, 1336*m*, 1322*m*, 1314*w*, 1301*w*, 1249*s*, 1219*s*, 1184*w*, 1098*m*, 1049*w*, 1031*s*, 1006*m*, 992*m*, 967*m*, 917*w*, 899*w*, 891*w*, 846*w*, 715*m*, 705*w*, 659*w*. ^{1}H-NMR: 1.19 (*dtm*, J_{gem} = 10.5, J(2,10-*exo*) = J(5,10-*exo*) = 3.5, $w_{½} \approx 2$ each, H_{exo}–C(10)); 1.5–1.6 (*m*, H_{endo}–C(7), H_{endo}–C(8)); 1.65–1.85 (*m*, H_{exo}–C(7), H_{exo}–C(8)); 1.96 (*s*, *exo*–CH_3COO–C(9)); 1.99 (*m*, $w_{½} \approx 13$, H–C(1), H–C(6)); 2.52 (*m*, $w_{½} \approx 12$, H–C(2), H–C(5)); 4.80 (*m*, $w_{½} \approx 5$, H_{endo}–C(9)); 5.92 (*m*, $w_{½} \approx 4$, H–C(3), H–C(4)). ^{13}C-NMR: 21.46 (*q*, *exo*–CH_3COO–C(9)); 27.03 (*t*, C(10)); 35.96 (*d*, C(1), C(6)); 40.48 (*t*, C(7), C(8)); 43.56 (*d*, C(2), C(5)); 81.21 (*d*, C(9)); 132.03 (*d*, C(3), C(4)); 170.62 (*s*, *exo*–CH_3COO–C(9)). MS: 192 (10, M^+, $C_{12}H_{16}O_2$), 132 (56), 131 (11), 126 (16), 117 (21), 104 (17), 93 (13), 91 (27), 84 (36), 83 (22), 79 (17), 77 (15), 67 (100), 66 (95), 65 (10), 43 (81), 41 (16), 39 (16).

Tetracyclo[5.3.0^{2,6}.0^{3,9}]decan-2-ol (**27**). IR: 3605*m*, 3300*m* (br.), 2940*s*, 2855*m*, 1469*m*, 1452*m*, 1441*w*, 1333*s*, 1313*m*, 1270*s*, 1265*m*, 1254*m*, 1237*w*, 1183*w*, 1168*m*, 1150*m*, 1099*s*, 1072*s*, 1031*m*, 986*m*, 956*w*, 938*m*, 921*m*, 913*w*, 871*w*, 856*w*, 622*w*. ^{1}H-NMR: 1.08 (*ddt*, J_{gem} = 12, J(7,8-*exo*) = 6.5, J(3 or 6,8-*exo*) = J(8-*exo*,9) = 2, H_{exo}–C(8)); 1.27 (*dm*, J_{gem} = 10.5, $w_{½} \approx 4$ each, among others J(9,10-*exo*) = 1.5, J(1,10-*exo*) = 1, H_{exo}–C(10)); 1.54 (*dm*, J_{gem} = 12, $w_{½} \approx 4$ each, among others J(8-*endo*,10-*endo*) = 1, J(8-*endo*,9) ≈ 1, H_{endo}–C(8)); 1.5–1.65 (*m*, H_{endo}–C(4), H_{endo}–C(5)); 1.67 (*m*, $w_{½} \approx 2$, HO–C(2)); 1.7–2.05 (*m*, H_{exo}–C(4), H_{exo}–C(5)); 1.79 (*dm*, J_{gem} = 10.5, $w_{½} \approx 4$ each, among others J(1,10-*endo*) = J(8-*endo*,10-*endo*) = 1, J(9,10-*endo*) = 0.5, H_{endo}–C(10)); 2.1–2.25 (*m*, H–C(3) or H–C(6), H–C(9)); 2.54 (*ddm*, J = 8, J = 6, $w_{½} \approx 3$ each, H–C(3), or H–C(6)); 2.61 (*dm*, J(1,7) = 6, $w_{½} \approx 3$ each, among others J(1,10-*endo*) = J(1,10-*exo*) = 1, H–C(1)). ^{13}C-NMR: 27.18, 27.51, 27.62, 38.95 (4 *t*, C(4), C(5), C(8), C(10)); 28.86, 43.02, 46.74, 50.75, 55.55 (5 *d*, C(1), C(3), C(6), C(7), C(9)); 77.23 (*s*, C(2)). MS: 150 (4, M^+, $C_{10}H_{14}O$), 95 (32), 84 (99), 83 (100), 82 (23), 79 (12), 67 (26), 66 (11), 55 (16), 39 (12).

anti-*Tricyclo[4.2.1.1^{2,5}]dec-9*-exo-*yl Acetate* (**28**). a) *From* **11**. A soln. of 100 mg (0.66 mmol) of **11** in 10 ml of Ac_2O/pyridine and a catalytical amount of 4-(*N*,*N*-dimethylamino)pyridine was kept for 18 h at r.t. Workup (ice/H_2O, Et_2O, 3 × 2N HCl, 2 × 1N $NaHCO_3$, 1 × sat. NaCl soln.) and CC on 30 g of silica gel in pentane/Et_2O 19:1 yielded 120.5 mg (94.5%) of **28**. IR: 2995*w*, 2940*s* (br.), 2880*m*, 1739*m* (sh), 1724*s*, 1487*w*, 1468*w*, 1449*w*, 1393*w*, 1363*m*, 1336*w*, 1314*w*, 1299*w*, 1281*w*, 1243*s*, 1212*w*, 1192*m*, 1166*w*, 1056*w*, 1033*m*, 1011*w*, 992*w*, 969*w*, 908*w*, 871*w*. ^{1}H-NMR: 0.86 (*dtm*, J_{gem} = 11.5, J(2,10-*exo*) = J(5,10-*exo*) = 3.5, $w_{½} \approx 2$, H_{exo}–C(10)); 1.45–1.8 (*m*, 2 H–C(3), 2 H–C(4), 2 H–C(7), 2 H–C(8)); 1.84 (*dm*, J_{gem} = 11.5, $w_{½} \approx 6$, H_{endo}–C(10)); 1.98 (*s*, *exo*–CH_3COO–C(9)); 2.0–2.15 (*m*, H–C(1), H–C(2), H–C(5), H–C(6)); 5.13 (*m*, $w_{½} \approx 4$, H_{endo}–C(9)). ^{13}C-NMR: 21.49 (*q*, *exo*–CH_3COO–C(9)); 26.52 (*t*, C(3), C(4)); 28.60 (*t*, C(7), C(8)); 30.80 (*t*, C(10)); 39.37 (*d*, C(2), C(5)); 43.41 (*d*, C(1), C(6)); 79.23 (*d*, C(9)); 170.72 (*s*, *exo*–CH_3COO–C(9)). MS: 194 (1, M^+, $C_{12}H_{18}O_2$), 152 (23), 134 (46), 119 (10), 106 (19), 95 (10), 93 (51), 92 (18), 91 (17), 81 (10), 80 (12), 79 (17), 67 (32), 66 (18), 43 (100), 41 (17), 28 (11).

b) *From* **25**. Hydrogenation (H_2, 5% Pd/C) of 10 mg (0.05 mmol) of **25** in Et_2O for 2 h gave after workup and CC on 3 g silica gel in pentane/Et_2O 19:1 9.5 mg (96%) of **28**.

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