136. The Novel Adamantane Isomer Tricyclo[4.4.0.0^{3,9}]decane (2-Homotwistbrendane)

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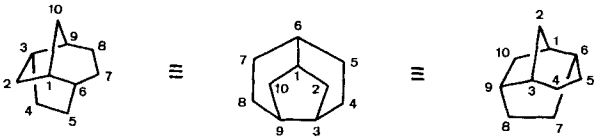
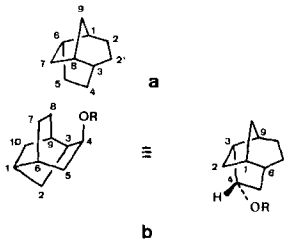
Two synthetic approaches to the novel $C_{10}H_{16}$ hydrocarbon tricyclo[4.4.0.0^{3,9}]decane (**1**; 2-homotwistbrendane), one of the 19 members of the adamantaneland, and its *Lewis*-acid-catalyzed rearrangement are described. One route starts from tricyclo[4.3.0.0^{3,8}]nonan-2-one (**2**; 2-twistbrendanone). The missing tenth C-atom is introduced by ring enlargement (*Tiffeneau-Demjanov* method). Starting from methyl 8,9,10-trinorborn-5-ene-2-*endo*-carboxylate (**8**), ring enlargement by one C-atom, regio- and stereoselective introduction of a C_1 unit to a 2-*endo*,6-*endo*-disubstituted bicyclo[3.2.1]octane, and ring closure by acyloin condensation are the key steps in the second approach.

Tricyclo[4.4.0.0^{3,9}]decane (**1**)[1]) of C_s symmetry belongs to the set of 19 isomeric tricyclic $C_{10}H_{16}$ compounds, known as 'adamantaneland' [1]. In the present communication, we describe two independent syntheses of the hitherto unknown hydrocarbon **1**[2]) and its *Lewis*-acid-catalyzed isomerization.



1

1. Synthesis of 1. – Inspection of the structure of the target hydrocabon **1** reveals the presence of a 2-*endo*-, 6-*endo*-disubstituted bicyclo[3.2.1]octane. The synthesis of **1** can be envisaged in the following two manners: Either starting from an already built-up tricyclic precursor and subsequently modifying its carbon skeleton or using a readily available bicyclic compound as starting material and performing the required additional ring closure. Both routes were successfully applied.



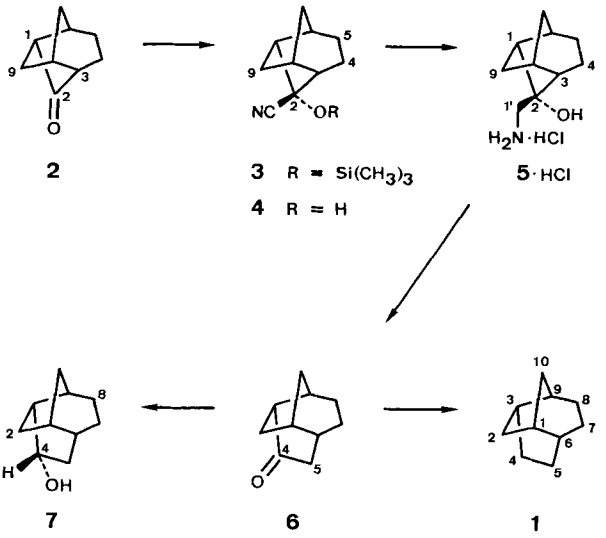
a **b**

[1]) Compound **1** is also called 2-homotwistbrendane (**a**).

[2]) In 1972 *Spurlock* and *Clark* [2], in a study on the 2-proto-adamantyl cation, assigned to one of the solvolysis products structure **b**, mainly 'for considerations of all rational 1,2-carbon and 1,3-hydride shifts'. However, repeating some to the solvolyses as described by the authors led to no compounds with tricyclo[4.4.0.0^{3,9}]decane skeleton.

1.1. *From Tricyclo[4.3.0.0^{3,8}]nonan-2-one* (**2**; *Scheme 1*). The obvious transformation to be carried out starting from tricyclo[4.3.0.0^{3,8}]nonan-2-one (**2**)[3]) [3] was the introduction of the missing tenth C-atom by ring enlargement. Treatment of **2** with trimethylsilyl cyanide and ZnI_2 as a catalyst stereoselectively yielded 87% of the siloxynitrile **3**[4]). Its hydrogenation in CH_3OH (saturated with HCl) in the presence of 10% Pd/C for 14 h quantitatively led to the amine hydrochloride **5**·HCl[5]). The reduction in an acidic medium exemplifies a method for the preparation of amino alcohols and their hydrochlorides superior to the well-established $LiAlH_4$ reduction [4], which in the case of **3** resulted only in poor yields of **5**.

Scheme 1



Ring enlargement, the key step in the synthesis of **1**, was accomplished applying the method of *Tiffeneau-Demjanov* [5]. From model studies one would expect that in the thermal [1,2]-sigmatropic rearrangement (suprafacial,suprafacial), migration of the C(2),C(3) bond to C(1′) should proceed with preference over a migration of the C(1),C(2) bond to C(1′), the latter requiring strong distortion of the molecule. Treatment of **5**·HCl with $NaNO_2$ in aq. AcOH, indeed, regioselectively provided a single C_{10} ketone[6]) to which we assigned the constitution **6** on the basis of the above argumentation. By optimizing the reaction conditions, a yield of 85% was achieved[7]). $LiAlH_4$ reduction of **6** exclusively gave the alcohol **7** with the OH group orientated towards C(7) (97%). Finally, ketone **6** was

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[3]) Compound **2** is also called 2-twistbrendanone (**c**) [3].

[4]) According to analytical GLC (*A*, 130°; see *Exper. Part*), only one stereoisomer was formed. The configuration at C(2) was assigned on the basis of the usual preference of an *exo*-attack in a bicyclo[2.2.1]heptane (= 8,9,10-trinorbornane), which corresponds to an attack of a nucleophile on the carbonyl group in **2** from the C(9) side.

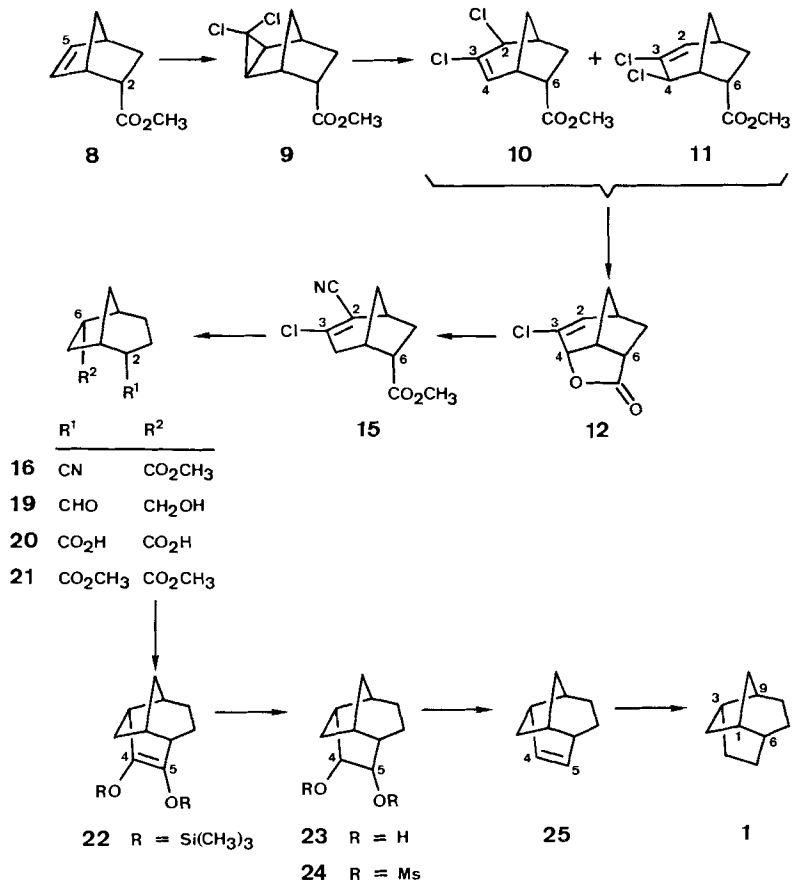
c

[5]) Shorter reaction times gave mixtures of the free cyanohydrin **4** and **5**·HCl.

[6]) No constitutional isomer could be detected by analytical GLC (A, 130°) (see *Exper. Part*).

[7]) a) 1¾ h at 0°, 2 h at 60°, 1¼ h at 66°: 85%; b) 1 h at 0°, 2 h at 60°, ¾ h at 65°: 66%; c) 4 h at 60°: 36%.

Scheme 2



converted to hydrocarbon **1** by *Wolff-Kishner* reduction (73%). The overall yield of the four step synthesis **2**→**3**→**5**·HCl→**6**→**1**, hence, was 54%. In accordance with the C_s symmetry of **1**, its ^{13}C-NMR spectrum shows only 6 signals (see *Exper. Part*).

1.2. *From Methyl 8,9,10-Trinorborn-5-ene-2-*endo*-carboxylate* (**8**) *(Scheme 2)*. Using the easily accessible *Diels-Alder* adduct **8** as starting material, conversion to **1** required ring enlargement by one C-atom followed by regio- and stereoselective introduction of a further C_1 unit to a properly functionalized 2-*endo*,6-*endo*-disubstituted bicyclo[3.2.1]octane as a prerequisite for a ring closure to the tricyclo[4.4.0.0^{3,9}]decane carbon skeleton.

Treatment of **8** in hexane at −10 to 0° with dichlorocarbene (generated from $CCl_3CO_2C_2H_5$/$NaOCH_3$) and subsequent refluxing of the crude dichlorocyclopropane **9** in acetone led to a 1.5:1 mixture of the ring-enlarged allylic chlorides **10** and **11** (quantitative yield with respect to converted **8**)[8]). It was reacted with 8% aq. KOH at room

[8]) It should be noted that reaction of **8** with the carbene equivalent phenyl(bromodichloromethyl)mercury (*Seyferth* reagent [6]) in benzene directly led to a 5.5:1 mixture **10**/**11**, however, only in 24% yield. Mainly dicarbene adducts (45%) were isolated.

temperature to give 76% of the desired lactone **12**[9])[10]). The latter served as substrate for the introduction of the missing C_1 unit. This was accomplished by regioselective nucleophilic attack of a cyanide anion (NaCN in hexamethylphosphoric triamide (HMPA) at 100°) at C(2) by way of an allylic substitution of the O-function at C(4)[11]) and re-isomerization of the intermediate C=C bond C(3),C(4) to C(2),C(3). Esterification of the crude product with diazomethane provided the α,β-unsaturated nitrile **15** (*ca.* 50%). Subsequent hydrogenation in CH_3OH and pyrrolidine as a base in the presence of $Pd/CaCO_3$ as a catalyst quantitatively gave the saturated cyano ester **16**[12]), a bicyclo[3.2.1]octane with both functional groups at C(2) and C(6) showing *endo*-configuration. Treatment of **16** with 3 equiv. of diisobutylaluminum hydride (DIBAH) at −78° followed by acidification (→**19**), *Jones* oxidation (→**20**) and esterification with diazomethane yielded 67% of the diester **21**.

The final ring closure to a tricyclo[4.4.0.0^{3,9}]decane was achieved by a modified acyloin condensation [11] yielding the disilylated acyloin **22** (45%). As a consequence of its low stability, it was instantly reduced first by H_2 in the presence of 10% Pd/C [12] and subsequently by $LiAlH_4$ in Et_2O to a mixture of diastereoisomeric alcohols **23** (67%; 31% for **21**→**23**), which was transformed to a corresponding mixture of methanesulfonates **24** (yield 100%). Elimination with anthrylsodium [13] gave the olefin **25** (44%). Its hydrogenation accomplished the second approach to hydrocarbon **1**.

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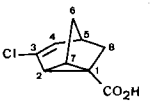
[9]) At room temperature, up to 23% of the tricyclic cyclopropanecarboxylic acid **13** were obtained as by-product. The latter became even the main product (**12**/**13** *ca.* 1:2) using a K_2CO_3 solution in CH_3OH/H_2O at r.t., whereas treatment of the mixture **10**/**11** with 8% aq. KOH under reflux afforded the acid **14** with inverted configuration at C(6) in high yield (82%).



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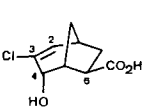
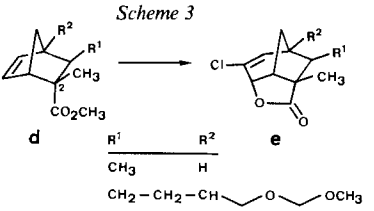


14

[10]) Analogous to our sequence **8**→**10**/**11**→**12** is the conversion of esters **d** to lactones **e** as described by *Schomburg* and *Landry* [7]. However, due to the CH_3 group at C(2), their results are slightly different from ours, especially because no compounds of the types **13** and **14** can be formed.

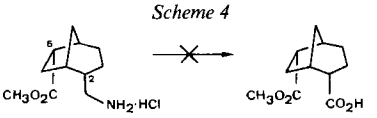
Scheme 3



[11]) The conversion **12**→**15** represents a vinylogous analogue to known substitutions by cyanide anions in normal esters giving acids (see *e.g.* [8]) as well as in saturated lactones leading to ω-cyano acids (see *e.g.* [9]).

[12]) In the absence of pyrrolidine using Pd catalysts on supports such as $BaSO_4$, charcoal, or *Chromosorb*, the amine hydrochloride **17**·HCl was obtained as main product. Efforts to convert the latter with Br_2 in a phosphate-buffered solution of pH 6 [10] to the acid **18** were unsuccessful.

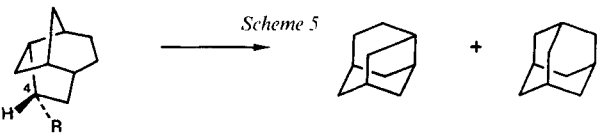
Scheme 4



17·HCl **18**

2. Adamantane Rearrangement of 1. – Tricyclo[4.4.0.$0^{3,9}$]decane (**1**) was treated with $AlBr_3$ in CS_2 at −75°. After 24 min (70% conversion), protoadamantane (**26**) and adamantane (**27**) (ratio 1:6) were the sole new products; this is in agreement with the proposed rearrangement pathway of **1** [1b].

Scheme 5



1 R = H **26** **27**

7 R = OH

Complementary to the *Lewis*-acid-catalyzed isomerization of **1** was the behaviour of the alcohol **7** on treatment with BF_3/Et_3SiH[13]). From the regioselectively generated carbenium ion at C(4), the rearranged hydrocarbons **26** and **27** were obtained in a 1:4 ratio.

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Experimental Part

General. Normal workup: The reaction mixture was taken up in the mentioned org. solvent, and the org. layer was washed with the mentioned aq. soln., dried over $MgSO_4$, filtered, and the solvent evaporated at *ca.* 50 Torr. CC = column chromatography. Capillary GLC: *Carlo Erba Fractovap 4160* using a 25 m × 0.33 mm *UCON 50 HB 5100* glass capillary column *(Method A)* or *Carlo Erba Fractovap Gl* using a 50 m × 0.33 mm *SE-52* glass capillary column *(Method B)*. IR spectra (CCl_4, if not mentioned otherwise): *Perkin-Elmer-297* spectrometer, bands in cm^{-1}. ^{1}H-NMR spectra (300 MHz, $CDCl_3$) and ^{13}C-NMR spectra (75.4 MHz, $CDCl_3$): *Bruker* WM-300; chemical shifts (δ) in ppm relative to TMS as internal standard; J = coupling constant (Hz), $w_{1/2}$ = half-width at half height (Hz). Mass spectra (MS): *Hitachi-Perkin-Elmer-RMU-6M* instrument at 70 eV ionizing electron energy, source temp. 180°, inlet temp. 200°; *m/z* values with relative intensities (% of base peak) of most important ions. A superscript (*e.g.* C(4)) indicates toward which C-atom a substituent is orientated.

Tricyclo[4.4.0.$0^{3,9}$]decane (**1**). *a) From* **6**. A soln. of 50 mg (0.33 mmol) of **6** in 5 ml of diethyleneglycol and 2 ml (41.2 mmol) of 100% $N_2H_4 \cdot H_2O$ was treated with 1.2 g (21.4 mmol) of KOH and stirred at 125° for 45 min. Within 30 min, the soln. was slowly heated up to 215° and kept at this temp. for 1 h. It was combined with the sublimate in the condenser (washed down from time to time), diluted with pentane, and washed once with H_2O. The dried pentane was distilled off at normal pressure through a *Vigreux* column to yield 33 mg (73%) of **1**, m.p. 200°. IR: 1472*m*, 1456*m*, 1344*w*, 1337*w*, 1320*w*, 1295*w*, 1261*w*, 1230*w*, 1179*w*, 1151*w*, 1130*w*, 1100*m*, 1027*w*, 949*w*, 895*w*, 878*w*. ^{1}H-NMR: 1.05–1.3, 1.45–1.65 (2*m*, 4H each, 2H–C(4), 2H–C(5), 2H–C(7), 2H–C(8)); 1.7–1.85 (*m*, 2H–C(2), 2H–C(10)); 2.06 (*m*, $w_{1/2} \approx 20$, H–C(6)); 2.22 (*m*, $w_{1/2} \approx 11$, H–C(3), H–C(9)); 2.32 (*d(quint.)*, $J(1,6) = 9.5$, $J(1,2^{C(10)}) = J(1,2^{C(5)}) = J(1,10^{C(2)}) = J(1,10^{C(7)}) = 2$, H–C(1)). ^{13}C-NMR: 26.73, 26.84 (2*t*, C(4), C(5), C(7), C(8)); 29.83 (*t*, C(2), C(10)); 31.96 (*d*, C(6)); 34.47 (*d*, C(3), C(9)); 35.02 (*d*, C(1)). MS: 136 (72, M^+, $C_{10}H_{16}$), 121 (36), 108 (18), 107 (30), 95 (74), 94 (100), 93 (39), 91 (15), 82 (19), 81 (49), 80 (42), 79 (68), 78 (10), 77 (20), 68 (12), 67 (59), 66 (13), 65 (10), 55 (17), 54 (19), 53 (18), 41 (38).

b) From **25**. Hydrogenation of 2 mg (0.015 mmol) of **25** in 2 ml of pentane with 5% Pd/C yielded (after distilling off the solvent through a *Vigreux* column) 1.1 mg (54%) of **1**.

2$^{C(4)}$-(Trimethylsiloxy)tricyclo[4.3.0.$0^{3,8}$]nonane-2$^{C(9)}$-carbonitrile (**3**). A mixture of 226 mg (1.66 mmol) of **2** [3], 1.2 ml (9.12 mmol) of $(CH_3)_3SiCN$ and 9 mg of dry ZnI_2 (12 h dried at 120°/0.05 Torr) was stirred at 70° for 1¼ h. Removal of excess $(CH_3)_3SiCN$ (r.t./12 Torr) and flash CC with pentane/Et_2O 9:1 yielded 339 mg (87%) of **3**. IR: 2225*w*, 1499*w*, 1473*w*, 1457*w*, 1444*w*, 1334*w*, 1323*w*, 1309*w*, 1281*w*, 1254*s*, 1225*w*, 1212*w*, 1186*m*, 1162*m*,

[13]) On 'ionic hydrogenation', see [14] and ref. cit. therein.

1136*s*, 1117*w*, 1075*w*, 1014*w*, 977*w*, 952*w*, 914*w*, 898*s*, 880*s*, 871*m*, 845*s*, 633*w*, 594*w*. ^{1}H-NMR: 0.27 (*s*, $(CH_3)_3Si$); 1.35–1.5 (*m*, 3H); 1.5–1.8 (*m*, 3H); 2.05 (*ddd*, $J \approx 11$, 10, 9, further $J < 1$, $H^{C(2)}$–C(5)); 2.07, 2.25, 2.45 (3*m*, $w_{1/2} \approx 14$, 12, 11, therein at 2.39 *dd*, $J = 5.5$, 2.5, further $J < 1$, H–C(1), H–C(3), H–C(6), H–C(8)); 2.30 (*ddd*, $J = 11.5$, 2.5, 2, further $J < 1$, $H^{C(2)}$–C(9)). MS: 235 (13, M^+, $C_{13}H_{21}NOSi$), 220 (27), 208 (12), 207 (30), 193 (29), 192 (12), 145 (17), 144 (11), 136 (26), 126 (11), 119 (15), 118 (24), 117 (15), 107 (17), 104 (10), 100 (12), 94 (31), 93 (20), 92 (49), 91 (21), 84 (12), 81 (44), 80 (18), 79 (73), 77 (17), 75 (49), 73 (100), 67 (15), 66 (19), 55 (20), 54 (17), 45 (24), 43 (10), 41 (23).

Hydrochloride of 2$^{C(9)}$-(Aminomethyl)tricyclo[4.3.0.0^{3,8}]nonan-2$^{C(4)}$-ol (**5**·*HCl*). Hydrogenation (14 h at r.t.) of 26 mg (0.11 mmol) of **3**, dissolved in 4 ml of HCl-sat. CH_3OH, with 10% Pd/C gave 22.5 mg (100%) of **5**·HCl, m.p. 222° (dec.). IR (KBr): 3700–2300*s* (br.), 3410*m* (br.), 1586*m*, 1484*s*, 1451*w*, 1380*w*, 1319*w*, 1308*w*, 1285*w*, 1274*w*, 1221*w*, 1211*w*, 1189*m*, 1164*m*, 1142*w*, 1132*w*, 1107*w*, 1072*w*, 1066*w*, 1039*m*, 1008*s*, 976*w*, 961*w*, 929*w*, 912*w*, 888*w*, 860*w*, 836*w*, 815*w*, 487*w*, 464*w*. ^{1}H-NMR (CD_3OD): 1.27 (*dm*, $J = 11$, $w_{1/2} \approx 4$, 1H); 1.35–1.55 (*m*, 2H); 1.55–1.85 (*m*, 4H); *ca.* 1.7, 2.05–2.2, 2.41 (3*m*, 1H, 2H ($w_{1/2} \approx 7$), and 1H ($w_{1/2} \approx 11$), resp., H–C(1), H–C(3), H–C(6), H–C(8)); 2.30 (*ddd*, $J \approx 11$, 10, 9, further $J < 1$, $H^{C(2)}$–C(5)); 2.85, 3.01 (*AB*, $J_{gem} = 13$, 2H–C(1′)). MS: 167 (7, M^+, $C_{10}H_{17}NO$), 150 (6), 149 (7), 137 (52), 136 (13), 122 (14), 119 (19), 109 (14), 95 (22), 93 (20), 91 (29), 86 (26), 81 (16), 80 (21), 79 (43), 78 (10), 77 (15), 68 (12), 67 (33), 66 (11), 59 (12), 58 (48), 55 (28), 53 (11), 43 (11), 41 (29), 38 (13), 36 (19), 32 (20), 31 (15), 30 (100).

Tricyclo[4.4.0.0^{3,9}]decan-4-one (**6**). A soln. of 146 mg (2.11 mmol) of $NaNO_2$ in 2 ml of H_2O was added dropwise to 215 mg (1.06 mmol) of **5**·HCl in 7 ml of H_2O and 270 µl of AcOH. After stirring for 1¾ h at 0°, 2 h at 60°, and 1¼ h at 66°, normal workup and flash CC with pentane/Et_2O 3:1 yielded 135 mg (85%) of **6**, m.p. 218–220°. IR: 1719*s*, 1491*w*, 1470*w*, 1459*w*, 1452*w*, 1414*m*, 1333*m*, 1330*m*, 1315*w*, 1294*w*, 1280*w*, 1255*w*, 1228*w*, 1209*w*, 1198*m*, 1167*w*, 1124*w*, 1094*w*, 1072*m*, 1019*w*, 970*w*, 944*w*, 915*w*, 905*w*, 892*w*, 867*w*, 847*w*, 698*w*. ^{1}H-NMR: 1.15–1.35 (*m*, 2H); 1.51 (*dddt*, $J_{gem} = 11$, $J(2^{C(10)},3) = 6$, further $J = 2.5$, 1.5, $H^{C(10)}$–C(2)); 1.5–1.65 (*m*, 1H); 1.65–1.95 (*m*, 5H); 2.37 (*m* $w_{1/2} \approx 19$, H–C(6)); 2.50 (*ddd*, $J(3,9) = 8$, $J = 6.5$, further $J < 1$, H–C(9)); 2.6–2.75 (*m*, H–C(1), H–C(5)); 2.84 (*ddd*, $J(3,9) = 8$, $J(2^{C(10)},3) = 6$, $J = 2$, H–C(3)). MS: 150 (63, M^+, $C_{10}H_{14}O$), 132 (15), 122 (15), 121 (11), 117 (10), 108 (16), 107 (22), 106 (91), 104 (22), 95 (11), 94 (20), 93 (57), 91 (35), 81 (42), 80 (100), 79 (100), 78 (19), 77 (28), 68 (18), 67 (62), 66 (49), 65 (15), 55 (27), 54 (21), 53 (22), 51 (10), 41 (41).

Tricyclo[4.4.0.0^{3,9}]decan-4$^{C(8)}$-ol (**7**). A soln. of 13 mg (0.087 mmol) of **6** in 3 ml of dry Et_2O, was treated with 10 mg (0.263 mmol) of $LiAlH_4$ and kept 2¼ h at r.t. Workup with sat. $(NH_4)_2SO_4$ soln./*Celite*, filtration, evaporation, and CC with pentane/Et_2O 2:1 yielded 12.5 mg (96%) of **7**, m.p. 226°. IR: 3620*m*, 3400*w* (br.), 1490*w*, 1469*w*, 1450*w*, 1436*w*, 1357*w*, 1315*w*, 1299*w*, 1282*w*, 1214*w*, 1229*m*, 1193*m*, 1103*m*, 1083*s*, 1075*s*, 1041*m*, 1007*s*, 970*m*, 955*w*, 903*w*, 867*w*, 847*w*, 653*w*, 595*w*. ^{1}H-NMR: 1.18 (*dd*, $J = 11$, 3.5, 1H); 1.2–1.4 (*m*, 4H); 1.48 (*ddd*, $J_{gem} = 13.5$, $J = 9.5$, 6, 1H); 1.57 (*dd*, $J = 11$, 3, 1H); 1.58 (*s*, $HO^{C(8)}$–C(4)); 1.76 (*ddddd*, $J_{gem} = 13.5$, $J = 9.5$, 9, 4.5, 2.5, 1H); 2.1–2.35 (*m*, H–C(1), $H^{C(2)}$–C(5), H–C(6), H–C(9)); 2.41 (*ddd*, $J(3,9) \approx 7$, $J(2^{C(10)},3) \approx 6.5$, $J(3,4^{C(2)}) = 5.5$, further $J < 1$, H–C(3)); 2.67 (*ddd*, $J_{gem} \approx 14$, $J = 9.5$, 8, further $J < 1$, $H^{C(4)}$–C(8)); 4.24 (*dd*, $J(4^{C(2)},5^{C(2)}) = 8.5$, $J(3,4^{C(2)}) = 5.5$, $H^{C(2)}$–C(4)). MS: 152 (2, M^+, $C_{10}H_{16}O$), 134 (69), 121 (10), 119 (28), 106 (23), 105 (25), 95 (14), 93 (63), 92 (100), 91 (57), 81 (22), 80 (87), 79 (88), 78 (27), 70 (11), 67 (74), 66 (62), 65 (11), 59 (13), 57 (17), 55 (20), 54 (14), 53 (15), 41 (40).

Carbene Addition to **8**. To a stirred soln. of 250 mg (1.64 mmol) of **8** [16] in 4 ml of dry hexane, 327 mg (6.07 mmol) of $NaOCH_3$ were added at −10° followed by 0.73 ml (5.27 mmol) of $CCl_3CO_2C_2H_5$ at such a rate that the temp. did not rise above 0°. The mixture was stirred below 0° for 2½ h, warmed up to r.t. within 30 min, and stirred at r.t. for further 20 h. After careful addition of H_2O, neutralization with 2N HCl, and normal workup (Et_2O, once sat. NaCl soln.), the crude mixture was poured into acetone and heated under reflux for 9 h. Standing at r.t. for 10 h, evaporation of the solvent, and CC with pentane/Et_2O 5:1 yielded, beside 88 mg (35%) of **8**, 247 mg (64%; 100% with respect to converted **8**) of a 1.5:1 mixture [14] **10**/**11**. *Methyl 2-*exo*,3-Dichlorobicyclo[3.2.1]oct-3-ene-6-*endo*-carboxylate* (**10**). IR: 1741*s*, 1630*w*, 1447*w*, 1434*w*, 1357*w*, 1330*w*, 1302*w*, 1289*w*, 1260*w*, 1197*m*, 1175*m*, 1101*w*, 1069*w*, 1036*w*, 963*w*, 916*w*, 894*w*, 878*w*, 854*w*, 701*w*. ^{1}H-NMR: 1.56 (*dddd*, $J_{gem} = 12$, $J(1,8^{C(6)} = 5.5$, $J(5,8^{C(6)}) = 3.5$, $J(4,8^{C(6)}) = 1.5$, further $J < 1$, $H^{C(6)}$–C(8)); 1.84 (*dddd*, $J_{gem} = 14.5$, $J(6exo,7endo) = 7$, $J(7endo,8^{C(3)}) = 2$ or 1.5, $J(1,7endo) = 1.5$ or 2, H_{endo}–C(7)); 2.16 (*d*, $J_{gem} = 12$, $w_{1/2} \approx 4$ each, $H^{C(3)}$–C(8)); 2.23 (*ddd*, $J_{gem} = 14.5$, $J(6exo,7exo) = 10.5$, $J(1,7exo) = 8$, H_{exo}–C(7)); 2.76 (*m*, $w_{1/2} \approx 15$, H–C(1)); 2.95 (*ddddd*, $J(4,5) = 7$, $J(5,6exo) = 5$, $J(5,8^{C(6)}) = 3.5$, $J(1,5) = 1.5$, $J(5,8^{C(3)}) = 1$, H–C(5)); 3.03 (*ddd*, $J(6exo,7exo) = 10.5$, $J(6exo,7endo) = 7$, $J(5,6exo) = 5$, H_{exo}–C(6)); 3.69 (*s*, CH_3OOC_{endo}–C(6)); 4.26 (*d*, $J(1,2endo) = 2.5$, H_{endo}–C(2)); 6.05 (*dd*, $J(4,5) = 7$, $J(4,8^{C(6)}) = 1.5$, H–C(4)). MS: 234 (2, M^+, $C_{10}H_{12}Cl_2O_2$), 201 (22), 199 (66), 169 (5), 167 (14), 141 (6), 139 (16), 115 (16), 113 (49), 105 (8), 103 (14), 87 (100), 77 (57), 55 (24), 51 (15), 41 (40).

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[14]) Ratio determined by ^{1}H-NMR.

*Methyl 3,4-*exo*-Dichlorobicyclo[3.2.1]oct-2-ene-6-*endo*-carboxylate* (**11**). ^{1}H-NMR: 1.5–1.65 (*m*, $H^{C(6)}$–C(8)); 1.97 (*ddd*, J_{gem} = 13, *J*(6*exo*,7*exo*) = 11, *J*(1,7*exo*) = 6, H_{exo}–C(7)); 2.14 (*ddd*, J_{gem} = 13, *J*(6*exo*,7*endo*) = 4.5, *J*(1,7*endo*) = 2.5, H_{endo}–C(7)); 2.23 (*d*, J_{gem} = 12, $w_{½} \approx 5$ each, $H^{C(3)}$–C(8)); 2.67 (*dddd*, *J*(1,2) = 7, *J*(1,7*exo*) = 6, *J*(1,$8^{C(6)}$) ≈ 3, *J*(1,7*endo*) = 2.5, further *J* < 1, H–C(1)); 3.10 (*m*, $w_{½} \approx 17$, H–C(5)); 3.21 (*ddd*, *J*(6*exo*,7*exo*) = 11, *J*(5,6*exo*) = 7.5, *J*(6*exo*,7*endo*) = 4.5, H_{exo}–C(6)); 3.74 (*s*, CH_3OOC_{endo}–C(6)); 4.30 (*d*, *J*(4*endo*,5) = 2.5, H_{endo}–C(4)); 6.18 (*dd*, *J*(1,2) = 7, *J*(2,$8^{C(6)}$) = 1, H–C(2)).

3-Chlorobicyclo[3.2.1]oct-2-ene-6,4-carbolactone (**12**). An emulsion of 32 mg (0.14 mmol) of the above 1.5:1 mixture **10**/**11** in 3 ml of 8% aq. KOH was stirred at r.t. for 5 h. Acidifying to pH 1 with 25% (*v*/*v*) H_2SO_4, normal workup (Et_2O, once 25% (*v*/*v*) H_2SO_4, once sat. NaCl soln.), and CC with pentane/Et_2O 1:3 gave 19 mg (76%) of **12**, m.p. 86–87°. IR ($CHCl_3$): 1775*s*, 1632*w*, 1459*w*, 1447*m*, 1380*w*, 1355*m*, 1337*m*, 1320*m*, 1291*m*, 1268*w*, 1167*m*, 1120*s*, 1094*w*, 1047*w*, 1032*m*, 1010*w*, 995*s*, 985*m*, 976*s*, 931*m*, 911*m*, 901*w*, 884*w*, 854*w*. ^{1}H-NMR: 1.75 (*dt*, J_{gem} = 12, *J*(1,$8^{C(6)}$) = *J*(5,$8^{C(6)}$) = 4.5, further *J* < 1, $H^{C(6)}$–C(8)); 1.92 (*dd*, J_{gem} = 12, *J*(7*endo*,$8^{C(3)}$) = 2, further *J* < 1, $H^{C(3)}$–C(8)); 1.94 (*ddd*, J_{gem} = 13.5, *J*(6*exo*,7*endo*) = 2.5, *J*(7*endo*,$8^{C(3)}$) = 2, H_{endo}–C(7)); 2.20 (*ddd*, J_{gem} = 13.5, *J*(6*exo*,7*exo*) = 12, *J*(1,7*exo*) = 5.5, H_{exo}–C(7)); 2.77 (*ddd*, *J*(1,2) = 7.5, *J*(1,7*exo*) = 5.5, *J*(1,$8^{C(6)}$) = 4.5, further *J* < 1, H–C(1)); 2.97 (*ddd*, *J*(6*exo*,7*exo*) = 12, *J*(5,6*exo*) = 7.5, *J*(6*exo*,7*endo*) = 2.5, H_{exo}–C(6)); 3.30 (*td*, *J*(4,5) = *J*(5,6*exo*) = 7.5, *J*(5,$8^{C(6)}$) = 4.5, further *J* < 1, H–C(5)); 5.04 (*d*, *J*(4,5) = 7.5, *J* < 1, H–C(4)); 6.46 (*d*, *J*(1,2) = 7.5, further *J* < 1, H–C(2)). MS: 186 (9), 184 (29, M^+, $C_9H_9C1O_2$), 142 (2), 140 (6), 112 (10), 105 (100), 101 (13), 91 (10), 77 (21), 65 (8), 51 (14).

In a further run under analogous conditions, 23% of *3-chlorotricyclo[3.2.1.$0^{2,7}$]oct-3-ene-1-carboxylic acid* (**13**) were obtained (beside 64% of **12**), m.p. 91–92°. IR ($CHCl_3$): 3500–2300*m* (br.), 1690*s*, 1628*m*, 1445*w*, 1436*m*, 1431*w*, 1333*m*, 1321*m*, 1280*s*, 1181*w*, 1150*m*, 1107*w*, 1076*m*, 1054*w*, 1018*w*, 990*w*, 972*w*, 955*w*, 915*w*, 872*m*, 844*w*, 827*w*. ^{1}H-NMR: 1.03 (*d*, J_{gem} = 12, $w_{½} \approx 2$ each, $H^{C(3)}$–C(6)); 1.57 (*d*, J_{gem} = 12, $w_{½} \approx 2$ each, $H^{C(4)}$–C(8)); 1.73 (*ddd*, J_{gem} = 12, *J*(5,$6^{C(1)}$) = 4.5, *J*($6^{C(1)}$,7) = 2.5, $H^{C(1)}$–C(6)); 1.93 (*dd*, J_{gem} = 12, *J*(5,$8^{C(6)}$) = 4.5, $H^{C(6)}$–C(8)); 2.22 (*dd*, *J*(2,7) = 7.5, *J*($6^{C(1)}$,7) = 2.5, further *J* < 1, $w_{½} \approx 5$, H–C(7)); 2.66 (*dt*, *J*(4,5) = 7.5, *J*(5,$6^{C(1)}$) = *J*(5,$8^{C(6)}$) = 4.5, H–C(5)); 2.69 (*dd*, *J*(2,7) = 7.5, *J*(2,4) = 3, H–C(2)); 3.2–5.6 (*m*, COOH); 6.01 (*dd*, *J*(4,5) = 7.5, *J*(2,4) = 3, H–C(4)). MS: 186 (14), 184 (42, M^+, $C_9H_9ClO_2$), 168 (5), 166 (15), 149 (16), 141 (32), 140 (13), 139 (100), 131 (10), 105 (15), 104 (17), 103 (91), 78 (11), 77 (62), 72 (45), 51 (23).

*3-Chloro-4-*endo*-hydroxybicyclo[3.2.1]oct-2-ene-6-*exo*-carboxylic Acid* (**14**). An emulsion of 31 mg (0.13 mmol) of a 5.5:1 mixture **10**/**11** in 1.5 ml of 8% aq. KOH was refluxed for 16 h. Extraction with Et_2O, acidifying with 20% H_2SO_4 to pH 1, and normal workup (Et_2O, once 20% H_2SO_4) led to 22 mg (82.5%) of **14**, which was recrystallized from Et_2O/CH_2Cl_2/pentane, m.p. 125–126°. IR ($CHCl_3$): 3590*m*, 3510*w*, 3450–2200*w* (br.), 1702*s*, 1635*w*, 1462*w*, 1446*w*, 1413*m*, 1375*m*, 1335*m*, 1316*m*, 1292*m*, 1153*w*, 1132*w*, 1063*m*, 1033*m*, 973*w*, 948*w*, 916*m*, 895*m*, 857*m*, 613*w*. ^{1}H-NMR: 1.2–5.0 (br. *m*, OH, COOH); 1.75–1.9 (*m*, 2H–C(8)); 1.98 (*ddd*, J_{gem} = 12.5, *J*(6*endo*,7*exo*) = 7.5, *J*(1,7*exo*) = 5.5, H_{exo}–C(7)); 2.14 (*ddd*, J_{gem} = 12.5, *J*(6*endo*,7*endo*) = 8.5, *J* = 2, H_{endo}–C(7)); 2.61 (*m*, $w_{½} \approx 16$, H–C(1)); 2.93 (*dd*, *J*(4*exo*,5) = 5.5, *J*(5,$8^{C(6)}$) ≈ 5, H–C(5)); 3.39 (*dd*, *J*(6*endo*,7*endo*) = 8.5, *J*(6*endo*,7*exo*) = 7.5, H_{endo}–C(6)); 4.47 (*d*, *J*(4*exo*,5) = 5.5, H_{exo}–C(4)); 6.10 (*d*, *J*(1,2) = 7, H–C(2)). MS: 204 (2), 202 (8, M^+, $C_9H_{11}ClO_3$), 184 (2), 168 (11), 167 (100), 149 (24), 139 (9), 121 (56), 112 (19), 103 (11), 101 (14), 95 (54), 93 (12), 91 (14), 77 (28), 73 (15), 67 (13), 65 (16), 55 (16), 53 (12), 51 (11), 41 (13).

*Methyl 2-Cyano-3-chlorobicyclo[3.2.1]oct-2-ene-6-*endo*-carboxylate* (**15**). To a soln. of 3.5 g (71.5 mmol) of NaCN (dried for 65 h at 100°/0.02 Torr) in 350 ml of dry HMPA at 75°, 6.6 g (35.8 mmol) of **12** were added at r.t. under Ar. After stirring for 27 h at 100°, the soln. became dark brown, HMPA was evaporated under high vacuum, the residue poured on 150 ml of 1N NaOH and washed 3 times with CH_2Cl_2, and the org. layer extracted twice with 150 ml of 1N NaOH. Acidification of the combined aq. layers to pH 1 with 25% (*v*/*v*) H_2SO_4, normal workup (Et_2O, once 25% (*v*/*v*) H_2SO_4, once sat. NaCl soln.), esterification with CH_2N_2, and flash CC with pentane/Et_2O 1:3 gave 3.774 g (47%, 54% with respect to converted **12**) of **15**, m.p. 69–71°. IR: 3020*w*, 2215*w*, 1739*s*, 1623*m*, 1444*w*, 1432*m*, 1345*m*, 1310*m*, 1280*w*, 1258*m*, 1201*m*, 1189*m*, 1168*s*, 1159*s*, 1097*w*, 1074*w*, 1047*w*, 1023*w*, 980*w*, 956*w*, 936*w*, 918*w*, 909*w*, 897*w*, 717*w*. ^{1}H-NMR: 1.75–1.9 (*m*, 2H–C(8)); 2.03 (*ddd*, J_{gem} = 13.5, *J*(6*exo*,7*exo*) = 11.5, *J*(1,7*exo*) = 6.5, H_{exo}–C(7)); 2.28 (*d*, J_{gem} = 20, $w_{½} \approx 4$ each, H_{endo}–C(4)); 2.45 (*ddd*, J_{gem} = 13.5, *J*(6*exo*,7*endo*) = 4.5, *J*(1,7*endo*) or *J*(7*endo*,$8^{C(3)}$) = 2, H_{endo}–C(7)); 2.70 (*dd*, J_{gem} = 20, *J*(4*exo*,5) = 4.5, $w_{½} \approx 3$ each, H_{exo}–C(4)); 2.8–2.9 (*m*, H–C(1), H–C(5)); 3.16 (*dddd*, *J*(6*exo*,7*exo*) = 11.5, *J*(5,6*exo*) = 6.5, *J*(6*exo*,7*endo*) = 4.5, *J*(4*exo*,6*exo*) = 1.5, H_{exo}–C(6)); 3.76 (*s*, $COOCH_3$). MS: 227 (1), 225 (3, M^+, $C_{11}H_{12}ClNO_2$), 196 (1), 194 (3), 168 (1), 166 (2), 140 (3), 138 (9), 102 (9), 87 (100), 77 (7), 55 (32).

*Methyl 2-*endo*-Cyanobicyclo[3.2.1]octane-6-*endo*-carboxylate* (**16**). Hydrogenation of 146 mg (0.65 mmol) of **15** in 80 µl (0.97 mmol) of pyrrolidine and 12 ml of CH_3OH with 103 mg of 5% Pd/$CaCO_3$ at r.t. for 2¼ h, workup (Et_2O, once 2N HCl), and CC with pentane/Et_2O 1:3 yielded 124 mg (100%) of **16**, m.p. 35–36°. IR: 2235*w*, 1737*s*, 1471*w*, 1455*m*, 1433*m*, 1351*w*, 1309*m*, 1269*w*, 1239*w*, 1198*s*, 1188*m*, 1180*m*, 1172*s*, 1153*s*, 1105*w*, 1058*w*,

1042*w*, 1018*w*, 967*w*, 912*m*. ^{1}H-NMR: 1.35–1.55 (*m*, among others $J = 7$, $J(4exo,5) = 2.5$, $J(4exo,6exo) = 1$, H_{exo}–C(4)); 1.48 (*dd*, $J_{gem} = 11.5$, $J(7endo,8^{C(3)}) = 2$, $H^{C(3)}$–C(8)); 1.6–1.95 (*m*, 2H–C(3), H_{endo}–C(4), $H^{C(6)}$–C(8)); 2.03 (*ddd*, $J_{gem} = 14.5$, $J(6exo,7exo) = 12$, $J(1,7exo) = 7$, H_{exo}–C(7)); 2.30 (*ddd*, $J_{gem} = 14.5$, $J(6exo,7endo) = 6.5$, $J(7endo,8^{C(3)}) = 2$, H_{endo}–C(7)); 2.45–2.6 (*m*, H–C(1), H–C(5)); 2.64 (*ddd*, $J = 9$, 7, $J(1,2exo) = 2$, H_{exo}–C(2)); 3.00 (*ddd*, $J(6exo,7exo) = 12$, $J(6exo,7endo) = 6.5$, $J(5,6exo) = 6$, further $J < 1$, H_{exo}–C(6)); 3.73 (*s*, $COOCH_3$). MS: 193 (5, M^+, $C_{11}H_{15}NO_2$), 178 (4), 166 (10), 162 (14), 161 (20), 134 (30), 133 (27), 132 (12), 117 (12), 107 (11), 106 (11), 92 (11), 87 (37), 81 (12), 80 (37), 79 (18), 55 (15), 41 (13), 39 (12), 32 (49), 28 (100).

*Hydrochloride of Methyl 2-*endo*-(Aminomethyl)bicyclo[3.2.1]octane-6-*endo*-carboxylate* (**17**·HCl). Hydrogenation of 34 mg (0.15 mmol) of **15** in 4 ml of CH_3OH and 3 drops of H_2O with 10% Pd/C at r.t. for 1¼ h yielded 31 mg (88%) of **17**·HCl, m.p. 242–244°. IR ($CHCl_3$): 3650–2300*s* (br.), 1724*s*, 1611*m*, 1511*m*, 1505*m*, 1457*m*, 1434*m*, 1406*w*, 1390*w*, 1350*w*, 1307*m*, 1178*m*, 1165*m*, 1154*m*, 1042*w*, 1000*w*, 966*w*, 913*w*, 878*w*. ^{1}H-NMR: 1.23, 1.4–1.7, 1.7–2.1 (3*m*, 1H, 4H, 3H); 1.83 (*ddd*, $J_{gem} = 14$, $J(6exo,7exo) = 11.5$, $J(1,7exo) = 6.5$, H_{exo}–C(7)); 2.33, 2.48 (*dd*, $J \approx 6$ each, $J < 1$, and *m*, $w_{½} \approx 13$, resp., H–C(1), H–C(5)); 2.77 (*B* of *ABX*, $J_{gem} = 13$, $J(2,1'_B) = 6$, H_B–C(1')); 2.84 (*A* of *ABX*, $J_{gem} = 13$, $J(2,1'_A) = 8.5$, H_A–C(1')); 2.94 (*ddd*, $J(exo,7exo) = 11.5$, $J(5,6exo) \approx 6$, $J(6exo,7endo) \approx 6$, H_{exo}–C(6)); 3.69 (*s*, $COOCH_3$); 7.8–8.65 (*m*, NH_3^+). MS: 198 (16), 197 (52, M^+, $C_{11}H_{19}NO_2$), 180 (11), 167 (10), 166 (27), 149 (3), 148 (13), 136 (11), 107 (19), 94 (18), 93 (17), 91 (14), 87 (49), 81 (12), 80 (39), 79 (51), 77 (12), 67 (17), 56 (12), 55 (15), 41 (19), 39 (12), 38 (11), 36 (32), 32 (28), 30 (100).

*Dimethyl Bicyclo[3.2.1]octane-2-*endo*,6-*endo*-dicarboxylate* (**21**). Under Ar, 0.48 ml of 1.12M DIBAH were added at −78° to 30 mg (0.16 mmol) of **16** in 3 ml of dry Et_2O. After stirring at −78° for ¾ h, warming up to r.t. within 1½ h, and further stirring at r.t. for 2½ h, 1 ml of sat. $(NH_4)_2SO_4$ soln. and subsequently 1 ml of 10% H_2SO_4 were added, and the mixture was stirred for 10 min at r.t. and then poured on 15 ml of 10% H_2SO_4. After normal workup (Et_2O, once sat. NaCl soln.), the residue (**19**) was taken up in acetone. *Jones* reagent was added at r.t. until the soln. remained orange. After 45 min stirring at r.t., i-PrOH was added till a green precipitate was formed. Filtration, evaporation of the solvent, dissolving the crude product (**20**) in Et_2O, esterification with CH_2N_2, evaporation, and CC with pentane/Et_2O 1:1 led to 23.5 g (67.5%) of **21**. IR: 1735*s*, 1472*w*, 1455*w*, 1433*m*, 1339*w*, 1307*m*, 1242*m*, 1228*m*, 1195*s*, 1172*s*, 1153*s*, 1107*w*, 1057*w*, 1043*w*, 1027*w*, 951*w*, 911*w*, 891*w*, 871*w*. ^{1}H-NMR: 1.35–1.55 (*m*, among others $J = 5$, $J(4exo,5) = 2$, H_{exo}–C(4)); 1.51 (*d*, $J_{gem} = 11.5$, $w_{½} \approx 4$ each, $H^{C(3)}$–C(8)); 1.65–1.8 (*m*, 2H–C(3), H_{endo}–C(4), $H^{C(6)}$–C(8)); 1.88 (*ddd*, $J_{gem} = 14$, $J(6exo,7exo) = 12$, $J(1,7exo) = 7$, H_{exo}–C(7)); 2.13 (*ddd*, $J_{gem} = 14$, $J(6exo,7endo) = 6$, $J(7endo,8^{C(3)}) = 2$, H_{endo}–C(7)); 2.4–2.55 (*m*, H–C(1), H–C(5)); 2.57 (*dd*, $J \approx 7$, $J \approx 5$, further $J < 1$, H_{exo}–C(2)); 2.93 (*dt*, $J(6exo,7exo) = 12$, $J(6exo,7endo) = J(5,6exo) = 6$, H_{exo}–C(6)); 3.66, 3.71 (2*s*, 2 $COOCH_3$). MS: 226 (3, M^+, $C_{12}H_{18}O_4$), 195 (15), 194 (34), 167 (31), 166 (100), 162 (24), 135 (21), 134 (39), 107 (35), 106 (13), 100 (12), 93 (12), 92 (27), 91 (14), 88 (23), 87 (54), 81 (19), 80 (48), 79 (49), 77 (11), 67 (12), 59 (16), 55 (18), 41 (17).

4,5-Bis(trimethylsiloxy)tricyclo[4.4.0.0^{3,9}]dec-4-ene (**22**). Under Ar, 185 mg (8.04 mmol) of Na were dispersed in 3 ml of boiling toluene (dist. over Na). After cooling to r.t., 1 ml (7.93 mmol) of $(CH_3)_3SiCl$ (dist. over CaH_2) and, dropwise, 380 mg (1.68 mmol) of **21** in 3.5 ml of toluene were added. On refluxing for 21 h, the soln. turned violet. Filtration, washing the residue with pentane, evaporation of the solvent (r.t./12 Torr), and distillation (95°/0.05 Torr) gave 236 mg (45.5%) of **22**.

Mixture of Tricyclo[4.4.0.0^{3,9}]decane-4,5-diols (**23**). A soln. of 230 mg (0.74 mmol) of **22** in 5 ml of abs. CH_3OH was hydrogenated with 82 mg of 10% Pd/C at r.t. for 1 h. After evaporation of CH_3OH, the residue was taken up in Et_2O and treated with 64 mg (1.68 mmol) of $LiAlH_4$. Stirring for 10 min at 0° and 45 min at r.t., workup with sat. $(NH_4)_2SO_4$ soln./*Celite*, filtration, evaporation, and CC with pentane/Et_2O 1:3 yielded 84 mg (67.5%) of a mixture of diastereoisomeric diols **23**. IR: 3630*w*, 3390*m* (br.), 1493*w*, 1475*w*, 1458*w*, 1406*w*, 1312*w*, 1299*w*, 1290*w*, 1270*w*, 1240*w*, 1210*w*, 1194*w*, 1175*w*, 1094*m*, 1066*s*, 1046*m*, 1027*m*, 1016*m*, 970*w*, 949*w*, 936*w*, 900*w*, 890*w*, 843*w*, 713*w*, 603*w*. ^{1}H-NMR: 1.15–1.3 (*m*, 2H); 1.33 (*dd*, $J_{gem} = 12$, $J = 3$, further $J < 1$, 1H); 1.4–1.55, 1.55–1.75 (2*m*, 2H each); 2.1–2.2, 2.25–2.5, 2.5–2.6 (3*m*, 1H, 5H, 1H, among others HO–C(4), HO–C(5)); 4.05–4.25 (*m*, H–C(4), H–C(5)). MS: 168 (3, M^+, $C_{10}H_{16}O_2$), 150 (13), 137 (18), 132 (24), 121 (11), 119 (25), 117 (31), 109 (20), 108 (10), 107 (13), 106 (20), 105 (10), 104 (95), 95 (20), 94 (21), 93 (54), 92 (41), 91 (53), 83 (11), 81 (45), 80 (47), 79 (100), 78 (34), 77 (36), 70 (28), 67 (43), 66 (17), 65 (17), 60 (11), 58 (19), 57 (32), 55 (28), 54 (46), 53 (25), 51 (12), 43 (12), 41 (62).

Mixture of Tricyclo[4.4.0.0^{3,9}]decane-4,5-diyl Bis(methanesulfonates) (**24**). A soln. of 24 mg (0.14 mmol) of **23**, 34 µl (0.44 mmol) of CH_3SO_2Cl and a catalytic amount of *p*-(*N*,*N*-dimethylamino)pyridine was stirred for 5½ h at r.t. Normal workup (in Et_2O, 4 times sat. $CuSO_4$, once sat. NaCl soln.) and drying (15 h, r.t./0.01 Torr) gave 46.5 mg (100%) of a mixture of diastereoisomeric sulfonates **24**. IR: 1496*w*, 1475*w*, 1414*w*, 1365*s*, 1346*s*, 1333*w*, 1314*w*, 1301*w*, 1292*w*, 1275*w*, 1240*w*, 1178*s*, 1105*w*, 1093*w*, 1060*w*, 1045*m*, 1034*w*, 1019*w*, 1007*m*, 966*s*, 949*m*,

903*w*, 893*m*, 883*m*, 863*s*, 841*w*, 696*w*, 669*w*. ^{1}H-NMR: 1.15–2.0 (*m*, 6H); 2.25–2.7 (*m*, 5H); 2.75 (*m*, $w_{1/2} \approx 16$, 1H); 3.09, 3.13 (2*s*, 2 CH_3SO_3); 5.05–5.15 (*m*, $w_{1/2} \approx 8$, H–C(4), H–C(5)). MS: no 324 ($C_{12}H_{20}O_6S_2$), 245 (1), 228 (4), 167 (9), 150 (14), 149 (100), 133 (20), 132 (48), 131 (49), 121 (79), 119 (12), 117 (28), 107 (10), 105 (18), 104 (16), 93 (72), 92 (13), 91 (65), 81 (23), 80 (20), 79 (77), 78 (18), 77 (20), 67 (34), 57 (28), 55 (21), 54 (23), 53 (13), 43 (14), 41 (34).

Tricyclo[4.4.0.0^{3,9}]dec-4-ene (**25**). So much of a 0.36M anthrylsodium soln. [13] (prepared by the reaction of 50 mg (2.17 mmol) of Na and 448 mg (2.52 mmol) of anthracene in 6 ml of abs. THF, 1 h at r.t.) was added at r.t. under Ar to a soln. of 115 mg (0.36 mmol) of **24** in 8 ml of abs. THF until the dark blue colour persisted. Stirring was continued for 17 h. Evaporation and sublimation (85°/12 Torr) gave 20.5 mg (43.5%; yield according to GLC (*B*, 90°): 83%) of **25**. IR: 3032*m*, 1619*w*, 1490*w*, 1459*m*, 1441*m*, 1412*m*, 1362*m*, 1322*m*, 1286*w*, 1250*w*, 1076*w*, 1059*w*, 891*m*, 876*w*, 836*w*, 695*s*. ^{1}H-NMR: 0.95–1.15 (*m*, $w_{1/2} \approx 21$, 2H); 1.23 (*dm*, $J = 9.5$, $w_{1/2} \approx 8$, 1H); 1.35–1.55 (*m*, 2H); 1.55–1.8 (*m*, 3H); 2.19 (*dtd*, $J = 8, 5.5, 2$, further $J < 1$, 1H); 2.41 (*ddd*, $J = 8, 4, 2$, 1H); 2.45–2.7 (*m*, 2H); 5.49 (*ddd*, $J(4,5) = 8$, $J(3,4)$ or $J(5,6) = 7.5$, $J = 1$, H–C(4) or H–C(5)); 6.31 (*dd*, $J(4,5) = 8$, $J(3,4)$ or $J(5,6) = 7.5$, further $J < 1$, H–C(4) or H–C(5)). MS: 134 (42, M^+, $C_{10}H_{14}$), 119 (32), 106 (20), 105 (26), 93 (43), 92 (95), 91 (100), 80 (42), 79 (60), 78 (25), 77 (42), 65 (12), 45 (15).

Rearrangement of **1** *with* $AlBr_3$ *in* CS_2. To 500 µl of an $AlBr_3$ soln. under Ar (prepared from 460 mg (1.72 mmol) of $AlBr_3$ and 3.7 ml of CS_2), precooled to –75°, 25 µl of a soln. of 2 mg (0.015 mmol) of **1** in 60 µl of CS_2 (also precooled to –75°) was added under stirring. After 24 min, the reaction was quenched by adding 2 ml of H_2O and worked up with 2 ml of pentane. GLC (*B*, 85°) showed a mixture of 30% of **1**, 10% of *protoadamantane* (**26**), and 60% of *adamantane* (**27**).

Ionic Hydrogenation of **7**. For 1 min, BF_3 (gas) was bubbled through a soln. of 5 mg (0.033 mmol) of **7** and 20 µl (0.13 mmol) of Et_3SiH in 3 ml of CH_2Cl_2 (filtered through basic Alox). After 10 min of stirring at r.t., GLC (*B*, 85°) showed a 1:4 mixture **26**/**27**.

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