92. C,C-Double Bond Participation in the Acid-Catalyzed Cyclization of 9*exo*-Methyl-*anti*^{10,11}-tricyclo[4.2.1.1^{2,5}]deca-3,7-diene-9*endo*,10*endo*-diol

Influence of Steric Compression on the Product Distribution

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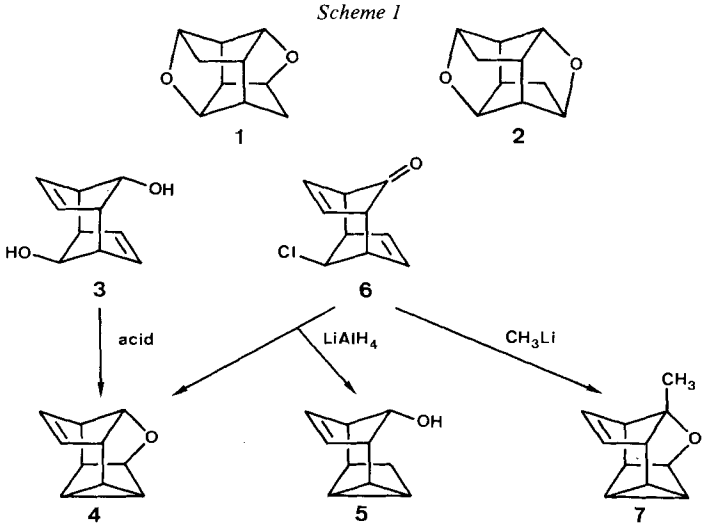
Summary

Acid treatment of 9*exo*-methyl-*anti*^{10,11}-tricyclo[4.2.1.1^{2,5}]deca-3,7-diene-9*endo*,10*endo*-diol (**8**) leads to the two isomeric pentacyclic ethers **7** and **9** by intramolecular nucleophilic substitution of a protonated OH-group with participation of a C,C-double bond.

The higher steric compression in diol **8** on the side of the tertiary OH-group at C(9) and the C(3),C(4)-double bond, accounts for the preferred formation of **7** over **9**.

In the course of our studies on heterodiamantanes and the structurally related pentacyclic diethers **1** and **2**, we observed that treatment of diol **3** with acid gave neither **1** nor **2** but quantitatively the pentacyclic monoether **4** [1]. This result was

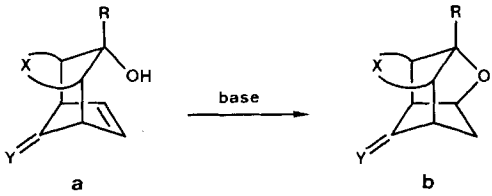
Scheme 1



interpreted in terms of an intramolecular substitution with participation of a C,C-double bond, favoured by the structurally enforced close proximity of the reacting centers. Analogously, **4** was also one of the products (**4/5** 1:3) from the reaction of the chloride **6** with lithium aluminum hydride [1] and its methyl analog **7** the sole product of the methyl lithium treatment of **6** [2].

To study the influence of steric compression in the above mentioned transformation **3**→**4**, the corresponding monomethylated diol **8** was also treated with acid[1]). From the two *a priori* possible pentacyclic monoethers **7** and **9**, we expected the former to be the predominant one, especially on the basis of the remarkable rate enhancements (10 to 10^2)[2]) observed in the base-catalyzed intramolecular cyclizations of type **a** alcohols to ethers **b** in replacing R = H by R = CH_3[3]). The results are listed in the *Table*.

Scheme 2



a **b**

R = H, CH_3
X = CH_2–CH_2–CH_2, CH_2–CH_2, CH=CH
Y = O, H,H

Indeed, **7** is always formed as the major ether even though the ratio **7/9** is solvent and acid concentration dependent, *i.e.* in diol **8** the tertiary OH-group at C(9) on the sterically more strained side of the molecule acts preferentially as a nucleophile substituting the protonated secondary OH-group at C(10) with participation of the C(3),C(4)-double bond (*Scheme 3*: **8**→**c**→**7**). On the other hand, the minor ether **9** as well as the *p*-toluenesulfonate **10** follow from the corresponding at HO–C(9) protonated intermediate **d**.

Table. *Treatment of diol* **8** *with acid and product distribution*

Run	Reaction conditions		Product distribution[a]) [%]					
	Acid	Time [min]	**8**	**7**	**9**	**10**	**11**	**12**
1	0.05 N *p*-TsOH in benzene	45	–	67	4	29	–	–
2	0.05 N *p*-TsOH in ether	45	–	84	10	5	1	–
3	0.05 N *p*-TsOH in benzene/ H_2O/dioxane 1:1:1	180	–	89	7	–	–	–
4	0.05 N HCl in $CHCl_3$	30	–	90	10	–	–	–
5	0.05 N HCl in ether	30	–	79	11	–	6	–
6	0.4 N HCl in ether	45	38	32	5	–	25	–

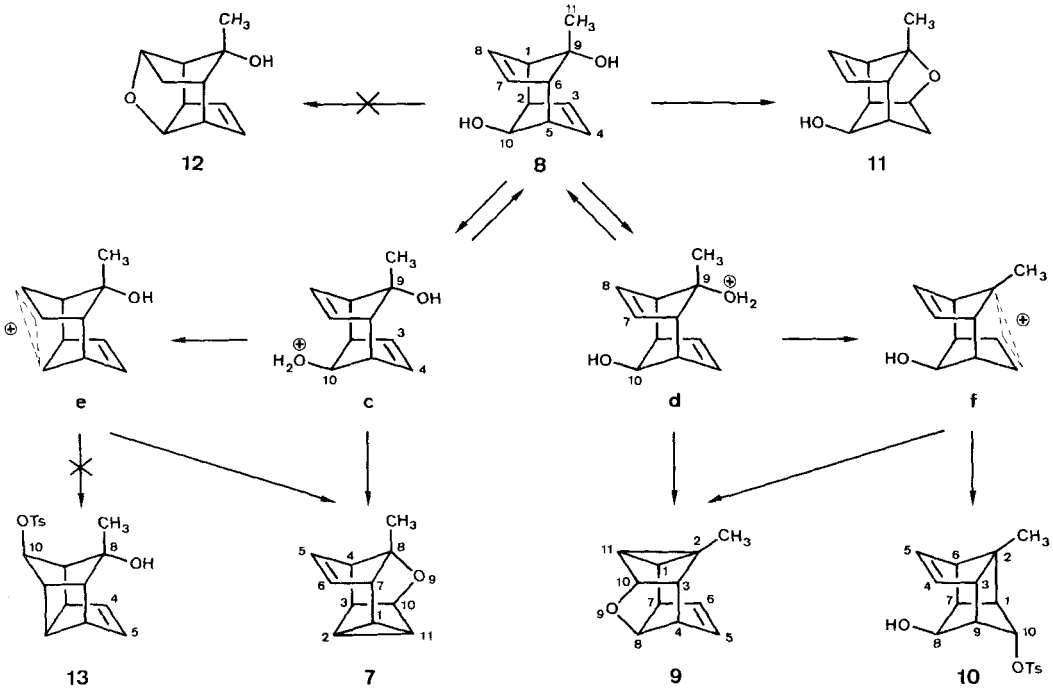
a) Run 1: isolated products; Run 2–6: composition determined by capillary GC.

1) It has to be mentioned that a recent communication by *Doecke & Garratt* [3] refers to the same topic. However, the authors' conclusions are quite different from ours.

2) Kinetic measurements to be published.

3) See [4] and the preceeding papers cited therein.

Scheme 3



That protonation of **8** is not the rate determining factor for the formation of the pentacyclic monoethers **7** and **9** is evident from *run 1:* the 17:1 ratio of **7**/**9** does not correspond to the ratio of the protonation of the secondary (**c**) *versus* the tertiary (**d**) OH-group, as manifested by the 2:1 ratio of the products **7** (67%) to **9** + **10** (33%).

The influence of varying the acid concentration is illustrated by the *runs 5* and *6*. In 0.4 N HCl/ethyl ether *(run 6)* diol **8** reacts slower (38% of unchanged **8** is recovered after 45 min) and less **7** and **9** are formed although still in practically the same ratio as in the 8 times more diluted (0.05 N) acid solution *(run 5)*. Significant at higher acid concentration *(run 6)*, however, becomes the protonation of the C(3), C(4)-double bond, *i.e.* the one on the sterically more compressed side of the molecule: 25% of the tetracyclic monoether **11** is formed[4]).

The formation of **7** and **9** *via* **c** and **d**, respectively, can *a priori* proceed either by a concerted nucleophilic attack of the free OH-group on the C, C-double bond and C, O-bond-breaking of the protonated OH-group or in a non-concerted way with the formation of the π-stabilized carbenium ions **e** and **f**[5]), respectively, the

[4]) It is noteworthy that none of the isomeric ether **12** resulting from protonation of the less strained C(7), C(8)-double bond is observed.

[5]) Studies on the analogous unsubstituted cation and the isolation of its corresponding *p*-toluenesulfonate were reported by *Paquette et al.* [5] [6]. It has to be noted that the authors describe the compounds as tetracyclo[5.2.1.$0^{2,6}$.$0^{3,9}$]decane systems, which does not correspond to the correct IUPAC numbering as tetracyclo[5.3.0.$0^{2,6}$.$0^{3,9}$]decanes.

latters being subsequently trapped by the remaining OH-group with participation of the neighbouring C, C-double bond.

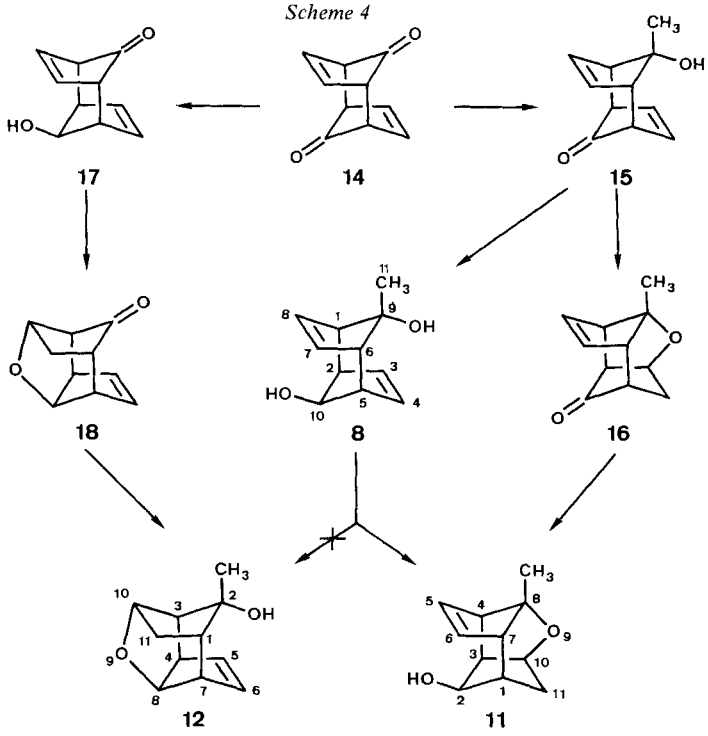
For the cyclization to **9**, a non-concerted mechanism seems to be very likely. Supporting evidence is gained from the *p*-toluenesulfonate **10** (*runs 1* and *2*), whose formation can most reasonably be formulated *via* the intermediate **f**. In benzene *(run 1)* the intermolecular reaction (**f** → **10**) even predominates over the intramolecular ether formation (**f** → **9**).

Cyclization to **7**, however, appears to be a concerted process. A non-concerted pathway would require the intermediate **e**, the less stable of the two π-stabilized carbenium ions **e** and **f**, and consequently lead to a product distribution of **7** < **9**. All experimental results are in clear contrast, *i.e.* always **7** > **9** and furthermore none of the *p*-toluenesulfonate **13** has been observed.

On the basis of our results, we conclude that in diol **8** the difference in steric compression on the two sides of the molecule and not the difference in the rate of protonation of the tertiary (→ **d**) *versus* the secondary (→ **c**) OH-group is the responsible factor leading to the observed product distribution[1]).

Synthesis of *8*, *11* and *12*. – The compounds **8**, **11** and **12** were all synthesized from the common intermediate **14** [7] [8]. Treatment of **14** with methyl lithium in ethyl ether at 0° afforded the tertiary alcohol **15** (73%) [9]. Subsequent reduction with lithium aluminum hydride yielded diol **8** (67%). The tetracyclic ether **11** (see *runs 2, 5* and *6*) was independently prepared by base-catalyzed cyclization of **8**

Scheme 4



(quant.) in 50% aq. NaOH-solution/CH_3OH 1:1. The full regioselectivity reflects the marked difference in reactivity of the two sides of diol **8**, the higher steric compression on the methylated side being the determining factor. A second approach to **11** was achieved by base-catalyzed cyclization (2 N aq. NaOH-solution/CH_3OH 1:1) of **15** to the ether **16** [9] (quant.) followed by lithium aluminium hydride reduction (71%). To assure that **12** was indeed not formed by acid treatment of diol **8**, it was independently prepared by methyl lithium addition to the ketone **18** (90%), whose preparation from diketone **14** [7] [8] *via* hydroxyketone **17** has already been reported [1] [10].

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Experimental Part

General remarks. Melting points (m.p.) were determined in sealed capillary tubes in an oil bath (*Büchi 510* apparatus) and are uncorrected. – IR. spectra (CCl_4) were recorded on a *Perkin-Elmer 297* spectrometer, bands are given in cm^{-1}. ^{1}H-NMR. spectra ($CDCl_3$) were measured on a *Varian EM-390* or *HA-100* or *Brucker WM-300* and ^{13}C-NMR. spectra ($CDCl_3$) on a *Varian XL-100* spectrometer. Chemical shifts (δ) are given in ppm relative to TMS as internal standard; J = spin coupling constant (Hz), $w_{1/2}$ = half width at half height (Hz). Mass spectra (MS.) were recorded on a *Hitachi-Perkin-Elmer RMU-6M* instrument at 70 eV ionizing electron energy, source temperature 180°, inlet temperature 200°. The most important ions are listed as *m/z* values with relative intensities (% of base peak) in parenthesis. Capillary GC. was performed on a *Carlo Erba Fractovap 4160* gas-chromatograph using an *UCON HB 5100* glass capillary column, length 20 m, diameter 0.33 mm; column chromatography on *Silicagel 60 Merck* (70–230 mesh ASTM).

Acid-catalyzed cyclizations of **8** (see *Table*). The diol **8** (0.01–0.1 mmol/ml) was treated with the indicated acid at r.t. After neutralization with sat. $NaHCO_3$-solution and extraction with ether, the product mixture was separated by column chromatography in CH_2Cl_2/AcOEt/cyclohexane 1:1:2 (run 1) or analyzed by capillary GC. (runs 2–6).

Data of 8-methyl-9-oxapentacyclo[5.4.0.0^{2,11}.0^{3,10}.0^{4,8}]undec-5-ene (**7**). – IR.: 3062*s*, 3020*w*, 1587*w*, 1446*w*, 1375*m*, 1349*w*, 1329*s*, 1310*w*, 1298*w*, 1288*w*, 1265*w*, 1256*m*, 1197*w*, 1164*w*, 1134*m*, 1124*s*, 1108*w*, 1092*w*, 1080*w*, 1049*s*, 1012*w*, 992*w*, 971*m*, 939*w*, 924*w*, 916*w*, 901*m*, 893*m*, 878*w*, 868*m*, 689*s*, 648*w*, 620*w*. – ^{1}H-NMR. (300 MHz): 1,25 (*s*, H_3C–C(8)); 1,33 (*t*×*d*, $J(1,2)=J(1,11)=6$ and $J(1,7)=4$, further J's ≤ 1, H–C(1)); 1.49 (*d*×*t*, $J(1,2)=6$ and $J(2,3)=J(2,11)=4$, further J's ≤ 1, H–C(2)); 1.82 (*d*×*d*, $J(3,4)=7$ and $J(4,5)=3$, H–C(4)); 2.11 (*d*×*d*×*d*, $J(1,11)=6$, $J(2,11)=4$ and $J(10,11)=3.5$, H–C(11)); 2.23 (*d*×*d*, $J(1,7)=4$ and $J(6,7)=3$, H–C(7)); 2.74 (*t*×*d*, $J(3,4)=J(3,10)=7$ and $J(2,3)=4$, further J's ≤ 1, H–C(3)); 4.76 (*d*×*d*, $J(3,10)=7$ and $J(10,11)=3.5$, further J's ≤ 1, H–C(10)); 5.72 (*d*×*d*, $J(5,6)=6$ and $J(4,5)=3$, H–C(5)); 6.16 (*d*×*d*, $J(5,6)=6$ and $J(6,7)=3$, H–C(6)). – MS.: 160 (14, M^+, $C_{11}H_{12}O$), 159 (24), 146 (11), 145 (81), 131 (59), 130 (12), 129 (17), 127 (13), 117 (83), 116 (39), 115 (100), 95 (10), 92 (17), 91 (86), 81 (21), 77 (16), 65 (15), 63 (11), 53 (11), 51 (15), 43 (37), 39 (24), 27 (11).

Data of 2-methyl-9-oxapentacyclo[5.4.0.0^{2,11}.0^{3,10}.0^{4,8}]undec-5-ene (**9**). – ^{1}H-NMR. (100 MHz)[6]: 1.02 (*t*, $J(1,7)=J(1,11)=4$, further J's ≤ 1, H–C(1)); 1.12 (*s*, H_3C–C(2)); 1.83 (*d*×*d*, $J(10,11)=6$ and $J(1,11)=4$, H–C(11)); 2.15 (*d*×*d*×*d*, $J(3,4)=7$, $J(4,8)=6$ and $J(4,5)=3$, H–C(4)); 2.3–2.6 (*m*, H–C(3) and H–C(7)); 4.46 (*t*×*d*, $J(4,8)=J(7,8)=6$, further $J=1$, H–C(8)); 4.77 (*d*×*d*, $J(10,11)=6$ and $J(3,10)=4$, further J's ≤ 1, H–C(10)); 5.75 (*d*×*d*, $J(5,6)=6$ and $J(4,5)=3$, H–C(5)); 6.10 (*d*×*d*, $J(5,6)=6$ and $J(6,7)=3$, H–C(6)).

[6]) Measured from a 3:1 mixture of **9** and **7**.

*Data of 8*endo-*hydroxy-2-methyl-tetracyclo[5.3.0.0^{2,6}.0^{3,9}]deca-4-en-10*exo-*yl* p-*toluene sulfonate* (**10**). – IR.: 3598*m*, 3048*w*, 1600*w*, 1447*w*, 1428*w*, 1376*s*, 1350*w*, 1330*w*, 1316*m*, 1307*w*, 1279*w*, 1245*w*, 1190*s*, 1178*s*, 1114*m*, 1100*w*, 1089*w*, 1075*m*, 1034*w*, 1015*w*, 983*s*, 964*s*, 938*w*, 912*w*, 887*m*, 859*w*, 690*w*, 684*m*, 663*m*. – ^{1}H-NMR. (100 MHz): 0.92 (*s*, H_3C–C(2)); 2.42 (*s*, 3 H, H_3C–C_6H_4); 2.3–2.8 (*m*, H–C(1), H–C(3), H–C(6), H–C(7) and H–C(9)); 3.09 (*d*, J(HO$_{endo}$–C(8),8*exo*) = 12, HO$_{endo}$–C(8)); 4.39 (*m*, $w_{1/2} \approx 26$, H$_{exo}$–C(8)); 4.52 (*t*, J(1,10) = J(9,10) = 2, H$_{endo}$–C(10)); 6.13 (*d*×*d*, J(4,5) = 6 and J(3,4) = 2, H–C(4)); 6.37 (*d*×*d*, J(4,5) = 6 and J(5,6) = 3, H–C(6)); 7.2–7.45 and 7.6–7.85 (2 *m*, each 2 H, H_3C–C_6H_4). – MS.: 332 (< 1, M^+, $C_{18}H_{20}O_4S$), 177 (5), 161 (16), 160 (90), 159 (21), 155 (13), 145 (41), 143 (11), 142 (27), 133 (13), 132 (53), 131 (100), 130 (19), 129 (14), 118 (12), 117 (59), 116 (14), 115 (17), 105 (23), 96 (31), 95 (68), 93 (17), 92 (20), 91 (84), 82 (15), 81 (23), 80 (15), 79 (21), 78 (18), 77 (24), 65 (19), 39 (9).

*Data of 8-methyl-9-oxatetracyclo[5.4.0.0^{3,10}.0^{4,8}]undec-5-en-2*endo-*ol* (**11**). – IR.: 3605*s*, 3052*w*, 1463*w*, 1449*w*, 1431*w*, 1377*m*, 1336*s*, 1300*w*, 1284*w*, 1271*m*, 1259*m*, 1233*w*, 1210*w*, 1200*w*, 1172*w*, 1159*w*, 1148*s*, 1124*w*, 1114*w*, 1094*w*, 1084*s*, 1033*w*, 1019*s*, 995*m*, 979*w*, 960*w*, 940*w*, 931*w*, 891*s*, 866*w*, 687*s*, 639*m*. – ^{1}H-NMR. (100 MHz): 1.21 (*s*, H_3C–C(8)); 1.45 (*d*×*t*, J(gem) = 12 and J(1,11*exo*) = J(10,11*exo*) = 4, H$_{exo}$–C(11)); 1.63 (*d*, J(gem) = 12, H$_{endo}$–C(11)); 2.15–2.5 (*m*, H–C(1), H–C(4) and H–C(7)); 2.86 (*d*×*d*×*d*×*d*, J(3,4) = 8, J(2*exo*,3) and J(3,10) each ≈ 4 and J(1,3) = 2, H–C(3)); 3.43 (*d*, J(2*exo*,HO$_{endo}$–C(2)) = 12, HO$_{endo}$–C(2)); 3,69 (*d*×*d*, J(2*exo*,HO$_{endo}$–C(2)) = 12 and J(2*exo*,3) ≈ 4, further J's ≤ 1, H$_{exo}$–C(2)); 4.65 (*m*, $w_{1/2} \approx 8$, H–C(10)); 6.15–6.4 (*m*, H–C(5) and H–C(6)). – MS.: 178 (100, M^+, $C_{11}H_{14}O_2$), 160 (2), 159 (2), 149 (4), 145 (5), 135 (17), 134 (5), 117 (44), 115 (10), 107 (13), 105 (15), 100 (21), 95 (27), 93 (13), 92 (33), 91 (39), 79 (57), 77 (21), 71 (16), 67 (17), 57 (40), 55 (12), 43 (66), 41 (14), 39 (13).

*Synthesis of 9*exo-*methyl*-anti^{9,10}-*tricyclo[4.2.1.1.1^{2,5}]deca-3,7-diene-9*endo,*10*endo-*diol* (**8**). To a solution of 76 mg (2 mmol) $LiAlH_4$ in 10 ml abs. ether, 147 mg (0.84 mmol) of **15** [9] were added at 0°. Stirring for 2 h, workup with sat. $(NH_4)_2SO_4$-solution and chromatography in CH_2Cl_2/AcOEt/cyclohexane 2:1:0.5 yielded 100 mg (67%) of **8**. – IR.: 3610*s*, 3045*w*, 3025*w*, 1452*w*, 1376*m*, 1330*s*, 1310*w*, 1264*m*, 1241*m*, 1216*s*, 1208*m*, 1146*m*, 1110*w*, 1091*s*, 1047*w*, 1003*m*, 960*w*, 951*w*, 884*w*, 687*m*. – ^{1}H-NMR. (80 MHz): 1.33 (*d*, J(H_3C_{exo}–C(9)), HO$_{endo}$–C(9)) = 2, H_3C_{exo}–C(9)); 2.4–2.9 (*m*, H–C(1), H–C(2), H–C(5) and H–C(6)); 3.85 (*d*×*m*, J(10*exo*,HO$_{endo}$–C(10)) = 13 and $w_{1/2}$ each ≈ 5. H$_{exo}$–C(10)); 4.10 (*d*, J(10*exo*,HO$_{endo}$–C(10)) = 13, HO$_{endo}$–C(10)); 5.17 (*qa*, J(H_3C_{exo}–C(9), HO$_{endo}$–C(9)) = 2, HO$_{endo}$–C(9)); 6.65 (*t*, J(1,7) = J(6,7) = 2 and J(1,8) = J(6,8) = 2, respectively, H–C(7) and H–C(8)); 6.82 (*t*, J(2,3) = J(3,5) = 2 and J(2,4) = J(4,5) = 2, respectively, H–C(3) and H–C(4)). – MS.: 178 (13, M^+, $C_{11}H_{14}O_2$), 160 (14), 159 (15), 145 (51), 132 (14), 131 (54), 130 (10), 129 (13), 117 (100), 116 (26), 115 (53), 105 (16), 96 (40), 95 (69), 93 (18), 92 (19), 91 (68), 82 (29), 81 (31), 79 (32), 78 (18), 77 (34), 67 (19), 66 (11), 65 (19), 57 (12), 55 (16), 53 (20), 51 (19), 43 (76), 41 (18), 39 (35).

*Synthesis of 8-methyl-9-oxatetracyclo[5.4.0.0^{3,10}.0^{4,8}]undec-5-en-2*endo-*ol* (**11**). A solution of 110 mg (0.63 mmol) **16** [9] in 5 ml abs. ether was added to a suspension of 41 mg (1.1 mmol) $LiAlH_4$ in 10 ml abs. ether. After stirring at r.t. under argon for 3 h, the mixture was hydrolyzed with sat. $(NH_4)_2SO_4$-solution, filtered through *Celite* and the solvent evaporated i.v. Chromatography in cyclohexane/AcOEt 1:1 gave 80 mg (71%) of **11**.

*Synthesis of 2*exo-*methyl-9-oxatetracyclo[5.4.0.0^{3,10}.0^{4,8}]undec-5-en-2*endo-*ol* (**12**). An ice-cooled solution of 48 mg (0.3 mmol) of **18** [1] [10] in 3 ml abs. ether was treated with 1 ml of *ca.* 1.6 N CH_3Li in ether. After 1 h of stirring at r.t. the mixture was hydrolyzed with ice and extracted with ether. Chromatography in cyclohexane/AcOEt 3:1 afforded 48 mg (90%) of **12**. – IR.: 3590*s*, 3050*w*, 1476*w*, 1444*w*, 1377*m*, 1354*s*, 1338*w*, 1301*m*, 1266*w*, 1188*s*, 1128*s*, 1114*w*, 1079*s*, 1055*w*, 1014*w*, 993*w*, 977*w*, 953*m*, 946*m*, 887*m*, 872*m*, 648*m*, 594*m*. – ^{1}H-NMR. (100 MHz): 1.07 (*d*, J(H_3C_{exo}–C(2), HO$_{endo}$–C(2)) = 1.5, H_3C_{exo}–C(2)); 1.55 (*d*, J(gem) = 12, H$_{endo}$–C(11)); 2.05 (*d*×*t*, J(gem) = 12 and J(1,11*exo*) = J(10,11*exo*) = 4, H$_{exo}$–C(11)); 2.18 and 2.45–2.8 (2 *m*, 1 H with $w_{1/2} \approx 10$ and 3 H, H–C(1), H–C(3), H–C(4) and H–C(7)); 4.33 (*t*, J(4,8) = J(7,8) = 4, H–C(8)); 4.41 (*qa*, J(H_3C_{exo}–C(2), HO$_{endo}$–C(2)) = 1.5, HO$_{endo}$–C(2)); 4.74 (*m*, $w_{1/2} \approx 11$, H–C(10)); 6.32 and 6.37 (2 *d*×*d*, J(5,6) = 6, J(4,5) = 3 and J(5,6) = 6, J(6,7) = 3, H–C(5) and H–C(6)). – MS.: 178 (87, M^+, $C_{11}H_{14}O_2$), 135 (23), 131 (25), 117 (44), 107 (25), 105 (26), 95 (32), 91 (54), 79 (60), 71 (79), 67 (23), 57 (21), 43 (100).

*Synthesis of 10*endo-*hydroxy-10*exo-*methyl*-anti^{9,10}-*tricyclo[4.2.1.1.2^{2,5}]deca-3,7-dien-9-one* (**15**). To a solution of *ca.* 2 mmol CH_3Li in 10 ml abs. ether, 80 mg (0.5 mmol) of fine powdered **14** [7] [8] were

added at 0°. After 80 min of stirring at 0° and 25 min at r.t. the mixture was hydrolyzed with ice. Extraction with ether and chromatography in cyclohexane/AcOEt 3:1 afforded 11 mg (13%) of **16** and 64 mg (73%) of **15** [9]. M.p. 107°. – IR.: 3602*s*, 3056*w*, 3014*w*, 1796*w*, 1760*s*, 1449*w*, 1374*m*, 1332*s*, 1319*w*, 1293*m*, 1238*m*, 1213*w*, 1180*w*, 1148*s*, 1101*m*, 1052*s*, 998*w*, 964*w*, 952*w*, 874*m*, 695*w*, 635*m*. – ^{1}H-NMR. (100 MHz): 1.31 (*d*, $J(H_3C_{exo}-C(10), HO_{endo}-C(10)) = 1.5$, $H_3C_{exo}-C(10)$); 2.60 (*d*×*t*, $J(1,2)$ and $J(5,6) = 6$, $J(2,3) = J(2,4) = 1.5$ and $J(3,5) = J(4,5) = 1.5$, respectively, H–C(2) and H–C(5)); 2.99 (*d*×*t*, $J(1,2)$ and $J(5,6) = 6$, $J(1,7) = J(1,8) = 2$ and $J(6,7) = J(6,8) = 2$, respectively, H–C(1) and H–C(6)); 4.20 (*qa*, $J(H_3C_{exo}-C(10), HO_{endo}-C(10)) = 1.5$, $HO_{endo}-C(10)$); 6.36 (*t*, $J(2,3) = J(3,5) = 1.5$ and $J(2,4) = J(4,5) = 1.5$, respectively, H–C(3) and H–C(4)); 7.06 (*t*, $J(1,7) = J(6,7) = 2$ and $J(1,8) = J(6,8) = 2$, respectively, H–C(7) and H–C(8)). – ^{13}C-NMR.: 30.13 (*qa*, $H_3C-C(10)$); 50.48 and 52.45 (2 *d*, C(1), C(2), C(5) and C(6)); 85.05 (*s*, C(10)); 138.35 and 139.96 (2 *d*, C(3), C(4), C(7) and C(8)); 195.89 (*s*, C(9)). – MS.: 176 (6, M^+, $C_{11}H_{12}O_2$), 161 (4), 158 (5), 148 (16), 133 (39), 129 (17), 115 (22), 105 (100), 95 (21), 91 (25), 79 (24), 78 (20), 77 (26), 65 (8), 55 (16), 51 (16), 43 (59).

Synthesis of 8-methyl-9-oxatetracyclo[5.4.0.0^{3,10}.0^{4,8}]undec-5-en-2-one (**16**). To a solution of 118 mg (0.67 mmol) **15** in 3 ml of methanol, 3 ml of 2N aq. NaOH were added. Stirring for 90 min at r.t., workup with pentane and chromatography in cyclohexane/AcOEt 1:1 yielded 117 mg (99%) of **16** [9]. M.p. 122°. – IR.: 3068*m*, 1759*s*, 1446*w*, 1377*m*, 1329*s*, 1282*w*, 1259*w*, 1236*w*, 1222*w*, 1182*w*, 1146*s*, 1102*s*, 1031*m*, 1021*m*, 990*w*, 977*w*, 964*m*, 942*m*, 892*s*, 668*m*, 621*w*, 592*w*. – ^{1}H-NMR. (100 MHz): 1.21 (*s*, $H_3C-C(8)$); 1.60 (*d*×*t*, J(gem) = 12.5 and $J(1,11exo) = J(10,11exo) = 3.5$, $H_{exo}-C(11)$); 1.86 (*d*, J(gem) = 12.5, $H_{endo}-C(11)$); 2.26 (*d*×*d*×*d*, $J(1,7) = 5$, $J(6,7) = 2.5$ and $J(4,7) = 1.5$, H–C(7)); 2.38 (*m*, $w_{1/2} \approx 10$, H–C(1)); 2.55–2.8 (*m*, H–C(3) and H–C(4)); 4.79 (*m*, $w_{1/2} \approx 9$, H–C(10)); 5.91 (*d*×*d*, $J(5,6) = 6$ and $J(4,5) = 2.5$, H–C(5)); 6.11 (*d*×*d*, $J(5,6) = 6$ and $J(6,7) = 2.5$, H–C(6)). – ^{13}C-NMR.: 18.75 (*qa*, $H_3C-C(8)$); 29.39 (*t*, C(11)); 50.90, 51.69, 53.18 and 59.39 (4 *d*, C(1), C(3), C(4) and C(7)); 77.00 (*d*, C(10)); 95.85 (*s*, C((8)); 129.88 and 137.83 (2 *d*, C(5) and C(6)); 211.66 (*s*, C(2)). – MS.: 176 (80, M^+, $C_{11}H_{12}O_2$), 133 (43), 105 (100), 95 (39), 92 (23), 91 (26), 79 (25), 77 (21), 43 (34).

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