79. Nucleophilic Addition to C,C-Double Bonds. IV[1]). Ether Formation by Intramolecular Addition to Unsymmetrically Alkyl-substituted C,C-Double Bonds

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Dedicated to Professor Dr. *George H. Büchi* on the occasion of his sixtieth birthday

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Summary

Tricyclic olefinic alcohols containing an unsymmetrically alkyl-substituted C,C-double bond were cyclized intramolecularly to their corresponding ethers under basic conditions: **9**→**12**, **10**→**17**+**18**, and **11**→**12** *(Scheme 3, Table 1).* The reactivity is mainly due to relieve of ground state strain.

Alcohol **9** (endocyclic double bond) isomerized under intramolecular assistance by the hydroxyl group to **11** (exocyclic double bond) before cyclization to **12** occurred *(Scheme 5).* The latter step being the faster one, no isomerization **11**→**9** was observed.

Recently we described several examples of base-catalyzed intramolecular ether formation with polycyclic olefinic alcohols of the general types **a** (→**b**) [2] [3], **c** (→**d**) [3] and **e** (→**f**) [1]. The reaction implies a nucleophilic attack of the

Table 1. *Base-catalyzed ether formation by treatment of the olefinic alcohols* **8**–**11** *with 1 molal* t-*BuOK in* t-*BuOH*

Run	Starting material	Reaction conditions		Yield	
		Temp. [°C]	Time [h]	Reisolated starting material	Isolated ether
1	**9**	90	24	85% **9**	5% **12**
2	**9**	150	24	–	90% **12**
3	**11**	25	113	50% **11**	25% **12**
4	**11**	90	6[a])	–	quant. **12**
5	**8**	90	24	87% **8**	7% **16**
6	**8**	150	24	–	quant. **16**
7	**10**	150	24	–	quant. **17**+**18**[b])

[a]) Required time for full conversion according to TLC.
[b]) Composition determined by capillary GLC.: 55% of **17** and 45% of **18**.

[1]) For Part III, see [1].

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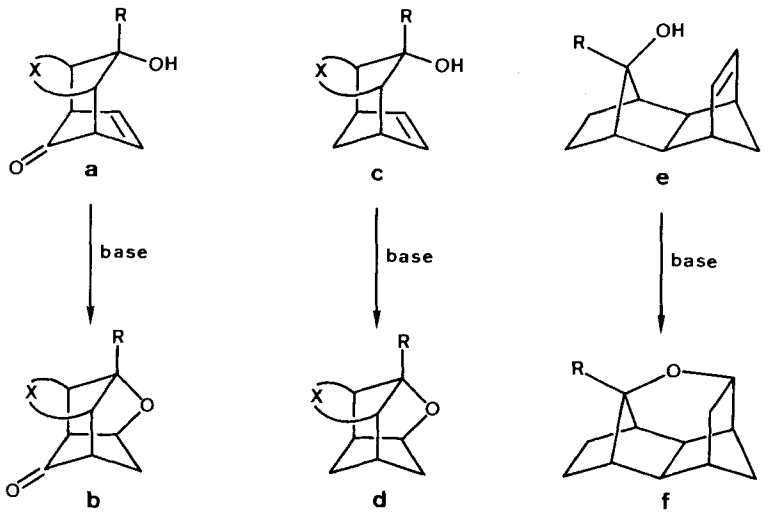
Scheme 1



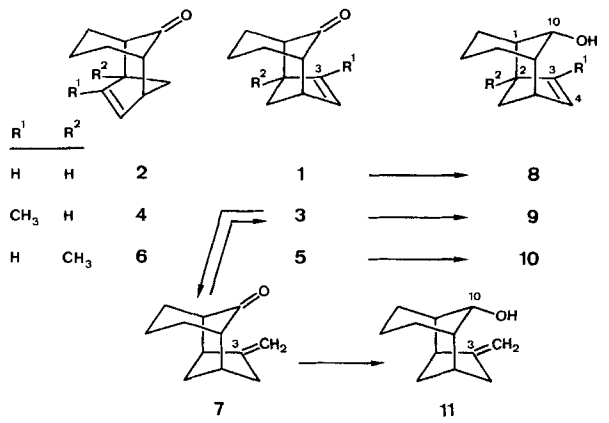
R ◻ H or alkyl X = CH=CH , CH_2–CH_2 or CH_2–CH_2–CH_2

alcohol O-atom on a C,C-double bond bearing no electron-attracting groups in conjugation. High steric compression alone (**c** and **e**) as well as in combination with electronic effects (**a**) is responsible for this most unusual reactivity.

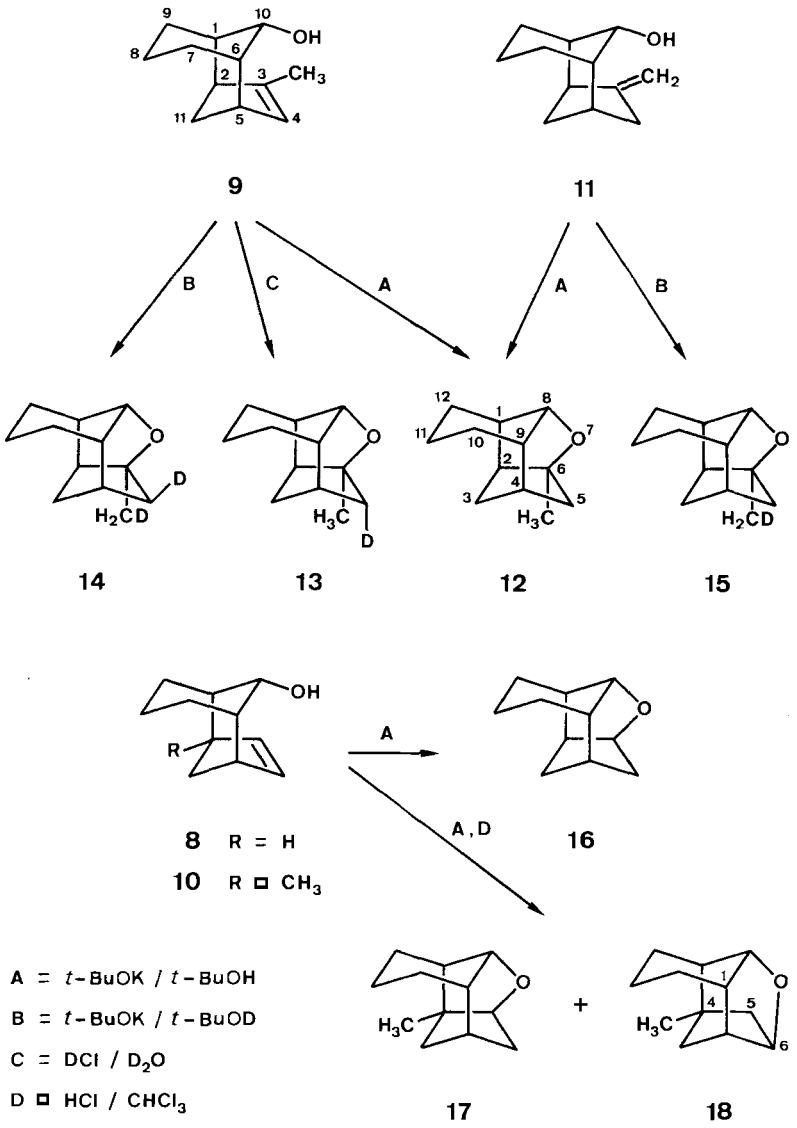
As part of our systematic investigations concerning the mechanism of such base-catalyzed ether formations, it was of great interest to study the behaviour of a substrate containing an unsymmetrically alkyl-substituted C,C-double bond. For this purpose we synthesized the olefinic alcohol **9**[2]), and for comparative experi-

[2]) The intermediate unmethylated ketones **1** and **2** were prepared according to [4] and the methylated ones **3**–**6** by analogy, starting from methylcyclopentadiene. Base-catalyzed isomerization (1 molal *t*-BuOK in *t*-BuOH at 150°) of **3** yielded a separable (1:1)-mixture of **3** and **7**. The alcohols **8**–**11** were obtained by $LiAlH_4$ reduction of the corresponding ketones **1**, **3**, **5** and **7**, respectively. For details s. exper. part.

Scheme 2



Scheme 3



ments also the closely related compounds **8**[2]), **10**[2]), and **11**[2]). The results of the cyclizations are summarized in *Scheme 3* and *Table 1*. Alcohol **9**, on treatment with 1 molal *t*-BuOK in *t*-BuOH (runs 1 and 2)[3]), cyclized at approximately the same rate as the unmethylated analog **8** (runs 5 and 6). Only ether **12**, the product of the regioselective ring closure to C(3), was formed. None of **22**, the *a priori*

[3]) All experiments were carried out under careful exclusion of oxygen to avoid oxidation to the corresponding ketones.

other possible ether, was detected. It was synthesized independently[4]), and on treatment with 1 molal *t*-BuOK in *t*-BuOH at 150° for 24 h remained unchanged. This clearly excludes **22** even as an intermediate in the cyclization of **9** to **12**.

Very spectacular was the result when alcohol **9** was treated in a deuteriated medium (1 molal *t*-BuOK in *t*-BuOD at 150°). Not the expected ether **13** was formed, which would correspond to incorporation of one deuterium atom regioselectively at C(5) of **13** and stereoselectivity from the *exo*-side by way of antiperiplanar addition (compare [3]), as in the case of the acid-catalyzed ring closure of **9** with 7% DCl in D_2O; instead the mainly dideuteriated ether **14**[5]) was isolated in 90% yield. According to the ^{1}H-NMR. spectra (100 and 360 MHz) of **14** in comparison with the ones of **12** (100 and 360 MHz) as well as with those (100 MHz) of **13**, **15** and **22** (s. below), one deuterium atom was incorporated in the *endo*-position at C(5)[6]) and a second one at the methyl group. The former results from a base-catalyzed isomerization of the C(3), C(4)-double bond to an exocyclic position (→ **g**) assisted by the alcohol group, before the alkoxide anion attacks the original endocyclic double bound. The latter gives conclusive evidence that the cyclization step **g** → **14** is faster than a possible back-isomerization **g** → **9**. This interpretation is supported by the formation of ether **15** on treatment of the alcohol **11** with 1 molal *t*-BuOK in *t*-BuOD: only one deuterium atom was incorporated, regioselectively at the methyl C-atom.

Base-catalyzed ring closure of the bridgehead methylated alcohol **10** shows little if any regioselectivity. Treatment of **10** with 1 molal *t*-BuOK in *t*-BuOH (run 7) resulted in an approximately 1:1 mixture of the ethers **17** and **18**. A significantly higher regioselectivity is observed under acidic conditions (HCl in $CHCl_3$, 16 h at RT.), where cyclization is initiated by protonation of the double bond: **17** and **18** were formed in an approximately 2:1 ratio. These two experiments together with our observation of a primary isotope effect of the order of 2 in the base-catalyzed ether formations of the structurally related olefinic alcohols **a** (X = CH=CH, R = H and X = CH_2–CH_2, R = H) might be indicative for a concerted addition of the nucleophile and a proton in the cyclization step.

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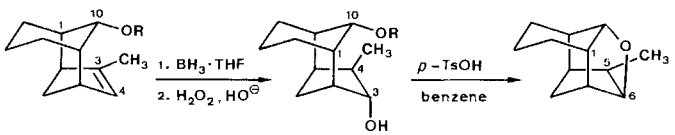
[4]) Ether **22** was prepared from alcohol **9** according to *Scheme 4*. For details s. exper. part.

Scheme 4

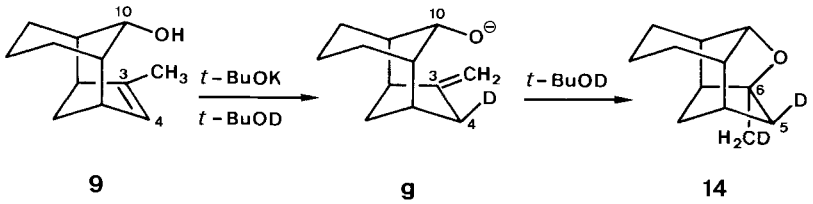


9 R = H **19** R = Ac **20** R = Ac **21** R = H **22**

[5]) Ether **14** was purified by chromatography on silicagel 'extra pure'. The deuterium distribution was determined by MS.: 2% d_0, 24% d_1, 67% d_2, 6% d_3, and 1% d_4.

[6]) The *endo*-position of D–C(5) in **14** was assigned from the absence of the *W*-coupling (J = 3.5 Hz) in the signal of H*endo*–C(3) and the disappearance of the signal corresponding to H*endo*–C(5) in the 360 MHz spectrum.

Scheme 5



9 **g** **14**

It has to be noted that the base-catalyzed cyclization **11** → **12** (runs 3 and 4) occurs at a higher rate than the ether formations **8** → **16** (runs 5 and 6) and **10** → **17** + **18** (run 7). One of the main factors for these differences in relative rates as well as for the observed regioselective formation of ether **12** (from **9** and **11**) appears to be the substitution pattern of the C-atom on which the negative charge development in the transition state takes place. The matter in under further investigation.

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Experimental Part

General remarks. See [5] and the following additional remarks: *Capillary GLC.* on a glass capillary column *UCON HB 5100*, length 20 m, diameter 0.33 mm. – *Column chromatography* on silicagel 60 *Merck* (70–230 mesh ASTM) or 60 *Merck* 'extra pure' (70–230 mesh ASTM). – *UV.-spectra* in C_2H_5OH-solutions. – *IR.-spectra* in CCl_4-solutions. – *^{1}H-NMR.-spectra* in the specified solvents. – *^{13}C-NMR.-spectra* in $CDCl_3$-solutions. – Recording conditions for *mass spectra* (MS.) if not specified: indirect introduction of the probe, inlet temperature ≈ 200°.

Cycloaddition to cyclopentadiene. Addition of 3-chloro-2-pyrrolidinocyclohexene [6] to cyclopentadiene in the presence of $AgBF_4$ in CH_2Cl_2 at −70° followed by hydrolysis as described in [4] and chromatography in ether/pentane 2:1 yielded beside 1% of ketone **2**, 72% of anti-*tricyclo-[4.3.1.1^{2,5}]undec-3-en-10-one* (**1**), m.p. 87–87.5° after recrystallization from hexane and sublimation at 84°/11 Torr. – UV.: 287 (30). – IR.: 3064*m*, 3042*w*, 1754*w*, 1728*s*, 1695*w*, 1668*w*, 1479*w*, 1454*m*, 1345*m*, 1279*w*, 1222*w*, 1147*w*, 1082*m*, 1045*m*, 954*m*, 920*w*, 715*m*. – ^{1}H-NMR. (CCl_4): 1.3–2.5 (*m*, 9 H); 2.72 (*m*, $w_{1/2} \approx 10$, H–C(2) and H–C(5)); 2.72 (*d*, J(11*endo*, 11*exo*) = 11, H*endo*–C(11)); 6.10 (*m*, $w_{1/2} \approx 4$, H–C(3) and H–C(4)). – ^{13}C-NMR.: 19.34 (*t*, C(8)); 28.95 (*t*, C(7) and C(9)); 34.97 (*t*, C(11)); 46.08 and 48.83 (2 *d*, C(1),C(6) and C(2),C(5)); 137.58 (*d*, C(3) and C(4)); 218.70 (*s*, C(10)). – MS.: 163 (3), 162 (28, M^+, $C_{11}H_{14}O$), 161 (4), 134 (9), 133 (8), 106 (12), 105 (12), 97 (37), 96 (100), 91 (33), 79 (23), 77 (22), 66 (24), 55 (16).

Cycloaddition to methylcyclopentadiene. At −70° under argon in the dark, 20 ml (*ca.* 250 mmol) of methylcyclopentadiene[7]) were added to a solution of 5 g (25.6 mmol) of $AgBF_4$ in 100 ml of CH_2Cl_2[8]). Subsequently a solution of 5.313 g (28.6 mmol) of 3-chloro-2-pyrrolidinocyclohexene [6] in 50 ml of CH_2Cl_2[8]) was added dropwise at a rate of *ca.* 1 ml/min. The mixture was stirred and allowed to reach RT. within 3 h, afterwards filtered, the solvent evaporated i.V. and the residue extracted 3 times with 100 ml of water. The water extract was washed with benzene and treated for 6½ h under reflux with a solution of 3 g of NaOH in 40 ml of methanol. Neutralization with 2N HCl, work-up with pentane, and chromatography of the yellow oil (*ca.* 3 g) in pentane/ether 3:1 yielded 2.157 g (48%) of **3**–**6** in a ratio of 37:3:54:6[9]). Ketones **5** and **6** were separated by rechromatography in benzene/AcOEt

[7]) Freshly cracked (oil bath temp. *ca.* 200°) and trapped at −70° (s. [7]).

[8]) Filtered through basic alumina.

[9]) Determined by capillary GLC.

Table 2. *Isomerization of the ketones* **3** *and* **7**

Run	Starting material	1 molal *t*-BuOK/ *t*-BuOH [ml]	Time [h]	Yield [%]	Product distribution	
					3 [%]	**7** [%]
1	**3**, 103 mg	2	16	96	53[a])	43[a])
2	**3**, 14 mg	1.5	24	96	51[b])	45[b])
3	**3**, 40 mg	2	168	78	43[a])	35[a])
4	**7**, 22 mg	2.5	24	95	48[b])	47[b])

[a]) Isolated material.
[b]) ^{1}H-NMR. analysis of the filtered (silicagel 'extra pure') reaction mixture.

20:1, and **3** and **5** were obtained by reduction of the remaining mixture, separation of the corresponding alcohols and independent reoxidations with pyridinium chlorochromate.

*Data of 3-methyl-*anti-*tricyclo[4.3.1.1^{2,5}]undec-3-en-10-one* (**3**). – UV.: 286 (30). – IR.: 3048*m*, 1762*w*, 1724*s*, 1697*w*, 1626*w*, 1480*w*, 1455*m*, 1443*m*, 1379*m*, 1343*w*, 1325*m*, 1273*w*, 1217*m*, 1154*m*, 1083*m*, 1047*m*, 1033*w*, 999*w*, 956*w*, 950*w*, 925*w*. – ^{1}H-NMR. (CCl_4): 1.3–2.5 (*m*, 10 H); 1.69 (*d*, *J*(H_3C–C(3), 4)= 1.5, H_3C–C(3)); 2.62 (*d*, *J*(11*endo*, 11*exo*)= 11, H*endo*–C(11)); 2.62 (*m*, $w^1/_2 \approx 10$, H–C(5)); 5.54 (*m*, $w^1/_2 \approx 6$, H–C(4)). – MS.: 178 (1), 177 (3.5), 176 (20, M^+, $C_{12}H_{16}O$), 175 (1.5), 161 (6), 148 (8), 133 (15), 120 (8), 105 (16), 97 (42), 96 (100), 91 (27), 79 (30), 67 (10), 55 (15).

*Data of 2-methyl-*anti-*tricyclo[4.3.1.1^{2,5}]undec-3-en-10-one* (**5**): UV.: 286 (25). – IR.: 3050*m*, 3028*w*, 1723*s*, 1474*w*, 1451*s*, 1376*m*, 1345*s*, 1279*w*, 1267*w*, 1224*w*, 1213*w*, 1193*w*, 1189*w*, 1161*w*, 1131*m*, 1082*m*, 1028*w*, 1009*w*, 994*w*, 931*w*, 922*w*, 912*w*. – ^{1}H-NMR. (CCl_4): 1.13 (*s*, H_3C–C(2)); 1.2–2.5 (*m*, 8 H); 1.48 (*d*×*d*, *J*(11*endo*, 11*exo*)= 11.5 and *J*(5, 11*exo*)= 4, H*exo*–C(11)); 2.59 (*d*, *J*(11*endo*, 11*exo*)= 11.5, H*endo*–C(11)); 2.70 (*m*, $w^1/_2 \approx 10$, H–C(5)); 5.75 (*d*, *J*(3,4)= 5.5, H–C(3)); 5.95 (*d*×*d*, *J*(3,4)= 5.5 and *J*(4,5)= 2.5, H–C(4)). – MS.: 176 (13, M^+, $C_{12}H_{16}O$), 161 (5), 148 (6), 143 (3), 133 (12), 120 (5), 119 (5), 105 (14), 97 (30), 96 (100), 91 (17), 79 (22), 67 (7), 55 (12).

*Data of 2-methyl-*syn-*tricyclo[4.3.1.1^{2,5}]undec-3-en-10-one* (**6**): IR.: 3052*w*, 1732*s*, 1717*s*, 1469*w*, 1445*m*, 1378*w*, 1360*w*, 1294*w*, 1233*w*, 1120*w*, 1093*w*, 866*w*. – ^{1}H-NMR. (CCl_4): 1.20 (*s*, H_3C–C(2)); 1.21 and 1.8–2.6 (2 *m*, 1 H, with $w^1/_2 \approx 12$ and 7 H); 1.42 and 1.49 (*AB*, *J*(11*endo*, 11*exo*)= 10, 2 H–C(11)); 2.88 (*m*, $w^1/_2 \approx 18$, H–C(5)); 6.06 (*d*, *J*(3,4)= 5.5, H–C(3)); 6.29 (*d*×*d*, *J*(3,4)= 5.5 and *J*(4,5)= 3.5, H–C(4)). – MS. (direct, <100°): 176 (10, M^+, $C_{12}H_{16}O$), 161 (6), 148 (6), 133 (13), 105 (19), 97 (33), 96 (100), 91 (18), 79 (22), 67 (7), 55 (11).

Isomerizations of the ketones **3** *and* **7**. The isomerizations **3** ⇄ **7** were carried out in oxygen-free 1 molal *t*-BuOK/*t*-BuOH solutions in sealed tubes at 150°. The results are summarized in *Table 2*.

*Data of 3-methylidene-*anti-*tricyclo[4.3.1.1^{2,5}]undecan-10-one* (**7**): UV.: 291 (25). – IR.: 3072*m*, 3032*w*, 1724*s*, 1688*w*, 1657*w*, 1478*w*, 1454*m*, 1432*w*, 1347*m*, 1309*w*, 1236*w*, 1217*m*, 1139*m*, 1082*m*, 1049*m*, 916*w*, 887*s*, 865*w*. – ^{1}H-NMR. (CCl_4): 1.1–2.5 (*m*, 11 H); 1.39 (*m*, $w^1/_2 \approx 22$, H*exo*–C(11)); 2.58 (*d*×*d*, *J*(11*endo*, 11*exo*)= 12.5 and *J*= 2.5, H*endo*–C(11)); 2.69 ($w^1/_2 \approx 12$, H–C(2)); 4.78 and 4.91 (2 *m*, $w^1/_2 \approx 4$ and 5, H_2C=C(3)). – MS.: 177 (5.5), 176 (35, M^+, $C_{12}H_{16}O$), 175 (0.5), 161 (2), 158 (2), 148 (7), 133 (8), 119 (7), 117 (6), 109 (7), 105 (12), 96 (68), 91 (22), 79 (100), 67 (10), 55 (10), 53 (10).

Synthesis of anti-*tricyclo[4.3.1.1^{2,5}]undec-3-en-10*endo-*ol* (**8**) [4]. To a solution of 100 mg (2.5 mmol) of $LiAlH_4$ in 10 ml abs. ether, 100 mg (0.62 mmol) of **1** were added at 0°, and the mixture was stirred at RT. for 2 h. Hydrolysis with sat. $(NH_4)_2SO_4$-solution, filtration, evaporation of the solvent i.V., and chromatography in pentane/ether 2:1 yielded 92 mg (91%) of **8**. – IR.: 3602*s*, 3044*m*, 1487*w*, 1462*w*, 1448*w*, 1430*w*, 1356*m*, 1339*m*, 1289*w*, 1222*s*, 1087*s*, 1070*s*, 1042*s*, 973*w*, 926*w*, 869*m*. – ^{1}H-NMR. ($CDCl_3$): 1.4–2.3 (*m*, 9 H); 2.59 (*m*, $w^1/_2 \approx 10$, H–C(2) and H–C(5)); 2.60 (*d*, *J*(11*endo*, 11*exo*)= 10, H*endo*–C(11)); 2.96 (*d*, *J*(10, HO–C(10))= 12, HO–C(10)); 3.64 (*d*×*m*, *J*(10, HO–C(10))= 12 and $w^1/_2 \approx 4$, H–C(10)); 6.43 (*m*, $w^1/_2 \approx 4$, H–C(3) and H–C(4)). – ^{13}C-NMR.: 17.84 (*t*, C(8)); 28.63 (*t*, C(7) and C(9)); 37.86 and 45.06 (2 *d*, C(1), C(6) and C(2), C(5)); 38.71 (*t*, C(11)); 75.71 (*d*, C(10)); 140.65 (*d*, C(3) and C(4)). – MS.: 164 (28, M^+, $C_{11}H_{16}O$), 146 (100), 131 (45), 118 (37), 117 (41), 105 (28), 104 (26), 91 (42), 81 (74), 80 (64), 79 (58), 66 (45), 55 (20).

Table 3. *Base- and acid-catalyzed cyclizations of the alcohols* **8**–**11**

Run	Starting material			Reaction conditions			Work-up	Column chromatography		Yield		
		[mg]	[mmol]	Medium [a]	Temp. [°C]	Time [h]	Solvent	Silicagel [g]	Solvent mixture Pentane/ether	Reisolated starting material [mg]	Ether [mg]	
1	**9**	10	0.06	A	90	24	pentane	9[b]	3:1	8.5	**12**	0.5
2	**9**	4	0.02	A	150	24	ether	6[b]	3:1	–	**12**	3.5
3	**11**	6	0.03	A	25	113	pentane	6[b]	3:1	3	**12**	1.5
4	**11**	14	0.08	A	90	6	pentane	–	–	–	**12**	14
5	**8**	7.5	0.05	A	90	24	pentane	6	1:1	6.5	**16**	0.5
6	**8**	16	0.1	A	150	24	pentane	–	–	–	**16**	16
7	**10**	26	0.15	A	150	24	pentane	–	–	–	**17**+**18**[c]	25
8	**9**	18	0.1	B	150	24	pentane	6[b]	6:1	–	**14**	16
9	**11**	14	0.08	B	90	24	pentane	6[b]	3:1	–	**15**	13.5
10	**9**	24	0.13	C	25	2	pentane	6[b]	6:1	–	**13**	19
11	**10**	8	0.05	D	25	16	pentane	–	–	–	**17**+**18**[d]	8

[a]) A: 1 molal *t*-BuOK/*t*-BuOH; B: 1 molal *t*-BuOK/*t*-BuOD; C: 3 ml of 7% DCl/D_2O; D: 1 ml of HCl-saturated $CHCl_3$.

[b]) *Merck* 'extra pure'.

[c]) Composition determined by capillary GLC.: 55% of **17** and 45% of **18**.

[d]) Composition determined by capillary GLC.: 65% of **17** and 35% of **18**.

*Synthesis of 3-methyl-*anti*-tricyclo[4.3.1.1^{2,5}]undec-3-en-10*endo*-ol* (**9**) *and 2-methyl-*anti*-tricyclo-[4.3.1.1^{2,5}]undec-3-en-10*endo*-ol* (**10**). A solution of 283 mg of **3/5** in 5 ml of abs. ether was treated with 76 mg (2 mmol) of $LiAlH_4$. After stirring at RT. for 45 min the mixture was hydrolyzed with sat. $(NH_4)_2SO_4$-solution, filtered, and the solvent evaporated i.V. Chromatography on silicagel 'extra pure' in pentane/ether 3:1 gave 88 mg (31%) of **9**, 72 mg (25%) of **9/10**, and 120 mg (42%) of **10**.

Data of **9**: IR.: 3592*s*, 3032*m*, 1620*w*, 1488*w*, 1463*w*, 1443*m*, 1378*w*, 1357*w*, 1326*w*, 1292*w*, 1268*w*, 1220*m*, 1092*m*, 1072*s*, 1043*s*, 1028*w*, 995*w*, 960*w*, 940*w*, 913*w*, 892*w*. – ^{1}H-NMR. ($CDCl_3$): 1.4–2.35 (*m*, 10 H); 1.89 (*d*, $J(H_3C-C(3),4) = 1.5$, $H_3C-C(3)$); 2.51 (*d*, $J(11endo, 11exo) = 10.5$, *Hendo*–C(11)); 2.56 (*m*, $w^1/_2 \approx 10$, H–C(5)); 2.94 (*d*, $J(10, HO-C(10)) = 11.5$, HO–C(10)); 3.64 (*d*×*m*, $J(10, HO-C(10)) = 11.5$ and $w^1/_2 \approx 4$, H–C(10)); 5.87 (*m*, $w^1/_2 \approx 6$, H–C(4)). – MS.: 178 (76, M^+, $C_{12}H_{18}O$), 160 (74), 145 (62), 131 (30), 120 (35), 119 (38), 107 (32), 106 (24), 105 (26), 97 (35), 93 (60), 91 (56), 81 (100), 80 (97), 67 (24), 55 (24).

Data of **10**: IR.: 3605*s*, 3030*m*, 1490*w*, 1460*m*, 1430*w*, 1379*w*, 1350*w*, 1343*w*, 1298*w*, 1229*s*, 1111*w*, 1061*s*, 949*w*, 932*w*, 919*w*, 870*w*, 665*m*. – ^{1}H-NMR. ($CDCl_3$): 1.21 (*s*, $H_3C-C(2)$); 1.41 (*d*×*d*, $J(11endo, 11exo) = 11$ and $J(5, 11exo) = 4$, *Hexo*–C(11)); 1.5–2.2 (*m*, 8 H); 2.44 (*d*, $J(11endo, 11exo) = 11$, *Hendo*–C(11)); 2.65 (*m*, $w^1/_2 \approx 11$, H–C(5)); 2.99 (*d*, $J(10, HO-C(10)) = 12$, HO–C(10)); 3.74 (*d*×*m*, $J(10, HO-C(10)) = 12$ and $w^1/_2 \approx 4$, H–C(10)); 6.10 (*d*, $J(3,4) = 5.5$, H–C(3)); 6.37 (*d*×*d*, $J(3,4) = 5.5$ and $J(4,5) = 3$, H–C(4)). – MS.: 178 (39, M^+, $C_{12}H_{18}O$), 160 (75), 145 (72), 131 (38), 119 (33), 107 (40), 93 (52), 91 (40), 81 (82), 80 (100), 79 (55), 67 (16), 53 (15).

*Synthesis of 3-methylidene-*anti*-tricyclo[4.3.1.1^{2,5}]undecan-10*endo*-ol* (**11**). A solution of 115 mg (0.65 mmol) of **7** in 5 ml of abs. ether was treated with 38 mg (1 mmol) of $LiAlH_4$ for 1 h at 0° followed by 1 h at RT. Work-up with sat. $(NH_4)_2SO_4$-solution, and chromatography on silicagel 'extra pure' in pentane/ether 2:1 yielded 105 mg (90%) of **11**, m.p. 56° after recrystallization from pentane and sublimation at 50°/11 Torr. – IR.: 3570*m*, 3065*w*, 3030*w*, 1646*w*, 1489*w*, 1462*m*, 1443*w*, 1361*w*, 1295*w*, 1235*w*, 1214*w*, 1094*w*, 1073*s*, 1047*m*, 885*m*. – ^{1}H-NMR. ($CDCl_3$): 1.20 (*d*×*m*, $J(11endo, 11exo) = 12$ and $w^1/_2 \approx 10$, *Hexo*–C(11)); 1.4–2.95 (*m*, 13 H); 2.73 (*d*, $J(10, HO-C(10)) = 8$, HO–C(10)); 3.63 (*d*×*m*, $J(10, HO-C(10)) = 8$ and $w^1/_2 \approx 4$, H–C(10)); 4.92 and 5.10 (2 *m*, $w^1/_2 \approx 4$ and 5, $H_2C=C(3)$). – MS.: 178 (9, M^+), 160 (22), 145 (12), 131 (12), 120 (14), 117 (13), 105 (13), 92 (100), 79 (32), 67 (15), 53 (12).

$C_{12}H_{18}O$ (178.28) Calc. C 80.85 H 10.18% Found C 80.79 H 10.18%

Cyclizations of the alcohols **8**–**11**. a) *Base-catalyzed cyclizations.* Argon atmosphere, sealed tubes, *ca.* 1 molal oxygen-free[10]) solutions of *t*-BuOK in *t*-BuOH or *t*-BuOD, respectively. The concentration of starting material in *t*-BuOH/*t*-BuOH(D) solution was 0.05 mmol/ml. Work-up with ether or pentane. The results are listed in *Table 3*.

b) *Acid-catalyzed cyclizations* (see *Table 3*). – *Data of 6-methyl-7-oxatetracyclo[6.4.0.0^{2,6}.0^{4,9}]-dodecane* (**12**): IR.: 3018*m*, 1494*w*, 1464*w*, 1452*w*, 1441*w*, 1377*s*, 1350*w*, 1321*m*, 1307*w*, 1275*w*, 1258*w*, 1189*m*, 1170*m*, 1155*w*, 1105*w*, 1099*w*, 1056*s*, 1050*w*, 1036*w*, 1008*w*, 965*m*, 953*w*, 935*w*, 915*m*, 888*m*, 862*w*. – ^{1}H-NMR. (CCl_4): 1.1–2.25 (*m*, 12 H); 1.28 (*s*, $H_3C-C(6)$); 1.32 (*d*×*d*, $J(5endo, 5exo) = 11$ and $J(4, 5exo) = 3.5$, *Hexo*–C(5)); 2.33 (*d*×*d*, $J(3endo, 3exo) = 12$ and $J(3endo, 5endo) = 3.5$, further $J \approx 1$, *Hendo*–C(3)); 3.70 (*m*, $w^1/_2 \approx 9$, H–C(8)). – ^{1}H-NMR. ($CDCl_3$, 360 MHz): 1.32 (*m*, $w^1/_2 \approx 24$, among others $J(3endo, 3exo) = 12$ and $J(2, 3exo) = 6$, *Hexo*–C(3)); 1.35–1.5, 1.6–2.0 and 2.22 (3 *m*, 1 H, 6 H and 1 H); 1.40 (*s*, $H_3C-C(6)$); 1.41 (*d*×*d*, $J(5endo, 5exo) = 11.2$ and $J(4, 5exo) = 3.7$, *Hexo*–C(5)); 1.84 (*d*×*d*, $J(5endo, 5exo) = 11.2$ and $J(3endo, 5endo) = 3.5$, *Hendo*–C(5)); 2.07 (*t*-like *m*, $J(1,2) \approx J(2, 3exo) \approx 6$ and $w^1/_2 \approx 4$, H–C(2)); 2.18 (*m*, $w^1/_2 \approx 11$, H–C(4)); 2.39 (*d*×*d*, $J(3endo, 3exo) = 12$ and $J(3endo, 5endo) = 3.5$, further $J \approx 1$, *Hendo*–C(3)); 3.88 (*m*, $w^1/_2 \approx 10$, H–C(8)). – MS.: 179 (4), 178 (24, M^+, $C_{12}H_{18}O$), 135 (5), 120 (100), 92 (30), 91 (30), 79 (15), 43 (18).

*Data of 5*exo*-deuterio-6-methyl-7-oxatetracyclo[6.4.0.0^{2,6}.0^{4,9}]dodecane* (**13**): IR.: 3018*m*, 2160*w*, 1493*w*, 1461*m*, 1442*w*, 1377*m*, 1351*w*, 1314*w*, 1301*w*, 1294*w*, 1190*w*, 1172*m*, 1154*w*, 1132*m*, 1100*m*, 1056*s*, 1038*w*, 985*w*, 970*w*, 952*w*, 930*m*, 899*w*, 883*m*. – ^{1}H-NMR. (CCl_4): main difference to **12**: 1.32 (signal of *Hexo*–C(5) disappeared). – MS.: 180 (3), 179 (20, M^+, $C_{12}H_{17}DO$), 178 (1.5), 136 (4), 120 (100), 92 (28), 91 (28), 79 (12), 43 (18).

*Data of 5*endo*-deuterio-6-deuteriomethyl-7-oxatetracyclo[6.4.0.0^{2,6}.0^{4,9}]dodecane* (**14**): IR.: 3015*m*, 2180*w*, 1493*w*, 1461*m*, 1441*w*, 1420*w*, 1369*w*, 1350*m*, 1321*m*, 1309*w*, 1187*w*, 1132*w*, 1098*m*, 1051*s*,

[10]) Argon was bubbled through the solution for 15 min.

1030*w*, 995*w*, 952*w*, 925*w*, 880*w*. – ^{1}H-NMR. ($CDCl_3$, 360 MHz): main differences to **12**: 1.40 (*m*, $H_2CD-C(6)$); 1.41 (*d*, $J(4,5exo)=3.7$, *Hexo*–C(5)); 1.84 (signal of *Hendo*–C(5) disappeared); 2.39 (*d*, $J(3endo,3exo)=12$, further $J\approx 1$, *Hendo*–C(3)). – MS.[5]): 182 (1), 181 (7), 180 (30), 179 (10), 178 (1), 120 (100).

Data of 6-deuteriomethyl-7-oxatetracyclo[6.4.0.0^{2,6}.0^{4,9}]dodecane (**15**): IR.: 3018*w*, 2180*w*, 1490*w*, 1462*w*, 1439*w*, 1418*w*, 1368*w*, 1349*w*, 1323*w*, 1307*w*, 1188*w*, 1150*w*, 1134*w*, 1095*w*, 1070*m*, 1052*s*, 1031*w*, 997*w*, 962*w*, 944*w*, 907*w*. – ^{1}H-NMR. (CCl_4): main difference to **12**: 1.28 (*m*, $H_2CD-C(6)$). – MS.: 180 (2), 179 (19, M^+, $C_{12}H_{17}DO$), 178 (3), 135 (4), 120 (100), 92 (27), 91 (25), 79 (12), 44 (11).

Data of 7-oxatetracyclo[6.4.0.0^{2,6}.0^{4,9}]dodecane (**16**): IR.: 3022*m*, 1494*w*, 1462*m*, 1439*w*, 1370*w*, 1349*w*, 1298*w*, 1232*w*, 1183*w*, 1164*w*, 1124*w*, 1094*m*, 1069*w*, 1044*s*, 1017*w*, 991*w*, 965*m*, 944*w*, 937*w*, 902*m*, 855*w*, 846*w*. – ^{1}H-NMR. (CCl_4): 1.0–2.2 (*m*, 9 H); 1.16 (*d*×*d*×*m*, among others $J(3endo,3exo)=12$ and $J(2,3exo)=6$, *Hexo*–C(3)); 1.34 (*d*×*t*, $J(5endo,5exo)=11$ and $J(4,5exo)=J(5exo,6)=4$, *Hexo*–C(5)); 1.83 (*d*×*d*, $J(5endo,5exo)=11$ and $J(3endo,5endo)=3.5$, *Hendo*–C(5)); 2.3–2.6 (*m*, H–C(2)); 2.36 (*d*×*d*, $J(3endo,3exo)=12$ and $J(3endo,5endo)=3.5$, *Hendo*–C(3)); 3.66 (*m*, $w^1/_2\approx 8$, H–C(8)); 4.43 (*d*×*d*×*d*, $J(2,6)=5$, $J(5exo,6)=4$ and $J(4,6)=1.5$, H–C(6)). – MS.: 165 (2), 164 (20, M^+, $C_{11}H_{16}O$), 146 (2), 135 (2), 121 (14), 120 (100), 105 (6), 92 (22), 91 (26), 79 (16), 67 (10), 55 (5), 53 (5).

Data of 2-methyl-7-oxatetracyclo[6.4.0.0^{2,6}.0^{4,9}]dodecane (**17**): IR.: 3018*m*, 1492*w*, 1463*m*, 1451*w*, 1376*w*, 1367*w*, 1350*w*, 1334*w*, 1298*m*, 1263*w*, 1122*w*, 1094*m*, 1073*w*, 1038*s*, 1019*w*, 1007*w*, 971*m*, 949*m*, 936*m*, 909*m*, 859*w*, 845*w*. – ^{1}H-NMR. (CCl_4): 1.02 (*d*×*m*, $J(3endo,3exo)=12$ and $w^1/_2\approx 6$, *Hexo*–C(3)); 1.10 (*s*, $H_3C-C(2)$); 1.2–2.0 (*m*, 9 H); 1.45 (*d*×*t*, $J(5endo,5exo)=11.5$ and $J(4,5exo)=J(5exo,6)=4$, *Hexo*–C(5)); 2.11 (*m*, $w^1/_2\approx 10$, H–C(4)); 2.25 (*d*×*d*, $J(3endo,3exo)=12$ and $J(3endo,5endo)=3$, further $J\approx 1$, *Hendo*–C(3)); 3.73 (*m*, $w^1/_2\approx 9$, H–C(8)); 3.88 (*d*×*d*, $J(5exo,6)=4$ and $J(4,6)=2$, H–C(6)). – MS.: 179 (3), 178 (18, M^+, $C_{12}H_{18}O$), 134 (100), 119 (34), 105 (33), 91 (19), 79 (13), 67 (9).

Data of 4-methyl-7-oxatetracyclo[6.4.0.0^{2,6}.0^{4,9}]dodecane (**18**): IR.: 3014*m*, 1491*w*, 1461*m*, 1442*w*, 1373*m*, 1343*w*, 1296*w*, 1265*w*, 1218*w*, 1143*w*, 1116*w*, 1092*w*, 1044*s*, 992*w*, 973*w*, 994*m*, 913*w*, 897*w*, 881*w*, 862*w*, 849*w*. – ^{1}H-NMR. (CCl_4): 0.96 (*s*, $H_3C-C(4)$); 1.00 (*m*, $w^1/_2\approx 22$, *Hexo*–C(3)); 1.17 (*d*×*d*, $J(5endo,5exo)=11.5$ and $J(5exo,6)=4$, *Hexo*–C(5)); 1.2–2.1 (*m*, 8 H); 1.61 (*d*×*d*, $J(5endo,5exo)=11.5$ and $J(3endo,5endo)=3.5$, *Hendo*–C(5)); 2.14 (*d*×*d*, $J(3endo,3exo)=12$ and $J(3endo,5endo)=3.5$, *Hendo*–C(3)); 2.46 (*qa*-like *m*, $w^1/_2\approx 18$, H–C(2)); 3.68 (*m*, $w^1/_2\approx 8$, H–C(8)); 4.41 (*d*×*d*, $J(2,6)=5$ and $J(5exo,6)=4$, H–C(6)). – MS.: 179 (10), 178 (60, M^+, $C_{12}H_{18}O$), 163 (16), 135 (39), 134 (100), 119 (40), 105 (37), 91 (26), 81 (30), 79 (31), 67 (20).

*Synthesis of 3-methyl-*anti*-tricyclo[4.3.1.1^{2,5}]undec-3-ene-10-*endo*-yl acetate* (**19**). Treatment of 38 mg (0.21 mmol) of **9** with 4 ml of Ac_2O/pyridine 1:1 yielded 39 mg (84%) of **19**. – IR.: 3030*w*, 1726*s*, 1633*w*, 1440*m*, 1366*s*, 1257*s*, 1232*s*, 1060*w*, 1032*s*, 883*w*. – ^{1}H-NMR. (CCl_4): 1.4–2.3 (*m*, 10 H); 1.73 (*d*, $J(H_3C-C(3),4)=1$, $H_3C-C(3)$); 1.85 (*s*, $CH_3COO-C(10)$); 2.42 (*d*, $J(11endo,11exo)=10$, *Hendo*–C(11)); 2.44 (*m*, $w^1/_2\approx 10$, H–C(5)); 4.62 (*m*, $w^1/_2\approx 4$, H–C(10)); 5.49 (*m*, $w^1/_2\approx 6$, H–C(4)). – MS.: 220 (18, M^+, $C_{14}H_{20}O_2$), 177 (5), 160 (100), 145 (43), 131 (25), 119 (17), 117 (21), 106 (17), 105 (18), 93 (31), 92 (26), 91 (35), 81 (46), 80 (37), 79 (39), 77 (25), 43 (58).

*Synthesis of 3*exo*-hydroxy-4*endo*-methyl-*anti*-tricyclo[4.3.1.1^{2,5}]undec-10*endo*-yl acetate* (**20**). A *ca.* 1M solution of BH_3 in THF (0.2 ml) was added dropwise to a solution of 28 mg (0.12 mmol) of **19** in 2 ml of abs. THF at 0°. After 1½ h of stirring at RT., 0.5 ml of H_2O, 0.5 ml of 3N NaOH and 0.2 ml of 30% H_2O_2 solution were added, and the mixture was stirred at 50° for 1 h. Extraction with ether and chromatography in cyclohexane/AcOEt 1:1 afforded 22 mg (77%) of **20**. – IR.: 3618*m*, 3450 br. *w*, 3030*w*, 3000*w*, 1732*s*, 1450*w*, 1367*m*, 1253*w*, 1233*s*, 1042*m*, 1027*w*, 999*m*. – MS.: 178 (25, M^+ ($C_{14}H_{22}O_3$) – 60), 163 (5), 160 (8), 147 (31), 123 (46), 121 (41), 120 (100), 91 (40), 81 (28), 79 (33), 67 (24), 55 (21), 43 (55).

*Synthesis of 4*endo*-methyl-*anti*-tricyclo[4.3.1.1^{2,5}]undecan-3*exo*,10*endo*-diol* (**21**). A solution of 20 mg (0.09 mmol) of **20** in 2 ml of 2N aq. NaOH/CH_3OH 1:1 was stirred at RT. for 18 h. Work-up with ether yielded 16 mg (91%) of **21**. – IR. (KBr): 3035*w*, 3005*w*, 1470*w*, 1382*w*, 1352*m*, 1295*w*, 1073*s*, 1046*w*, 1004*s*, 961*w*, 941*w*, 926*w*. – MS.: 178 (48, M^+ ($C_{12}H_{20}O_2$) – 18), 121 (27), 120 (100), 92 (24), 91 (34), 81 (18), 79 (24), 67 (12), 55 (9).

*Synthesis of 5*endo*-methyl-7-oxatetracyclo[6.4.0.0^{2,6}.0^{4,9}]dodecane* (**22**). A suspension of 15 mg (0.08 mmol) of **21** and **5** mg of *p*-TsOH in 4 ml of benzene was stirred at RT. for 30 min. Work-up with ether, washing twice with 1N $NaHCO_3$ and once with NaCl-solution followed by

chromatography in pentane/ether 3:1 gave 11 mg (81%) of **22**. – IR.: 3025*m*, 1462*w*, 1373*w*, 1300*w*, 1095*m*, 1049*s*, 947*m*, 916*m*, 893*m*. – ^{1}H-NMR. (CCl_4): 1.16 (*d*, *J*(5, H_3C–C(5))=6, H_3C–C(5)); 1.18 (*m*, $w^1/_2 \approx 24$, H*exo*–C(3)); 1.3–2.2 (*m*, 10 H); 2.32 (*d*, *J*(3*endo*,3*exo*)=12, H*endo*–C(3)); 2.49 (*m*, $w^1/_2 \approx 22$, H–C(2)); 3.65 (*m*, $w^1/_2 \approx 8$, H–C(8)); 4.12 (*m*, $w^1/_2 \approx 10$, H–C(6)). – MS.: 178 (53, M^+, $C_{12}H_{18}O$), 163 (3), 160 (3), 120 (100), 92 (32), 91 (36), 79 (24), 67 (14), 41 (17).

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