# Nucleophilic Addition to C=C Bonds

Part X[1])

## Influence of Alkyl Substituents in Allylic Position and at the C=C Bond on the Regioselectivity and the Rate of Base-Catalyzed Intramolecular Cyclizations of Unsaturated Alcohols

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Dedicated to Professor *Dieter Seebach* on the occasion of his 65th birthday

A mechanistic model is presented for the base-catalyzed intramolecular cyclization of polycyclic unsaturated alcohols of type **A** to ethers **D** (*Scheme 1*). The alkoxide anion **B** is formed first in a fast acid-base equilibrium. For the subsequent reaction to **D**, a carbanion-like transition state **C** is proposed. This mechanism is in full agreement with our results regarding the influence of substituents on the regioselectivity and the rate of cyclization. We studied the effect of alkyl substituents in allylic position (alkylated endocylic olefinic alcohols **1**–**3**) and, especially, at the exocyclic double bond (**12**–**15**). The fastest cyclization ($k_{rel} = 1$) is **12** → **16**, which proceeds *via* a primary carbanion-like transition state (**E**: $R^1 = R^2 = H$). The corresponding processes **13** → **17** and **14** → **17** are characterized by a less-stable secondary carbanion-like transtition state (**E**: $R^1 = Me$, $R^2 = H$, or *vice versa*) and are slower by a factor of $10^4$. The slowest reaction ($k_{rel}$ *ca.* $10^{-6}$) is the cyclization **15** → **18** *via* a tertiary carbanion-like transition state (**E**: $R^1 = R^2 = Me$).

**1. Introduction.** – Based on kinetic data, we present a mechanistic model for the base-catalyzed intramolecular cyclization of olefinic alcohols of the general type **A** to ethers **D** (*Scheme 1*). The spatial proximity of the reacting centers allows the primarily formed alkoxide anion **B** to add to a C=C bond bearing no electron-attracting substituents. Thereby, a carbanion-like transition state **C** has been proposed [1][3]). As a consequence, alkyl substituents in allylic position, and especially such at the double bond itself, are expected to strongly influence the regioselectivity and the rate of cyclization. This is fully confirmed by the hereby described studies on the behavior of the three bridgehead-alkylated endocyclic olefinic alcohols **1**–**3** relative to their unsubstitued analogue **4** (*cf. Scheme 2*), as well as the behaviour of the four differently substituted alcohols **12**–**15** with exocyclic C=C bonds (*cf. Scheme 3*).

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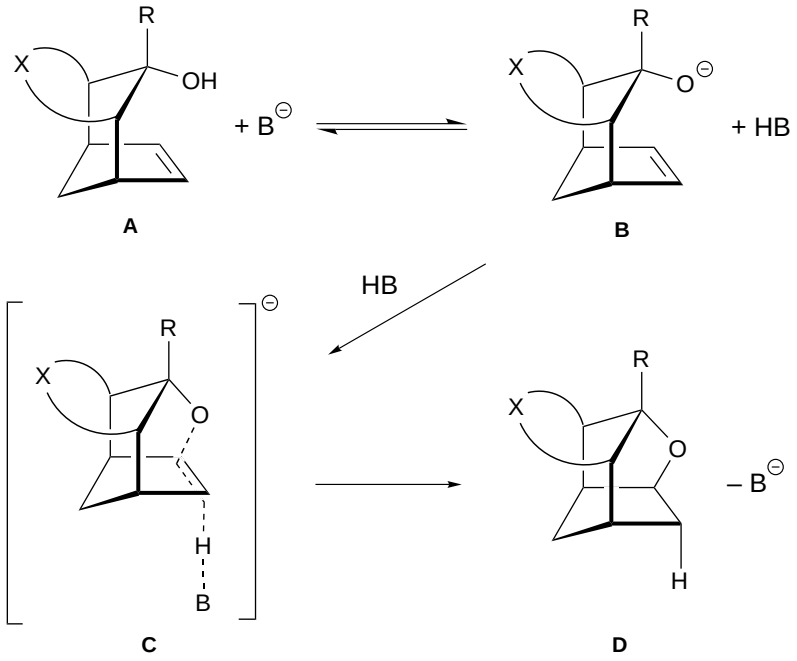
[1]) Part IX: [1].

[2]) Present adress: *Syngenta Crop Protection* AG, CH-4002 Basel.

[3]) For related examples in analogous systems, see, *e.g.*, [2].

*Scheme 1*




**2. Results and Discussion.** – 2.1. *Bridgehead-Alkylated Endocyclic Olefins* (*Scheme 2*). The product distributions in the base-catalyzed cyclizations of **1**[4]), **2**, and **3** are listed in *Table 1* (*Entries 1*, *3*, and *5*). The results suggest a transition state of type **E**, *i.e.*, protonation by the solvent preferentially occurs at the sterically less-hindered $sp^2$-C-atom, and regioselectivity increases with increasing size of the alkyl substituent R.

The relative cyclization rates ($k_{rel}$) of **1**–**3** compared to the unsubstituted analogue **4** ($k_{rel} = 1$) are listed in *Table 2* (*Entries 1–3* and *4*, resp.). The rates of formation of the *C*(2)-alkylated ethers **5** (R = Me) and **7** (R = Et) are comparable. However, the formation of **9** (R = i-Pr) is approximately twice as fast. This seems to be a consequence of the sterically hindered solvation in the transition state caused by the bulky isopropyl group.

In contrast, but to be expected for a carbanion-like transition state of type **C**, the relative rates of formation of the *C*(4)-alkylated ethers **8** (R = Et) and **10** (R = i-Pr) are similar and significantly smaller than for **6** (R = Me). The total relative cyclization rate $k_{rel}$ (tot) is practically not influenced by the substitution pattern at C(2), as shown by

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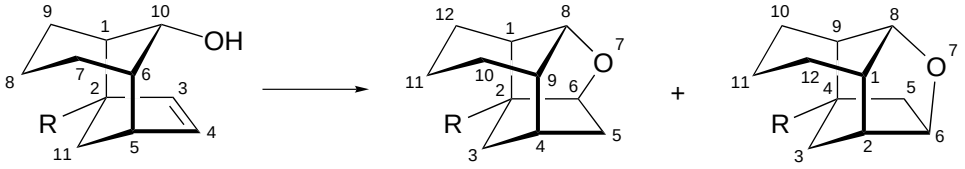
[4]) The alcohols **1**, **4**, **12** and their corresponding ethers **5** and **6**, as well as **11** and **16**, resp., have already been described [3].

*Scheme 2*



**1** R = Me
**2** R = Et
**3** R = i-Pr
**4** R = H

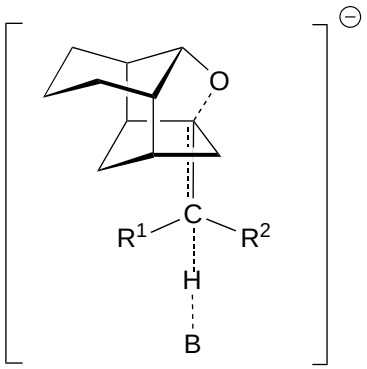
**5** R = Me
**7** R = Et
**9** R = i-Pr
**11** R = H

**6** R = Me
**8** R = Et
**10** R = i-Pr

Table 1. *Base- and Acid-Catalyzed Cyclizations of Compounds* **1**–**3**

| *Entry* | Reactant | Condition | | | | Products | Ratio[a]) | Yield[b]) |
|---|---|---|---|---|---|---|---|---|
| | | Base | Acid | *T* [°] | Time [h] | | | |
| *1* | **1** R = Me | [c]) | | 150 | 24 | **5**/**6** | 55 : 45 | quant. |
| *2* | **1** R = Me | | [d]) | r.t. | 16 | **5**/**6** | 65 : 35 | quant. |
| *3* | **2** R = Et | [c]) | | 160 | 16 | **7**/**8** | 68 : 32 | 98% |
| *4* | **2** R = Et | | [e]) | r.t. | 25 | **7**/**8** | 80 : 20 | 87% |
| *5* | **3** R = i-Pr | [c]) | | 160 | 16 | **9**/**10** | 85 : 15 | quant. |
| *6* | **3** R = i-Pr | | [e]) | r.t. | 16 | **9**/**10** | 95 : 5 | 90% |

[a]) Determined by capillary GLC. [b]) Isolated. [c]) *t*-BuOK/*t*-BuOH (1.19M). [d]) HCl/$CHCl_3$. [e]) HCl/$Et_2O$.



**E**

the corresponding values for **4** (R = H), **1** (R = Me), and **2** (R = Et). A somewhat higher total rate is only observed for **3** (R = i-Pr). This can, again, be ascribed to different solvations in the transition state.

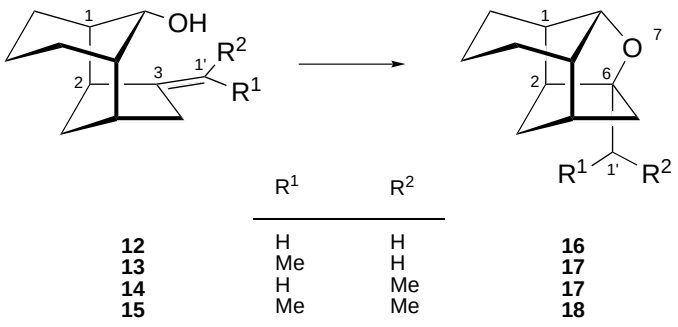
For comparison, compounds **1**–**3** were also cyclized under acidic conditions (*cf. Table 1*, *Entries 2*, *4*, and *6*). Here, ether formation proceeds more regioselectively. The first step of these electrophilic additions is the protonation of the C=C bond, and hyperconjugative effects probably come into play [4][5].

Table 2. *Relative Cyclization Rates of the Bridgehead-Substituted Alcohols* **1**–**4** *in* t-*BuOK*/t-*BuOH at 130°*

| *Entry* | Reactant | Products | | |
|---|---|---|---|---|
| | | R–C(2) ($k_{rel}$) | R–C(4) ($k_{rel}$) | $k_{rel}$ (tot) |
| *1* | **1** R = Me | **5** (0.69) | **6** (0.50) | 1.19 |
| *2* | **2** R = Et | **7** (0.66) | **8** (0.30) | 0.96 |
| *3* | **3** R = i-Pr | **9** (1.29) | **10** (0.29) | 1.58 |
| *4* | **4** R = H | **11** | | 1 |

2.2. *Alkylated Exocyclic Olefins* (*Scheme 3*). The unsaturated alcohols **12** and **13**–**15** possess the same polycyclic C skeleton and differ only in the substitution pattern of the exocyclic double bond. The relative rates of base-catalyzed ether formation are listed in *Table 3* (*Entries 1–4*). For comparison, the relative cyclization rate for the conversion **4** → **11** (*Entry 5*) is also included. As expected, the rates strongly depend on the substitution pattern at the C-atom that becomes negatively charged in the transition state **E**. The fastest cyclization ($k_{rel} = 1$) is **12** → **16**, which proceeds *via* a primary carbanion-like transition state (**E**: $R^1 = R^2 = H$). The corresponding processes **13** → **17** and **14** → **17**, which are characterized by a less stable secondary carbanion-like transition state (**E**: $R^1$ = Me, $R^2$ = H, or $R^1$ = H, $R^2$ = Me) are four orders of magnitude slower. Finally, the cyclization **15** → **18**, which proceeds *via* a tertiary carbanion-like transition state (**E**: $R^1 = R^2$ = Me), is the slowest ($k_{rel}$ *ca.* $10^{-6}$).

*Scheme 3*




| | $R^1$ | $R^2$ | |
|---|---|---|---|
| **12** | H | H | **16** |
| **13** | Me | H | **17** |
| **14** | H | Me | **17** |
| **15** | Me | Me | **18** |

Table 3. *Relative Cyclization Rates of Compounds* **12**–**15** *and* **4** *in* t-*BuOK*/t-*BuOH at 130°*

| *Entry* | Reactant | Product | $k_{rel}$ |
|---|---|---|---|
| *1* | **12** | **16** | 1 |
| *2* | **13** | **17** | $1.8 \cdot 10^{-4}$ |
| *3* | **14** | **17** | $2.7 \cdot 10^{-4}$ |
| *4* | **15** | **18** | *ca.* $10^{-6}$ |
| *5* | **4** | **11** | $4.5 \cdot 10^{-3}$ |

Comparison of the rates of ether formation in the case of **13** and **14** (exocyclic C=C bond) relative to **4** (endocyclic C=C bond) allows one to assess the influence of steric compression on the cyclization rate for compounds with a very similar substitution

pattern at the reacting centers. Although, in each case, cyclization proceeds *via* a secondary carbanion-like transition state, **4** cyclizes *ca.* 10 times faster than **13** and **14**. This reflects the higher steric compression between the OH group and the C=C bond in **4**. The small difference in reactivity of **13** and **14** is probably due to different ground-state strains, a consequence of the (*E*)- *vs.* (*Z*)-configured C=C bonds. Models show a much stronger interaction in **14** between the (*Z*)-configured Me group and H–C(2) at the bridgehead than between the (*E*)-configured Me group and $H_{endo}$–C(4) in **13**[5]).

**3. Synthesis of the Unsaturated Alcohols.** – Addition of 1-(6-chlorocyclohex-1-enyl)pyrrolidine (**19**) [6] to ethylcyclopentadiene (**20** ⇄ **21** ⇄ **22**) [7] in the presence of $AgBF_4$ [8] followed by hydrolysis of the intermediary pyrrolidinium salts afforded 39% of a 58:32:6:4 mixture of **23**/**24**/**25**/**26** (partially separable by column chromatography (CC) into mixtures of **23**/**24** and **24**/**25**) (*Scheme 4*). Analogous reaction with isopropylcyclopentadiene (**27** ⇄ **28** ⇄ **29**) [9] yielded 45% of a 41:33:6:4:16 mixture of **30**/**31**/**32**/**33**/**34**[6]) (partially separable by CC into mixtures of **31**/**32**/**33** and **30**/**34**).

Treatment of **23**/**24** with $LiAlH_4$ yielded 81% of the two alcohols **2** and **35**, which were separated and re-oxidized with pyridinium chlorochromate to yield pure **23** (34%) and **24** (76%), respectively. Analogously, the mixture **24**/**25** was reduced (87%) to the corresponding alcohols **35** and **36**.

The isomerization of the endocyclic C=C bond of **24** was achieved by treatment with *t*-BuOK/*t*-BuOH at 160° for 72 h, which resulted in a 2:1 mixture of **37**/**38** (thermodynamic equilibrium). The former could partially be separated chromatographically. The latter was characterized in the mixture with **37**. Reduction of **37**/**38** with $LiAlH_4$ afforded 68% of a mixture of the alcohols **13** and **14** from which **13** was partially separated by CC (*Scheme 5*). For cyclization experiments, **14** was used in a mixture with **13**.

The configurations of the C=C bonds in **13** and **14** were assigned on the basis of $^{13}$C-NMR measurements. In the spectrum of **13**, with the (*E*)-configured Me group oriented towards C(4), the bridgehead C(2)-atom appears as a dublett at $\delta$ 47.30 ppm, and C(4) as a triplett at 34.36 ppm. In **14**, with the (*Z*)-configured Me group oriented towards C(2), C(2) appears as a dublett at 39.19 ppm, which reflects steric interaction with the Me group. The signal for the less-deshielded C(4)-atom appears as a triplett at 37.29 ppm.

$LiAlH_4$-promoted reduction of the mixture of the ketones **30**/**34** and **31**/**32**/**33** yielded a separable mixture of the corresponding alcohols **3**, **39** (97%) and **40**–**42** (81%), respectively. Individual pyridinium chlorochromate (PCC) oxidations of these compounds led to the corresponding ketones **30** (60%), **34** (71%), **31** (73%), **32** (69%), and **33** (62%) (*Scheme 5*).

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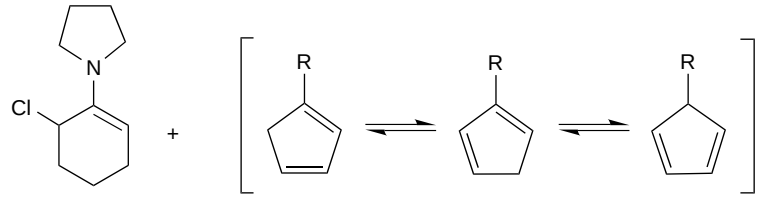
[5]) The product distribution of these base-catalyzed isomerization of **24** to the ketones **37** and **38** (the precursors of alcohols **13** and **14**, resp.) under thermodynamic control confirms the higher stability of **37** with the (*E*)-configured Me group directed towards C(4), *cf. Chapt. 3* and *Exper. Part.*

[6]) The formation of **34** is noteworthy since it implies a formal [3+4] cycloaddition corresponding to an overall oxidation of isopropylcyclopentadiene.

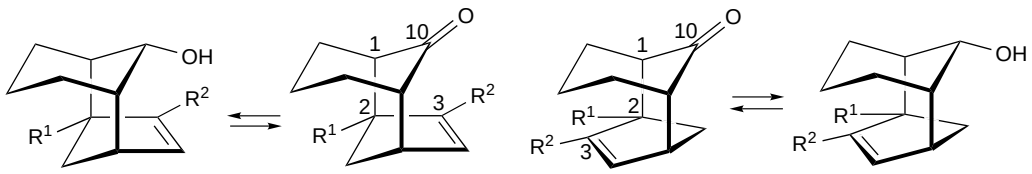
*Scheme 4*



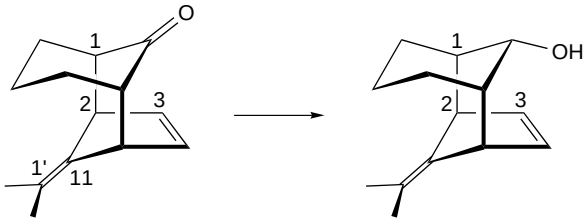

**19** **20** **21** **22** R = Et

**27** **28** **29** R = i-Pr

1. $AgBF_4$, $CH_2Cl_2$, –78°
2. aq. NaOH/MeOH, reflux

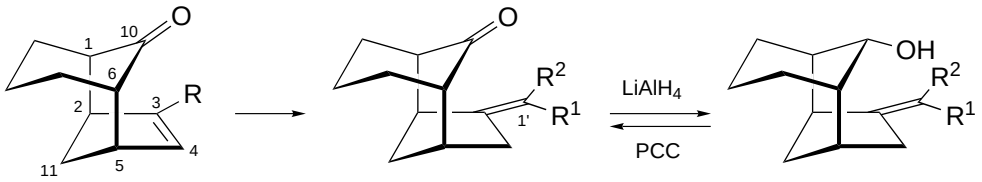



| | | $R^1$ | $R^2$ | | |
|---|---|---|---|---|---|
| **2** | **23** | Et | H | **25** | **36** |
| **35** | **24** | H | Et | **26** | |
| **3** | **30** | i-Pr | H | **32** | **41** |
| **40** | **31** | H | i-Pr | **33** | **42** |




**34** **39**

*Scheme 5*




| | | $R^1$ | $R^2$ | |
|---|---|---|---|---|
| **24** R = Et | **37** | Me | H | **13** |
| | **38** | H | Me | **14** |
| **31** R = i-Pr | **43** | Me | Me | **15** |

Irreversible isomerization of ketone **31** by *t*-BuOK/*t*-BuOH at 160° for 18 h led to **43** with an exocyclic C=C bond[7]). This compound was quantitatively reduced to the alcohol **15** by exposure to $LiAlH_4$.

## Experimental Part

1. *General*. Oxygen-free solns. were generated by bubbling Ar gas for 15 min through the medium. Product distributions were determined by capillary gas chromatography (GC) at 150–170°: Analytical data for the prepared compds. can be found at the end of the *Exper. Part*. For all other details, including kinetic measurements, see [1].

2. *Cylization Procedures* (*cf. Tables 1–3*). Base-catalyzed cyclizations: Ar atmosphere, sealed tubes, *ca.* 1.2 molal of $O_2$-free solns. in *t*-BuOK/*t*-BuOH. Representative examples of base- and acid-catalyzed cyclizations are given below.

*Treatment of* **2** *with* t-*BuOK*/t-*BuOH*. An $O_2$-free soln. of 130 mg (0.68 mmol) of **2** in 1.5 ml of 1.19 molal *t*-BuOK/*t*-BuOH was heated for 16 h in a sealed tube at 160°. Workup with pentane and CC ($SiO_2$; pentane/$Et_2O$ 6:1) yielded 48 mg (37%) of **7**, 5 mg (4%) of **8**, and 75 mg (58%) of **7**/**8** in a ratio of 52:48.

*Treatment of* **2** *with HCl*. A soln. of 30 mg (0.16 mmol) of **2** in 4 ml of $Et_2O$ was treated with 1 ml of HCl-sat. MeOH and was stirred for 25 h at r.t. $Et_2O$ was added, and the org. phase was washed twice with 1N $NaHCO_3$ and twice with sat. NaCl soln. CC ($SiO_2$; pentane/$Et_2O$ 6:1) to afford 11 mg (37%) of **7**, 1 mg (3%) of **8**, and 14 mg (47%) of **7**/**8** in a ratio of 2:1.

*Treatment of* **3** *with* t-*BuOK*/t-*BuOH*. An $O_2$-free soln. of 39 mg (0.19 mmol) of **3** in 2 ml of 1.19 molal *t*-BuOK/*t*-BuOH was heated for 16 h in a sealed tube at 160°. Workup with pentane and CC ($SiO_2$; pentane/$Et_2O$ 6:1) yielded 26 mg (67%) of **9** and 12 mg (58%) of **9**/**10** in a ratio of 1:1.

*Treatment of* **3** *with HCl*. A soln. of 10 mg (0.05 mmol) of **3** in 2 ml of $Et_2O$ was treated with 1 ml of HCl-sat. MeOH and was stirred for 16 h at r.t. Workup and CC ($SiO_2$; pentane/$Et_2O$ 6:1) afforded 9 mg (90%) of **9**/**10** in a ratio of 95:5.

*Treatment of* **15** *with* t-*BuOK*/t-*BuOH*. An $O_2$-free soln. of 10 mg (0.05 mmol) of **15** in 1 ml of 1.19M *t*-BuOK/*t*-BuOH was heated for 20 h in a sealed tube at 190°. Workup with pentane and CC ($SiO_2$; pentane/$Et_2O$ 3:1) yielded 9 mg (90%) of **18**.

3. *Syntheses. Cycloaddition to Ethylcyclopentadiene*. At −70° under Ar in the dark, *ca.* 30 ml (*ca.* 260 mmol) of ethylcyclopentadiene [7][8]) were added to a soln. of 5 g (25.6 mmol) of $AgBF_4$ in 100 ml of

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7) On longer heating, **43** and **44** tend to decompose, the former faster than the latter. This allowed us to isolate **44** as a single compound without separating the mixture.

8) Freshly cracked (b.p. 95–105°, salt-bath temp. 220–240°), trapped at −70°.

$CH_2Cl_2$[9]). A soln. of *ca.* 6 g (*ca.* 32 mmol) of **19** [6] in 50 ml of acid-free $CH_2Cl_2$[9]) was added dropwise over 1 h. The mixture was stirred, allowed to reach r.t. within 3 h, filtered through *Celite*, and the solvent was evaporated *in vacuo*. The residue was extracted several times with $H_2O$. The aq. extracts were combined, washed with benzene (3×), treated with a soln. of 4 g of NaOH in 40 ml of MeOH, and refluxed for 6 h. Neutralization with 2N aq. HCl soln., workup with pentane and CC ($SiO_2$; pentane/$Et_2O$ 3:1) yielded 1.9 g (39%) of **23**/**24**/**25**/**26** in a ratio of 58:32:6:4. CC in pentane/$Et_2O$ 6:1 yielded mixtures of **23**/**24** and **24**/**25**, resp.

*Cycloaddition to Isopropylcyclopentadiene.* Following the above procedure with 5 g (25.6 mmol) of $AgBF_4$, 6.2 g (33 mmol) of **19** [6], and 29 g (269 mmol) of isopropylcyclopentadiene [9], 1.96 g (45%) of **30**/**31**/**32**/**33**/**34** in a ratio of 41:33:6:4:16 were obtained. Repeated CC ($SiO_2$; pentane/$Et_2O$ 6:1) yielded mixtures of **32**/**32**/**33** and **30**/**34**, resp.

*Reduction of* **23**/**24** *with* $LiAlH_4$. A soln. of 1.75 g (9.2 mmol) of **23**/**24** in 15 ml of anh. $Et_2O$ was treated at 0° with 400 mg (10.5 mmol) of $LiAlH_4$ and stirred for 15 min at 0° and for 30 min at r.t. Usual workup and CC ($SiO_2$; pentane/$Et_2O$ 3:1) yielded 1.01 g (57%) of **2** and 414 mg (24%) of **35**.

*2-Ethyl*-anti$^{10,11}$-*tricyclo[4.3.1.1*$^{2,5}$*]undec-3-en-10-one* (**23**). A soln. of 99 mg (0.52 mmol) of **2** in 15 ml of $CH_2Cl_2$ was treated with 27 mg (0.33 mmol) of AcONa and 190 mg (0.88 mmol) of pyridinium chlorochromate and stirred for 2 h at r.t. Usual workup and CC ($SiO_2$; pentane/$Et_2O$ 3:1) afforded 33 mg (34%) of **23**.

*3-Ethyl*-anti$^{10,11}$-*tricyclo[4.3.1.1*$^{2,5}$*]undec-3-en-10-one* (**24**). A soln. of 330 mg (1.72 mmol) of **35** in 25 ml of $CH_2Cl_2$ was treated with 30 mg (0.4 mmol) of AcONa and 730 mg (3.4 mmol) of pyridinium chlorochromate and stirred for 2 h at r.t. Standard workup and CC ($SiO_2$; pentane/$Et_2O$ 3:1) afforded 250 mg (76%) of **24**.

*Reduction of* **24**/**25** *with* $LiAlH_4$. A soln. of 575 mg (3 mmol) of **24**/**25** in 30 ml of anh. $Et_2O$ was treated at 0° with 230 mg (6 mmol) of $LiAlH_4$ and stirred for 15 min at 0° and for 45 min at r.t. Standard workup and CC ($SiO_2$; pentane/$Et_2O$ 3:1) yielded 330 mg (57%) of **35**, 47 mg (8%) of **36**, and 125 mg (22%) of **35**/**36**.

*Base-Catalyzed Isomerization of* **24** *to* **37**/**38**. An $O_2$-free soln. of 25 mg (0.13 mmol) of **24** in 2 ml of 1.2M *t*-BuOK/*t*-BuOH was heated for 16 h in a sealed tube under argon at 150°. Workup with pentane and CC ($SiO_2$; pentane/$Et_2O$ 12:1) yielded 10 mg (40%) of **37** and 13 mg (52%) of **37**/**38** in a ratio of *ca.* 1:1.

*Thermodynamic Equilibrium between* **37** *and* **38**. An $O_2$-free soln. of 10 mg (0.05 mmol) of a mixture of **37**/**38** in 2 ml of 1.2 molal *t*-BuOK/*t*-BuOH was heated for 72 h in a sealed tube under argon at 160°. Workup with pentane and CC ($SiO_2$; pentane/$Et_2O$ 12:1) quantitatively led to **37**/**38** in a ratio of 66:34, which, on longer heating, did not change anymore.

*Reduction of* **37**/**38** *with* $LiAlH_4$. A soln. of 210 mg (3 mmol) of **37**/**38** in 6 ml of anh. $Et_2O$ was treated at 0° with 76 mg (2 mmol) of $LiAlH_4$ and stirred for 15 min at 0° and for 45 min at r.t. Usual workup and CC ($SiO_2$; pentane/$Et_2O$ 6:1) yielded 35 mg (17%) of **13** and 116 mg (51%) of **13**/**14** in a ratio of 45:55.

*Base-Catalyzed Isomerization of* **35** *to* **13**/**14** and **17**. An $O_2$-free soln. of 25 mg (0.13 mmol) of **35** in 1 ml of 1.2 molal *t*-BuOK/*t*-BuOH was heated for 16 h in a sealed tube under Ar at 150°. Workup with pentane and CC ($SiO_2$; pentane/$Et_2O$ 3:1) yielded 19 mg (76%) of **17** and 6 mg (24%) of **37**/**38** in a ratio of 9:1.

*Reduction of* **31**/**32**/**33** *with* $LiAlH_4$. A soln. of 370 mg (1.81 mmol) of **31**/**32**/**33** in 10 ml of anh. $Et_2O$ was treated at 0° with 95 mg (2.5 mmol) of $LiAlH_4$ and stirred for 15 min at 0° and for 45 min at r.t. Usual workup and CC ($SiO_2$; pentane/$Et_2O$ 3:1) yielded 219 mg (59%) of **40**, 23 mg (6%) of **41**, 24 mg (7%) of **42**, and 33 mg (9%) of mixtures thereof.

*Reduction of* **30**/**34** *with* $LiAlH_4$. Analogous procedure as for the reduction of **31**/**32**/**33**. From a soln. of 289 mg (1.42 mmol) of **30**/**34** in anh. $Et_2O$, 226 mg (77%) of **3**, and 58 mg (20%) of **39** were obtained after CC (pentane/$Et_2O$ 3:1).

*2-Isopropyl*-anti$^{10,11}$-*tricyclo[4.3.1.1*$^{2,5}$*]undec-3-en-10-one* (**30**). A soln. of 64 mg (0.31 mmol) of **3** in 10 ml of $CH_2Cl_2$ was treated with 26 mg (0.19 mmol) of AcONa and 109 mg (0.5 mmol) of pyridinium chlorochromate and stirred for 2 h at r.t. Standard workup and CC ($SiO_2$; pentane/$Et_2O$ 3:1) afforded 38 mg (60%) of **30**.

*3-Isopropyl*-anti$^{10,11}$-*tricyclo[4.3.1.1*$^{2,5}$*]undec-3-en-10-one* (**31**). Same procedure as for the preparation of **30**. From 191 mg (0.93 mmol) of **40**, 139 mg (73%) of **31** were obtained after CC ($SiO_2$; pentane/$Et_2O$ 6:1).

*2-Isopropyl*-syn$^{10,11}$-*tricyclo[4.3.1.1*$^{2,5}$*]undec-3-en-10-one* (**32**). Same procedure as for the preparation of **30**. From 20 mg (0.1 mmol) of **41**, 14 mg (69%) of **32** were obtained after CC ($SiO_2$; pentane/$Et_2O$ 3:1).

*3-Isopropyl*-syn$^{10,11}$-*tricyclo[4.3.1.1*$^{2,5}$*]undec-3-en-10-one* (**33**). Same procedure as for the preparation of **30**. From 16 mg (0.08 mmol) of **42**, 10 mg (73%) of **33** were obtained after CC ($SiO_2$; pentane/$Et_2O$ 3:1).

*11-Isopropylidene*-anti$^{10,11}$-*tricyclo[4.3.1.1*$^{2,5}$*]undec-3-en-10-one* (**34**). Same procedure as for the preparation of **30**. From 191 mg (0.93 mmol) of **39**, 139 mg (73%) of **34** were obtained after CC ($SiO_2$; pentane/$Et_2O$ 6:1).

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9) Filtered through a pad of basic alumina.

*Base-Catalyzed Isomerization of* **31** *to* **43**. *Method A*. An $O_2$-free soln. of 80 mg (0.39 mmol) of **31** in 1 ml of 1.19*m* *t*-BuOK/*t*-BuOH was heated for 18 h in a sealed tube under Ar at 160°. Workup with pentane and CC ($SiO_2$; pentane/$Et_2O$ 6:1) yielded 77 mg (96%) of **31**/**43** in a ratio of 27:73.

*Method B*. In analogy to *Method A*, 70 mg (0.34 mmol) of **31** in 1 ml of 1.19 molal *t*-BuOK/*t*-BuOH were heated for 72 h at 200°. Workup and CC ($SiO_2$; pentane/$Et_2O$ 6:1) afforded 39 mg (56%) of **43** as the only product.

*3-Isopropylidene*-anti*[10,11]-tricyclo[4.3.1.1.2,5]undecan-10*-endo-*ol* (**15**). A soln. of 30 mg (0.15 mmol) of **43** in anh. $Et_2O$ was treated at 0° with 30 mg (0.8 mmol) of $LiAlH_4$ and stirred for 15 min at 0° and for 45 min at r.t. Usual workup and CC ($SiO_2$; pentane/$Et_2O$ 3:1) yielded 30 mg (99%) of **15**.

4. *Analytical and Spectral Data*[10])[11]). – *2-Ethyl*-anti*[10,11]-tricyclo[4.3.1.1*$^{2,5}$*]undec-3-en-10*-endo-*ol* (**2**). IR ($CCl_4$): 3602*s*, 3040*w*, 3028*w*, 1488*w*, 1459*m*, 1429*w*, 1379*w*, 1358*w*, 1348*w*, 1294*w*, 1271*w*, 1224*s*, 1192*w*, 1100*w*, 1086*w*, 1076*w*, 1060*s*, 1036*m*, 968*w*, 929*w*, 655w. $^1$H-NMR (300 MHz, $CDCl_3$): 0.87 (*t*, *J*(1′,2′) = 7.5, Me−C(1′)); 1.4–2.1 (*m*, H−C(1), H−C(6), 2 H−C(7), 2 H−C(8), 2 H−C(9), $H_{exo}$−C(11)); 1.53 (*q*, *J*(1′,2′) = 7.5, 2 H−C(1′)); 2.31 (*d*, $J_{gem}$ = 11, $H_{endo}$−C(11)); 2.70 (*td*, *J*(5,6) = *J*(5,11-*exo*) = 4, *J*(4,5) = 3, H−C(5)); 3.01 (*dm*, *J*($HO_{endo}$−C(10),10-*exo*) = 11.5, $w_{1/2} \approx 5$ each, $HO_{endo}$−C(10)); 3.77 (*dm*, *J*($HO_{endo}$−C(10),10-*exo*) = 11.5, $w_{1/2} \approx 5$ each, $H_{exo}$−C(10)); 6.19 (*d*, *J*(3,4) = 6, H−C(3)); 6.42 (*dd*, *J*(3,4) = 6, *J*(4,5) = 3, H−C(4)). MS: 192 (17, $M^+$, $C_{13}H_{20}O^+$), 175 (8), 174 (51), 159 (21), 146 (18), 145 (100), 135 (8), 133 (21), 132 (7), 131 (15), 121 (30), 120 (13), 119 (14), 118 (7), 117 (20), 108 (26), 107 (33), 106 (20), 105 (26), 98 (7), 97 (8), 96 (6), 95 (29), 94 (63), 93 (29), 92 (14), 91 (52), 83 (7), 82 (6), 81 (71), 80 (17), 79 (94), 78 (10), 77 (29), 70 (7), 67 (25), 65 (10), 57 (8), 55 (18), 53 (11), 43 (11), 41 (28), 39 (14), 29 (12), 27 (11).

*2-Isopropyl*-anti*[10,11]-tricyclo[4.3.1.1*$^{2,5}$*]undec-3-en-10*-endo-*ol* (**3**). IR ($CCl_4$): 3595*s*, 3038*w*, 1485*w*, 1460*w*, 1428*w*, 1386*w*, 1369*w*, 1364*w*, 1300*w*, 1295*w*, 1263*w*, 1225*s*, 1191*w*, 1125*w*, 1108*w*, 1089*w*, 1072*m*, 1055*s*, 1048*w*, 1004*w*, 969*w*, 945*w*, 932*w*, 922*w*, 866*w*, 651*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 0.85, 0.98 (2*d*, *J*(Me−C(1′), H−C(1′)) = 7 each, 2 Me−C(1′)); 1.5–2.1 (*m*, 2 H−C(7), 2 H−C(8), 2 H−C(9), $H_{exo}$−C(11)); 1.98 (*sept.*, *J*(Me−C(1′),1′) = 7, H−C(1′)); 1.99 (*m*, $w_{1/2} \approx 11$, H−C(1)); 2.27 (*m*, $w_{1/2} \approx 11$, H−C(6)); 2.28 (*d*, $J_{gem}$ = 10.5, $H_{endo}$−C(11)); 2.71 (*m*, $w_{1/2} \approx 12$, H−C(5)); 2.97 (*d*, *J*($HO_{endo}$−C(10),10-*exo*) = 12, $HO_{endo}$−C(10)); 3.78 (*dm*, *J*($HO_{endo}$−C(10),10-*exo*) = 12, $w_{1/2} \approx 5$ each, $H_{exo}$−C(10)); 6.24 (*d*, *J*(3,4) = 6, H−C(3)); 6.24 (*dd*, *J*(3,4) = 6, *J*(4,5) = 3, H−C(4)). MS: 206 (18, $M^+$, $C_{14}H_{22}O^+$), 188 (33), 173 (43), 147 (13), 146 (12), 145 (67), 135 (28), 131 (15), 122 (18), 121 (22), 120 (17), 119 (25), 117 (19), 109 (25), 108 (49), 107 (43), 106 (16), 93 (95), 91 (75), 81 (100), 79 (60), 77 (46), 69 (14), 67 (44), 65 (20), 56 (19), 55 (33), 53 (24), 51 (11), 43 (52), 41 (87), 39 (38), 29 (26), 27 (39).

*2-Ethyl-7-oxatetracyclo[6.4.0.0*$^{2,6}$*.0*$^{4,9}$*]dodecane* (**7**). IR ($CCl_4$): 3018*w*, 1494*w*, 1463*w*, 1443*w*, 1380*w*, 1370*w*, 1352*w*, 1335*w*, 1325*w*, 1301*w*, 1265*w*, 1223*w*, 1180*w*, 1138*w*, 1121*w*, 1098*w*, 1079*w*, 1070*w*, 1049*s*, 1038*m*, 1022*w*, 991*w*, 972*m*, 959*w*, 949*w*, 920*m*, 906*w*, 890*w*, 870*w*, 863*m*, 849*m*. $^1$H-NMR (300 MHz, $CDCl_3$): 0.90 (*t*, *J*(1′,2′) = 8, Me−C(2)); 1.17 (*dm*, $J_{gem}$ = 12, $w_{1/2} \approx 6$ each, $H_{exo}$−C(3)); 1.3–2.0 (*m*, H−C(9), 2 H−C(10), 2 H−C(11), 2 H−C(12)); 1.46 (*dt*, $J_{gem}$ = 11.5, *J*(4,5-*exo*) = *J*(5-*exo*,6) = 4, $H_{exo}$−C(5)); 1.55 (*q*, *J*(1′,2′) = 8, 2 H−C(1′)); 1.86 (*dm*, $J_{gem}$ = 11.5, *J*(3-*endo*,5-endo) = 4, $H_{endo}$−C(5)); 1.97 (*m*, $w_{1/2} \approx 18$, H−C(1)); 2.19 (*m*, $w_{1/2} \approx 8$, H−C(4)); 2.26 (*dd*, $J_{gem}$ = 12, *J*(3-*endo*, 5-*endo*) = 4, $H_{endo}$−C(3)); 3.89 (*t*, *J*(1,8) = *J*(8,9) = 4, H−C(8)); 4.4 (*dd*, *J*(5-*exo*,6) = 4, *J*(4,6) = 2, H−C(6)). MS: 192 (17, $M^+$, $C_{13}H_{20}O^+$), 149 (13), 148 (72), 147 (22), 120 (20), 119 (100), 105 (12), 93 (11), 91 (36), 81 (10), 79 (22), 77 (13), 67 (14), 54 (10), 53 (9), 41 (23), 39 (12), 29 (9), 27 (9).

*4-Ethyl-7-oxatetracyclo[6.4.0.0*$^{2,6}$*.0*$^{4,9}$*]dodecane* (**8**). IR ($CCl_4$): 3018*w*, 1492*w*, 1461*m*, 1441*w*, 1380*w*, 1369*w*, 1349*w*, 1334*w*, 1311*w*, 1301*w*, 1268*w*, 1252*w*, 1216*w*, 1144*w*, 1125*w*, 1112*w*, 1095*w*, 1049*s*, 1025*w*, 998*w*, 988*w*, 974*w*, 949*w*, 919*m*, 905*w*, 896*w*, 868*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 0.82 (*t*, *J*(1′,2′) = 7.5, Me−C(1′)); 1.07 (*dd*, $J_{gem}$ = 12, *J*(2,3-*exo*) = 6, $H_{exo}$−C(3)); 1.1–1.3 (*m*, $H_{exo}$−C(11)); 1.18 (*dd*, $J_{gem}$ = 11.5, *J*(5-*exo*,6) = 4, $H_{exo}$−C(5)); 1.35–2.0 (*m*, H−C(9), 2 H−C(10), $H_{endo}$−C(11), 2 H−C(12)); 1.70 (*dd*, $J_{gem}$ = 11.5, *J*(3-*endo*,5-*endo*) = 4, $H_{endo}$−C(5)); 2.09 (*m*, $w_{1/2} \approx 15$, H−C(1)); 2.12 (*dd*, $J_{gem}$ = 12, *J*(3-*endo*,5-*endo*) = 4, $H_{endo}$−C(3)); 2.54 (*q*, *J*(1,2) = *J*(2,3-*exo*) = *J*(2,6) = 6, H−C(2)); 3.86 (*t*, *J*(1,8) = *J*(8,9) = 4, H−C(8)); 4.59 (*dd*, *J*(2,6) = 6, *J*(5-*exo*,6) = 4, H−C(6)). MS: 192 (67, $M^+$, $C_{13}H_{20}O^+$), 164 (10), 163 (50), 149 (39), 148 (61), 145 (22), 135 (21), 133 (13), 121 (17), 120 (20), 119 (100), 117 (11), 111 (13), 109 (16), 107 (21), 105 (21), 96 (21), 95 (35), 94 (25), 93 (29), 91 (53), 81 (32), 80 (12), 79 (55), 77 (26), 67 (32), 65 (12), 55 (21), 53 (16), 41 (40), 39 (19), 29 (13), 28 (16), 27 (15).

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[10]) Reference data for **1**, **4**–**6**, **11**, **12**, and **16**: [3]; **19**: [6]; **20**–**22**: [7]; and **27**–**29**: [9]. No precise data (except for mixtures) are available for **10**, **25**, **26**, and **38**.

[11]) The prefixes '*syn*' and '*anti*' are used for isomers with the two bridges $CH_2$(10) and $CH_2$(11) on the same and opposite sides, resp., of the plane defined by C(1)−C(2)−C(5)−C(6).

*2-Isopropyl-7-oxatetracyclo[6.4.0.0$^{2,6}$.0$^{4,9}$]dodecane* (**9**). IR ($CCl_4$): 3024*m*, 1491*w*, 1485*w*, 1452*s*, 1385*m*, 1368*m*, 1351*w*, 1348*w*, 1320*w*, 1306*w*, 1298*w*, 1266*w*, 1226*w*, 1191*w*, 1172*w*, 1145*w*, 1136*w*, 1097*w*, 1080*w*, 1072*w*, 1051*s*, 1028*s*, 1012*w*, 999*w*, 975*m*, 959*w*, 951*w*, 938*w*, 921*m*, 905*w*, 889*w*, 863*m*, 845*m*, 684*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 0.90, 0.94 (2*d*, *J*(Me–C(1′),1′) = 7 each, 2 Me–C(1′)); 1.20 (*dm*, $J_{gem}$ = 12, $w_{1/2} \approx 7$, $H_{exo}$–C(3)); 1.3–1.5 (*m*, $H_{exo}$–C(11)); 1.43 (*dt*, $J_{gem}$ = 11.5, *J*(4,5-*exo*) = *J*(5-*exo*,6) = 4, $H_{exo}$–C(5)); 1.5–2.0 (*m*, 6 H); 1.77 (*sept.*, *J*(Me–C(1′),1′) = 7, H–C(1′)); 1.84 (*dd*, $J_{gem}$ = 11.5, *J*(3-*endo*,5-*endo*) = 3.5, $H_{endo}$–C(5)); 2.12 (*m*, $w_{1/2} \approx 14$, H–C(1)); 2.19 (*m*, $w_{1/2} \approx 9$, H–C(4)); 2.28 (*dd*, $J_{gem}$ = 12, *J*(3-*endo*,5-*endo*) = 3.5, $H_{endo}$–C(3)); 3.95 (*t*, *J*(1,8) = *J*(8,9) = 4, H–C(8)); 4.19 (*dd*, *J*(5-*exo*,6) = 4, *J*(4,6) = 2, H–C(6)). MS: 206 (15, $M^+$, $C_{14}H_{22}O^+$), 163 (13), 162 (47), 147 (27), 120 (19), 119 (100), 118 (18), 105 (11), 91 (33), 79 (16), 77 (11), 67 (12), 55 (10), 43 (13), 41 (23), 28 (11).

*3-Ethylidene$^{C(4)}$*-anti$^{10,11}$*-tricyclo[4.3.1.1.$^{2,5}$]undecan-10*-endo-*ol* (**13**). IR ($CCl_4$): 3548*s*, 3030*w*, 1490*w*, 1464*w*, 1446*w*, 1429*w*, 1378*w*, 1363*w*, 1346*w*, 1324*w*, 1298*w*, 1284*w*, 1274*w*, 1235*w*, 1222*m*, 1175*w*, 1095*w*, 1076*w*, 1056*s*, 1043*w*, 1030*w*, 974*w*, 956*w*, 911*w*, 878*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 1.18 (*dt*, $J_{gem}$ = 12, *J*(2,11-*exo*) = *J*(5,11-*exo*) = 4, $H_{exo}$–C(11)); 1.45–2.1 (*m*, H–C(1), H–C(6), 2 H–C(7), 2 H–C(8), 2 H–C(9); 1.62 (*dm*, *J*(1′,2′) = 6.5, $w_{1/2} \approx 4$ each, Me–C(1′)); 2.14 (*dm*, $J_{gem}$ = 16, $w_{1/2} \approx 13$ each, $H_{exo}$–C(4)); 2.34 (*m*, $w_{1/2} \approx 12$, H–C(5)); 2.39 (*dd*, $J_{gem}$ = 12, *J*(4-*endo*,11-*endo*) = 3, $H_{endo}$ – C(11)); 2.58 (*m*, $w_{1/2} \approx 11$, H–C(2)); 2.69 (*dm*, $J_{gem}$ = 16, $w_{1/2} \approx 9$ each, $H_{endo}$–C(4)); 2.70 (*d*, *J*($HO_{endo}$–C(10),10-*exo*) = 8.5, $HO_{endo}$–C(10)); 3.65 (*dm*, *J*($HO_{endo}$–C(10),10-*exo*) = 8.5, $w_{1/2} \approx 6$ each, $H_{exo}$–C(10)); 5.55 (*m*, $w_{1/2} \approx 20$, H–C(1′)). $^{13}$C-NMR (75 MHz, $CDCl_3$): 14.29 (*q*, C(2′)); 17.43 (*t*, C(8)); 29.88, 30.24 (2*t*, C(7), C(9)); 32.08 (*t*, C(11)); 34.36 (*t*, C(4)); 38.94, 40.36 (2*d*, C(1), C(6)); 42.03 (*d*, C(5)); 47.30 (*d*, C(2)); 75.42 (*d*, C(10)); 115.47 (*d*, C(1′)); 146.62 (*s*, C(3)).

*3-Ethylidene$^{C(2)}$*-anti$^{10,11}$*-tricyclo[4.3.1.1.$^{2,5}$]undecan-10*-endo-*ol* (**14**). $^{13}$C-NMR (75 MHz, $CDCl_3$)[12]: 14.55 (*q*, C(2′)); 17.61 (*t*, C(8)); 30.10, 30.34 (2*t*, C(7), C(9)); 31.96 (*t*, C(11)); 37.29 (*t*, C(4)); 39.19 (*d*, C(2)); 39.54, 40.36 (2*d*, C(1), C(6)); 42.45 (*d*, C(5)); 75.42 (*d*, C(10)); 116.49 (*d*, C(1′)); 146.02 (*s*, C(3)).

*3-Isopropylidene*-anti$^{10,11}$*-tricyclo[4.3.1.1.$^{2,5}$]undecan-10*-endo-*ol* (**15**). IR ($CCl_4$): 3540*s*, 3030*w*, 1490*w*, 1463*w*, 1445*m*, 1435*w*, 1429*w*, 1371*m*, 1362*w*, 1302*w*, 1276*w*, 1242*w*, 1224*m*, 1148*w*, 1082*w*, 1070*s*, 1041*m*, 914*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 1.15 (*dt*, $J_{gem}$ = 12, *J*(2,11-*exo*) = *J*(5,11-*exo*) = 4, $H_{exo}$–C(11)); 1.45–2.1 (*m*, 8 H); 1.65, 1.92 (2*m*, $w_{1/2} \approx 4$ and 5, resp., $(Me)_2C$=C(3)); 2.17 (*dm*, $J_{gem}$ = 16, $w_{1/2} \approx 13$, $H_{exo}$–(4)); 2.32 (*m*, $w_{1/2} \approx 12$, H–C(5)); 2.40 (*dd*, $J_{gem}$ = 12, *J*(4-*endo*,11-*endo*) = 3, $H_{endo}$–C(11)); 2.60 (*dm*, $J_{gem}$ = 16, $w_{1/2} \approx 7$ each, $H_{endo}$–C(4)); 2.79 (*m*, $w_{1/2} \approx 10$, H–C(2)); 3.00 (*d*, *J*($HO_{endo}$–C(10),10-*exo*) = 10, $HO_{endo}$–C(10)); 3.61 (*dm*, *J*($HO_{endo}$–C(10),10-*exo*) = 10, $w_{1/2} \approx 5$ each, $H_{exo}$–C(10)). MS: 206 (25, $M^+$, $C_{14}H_{22}O^+$), 188 (33), 173 (23), 145 (21), 133 (11), 121 (14), 120 (67), 114 (35), 107 (100), 106 (27), 105 (90), 93 (21), 92 (10), 91 (56), 81 (14), 79 (27), 77 (18), 67 (17), 55 (13), 53 (10), 43 (11), 41 (31), 39 (12), 32 (14), 28 (61).

*6-Ethyl-7-oxatetracyclo[6.4.0.0$^{2,6}$.0$^{4,9}$]dodecane* (**17**). IR ($CCl_4$): 3018*w*, 1492*w*, 1485*w*, 1461*w*, 1441*w*, 1369*w*, 1352*w*, 1317*w*, 1302*w*, 1273*w*, 1254*w*, 1215*w*, 1191*w*, 1178*w*, 1135*w*, 1096*w*, 1084*w*, 1051*s*, 1040*w*, 1022*w*, 969*m*, 948*w*, 913*w*, 902*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 0.76 (*t*, *J*(1′,2′) = 7.5, Me–C(1′)); 1.25 (*dm*, $J_{gem}$ = 12, $w_{1/2} \approx 11$ each, $H_{exo}$–C(3)); 1.45–1.55 (*m*, $H_{exo}$–C(11)); 1.41 (*dd*, $J_{gem}$ = 11.5, *J*(4,5-*exo*) = 4, $H_{exo}$–C(5)); 1.6–2.0 (*m*, H–C(9), 2 H–C(10), $H_{endo}$–C(11), 2 H–C(12)); 1.70 (*q*, *J*(1′,2′) = 7.5, 2 H–C(1′)); 1.80 (*dd*, $J_{gem}$ = 11.5, *J*(3-*endo*,5-*endo*) = 3.5, $H_{endo}$–C(5)); 2.1–2.25 (*m*, H–C(1), H–C(2), H–C(4)); 2.39 (*dd*, $J_{gem}$ = 12, *J*(3-*endo*,5-*endo*) = 3.5, $H_{endo}$–C(3)); 3.98 (*m*, $w_{1/2} \approx 7$, H–C(8)). MS: 192 (20, $M^+$, $C_{13}H_{20}O^+$), 135 (9), 121 (14), 120 (100), 105 (8), 93 (10), 92 (30), 91 (37), 81 (8), 79 (15), 78 (7), 77 (8), 67 (8), 57 (16), 41 (9), 29 (10), 28 (16).

*6-Isopropyl-7-oxatetracyclo[6.4.0.0$^{2,6}$.0$^{4,9}$]dodecane* (**18**). IR ($CCl_4$): 3018*w*, 1491*w*, 1461*m*, 1440*w*, 1381*w*, 1361*w*, 1351*w*, 1318*w*, 1301*w*, 1283*w*, 1272*w*, 1254*w*, 1184*w*, 1161*w*, 1140*w*, 1095*w*, 1051*s*, 1000*w*, 983*w*, 959*w*, 942*w*, 960*w*, 965*w*, 905*w*, 858*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 0.95, 0.96 (2*d*, *J*(Me–C(1′),1′) = 7 each, 2 (Me)–C(1′)); 1.19 (*dm*, $J_{gem}$ = 12, $w_{1/2} \approx 14$ each, $H_{exo}$–C(3)); 1.35–1.55 (*m*, $H_{exo}$–C(11)); 1.48 (*dd*, $J_{gem}$ = 11, *J*(4,5-*exo*) = 4, $H_{exo}$–C(5)); 1.6–2.0 (*m*, 6 H); 1.75 (*dd*, $J_{gem}$ = 11, *J*(3-*endo*,5-*endo*) = 3.5, $H_{endo}$–C(5)); 1.84 (*sept.*, *J*(Me–C(1′),1′) = 7, H–C(1′)); 2.11 (*m*, $w_{1/2} \approx 14$, H–C(4)); 2.15–2.25 (*m*, H–C(1), H–C(2)); 2.41 (*dd*, $J_{gem}$ = 12, *J*(3-*endo*,5-*endo*) = 3.5, $H_{endo}$–C(3)); 3.90 (*t*, *J*(1,8) = *J*(8,9) = 4, H–C(8)). MS: 206 (26, $M^+$, $C_{14}H_{22}O^+$), 135 (10), 121 (19), 120 (100), 93 (13), 92 (27), 91 (38), 79 (17), 67 (11), 43 (19), 41 (17).

*2-Ethyl*-anti$^{10,11}$*-tricyclo[4.3.1.1$^{2,5}$]undec-3-en-10-one* (**23**). IR ($CCl_4$): 3055*w*, 3030*w*, 1724*s*, 1454*m*, 1379*w*, 1448*m*, 1275*w*, 1222*w*, 1215*w*, 1173*w*, 1159*w*, 1135*w*, 1121*w*, 1091*w*, 1078*w*, 1030*w*, 973*w*, 921*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 0,91 (*d*, *J*(1′,2′) = 7.5, Me–C(1′)); 1.45–1.7 (*m*, $H_{exo}$–C(8)); 1.54 (*q*, *J*(1′,2′) = 7.5, 2 H–C(1′)); 1.64 (*dd*, $J_{gem}$ = 11.5, *J*(5,11-*exo*) = 4.5, $H_{exo}$–C(11)); 1.7–1.85 (*m*, $H_{endo}$–C(8)); 1.9–2.2 (*m*, 2 H–C(7), 2 H–C(9)); 2.26 (*m*, $w_{1/2} \approx 17$, H–C(1)); 2.39 (*m*, $w_{1/2} \approx 20$, H–C(6)); 2.51 (*d*, $J_{gem}$ = 11.5,

[12]) From a mixture of **13**/**14** 45:55.

$H_{endo}$–C(11)); 2.78 (*td*, *J*(5,6) = *J*(5,11-*exo*) = 4.5, *J*(4,5) = 3, H–C(5)); 5.88 (*dd*, *J*(3,4) = 6, *J*(3,5) *ca.* 1, H–C(3)); 6.05 (*dd*, *J*(3,4) = 6, *J*(4,5) = 3, H–C(5)). MS: 190 (5, $M^+$, $C_{13}H_{18}O^+$), 175 (2), 162 (5), 161 (9), 147 (4), 134 (6), 133 (22), 129 (3), 128 (3), 121 (4), 120 (4), 119 (12), 117 (4), 105 (16), 98 (5), 97 (34), 96 (100), 95 (16), 94 (21), 93 (23), 92 (11), 91 (34), 87 (5), 79 (42), 78 (8), 77 (22), 69 (5), 67 (13), 65 (9), 55 (18), 53 (7), 51 (6), 43 (11), 41 (19), 49 (14), 27 (12).

*3-Ethyl*-anti*[10,11]-tricyclo[4.3.1.1[2,5]]undec-3-en-10-one* (**24**). IR ($CCl_4$): 3050*w*, 3035*w*, 1722*s*, 1616*w*, 1454*m*, 1376*w*, 1341*w*, 1310*w*, 1288*w*, 1206*w*, 1150*w*, 1078*w*, 1041*w*, 1035*w*, 955*w*, 945*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 1.00 (*t*, *J*(1′,2′) = 7.5, Me–C(1′)); 1.45–1.65, 1.7–1.85 (2*m*, 2 H–C(8)); 1.73 (*dtt*, $J_{gem}$ = 11.5, *J*(2,11-*exo*) = *J*(5,11-*exo*) = 4.5, *J*(1,11-*exo*) = *J*(6,11-*exo*) = 1.5, $H_{exo}$–C(11)); 1.9–2.2 (*m*, 2 H–C(7), 2 H–C(9)); 2.06 (*qd*, *J*(1′,2′) = 7.5, *J*(2′,4) = 2, 2 H–C(1′)); 2.38, 2.47 (2*m*, $w_{1/2} \approx 20$ each, H–C(1), H–C(6)); 2.55 (*t*, *J*(1,2) = *J*(2,11-*exo*) = 4.5, H–C(2)); 2.70 (*d*, $J_{gem}$ = 11.5, $H_{endo}$–C(11)); 2.71 (*m*, $w_{1/2} \approx 10$, H–C(5)); 5.63 (*m*, $w_{1/2} \approx 6$, H–C(4)). MS: 190 (9, $M^+$, $C_{13}H_{18}O^+$), 161 (9), 133 (17), 105 (11), 98 (8), 97 (30), 96 (100), 95 (16), 94 (22), 93 (32), 92 (18), 91 (29), 79 (31), 77 (15), 67 (11), 55 (11), 28 (37).

*2-Isopropyl*-anti*[10,11]-tricyclo[4.3.1.1[2,5]]undec-3-en-10-one* (**30**). IR ($CCl_4$): 3052*w*, 3030*w*, 1724*s*, 1452*m*, 1385*m*, 1378*w*, 1349*m*, 1277*w*, 1262*w*, 1218*w*, 1188*w*, 1149*w*, 1135*w*, 1099*w*, 1089*w*, 1052*w*, 1035*w*, 978*w*, 921*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 0.92, 0.93 (2*d*, *J*(Me–C(1′),1′) = 7 each, 2 (Me–C(1′)); 1.45–1.65 (*m*, $H_{exo}$–C(8)); 1.65–2.0 (*m*, 2 H–C(7), $H_{endo}$–C(8), 2 H–C(9)); 1.78 (*dm*, $J_{gem}$ = 11.5, $w_{1/2} \approx 9$ each, $H_{exo}$–C(11)); 1.85 (*sept.*, *J*(Me–C(1′), H–C(1′)) = 7, H–C(1′)); 2.37 (*m*, $w_{1/2} \approx 20$, H–C(1)); 2.45–2.55 (*m*, H–C(6)); 2.51 (*d*, $J_{gem}$ = 11.5, $H_{endo}$–C(11)); 2.79 (*td*, *J*(5,6) = *J*(5,11-*exo*) = 4.5, H–C(5)); 5.92 (*d*, *J*(3,4) = 6, H–C(3)); 6.03, (*dd*, *J*(3,4) = 6, *J*(4,5) = 3, H–C(4)). MS: 204 (17, $M^+$, $C_{14}H_{20}O^+$): 189 (15), 161 (26), 133 (29), 119 (10), 109 (13), 108 (37), 107 (71), 106 (21), 105 (22), 97 (37), 96 (100), 95 (10), 93 (34), 91 (54), 79 (29), 77 (22), 67 (18), 65 (11), 55 (20), 43 (14), 41 (29), 39 (15), 28 (10), 27 (14).

*3-Isopropyl*-anti*[10,11]-tricyclo[4.3.1.1[2,5]]undec-3-en-10-one* (**31**). IR ($CCl_4$): 3058*w*, 3032*w*, 1724*s*, 1612*w*, 1452*m*, 1381*w*, 1363*w*, 1341*w*, 1310*m*, 1288*w*, 1269*w*, 1233*w*, 1210*w*, 1157*w*, 1148*w*, 1082*m*, 1062*w*, 1039*m*, 959*w*, 949*w*, 921*w*, 870*w*, 678*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 1.00, 1.01 (2*d*, *J*(Me–C(1′),1′) = 7 each, 2 Me–C(1′)); 1.45–1.65 (*m*, $H_{exo}$–C(8)); 1.65–1.85 (*m*, $H_{endo}$–C(8)); 1.70 (*dt*, $J_{gem}$ = 11.5, *J*(2,11-*exo*) = *J*(5,11-*exo*) = 4.5, $H_{exo}$–C(11)); 1.9–2.2 (*m*, 2 H–C(7), 2 H–C(9)); 2.28 (*sept.d*, *J*(Me–C(1′),1′) = 7, *J*(4,1′) = 1.5, H–C(1′)); 2.39, 2.48 (2*m*, $w_{1/2} \approx 18$ each, H–C(1), H–C(6)); 2.6–2.75 (*m*, H–C(2), H–C(5)); 2.71 (*d*, $J_{gem}$ = 11.5, $H_{endo}$–C(11)); 5.62 (*m*, $w_{1/2} \approx 6$, H–C(4)). MS: 204 (9, $M^+$, $C_{14}H_{20}O^+$), 161 (12), 133 (15), 108 (28), 107 (100), 106 (33), 105 (16), 97 (27), 96 (62), 93 (21), 91 (41), 79 (23), 77 (17), 67 (13), 55 (15), 41 (23), 39 (12), 27 (10).

*2-Isopropyl*-syn*[10,11]-tricyclo[4.3.1.1[2,5]]undec-3-en-10-one* (**32**). IR ($CCl_4$): 3055*w*, 1718*s*, 1465*m*, 1442*w*, 1388*w*, 1370*w*, 1359*w*, 1289*m*, 1235*w*, 1195*w*, 1169*w*, 1099*w*, 1089*w*, 1054*w*, 1025*w*, 946*w*, 935*w*, 908*w*, 859*w*, 827*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 0.91, 0.92 (2*d*, *J*(Me–C(1′),1′) = 7 each, 2 Me–C(1′)); 1.1–1.3 (*m*, $H_{endo}$–C(8)); 1.36 (*d*, $J_{gem}$ = 11, $H_{endo}$–C(11)); 1.56 (*dd*, $J_{gem}$ = 11, *J*(5,11-*exo*) = 4.5, $H_{exo}$–C(11)); 1.72 (*sept.*, *J*(Me–C(1′),1′) = 7, H–C(1′)); 1.9–2.15 (*m*, 2 H–C(7), $H_{exo}$–C(8), 2 H–C(9)); 2.44 (*m*, $w_{1/2} \approx 11$, H–C(1)); 2.54 (*m*, $w_{1/2} \approx 18$, H–C(6)); 2.94 (*dddd*, *J*(5,6) = 9, *J*(5,11-*exo*) = 4.5, *J*(4,5) = 3.5, *J*(3,5) = 1, H–C(5)); 6.30 (*dd*, *J*(3,4) = 5.5, *J*(3,5) = 1, H–C(3)); 6.38 (*dd*, *J*(3,4) = 5.5, *J*(4,5) = 3.5, H–C(4)). MS: 204 (24, $M^+$, $C_{14}H_{20}O^+$), 189 (11), 161 (27), 133 (33), 199 (14), 109 (13), 108 (37), 107 (78), 106 (17), 105 (26), 97 (31), 96 (100), 95 (14), 93 (41), 91 (60), 79 (30), 77 (25), 69 (10), 67 (21), 65 (13), 55 (18), 43 (14), 41 (34), 39 (17), 28 (18), 27 (13).

*3-Isopropyl*-syn*[10,11]-tricyclo[4.3.1.1[2,5]]undec-3-en-10-one* (**33**). IR ($CCl_4$): 3055*w*, 1723*s*, 1621*w*, 1465*m*, 1442*w*, 1381*w*, 1363*w*, 1321*w*, 1315*w*, 1281*m*, 1239*w*, 1088*w*, 912*w*, 879*m*. $^1$H-NMR (300 MHz, $CDCl_3$): 1.11, 1.22 (2*d*, *J*(Me–C(1′),1′) = 7 each, 2 Me–C(1′)); 1.15–1.35 (*m*, $H_{endo}$–C(8)); 1.55 (*d*, $J_{gem}$ = 11, $H_{endo}$–C(11)); 1.67 (*dt*, $J_{gem}$ = 11, *J*(2,11-*exo*) = *J*(5,11-*exo*) = 4, $H_{exo}$–C(11)); 1.8–2.2 (*m*, 2 H–C(7), $H_{exo}$–C(8), 2 H–C(9)); 2.44 (*sept.d*, *J*(Me–C(1′),1′) = 7, *J*(4,1′) = 2, H–C(1′)); 2.55–2.65 (*m*, H–C(1), H–C(6)); 2.85–2.95 (*m*, H–C(2), H–C(5)); 5.92 (*m*, $w_{1/2} \approx 7$, H–C(4)). MS: 204 (7, $M^+$, $C_{14}H_{20}O^+$), 161 (18), 133 (19), 109 (10), 108 (30), 107 (100), 106 (31), 105 (21), 97 (27), 96 (60), 93 (27), 91 (50), 79 (29), 77 (20), 67 (16), 65 (10), 55 (18), 43 (14), 41 (28), 39 (14), 28 (19), 27 (11).

*11-Isopropylidene*-anti*[10,11]-tricyclo[4.3.1.1[2,5]]undec-3-en-10-one* (**34**). M.p. 128°. IR ($CCl_4$): 3060*w*, 1726*s*, 1441*m*, 1372*w*, 1352*w*, 1340*w*, 1334*w*, 1326*w*, 1290*w*, 1280*w*, 1236*m*, 1220*w*, 1185*w*, 1126*w*, 1165*w*, 1078*m*, 1026*w*, 989*w*, 970*w*, 930*w*, 920*w*, 889*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 1.3–1.5 (*m*, 2 H–C(7), $H_{endo}$–C(8), 2 H–C(9)); 1.79 (*s*, $(Me)_2C$=C(11)); 2.52 (*m*, $w_{1/2} \approx 15$, H–C(1), H–C(6)); 3.45 (*m*, $w_{1/2} \approx 9$, H–C(2), H–C(5)); 6.23 (*dd*, *J*(2,3) = *J*(4,5) = 2, *J*(2,4) = *J*(3,5) = 1, H–C(3), H–C(4)). MS: 202 (11, $M^+$, $C_{14}H_{18}O^+$), 187 (19), 159 (13), 131 (11), 91 (17), 32 (24), 28 (100).

*3-Ethyl*-anti*[10,11]-tricyclo[4.3.1.1[2,5]]undec-3-en-10*-endo-*ol* (**35**). IR ($CCl_4$): 3592*s*, 3035*w*, 1611*w*, 1486*w*, 1458*m*, 1450*w*, 1438*m*, 1380*m*, 1375*w*, 1355*w*, 1330*w*, 1317*w*, 1289*w*, 1221*m*, 1091*w*, 1070*s*, 1038*s*, 944*w*, 931*w*, 915*w*,

892*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 1.11 (*t*, $J(1',2')=7.5$, Me–C(1′)); 1.6–2.15 (*m*, 2 H–C(7), 2 H–C(8), 2 H–C(9)); 1.64 (*dt*, $J_{gem}=10.5$, $J(2,11\text{-}exo)=J(5,11\text{-}exo)=4$, $H_{exo}$–C(11)); 1.97 (*m*, $w_{1/2}\approx 11$, H–C(1)); 2.08 (*m*, $w_{1/2}\approx 11$, H–C(6)); 2.25 (*q*, $J(1',2')=7.5$, 2 H–C(1′)); 2.35 (*t*, $J(1,2)=J(2,11\text{-}exo)=4$, H–C(2)); 2.56 (*d*, $J_{gem}=10.5$, $H_{endo}$–C(11)); 2.60 (*m*, $w_{1/2}\approx 10$, H–C(5)); 2.96 (*dm*, $J(HO_{endo}\text{–}C(10),10\text{-}exo)=12$, $w_{1/2}\approx 4$ each, $HO_{endo}$–C(10)); 3.67 (*dm*, $J(HO_{endo}\text{–}C(10),10\text{-}exo)=12$, $w_{1/2}\approx 5$ each, $HO_{exo}$–C(10)); 5.91 (*m*, $w_{1/2}\approx 7$, H–C(4)). MS: 192 (36, $M^+$, $C_{13}H_{20}O^+$), 175 (6), 174 (38), 163 (9), 159 (20), 146 (12), 145 (64), 135 (15), 133 (15), 131 (15), 121 (29), 120 (100), 119 (15), 118 (12), 117 (19), 111 (10), 109 (7), 108 (18), 107 (28), 106 (26), 105 (33), 98 (14), 97 (9), 95 (31), 94 (42), 93 (37), 92 (49), 91 (87), 83 (8), 81 (63), 80 (17), 79 (87), 78 (15), 77 (30), 67 (29), 65 (12), 57 (22), 55 (19), 53 (14), 43 (9), 41 (33), 39 (17), 29 (18), 28 (9), 27 (12).

*2-Ethyl*-syn*[10,11]-tricyclo[4.3.1.1[2,5]]undec-3-en-10*-endo-*ol* (**36**). IR ($CCl_4$): 3660*m*, 3470*w* (br.), 3048*w*, 3020*w*, 1459*m*, 1377*w*, 1345*w*, 1330*w*, 1286*w*, 1278*w*, 1244*w*, 1230*w*, 1198*w*, 1154*w*, 1109*w*, 1082*w*, 1075*w*, 1055*s*, 1028*w*, 1020*w*, 964*w*, 935*w*, 912*w*, 894*w*, 872*w*, 656*m*. $^1$H-NMR (100 MHz, $CDCl_3$): 0.88 (*t*, $J(1',2')=7.5$, Me–C(1′)); 1.0–2.3 (*m*, H–C(1), H–C(6), 2 H–C(7), 2 H–C(8), 2 H–C(9), 2 H–C(1′), $H_{exo}$–C(11)); 1.62 (*s*, $HO_{endo}$–C(10)); 2.66 (*dt*, $J(5,6)=8$, $J(4,5)=J(5,11\text{-}exo)=3$, H–C(5)); 2.95 (*d*, $J_{gem}=10$, $H_{endo}$–C(11)); 4.91 (*m*, $w_{1/2}\approx 4$, $H_{exo}$–C(10)); 6.03 (*d*, $J(3,4)=5$, H–C(3)); 6.25 (*dd*, $J(3,4)=5$, $J(4,5)=3$, H–C(4)). MS: 192 (3, $M^+$, $C_{13}H_{20}O^+$), 174 (23), 159 (7), 145 (26), 131 (10), 121 (8), 119 (9), 117 (19), 107 (14), 106 (24), 105 (24), 95 (18), 94 (37), 93 (28), 92 (18), 91 (94), 81 (52), 80 (16), 79 (100), 78 (25), 77 (59), 67 (27), 65 (24), 57 (22), 55 (26), 53 (25), 51 (16), 43 (10), 41 (42), 39 (35), 29 (34), 27 (49).

*3-Ethylidene$^{C(4)}$*-anti*[10,11]-tricyclo[4.3.1.1[2,5]]undecan-10-one* (**37**). IR ($CCl_4$): 3032*w*, 1721*s*, 1468*w*, 1445*m*, 1377*w*, 1349*w*, 1306*w*, 1230*w*, 1219*w*, 1165*w*, 1135*w*, 1083*w*, 1046*w*, 945*w*, 915*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 1.2–1.45 (*m*, $H_{exo}$–C(8)); 1.39 (*dtt*, $J_{gem}=12.5$, $J(2,11\text{-}exo)=J(5,11\text{-}exo)=4$, $J(1,11\text{-}exo)=J(6,11\text{-}exo)\approx 1$, $H_{exo}$–C(11)); 1.53 (*dm*, $J(1',2')=7$, $w_{1/2}\approx 4$ each, Me–C(1′)); 1.6–1.8 (*m*, $H_{endo}$–C(8)); 2.0–2.3 (*m*, 2 H–C(7), 2 H–C(9)); 2.01 (*dm*, $J_{gem}=16$, $w_{1/2}\approx 8$ each, $H_{endo}$–C(4)); 2.21 (*dm*, $J_{gem}=16$, $w_{1/2}\approx 12$ each, $H_{exo}$–C(4)); 2.34 (*m*, $w_{1/2}\approx 16$, H–C(1), H–C(6)); 2.47 (*m*, $w_{1/2}\approx 12$, H–C(5)); 2.62 (*dd*, $J_{gem}=12.5$, $J(4\text{-}endo,11\text{-}endo)=2.5$, $H_{endo}$–C(11)); 2.73 (*m*, $w_{1/2}\approx 11$, H–C(2)); 5.42 (*qt*, $J(1',2')=7$, $J(1',2)=J(1',4\text{-}endo)=2.5$, H–C(1′)). MS: 190 (4, $M^+$, $C_{13}H_{18}O^+$), 96 (11), 94 (42), 93 (100), 92 (8), 91 (21), 77 (15), 41 (8).

*11-Isopropylidene-anti[10,11]-tricyclo[4.3.1.1[2,5]]undec-3-en-10*-endo-*ol* (**39**). M.p. 77°. IR ($CCl_4$): 3594*s*, 3048*w*, 1463*w*, 1442*w*, 1426*w*, 1372*w*, 1349*w*, 1289*w*, 1280*w*, 1223*w*, 1215*w*, 1105*w*, 1086*m*, 1060*s*, 1036*w*, 968*w*, 947*w*, 929*w*, 888*w*, 869*w*, 702*m*, 658*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 1.25–1.45 (*m*, $H_{endo}$–C(8)); 1.6–2.0 (*m*, 2 H–C(7), $H_{exo}$–C(8), 2 H–C(9)); 1.64 (*s*, $(Me)_2C{=}C(11)$); 2.22 (*m*, $w_{1/2}\approx 10$, H–C(1), H–C(6)); 3.00 (*d*, $J(HO_{endo}\text{–}C(10),10\text{-}exo)=12$, $HO_{endo}$–C(10)); 3.37 (*m*, $w_{1/2}\approx 9$, H–C(2), H–C(5)); 3.62 (*dm*, $J(HO_{endo}\text{–}C(10),10\text{-}exo)=12$, $w_{1/2}\approx 5$ each, $H_{exo}$–C(10)); 4.54 (*dd*, $J(2,3)=J(4,5)=2$, $J(2,4)=J(3,5)=1$, H–C(3), H–C(4)). MS: 204 (16, $M^+$, $C_{14}H_{20}O^+$), 189 (35), 186 (20), 171 (57), 157 (13), 143 (28), 133 (15), 129 (15), 126 (44), 119 (30), 117 (16), 115 (12), 109 (27), 108 (21), 107 (36), 105 (43), 93 (20), 91 (100), 81 (46), 79 (35), 77 (29), 70 (7), 67 (17), 65 (18), 55 (16), 53 (15), 51 (11), 43 (11), 41 (43), 40 (26), 29 (11), 28 (15), 27 (16).

*3-Isopropyl*-anti*[10,11]-tricyclo[4.3.1.1[2,5]]undec-3-en-10*-endo-*ol* (**40**). IR ($CCl_4$): 3578*s*, 3028*w*, 1606*w*, 1485*w*, 1460*m*, 1446*w*, 1425*w*, 1381*w*, 1365*w*, 1355*w*, 1346*w*, 1318*w*, 1295*w*, 1222*w*, 1558*w*, 1091*w*, 1071*s*, 1040*m*, 1002*w*, 959*w*, 948*w*, 938*w*, 917*w*, 898*w*, 870*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 1.09, 1.12 (2*d*, $J(Me\text{–}C(1'),H\text{–}C(1'))=7$ each, $(Me)_2C(1')$); 1.55–2.15 (*m*, H–C(1), H–C(6), 2 H–C(7), 2 H–C(8), 2 H–C(9), $H_{exo}$–C(11)); 2.4–2.5 (*m*, H–C(2)); 2.45 (*sept.d*, $J(Me\text{–}C(1'),1')=7$, $J(1',4)=2$, H–C(1′)); 2.53–2.62 (*m*, H–C(5)); 2.57 (*d*, $J_{gem}=10.5$, $H_{endo}$–C(11)); 2.93 (*d*, $J(HO_{endo}\text{–}C(10),10\text{-}exo)=12$, $HO_{endo}$–C(10)); 3.68 (*dm*, $J(HO_{endo}\text{–}C(10),10\text{-}exo)=12$, $w_{1/2}\approx 5$ each, $H_{exo}$–C(10)); 5.91 (*m*, $w_{1/2}\approx 6$, H–C(4)). MS: 206 (33, $M^+$, $C_{14}H_{22}O^+$), 188 (33), 173 (50), 63 (14), 159 (6), 145 (62), 135 (22), 133 (12), 131 (16), 121 (29), 120 (83), 119 (38), 117 (21), 109 (31), 108 (43), 107 (75), 106 (41), 105 (84), 93 (82), 91 (85), 81 (100), 79 (62), 77(43), 69 (16), 67 (46), 65 (19), 57 (13), 55 (31), 53 (22), 51 (10), 43 (46), 41 (66), 40 (29), 29 (19), 28 (15), 27 (25).

*2-Isopropyl*-syn*[10,11]-tricyclo[4.3.1.1[2,5]]undec-3-en-10*-endo-*ol* (**41**). M.p. 75°. IR ($CCl_4$): 3612*m*, 3480 (br.), 3045*w*, 1465*m*, 1449*w*, 1384*w*, 1366*w*, 1320*w*, 1278*w*, 1245*w*, 1203*w*, 1092*w*, 1065*s*, 1041*w*, 1034*w*, 1028*w*, 974*w*, 939*w*, 919*w*, 879*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 0.91, 0.93 (2*d*, $J(Me\text{–}C(1'),1')=7$ each, $(Me)_2C(1')$); 1.2–1.4 (*m*, $H_{endo}$–C(8)); 1.37 (*dd*, $J_{gem}=9.5$, $J(5,11\text{-}exo)=4$, $H_{exo}$–C(11)); 1.5–2.15 (*m*, H–C(1), H–C(6), 2 H–C(7), $H_{exo}$–C(8), 2 H–C(9)); 1.54 ($HO_{endo}$–C(10)); 1.62 (*sept.*, $J(Me\text{–}C(1'),1')=7$, H–C(1′)); 2.69 (*ddd*, $J(5,6)=9$, $J(5,11\text{-}exo)=4$, $J(4,5)=3.5$, H–C(5)); 2.99 (*d*, $J_{gem}=9.5$, $H_{endo}$–C(11)); 3.90 (*m*, $w_{1/2}\approx 5$, $H_{exo}$–C(10)); 6.17 (*d*, $J(3,4)=6$, H–C(3)); 6.24 (*dd*, $J(3,4)=6$, $J(4,5)=3.5$, H–C(4)). MS: 206 (6, $M^+$, $C_{14}H_{22}O^+$), 188 (27), 173 (53), 145 (72), 135 (13), 131 (19), 121 (16), 120 (18), 119 (22), 117 (25), 109 (31), 108 (78), 107 (66), 106 (22), 105 (97), 93 (88), 91 (78), 81 (100), 79 (56), 77 (44), 69 (13), 67 (38), 65 (19), 57 (16), 55 (28), 53 (19), 43 (41), 41 (66), 39 (30), 29 (19), 27 (27).

*3-Isopropyl*-syn*-tricyclo[4.3.1.1$^{2,5}$]undec-3-en-10*-endo-*ol* (**42**). M.p. 116°. IR ($CCl_4$): 3615*m*, 3500 (br.), 3045*w*, 3015*w*, 1465*m*, 1449*w*, 1379*w*, 1362*w*, 1315*w*, 1291*w*, 1278*w*, 1242*w*, 1230*w*, 1106*w*, 1092*w*, 1068*m*, 1041*w*, 963*w*, 915*w*, 892*w*, 876*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 1.01, 1.12 (2*d*, *J*(Me–C(1′),H–C(1′)) = 7 each, $(Me)_2$C(1′)); 1.2–1.35 (*m*, $H_{endo}$–C(8)); 1.57 (*dt*, $J_{gem}$ = 10, *J*(2,11-*exo*) = *J*(5,11-*exo*) = 3.5, $H_{exo}$–C(11)); 1.62 (*m*, $w_{1/2} \approx 4$, $HO_{endo}$–C(10)); 1.6–2.1 (*m*, H–C(1), H–C(6), 2 H–C(7), $H_{exo}$–C(8), 2 H–C(9)); 2.33 (*sept.d*, *J*(Me–C(1′),H–C(1′)) = 7, *J*(1′,4) = 2, H–C(1″)); 2.58 (*dm*, *J*(1,2) = 9.5, $w_{1/2} \approx 9$ each, H–C(2)); 2.6–2.65 (*m*, H–C(5)); 3.14 (*dm*, $J_{gem}$ = 10, $w_{1/2} \approx 4$ each, $H_{endo}$–C(11)); 3.90 (*m*, $w_{1/2} \approx 5$, $H_{exo}$–C(10)); 5.78 (*m*, $w_{1/2} \approx 7$, H–C(4)). MS: 206 (15, $M^+$, $C_{14}H_{22}O^+$), 188 (19), 173 (36), 163 (23), 145 (69), 135 (23), 131 (15), 121 (15), 120 (20), 119 (27), 117 (25), 109 (31), 108 (53), 107 (49), 106 (28), 105 (69), 97 (12), 95 (14), 92 (15), 91 (73), 83 (15), 81 (100), 80 (18), 79 (59), 78 (13), 77 (45), 69 (16), 67 (47), 65 (18), 57 (14), 55 (28), 53 (19), 43 (38), 41 (62), 39 (27), 29 (18), 28 (13), 27 (23).

*3-Isopropylidene*-anti*-tricyclo[4.3.1.1$^{2,5}$]undecan-10-one* (**43**). IR ($CCl_4$): 3030*w*, 1723*s*, 1478*w*, 1453*m*, 1445*w*, 1371*w*, 1349*w*, 1311*w*, 1322*w*, 1220*w*, 1168*w*, 1148*w*, 1145*w*, 1090*w*, 1082*w*, 1044*w*, 950*w*, 914*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 1.2–1.45 (*m*, $H_{exo}$–C(8)); 1.36 (*dt*, $J_{gem}$ = 12.5, *J*(2,11-*exo*) = *J*(5,11-*exo*) = 4, $H_{exo}$–C(11)); 1.56, 1.65 (2*m*, $w_{1/2} \approx 4$ and 5, resp., $(Me)_2$C=C(3)); 1.6–1.8 (*m*, $H_{endo}$–C(8)); 1.98 (*dm*, $J_{gem}$ = 16, $w_{1/2} \approx 7$ each, $H_{endo}$–C(4)); 2.0–2.45 (*m*, 8 H); 2.63 (*dd*, $J_{gem}$ = 12.5, *J*(4-*endo*,11-*endo*) = 3, $H_{endo}$–C(11)); 2.95 (*m*, $w_{1/2} \approx 12$, H–C(2)). MS: 204 (5, $M^+$, $C_{14}H_{20}O^+$), 108 (16), 107 (100), 91 (23), 79 (8), 77 (6), 41 (9), 28 (13).

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