150. Syntheses and PE-Spectroscopic Investigations of 2,6- and 3,5-Bridged 1,4-Dimethylidenecyclohexanes

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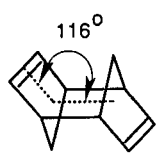
Three 1,4-dimethylidenecyclohexanes, bridged in the 2,6- and 3,5-positions by two ethano (**4**), one ethano and one propano (**5**), and two propano bridges (**6**) have been synthesized. The interaction of the two exocyclic methylidene groups has been investigated by He(I) photoelectron (PE) spectroscopy. It revealed a slightly larger energy difference (0.8 eV) for **4** and **5** as compared to the parent 1,4-dimethylidenecyclohexane (**7**) (0.7 eV). The interpretation of the PE spectra was based on the comparison with PE data of related systems and with the results of semiempirical calculations on **4**–**6**.

Introduction. – A comparison of the PE spectra of *anti*-tricyclo[4.2.1.$1^{2,5}$]deca-3,7-diene (**1**), *anti*-tricyclo[4.2.0.$0^{2,5}$]octa-3,7-diene (**2**), and *anti*-tricyclo[6.4.0.$0^{2,7}$]dodeca-3,5,9,11-tetraene (**3**) indicates a strong variation of the energy difference between the two highest occupied MOs [1][4]). This was partly ascribed to the different overlap of the π- and σ-frames in **1**–**3** as indicated by the different dihedral angles in the *Formulae*. To further check this argumentation, we have synthesized **4**–**6**. These molecules can be looked at as derivatives of 1,4-dimethylidenecyclohexane (**7**) in which the angles Θ and Θ' are varied (see **7**) by the different bridges between the centers a–d and b–c, respectively. The different



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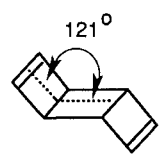

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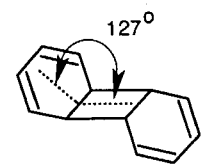

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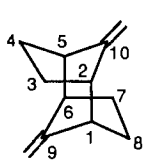
[4]) In **1**–**3**, *anti* refers to the position of the two chromophors relative to the central planar moiety of the structure; in all other compounds, *anti* refers to the position of the main and secondary bridges to each other; substituents are *endo* if they point towards the central 'cage' of the structure, and *exo* if they point outwards.



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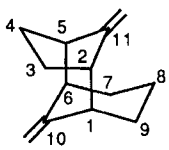

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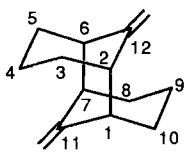

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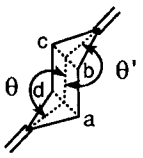

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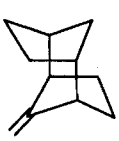

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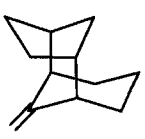

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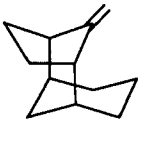

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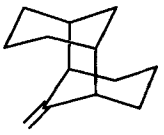

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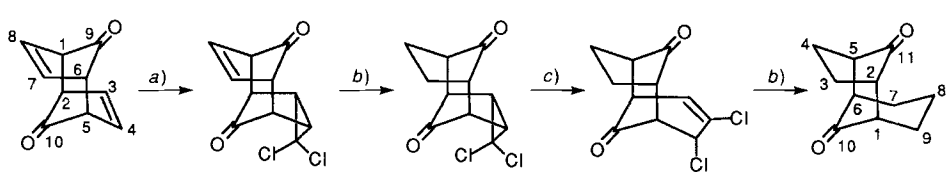
dihedral angles should influence the overlap integral between the π-MOs of the double bonds and the σ-bonds a–b and c–d. Furthermore, **4–6** as well as the monofunctional species such as **8–11** (which can be looked at as derivatives of methylidenecyclohexane (**12**)) impose the question of the conformation of the cyclohexane ring(s). The interaction of the π systems with the σ skeleton can be investigated by He(I) photoelectron (PE) spectroscopy, while the conformational problems can be solved by NMR spectroscopy. In the following, we report on the synthesis of **4–6** and **8–11** and discuss the spectroscopic results.

Syntheses of the Dienes 4–6 and the Monoenes 8–11. – Starting materials for the syntheses of the tricyclic dimethylidene compounds **4–6** were the corresponding diketones **13** [2], **14**[5]), and **19** [3], respectively. The strategy for converting the carbonyl into a methylidene group included addition of methyllithium (MeLi) and subsequent H_2O elimination (*Scheme 2*). The diketones showed remarkable differences in reactivity. Depending on the ring size (the 5/5-membered-ring diketone **13** being the most reactive one) and on the solvent used, the addition of MeLi led preferentially either to the

[5]) Diketone **14** was prepared (*Scheme 1*) from the known 5/5-membered-ring diketone **15** [2]: dichlorocarbene addition (→ **16** [3]), reduction of the remaining double bond (→ **17**), thermal ring opening (→ **18**), and subsequent reduction with H_2, Pd/C, led to **14** (see *Exper. Part*).

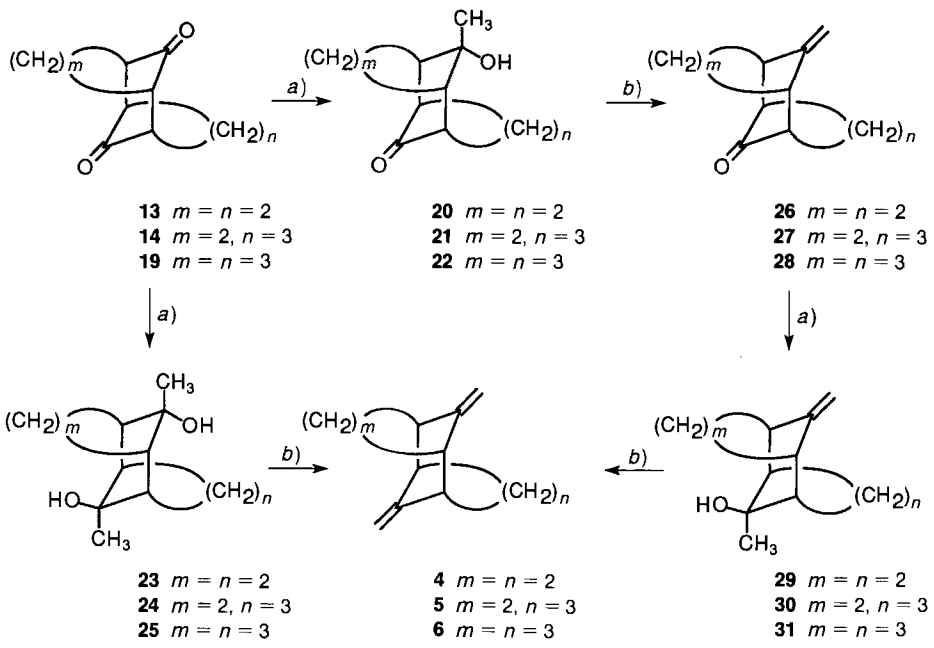
Scheme 1



15 **16** **17** **18** **14**

a) $CHCl_3$, NaOH. *b*) H_2, Pd/C. *c*) ΔT.

Scheme 2



a) MeLi. *b*) $SOCl_2$/pyridine.

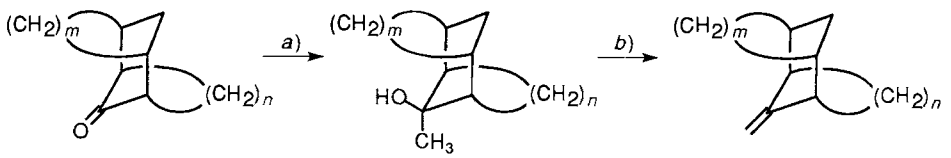
Table 1. *Addition of Methyllithium to the Diketones* **13**, **14**, *and* **19**

Diketone	Products		
	Et_2O	Et_2O/dioxane	THF
13	hydroxy ketone **20**/diol **23**	diol **23**	diol **23**
14	hydroxy ketone **21**		diol **24**
19	no reaction	hydroxy ketone **22**	hydroxy ketone **22**/diol **25** 1:3

monohydroxy ketones **20–22** or directly to the diols **23–25**. Some of the results are summarized in *Table 1*. Subsequent H_2O elimination was easily achieved by treatment of the tertiary alcohols with thionyl chloride ($SOCl_2$) in pyridine. Thus, the diols **23–25**, without isolating an intermediate, gave the desired dimethylidene compounds **4–6**, whereas the monoalcohols **20–22** led to the monomethylidene ketones **26**[6])–**28**. The latters, by repeating the treatment with MeLi and $SOCl_2$ once more, were easily converted too (*via* **29–31**) to the corresponding dimethylidene compounds **4–6**.

[6]) Monomethylidene ketone **26** could also be obtained from the diketone **13** [2] by a *Wittig* reaction (NaH in DMSO, Ph_3PMeBr).

Scheme 3



32 $m = n = 2$
33 $m = 2, n = 3$
34 $m = 3, n = 2$
35 $m = n = 3$

36 $m = n = 2$
37 $m = 2, n = 3$
38 $m = 3, n = 2$
39 $m = n = 3$

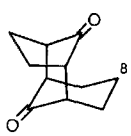
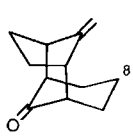
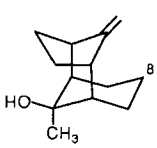
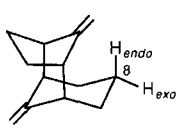
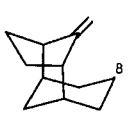
8 $m = n = 2$
9 $m = 2, n = 3$
10 $m = 3, n = 2$
11 $m = n = 3$

a) MeLi. *b*) $SOCl_2$/pyridine.

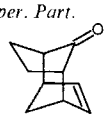
The monoolefins **8**[7])–**11**, required for comparative PE spectroscopy measurements, were synthesized analogously from the corresponding monoketones **32** [5], **33** [6], **34** [6], and **35**[8]) *via* the tertiary alcohols **36**–**39** (*Scheme 3*).

Interesting features are observed in several of the NMR-spectra: *i*) Of the two geminal methylene protons at the unsubstituted 6-membered ring position opposite to a carbonyl or a methylidene group of the methylene bridge, it is always the *exo*-proton[4]) that is more shielded by *ca.* 1 ppm than the *endo*[4]) one (see *Tables 2* and *3*). This assignment is the unequivocal result, *e.g.* for the 5/6-membered diene **5**, from a 400-MHz COSY spectrum, a 2D $^{13}C/^{1}H$-shift correlation 100/400 MHz spectrum, and 1D $^{1}H/^{1}H$-NOE experiments. *ii*) The unsubstituted 6-membered ring varies its conformation depending on the functional group at the opposite methylene bridge. From the observed coupling constants, it

Table 2. *^{1}H-NMR Chemical Shifts* δ [ppm] *of the 5/6-Membered-Ring Compounds* **14**, **27**, **30**, **5**, *and* **10**

					
	14	**27**	**30**	**5**	**10**
H_{endo}–C(8)[4])	2.0–2.35	1.97–2.18	2.0–2.15	2.01	2.28–2.45
H_{exo}–C(8)[4])	1.4–1.55	1.1–1.25	1.14–1.27	1.19	1.21–1.33

[7]) The preparation of **8** *via* **36** was already described by *Siemionko* and *Berson* [4]. Detailed analytical data of **8** and **36** are given in the *Exper. Part.*



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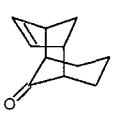

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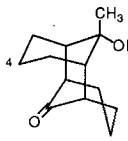
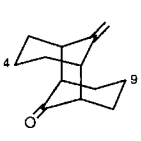
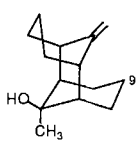
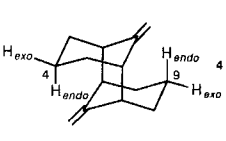
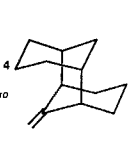
[8]) The ketones **34** and **35** [7] were prepared from the known keto olefins **40** and **41** [8] in analogy to the synthesis of diketone **14**[5]).

Table 3. *^{1}H-NMR Chemical Shifts* δ [ppm] *of the 6/6-Membered-Ring Compounds* **22**, **28**, **31**, **6**, *and* **11**

	 **22**	 **28**	 **31**	 **6**	 **11**
H_{endo}–C(4)[4]	1.5–1.7	1.65–1.95		2.44	2.35–2.52
H_{endo}–C(9)[4]		2.58	2.23	2.44	
H_{exo}–C(4)[4]	1.2–1.5	1.38–1.50		1.19	1.15–1.28
H_{exo}–C(9)[4]		1.21	1.11	1.19	

is conclusive that a tertiary alcohol function (*Table 4*) forces the unsubstituted cyclohexane ring into a boat conformation, whereas a carbonyl and/or a methylidene group (*Table 5*) allows it to adopt a chair conformation. The conclusions are mainly based on dihedral-angle arguments of appropriate H-atoms (resulting from stereomodels).

A special case is the 5/6-membered-ring diene **5**. As it happened, both methylene protons H_{endo}–C(7)/H_{exo}–C(7) and H_{endo}–C(9)/H_{exo}–C(9), respectively, have the same chemical shift, and their coupling constants with the neighboring methylene protons H_{endo}–C(8) (δ = 2.01) and H_{exo}–C(8) (δ = 1.19) are equal, *i.e.*, an average of 7 Hz. Thus for diene **5**, a dynamic process is observed under the time scale of the ^{1}H-NMR measurement at room temperature.

Table 4. *^{1}H-NMR Coupling Constants* J [Hz] *at the Cyclohexane Ring Opposite to a Tertiary Alcohol Function in* **21**, **22**, *and* **31**

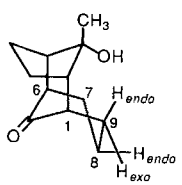
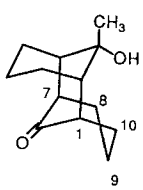
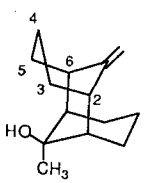
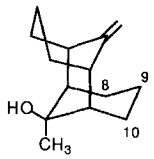
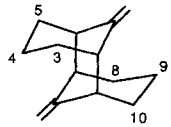
 **21**	 **22**	 **31**
H_{endo}–C(7), H_{endo}–C(9)(3.02 ppm)[4]	H_{endo}–C(8), H_{endo}–C(10) (2.90 ppm)[4]	H_{endo}–C(3), H_{endo}–C(5) (2.31 ppm)[4]
J_{gem} = 12	J_{gem} = 14	J_{gem} = 14
J(7*endo*,8*exo*) = *J*(8*exo*,9*endo*) = 12	*J*(8*endo*,9*exo*) = *J*(9*exo*,10*endo*) = 11.5	*J*(3*endo*,4*exo*) = *J*(4*exo*,5*endo*) = 11
J(7*endo*,8*endo*) = *J*(8*endo*,9*endo*) = 7.5	*J*(8*endo*,9*endo*) = *J*(9*endo*,10*endo*) = 7.5	*J*(3*endo*,4*endo*) = *J*(4*endo*,5*endo*) = 8.5
J(1,9*endo*) = *J*(6,7*endo*) = 1.5	*J*(1,10*endo*) = *J*(7,8*endo*) = 1.5	*J*(2,3*endo*) = *J*(5*endo*,6) = 1.5
H_{exo}–C(7), H_{exo}–C(9) (2.05 ppm)[4]	H_{exo}–C(8), H_{exo}–C(10) (2.20 ppm)[4]	
J_{gem} = 12	J_{gem} = 14	
J(1,9*exo*) = *J*(6,7*exo*) = 12	*J*(1,10*exo*) = *J*(7,8*exo*) = 11	
J(7*exo*,8*exo*) = *J*(8*exo*,9*exo*) = 7.5	*J*(8*exo*,9*exo*) = *J*(9*exo*,10*exo*) = 8.5	
J(7*exo*,8*endo*) = *J*(8*endo*,9*exo*) = 1.5	*J*(8*exo*,9*endo*) = *J*(9*endo*,10*exo*) = 2	
H_{endo}–C(8) (1.51 ppm)[4]		
J_{gem} = 14		
J(7*endo*,8*endo*) = *J*(8*endo*,9*endo*) = 7.5		
J(7*exo*,8*endo*) = *J*(8*endo*,9*exo*) = 1.5		

Table 5. *^{1}H-NMR Coupling Constants* J [Hz] *at the Cyclohexane Ring Opposite to a Methylidene Group in* **31** *and* **6**

31 	**6** 
H_{endo}–C(9) (2.23 ppm)	H_{endo}–C(4), H_{endo}–C(9) (2.44 ppm)
$J_{gem} = 14.5$	$J_{gem} = 14.5$
$J(8exo,9endo) = J(9endo,10exo) = 11.5$	$J(3exo,4endo) = J(4endo,5exo) = J(8exo,9endo) = J(9endo,10exo) = 11.5$
$J(8endo,9endo) = J(9endo,10endo) = 9$	$J(3endo,4endo) = J(4endo,5endo) = J(8endo,9endo) = J(9endo,10endo) = 6.5$
H_{exo}–C(9) (1.11 ppm)	H_{exo}–C(4), H_{exo}–C(9) (1.19 ppm)
$J_{gem} = 14.5$	$J_{gem} = 14.5$
$J(8exo,9exo) = J(9exo,10exo) = 9$	$J(3exo,4exo) = J(4exo,5exo) = J(8exo,9exo) = J(9exo,10exo) = 7$
$J(8endo,9exo) = J(9exo,10endo) = 0.5$	$J(3endo,4exo) = J(4exo,5endo) = J(8endo,9exo) = J(9exo,10endo) = 2.5$

The Photoelectron Spectra of Dienes 4–6. – The tricyclic dimethylidene compounds **4–6** are good models for sterically rigid nonconjugated double bonds which are interconnected by two ethano bridges. The method of choice to study the interactions among π-units in the He(I) PE spectroscopy which has been applied in many cases [9]. For **4–6**, we expect a similar interaction between the two double bonds as in 1,4-dimethylidenecyclohexane (**7**) [10]. The PE spectra of the three dienes **4–6** are shown in *Fig. 1*, and the first vertical ionization energies ($I_{v,j}$) of the four dienes **4–7** together with those of the five corresponding monoenes **8–11** are listed in *Table 6*.

The PE spectra of the monoenes exhibit one band which is well separated from strongly overlapping bands. A comparison of the ionization energies shows that there is a shift of the first band from 9.13 eV (**12**) to 8.54 eV (**11**). A shift towards lower energy has also been encountered in going from 2-methylidene-8,9,10-trinorbornane (9.04 eV) [11] to 2-methylidenebicyclo[2.2.2]octane (8.87 eV) [11]. The assignment of the first band of the monoenes **8–12** to the ejection of electrons from the π-MO is confirmed by taking into account the ionization energies of other 1,1-dialkylethylenes [11] [12] as well as the fine structure of the first band in **8** (1210 cm^{-1}), **9** (1290 cm^{-1}), and **11** (1290 cm^{-1}). A comparison of the first two bands of the dienes **4–7** (the observed split being 0.6–0.9 eV) with those of the corresponding monoenes **8–12** suggests the formers to be due to the ionization from the π-MOs.

Our empirical interpretation can be checked by means of MO calculations. We made the assumption (*Koopmans'* theorem [13]) that the recorded vertical ionization energies ($I_{v,j}$) can be set equal to the negative values of the calculated orbital energies ($-\varepsilon_j$), which usually is valid for larger hydrocarbons.

The MO energies of the dienes **4–7** and the monoenes **8–12** have been calculated applying the MINDO/3 [14] and the MNDO/2 [15] method (*Table 6*). Since the detailed structures of the compounds are not known, their geometries were optimized using the MMX force-field program [16]. It can be seen that the results obtained by both methods

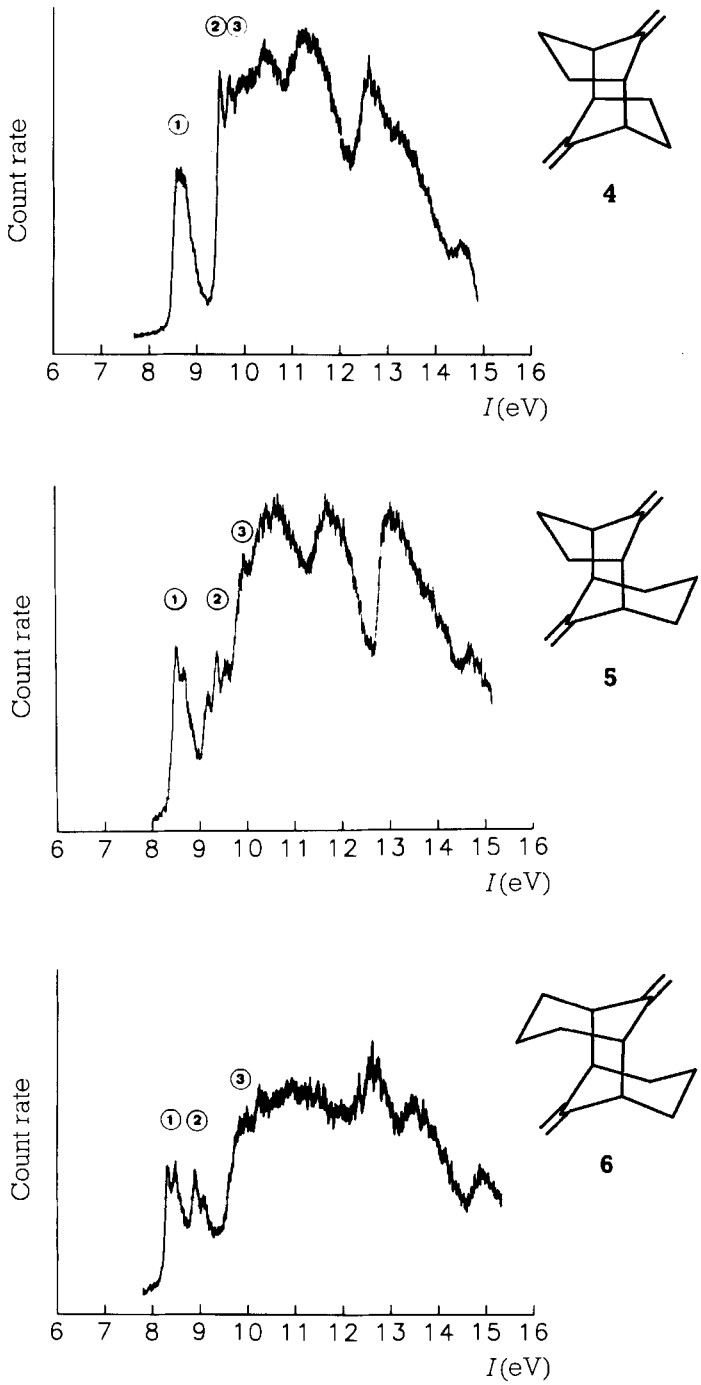
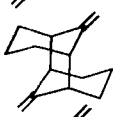


Fig. 1. *The PE spectra of the dienes* **4**–**6**

Table 6. *Comparison Between the Recorded Vertical Ionization Energies ($I_{v,j}$) of the Dienes* **4–7** *and the Monoenes* **8–12** *with Calculated Orbital Energies (ε_j).* All values in eV.

Compound	Band	$I_{v,j}$	Assignment	$-\varepsilon_j$ (MINDO/3)	$-\varepsilon_j$ (MNDO/2)
 **4**	1	8.6	$10a_g(\pi^+)$	9.02	9.56
	2	9.47	$9b_u(\pi^-)$	9.81	10.08
	3	9.7	$7a_u(\sigma)$	9.75	11.35
 **5**	1	8.50	$21a'(\pi^+)$	8.94	9.55
	2	9.36	$20a'(\pi^-)$	9.59	10.00
	3	10.05	$14a''(\sigma)$	9.89	11.42
 **6**	1	8.50	$12a_g(\pi^+)$	8.85	9.54
	2	8.90	$11b_u(\pi^-)$	9.54	9.94
	3	9.9	$7b_g(\sigma)$	9.80	11.33
 **7**	1	8.88	$7a_g(\pi^+)$	9.11	9.59
	2	9.56	$6b_u(\pi^-)$	9.89	10.07
	3	10.7	$4b_g(\sigma)$	10.16	11.74
 **8**	1	8.95	$18a'(\pi)$	9.29	9.78
	2	9.95	$12a''(\sigma)$	9.81	11.41
 **9**	1	8.80	$20a'(\pi)$	9.20	9.78
	2	9.85	$13a''(\sigma)$	9.84	11.39
 **10**	1	8.72	$20a'(\pi)$	9.10	9.69
	2	9.75	$13a''(\sigma)$	9.79	11.21
 **11**	1	8.54	$22a'(\pi)$	9.06	9.71
	2	9.6	$14a''(\sigma)$	9.75	11.23
 **12**	1	9.13	$12a'(\pi)$	9.37	9.80
	2	10.64	$8a''(\sigma)$	10.20	11.71

indeed confirm our empirical assignment. For the monoenes where the HOMO is predicted to be of π type, there is always a sizeable gap between the π- and σ-MOs. The π-MO is considerably delocalized due to σ/π mixing as discussed below.

Final Remarks. – To estimate the π/σ interactions prevailing in **4–6**, we have analyzed the interactions in **4** quantitatively. The geometry of **4** was optimized at the *Hartree-Fock* level using the 3-21G basis set [16] assuming C_{2h} symmetry. For the analysis, we make use of a procedure first suggested by *Heilbronner* and *Schmelzer* [17], later modified by *Imamura* and *Ohsaku* [18]. It is based on the *Fock* matrix in a localized basis set. The first step is the transformation of the canonical *Hartree-Fock* orbitals (CMOs) into a set of localized orbitals by means of the *Weinhold* natural bond orbital (NBO) localization procedure [19]. *Fig. 2* shows those symmetry-adapted NBOs which interact significantly with the π orbitals. We have divided them in three groups TB1, TB2, and TB3. A

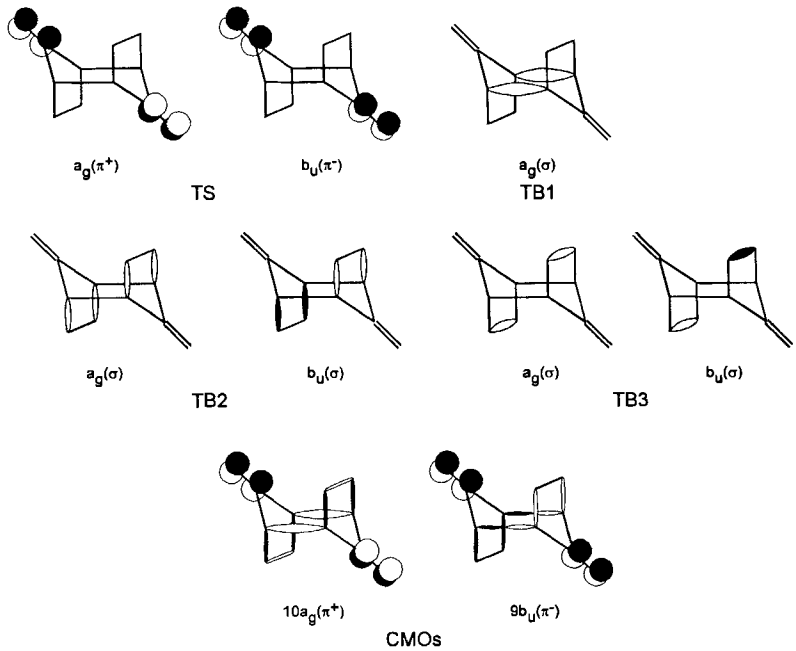


Fig. 2. *Symmetry-adapted NBOs which contribute to the π/σ interaction in* **4** *and the resulting canonical MOs $10a_g(\pi^+)$ and $9b_u(\pi^-)$.* For the meaning of TB1–TB3, see text and *Fig. 3.*

schematical drawing of the canonical MOs, 10 a_g (π^+) anf 9 b_u (π^-) as linear combination of the NBOs is shown at the bottom.

In *Fig. 3*, we divide the π/σ interaction in several steps. At the left, the energy of the localized π-orbitals of **4** (−10.02 eV) is shown. Allowing through-space (TS) interaction between them leads to a small split due to their large separation. The interaction with a_g (σ) (TB1) yields a destabilization of a_g (π^+) and thus a reversal of the original sequence. In the second step (TB2), both levels are destabilized, π^+ by 0.49 eV and π^- by only 0.21 eV. In the third step (TB3), only the a_g (σ) NBO is effective. The interaction with the NBO b_u (σ) is minute due to a very large energy difference between the basis orbital energies and much smaller coefficients. Finally, it results a split of 0.77 eV. To derive the CMOs, we find that π^- is lowered considerably due to an admixture of the b_u (σ^*) NBO localized at the bonds C(1)–C(2) and C(5)–C(6).

Table 7. *Calculated* (MMX) *Dihedral Angles* (Θ and Θ') *and Observed Energy Differences* ($\Delta I_v(\pi)$) *of the Dienes* **4**–**7**

	Θ[a])	Θ'[a])	$\Delta I_v(\pi)$
4	120	120	0.87
5	122	128	0.86
6	129	129	0.59
7	128	128	0.68

[a]) For definition of Θ and Θ', see **7**.

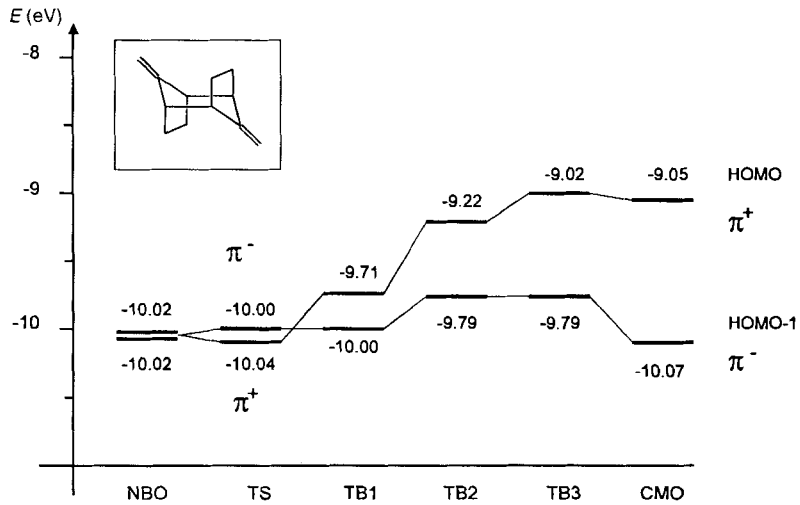


Fig. 3. *Through-space*(TS)- *and through-bond*(TB)-*interaction diagram for* **4**. NBO: energy of the localized π-NBOs; TS: energy after through-space interaction; TB1: energy after taking into consideration the NBOs TB1 of *Fig. 2*; TB2 and TB3 have a similar meaning as TB1; CMO: energy of the canonical molecular orbitals.

The PE spectra of the dienes **4**–**7** reveal a split of 0.6–0.9 eV between the π bands. The larger split found in the PE spectra of **4** and **5** as compared to **6** and **7** is ascribed to a better overlap between the σ-MOs which are localized in the C(a)–C(b) and C(c)–C(d) bonds of the central cyclohexane moiety (see **7**). This overlap should depend on the dihedral angles Θ and Θ' between the planes of the π systems and the plane spanned by C(a), C(b), C(c), and C(d). Corresponding values for the dienes **4**–**7** derived by force field calculation (MMX) [20] [8a] are given in *Table 7*. A maximum of interaction is encountered for **4** and a minimum for **6**.

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Experimental Part

General. For a representative procedure for the MeLi addition to ketones (under Ar in Et_2O, Et_2O dioxane, or THF), see the addition to **19**, and for the conversion of tertiary alcohols to olefins, see **5** from **30**. Column chromatography (CC): *Merck* silica gel *60*, 70–230 mesh. Flash chromatography (FC): silica gel *Merck 60*, 230–400 mesh. Gas chromatography: capillary GC von *UCON 50 HB 5100* (polar) or *SE 52 Sil* (apolar); prep. GC on 20% *SE 30*. Melting points (M.p.): in capillary tubes; not corrected. He(I) PE Spectra: *PS-18* spectrometer (*Perkin-Elmer*, Beaconsfield); at r.t.; calibration with Ar (15.76 and 15.94 eV) and Xe (12.13 and 13.44 eV); resolution, 20 meV on the $^2P_{3/2}$ Ar line. IR Spectra: $\tilde{\nu}_{max}$ in cm^{-1}. ^1H- and ^{13}C-NMR Spectra[4]): at the indicated frequencies and in the mentioned solvents; δ in ppm rel. to $SiMe_4$, J in Hz. MS: 70 eV/180° by the indirect method *A* (200°) or the direct method *B* (temp. indicated).

9,10-Dimethylidene-anti-*tricyclo[4.2.1.1^{2,5}]decane* (**4**). M.p. 122° (after sublimation at 72°/8 Torr). IR (CCl_4): 3067*m*, 1678*m*, 1670*m*, 1467*m*, 1452*m*, 1436*m*, 1426*w*, 1309*w*, 1298*m*, 1278*w*, 1230*w*, 1155*w*, 1143*m*, 1056*w*, 974*w*, 956*m*, 844*s*, 863*m*, 706*m*, 672*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.40–1.57, 1.58–1.77 (2*m*, 2 H–C(3), 2 H–C(4), 2 H–C(7), 2 H–C(8)); 2.30 (*m*, $w_{1/2} \approx 6$, H–C(1), H–C(2), H–C(5), H–C(6)). ^{13}C-NMR (25 MHz, $CDCl_3$): 27.50 (*t*, C(3), C(4), C(7), C(8)); 48.07 (*d*, C(1), C(2), C(5), C(6)); 102.68 (*t*, CH_2=C(9), CH_2=C(10)); 155.60 (*s*, C(9), C(10)). MS (*A*): 160 (2, M^+), 159 (1), 145 (3), 131 (7), 117 (9), 91 (13), 81 (100), 80 (99).

10,11-Dimethylidene-anti-*tricyclo[4.3.1.1^{2,5}]undecane* (**5**). To a soln. of 50 mg (0.26 mmol) of **30** in 3 ml of Et_2O (filtered through Alox *B*) were added 50 drops of pyridine. After cooling to 15°, 25 drops of $SOCl_2$ were added slowly, and the mixture was stirred for 4 h at r.t. Workup (poured on 50 g of ice and 2 ml of sat. aq. $CuSO_4$ soln., 3 × 30 ml of Et_2O, 50 ml of sat. aq. NaCl soln.), evaporation of the solvent through a *Vigreux* column, CC (50 g of silica gel, pentane), and sublimation at 120°/18 Torr led to 27 mg (60%) of **5**. M.p. 158°. IR (CCl_4): 3065*m*, 1668*m*, 1657*m*, 1458*m*, 1439*m*, 1405*w*, 1286*w*, 1223*w*, 1154*w*, 1121*w*, 1071*m*, 991*w*, 896*w*, 881*s*, 700*w*, 691*w*, 650*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.19 (*dtt*, $J_{gem} = 14$, $J(7endo,8exo) = J(8exo,9endo) = 7$, $J(7exo,8exo) = J(8exo,9exo) = 7$, H_{exo}–C(8)); 1.40–1.54 (*m*, 2 H–C(3), 2 H–C(4)); 1.78 (*ddd*, $J(7,8endo) = J(8endo,9) = 7$, $J(7,8exo) = J(8exo,9) = 7$, $J(1,9) = J(6,7) = 4.5$, 2 H–C(7), 2 H–C(9)); 2.01 (*dtt*, $J_{gem} = 14$, $J(7endo,8endo) = J(8endo,9endo) = 7$, $J(7exo,8endo) = J(8endo,9exo) = 7$, H_{endo}–C(8)); 2.28 (*dt*, $J(1,2) = J(5,6) = 5$, $J(1,9endo) = J(6,7,endo) = J(1,9exo) = J(6,7exo) = 4.5$, H–C(1), H–C(6)); 2.37 (*m*, $w_{1/2} \approx 12$, H–C(2), H–C(5)); 4.71 (*s*, CH_2=C(10)); 4.75 (*s*, CH_2=C(11)). ^{13}C-NMR (100 MHz, $CDCl_3$): 18.44 (*t*, C(8)); 26.59 (*t*, C(3), C(4)); 30.51 (*t*, C(7), C(9)); 46.97 (*d*, C(1), C(6)); 48.06 (*d*, C(2), C(5)); 103.70 (*t*, CH_2=C(10)); 106.95 (*t*, CH_2=C(11)); 152.67 (*s*, C(10)); 156.43 (*s*, C(11)). MS (*A*): 174 (7, M^+), 159 (4), 145 (9), 138 (22), 131 (14), 117 (12), 105 (8), 95 (59), 94 (100), 81 (70).

11,12-Dimethylidene-anti-*tricyclo[5.3.1.1^{2,6}]dodecane* (**6**). M.p. 192° (after sublimation at 140°/normal pressure). IR (CCl_4): 3070*m*, 1653*m*, 1465*m*, 1440*m*, 1327*w*, 1309*w*, 1280*w*, 1116*w*, 1056*w*, 966*w*, 884*s*, 857*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.19 (*dtt*, $J_{gem} = 14.5$, $J(3exo,4exo) = J(4exo,5exo) = J(8exo,9exo) = J(9exo,10exo) = 7$, $J(3endo,4exo) = J(4exo,5endo) = J(8endo,9exo) = J(9exo,10endo) = 2.5$, H_{exo}–C(4), H_{exo}–C(9)); 1.68–1.91 (*m*, 2 H–C(3), 2 H–C(5), 2 H–C(8), 2 H–C(10)); 2.44 (*dtt*, $J_{gem} = 14.5$, $J(3exo,4endo) = J(4endo,5exo) = J(8exo,9endo) = J(9endo,10exo) = 11.5$, $J(3endo,4endo) = J(4endo,5endo) = J(8endo,9endo) = J(9endo,10endo) = 6.5$, H_{endo}–C(4), H_{endo}–C(9)); 2.49 (*m*, $w_{1/2} \approx 8$, H–C(1), H–C(2), H–C(6), H–C(7)); 4.71 (*s*, CH_2=C(11), CH_2=C(12)). ^{13}C-NMR (75 MHz, $CDCl_3$): 18.67 (*t*, C(4), C(9)); 36.09 (*t*, C(3), C(5), C(8), C(10)); 47.26 (*d*, C(1), C(2), C(6), C(7)); 103.91 (*t*, CH_2=C(11), CH_2=C(12)); 158.01 (*s*, C(11), C(12)). MS (*A*): 189 (6, $[M + 1]^+$), 188 (43, M^+), 173 (16), 145 (21), 131 (15), 106 (21), 96 (30), 95 (100), 94 (92).

9-Methylidene-anti-*tricyclo[4.2.1.1^{2,5}]decane* (**8**)[7]. IR ($CDCl_4$): 3075*m*, 1677*m*, 1489*w*, 1462*m*, 1450*w*, 1445*w*, 1418*w*, 1315*m*, 1288*w*, 1203*w*, 1148*w*, 992*w*, 978*w*, 883*s*, 855*w*, 704*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.02 (*dt*, $J_{gem} = 11.5$, $J(2,10exo) = 3.5$, H_{exo}–C(10)); 1.35–1.52 (*m*, H_{endo}–C(3), H_{endo}–C(4)); 1.48–1.63 (*m*, H_{exo}–C(7), H_{exo}–C(8)); 1.58–1.75 (*m*, H_{exo}–C(3), H_{exo}–C(4), H_{endo}–C(7), H_{endo}–C(8)); 1.97–2.10 (*m*, H–C(2), H–C(5), H_{endo}–C(10)); 2.22 (*m*, $w_{1/2} \approx 13$, H–C(1), H–C(6)); 4.55 (*s*, CH_2–C(9)). ^{13}C-NMR (75 MHz, $CDCl_3$): 27.61, 28.97 (2*t*, C(3), C(4), C(7), C(8)); 31.65 (*t*, C(10)); 41.27 (*d*, C(2), C(5)); 46.81 (*d*, C(1), C(6)); 99.97 (*t*, CH_2=C(9)); 157.59 (*s*, C(9)). MS (*A*): 148 (4, M^+), 133 (4), 119 (11), 105 (9), 91 (24), 81 (100).

10-Methylidene-anti-*tricyclo[4.3.1.1^{2,5}]undecane* (**9**). IR (CCl_4): 3075*w*, 1660*m*, 1558*w*, 1488*w*, 1456*m*, 1442*w*, 1320*w*, 890*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.99 (*dtt*, $J_{gem} = 12$, $J(2,11exo) = J(5,11exo) = 4$, $J(1,11exo) = J(6,11exo) = 1.5$, H_{exo}–C(11)); 1.27–1.50 (*m*, H_{exo}–C(8), 4 H); 1.50–1.63 (*m*, H_{endo}–C(8)); 1.63–1.77 (*m*, 2 H); 1.77–1.90 (*m*, 2 H); 2.08, 2.16 (2*m*, $w_{1/2} \approx 13$, 16, H–C(1), H–C(2), H–C(5), H–C(6)); 2.29 (*dm*, $J_{gem} = 12$, $w_{1/2} \approx 5$ each, H_{endo}–C(11)); 4.59 (*s*, CH_2=C(10)). ^{13}C-NMR (75 MHz, $CDCl_3$): 18.65 (*t*, C(8)); 24.65 (*t*, C(3), C(4)); 29.36 (*t*, C(7), C(9)); 42.10, 44.28 (2*d*, C(1), C(2), C(5), C(6)); 105.89 (*t*, CH_2=C(10)); 153.28 (*s*, C(10)). MS (*A*): 162 (22, M^+), 147 (7), 134 (16), 133 (37), 119 (41), 108 (11), 105 (23), 96 (100), 95 (92), 91 (76).

11-Methylidene-anti-*tricyclo[4.3.1.1^{2,5}]undecane* (**10**). IR (CCl_4): 3075*w*, 1670*w*, 1483*w*, 1467*m*, 1413*w*, 883*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.20 (*dm*, $J_{gem} = 13$, $w_{1/2} \approx 5$ each, H_{exo}–C(10)); 1.21–1.33 (*m*, H_{exo}–C(8)); 1.45–1.65 (*m*, 4 H); 1.65–1.78 (*m*, 6 H); 1.89 (*dm*, $J_{gem} = 13$, $w_{1/2} \approx 10$ each, H_{endo}–C(10)); 2.28–2.45 (*m*, H_{endo}–C(8)); 2.39 (*m*, $w_{1/2} \approx 9$, H–C(2), H–C(5)); 4.60 (*s*, CH_2–C(11)). ^{13}C-NMR (75 MHz, $CDCl_3$): 17.69 (*t*, C(8)); 27.01 (*t*, C(3), C(4)); 27.28 (*t*, C(10)); 29.28 (*t*, C(7), C(9)); 36.51 (*d*, C(1), C(6)); 47.01 (*d*, C(2), C(5)); 101.05 (*t*, CH_2=C(11)); 159.14 (*s*, C(11)). MS (*A*): 162 (22, M^+), 147 (8), 133 (10), 119 (16), 106 (17), 93 (26), 91 (29), 81 (86), 80 (100).

11-Methylidene-anti-*tricyclo[5.3.1.1^{2,6}]dodecane* (**11**). IR (CCl_4): 3075*m*, 1653*m*, 1496*w*, 1467*m*, 1458*m*, 1445*w*, 1414*w*, 1290*w*, 880*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.15–1.28 (*m*, H_{exo}–C(4)); 1.32 (*dm*, $J_{gem} = 13$, $w_{1/2} \approx 6$ each, H_{exo}–C(12)); 1.40–1.52 (*m*, H_{exo}–C(9)); 1.60–1.72, 1.72–2.0 (2*m*, 2 H–C(3), 2 H–C(5), 2 H–C(8), 2 H–C(10)); 1.72–2.0 (*m*, H–C(2), H–C(6), H_{endo}–C(9)); 2.35–2.52 (*m*, H–C(1), H–C(7), H_{endo}–C(4), H_{endo}–C(12)); 4.63 (*s*, CH_2=C(11)). ^{13}C-NMR (75 MHz, $CDCl_3$): 18.83 (*t*, C(9)); 20.25 (*t*, C(4)); 28.80 (*t*, C(12));

32.48, 34.16 (2*t*, C(3), C(5), C(8), C(10)); 37.61 (*d*, C(2), C(6)); 45.22 (*d*, C(1), C(7)); 103.88 (*t*, CH_2=C(11)); 158.43 (*s*, C(11)). MS (*A*): 176 (33, M^+), 161 (14), 147 (9), 135 (26), 134 (30), 133 (23), 119 (16), 105 (19), 95 (49), 93 (35), 91 (48), 81 (41), 80 (100).

anti-*Tricyclo[4.3.1.1^{2,5}]undecane-10,11-dione* (**14**). Reduction of 400 mg (1.63 mmol) of **18** in 35 ml of MeOH and 6 ml of H_2O with H_2 over 150 mg of 10% Pd/C for 20 h at r.t., filtration of the mixture through *Celite* and FC (130 mg of silica gel, CH_2Cl_2/pentane 5:1) led to 284 mg (98%) of **14**. M.p. 153° (after recrystallization from CH_2Cl_2/hexane and sublimation at 115°/2.5 Torr). IR (CCl_4): 1750*s*, 1728*s*, 1478*m*, 1467*m*, 1450*m*, 1445*m*, 1350*w*, 1332*w*, 1302*m*, 1285*m*, 1242*m*, 1182*w*, 1175*w*, 1118*w*, 1086*m*, 1005*m*, 915*w*, 888*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.4–1.55 (*m*, H_{exo}–C(8)); 1.65–1.95 (*m*, 2 H–C(3), 2 H–C(4)); 2.0–2.35 (*m*, 2 H–C(7), 2 H–C(9), H_{endo}–C(8)); 2.41 (*m*, $w_{1/2} \approx 12$, H–C(2), H–C(5)); 2.60 (*m*, $w_{1/2} \approx 9$, H–C(1), H–C(6)). ^{13}C-NMR (75 MHz, $CDCl_3$): 17.02 (*t*, C(8)); 20.72 (*t*, C(3), C(4)); 32.89 (*t*, C(7), C(9)); 47.33 (*d*, C(1), C(6)); 55.78 (*d*, C(2), C(5)); 216.08, 216.73 (2*s*, C(10), C(11)). MS (*A*): 178 (100, M^+), 160 (11), 150 (4), 122 (21), 107 (20), 93 (49), 80 (68).

3-exo,*4*-exo-*(Dichloromethano)*-anti-*tricyclo[4.2.1.1^{2,5}]decane-9,10-dione* (**17**). Hydrogenation (H_2, 50 mg of 10% Pd/C) of 450 mg (1.85 mmol) of **16** [3] in 20 ml of AcOEt for 14 h at r.t., addition of 0.3 ml of CH_2Cl_2, filtration through *Celite*, washing the latter with 5 ml of CH_2Cl_2, and CC (30 g of silica gel, pentane/Et_2O 3:1) gave 436 mg (99%) of **17**. M.p. 160° (after recrystallization from CH_2Cl_2/hexane and sublimation at 130°/0.01 Torr). IR (CCl_4): 1790*w*, 1768*s*, 1760*s*, 1720*w*, 1670*w*, 1462*m*, 1448*w*, 1245*m*, 1200*w*, 1192*m*, 1108*m*, 1028*m*, 987*m*, 907*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.75–1.95, 1.95–2.15 (2*m*, *AA'BB*, 2 H–C(7), 2 H–C(8)); 2.40 (*s*, H_{endo}–C(3), H_{endo}–C(4)); 2.56 (*m*, $w_{1/2} \approx 14$, H–C(1), H–C(6)); 2.73 (*d*, $J(1,2) = J(5,6) = 6$, H–C(2), H–C(5)). ^{13}C-NMR (25 MHz, $CDCl_3$): 22.18 (*t*, C(7), C(8)); 33.66 (*d*, C(3), C(4)); 49.30, 51.10 (2*d*, C(1), C(6), C(2), C(5)); 62.89 (*s*, C(11)); 207.30, 208.97 (2*s*, C(9), C(10)). MS (*B*, 130°): 246 (3, $[M + 2]^+$), 244 (4, M^+), 220 (3), 218 (14), 216 (22), 211 (11), 209 (31), 150 (75), 148 (100), 117 (22), 115 (33), 113 (78). Anal. calc. for $C_{11}H_{10}Cl_2O_2$ (214.11): C 53.90, H 4.11; found: C 54.03, H 4.22.

8,9-exo-*Dichloro*-anti-*tricyclo[4.3.1.1^{2,5}]undec-7-ene-10,11-dione* (**18**). In a sealed glas tube, 436 mg (1.78 mmol) of **17** were kept at 160° for 1 h. Filtration in 50 ml of CH_2Cl_2 through a small amount of silica gel yielded 436 mg (quant.) of crude **18**. M.p. 249° (after recrystallization from CH_2Cl_2/hexane and sublimation at 145°/0.05 Torr). IR (KBr): 3065*w*, 1750*s*, 1738*s*, 1623*w*, 1466*w*, 1452*w*, 1361*w*, 1332*w*, 1296*m*, 1235*m*, 1203*w*, 1113*m*, 1072*w*, 1046*w*, 1011*m*, 990*w*, 980*w*, 950*m*, 902*m*, 892*m*, 868*w*, 848*w*, 806*w*, 754*w*, 742*m*. ^{1}H-NMR (300 MHz, (D_5)pyridine): 1.55–1.9 (*m*, 2 H–C(3), 2 H–C(4)); 2.53 (*m*, $w_{1/2} \approx 15$, H–C(5)); 2.63 (*m*, $w_{1/2} \approx 13$, H–C(2)); 3.18 (*ddd*, $J(6,7) = 6.5$, $J(5,6) = 5.5$, $J(1,6) = 3$, H–C(6)); 3.28 (*ddd*, $J(1,2) = 5$, $J(1,6) = 3$, $J(1,9) = 1.5$, H–C(1)); 5.52 (*dd*, $J(1,9) = 1.5$, $J(3,7) = 0.5$, H–C(9)); 6.27 (*dd*, $J(6,7) = 6.5$, $J(7,9) = 0.5$, H–C(7)). MS (*A*): 248 (3, $[M + 4]^+$), 246 (21, $[M + 2]^+$), 244 (31, M^+), 211 (4), 209 (14), 183 (5), 181 (16), 155 (6), 153 (18), 125 (28), 117 (35), 91 (36), 83 (100), 82 (78). Anal. calc. for $C_{11}H_{10}Cl_2O_2$ (214.11): C 53.90, H 4.11; found: C 53.84, H 4.10.

10-endo-*Hydroxy-10*-exo-*methyl*-anti-*tricyclo[4.2.1.1^{2,5}]decan-9-one* (**20**). M.p. 110°. IR (CCl_4): 3618*m*, 3472*m* (br.), 3008*m*, 1747*s*, 1722*w*, 1482*m*, 1451*m*, 1440*w*, 1378*m*, 1325*m*, 1282*m*, 1247*m*, 1182*m*, 1154*m*, 1119*s*, 1077*m*, 1041*m*, 1004*m*, 978*m*, 964*m*, 948*m*, 921*m*, 682*w*, 655*w*. ^{1}H-NMR (100 MHz, $CDCl_3$): 1.35 (*s*, Me_{exo}–C(10)); 1.4–1.9 (*m*, 2 H–C(3), 2 H–C(4), H_{exo}–C(7), H_{exo}–C(8)); 1.57 (*s*, OH_{endo}–C(10)); 1.96, 2.11 (2*m*, $w_{1/2} \approx 12$, 10, H–C(1), H–C(2), H–C(5), H–C(6)); 2.6–2.8 (*m*, H_{endo}–C(7), H_{endo}–C(8)). MS (*B*, 100°): 180 (24, M^+), 165 (9), 162 (20), 152 (11), 147 (9), 137 (22), 119 (31), 109 (37), 97 (35), 93 (37), 91 (30), 84 (41), 79 (36), 71 (82), 43 (100).

11-endo-*Hydroxy-11*-exo-*methyl*-anti-*tricyclo[4.3.1.1^{2,5}]undecan-10-one* (**21**). To a soln. of 5.8 mg (32.5 μmol) of **14** in 2 ml of Et_2O (filtered through Alox *B*) under Ar were added dropwise 2 ml of 1.6M MeLi in Et_2O over 10 min at r.t., and the mixture was stirred for 17 h at r.t. Workup (1 ml of H_2O, 3 × 5 ml of Et_2O) and CC (5 g of silica gel, pentane/Et_2O 2:1) gave 4.7 mg (76%) of **21**. M.p. 131°. IR ($CHCl_3$): 3610*m*, 3450*w* (br.), 1709*s*, 1477*m*, 1447*m*, 1376*w*, 1160*w*, 1133*m*, 1083*m*, 1043*m*, 981*m*, 952*w*, 918*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.23–1.33 (*m*, H_{endo}–C(3), H_{endo}–C(4)); 1.25–1.42 (*m*, H_{exo}–C(8)); 1.32 (*s*, OH_{endo}–C(11)); 1.37 (*s*, Me_{exo}–C(11)); 1.51 (*dtt*, $J_{gem} = 14$, $J(7endo,8endo) = J(8endo,9endo) = 7.5$, $J(7exo,8endo) = J(8endo,9exo) = 1.5$, H_{endo}–C(8)); 1.65–1.77 (*m*, H_{exo}–C(3), H_{exo}–C(4)); 2.03 (*m*, $w_{1/2} \approx 8$, H–C(2), H–C(5)); 2.05 (*dddd*, $J_{gem} = 12$, $J(1,9exo) = J(6,7exo) = 12$, $J(7exo,8exo) = J(8exo,9exo) = 7.5$, $J(7exo,8endo) = J(8endo,9exo) = 1.5$, H_{exo}–C(7), H_{exo}–C(9)); 2.36 (*ddd*, $J(1,9exo) = J(6,7exo) = 12$, $J(1,2) = J(5,6) = 4.5$, $J(1,9endo) = J(6,7endo) = 1.5$, H–C(1), H–C(6)); 3.02 (*dddd*, $J_{gem} = 12$, $J(7endo,8exo) = J(8exo,9endo) = 12$, $J(7endo,8endo) = J(8endo,9endo) = 7.5$, $J(1,9endo) = J(6,7endo) = 1.5$, H_{endo}–C(7), H_{endo}–C(9)). ^{13}C-NMR (75 MHz, $CDCl_3$): 17.20 (*t*, C(8)); 24.80 (*t*, C(3), C(4)); 29.95 (*q*, Me_{exo}–C(11)); 30.23 (*t*, C(7), C(9)); 48.01 (*d*, C(1), C(6)); 52.59 (*d*, C(2), C(5)); 80.41 (*s*, C(11)); 222.90 (*s*, C(10)). MS (*A*): 195 (17, $[M + 1]^+$), 194 (16, M^+), 176 (45), 151 (71), 133 (79), 123 (44), 109 (61), 96 (79), 81 (85), 81 (100), 43 (94).

12-endo-*Hydroxy-12*-exo-*methyl*-anti-*tricyclo[5.3.1.1^{2,6}]dodecan-11-one* (**22**). To a soln. of 35.5 mg (0.165 mmol) of **19** in 1.5 ml of Et_2O and 2 ml of dioxane under Ar at −70° were added dropwise 5 ml of 1.6M MeLi

in Et_2O, and the mixture was stirred for 4 h at r.t. Workup (ice, CH_2Cl_2) and filtration through 15 g of silica gel in Et_2O gave 40 mg (97%) of **22**. M.p. 163° (after sublimation at 115°/0.04 Torr). IR (CCl_4): 3607*m*, 3430*w* (br.), 1725*w*, 1710*s*, 1478*m*, 1459*w*, 1444*m*, 1372*w*, 1295*w*, 1246*w*, 1133*m*, 1086*m*, 1032*w*, 936*w*, 896*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.2–1.5 (*m*, H_{exo}–C(4), H_{exo}–C(9)); 1.24 (*s*, OH_{endo}–C(12)); 1.45 (*s*, Me_{exo}–C(12)); 1.5–1.7 (*m*, H_{endo}–C(4), H_{endo}–C(9)); 1.5–1.7, 1.87–2.05 (2*m*, 2 H–C(3), 2 H–C(5)); 2.10 (*m*, $w_{1/2} \approx 9$, H–C(2), H–C(6)); 2.20 (*dddd*, $J_{gem} = 14$, $J(1,10exo) = J(7,8endo) = 11$, $J(8exo,9exo) = J(9exo,10exo) = 8.5$, $J(8exo,9endo) = J(9endo,10exo) = 2$, H_{exo}–C(8), H_{exo}–C(10)); 2.47 (*dd*, $J(1,10exo) = J(7,8exo) = 11$, $J(1,2) = J(6,7) = 1.5$, H–C(1), H–C(7)); 2.90 (*dddd*, $J_{gem} = 14$, $J(8endo,9exo) = J(9exo,10endo) = 11.5$, $J(8endo,9endo) = J(9endo,10endo) = 7.5$, $J(1,10endo) = J(7,8endo) = 1.5$, H_{endo}–C(8), H_{endo}–C(10)). MS (*B*): 209 (2, $[M + 1]^+$), 208 (2, M^+), 190 (16), 165 (18), 149 (10), 147 (12), 109 (15), 97 (26), 96 (100), 95 (46), 94 (41), 81 (23), 79 (20), 67 (20), 55 (15), 43 (33).

9-exo,*10*-exo-*Dimethyl*-anti-*tricyclo[4.2.1.1^{2,5}]decane-9*-endo,*10*-endo-*diol* (**23**). M.p. 182.5°. IR (CCl_4): 3625*m*, 3300*w* (br.), 3025*w*, 1488*m*, 1448*m*, 1338*w*, 1283*m*, 1182*s*, 1106*m*, 958*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.17 (*s*, OH_{endo}–C(9), OH_{endo}–C(10)); 1.39 (*s*, Me_{exo}–C(9), Me_{exo}–C(10)); 1.45–1.64 (*m*, H_{exo}–C(3), H_{exo}–C(4), H_{exo}–C(7), H_{exo}–C(8)); 1.80 (*m*, $w_{1/2} \approx 6$, H–C(1), H–C(2), H–C(5), H–C(6)); 2.50–2.69 (*m*, H_{endo}–C(3), H_{endo}–C(4)). MS (*A*): 196 (0.5, M^+), 178 (9), 163 (19), 137 (20), 135 (42), 71 (49), 43 (100).

10-exo,*11*-exo-*Dimethyl*-anti-*tricyclo[4.3.1.1^{2,5}]undecane-10*-endo,*11*-endo-*diol* (**24**). M.p. 196–200° (sealed capillary tube). IR (KBr): 1474*m*, 1442*m*, 1402*w*, 1473*m*, 1358*s*, 1350*w*, 1318*w*, 1263*m*, 1204*m*, 1190*s*, 1135*w*, 1108*s*, 1042*m*, 972*m*, 955*w*, 939*s*, 856*w*, 812*w*, 803*w*, 786*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.93, 1.15 (2*s*, OH_{endo}–C(10), OH_{endo}–C(11)); 1.2–1.4 (*m*, H_{exo}–C(8)); 1.33, 1.39 (2*s*, Me_{exo}–C(10), Me_{exo}–C(11)); 1.46–1.56 (*m*, H_{exo}–C(3), H_{exo}–C(4)); 1.68–1.78, 1.98–2.10 (2*m*, 2 H–C(7), 2 H–C(9), H–C(1), H–C(2), H–C(5), H–C(6)); 1.78–1.95 (*m*, H_{endo}–C(8)); 2.10–2.20 (*m*, H_{endo}–C(3), H_{endo}–C(4)). ^{13}C-NMR (100 MHz, $CDCl_3$): 17.28 (*t*, C(8)); 25.99 (*t*, C(3), C(4)); 29.32 (*t*, C(7), C(9)); 31.38, 31.47 (2*q*, Me_{exo}–C(10), Me_{exo}–C(11)); 44.12, 47.93 (2*d*, C(1), C(2), C(5), C(6)); 75.98, 78.07 (2*s*, C(10), C(11)). MS (*A*): 192 (15, $[M - 18]^+$), 177 (21), 149 (34), 121 (13), 110 (21), 107 (13), 93 (22), 81 (21), 71 (23), 67 (18), 43 (100).

11-exo-*12*-exo-*Dimethyl*-anti-*tricyclo[5.3.1.1^{2,6}]dodecane-11*-endo,*12*-endo-*diol* (**25**). To a soln. of 31.5 mg (0.163 mmol) of **19** in 16 ml of THF under Ar at −70° were added dropwise over 5 min 1.6 ml of 1.6M MeLi in Et_2O, and the mixture was stirred at r.t. for 12 h. Workup (ice, CH_2Cl_2) and CC (30 g of silica gel, pentane/Et_2O 3:1) led to 7.5 mg (22%) of **22** and 25.5 mg (70%) of **25**. M.p. 269° (sealed capillary tube, after sublimation at 130°/0.3 Torr). IR (KBr): 3012*m*, 1468*w*, 1443*m*, 1371*s*, 1363*s*, 1328*m*, 1250*m*, 1204*m*, 1166*w*, 1140*m*, 1112*s*, 1051*w*, 1018*m*, 967*m*, 932*s*, 891*w*, 797*w*, 688*w*, 643*w*. ^{1}H-NMR (300 MHz, (D_5)pyridine): 1.47–1.63 (*m*, H_{exo}–C(4), H_{exo}–C(9)); 1.70 (*s*, Me_{exo}–C(11), Me_{exo}–C(12)); 2.03 (*m*, $w_{1/2} \approx 12$, H–C(1), H–C(2), H–C(6), H–C(7)); 2.2–2.6 (*m*, 2 H–C(3), 2 H–C(5), 2 H–C(8), 2 H–C(9)); 2.36–2.53 (*m*, H_{endo}–C(4), H_{endo}–C(9)). ^{13}C-NMR (75 MHz, (D_5)pyridine): 17.19 (*t*, C(4), C(9)); 30.35 (*t*, C(3), C(5), C(8), C(10)); 30.98 (*q*, Me_{exo}–C(11), Me_{exo}–C(12)); 47.05 (*d*, C(1), C(2), C(6), C(7)); 71.82 (*s*, C(11), C(12)). MS (*B*): 206 (41, $[M - 18]^+$), 191 (44), 173 (20), 163 (42), 43 (100).

10-Methylidene-anti-*tricyclo[4.2.1.1^{2,5}]decan-9-one* (**26**). M.p. 166° (after sublimation at 88°/12 Torr). IR (CCl_4): 3074*w*, 1753*s*, 1729*m*, 1680*w*, 1670*w*, 1466*m*, 1442*m*, 1325*w*, 1283*w*, 1256*w*, 1179*w*, 1144*m*, 1037*m*, 942*m*, 896*s*, 710*w*, 697*w*. ^{1}H-NMR (100 MHz, $CDCl_3$): 1.5–1.9 (*m*, 2 H–C(3), 2 H–C(4), 2 H–C(7), 2 H–C(8)); 2.12, 2.48 (2*m*, $w_{1/2} \approx 12$ each, H–C(1), H–C(2), H–C(5), H–C(6)); 4.94 (*s*, CH_2=C(10)). ^{13}C-NMR (25 MHz, $CDCl_3$): 22.21 (*t*, C(7), C(8)); 26.86 (*t*, C(3), C(4)); 48.41, 50.20 (2*d*, C(1), C(2), C(5), C(6)); 106.54 (*t*, CH_2=C(10)); 152.26 (*s*, C(10)); 216.73 (*s*, C(9)). MS (*B*, 90°): 162 (74, M^+), 147 (20), 133 (13), 119 (47), 105 (39), 91 (82), 82 (100).

11-Methylidene-anti-*tricyclo[4.3.1.1^{2,5}]undecan-10-one* (**27**). M.p. 165°. IR (CCl_4): 3070*m*, 1724*s*, 1676*w*, 1462*m*, 1441*m*, 1413*w*, 1348*w*, 1301*w*, 1277*w*, 1226*m*, 1153*w*, 1109*w*, 1096*w*, 1036*m*, 941*w*, 893*s*, 692*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.1–1.25 (*m*, H_{exo}–C(8)); 1.47–1.56 (*m*, H_{endo}–C(3), H_{endo}–C(4)); 1.63–1.75 (*m*, H_{exo}–C(3), H_{exo}–C(4)); 1.97–2.18 (*m*, 2 H–C(7), 2 H–C(9), H_{endo}–C(8)); 2.36 (*m*, $w_{1/2} \approx 14$, H–C(1), H–C(6)); 2.61 (*m*, $w_{1/2} \approx 12$, H–C(2), H–C(5)); 4.98 (*s*, CH_2=C(11)). ^{13}C-NMR (100 MHz, $CDCl_3$): 18.09 (*t*, C(8)); 26.03 (*t*, C(3), C(4)); 31.88 (*t*, C(7), C(9)); 47.92 (*d*, C(1), C(6)); 53.98 (*d*, C(2), C(5)); 106.89 (*t*, CH_2=C(11)); 153.37 (*s*, C(11)); 220.36 (*s*, C(10)). MS (*A*): 177 (7, $[M + 1]^+$), 176 (50, M^+), 161 (6), 148 (8), 133 (16), 119 (25), 96 (100), 79 (57).

12-Methylidene-anti-*tricyclo[5.3.1.1^{2,6}]dodecan-11-one* (**28**). M.p. 178° (after sublimation at 90°/12 Torr). IR (CCl_4): 3074*m*, 1725*s*, 1708*m*, 1692*w*, 1655*m*, 1470*m*, 1442*m*, 1408*w*, 1366*m*, 1339*w*, 1303*m*, 1264*w*, 1232*m*, 1174*w*, 1123*w*, 1088*w*, 1078*m*, 1057*m*, 970*w*, 903*m*, 892*s*, 872*s*, 705*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.21 (*dtt*, $J_{gem} = 14.5$, $J(8exo,9exo) = J(9exo,10exo) = 6.5$, $J(8endo,9exo) = J(9exo,10endo) = 2.5$, H_{exo}–C(9)); 1.38–1.50 (*m*, H_{exo}–C(4)); 1.65–1.95 (*m*, 2 H–C(3), 2 H–C(5), H_{endo}–C(4)); 2.02–2.25 (*m*, 2 H–C(8), 2 H–C(10)); 2.48 (*m*, $w_{1/2} \approx 10$, H–C(1), H–C(7)); 2.58 (*dtt*, $J_{gem} = 14.5$, $J(8exo,9endo) = J(9endo,10exo) = 12$,

J(8*endo*,9*endo*) = *J*(9*endo*,10*endo*) = 7, H_{endo}–C(9)); 2.78 (*m*, $w_{1/2} \approx 7$, H–C(2), H–C(6)); 4.87 (*s*, CH_2=C(12)). MS (*B*): 191 (19, $[M+1]^+$), 190 (100, M^+), 175 (7), 172 (10), 162 (14), 157 (11), 147 (19), 133 (37), 119 (20), 96 (86). Anal. calc. for $C_{13}H_{18}O$ (190.29): C 82.06, H 9.54; found: C 81.74, H 9.48.

9-exo-*Methyl-10-methylidene*-anti-*tricyclo[4.2.1.1*^{2,5}*]decan-9*-endo-*ol* (**29**). M.p. 76° (after sublimation at 74°/9 Torr). IR (CCl_4): 3618*m*, 3488*w* (br.), 3063*w*, 1678*w*, 1670*m*, 1469*m*, 1452*w*, 1442*m*, 1438*w*, 1373*m*, 1279*m*, 1208*s*, 1178*m*, 1113*s*, 1075*m*, 984*w*, 965*m*, 940*m*, 927*m*, 879*s*, 859*m*. ^{1}H-NMR (100 MHz, CCl_4): 0.92 (*s*, OH_{endo}–C(9)); 1.22 (*s*, Me_{exo}–C(9)); 1.3–1.8 (*m*, 2 H–C(7), 2 H–C(8), H–C(1), H–C(6), H_{exo}–C(3), H_{exo}–C(4)); 2.24 (*m*, $w_{1/2} \approx 11$, H–C(2), H–C(5)); 2.4–2.6 (*m*, H_{endo}–C(3), H_{endo}–C(4)); 4.50 (*s*, CH_2=C(10)). MS (*A*): 178 (10, M^+), 163 (20), 160 (48), 145 (59), 135 (100), 131 (66), 120 (40), 105 (43), 93 (64), 81 (97).

10-exo-*Methyl-11-methylidene*-anti-*tricyclo[4.3.1.1*^{2,5}*]undecan-10*-endo-*ol* (**30**). M.p. 153°. IR ($CHCl_3$): 3595*m*, 3061*w*, 1670*m*, 1474*m*, 1468*m*, 1456*m*, 1445*s*, 1379*m*, 1315*w*, 1281*w*, 1262*w*, 1122*w*, 1105*m*, 1092*s*, 953*m*, 917*s*, 884*s*, 833*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.04 (*s*, OH_{endo}–C(10)); 1.14–1.27 (*m*, H_{exo}–C(8)); 1.26 (*s*, Me_{exo}–C(10)); 1.38–1.48 (*m*, H_{exo}–C(3), H_{exo}–C(4)); 1.62–1.73, 1.92–2.10 (2*m*, 2 H–C(7), 2 H–C(9)); 1.75 (*m*, $w_{1/2} \approx 13$, H–C(1), H–C(6)); 2.0–2.15 (*m*, H_{endo}–C(8)); 2.15–2.23 (*m*, H_{endo}–C(3), H_{endo}–C(4)); 2.44 (*m*, $w_{1/2} \approx 12$, H–C(2), H–C(5)); 4.66 (*s*, CH_2=C(11)). ^{13}C-NMR (75 MHz, $CDCl_3$): 13.38 (*t*, C(8)); 26.91 (*t*, C(3), C(4)); 29.17 (*t*, C(7), C(9)); 31.40 (*q*, Me_{exo}–C(10)); 46.68 (*d*, C(1), C(6)); 48.51 (*d*, C(2), C(5)); 74.94 (*s*, C(10)); 100.97 (*t*, CH_2=C(11)); 157.75 (*s*, C(11)). MS (*A*): 193 (2, $[M+1]^+$), 192 (15, M^+), 177 (34), 174 (20), 159 (29), 149 (64), 145 (24), 94 (100), 81 (91), 67 (34), 43 (50).

11-exo-*Methyl-12-methylidene*-anti-*tricyclo[5.3.1.1*^{2,6}*]dodecan-11*-endo-*ol* (**31**). IR (CCl_4): 3608*m*, 3067*w*, 3012*w*, 1602*m*, 1475*m*, 1445*m*, 1372*w*, 1317*w*, 1251*w*, 1138*m*, 1113*m*, 1087*m*, 1056*w*, 1031*w*, 950*w*, 933*w*, 897*w*, 888*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.11 (*dtt*, J_{gem} = 14.5, *J*(8*exo*,9*exo*) = *J*(9*exo*,10*exo*) = 9, *J*(8*endo*,9*exo*) = *J*(9*exo*,10*endo*) = 0.5, H_{exo}–C(9)); 1.35–1.52 (*m*, 2 H–C(4)); 1.36 (*s*, Me_{exo}–C(11)); 1.52 1.65 (*m*, H_{exo}–C(8), H_{exo}–C(10)); 1.75 (*m*, $w_{1/2} \approx 10$, H–C(1), H–C(7)); 1.83–2.05 (*m*, H_{exo}–C(3), H_{exo}–C(5), H_{endo}–C(8), H_{endo}–C(10)); 2.23 (*dtt*, J_{gem} = 14.5, *J*(8*exo*,9*endo*) = *J*(9*endo*,10*exo*) = 11.5, *J*(8*endo*,9*endo*) = *J*(9*endo*,10*endo*) = 9, H_{endo}–C(9)); 2.31 (*dddd*, J_{gem} = 14, *J*(3*endo*,4*exo*) = *J*(4*exo*,5*endo*) = 11, *J*(3*endo*,4*endo*) = *J*(4*endo*,5*endo*) = 8.5, *J*(2,3*endo*) = *J*(5*endo*,6) = 1.5, H_{endo}–C(3), H_{endo}–C(5)); 2.56 (*ddd*, *J*(2,3*exo*) = *J*(5*exo*,6) = 10, *J*(2,3*endo*) = *J*(5*endo*,6) = 1.5, *J*(1,2) = *J*(6,7) ≈ 1.5, H–C(2), H–C(6)); 4.74 (*s*, CH_2=C(12)). MS (*B*, < 100°): 207 (5, $[M+1]^+$), 206 (31, M^+), 191 (29), 188 (64), 173 (73), 163 (24), 159 (37), 145 (46), 95 (100), 94 (92), 43 (73).

9-exo-*Methyl*-anti-*tricyclo[4.2.1.1*^{2,5}*]decan-10*-endo-*ol* (**36**)[7]. M.p. 96°. IR (CCl_4): 3625*w*, 1473*m*, 1452*w*, 1445*w*, 1377*w*, 1315*w*, 1283*m*, 1218*m*, 1184*m*, 1108*s*, 982*m*, 939*w*, 909*s*. ^{1}H-NMR (90 MHz, $CDCl_3$): 1.00 (*dt*, J_{gem} = 11, *J*(2,10*exo*) = *J*(5,10*exo*) = 3, H_{exo}–C(10)); 1.15–1.8 (*m*, 2 H–C(7), 2 H–C(8), H–C(1), H–C(6), H_{exo}–C(3), H_{exo}–C(4), OH_{endo}–C(9)); 1.30 (*s*, Me_{exo}–C(9)); 1.9–2.3 (*m*, H–C(2), H–C(5), H_{endo}–C(10)); 2.3–2.65 (*m*, H_{endo}–C(3), H_{endo}–C(4)). ^{13}C-NMR (75 MHz, $CDCl_3$): 28.53, 30.09 (2*t*, C(3), C(4), C(7), C(8)); 31.70 (*q*, Me_{exo}–C(9)); 33.82 (*t*, C(10)); 41.27, 44.94 (2*d*, C(1), C(2), C(5), C(6)); 81.97 (*s*, C(9)). MS (*A*): 166 (46, M^+), 151 (10), 148 (5). 137 (34), 133 (8), 123 (40), 108 (29), 81 (57), 79 (36), 71 (74), 67 (42), 43 (100).

10-exo-*Methyl*-anti-*tricyclo[4.3.1.1*^{2,5}*]undecan-10*-endo-*ol* (**37**). M.p. 109–110°. IR (CCl_4): 3655*m*, 3500*w* (br.), 1340*w*, 1315*m*, 1297*m*, 1222*m*, 1204*w*, 1178*w*, 1155*w*, 1117*m*, 1026*w*, 954*s*, 936*m*, 894*w*, 818*w*, 778*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.94 (*dt*, J_{gem} = 12, *J*(2,11*exo*) = *J*(5,11*exo*) = 4, H_{exo}–C(11)); 1.04 (*s*, OH_{endo}–C(10)); 1.22 (*s*, Me_{exo}–C(10)); 1.40–1.50 (*m*, H_{exo}–C(3), H_{exo}–C(4)); 1.50–1.66 (*m*, 4 H); 1.66 (*dm*, J_{gem} = 12, $w_{1/2} \approx 4$ each, H_{endo}–C(11)); 1.70–1.88 (*m*, 1 H); 1.98 2.22 (*m*, H–C(1), H–C(2), H–C(5), H–C(6), and 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 16.58 (*t*, C(8)); 28.49 (*t*, C(3), C(4)); 29.03 (*t*, C(7), C(9)); 31.32 (*q*, Me_{exo}–C(10)); 31.40 (*t*, C(11)); 42.60, 43.41 (2*d*, C(1), C(2), C(5), C(6)); 75.26 (*s*, C(10)). MS (*A*): 180 (87, M^+), 165 (24), 162 (8), 151 (18), 147 (20), 137 (26), 133 (13), 123 (62), 119 (22), 95 (64), 81 (87), 67 (74), 43 (100).

11-exo-*Methyl*-anti-*tricyclo[4.3.1.1*^{2,5}*]undecan-11*-endo-*ol* (**38**). M.p. 104°. IR (CCl_4): 3615*m*, 3500*m* (br.), 1492*m*, 1470*m*, 1446*m*, 1370*m*, 1310*w*, 1171*m*, 1130*m*, 1106*m*, 1084*m*, 968*m*, 951*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.22 (*s*, Me_{exo}–C(11)); 1.22–1.33 (*m*, 3 H); 1.3–1.4 (*m*, OH_{endo}–C(11)); 1.45–1.75 (*m*, 5 H); 1.64, 1.82 (2*m*, $w_{1/2}$ = 8, 10, H–C(1), H–C(2), H–C(5), H–C(6)); 1.75–1.95 (*m*, 2 H); 2.05–2.18 (*m*, 2 H). MS (*A*): 180 (50, M^+), 165 (19), 162 (16), 147 (8), 137 (100), 133 (12), 122 (34), 81 (93), 71 (82), 67 (41), 43 (95).

11-exo-*Methyl*-anti-*tricyclo[5.3.1.1*^{2,6}*]dodecan-11*-endo-*ol* (**39**). M.p. 142–143°. IR (CCl_4): 3610*w*, 1494*w*, 1470*w*, 1434*m*, 1370*m*, 1136*w*, 1118*w*, 1080*w*, 950*m*, 911*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.32 (*s*, Me_{exo}–C(11)); 1.4–1.65 (*m*, 8 H); 1.65–2.15 (*m*, 11 H). MS (*A*): 194 (4, M^+), 179 (5), 176 (4), 161 (8), 151 (8), 137 (13), 95 (38), 81 (37), 80 (100).

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