

15. Interaction between Exocyclic *s-cis*-Butadiene and Homoconjugated Functions. Preparation and *Diels-Alder* Reactivity of Remotely Substituted 2,3-Dimethylidenebicyclo[2.2.2]octanes¹⁾

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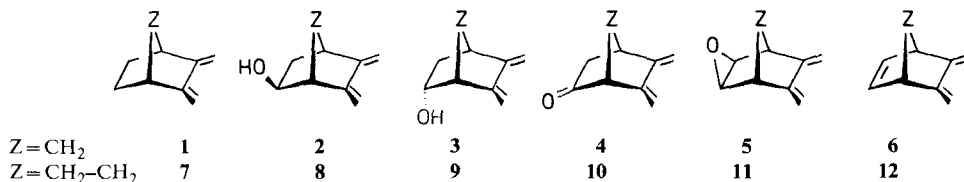
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(23. X. 81)

Summary

The preparations of 5,6-dimethylidene-2-*exo*-bicyclo[2.2.2]octanol (**8**), its *endo* isomer **9**, 5,6-dimethylidene-2-bicyclo[2.2.2]octanone (**10**) and 2-*exo*,3-*exo*-epoxy-5,6-dimethylidenebicyclo[2.2.2]octane (**11**) are described. The kinetics of their cycloaddition to tetracyanoethylene has been measured in toluene at 25° together with those of 2,3-dimethylidenebicyclo[2.2.2]octane (**7**) and 5,6-dimethylidenebicyclo[2.2.2]oct-2-ene (**12**). The effects of remote substitution on the *Diels-Alder* reactivity of 2,3-dimethylidenebicyclo[2.2.2]octanes are compared with those observed in the 2,3-dimethylidenenorbornane series (**1–6**).

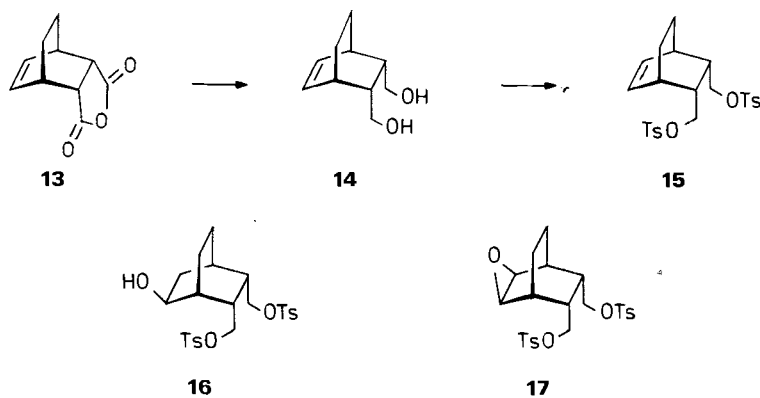
Introduction. – The spectroscopic [2] and chemical properties of an exocyclic *s-cis*-butadiene moiety grafted onto a rigid skeleton can be modified by remote substitution [3–9]. For instance, the carbonyl group in 5,6-dimethylidene-2-norbornanone (**4**) causes a significant rate retardation effect [7] in the *Diels-Alder* addition compared of the behavior of 2,3-dimethylidenenorbornane (**1**)⁴⁾. The effect is larger than that introduced by hydroxyl groups (*e. g.* **2** and **3**) [7], but not as large as that observed for the 2-*exo*,3-*exo*-epoxy-5,6-dimethylidenenorbornane (**5**) [8] [9] relative to the parent diene **1**. The introduction of a homoconjugated endocyclic double bond (*e. g.* **6**) leads also to a decrease of the *Diels-Alder* reactivity of the exocyclic diene moiety grafted onto norbornane and 7-oxanorbornane skeletons [8].



- ¹⁾ Interactions between non-conjugated chromophores, Part 13; Part 12, [1]. An exocyclic butadiene moiety means that each double bond is in an exocyclic position on the ring skeleton.
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- ⁴⁾ According to the IUPAC nomenclature 'bicyclo[2.2.1]heptane' is now called '8,9,10-trinorbornane'; for commodity reasons we use the abolished name 'norbornane'.

We report now the preparation of the dienols **8** and **9**, the dienone **10** and the epoxydiene **11**, four new exocyclic *s-cis*-butadienes grafted onto the bicyclo[2.2.2]octane skeleton. We have measured the rate constants of the cycloadditions of **7–12** to tetracyanoethylene (TCE) and compare the remote-substituent effects on the *Diels-Alder* reactivity of these dienes with those observed for **1–6**. We have found that the hydroxyl- and oxo-substituent effects are similar for the two series. However, the rate-retardation effect introduced by a homoconjugated *exo*-epoxy group or an endocyclic double bond are significantly larger in the norbornane than in the bicyclo[2.2.2]octane series.

Results. – The *Diels-Alder* adduct **13** of maleic anhydride to 1,3-cyclohexadiene was reduced ($\text{LiAlH}_4/\text{THF}$) to the diol **14** which gave the bis(*p*-toluenesulfonate) **15** ($\text{TsCl}/\text{pyridine}$; 0°) [**3a**]. Double elimination of TsOH (*t*-BuOK/DMSO) led to the triene **12** [**3a**]. Catalytic hydrogenation of **15** followed by double elimination of TsOH gave the diene **7** [**3a**]. Hydroboration of **15** followed by oxidative work up yielded the *exo*-alcohol **16** in 90% isolated yield. Treatment with *t*-BuOK in DMSO gave **8** (77%). *Collins* oxidation of **8** furnished the ketone **10** (70%) which was reduced to a 1:1 mixture of the alcohols **8** and **9**. The *endo*-isomer **9** was isolated by column chromatography on silica gel (43%). Epoxidation of **15** with (*m*-chloroperbenzoic acid in CH_2Cl_2) (\rightarrow **17**) followed by double elimination of TsOH (*t*-BuOK/DMSO) furnished the epoxydiene **11** (66%).



The high *exo*-stereoselectivity of the hydroboration and epoxidation of **15** must be due to the bulk of the two *endo*-tosyloxymethyl substituents that prohibits the approach of the electrophilic reagents onto the *endo*-face of the endocyclic double bond.

The structures of the dienes **8–11** were given by their elemental analysis, their spectroscopic data, their mode of formation and their cycloadditions with dimethyl acetylenedicarboxylate and TCE giving the corresponding adducts **18–21** and **22–25**, respectively. The *exo*-configuration of the alcohol **8** was given by the ^{13}C -NMR. spectrum together with the use of a lanthanide shift reagent ($\text{Yb}(\text{dpm})_3$) (*cf.* Table 1). Similarly, the *exo*-position of the epoxy groups in **11** was confirmed by the lanthanide induced shifts in its ^1H -NMR. spectrum (see *Exper. Part*).

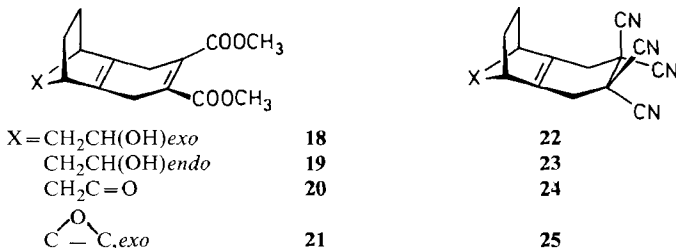
Table 1. ^{13}C -NMR. data of dimethylidenebicyclo[2.2.2]octanes 7–12 (in CDCl_3 , 15.08 MHz, spectrum width 3750 Hz, 4096 points, FT. Mode; chemical shifts in ppm, TMS as internal standard ($=0.0$ ppm); J in Hz)^{a)}

	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	$\text{CH}_2=\text{C}(5)$	$\text{CH}_2=\text{C}(6)$
7	37.0	26.7	26.7	37.0	150.0	150.0	26.7	26.7	103.5	103.5 ^{b)}
8	44.2 <i>d, J=132</i> (44.7)	68.6 <i>d, J=147</i> (100)	37.2 <i>t, J=130</i> (46.8)	36.8 <i>d, J=137</i> (24.2)	147.9 <i>br.s</i> (16.4)	146.5 <i>br.s</i> (19.3)	25.8 <i>t, J=130</i> (24.4)	18.2 <i>t, J=130</i> (33.7)	103.4 <i>t, J=159</i> (9.4)	105.5 <i>t, J=159</i> (10.3) ^{c)}
9	44.4 <i>d, J=137</i>	68.5 <i>d, J=148</i>	38.9 <i>t, J=131</i>	36.2 <i>d, J=137</i>	148.4 <i>br.s</i>	143.9 <i>br.s</i>	24.8 <i>t, J=130</i>	22.9 <i>t, J=130</i>	103.6 <i>t, J=160</i>	108.1 <i>t, J=160</i>
10	54.8 <i>d, J=144</i> (42.5)	211.3 <i>br.s</i> (100)	44.2 <i>t, J=134</i> (42.8)	38.2 <i>d, J=139</i> (20.4)	145.9 <i>br.s</i> (15.2)	141.4 <i>br.s</i> (18.1)	24.9 <i>t, J=133</i> (14.8)	23.9 <i>t, J=133</i> (17.9)	105.2 <i>t, J=158</i> (8.7)	108.1 <i>t, J=158</i> (10.1) ^{c)}
11	40.2 <i>d, J=140</i>	53.4 <i>d, J=185</i>	53.4 <i>d, J=185</i>	40.2 <i>d, J=140</i>	145.6 <i>br.s</i>	145.6 <i>br.s</i>	23.9 <i>t, J=134</i>	23.9 <i>t, J=134</i>	106.6 <i>t, J=156</i>	106.6 <i>t, J=156</i>
12	42.3	133.2	133.2	42.3	147.4	147.4	26.2	26.2	102.6	102.6 ^{b)}

a) Signal attributions confirmed by analogy with the ^{13}C -NMR. data of dimethylidenenorbornane derivatives [2e].

b) Taken from [2d].

c) Relative lanthanide induced shifts due to added $\text{Yb}(\text{dpm})_3$. Linear induced shifts were observed for concentration ratios: $0.05 < [\text{Yb}(\text{dpm})_3]/[\text{diene}] < 0.4$; a correlation coefficient > 0.999 was obtained for 4–7 successive additions of the lanthanide chelate to the solution of the compound under investigation.



The Table 2 summarizes our kinetic data of the *Diels-Alder* additions of the dienes 1, and 6–12 to TCE in toluene. The expected adducts were the only products formed and could be isolated in good yield (see *Exper. Part*). The reactions were followed for at least 3 half-lives and were found to obey pseudo-first-order rate laws

Table 2. Kinetic data of the cycloadditions of dienes 1 and 6–12 to TCE in toluene at $25.0 \pm 0.05^\circ\text{C}$

Diene	1	6	7	8	9	10	11	12
$10^3 \cdot k^{\text{II}}/[\text{mol}]^{-1}\text{s}^{-1}$	69 ^{a)}	5.3 ^{b)} ± 0.02	1900 ± 100	435 ± 15	360 ± 20	30 ± 1	85 ± 4	670 ± 15
k_{rel}	1/28	1/360	(1.)	1/4	1/5	1/63	1/22	1/2.8

a) Interpolated from the data in [9]; it differs somewhat from the data reported in [10] due to different solvents (toluene vs. dioxane).

b) See [8b].

(k^I) for the disappearance of the TCE toluene complex ($\lambda_{\max} = 405 \text{ nm}$) when a 30- to 1000fold excess of the dienes **1** and **6–12** was used. There was no observable effect on the second-order rate constant k^{II} due to changes of the initial concentration of the cycloaddends ($[\text{TCE}] = (1.5\text{--}4.5) \cdot 10^{-4} \text{ M}$; $[\text{diene}] = 5 \cdot 10^{-3}\text{--}2 \cdot 10^{-1} \text{ M}$) and due to changes in their initial concentration ratios.

Discussion. – The reactivity differences observed here are not very large on an absolute scale; nevertheless, we think that they are significant when considering the fact that all our dienes are grafted on very similar skeletons and that we are dealing with remote-substituent effects. Our kinetic data must be compared with the *Diels-Alder* additions of systems with different substituents attached directly to the diene moiety [11] [12] (*e. g.*: rate constant ratio for the addition of TCE to isoprene *vs.* 2-methoxybutadiene = 1:40 [12]). The comparison of the rate constant of the cycloaddition of the alcohols **8** and **9** with that of the parent diene **7** shows a small retardation effect due to the hydroxyl group. It is comparable to the hydroxyl substituent effect in the 2,3-dimethylidene-norbornane series (rate constant ratio for the addition of TCE to **2** *vs.* **1** = 1:4 [7]). The rate retardation effect of the homoconjugated carbonyl group in **4** and **10** is larger than that introduced by a hydroxyl group. It is similar in both the norbornane and bicyclo[2.2.2]octane series. Interestingly, the rate retardation effect due to the introduction of an *exo*-oxirane ring is about 10 times smaller (rate constant ratio of the TCE addition to **11** *vs.* **7** = 1:22 at 25°) in the bicyclo[2.2.2]octane than in the norbornane series (**5** *vs.* **1** = 1:178 at 20° [9]). This can be attributed to a smaller overlap of the LUMO localized on the oxirane ring and the HOMO localized on the exocyclic diene moiety in **11** than in **5** (*cf.* [6] [9]), due to the larger distance between the two homoconjugated functions in the bicyclo[2.2.2]octane than in the norbornane systems (*cf.* the PE. spectra of norbornadiene and bicyc-

Table 3. *Electronic properties and calculated s-cis-butadiene 1,4-distances of dienes 1–12.*

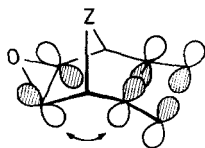
Diene	$\lambda_{\max}[\text{nm}]$ in isooctane	IP. ^{a)} [eV]	$\epsilon_{\text{HOMO}}^{\text{b)}$ [eV]	$\epsilon_{\text{LUMO}}^{\text{b)}$ [eV]	Distance between ^{b)} methylidene C-atoms [Å]
1	248 c)e)	8.41	–9.15	0.43	3.199
2	245.5e)		–9.23	0.33	3.192
3	244.5d)		–9.13	0.44	3.193
4	248 c)		–9.41	0.14	3.196
5	239 c)		–9.39	0.23	3.193
6	240 f)	8.48	–9.15	0.46	3.202
7	252 a)e)	8.37	–9.10	0.38	3.092
8	251		–9.18	0.31	3.090
9	248		–9.09	0.39	3.092
10	251.5		–9.37	0.09	3.096
11	247.5		–9.326	0.20	3.093
12	252	8.33	–9.10	0.41	3.093

a) See [2b].

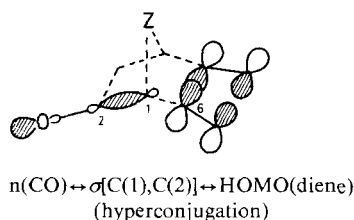
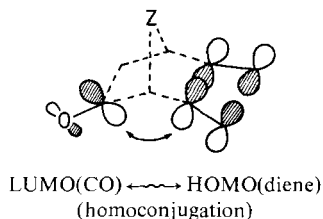
b) By MNDO calculations, with complete minimization of the geometries [16].

c) [7]. d) [17]. e) [18]. f) [3a].

lo[2.2.2]octadiene [13], and the geometries of bicyclo[2.2.2]octanes [14] and norbornanes [15]). The epoxy-diene interaction is assumed to increase the ionization potential (*i. e.* to lower the HOMO energy) of **5** and **11** with respect to the parent dienes **1** and **7** as suggested by MO calculations (see *Table 3* and [6]).



The *exo*-epoxy group introduces a hypsochromic shift of *ca.* 9 nm on the $V \leftarrow N$ transition of the homoconjugated diene in **5** (*vs.* **1**) and of only 4–5 nm in **11** (*vs.* **7**). This observation is also consistent with a smaller interaction between the epoxy and diene chromophores in the bicyclo[2.2.2]octane than in the norbornane series.



The observation of a similar rate retardation effect of the oxo group in **4** and **10** is somewhat surprising if one assumes the homoconjugated carbonyl group to act as an electron withdrawing substituent as does the *exo*-epoxy group. MO calculations as well as experimental observations (*e. g.*: regioselectivity of the electrophilic additions to 5-norbornen-2-one and other norbornene derivatives [19]; the CD. spectrum of **4** [5] and the regioselectivity of its cycloadditions to strong dienophiles [20]) have suggested that a carbonyl group homoconjugated to a π -system can act as an electron-donating group because of the $n(\text{C}=\text{O}) \leftrightarrow \sigma[\text{C}(1), \text{C}(2)] \leftrightarrow \pi[\text{C}(6)]$ hyperconjugative interaction. The relative importance of this through-bond effect [21] that competes with the opposite through-space effect (the latter would make **10** to react faster than **4** with TCE), depends upon the alignment of the $\sigma[\text{C}(1), \text{C}(2)]$ -bond with the p-orbital of the π -system at C(6) and upon the polarizability of the transmitting σ -bond. Accordingly, and considering the geometries of the bicyclo[2.2.2]octane [14] and norbornane systems [15], the oxo function is more electron-donating in **4** than in **10**, and consequently makes **4** to react faster with strong dienophiles than expected from a model assuming only the LUMO (carbonyl) \leftrightarrow HOMO (diene) interaction.

The rate retardation effect of the endocyclic double bond in **12** (compared with **7**) is insignificant. It is much smaller than that observed in the norbornane (*Table 2*) and 7-oxanorbornane series [8]. This could also be attributed to a weaker homoconjugative interaction (involving the LUMO localized on the endocyclic double bond and the HOMO localized on the exocyclic diene) in **12** than in **6**. Nevertheless, it is possible that the *Diels-Alder* reactivity of our dienes is driven by other factors than the polarizability of the diene (*i. e.* IP.'s). The relatively large reactivity difference

between **1** and **7** has been attributed to the different 1,4-distances between the olefinic methylenic C-atoms [10]. X-Ray diffraction data on the *endo*-irontricarbonyl complexes of tetramethylenedibicyclo[2.2.2]octane [22] and -bicyclo[2.2.2]oct-2-ene [23] did not allow to detect any significant change in the 1,4-distance of the uncoordinated diene moiety. Thus, the *Diels-Alder* reactivity of **7** and **12** is consistent with that observation and confirms the weak interaction between the homoconjugated olefinic chromophores (see also the UV.- and PE.-spectroscopy data (Table 3) and *Diels-Alder* reactivity of the above complexes [23]).



The relatively large difference in *Diels-Alder* reactivity between **6** and **1** is surprising since we do not expect the 1,4-distance between the methylenic C-atoms of **1** and **6** to vary significantly neither (see the MNDO-minimized geometries in Table 3). Thus an explanation based on electronic or/and strain factors must be maintained in the latter case. Further data with other exocyclic dienes must be gathered to substantiate the hypotheses presented here.

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Experimental Part

General Remarks. See [24].

Kinetic measurements. See [9].

Synthesis of bicyclo[2.2.2]oct-5-ene-2endo,3endo-dimethanol (14). The *Diels-Alder* adduct **13** of maleic anhydride to 1,3-cyclohexadiene [3a] (10 g, 0.056 mol) in anh. THF (50 ml) was added dropwise under N₂ to a stirred suspension of LiAlH₄ (8 g, 0.21 mol) in THF (150 ml). After heating under reflux for 8 h, the mixture was allowed to cool to RT. and slowly hydrolyzed with water (15 ml). The inorganic salts were removed by filtration on silica gel (10 g), and the solution was evaporated i. V. The residue was dissolved in dry CHCl₃ (80 ml), and dried over MgSO₄. After evaporation, the crude **14** was recrystallized from CHCl₃/pentane 9:1 giving 7.4 g (79%) of colorless crystals, m. p. 107–108°. – UV (95% ethanol): final absorption. – IR. (KBr): 3300, 2950, 2880, 1620, 1460, 1440, 1375, 1355, 1330, 1290, 1220, 1170, 1115, 1080, 1030, 1020, 980, 960, 910, 870, 820, 720. – ¹H-NMR. (CDCl₃): 6.1 (*m*, 2 H); 4.25 (*br. s*, 2 H); 3.5 (*m*, 4 H); 2.4 (*m*, 2 H); 2.2 (*m*, 2 H); 1.75–1.0 (*m*, 4 H). – MS. (70 eV): 168 (5), 151 (18), 136 (14), 137 (17), 122 (46), 121 (41), 119 (39), 117 (42), 115 (15), 109 (37), 107 (44), 106 (38), 105 (39), 104 (45), 97 (23), 96 (40), 95 (41), 94 (82), 93 (78), 92 (81), 91 (100).

C₁₀H₁₆O₂ (168.23) Calc. C 71.39 H 9.58% Found C 71.32 H 9.54%

Synthesis of bicyclo[2.2.2]oct-5-ene-2endo,3endo-dimethyl bis(p-toluenesulfonate) (15). The diol **14** (6 g, 0.026 mol) was added portionwise to a stirred mixture of *p*-toluenesulfonyl chloride (TsCl; 30 g, 0.16 mol) and anh. pyridine at 0° and under N₂. After 48 h at 0°, the mixture was poured dropwise onto vigorously stirred ice-water (250 g). The yellowish precipitate (11.8 g, 97%) was recrystallized from CHCl₃/ether 9:3 giving 10.3 g (85%) of **15** as a white solid, m. p. 101–102°. – IR. (KBr): 3050, 2960, 2880, 1930, 1820, 1720, 1650, 1600, 1500, 1365, 1190, 1175, 1100, 955, 875, 815. – ¹H-NMR. (CDCl₃): 8.–7.25 (*m*, 8 H); 6.0 (*m*, 2 H); 4.0–3.5 (*m*, 4 H); 2.5 (*m*, 8 H); 2.2 (*m*, 2 H); 1.6–1.0 (*m*, 4 H). – MS. (70 eV): 476 (4), 397 (7), 326 (10), 305 (6), 304 (8), 264 (11), 262 (13), 236 (7), 225 (25), 172 (30), 167 (15), 166 (20), 165 (62), 150 (35), 149 (31), 133 (30), 132 (85), 131 (18), 117 (30), 104 (70), 91 (100).

C₂₄H₂₈O₆S₂ (476.61) Calc. C 60.48 H 5.92% Found C 60.55 H 5.99%

Synthesis of 5exo-hydroxybicyclo[2.2.2]octane-2endo,3endo-dimethyl bis(p-toluenesulfonate) (16). The diester **15** (10 g, 0.02 mol) was added portionwise under N₂ to a stirred suspension of NaBH₄ (1.2 g, 0.032 mol) in anh. THF (50 ml). After cooling to 0°, Et₂O·BF₃ (5 g, 0.035 mol, freshly distilled) was added dropwise under N₂ and vigorous stirring. After the addition, the mixture was stirred at RT. for 12 h and then cooled to 0°. Water (10 ml) 3N KOH (20 ml) and 30%-solution H₂O₂ (20 ml) were added successively and dropwise. After 24 h at RT. the salts were filtered off on silica gel. The solution was evaporated i. V., the residue dissolved in CHCl₃, washed with water, the solution dried (MgSO₄), and evaporated i. V. The crude alcohol was recrystallized from CHCl₃/pentane 9:1 yielding 9.3 g (90%) of **16** as a white solid, m. p. 110–111°. – IR. (KBr): 3600, 3050, 2950, 2880, 1930, 1810, 1750, 1600, 1365, 1190, 1175, 1100, 960. – ¹H-NMR. (CDCl₃): 8.0–7.25 (*m*, 8 H); 4.25–3.75 (*m*, 5 H); 2.5 (*s*, 6 H); 2.25–1.0 (*m*, 11 H). – MS. (70 eV): 477 (0.6), 398 (1), 345 (3), 305 (7), 227 (5), 213 (4), 201 (2), 173 (100), 155 (11), 151 (15), 133 (37), 91 (10), 47 (11), 31 (92).

C₂₄H₃₀O₇S₂ (494.61) Calc. C 58.28 H 6.11% Found C 58.36 H 6.27%

Synthesis of 5exo,6exo-epoxybicyclo[2.2.2]octane-2endo,3endo-dimethyl bis(p-toluenesulfonate) (17). *m*-Chloroperbenzoic acid (2.5 g, 0.014 mol) in CH₂Cl₂ (30 ml) was added to **15** (4 g, 8.4 mmol) in CH₂Cl₂ (20 ml). After heating under reflux for 3 days, the mixture was washed with sat. aq. Na₂CO₃-solution (3 times 20 ml) and H₂O (2 times 10 ml), dried (MgSO₄) and evaporated i. V.: 3 g (73%) **17**, viscous oil. – IR. (film): 3020, 2950, 2880, 1930, 1800, 1720, 1600, 1365, 1185, 1170, 1095, 955. – ¹H-NMR. (CDCl₃): 8.0–7.25 (*m*, 8 H); 4.2–4.0 (*m*, 4 H); 3.15 (*m*, 2 H); 2.5 (*s*, 6 H); 2.25 (*m*, 2 H); 2.0–1.5 (*m*, 2 H); 1.45–1.0 (*m*, 2 H). – MS. (70 eV): 446 (1), 369 (0.5), 337 (0.7), 321 (5), 309 (6), 273 (7), 245 (15), 218 (30), 191 (42), 155 (85), 149 (37), 148 (35), 109 (30), 107 (32), 105 (40), 91 (100).

C₂₄H₂₈O₇S₂ (492.52) Calc. C 58.52 H 5.73% Found C 58.59 H 5.81%

Synthesis of 5,6-dimethylidene-2exo-bicyclo[2.2.2]octanol (8). *t*-BuOK (7 g, 0.062 mol) was added portionwise under N₂ to a stirred solution of **16** (9.6 g, 0.019 mol) in anh. DMSO (200 ml). After stirring at RT. for 5 h the mixture was poured onto ice-water (250–300 g) and extracted with pentane (100 ml, 5 times). The extract was washed with sat. NaCl-solution (150 ml, 3 times) and water (200 ml, 3 times), dried (MgSO₄) and evaporated i. V. The crude **8** was recrystallized from pentane/ether 9:1 yielding 2.2 g (77%) of colorless crystals, m. p. 58°. – UV. (isooctane): 246 (8100), 251 (8100), 260.5 (5070). UV. (ethanol/water 95:5): 246 (8200), 251 (8200), 260.5 (5150). – IR. (KBr): 3400, 3100, 2950, 1620, 1155, 1100, 900, 885. – ¹H-NMR. (CDCl₃): 5.35 (*s*, 1 H); 5.25 (*s*, 1 H); 4.8 (*s*, 1 H); 4.7 (*s*, 1 H); 4.2–3.9 (*m*, 1 H); 2.5–1.0 (*m*, 9 H). – ¹³C-NMR.: see Table I. – MS. (70 eV): 150 (23), 133 (4), 132 (16), 131 (10), 121 (11), 119 (14), 117 (39), 108 (28), 107 (22), 106 (100), 105 (27), 104 (11), 93 (17), 91 (69), 79 (16), 78 (17), 77 (10).

C₁₀H₁₄O (150.20) Calc. C 79.95 H 9.39% Found C 79.95 H 9.48%

Synthesis of 5,6-dimethylidene-2-bicyclo[2.2.2]octanone (10). CrO₃ (12.5 g, 0.125 mol) was added slowly and portionwise to a stirred mixture of anh. pyridine (20 g) and CH₂Cl₂ (125 ml) cooled to 0°. After the addition, the mixture was stirred for 15 min, then **8** (1.5 g, 0.01 mol) was added, and the mixture allowed to warm to RT. and stirred for 3 h. Then the precipitate was filtered off on silica gel (20 g) and the solution evaporated i. V. The residue was dissolved in Et₂O (100 ml) and washed successively with 1N HCl (50 ml, 5 times) and water (100 ml). After drying (MgSO₄), the ethereal solution was distilled i. V.: 1 g (70%) of **10** as a colorless oil, b. p. 30°/0.5 Torr. – UV. (isooctane): 251.5 (6700), 299 (280), 289 (310), 307 (220); identical UV. in EtOH/H₂O 95:5. – IR. (film): 3090, 2950, 2920, 2880, 1735, 1615, 1400, 1100, 895. – ¹H-NMR. (CDCl₃)⁵: 5.45 (*br. s*, HCH=C(6) *cis* to C(5)–C(6)[21.4]); 5.4 (*br. s*, HCH=C(5) *cis* to C(5)–C(6)[19.4]); 4.9 (*br. s*, HCH=C(5) *trans* to C(5)–C(6)[17.4], and HCH=C(6) *trans* to C(5)–C(6)[29.6]); 3.05 (*m*, H–C(4)[27.6]); 2.75 (*m*, H–C(1)[100]); 2.3 (*m*, 2 H–C(3)[94]); 1.85 (*m*, 2 H–C(7), 2 H–C(8)). – ¹³C-NMR.: see Table I. – MS. (70 eV): 148 (34), 120 (32), 106 (18), 105 (51), 104 (33), 103 (12), 92 (29), 91 (100), 79 (21), 78 (28), 77 (22), 65 (6).

C₁₀H₁₂O (148.19) Calc. C 81.04 H 8.16% Found C 80.90 H 8.20%

Synthesis of 5,6-dimethylidene-2endo-bicyclo[2.2.2]octanol (9). The ketone **10** (0.5 g, 3.4 mmol) in anh. THF (2 ml) was added to a suspension of LiAlH₄ (0.25 g, 6.6 mmol) in anh. THF (10 ml). After stirring at RT. for 1 h, water (1 ml) was added slowly and the mixture filtered on silica gel (1 g, washed with THF). The solution was evaporated i. V. and the residue dissolved in pentane (50 ml). After drying

5) The relative lanthanide-induced shifts due to Eu(dpm)₃ are given in brackets.

(MgSO₄), the solution was evaporated i. V. giving a 1:1 mixture of **8** and **9** which was separated by column chromatography on silica gel (AcOEt/hexane 1:2). The second fraction contained 0.22 g (43%) of **9**, colorless crystals, m. p. 66–67°. – UV. (isooctane): 248 (7950). – UV. (ethanol/H₂O 95:5): 248 (8200). – IR. (KBr): 3300, 3220, 3080, 2950, 2875, 1620, 1445, 1335, 1310, 1090, 1040, 880. – ¹H-NMR. (CDCl₃): 5.45 (br. s, 1 H); 5.25 (br. s, 1 H); 4.85 (br. s, 1 H); 4.75 (br. s, 1 H); 3.9 (m, 1 H); 2.4 (m, 2 H); 2.15 (m, 1 H); 1.75–1.25 (m, 6 H). – ¹³C-NMR.: see Table 1. – MS. (70 eV): 150 (13), 132 (9), 131 (12), 121 (14), 119 (15), 117 (30), 115 (14), 108 (31), 106 (75), 105 (30), 93 (60), 91 (100), 79 (35), 78 (36), 77 (34), 65 (11).

C₁₀H₁₄O (150.20) Calc. C 79.95 H 9.39% Found C 79.81 H 9.62%

Synthesis of 2exo,3exo-epoxy-5,6-dimethylidenebicyclo[2.2.2]octane (11) *t*-BuOK (2 g, 18 mmol) was added portionwise under N₂ to a stirred solution of **17** (3 g, 6 mmol) in anh. DMSO (100 ml). After stirring at RT. for 10 h, the mixture was poured onto ice-water (200 g) and extracted with pentane (5 times, 100 ml). The organic extract was washed successively with sat. NaCl-solution and water, dried (MgSO₄) and evaporated i. V. The crude **11** was purified by chromatography on silica gel (CHCl₃/pentane 2:1): 0.6 g (66%) of colorless crystals, m. p. 68° (pentane). – UV. (isooctane): 241.5 (8200), 247.5 (8400), 256.5 (5300). – UV. (ethanol/H₂O 95:5): 241.5 (8800), 247.5 (8800), 256.5 (5200). – IR. (KBr): 3020, 2950, 2940, 1640, 1620, 1460, 1400, 1345, 1235, 1140, 1010, 945, 900, 865, 800. – ¹H-NMR. (CDCl₃)⁵: 5.4 (s, HCH=C(5) and HCH=C(6), both *cis* to C(5)–C(6)[14.9]); 4.85 (s, HCH=C(5) and HCH=C(6), both *trans* to C(5)–C(6)[16.8]); 3.25 (m, H–C(2) and H–C(3)[100]); 2.75 (m, H–C(1) and H–C(4)[37.3]); 1.85 (m, H–C(7) and H–C(8), both *syn* to epoxy [55.1]); 1.3 (m, H–C(7) and H–C(8), both *anti* to epoxy [28.5]). – ¹³C-NMR.: see Table 1. – MS. (70 eV): 148 (8), 131 (5), 121 (4), 119 (16), 117 (17), 105 (4), 91 (5), 87 (50), 85 (100), 83 (100), 50 (8), 49 (12), 48 (31), 47 (38).

C₁₀H₁₂O (148.19) Calc. C 81.04 H 8.16% Found C 81.23 H 8.11%

Synthesis of dimethyl 9exo-hydroxytricyclo[6.2.2.0^{2,7}]dodeca-2(7),4-diene-4,5-dicarboxylate (18) A mixture of **8** (0.3 g, 2 mmol), Et₂O (25 ml) and freshly distilled dimethyl acetylenedicarboxylate (0.3 g, 2.1 mmol) was stirred at RT. for 3 h. After removal of the solvent i. V., the crude adduct was recrystallized from pentane/AcOEt 1:2 yielding 0.51 g (87%) **18**, colorless crystals, m. p. 91–92°. – IR. (KBr): 3450, 3000, 2950, 2870, 2820, 1730, 1650, 1435, 1265, 1065, 1050, 1000. – ¹H-NMR. (CDCl₃): 3.8 (m, 1 H); 3.75 (br. s, 6 H); 3.05 (br. s, 4 H); 2.25 (m, 2 H); 2.1–1.6 (m, 3 H); 1.5–1.0 (m, 3 H). – MS. (70 eV): 292 (8), 261 (18), 260 (15), 259 (24), 258 (22), 248 (30), 246 (17), 243 (11), 242 (13), 230 (19), 217 (23), 216 (100), 215 (89), 213 (30), 201 (23), 189 (18), 188 (10), 187 (18), 157 (35), 130 (30), 129 (79), 128 (81), 127 (36), 115 (65), 105 (20), 103 (17), 91 (67).

C₁₆H₂₀O₅ (292.27) Calc. C 65.74 H 6.90% Found C 65.49 H 6.97%

Synthesis of dimethyl 9endo-hydroxytricyclo[6.2.2.0^{2,7}]dodeca-2(7),4-diene-4,5-dicarboxylate (19) Same procedure as for **18**, using **9**. Yield 94%, m. p. 93–94°. – IR. (KBr): 3300, 2950, 2860, 2820, 1735, 1715, 1700, 1650, 1440, 1290, 1270, 1250, 1160, 1100. – ¹H-NMR. (CDCl₃): 3.8 (m, 1 H); 3.75 (br. s, 6 H); 3.1 (br. s, 4 H); 2.4 (m, 2 H); 2.15–1.8 (m, 1 H); 1.75–1.0 (m, 5 H). – MS. (70 eV): 292 (7), 261 (19), 260 (17), 259 (21), 258 (20), 248 (40), 230 (15), 216 (100), 215 (85), 201 (25), 188 (21), 187 (19), 157 (14), 130 (27), 129 (81), 128 (76), 127 (26), 115 (43), 105 (15), 91 (27).

C₁₆H₂₀O₅ (292.27) Calc. C 65.74 H 6.90% Found C 65.60 H 6.96%

Synthesis of dimethyl 9-oxotricyclo[6.2.2.0^{2,7}]dodeca-2(7),4-diene-4,5-dicarboxylate (20) Same procedure as for **18**, using **10**. Yield 85%, viscous oil, after column chromatography on silica gel (hexane/AcOEt 1:2). – IR. (film): 2960, 2880, 1730, 1650, 1440, 1270, 1070, 1045. – ¹H-NMR. (CDCl₃): 3.75 (br. s, 6 H); 3.1 (br. s, 4 H); 2.9 (m, 1 H); 2.7 (m, 1 H); 2.05 (m, 2 H); 2.0–1.45 (m, 4 H). – MS. (70 eV): 290 (10), 259 (29), 258 (36), 248 (46), 217 (29), 216 (100), 201 (21), 189 (24), 188 (18), 187 (15), 173 (7), 171 (10), 159 (10), 158 (21), 157 (43), 156 (12), 155 (11), 143 (15), 141 (14), 130 (40), 129 (95), 128 (80), 127 (40), 117 (8), 116 (11), 115 (62), 105 (18), 103 (15), 102 (12), 91 (45), 79 (15), 78 (16), 77 (30), 59 (35).

C₁₆H₁₈O₅ (290.25) Calc. C 66.20 H 6.25% Found C 66.32 H 6.36%

Synthesis of dimethyl 9exo,10exo-epoxytricyclo[6.2.2.0^{2,7}]dodeca-2(7),4-diene-4,5-dicarboxylate (21) Same procedure as for **18**, using **11**. After recrystallization from CH₂Cl₂/pentane 9:1, 85% of colorless crystals, m. p. 82–83°. – IR. (KBr): 3030, 3020, 2970, 2920, 2880, 2840, 1745, 1725, 1650, 1440, 1420, 1410, 1340, 1330, 1290, 1280, 1260, 1255, 1140, 1070, 1005, 850. – ¹H-NMR. (CDCl₃): 3.8 (br. s, 6 H); 3.25 (m, 2 H); 3.15 (br. s, 4 H); 2.75 (m, 2 H); 2.0–1.75 (m, 2 H); 1.0–0.8 (m, 2 H). – MS. (70 eV): 290 (10), 259 (17),

258 (19), 257 (18), 231 (10), 230 (13), 229 (15), 205 (14), 204 (14), 203 (30), 202 (15), 201 (15), 199 (25), 190 (13), 189 (100), 171 (15), 170 (14), 169 (15), 155 (10), 153 (8), 143 (20), 142 (19), 141 (31), 129 (25), 128 (50), 127 (23), 116 (15), 115 (52), 105 (10), 103 (11), 102 (10), 91 (20), 89 (10).

$C_{16}H_{18}O_5$ (290.31) Calc. C 66.20 H 6.25% Found C 66.27 H 6.31%

Synthesis of 9exo-hydroxytricyclo[6.2.2.0^{2,7}]dodec-2(7)-ene-4,4,5,5-tetracarbonitrile (22). A mixture of **8** (0.3 g, 2 mmol), anh. benzene (15 ml) and TCE (0.256 g, 2 mmol) was stirred at RT. for 5 h. After evaporation of the solvent i. v., the crude adduct was recrystallized from CH_2Cl_2 /pentane 9:1 yielding 0.5 g (90%) of white powder, m. p. 166–167°. – IR. (KBr): 3560, 3360, 2950, 2875, 2250, 1470, 1435, 1285, 1050, 1000. – ¹H-NMR. (D_6 -acetone): 3.8 (m, 1 H); 3.5 (br. s, 4 H); 2.45 (m, 2 H); 2.1–1.0 (m, 6 H). – MS. (70 eV): 278 (7), 260 (10), 235 (40), 234 (100), 233 (20), 232 (15), 208 (9), 207 (25), 206 (27), 205 (8), 194 (20), 181 (18), 180 (45), 179 (30), 156 (55), 149 (40), 106 (95), 105 (81), 91 (98).

$C_{16}H_{14}N_4O$ (278.29) Calc. C 69.05 H 5.07% Found C 68.90 H 4.98%

Synthesis of 9endo-hydroxytricyclo[6.2.2.0^{2,7}]dodec-2(7)-ene-4,4,5,5-tetracarbonitrile (23). Same procedure as for **22**, using **9**. Yield 88%, m. p. 185° (dec.). – IR. (KBr): 3460, 3380, 2950, 2875, 2250, 1470, 1435, 1235, 1050, 1000, 930, 830, 820. – ¹H-NMR. (D_6 -acetone): 4.1 (m, 1 H); 2.8 (m, 2 H); 2.4 (m, 4 H); 2.0–1.0 (m, 6 H). – MS. (70 eV): 278 (12), 260 (19), 235 (52), 234 (100), 233 (35), 232 (25), 207 (30), 206 (31), 194 (25), 181 (27), 180 (49), 179 (37), 156 (68), 106 (91), 105 (80), 91 (98).

$C_{16}H_{14}N_4O$ (278.29) Calc. C 69.05 H 5.07% Found C 68.93 H 4.96%

Synthesis of 9oxotriacyclo[6.2.2.0^{2,7}]dodec-2(7)-ene-4,4,5,5-tetracarbonitrile (24). Same procedure as for **22**, using **10**. Yield 86%, colorless powder, m. p. 190° (dec.). – IR. (KBr): 2995, 2970, 2940, 2890, 2260, 1730, 1460, 1440, 1410, 1240, 1105, 1090, 970, 930. – ¹H-NMR. (D_6 -acetone): 3.6 (m, 4 H); 3.05 (m, 2 H); 2.1 (m, 2 H); 2.0–1.45 (m, 4 H). – MS. (70 eV): 276 (18), 235 (20), 234 (100), 233 (10), 208 (5), 207 (8), 206 (7), 194 (6), 181 (5), 180 (15), 179 (5), 156 (25), 140 (8), 107 (5), 106 (60), 105 (22), 104 (10), 92 (10), 91 (82), 79 (10), 78 (24), 77 (15).

$C_{16}H_{12}N_4O$ (276.27) Calc. C 69.55 H 4.38% Found C 69.48 H 4.33%

Synthesis of 9exo,10exo-epoxytricyclo[6.2.2.0^{2,7}]dodec-2(7)-ene-4,4,5,5-tetracarbonitrile (25). Same procedure as for **22**, using **11**. Yield 84%, colorless crystals, m. p. 163–4°. – IR. (KBr): 3050, 3000, 2970, 2940, 2860, 2260, 1440, 1400, 1330, 1240, 1150, 850. – ¹H-NMR. (D_6 -acetone): 3.6 (m, 4 H); 3.3 (m, 2 H); 2.9 (m, 2 H); 2.0–1.7 (m, 2 H); 1.15–0.8 (m, 2 H). – MS. (70 eV): 276 (10), 234 (20), 232 (8), 190 (65), 189 (31), 188 (32), 149 (30), 131 (78), 130 (42), 129 (70), 128 (69), 115 (40), 105 (41), 91 (100).

$C_{16}H_{12}N_4O$ (276.27) Calc. C 69.55 H 4.38% Found C 69.39 H 4.31%

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