

139. Syntheses and Tandem *Diels-Alder* Reactivities of 7,7-Diphenyl-[2.2.1]hericene (= 7-(Diphenylmethylidene)-2,3,5,6-tetramethylidenebicyclo[2.2.1]heptane) and 7-Oxa[2.2.1]hericene (= 2,3,5,6-Tetramethylidenebicyclo[2.2.1]heptan-7-one)¹⁾

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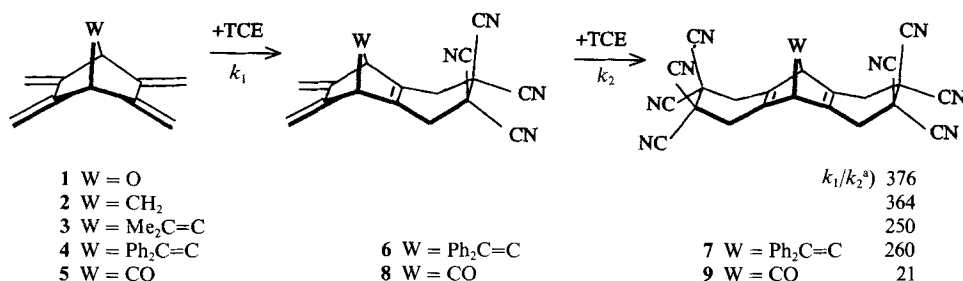
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Syntheses of 7,7-diphenyl[2.2.1]hericene (**4**) and 7-oxa[2.2.1]hericene (**5**) are presented. Rate constants k_1 and k_2 of the two successive *Diels-Alder* additions of ethylenetetracarbonitrile (TCE) to **4** and to **5** have been evaluated. At 25° in toluene, the rate-constant ratio $k_1/k_2 = 260$ and 21 for **4** and **5**, respectively. These results are compared with those reported for the tandem *Diels-Alder* reactivity of 2,3,5,6-tetramethylidenebicyclo[2.2.1]heptane and other derivatives.

Introduction. – The 2,3,5,6-tetramethylidenebicyclo[2.2.1]heptane derivatives **1** [4], **2** [5], and **3** [2] are useful starting materials for the preparation of linearly annellated six-membered ring systems. The rate constants k_1 of their *Diels-Alder* additions to a first equivalent of a given dienophile (e.g. ethylenetetracarbonitrile (TCE), see *Scheme 1*) are significantly larger than those (k_2) of the reactions of the second equivalent of dienophile [6]. This principle (tandem *Diels-Alder* additions with decreasing reactivity) has been exploited with tetraene **1** in our doubly convergent syntheses of anthracyclinones [7].

One of the dominating factors responsible for the relatively large rate-constant ratios k_1/k_2 in the tandem *Diels-Alder* additions of **1–3** is believed to be the change in exothermicity between the two successive cycloadditions [5] [6]. We have now prepared the two

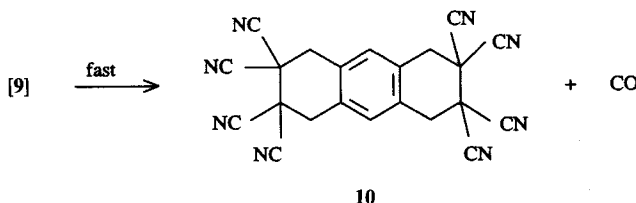
Scheme 1



^{a)} At 25° in toluene

¹⁾ For the [*l.m.n*]hericene coinage, see [1–3].

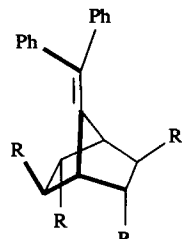
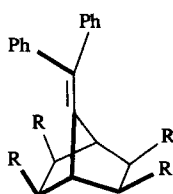
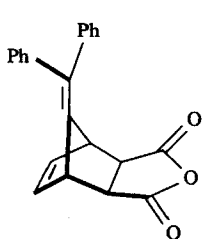
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new [2.2.1]hericene derivatives **4** and **5** and have evaluated their tandem *Diels-Alder* reactivity toward TCE. While 7,7-diphenyl[2.2.1]hericene (**4**) gave mono-adduct **6** and bis-adduct **7** with a rate-constant ratio k_1/k_2 nearly the same as those measured for the TCE cycloadditions to 7,7-dimethyl[2.2.1]hericene (**3**) and tetraenes **1** and **2**, a significantly smaller k_1/k_2 value was evaluated for the two successive *Diels-Alder* additions of 7-oxa[2.2.1]hericene (**5**; see *Scheme 1*). The bis-adduct **9** expected for the TCE addition to the mono-adduct **8** was not observed as it underwent a facile cheletropic elimination of CO [**8**] [**9**] to give the benzene derivative **10**. The possible origins of the relatively low ratio k_1/k_2 observed for the tandem *Diels-Alder* additions of **5** will be discussed³⁾).

Synthesis of 7,7-Diphenyl[2.2.1]hericene. – The *Diels-Alder* adduct **11** of maleic anhydride to 6,6-diphenylfulvene [**12**] was biscoxylated (3 atm CO, CuCl₂, anh. MeOH, cat. Pd/C, 25°) [**2**] giving the all-*exo* methyl tetraester **12** (50%). Products arising from the carboxylation of the diphenylethylidene moiety were not observed. Reduction of **12** with LiAlH₄ in anh. THF afforded tetrol **13** (73%) which was transformed into the corresponding tetrachloride **14** (50%) on treatment with SOCl₂ and pyridine. In the presence of an excess of *t*-BuOK in THF, **14** eliminated 4 equiv. of HCl giving 7,7-diphenyl[2.2.1]hericene (**4**) in 69% yield.

Attempts to cleave the C=C bond in **14** with ozone and of epoxidation with various peracids all failed. Furthermore, **14** was perfectly stable when heated with KMnO₄ in

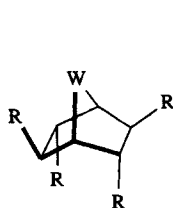


³⁾ Disclosure of our synthesis of **5** and of its matrix irradiation giving CO and 2,3,5,6-tetramethylidene-1,4-cyclohexanediyl diradical ('1,2,4,5-tetramethylidenebenzene') was made first by Prof. J. A. Berson, conferences at the University of Chicago, May 19, 1986; University of Washington, May 30, 1986; IUPAC meeting, Tokyo, Aug. 25, 1986; University of Maryland, Oct. 15, 1986; University of Technology, Nov. 20, 1986; see also [10].

⁴⁾ For the photoelectron spectrum of **5** and a study on the interaction between the homoconjugated carbonyl and olefinic functions, see [11].

C_6H_6 with [18]crown-6 [13]. Under the same conditions, the all-*trans* isomer **17** was also inert. The latter was obtained in the following way. Treatment of **12** with abs. MeOH and anh. K_2CO_3 gave the all-*trans* tetraester **15** (81%) which was reduced to tetrol **16** (78%). Treatment of **16** with $SOCl_2$ and pyridine gave **17** (61%).

Synthesis of 7-Oxa[2.2.1]hericene. – Since all our attempts to generate 2,3,5,6-tetrakis(chloromethyl)bicyclo[2.2.1]heptan-7-one (**18**) from **17** failed, we turned to the derivatives **19** and **20**. The all-*exo* tetrachloride **19** was the precursor of 7,7-dimethyl[2.2.1]hericene [2]. Attempts to cleave its double bond with ozone led exclusively to the formation of epoxide **21** [14]. Assuming that steric effects due to the four *exo* chloromethyl groups in **19** were responsible for the inertness of this compound toward double-bond cleavage with O_3 , we prepared its all-*trans* isomer **20** in a way similar to that of **17**. Treatment of the all-*exo* tetraester **22** [2] with a catalytical amount of anh. K_2CO_3 in MeOH gave the all-*trans* tetraester **23** quantitatively. Reduction with $LiAlH_4$ in THF yielded tetrol **24** (73%). Treatment with an excess of $SOCl_2$ and pyridine afforded the corresponding tetrachloride **20** in 55% yield. Ozonolysis of **20** (MeOH, -78°) followed



18 R = CH_2Cl ,

W = C=O

20 R = CH_2Cl ,

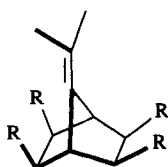
W = C=CMe₂

23 R = COOMe,

W = C=CMe₂

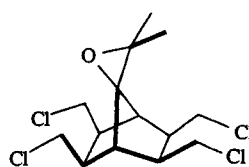
24 R = CH_2OH ,

W = C=CMe₂

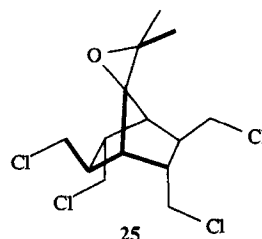


19 R = CH_2Cl

22 R = COOMe



21



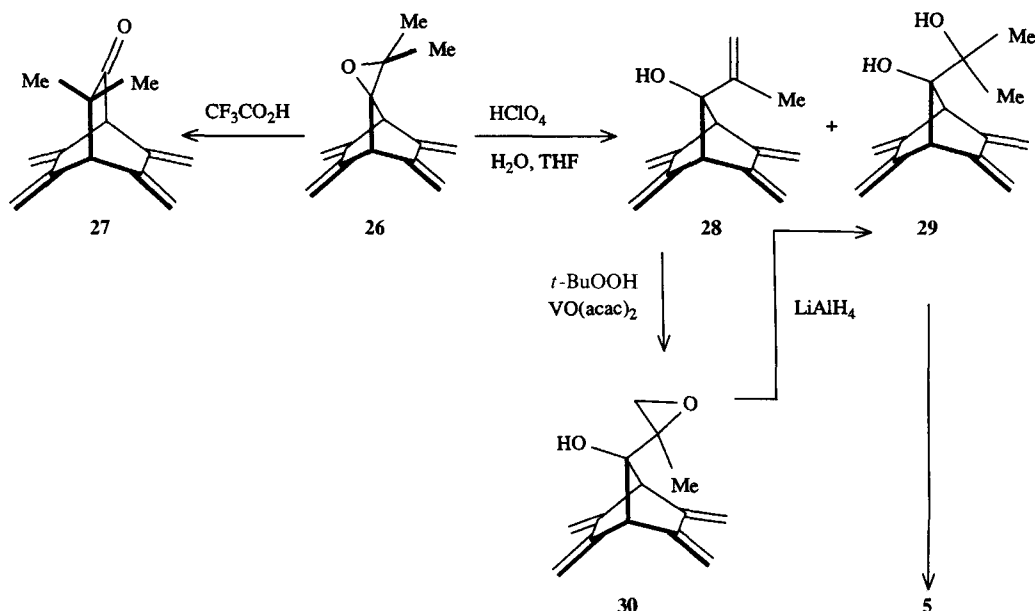
25

by workup with Me_2S gave a mixture from which the epoxide **25** (65%) and ketone **18** (25%) could be isolated by chromatography on silica gel. Attempts to eliminate HCl from **18** under various basic conditions (*e.g.* *t*-BuOK/THF, *t*-BuOK/DMSO, CsF in DMF/HMPA [15], *etc.*) all failed to give **5** and led to decomposition.

Quadruple elimination of HCl from **21** afforded the epoxytetraene **26** [14]. On treatment with CF_3COOH (CH_2Cl_2 , 0°), **26** was isomerized into the tetraene ketone **27** (60%, isolated)⁵, a rapidly polymerizing compound. In the presence of $HClO_4$ in H_2O /THF (20° , 15 h), **26** was transformed into a mixture from which 50% of pentaenol **28** and 30% of tetraenediol **29** were isolated by flash chromatography on silica gel. Oxidation of **29**

⁵) For the syntheses of 5,6,7,8-tetramethylidenebicyclo[2.2.2]octan-2-one and other derivatives, see [16].

Scheme 2

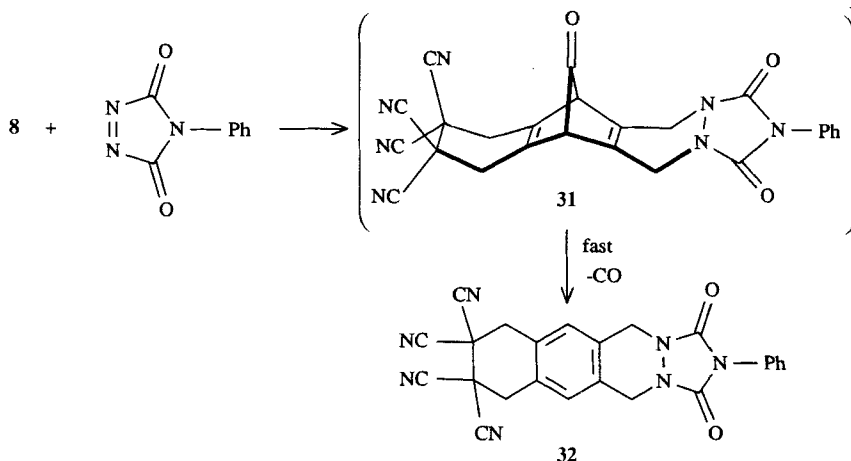


with pyridinium chlorochromate suspended in CH_2Cl_2 , gave the desired tetraenone **5** in 48% yield. The latter has a strong tendency to polymerize. Epoxidation of the allylic-alcohol moiety of pentaene **28** with $t\text{-BuOOH}$ in the presence of a catalytical amount of $\text{VO}(\text{acac})_2$ [17] (C_6H_6 , 40° , 3 h) allowed one to isolate the corresponding epoxide **30** (46%). The latter was reduced with LiAlH_4 (THF , 80° , 2 days) to diol **29** (52%), the precursor of **5** (Scheme 2).

The structures of the compounds **12–30** were given by their data, combustion analysis, mode of formation, and reactivity. The relative configuration (*exo* vs. *endo*) of the substituents at C(2), C(3), C(5), and C(6) in **12–25** was given by the vicinal coupling constants observed between the protons at these centres and the bridgehead protons $\text{H}-\text{C}(1)$, $\text{H}-\text{C}(4)$ [18]. The UV absorption spectrum of 7,7-diphenyl[2.2.1]hericene (**4**) was dominated by the absorption of the diphenylethylidene chromophore. Interaction between the two homoconjugated *s-cis*-butadiene moieties in **5** and **26–30** was evidenced by their UV absorption spectra (see *Exper. Part*) which showed typical splittings of the $\text{V} \leftarrow \text{N}$ transitions as in the case of tetraenes **1**, **2**, and 7,7-dimethyl[2.2.1]hericene (**3**) [2] [4a].

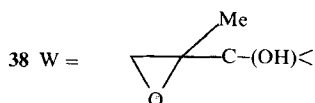
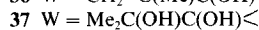
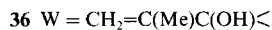
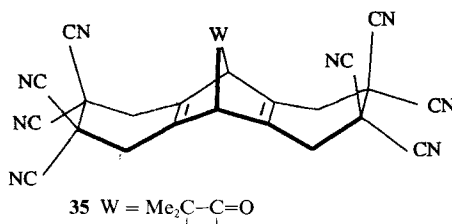
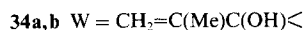
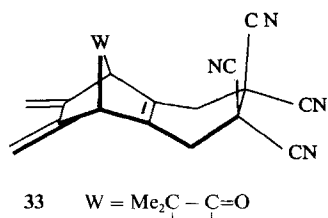
Tandem Diels-Alder Reactivities. – In the presence of 1 equiv. of TCE in acetone, 7,7-diphenyl[2.2.1]hericene (**4**) gave the corresponding mono-adduct **6** (82%, isolated). With 2 or more equiv. of TCE (acetone, 20° , 50 h), the bis-adduct **7** was obtained in 95% yield. The rate constants $k_1 = (3.8 \pm 0.3) \cdot 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_2 = (1.5 \pm 0.2) \cdot 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 25° in toluene were evaluated for the two successive cycloadditions. The reactions were followed by UV absorption spectroscopy [5] or/and 80-MHz ^1H -NMR for various concentrations of **4** and TCE for at least 3 half-lives.

In the presence of 0.9 to 1 equiv. of TCE in benzene (20°, 4 h), 7-oxa[2.2.1]hericene (**5**) gave the corresponding mono-adduct **8** in 67% isolated yield. With an excess of TCE in acetone, 2 equiv. of the dienophile added to **5** (20°, 15 h) giving 1,2,3,5,6,7,8-hexahydroanthracene-2,2,3,3,6,6,7,7-octacarbonitrile (**10**; 61%). No trace of the bis-adduct **9** could be detected during the reaction by 360-MHz ¹H-NMR at 25°. Mono-adduct **8** added to 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione in THF already at –50° and afforded the aromatic derivative **32**. In this case also, no trace of the intermediate product **31** could be detected neither by 360-MHz ¹H-NMR nor by 90-MHz ¹³C-NMR during the cycloaddition (–40° and –50°). As expected for bicyclo[2.2.1]hepta-2,5-dien-7-one [8], the cheletropic elimination of CO is already a fast process at such low temperatures.



The rate constants $k_1 = (4.3 \pm 0.4) \cdot 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_2 = (0.20 \pm 0.02) \cdot 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 25° in toluene were evaluated by 360-MHz ¹H-NMR for various concentrations of tetraenone **5** and TCE.

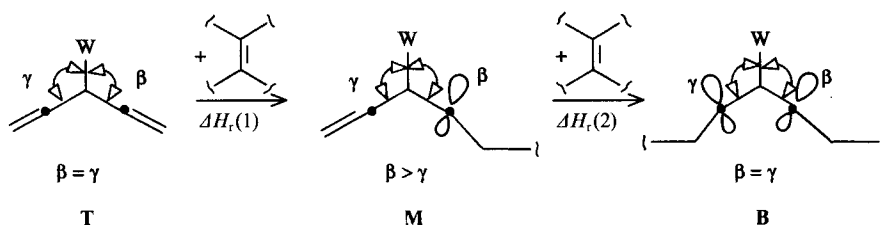
The polyenes **27–30** also added to TCE and gave the corresponding mono- and bis-adducts. In the case of pentenol **28**, two isomeric adducts **34a** and **34b** were obtained in a



3:2 ratio. Unfortunately, their relative configuration could not be established unambiguously. The mono-adducts **33**, **34a**, and **34b** and bis-adducts **35–38** were isolated and characterized.

Discussion. – Although no thermochemical measurements have been done thus far, it is believed that one of the dominating factor responsible of the relatively high rate-constant ratio k_1/k_2 for the tandem *Diels-Alder* reactions of a given dienophile to tetranes **1**, **2**, and 7,7-dimethyl[2.2.1]hericene (**3**) is the change in the exothermicity of the two successive cycloadditions ($|\Delta H_r(1)| > |\Delta H_r(2)|$) [2] [5–6]. When going from mono-adduct **M** of a corresponding tetraene **T** to the corresponding bis-adduct **B** (Scheme 3), the strain increases more than when going from **T** to the corresponding **M**. Most of the strain in bicyclo[2.2.1]hept-2-ene, and more so in bicyclo[2.2.1]hepta-2,5-diene [19] systems, arises from bond-angle deformation at the bridgehead centres C(1) and C(4). This was suggested by force-field [20] and *ab initio* MO calculations [21]. It was confirmed by X-ray crystallographic data of bicyclo[2.2.1]hept-2-ene and bicyclo[2.2.1]hepta-2,5-diene derivatives [20]. When going from **T** to **M**, the bridge W(7) is tilted toward the exocyclic diene moiety. The larger value observed for the angle β (between plane C(1), C(4), W(7) and mean plane C(1), C(2), C(3), C(4)) than for the angle γ (between plane C(1), C(4), W(7) and mean plane C(1), C(4), C(5), C(6)) was attributed to the difference in bond length between the π (C(2), C(3)) and σ (C(5), C(6)) bonds and to electronic repulsions between the π (C(2), C(3)) endocyclic double bond and bridge W(7) [5] [20] [21]. Introduction of the second endocyclic double bond at C(5), C(6) when going from **M** to **B** leads to a much greater strain increase for the same reasons, thus making reactions **M**→**B** ($\Delta H_r(2)$) less exothermic than corresponding reactions **T**→**M** ($\Delta H_r(1)$).

Scheme 3



MO calculations [21] predicted that the tilt $\beta - \gamma$ can be modulated by specific interactions involving the W(7) bridge and the π -systems at C(2), C(3) on one hand and at C(5), C(6) on the other hand. This hypothesis was confirmed also by comparison of the experimental $\beta - \gamma$ values determined by X-ray crystallography of bicyclo[2.2.1]hept-2-ene systems with various bridges W(7). For instance, while an average tilt $\beta - \gamma = 7^\circ$ was found for bicyclo[2.2.1]hept-2-enes (W = CH₂), a somewhat higher value $\beta - \gamma \approx 10^\circ$ was obtained for 7-oxabicyclo[2.2.1]hept-2-ene derivatives (W = O). Most striking in our context was the finding that $\beta - \gamma = 4.5^\circ$ only for bicyclo[2.2.1]hept-2-en-7-ones (W = CO), whereas a 'normal' value $\beta - \gamma = 7^\circ$ was measured for 7-isopropylidenebicyclo[2.2.1]hept-2-ene derivatives (W = Me₂C=C) [20]. This latter result can be interpreted in terms of a possible stabilizing $\pi_{CO}^* - \pi$ (C(2), C(3)) interaction in bicyclo[2.2.1]hept-2-en-7-ones [22] which diminishes the tilt $\beta - \gamma$ and the strain of these systems compared

with the corresponding 7-isopropylidene derivatives. We thus propose that the strain increase when going from mono-adduct **8** to bis-adduct **9** compared with that when going from 7-oxa[2.2.1]hericene (**5**) to **8** is a smaller value than the strain increase when going from **6** to **7** compared with that when going from 7,7-diphenyl[2.2.1]hericene (**4**) to **6**. Accordingly, we expect the rate-constant ratio k_1/k_2 for the tandem *Diels-Alder* additions of **5** to be smaller than for the same reactions of [2.2.1]hericene **3** and **4**, and tetraenes **1**, **2**, as observed (*Scheme 1*). This interpretation is tentative only; more quantitative kinetic and thermochemical data, as well as an X-ray structure of *Diels-Alder* mono-adducts of **5** are necessary to put it on firmer grounds.

We do not believe that the cheletropic elimination of CO in bis-adduct **9** giving **10** affects significantly the rate constant k_2 (e.g. through the coupling of both the cycloaddition and elimination reactions) since *Warrener et al.* [9] have reported that the *Diels-Alder* addition of 4-(*p*-tolyl)-3*H*-1,2,4-triazole-3,5(4*H*)-dione to 1,4-dimethyl-5,6-dimethylidene-2,3-diphenylbicyclo[2.2.1]hept-2-ene gives the corresponding bicyclo[2.2.1]hepta-2,5-dien-7-one derivative which was observable at -40° , but underwent fast CO elimination at 20° .

Conclusion. – The 3',3'-dimethyl-2,3,5,6-tetramethylidenespiro[bicyclo[2.2.1]heptane-7,2'-oxirane] (**26**) [14] was isomerized into 3,3-dimethyl-5,6,7,8-tetramethylidenebicyclo[2.2.2]octan-2-one (**27**) with CF_3COOH . With aq. HClO_4 in THF, **26** gave a mixture of 2,3,5,6-tetramethylidene-7-(propen-2'-yl)bicyclo[2.2.1]heptan-7-ol (**28**) and 7-(2'-hydroxypropan-2'-yl)-2,3,5,6-tetramethylidenebicyclo[2.2.1]heptan-7-ol (**29**). Oxidative cleavage of diol **29** afforded 7-oxa[2.2.1]hericene (**5**). The synthesis of 7,7-diphenyl[2.2.1]hericene (**4**) is also reported. As for **1–3**, a relatively large reactivity difference ($k_1/k_2 = 260$) was observed for the two successive *Diels-Alder* additions of TCE to **4** (*Scheme 1*). In contrast, a significantly smaller rate-constant ratio ($k_1/k_2 = 21$) was measured for the tandem cycloaddition of TCE to **5**. Thus, as for 2,3,5,6-tetramethylidenebicyclo[2.2.2]octane derivatives [6] [23], the rate-constant ratio k_1/k_2 of the tandem *Diels-Alder* additions of a given dienophile to 2,3,5,6-tetramethylidenebicyclo[2.2.1]heptanes depends on the nature of the bridge W(7).

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Experimental Part

General. See [24].

Tetramethyl 7-(Diphenylmethylidene)bicyclo[2.2.1]heptane-2-exo,3-exo,5-exo,6-exo-tetracarboxylate (12). A degassed mixture of 10% Pd/C (95.3 g, 0.71 mol), *Diels-Alder* adduct of maleic anhydride to 6,6-diphenylfulvene [12] (46.4 g, 0.14 mol), and abs. MeOH (375 ml) was pressurized with CO (3 atm) and shaken in a 2-l *Parr* flask at 20° for 60 h. The solvent was evaporated and the residue triturated with CHCl_3 (650 ml) and sat. aq. NaHCO_3 soln. (500 ml). After filtration on *Celite*, the org. phase was washed with sat. aq. NaHCO_3 soln. (450 ml, 4 times) and H_2O (450 ml, twice), dried (MgSO_4), and evaporated and the residue recrystallized from Et_2O (100 ml), yielding 34.7 g (50%), colourless powder. M.p. $132\text{--}133^\circ$ (MeOH). UV (95% EtOH): 202 (60000), 240 (25000). IR (KBr): 3040, 2880, 1730, 1440, 1320, 1290, 1250, 1200, 1170, 1150, 1020, 900. $^1\text{H-NMR}$ (80 MHz, CDCl_3): 7.37 (m, 2 Ph); 3.60 (s, 4 MeOOC); 3.45 (s, H-C(1), H-C(4)); 2.93 (s, H-C(2), H-C(3), H-C(5), H-C(6)). $^{13}\text{C-NMR}$ (90.55 MHz, CDCl_3): 171.3 (s, COO); 141.3 (s, arom. C); 137.7 (s, C=C(7)); 135.5 (s, C(7)); 129.2, 127.5, 126.6 (3d, $^1J(\text{C}, \text{H}) = 154$, arom. CH); 51.7 (q, $^1J(\text{C}, \text{H}) = 146$, CH_3O); 49.3 (d, $^1J(\text{C}, \text{H}) = 136$, C(2), C(3), C(5), C(6)); 43.9

(*dd*, $^1J(\text{C}, \text{H}) = 152$, $^3J(\text{C}, \text{H}) = 7$, $\text{C}(1)$, $\text{C}(4)$). MS (70 eV): 492 (M^+), 461 (11), 348 (22), 315 (85), 288 (39), 229 (65), 145 (31), 113 (75), 59 (100). Anal. calc. for $\text{C}_{28}\text{H}_{28}\text{O}_8$ (492.53): C 68.28, H 5.73; found: C 68.23, H 5.70.

7-(Diphenylmethylidene)bicyclo[2.2.1]heptane-2-exo,3-exo,5-exo,6-exo-tetramethanol (**13**). A soln. of **12** (25 g, 0.05 mmol) in anhyd. THF (65 ml) was added dropwise to a vigorously stirred suspension of LiAlH_4 (5.8 g, 0.15 mol) in anhyd. THF (190 ml) at 0° and under N_2 . After heating under reflux overnight, the mixture was cooled to 20° and H_2O (20 ml) was added dropwise until formation of a white suspension. The precipitate was eliminated by quick filtration through silica gel. The residue was extracted with boiling EtOH (120 ml, 3 times). The alcoholic extracts were evaporated and the residue recrystallized from MeOH, yielding 14 g (73%), white powder. M.p. $197\text{--}199^\circ$ (MeOH). IR (KBr): 3280, 2940, 2900, 1600, 1480, 1450, 1380, 1350, 1320, 1230, 1060, 1040, 1000. $^1\text{H-NMR}$ (80 MHz, D_2O): 7.2 (*m*, 2 Ph); 4.77 (*s*, OH); 3.85–3.40 (*m*, 4 CH_2OH); 2.6 (*s*, $\text{H-C}(1)$, $\text{H-C}(4)$); 2.5–2.3 (*m*, $\text{H-C}(2)$, $\text{H-C}(3)$, $\text{H-C}(5)$, $\text{H-C}(6)$). $^{13}\text{C-NMR}$ (90.55 MHz, D_2O ; internal reference dioxane, $\delta(\text{C}) = 67.4$ ppm): 145.2 (*s*, arom. C); 143.7 (*s*, $\text{C}=\text{C}(7)$); 134.7 (*s*, $\text{C}(7)$); 130.1, 129.1, 127.0 (3*d*, $^1J(\text{C}, \text{H}) = 154$, arom. CH); 62.7 (*t*, $^1J(\text{C}, \text{H}) = 142$, CH_2OH); 48.4 (*d*, $^1J(\text{C}, \text{H}) = 136$, $\text{C}(2)$, $\text{C}(3)$, $\text{C}(5)$, $\text{C}(6)$); 45.9 (*d*, $^1J(\text{C}, \text{H}) = 152$, $\text{C}(1)$, $\text{C}(4)$). MS (70 eV): 380 (6, M^+), 362 (12), 312 (4), 274 (24), 215 (50), 167 (98), 91 (100). Anal. calc. for $\text{C}_{24}\text{H}_{28}\text{O}_4$ (380.49): C 75.76, H 7.42; found: C 75.63, H 7.32.

2-exo,3-exo,5-exo,6-exo-Tetrakis(chloromethyl)-7-(diphenylmethylidene)bicyclo[2.2.1]heptane (**14**). At 0° , **13** (12 g, 0.032 mol) was added portionwise and slowly into a stirred soln. of SOCl_2 (18.76 g, 0.158 mol, 11.1 ml) in anhyd. pyridine (9.97 g, 0.126 mol, 10.3 ml) under N_2 . When the mixture became viscous, SOCl_2 (31.1 g, 0.262 mol, 19 ml) was added slowly. The temp. was allowed to reach 60° in 30 min and the mixture stirred for 150 min (the temp. should not rise above 60°). After cooling to 20° , CH_2Cl_2 (30 ml) was added. Then, H_2O (10 ml) was added dropwise (destruction of excess of SOCl_2). The org. layer was washed with H_2O (15 ml, 3 times), sat. aq. NaHCO_3 soln. (20 ml, 4 times), and H_2O (20 ml, twice), dried (MgSO_4), and evaporated giving 7.1 g (50%), colourless powder which was recrystallized from CHCl_3 . M.p. $144\text{--}146^\circ$. UV (95% EtOH): 205 (66000), 229 (26000), 243 (30000). IR (KBr): 3100, 2980, 1700, 1500, 1450, 1340, 1260, 1070, 1030, 920, 890. $^1\text{H-NMR}$ (80 MHz, CDCl_3): 7.2 (*m*, 2 Ph); 3.72, 3.45 (2*m*, 4 CH_2Cl); 2.95 (*s*, $\text{H-C}(1)$, $\text{H-C}(4)$); 2.35 (*m*, $\text{H-C}(2)$, $\text{H-C}(3)$, $\text{H-C}(5)$, $\text{H-C}(6)$). $^{13}\text{C-NMR}$ (90.55 MHz, CDCl_3): 140.6 (*s*, arom. C); 140.2 (*s*, $\text{C}=\text{C}(7)$); 137.5 (*s*, $\text{C}(7)$); 128.6, 128.5, 128.4 (3*d*, $^1J(\text{C}, \text{H}) = 154$, arom. CH); 46.8 (*d*, $^1J(\text{C}, \text{H}) = 158$, $\text{C}(1)$, $\text{C}(4)$); 43.3 (*d*, $^1J(\text{C}, \text{H}) = 150$, CH_2Cl). MS (70 eV): 458 (12), 456 (46), 454 (100, M^+), 452 (76), 417 (26), 403 (48), 327 (66), 228 (50), 165 (86), 91 (100). Anal. calc. for $\text{C}_{24}\text{H}_{24}\text{Cl}_4$ (454.27): C 63.46, H 5.33; found: C 63.46, H 5.37.

7-(Diphenylmethylidene)-2,3,5,6-tetramethylidenebicyclo[2.2.1]heptane (**4**). *t*-BuOK (3.7 g, 33 mmol) was added portionwise to a stirred soln. of **14** (1.5 g, 3.3 mmol) in anhyd. THF (40 ml) cooled to 0° . The mixture was stirred at 20° for 45 min, and then heated under reflux for 3 h. After cooling to 20° , H_2O (20 ml) was added, the mixture extracted with hexane (40 ml, 5 times), the combined org. extract washed with H_2O (50 ml, 3 times), dried (MgSO_4), and evaporated and the residue recrystallized from hexane, yielding 0.7 g (69%), white powder. M.p. $131\text{--}133^\circ$ (dec.). UV (95% EtOH): 228 (22500), 245 (sh, 24000), 250 (25500). UV (isooctane): 229 (22100), 245 (sh, 23800), 250 (24000). IR (KBr): 3070, 3000, 2990, 2940, 2820, 1780, 1650, 1470, 1400, 1320, 1300, 780, 720. $^1\text{H-NMR}$ (80 MHz, CDCl_3): 7.3 (*m*, 2 Ph); 5.3, 5.0 (2*s*, 4 $\text{CH}_2=\text{C}$); 3.98 (*s*, $\text{H-C}(1)$, $\text{H-C}(4)$). $^{13}\text{C-NMR}$ (90.55 MHz, CDCl_3): 147.9 (*m*, $\text{C}(2)$, $\text{C}(3)$, $\text{C}(5)$, $\text{C}(6)$); 143.6 (*s*, $\text{C}=\text{C}(7)$); 142.1 (*s*, arom. C); 141.2 (*s*, $\text{C}(7)$); 129.9, 127.9, 126.9 (3*d*, $^1J(\text{C}, \text{H}) = 154$, arom. CH); 101.7 (*t*, $^1J(\text{C}, \text{H}) = 160$, $\text{CH}_2=\text{C}$); 58.0 (*dm*, $^1J(\text{C}, \text{H}) = 150$, $\text{C}(1)$, $\text{C}(4)$). MS (70 eV): 308 (93, M^+), 293 (34), 278 (24), 215 (100), 202 (49), 189 (25), 178 (38), 165 (31), 115 (31), 91 (28). Anal. calc. for $\text{C}_{24}\text{H}_{20}$ (308.43): C 93.46, H 6.54; found: C 93.55, H 6.47.

Tetramethyl 7,7-(Diphenylmethylidene)bicyclo[2.2.1]heptane-2-exo,3-endo,5-exo,6-endo-tetracarboxylate (**15**). A soln. of **12** (10 g) and anhyd. K_2CO_3 in anhyd. MeOH (dried over Mg/I_2) was stirred at 20° overnight. After filtration on silica gel (10 g), the solvent was evaporated, the residue dissolved in CH_2Cl_2 (150 ml), and the soln. washed with H_2O (50 ml, 3 times), dried (MgSO_4), and evaporated, yielding 8.1 g (81%), colourless powder. IR (KBr): 3040, 2970, 1740, 1440, 1380, 1350, 1320. $^1\text{H-NMR}$ (80 MHz, CDCl_3): 7.41 (*m*, 2 Ph); 3.83, 3.74 (2*s*, 4 MeO); 3.72 (*t*, $J = 7$, $\text{H-C}(1)$, $\text{H-C}(5)$); 3.38 (*d*, $J = 7$, $\text{H-C}(1)$, $\text{H-C}(4)$); 3.18 (*m*, $\text{H-C}(3)$, $\text{H-C}(6)$). MS (70 eV): 492 (26, M^+), 461 (22), 445 (18), 382 (35), 358 (31), 300 (24), 110 (55), 59 (100).

7-(Diphenylmethylidene)bicyclo[2.2.1]heptane-2-exo,3-endo,5-exo,6-endo-tetramethanol (**16**). A soln. of **15** (12 g, 0.025 mol) in anhyd. THF (40 ml) was added dropwise to a stirred suspension of LiAlH_4 (2.9 g, 70 mmol) in anhyd. THF (100 ml) at 0° and under N_2 . The mixture was then heated under reflux for 10 h. After cooling to 20° , H_2O (11 ml) was added dropwise under vigorous stirring. The mixture was immediately filtered on silica gel. The precipitate/silica gel was extracted with boiling EtOH (80 ml, 3 times), the combined extract evaporated, and the residue recrystallized from MeOH, yielding 7.5 g (78%), colourless powder. M.p. $201\text{--}203^\circ$. IR (KBr): 3290, 2930, 2900, 2870, 1590, 1500, 1465, 1310, 1040. $^1\text{H-NMR}$ (80 MHz, D_2O): 7.27 (*m*, 2 Ph); 3.85, 3.42 (2*m*, 4 CH_2OH); 2.62

(*d*, *J* = 7, H–C(1), H–C(4)); 2.30 (*m*, H–C(2), H–C(3), H–C(5), H–C(6)). MS (70 eV): 380 (8, *M*⁺), 362 (24), 344 (10), 168 (59), 126 (29) 91 (100).

2-*exo*,3-*endo*,5-*exo*,6-*endo*-Tetrakis(chloromethyl)-7-(diphenylmethylenidene)bicyclo[2.2.1]heptane (**17**). At 0°, **16** (8 g, 21 mmol) was added portionwise to a soln. of SOCl₂ (12.5 g, 0.11 mol, 7.4 ml) and pyridine (6.6 g, 6.8 ml, 0.08 mol). SOCl₂ (20.7 g, 12.6 ml, 0.17 mol) was added and the mixture heated to 60° for 3 h. After cooling to 20°, CH₂Cl₂ (20 ml) was added and the excess of SOCl₂ destroyed by dropwise addition of H₂O (8 ml). The org. phase was washed with H₂O (15 ml, 3 times), sat. aq. NaHCO₃ soln. (20 ml, 4 times), and H₂O (20 ml, twice), dried (MgSO₄), and evaporated, yielding 2.9 g (61%), white powder. M.p. 139–141° (CHCl₃). IR (KBr): 3100, 2970, 1510, 1430, 1340, 1280, 1250, 1020. ¹H-NMR (80 MHz, CDCl₃): 7.35 (*m*, 2 Ph); 4.0–3.4 (*m*, 4 CH₂Cl); 2.95 (*d*, *J* = 7, H–C(1), H–C(4)); 2.5–1.8 (*m*, H–C(2), H–C(3), H–C(5), H–C(6)). MS (70 eV): 458 (8), 456 (31), 454 (36, *M*⁺), 452 (35), 419 (21), 401 (53), 248 (29), 165 (70), 124 (23), 91 (100).

11-(Diphenylmethylenidene)-9,10-dimethylenetricyclo[6.2.1.0^{2,7}]undec-2(7)-ene-4,4,5,5-tetracarbonitrile (**6**). A mixture of **4** (40 mg, 0.13 mmol), freshly sublimed TCE (33 mg, 0.26 mmol), and acetone (82 ml) was stirred at 20° for 10 h. After staying overnight at –20°, the precipitate was collected and recrystallized from CH₂Cl₂, yielding 60 mg (82%), white powder. M.p. 239–241°. UV (95% EtOH): 202 (38000), 225 (19000), 265 (11000). IR (KBr): 3100, 3020, 2940, 1500, 1450, 1230, 900, 870. ¹H-NMR (80 MHz, CD₃COCD₃): 7.27 (*m*, 2 Ph); 5.4, 5.2 (2*s*, CH₂=C(9), CH₂=C(10)); 3.99 (*s*, H–C(1), H–C(8)); 3.71, 3.52 (2*s*, CH₂(3), CH₂(6)). ¹³C-NMR (90.55 MHz, CD₃COCD₃): 146.5 (*m*, C(9), C(10)); 144.0 (*s*, C=C(11)); 141.6 (*s*, arom. C); 140.9 (*s*, C(11)); 129.7, 127.8, 126.8 (3*d*, ¹J(C,H) = 154, arom. CH); 111.8, 111.2 (2*s*, CN); 101.9 (*t*, ¹J(C,H) = 160, CH₂=C(9), CH₂=C(10)); 58.3 (*d*, ¹J(C,H) = 150, C(1), C(4)); 37.4 (*t*, ¹J(C,H) = 140, C(2), C(3)). MS (70 eV): 436 (40, *M*⁺), 308 (43), 255 (37), 215 (36), 191 (53), 178 (93), 58 (100). Anal. calc. for C₃₀H₂₀N₄ (436.52): C 82.55, H 4.62; found: C 82.71, H 4.61.

15-(Diphenylmethylenidene)tetracyclo[6.6.1.0^{2,7}.0^{9,14}]pentadeca-2(7),9(14)-diene-4,4,5,5,11,11,12,12-octacarbonitrile (**7**). A mixture of **4** (120 mg, 0.65 mmol), freshly sublimed TCE (166 mg, 1.3 mmol) and acetone (27 ml) was allowed to stay at 20° for 20 h. After cooling to –20°, a few drops of pentane were added. The precipitate was collected and dried *in vacuo*, yielding 350 mg (95%), colourless crystals. M.p. > 250° (dec.). UV (95% EtOH): 205 (41000). IR (KBr): 3080, 3060, 3010, 2970, 1650, 1600, 1490, 1430, 1230, 1120, 1020, 760. ¹H-NMR (80 MHz, CD₃COCD₃): 7.5–7.1 (*m*, 2 Ph); 4.25 (*s*, H–C(1), H–C(8)); 3.9 (*s*, CH₂(3), CH₂(6), CH₂(10), CH₂(13)).

Tetramethyl 7-Isopropylidenebicyclo[2.2.1]heptane-2-*exo*,3-*endo*,5-*exo*,6-*endo*-tetracarboxylate (**23**). A soln. of tetraester **22** [2] [14] (15 g) and anh. K₂CO₃ (5 g) in anh. MeOH (freshly distilled from Mg/I₂) was allowed to stand at 20° for 8 h. The soln. was filtered through silica gel (15 g) and evaporated and the residue dried over P₂O₅ and paraffin *in vacuo*: 15 g (100%), white crystals. M.p. 102–103° (Et₂O). IR (CHCl₃): 3040, 2970, 1750, 1725, 1440, 1380, 1320, 1285, 1265. ¹H-NMR (80 MHz, CDCl₃): 3.67, 3.75 (2*s*, 4 MeO); 3.4 (*d*, *J* = 7, H–C(1), H–C(4)); 3.2 (*t*, *J* = 7, H_{endo}–C(2), H_{endo}–C(5)); 2.96 (*m*, H_{exo}–C(3), H_{exo}–C(6)); 1.62 (*s*, 2 Me). ¹³C-NMR (90.55 MHz, CDCl₃): 173.5, 171.9 (2*s*, COO); 135.4 (*m*, C(7)); 121.1 (*m*, C=C(7)); 52.0 (*q*, ¹J(C,H) = 146, CH₃O); 47.5, 43.8 (2*d*, ¹J(C,H) = 136, C(2), C(3), C(5), C(6)); 43.5 (*d*, ¹J(C,H) = 152, C(1), C(4)); 20.1 (*qq*, ¹J(C,H) = 126, ³J(C,H) = 5, 2 Me). MS (70 eV): 368 (17, *M*⁺), 337 (28), 335 (25), 276 (58), 248 (100), 189 (70), 164 (70), 145 (40), 113 (60). Anal. calc. for C₁₈H₂₄O₈ (368.39): C 58.69, H 6.57; found: C 58.76, H 6.53.

7-Isopropylidenebicyclo[2.2.1]heptane-2-*exo*,3-*endo*,5-*exo*,6-*endo*-tetramethanol (**24**). A soln. of **23** (15 g, 0.04 mol) in anh. THF (80 ml) was added dropwise to a stirred suspension of LiAlH₄ (4.7 g, 0.122 mol) in anh. THF (160 ml) at 0° and under N₂. The mixture was heated under reflux for 4 h. After cooling to 20°, H₂O (16 ml) was added dropwise and the mixture heated under reflux for 1 h. The boiling soln. was filtered quickly through silica gel (80 g). The salts/silica gel were extracted with boiling EtOH (1 h of heating, 200 ml, 4 times). The extracts and THF soln. were combined and evaporated. The residue was recrystallized from MeOH at –15°, yielding 7.5 g (73%), colourless crystals. M.p. 169–171°. IR (KBr): 3290, 2920, 2900, 2860, 1480, 1440, 1350, 1070, 1040, 1020. ¹H-NMR (80 MHz, D₂O): 4.80 (*s*, OH); 3.75, 3.42 (2*m*, 4 CH₂O); 2.75 (*d*, *J* = 7, H–C(1), H–C(4)); 1.77 (*s*, 2 Me); 1.65 (*m*, H–C(2), H–C(3), H–C(5), H–C(6)). ¹³C-NMR (90.55 MHz, D₂O; internal ref.: dioxane, δ(C) = 67.4 ppm): 137.9 (*m*, C(7)); 121.5 (*m*, C=C(7)); 49.9, 46.7 (*t*, ¹J(C,H) = 152, CH₂OH); 48.1, 45.1 (2*dm*, ¹J(C,H) = 134, C(2), C(3), C(5), C(6)); 45.1 (*dm*, ¹J(C,H) = 148, C(1), C(4)); 20.4 (*qq*, ¹J(C,H) = 126, ³J(C,H) = 5, Me). MS (70 eV): 256 (40, *M*⁺), 238 (29), 202 (100), 191 (87), 184 (73). Anal. calc. for C₁₄H₂₄O₄ (256.34): C 65.60, H 9.44; found: C 65.54, H 9.52.

2-*exo*,3-*endo*,5-*exo*,6-*endo*-Tetrakis(chloromethyl)-7-isopropylidenebicyclo[2.2.1]heptane (**20**). At 0°, **24** (4 h, 16 mmol) was added portionwise to a stirred soln. of freshly distilled SOCl₂ (9.28 g, 80 mmol) and anh. pyridine (4.93 g, 62 mmol) under N₂. When the mixture became viscous, SOCl₂ (15.4 g, 129 mmol) was added slowly. The mixture was heated to 55° for 2½ h. After cooling to 20°, CH₂Cl₂ (25 ml) was added, then H₂O (9 ml) dropwise and under vigorous stirring. The org. phase was washed with H₂O (10 ml, twice), sat. aq. NaHCO₃ soln. (15 ml, twice), and H₂O (15 ml, twice), dried (MgSO₄), and evaporated and the residue recrystallized from CHCl₃, yielding 2.8 g

(55%), colourless crystals. M.p. 84–85°. UV (95% EtOH): final absorption, $\epsilon_{210} = 110$. IR (CHCl₃): 2975, 2925, 1400, 1380, 1300. ¹H-NMR (80 MHz, CDCl₃): 3.17–3.92 (*m*, 4 CH₂Cl); 2.85 (*d*, *J* = 7, H–C(1), H–C(4)); 1.85 (*m*, H–C(2), H–C(3), H–C(5), H–C(6)); 1.71 (*s*, 2 Me). ¹³C-NMR (90.55 MHz, CDCl₃): 136.7 (*m*, C(7)); 121.6 (*m*, C=C(7)); 47.4, 41.6 (*dm*, ¹*J*(C, H) = 134, C(2), C(3), C(5), C(6)); 47.7, 44.0 (*r*, ¹*J*(C, H) = 152, CH₂Cl); 44.1 (*dm*, ¹*J*(C, H) = 148, C(1), C(4)); 20.3 (*q*, ¹*J*(C, H) = 126, Me). MS (70 eV): 332 (14), 339 (29), 328 (33), 317 (16), 283 (35), 279 (100), 245 (27), 239 (45), 191 (60), 155 (80), 91 (98). Anal. calc. for C₁₄H₂₀Cl₄ (330.13): C 50.94, H 6.11; found: C 50.82, H 6.00.

Ozonolysis of 20. Oxygen (O₂) containing 3–4% of O₃ (1.5 l/min) was bubbled through a soln. of **20** (0.74 g, 2.24 mmol) in MeOH (80 ml) cooled to –78° for 2½ h. After addition of Me₂S (1 ml), the soln. was allowed to warm up to 0° and kept at that temp. for 3–4 h. The solvent was evaporated and the residue purified and separated by column chromatography on silica gel (15 g, AcOEt/hexane 1:9). The 1st fraction gave **25**, oil which crystallized from CH₂Cl₂/hexane 1:4, yielding 503 mg (65%). The 2nd fraction gave **18**, oil which crystallized from CH₂Cl₂/hexane 1:9, yielding 170 mg (25%).

2-exo,3-endo,5-exo,6-endo-Tetrakis(chloromethyl)-3',3'-dimethylspiro[bicyclo[2.2.1]heptane-7,2'-oxirane] (25). Colourless crystals. M.p. 96–98°. IR (CH₂Cl₂): 3000, 2980, 2960, 1450, 1370, 1260, 1180, 780. ¹H-NMR (80 MHz, CDCl₃): 3.12–4.12 (*m*, 4 CH₂Cl); 1.67–2.67 (*m*, H–C(1), H–C(2), H–C(3), H–C(4), H–C(5), H–C(6)); 1.37 (*s*, 2 Me). ¹³C-NMR (90.55 MHz, CDCl₃): 79.4 (*m*, C(7)); 59.2 (*m*, C(3')); 49.5, 45.8 (*2dm*, ¹*J*(C, H) = 154, C(2), C(3), C(5), C(6)); 44.5, 42.7 (*2t*, ¹*J*(C, H) = 150, 4 CH₂Cl); 42.9 (*d*, ¹*J*(C, H) = 146, C(1), C(4)); 22.3 (*qq*, ¹*J*(C, H) = 128, ³*J*(C, H) = 3, Me). MS (70 eV): 348 (26), 246 (52, *M*⁺), 344 (39), 309 (55), 297 (40), 295 (35), 253 (60), 117 (36), 91 (94), 77 (87), 70 (100). Anal. calc. for C₁₄H₂₀Cl₄O (346.13): C 48.58, H 5.83; found: C 48.55, H 5.86.

2-exo,3-endo,5-exo,6-endo-Tetrakis(chloromethyl)bicyclo[2.2.1]heptan-7-one (18). Colourless crystals, soluble in polar solvents. M.p. 83–84°. UV (isooctane): 294 (27). IR (CH₂Cl₂): 3070, 3000, 2695, 2310, 1785, 1485, 1260, 1170, 1140, 895. ¹H-NMR (80 MHz, CDCl₃): 3.3–4.1 (*m*, 4 CH₂Cl); 1.9–2.6 (*m*, H–C(1), H–C(2), H–C(3), H–C(4), H–C(5), H–C(6)). ¹³C-NMR (90.55 MHz, CDCl₃): 206.9 (*s*, CO); 48.1 (*d*, ¹*J*(C, H) = 148, C(1), C(4)); 46.4, 42.9 (*2t*, ¹*J*(C, H) = 152, CH₂Cl); 41.5, 37.3 (*2d*, ¹*J*(C, H) = 140, C(2), C(3), C(5), C(6)). MS (70 eV): 306 (6, *M*⁺), 304 (13), 302 (10), 271 (19), 267 (31), 255 (52), 253 (54), 203 (25), 191 (33), 153 (57), 117 (49), 103 (100), 91 (72).

3,3-Dimethyl-5,6,7,8-tetramethyldenebicyclo[2.2.2]octan-2-one (27). CF₃COOH (750 µl, 10 mmol) was added to a soln. of **26** (1.8 g, 9 mmol) in CH₂Cl₂ (20 ml) at 0° and under N₂. After staying at 20° for 10 min, the soln. was washed with H₂O (30 ml, twice), dried (MgSO₄), and evaporated. The oily residue was purified by column chromatography on Florisil (50 g, CH₂Cl₂) and by recrystallization from hexane at –20°, yielding 1 g (60%), colourless crystals, polymerizing rapidly at 20°. M.p. 37–38°. UV (isooctane): 233 (9250), 242 (11 200), 250 (11 700), 261 (7700). UV (95% EtOH): 244 (10 200), 252 (11 700). IR (CH₂Cl₂): 3100, 2980, 2940, 1735, 1095, 895. ¹H-NMR (80 MHz, CDCl₃): 5.40, 5.37, 4.35 (3*s*, 4 CH₂=C); 3.66 (*s*, H–C(1)); 2.87 (*s*, H–C(4)); 1.0 (*s*, 2 Me). ¹³C-NMR (90.55 MHz, CDCl₃): 208.7 (*s*, CO); 142.9 (*s*, C(5), C(8)); 139.4 (*s*, C(6), C(7)); 108.4, 107.5 (2*r*, ¹*J*(C, H) = 162, 4 CH₂=C); 66.7, 60.6 (2*d*, ¹*J*(C, H) = 148, C(1), C(4)); 46.7 (*s*, C(3)); 24.1 (*qm*, ¹*J*(C, H) = 126, Me). MS (70 eV): 200 (*M*⁺), 185 (17), 172 (37), 157 (60), 142 (77), 129 (80), 115 (100), 91 (45), 77 (55), 65 (51). Anal. calc. for C₁₄H₁₆O (200.28): C 83.96, H 8.05; found: C 83.17, H 7.88.

Acidic Hydrolysis of Epoxide 26. Aq. 35% HClO₄ soln. (2 ml) was added dropwise to a stirred soln. of **26** (2.5 g, 12.5 mmol) in THF (170 ml) and H₂O (30 ml). After stirring at 20° overnight, NaCl was added until saturation and the mixture extracted with CH₂Cl₂ (50 ml, 5 times). The combined org. phase was washed with sat. aq. NaCl soln. (100 ml, 5 times), dried (MgSO₄), and evaporated. The oily residue was purified and separated by flash column chromatography on silica gel (200 g, CH₂Cl₂). The 1st fraction (*R*_f 0.5) gave 1.15 g (50%) of **28** after recrystallization from hexane. The 2nd fraction (*R*_f 0.1) gave 0.82 g (30%) of **29** after recrystallization from CH₂Cl₂/hexane.

2,3,5,6-Tetramethyldene-7-(propen-2'-yl)bicyclo[2.2.1]heptan-2-ol (28). Colourless crystals. M.p. 43–45°. UV (isooctane): 223 (11 150), 230 (12 300), 237 (11 100), 257 (7000). UV (95% EtOH): 223 (11 500), 230 (13 200), 236 (12 100), 252 (7700). IR (CH₂Cl₂): 3400, 3040, 2990, 1610, 1600, 1460, 1440, 1380, 1240, 1190, 1080, 1000, 980. ¹H-NMR (80 MHz, CDCl₃): 5.43, 5.23, 5.11, 4.95 (4*s*, 4 CH₂=C); 5.05 (*s*, CH₂(1')); 3.4 (*s*, H–C(1), H–C(4)); 1.8 (*s*, CH₃). ¹³C-NMR (90.55 MHz, CDCl₃): 147.3, 146.9 (2*s*, C(2), C(3), C(5), C(6)); 142.4 (*s*, C(2')); 115.2 (*td*, ¹*J*(C, H) = 156, ³*J*(C, H) = 6, CH₂(1')); 104.7, 103.1 (2*d*, ¹*J*(C, H) = 156, CH₂–C(2), CH₂=C(3), CH₂=C(5), CH₂=C(6)); 85.6 (*s*, C(7)); 61.7 (*d*, ¹*J*(C, H) = 148, C(1), C(4)); 18.6 (*qm*, ¹*J*(C, H) = 126, CH₃). MS (70 eV): 200 (5, *M*⁺), 185 (5), 172 (18), 158 (50), 143 (22), 128 (18), 115 (20), 91 (21), 77 (16), 70 (100). Anal. calc. for C₁₄H₁₆O (200.28): C 83.96, H 8.05; found: C 83.80, H 8.03.

7-(2'-Hydroxypropen-2'-yl)-2,3,5,6-tetramethyldenebicyclo[2.2.1]heptan-2-ol (29). Colourless crystals. M.p. 74–76°. UV (isooctane): 223 (sh, 7560), 231 (8900), 238 (9200), 250 (7500). UV (95% EtOH): 222 (sh, 8500),

229 (9650), 237 (9500), 251 (7500). IR (CH_2Cl_2): 3600, 3360, 2940, 2860, 1390, 1370, 1350, 1120, 1110. $^1\text{H-NMR}$ (80 MHz, CDCl_3): 5.30, 5.17, 5.13, 4.93 (4s, $\text{CH}_2=\text{C}(2)$, $\text{CH}_2=\text{C}(3)$, $\text{CH}_2=\text{C}(5)$, $\text{CH}_2=\text{C}(6)$); 3.25 (s, $\text{H}-\text{C}(1)$, $\text{H}-\text{C}(4)$); 1.27 (s, 2 Me). $^{13}\text{C-NMR}$ (90.55 MHz, CDCl_3): 148.0, 147.9 (2s, C(2), C(3), C(5), C(6)); 104.2, 104.0 (2t, $^1J(\text{C}, \text{H}) = 160$, $\text{CH}_2=\text{C}$); 87.2 (s, C(7)); 74.3 (s, C(2')); 60.9 (d, $^1J(\text{C}, \text{H}) = 158$, C(1), C(4)); 25.8 (qm, $^1J(\text{C}, \text{H}) = 126$, Me). MS (70 eV): 218 (3, M^+), 203 (4), 200 (4), 185 (4), 159 (30), 143 (33), 132 (71), 118 (49), 107 (7), 92 (35), 78 (23), 64 (100). Anal. calc. for $\text{C}_{14}\text{H}_{18}\text{O}_2$ (218.29): C 77.03, H 8.31; found: C 76.91, H 8.21.

2,3,5,6-Tetramethylidenebicyclo[2.2.1]heptan-7-one (5). A soln. of **29** (0.2 g, 0.9 mmol) in anh. CH_2Cl_2 (5 ml) was added dropwise to a vigorously stirred suspension of pyridinium chlorochromate (0.6 g, 2.75 mmol) in anh. CH_2Cl_2 cooled to 0° . The mixture was then stirred at 20° for 2 h, and anh. Et_2O (40 ml) was added. After decantation, the black residue was washed with Et_2O (20 ml, 3 times). The org. soln. were combined and filtered at 0° (Büchner). The solvent was evaporated and the greenish residue purified by column chromatography on Florisil (70 g, CH_2Cl_2) yielding a 1st fraction containing **5** (R_f 0.74, CH_2Cl_2 , silica gel) and a 2nd fraction containing 20 mg (10%) of **29**. The soln. containing **5** was concentrated to ca. 5 ml, and hexane (5 ml) was added. After concentration to 5 ml, the soln. was cooled in liq. N_2 which led to precipitation of **5** that was collected by decantation under N_2 , yielding 70 mg (48%), colourless crystals. M.p. $56-57^\circ$ (pentane). UV (isooctane): 206 (10 150), 213 (9225), 258 (12 300), 282 (sh, 4730). UV (CH_3CN): 260 (13 800), 285 (sh, 3000), 311 (390), 327 (220); UV (95% EtOH): 219 (sh, 15 400), 226 (15 600), 235 (13 500), 251 (sh, 9100). IR (CHCl_3): 3110, 3000, 2985, 2940, 2245, 1795, 1635, 1270, 1225, 1170. $^1\text{H-NMR}$ (80 MHz, CDCl_3): 207.2 (s, C(7)); 142.5 (s, C(2), C(3), C(5), C(6)); 103.8 (t, $^1J(\text{C}, \text{H}) = 160$, $\text{CH}_2=\text{C}$); 62.4 (d, $^1J(\text{C}, \text{H}) = 155$, C(1), C(4)). Anal. calc. for $\text{C}_{11}\text{H}_{10}\text{O}$ (158.21): C 83.52, H 6.37; found: C 83.42, H 6.54.

2,3,5,6-Tetramethylidene-7-(2'-methyloxiran-2'-yl)bicyclo[2.2.1]heptan-7-ol (30). To a soln. of **28** (250 mg, 1.25 mmol) in anh. benzene (5 ml), $\text{VO}(\text{acac})_2$ (2 mg) in C_6H_6 (1 ml) and $t\text{-BuOOH}$ (200 mg, 223 μl) in C_6H_6 (1 ml) were added and stirred at 40° for 3 h. After cooling to 20° , the solvent was evaporated and the greenish, oily residue purified by column chromatography on silica gel (100 g, AcOEt /hexane 1:1) yielding 125 mg (46%) of **30** after recrystallization from pentane, colourless crystal. M.p. $70-71^\circ$. UV (isooctane): 223 (sh, 12 000), 240 (9000), 245 (8000). UV (95% EtOH): 207 (16 000), 223 (sh, 13 500), 240 (13 000), 245 (12 300), 299 (6800). IR (CH_2Cl_2): 3540, 3010, 2990, 2960, 1710, 1380, 1240, 1200, 1060, 890. $^1\text{H-NMR}$ (80 MHz, CDCl_3): 5.4, 5.05 (2m, $\text{CH}_2=\text{C}(2)$, $\text{CH}_2=\text{C}(3)$, $\text{CH}_2=\text{C}(5)$, $\text{CH}_2=\text{C}(6)$); 3.3 (s, OH); 3.1 (s, $\text{CH}_2(3')$); 2.73, 2.35 (2s, $\text{H}-\text{C}(1)$, $\text{H}-\text{C}(4)$); 1.42 (s, CH_3). $^{13}\text{C-NMR}$ (90.55 MHz, CDCl_3): 147.4, 147.2, 147.1, 145.7 (4s, C(2), C(3), C(5), C(6)); 104.2, 103.7, 103.5 (3t, $^1J(\text{C}, \text{H}) = 156$, $\text{CH}_2=\text{C}(2)$, $\text{CH}_2=\text{C}(3)$, $\text{CH}_2=\text{C}(5)$, $\text{CH}_2=\text{C}(6)$); 84.4 (s, C(2')); 60.9, 60.6, (2dm, $^1J(\text{C}, \text{H}) = 150$, C(1), C(4)); 58.8 (s, C(7)); 56.6 (tm, $^1J(\text{C}, \text{H}) = 172$, C(3')); 18.6 (q, $^1J(\text{C}, \text{H}) = 126$, CH_3). MS (70 eV): 216 (3.5, M^+), 170 (25), 155 (37), 143 (44), 129 (86), 115 (100), 103 (17), 91 (70). Anal. calc. for $\text{C}_{14}\text{H}_{16}\text{O}_2$ (216.28): C 77.75, H 7.46; found: C 76.76, H 7.38.

9,10-Dimethylidene-11-oxotricyclo[6.2.1.0^{2,7}]undec-2(7)-ene-4,4,5,5-tetracarbonitrile (8). A soln. of **5** (10 mg, 0.063 mmol) and freshly sublimed TCE (8 mg, 0.062 mmol) was allowed to stand at 20° for 4 h. After the addition of pentane (1 ml) and cooling to -20° , the precipitate was collected, recrystallized from CH_2Cl_2 , and dried *in vacuo*, yielding 12 mg (67%), colourless crystals. M.p. $> 200^\circ$ (dec.). UV (95% EtOH): 206 (31 000), 238 (9500), 301 (1000). IR (CH_2Cl_2): 3120, 3000, 2940, 2245, 1790, 1650, 1290, 1240, 1100, 980, 900. $^1\text{H-NMR}$ (80 MHz, CD_3COD_3): 5.62, 5.32 (2s, $\text{CH}_2=\text{C}(9)$, $\text{CH}_2=\text{C}(10)$); 3.82 (s, $\text{H}-\text{C}(1)$, $\text{H}-\text{C}(8)$); 3.75 (m, $\text{CH}_2(3)$, $\text{CH}_2(6)$). $^{13}\text{C-NMR}$ (90.55 MHz, CD_3COD_3): 206.5 (s, C(11)); 146.4 (m, C(9), C(10)); 137.8 (m, C(2), C(7)); 111.7, 111.0 (2s, CN); 102.2 (t, $^1J(\text{C}, \text{H}) = 136$, $\text{CH}_2=\text{C}(9)$, $\text{CH}_2=\text{C}(10)$); 57.2 (dm, $^1J(\text{C}, \text{H}) = 130$, C(1), C(8)); 40.1 (s, C(4), C(5)); 31.7 (t, $^1J(\text{C}, \text{H}) = 140$, C(3), C(6)). MS (70 eV): 286 (0.4, M^+), 258 (75), 206 (25), 154 (29), 137 (21), 100 (35), 91 (100), 80 (21).

1,2,3,4,5,6,7,8-Octahydroanthracene-2,2,3,3,6,6,7,7-octacarbonitrile (10). A mixture of **5** (20 mg, 0.127 mmol) and freshly sublimed TCE (32 mg, 0.25 mmol) in acetone (1.5 ml) was stirred at 20° for 15 h. The solvent was evaporated and the residue recrystallized from $\text{CH}_3\text{CN}/\text{Et}_2\text{O}$ /petroleum ether 1:1:5 yielding 30 mg (61%), beige powder. M.p. $> 200^\circ$. UV (95% EtOH): 207 (43 000), 220 (sh, 16 000), 225 (sh, 1400), 271 (1000), 280 (9000). IR (KBr): 2990, 2920, 1520, 1435, 1350, 1300, 1250, 1130, 1050, 1000, 970. $^1\text{H-NMR}$ (80 MHz, CD_3COCD_3): 7.59 (s, $\text{H}-\text{C}(9)$, $\text{H}-\text{C}(10)$); 4.25 (s, $\text{CH}_2(1)$, $\text{CH}_2(4)$, $\text{CH}_2(5)$, $\text{CH}_2(8)$). MS (70 eV): 386 (10, M^+), 258 (100), 130 (11), 115 (7).

1,3,15-Dioxo-14-phenyl-12,14,16-triazatetracyclo[8.7.0.0^{3,8}.0^{12,16}]heptadeca-1,3(8),9-triene-5,5,6,6-tetracarbonitrile (32). At 20° , 4-phenyl-3H-1,2,4-triazole-3,5(4H)-dione (6.5 mg, 0.03 mmol) was added to a soln. of **8** (4.7 mg, 0.03 mmol). After stirring at 20° for 5 min, the soln. was cooled to -20° . The precipitate was collected, yielding 11 mg (84%), beige powder, m.p. $> 220^\circ$. IR (KBr): 2990, 2920, 2280, 1770, 1725, 1610, 1510, 1420, 1300, 1290, 1250, 1070, 950. $^1\text{H-NMR}$ (80 MHz, CD_3COCD_3): 7.4-7.6 (m, $\text{H}-\text{C}(2)$, $\text{H}-\text{C}(9)$, Ph); 4.45 (m, $\text{CH}_2(4)$, $\text{CH}_2(7)$); 4.25 (s, $\text{CH}_2(11)$, $\text{CH}_2(17)$). MS (70 eV): 437 (4, M^+), 408 (4), 258 (100), 213 (16), 200 (32), 130 (11), 115 (9), 91 (21).

9,9-Dimethyl-11,12-dimethylidene-10-oxotricyclo[6.2.2.0^{2,7}]dodec-2(7)-ene-4,4,5,5-tetracarbonitrile (33). A soln. of **27** (150 mg, 0.75 mmol) and freshly sublimed TCE (96 mg, 0.75 mmol) in anh. C₆H₆ (5 ml) was allowed to stand at 20° for 2 h. The solvent was evaporated and the residue recrystallized from CH₂Cl₂, yielding 246 mg (100%), colourless crystals. M.p. > 200° (dec.). UV (95% EtOH): 247 (7500), 296 (1100). IR (KBr): 2980, 2970, 2280, 1720, 1620, 1440, 1380, 1240, 1060, 900. ¹H-NMR (80 MHz, CD₂Cl₂): 5.65, 5.25 (2s, CH₂=C(11), CH₂=C(12)); 3.85 (s, H-C(1)); 3.7 (m, CH₂(3), CH₂(6)); 3.35 (s, H-C(8)); 1.1, 1.05 (2s, 2 MeC(9)). MS (70 eV): 328 (3, M⁺), 258 (100), 230 (24), 199 (9), 140 (13), 130 (100), 123 (35), 91 (34). Anal. calc. for C₂₀H₁₆N₄O (328.38): C 73.15, H 4.91; found: C 73.35, H 4.78.

15,15-Dimethyl-16-oxotetracyclo[6.6.2.0^{2,7}.0^{9,14}]hexadeca-2(7),9(14)-diene-4,4,5,5,11,11,12,12-octacarbonitrile (35). A mixture of **27** (30 mg, 0.3 mmol) and freshly sublimed TCE (38 mg, 0.15 mmol) in acetone (2 ml) was stirred at 20° for 30 h. The solvent was evaporated and the residue recrystallized from CH₃CN/CH₂Cl₂ yielding 51 mg (75%), white powder. M.p. > 250°. UV (95% EtOH): 292 (520). IR (KBr): 3000, 2960, 2270, 1740, 1480, 1380, 1370, 1240, 1000, 960. ¹H-NMR (80 MHz, CD₃COCD₃): 4.15 (s, H-C(1)); 3.77 (m, H-C(8), CH₂(3), CH₂(6), CH₂(10), CH₂(13)); 1.15 (s, 2 Me). Anal. calc. for C₂₆H₁₆N₈O (456.47): C 68.41, H 3.53; found: C 67.59, H 3.76.

TCE Mono-adducts of 28. A mixture of **28** (200 mg, 1 mmol) and freshly sublimed TCE (128 mg, 1 mmol) in anh. C₆H₆ (10 ml) was allowed to stand at 20° for 3 h. The solvent was evaporated and the residue recrystallized from CH₂Cl₂, yielding 325 mg (98%) of a 3:2 mixture **34a/34b** (by 360-MHz ¹H-NMR). Separation by column chromatography on silica gel (25 g, AcOEt/hexane 1:1) gave a 1st fraction containing 195 mg (60%) of **34a** and a 2nd fraction containing 130 mg (40%) of **34b**.

11-syn-Hydroxy-9,10-dimethylidene-11-(propen-2'-yl)tricyclo[6.2.1.0^{2,7}]undec-2(7)-ene-4,4,5,5-tetracarbonitrile (34a). White powder, recrystallized from CH₂Cl₂. M.p. > 230°. The configuration 11-syn-hydroxy was assigned tentatively to the less polar adduct. UV (95% EtOH): 208 (17000), 215 (13000), 244 (9600). IR (KBr): 3540, 2950, 2910, 2850, 2260, 1710, 1650, 1450, 1410, 1240, 1180. ¹H-NMR (80 MHz, CD₃COCD₃): 5.3, 5.15 (2s, CH₂=C(9), CH₂=C(10)); 4.95 (s, CH₂=C(2')); 3.6 (s, CH₂(3), CH₂(6)); 3.4 (s, H-C(1), H-C(8)); 1.85 (s, Me). MS (70 eV): 328 (2, M⁺), 310 (10), 276 (15), 103 (61), 95 (100), 83 (61), 75 (72), 63 (79), 51 (70). Anal. calc. for C₂₀H₁₆N₄O (328.38): C 73.15, H 4.91; found: C 73.26, H 4.96.

11-anti-Hydroxy-9,10-dimethylidene-11-(propen-2'-yl)tricyclo[6.2.1.0^{2,7}]undec-2(7)-ene-4,4,5,5-tetracarbonitrile (34b). The 2nd fraction obtained above was recrystallized from CH₂Cl₂. M.p. > 220°. UV (95% EtOH): 215 (11000), 244 (10000). IR (KBr): 3540, 3040, 2990, 2970, 2970, 2920, 1650, 1430, 1350, 1220, 1190, 1070, 1000. ¹H-NMR (360 MHz, CD₃COCD₃): 5.5, 5.15 (2s, CH₂=C(10)); 5.05 (s, CH₂=C(2')); 3.55 (s, CH₂(3), CH₂(6)); 3.50 (s, H-C(1), H-C(8)); 1.85 (s, CH₃). MS (70 eV): 328 (4, M⁺), 310 (6), 176 (12), 109 (41), 96 (100), 81 (69), 79 (61), 64 (54), 51 (74). Anal. calc. for C₂₀H₁₆N₄O (328.38): C 73.15, H 4.91; found: C 73.50, H 5.00.

15-Hydroxy-15-(propen-2'-yl)tetracyclo[6.6.1.0^{2,7}.0^{9,14}]pentadeca-2(7),9(14)-diene-4,4,5,5,11,11,12,12-octacarbonitrile (36). A soln. of **28** (30 mg, 0.15 mmol) and freshly sublimed TCE (38 mg, 0.3 mmol) in anh. C₆H₆ (3 ml) was allowed to stand at 20° for 27 h. Pentane (1 ml) was added and the soln. cooled to 0°. The precipitate was collected, dried *in vacuo*, yielding 58 mg (85%), beige crystals. M.p. > 260°. UV (95% EtOH): final absorption, ε₂₁₀ = 410. IR (KBr): 3580, 3440, 2980, 2960, 2260, 1480, 1260, 1200, 1070, 990, 900, 860. ¹H-NMR (80 MHz, CD₃COCD₃): 5.07–4.8 (m, CH₂=C(2')); 3.82 (s, H-C(1), H-C(8)); 3.57 (m, CH₂(3), CH₂(6), CH₂(10), CH₂(13)); 1.77 (s, CH₃). MS (70 eV): 456 (8, M⁺), 427 (19), 258 (100), 129 (10), 115 (30), 70 (56), 45 (90). Anal. calc. for C₂₆H₁₆N₈O (456.47): C 68.41, H 3.53; found: C 68.08, H 3.47.

15-Hydroxy-15-(2'-hydroxypropan-2'-yl)tetracyclo[6.6.1.0^{2,7}.0^{9,14}]pentadeca-2(7),9(14)-diene-4,4,5,5,11,11,12,12-octacarbonitrile (37). A soln. of **29** (70 mg, 0.32 mmol) and freshly sublimed TCE (82 mg, 0.64 mmol) in anh. acetone (3 ml) was stirred at 20° for 20 h. Pentane (1 ml) was added and the soln. cooled to –10°. The precipitate was collected and dried *in vacuo*, yielding 121 mg (80%), beige crystals. M.p. > 285°. IR (KBr): 3580, 3440, 2990, 2260, 1650, 1475, 1380, 1360, 1260, 1230, 1130, 1120, 1070, 980, 900. ¹H-NMR (80 MHz, CD₃COCD₃): 3.67 (m, H-C(1), H-C(8), CH₂(3), CH₂(6), CH₂(10), CH₂(13)); 1.32 (s, 2 Me); 2.8 (s, 2 OH). MS (70 eV): 474 (5, M⁺), 456 (100), 373 (71), 110 (21), 59 (61), 45 (10).

15-Hydroxy-15-(2'-methyloxiran-2'-yl)tetracyclo[6.6.1.0^{2,7}.0^{9,14}]pentadeca-2(7),9(14)-diene-4,4,5,5,11,11,12,12-octacarbonitrile (38). A soln. of **30** (170 mg, 0.79 mmol) and freshly sublimed TCE (201 mg, 1.58 mmol) in anh. C₆H₆ (10 ml) was allowed to stand at 20° for 24 h. The solvent was evaporated and the residue recrystallized from acetone/Et₂O, yielding 300 mg (81%), white powder. M.p. > 230° (dec.). UV (95% EtOH): final absorption, ε₂₀₅ = 5600. IR (KBr): 3520, 2980, 2970, 2260, 1710, 1670, 1440, 1380, 1230, 1080, 1060, 920, 900. ¹H-NMR (80 MHz, CD₃COCD₃): 3.6 (m, CH₂(3)); 3.1 (m, H-C(1), CH₂(3), CH₂(6), H-C(8), CH₂(10), CH₂(13)); 1.45 (s, CH₃).

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