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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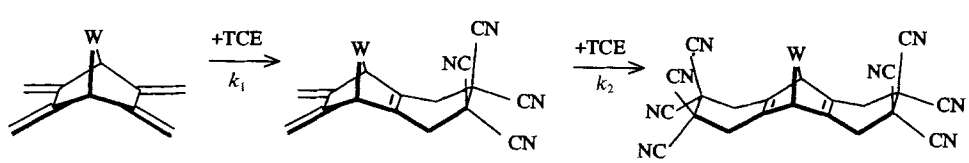
(24. V. 88)

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

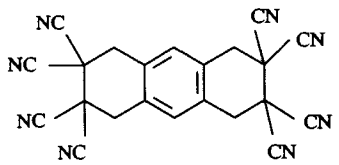


			k_1/k_2[a])
1 W = O			376
2 W = CH_2			364
3 W = Me_2C=C			250
4 W = Ph_2C=C	**6** W = Ph_2C=C	**7** W = Ph_2C=C	260
5 W = CO	**8** W = CO	**9** W = CO	21

[a]) At 25° in toluene

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

[2]) Present address: *Vis Farmaceutici*, Viale delle Industrie 54, I-35129 Padova (Italy).

[9] fast →  + CO

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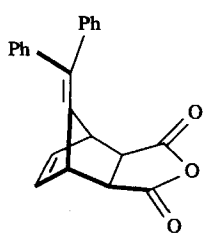
new [2.2.1]hericene derivatives **4** and **5** and have evaluated their tandem *Diels-Alder* reactivity toward TCE. While 7,7-diphenyl[2.2.1]hericene (**4**) gave mono-adduct **6** and bis-adduct **7** with a rate-constant ratio k_1/k_2 nearly the same as those measured for the TCE cycloadditions to 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 discussed[3][4]).

Synthesis of 7,7-Diphenyl[2.2.1]hericene. – The *Diels-Alder* adduct **11** of maleic anhydride to 6,6-diphenylfulvene [12] was biscarboxylated (3 atm CO, $CuCl_2$, 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 $LiAlH_4$ in anh. THF afforded tetrol **13** (73%) which was transformed into the corresponding tetrachloride **14** (50%) on treatment with $SOCl_2$ 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 $KMnO_4$ in



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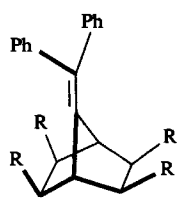
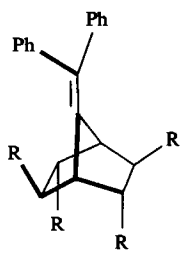


12 R = COOMe
13 R = CH_2OH
14 R = CH_2Cl



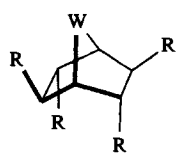
15 R = COOMe
16 R = CH_2OH
17 R = CH_2Cl

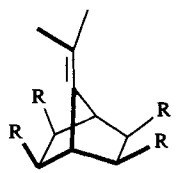
[3]) Disclosure of our synthesis of **5** and of its matrix irradiation giving CO and 2,3,5,6-tetramethylidene-1,4-cyclohexanediyl diradical ('1,2,4,5-tetramethylidenebenzene') was made first by *Prof. J. A. Berson*, conferences at the University of Chicago, May 19, 1986; University of Washington, May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

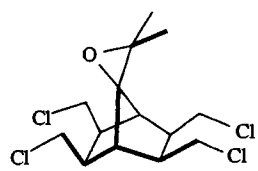
[4]) For the photoelectron spectrum of **5** and a study on the interaction between the homoconjugated carbonyl and olefinic functions, see [11].

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

19 R = CH_2Cl

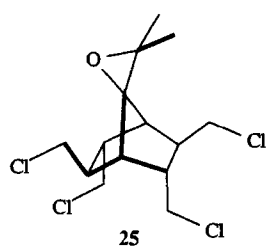
20 R = CH_2Cl, W = C=CMe_2

21

22 R = COOMe

23 R = COOMe, W = C=CMe_2

24 R = CH_2OH, W = C=CMe_2



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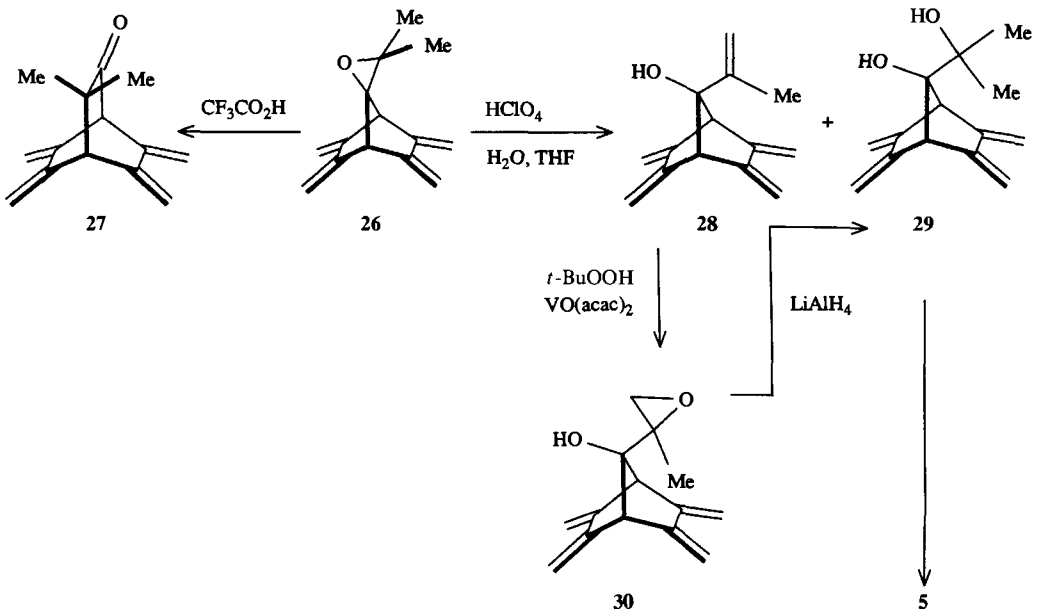
by workup with Me_2S gave a mixture from which the epoxide **25** (65%) and ketone **18** (25%) could be isolated by chromatography on silica gel. Attempts to eliminate HCl from **18** under various basic conditions (*e.g.* *t*-BuOK/THF, *t*-BuOK/DMSO, CsF in DMF/HMPA [15], *etc.*) all failed to give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

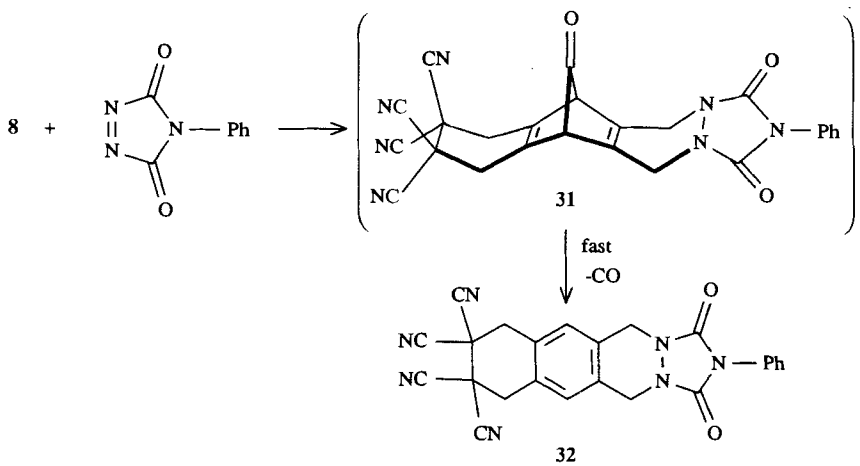


with pyridinium chlorochromate suspended in CH_2Cl_2 gave the desired tetraenone **5** in 48% yield. The latter has a strong tendency to polymerize. Epoxidation of the allylic-alcohol moiety of pentaene **28** with *t*-BuOOH in the presence of a catalytical amount of $VO(acac)_2$ [17] (C_6H_6, 40°, 3 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 H–C(1), H–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 V←N transitions as in the case of tetraenes **1**, **2**, and 7,7-dimethyl[2.2.1]hericene (**3**) [2] [4a].

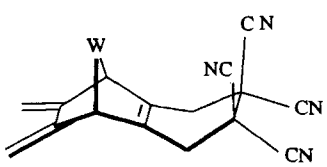
Tandem *Diels-Alder* Reactivities. – In the presence of 1 equiv. of TCE in acetone, 7,7-diphenyl[2.2.1]hericene (**4**) gave the corresponding mono-adduct **6** (82%, isolated). With 2 or more equiv. of TCE (acetone, 20°, 50 h), the bis-adduct **7** was obtained in 95% yield. The rate constants $k_1 = (3.8 \pm 0.3) \cdot 10^{-3} dm^3 mol^{-1} s^{-1}$ and $k_2 = (1.5 \pm 0.2) \cdot 10^{-5} dm^3 mol^{-1} s^{-1}$ at 25° in toluene were evaluated for the two successive cycloadditions. The reactions were followed by UV absorption spectroscopy [5] or/and 80-MHz ^{1}H-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 ^{1}H-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 ^{1}H-NMR nor by 90-MHz ^{13}C-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.



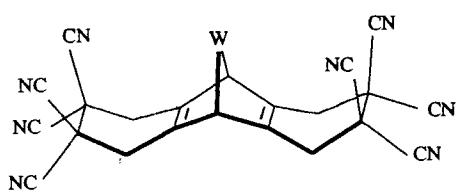
The rate constants $k_1 = (4.3 \pm 0.4) \cdot 10^{-3}$dm^{3}mol^{-1}s^{-1} and $k_2 = (0.20 \pm 0.02) \cdot 10^{-3}$dm^{3}mol^{-1}s^{-1} at 25° in toluene were evaluated by 360-MHz ^{1}H-NMR for various concentrations of tetraenone **5** and TCE.

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



33 W = $Me_2C-\underset{|}{\overset{|}{C}}=O$

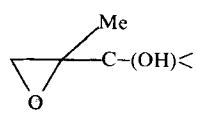
34a,b W = CH_2=C(Me)C(OH)<



35 W = $Me_2C-\underset{|}{\overset{|}{C}}=O$

36 W = CH_2=C(Me)C(OH)<

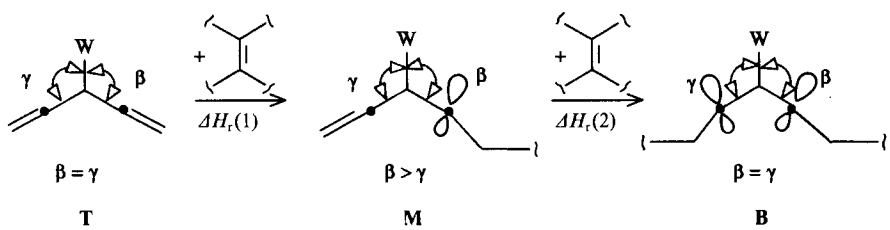
37 W = $Me_2C(OH)C(OH)<$

38 W = 

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 $\beta - \gamma = 7°$ was found for bicyclo[2.2.1]hept-2-enes (W = CH_2), a somewhat higher value $\beta - \gamma \approx 10°$ was obtained for 7-oxabicyclo[2.2.1]hept-2-ene derivatives (W = O). Most stricking in our context was the finding that $\beta - \gamma = 4.5°$ only for bicyclo[2.2.1]hept-2-en-7-ones (W = CO), whereas a 'normal' value $\beta - \gamma = 7°$ was measured for 7-isopropylidenebicyclo[2.2.1]hept-2-ene derivatives (W = Me_2C=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 the 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 dot 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. 132–133° (MeOH). UV (95% EtOH): 202 (60000), 240 (25000). IR (KBr): 3040, 2880, 1730, 1440, 1320, 1290, 1250, 1200, 1170, 1150, 1020, 900. ^{1}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}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 (3*d*, ^1J(C,H) = 154, arom. CH); 51.7 (*q*, ^1J(C,H) = 146, CH_3O); 49.3 (*d*, ^1J(C,H) = 136, C(2), C(3), C(5), C(6)); 43.9

(*dd*, ^1J(C,H) = 152, ^3J(C,H) = 7, C(1), 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 $C_{28}H_{28}O_8$ (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 anh. THF (65 ml) was added dropwise to a vigourously stirred suspension of $LiAlH_4$ (5.8 g, 0.15 mol) in anh. 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. 197–199° (MeOH). IR (KBr): 3280, 2940, 2900, 1600, 1480, 1450, 1380, 1350, 1320, 1230, 1060, 1040, 1000. ^{1}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*, H–C(1), H–C(4)); 2.5–2.3 (*m*, H–C(2), H–C(3), H–C(5), H–C(6)). ^{13}C-NMR (90.55 MHz, D_2O; internal reference dioxane, δ(C) = 67.4 ppm): 145.2 (*s*, arom. C); 143.7 (*s*, *C*=C(7)); 134.7 (*s*, C(7)); 130.1, 129.1, 127.0 (3*d*, ^1J(C,H) = 154, arom. CH); 62.7 (*t*, ^1J(C,H) = 142, CH_2OH); 48.4 (*d*, ^1J(C,H) = 136, C(2), C(3), C(5), C(6)); 45.9 (*d*, ^1J(C,H) = 152, C(1), C(4)). MS (70 eV): 380 (6, M^+), 362 (12), 312 (4), 274 (24), 215 (50), 167 (98), 91 (100). Anal. calc. for $C_{24}H_{28}O_4$ (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 anh. 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. 144–146°. UV (95% EtOH): 205 (66000), 229 (26000), 243 (30000). IR (KBr): 3100, 2980, 1700, 1500, 1450, 1340, 1260, 1070, 1030, 920, 890. ^{1}H-NMR (80 MHz, $CDCl_3$): 7.2 (*m*, 2 Ph); 3.72, 3.45 (2*m*, 4 CH_2Cl); 2.95 (*s*, H–C(1), H–C(4)); 2.35 (*m*, H–C(2), H–C(3), H–C(5), H–C(6)). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 140.6 (*s*, arom. C); 140.2 (*s*, *C*=C(7)); 137.5 (*s*, C(7)); 128.6, 128.5, 128.4 (3*d*, ^1J(C,H) = 154, arom. CH); 46.8 (*d*, ^1J(C,H) = 158, C(1), C(4)); 43.3 (*d*, ^1J(C,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 $C_{24}H_{24}Cl_4$ (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 anh. 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. 131–133° (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}H-NMR (80 MHz, $CDCl_3$): 7.3 (*m*, 2 Ph); 5.3, 5.0 (2*s*, 4 CH_2=C); 3.98 (*s*, H–C(1), H–C(4)). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 147.9 (*m*, C(2), C(3), C(5), C(6)); 143.6 (*s*, *C*=C(7)); 142.1 (*s*, arom. C); 141.2 (*s*, C(7)); 129.9, 127.9, 126.9 (3*d*, ^1J(C,H) = 154, arom. CH); 101.7 (*t*, ^1J(C,H) = 160, CH_2=C); 58.0 (*dm*, ^1J(C,H) = 150, C(1), 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 $C_{24}H_{20}$ (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 anh. K_2CO_3 in anh. 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}H-NMR (80 MHz, $CDCl_3$): 7.41 (*m*, 2 Ph); 3.83, 3.74 (2*s*, 4 MeO); 3.72 (*t*, *J* = 7, H–C(1), H–C(5)); 3.38 (*d*, *J* = 7, H–C(1), H–C(4)); 3.18 (*m*, H–C(3), 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 anh. THF (40 ml) was added dropwise to a stirred suspension of $LiAlH_4$ (2.9 g, 70 mmol) in anh. 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 vigourous 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. 201–203°. IR (KBr): 3290, 2930, 2900, 2870, 1590, 1500, 1465, 1310, 1040. ^{1}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-(diphenylmethylidene)bicyclo[2.2.1]heptane (**17**). At 0°, **16** (8 g, 21 mmol) was added portionwise to a soln. of $SOCl_2$ (12.5 g, 0.11 mol, 7.4 ml) and pyridine (6.6 g, 6.8 ml, 0.08 mol). $SOCl_2$ (20.7 g, 12.6 ml, 0.17 mol) was added and the mixture heated to 60° for 3 h. After cooling to 20°, CH_2Cl_2 (20 ml) was added and the excess of $SOCl_2$ destroyed by dropwise addition of H_2O (8 ml). The org. phase 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, yielding 2.9 g (61%), white powder. M.p. 139–141° ($CHCl_3$). IR (KBr): 3100, 2970, 1510, 1430, 1340, 1280, 1250, 1020. ^{1}H-NMR (80 MHz, $CDCl_3$): 7.35 (*m*, 2 Ph); 4.0–3.4 (*m*, 4 CH_2Cl); 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-(Diphenylmethylidene)-9,10-dimethylidenetricyclo[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 CH_2Cl_2, 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. ^{1}H-NMR (80 MHz, CD_3COCD_3): 7.27 (*m*, 2 Ph); 5.4, 5.2 (2*s*, CH_2=C(9), CH_2=C(10)); 3.99 (*s*, H–C(1), H–C(8)); 3.71, 3.52 (2*s*, CH_2(3), CH_2(6)). ^{13}C-NMR (90.55 MHz, CD_3COCD_3): 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, *C*H_2=C(9), *C*H_2=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 $C_{30}H_{20}N_4$ (436.52): C 82.55, H 4.62; found: C 82.71, H 4.61.

15-(Diphenylmethylidene)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. ^{1}H-NMR (80 MHz, CD_3COCD_3): 7.5–7.1 (*m*, 2 Ph); 4.25 (*s*, H–C(1), H–C(8)); 3.9 (*s*, CH_2(3), CH_2(6), CH_2(10), CH_2(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. K_2CO_3 (5 g) in anh. MeOH (freshly distilled from Mg/I_2) 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 P_2O_5 and paraffin *in vacuo*: 15 g (100%), white crystals. M.p. 102–103° (Et_2O). IR ($CHCl_3$): 3040, 2970, 1750, 1725, 1440, 1380, 1320, 1285, 1265. ^{1}H-NMR (80 MHz, $CDCl_3$): 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). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 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, CH_3O); 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 $C_{18}H_{24}O_8$ (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 $LiAlH_4$ (4.7 g, 0.122 mol) in anh. THF (160 ml) at 0° and under N_2. The mixture was heated under reflux for 4 h. After cooling to 20°, H_2O (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. ^{1}H-NMR (80 MHz, D_2O): 4.80 (*s*, OH); 3.75, 3.42 (2*m*, 4 CH_2O); 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)). ^{13}C-NMR (90.55 MHz, D_2O; 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, CH_2OH); 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 $C_{14}H_{24}O_4$ (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 $SOCl_2$ (9.28 g, 80 mmol) and anh. pyridine (4.93 g, 62 mmol) under N_2. When the mixture became viscous, $SOCl_2$ (15.4 g, 129 mmol) was added slowly. The mixture was heated to 55° for 2½ h. After cooling to 20°, CH_2Cl_2 (25 ml) was added, then H_2O (9 ml) dropwise and under vigourous stirring. The org. phase was washed with H_2O (10 ml, twice), sat. aq. $NaHCO_3$ soln. (15 ml, twice), and H_2O (15 ml, twice), dried ($MgSO_4$), and evaporated and the residue recrystallized from $CHCl_3$, yielding 2.8 g

(55%), colourless crystals. M.p. 84–85°. UV (95% EtOH): final absorption, $\varepsilon_{210} = 110$. IR ($CHCl_3$): 2975, 2925, 1400, 1380, 1300. ^{1}H-NMR (80 MHz, $CDCl_3$): 3.17–3.92 (*m*, 4 CH_2Cl); 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). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 136.7 (*m*, C(7)); 121.6 (*m*, *C*=C(7)); 47.4, 41.6 (*dm*, ^1J(C,H) = 134, C(2), C(3), C(5), C(6)); 47.7, 44.0 (*t*, ^1J(C,H) = 152, CH_2Cl); 44.1 (*dm*, ^1J(C,H) = 148, C(1), C(4)); 20.3 (*q*, ^1J(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 $C_{14}H_{20}Cl_4$ (330.13): C 50.94, H 6.11; found: C 50.82, H 6.00.

Ozonolysis of **20**. Oxygen (O_2) containing 3–4% of O_3 (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 Me_2S (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 CH_2Cl_2/hexane 1:4, yielding 503 mg (65%). The 2nd fraction gave **18**, oil which crystallized from CH_2Cl_2/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 (CH_2Cl_2): 3000, 2980, 2960, 1450, 1370, 1260, 1180, 780. ^{1}H-NMR (80 MHz, $CDCl_3$): 3.12–4.12 (*m*, 4 CH_2Cl); 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). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 79.4 (*m*, C(7)); 59.2 (*m*, C(3')); 49.5, 45.8 (2*dm*, ^1J(C,H) = 154, C(2), C(3), C(5), C(6)); 44.5, 42.7 (2*t*, ^1J(C,H) = 150, 4 CH_2Cl); 42.9 (*d*, ^1J(C,H) = 146, C(1), C(4)); 22.3 (*qq*, ^1J(C,H) = 128, ^3J(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 $C_{14}H_{20}Cl_4O$ (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 (CH_2Cl_2): 3070, 3000, 2695, 2310, 1785, 1485, 1260, 1170, 1140, 895. ^{1}H-NMR (80 MHz, $CDCl_3$): 3.3–4.1 (*m*, 4 CH_2Cl); 1.9–2.6 (*m*, H–C(1), H–C(2), H–C(3), H–C(4), H–C(5), H–C(6)). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 206.9 (*s*, CO); 48.1 (*d*, ^1J(C,H) = 148, C(1), C(4)); 46.4, 42.9 (2*t*, ^1J(C,H) = 152, CH_2Cl); 41.5, 37.3 (2*d*, ^1J(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-tetramethylidenebicyclo[2.2.2]octan-2-one (**27**). CF_3COOH (750 µl, 10 mmol) was added to a soln. of **26** (1.8 g, 9 mmol) in CH_2Cl_2 (20 ml) at 0° and under N_2. After staying at 20° for 10 min, the soln. was washed with H_2O (30 ml, twice), dried ($MgSO_4$), and evaporated. The oily residue was purified by column chromatography on *Florisil* (50 g, CH_2Cl_2) 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 (CH_2Cl_2): 3100, 2980, 2940, 1735, 1095, 895. ^{1}H-NMR (80 MHz, $CDCl_3$): 5.40, 5.37, 4.35 (3*s*, 4 CH_2=C); 3.66 (*s*, H–C(1)); 2.87 (*s*, H–C(4)); 1.0 (*s*, 2 Me). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 208.7 (*s*, CO); 142.9 (*s*, C(5), C(8)); 139.4 (*s*, C(6), C(7)); 108.4, 107.5 (2*t*, ^1J(C,H) = 162, 4 CH_2=C); 66.7, 60.6 (2*d*, ^1J(C,H) = 148, C(1), C(4)); 46.7 (*s*, C(3)); 24.1 (*qm*, ^1J(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 $C_{14}H_{16}O$ (200.28): C 83.96, H 8.05; C 83.17, H 7.88.

Acidic Hydrolysis of Epoxide **26**. Aq. 35% $HClO_4$ soln. (2 ml) was added dropwise to a stirred soln. of **26** (2.5 g, 12.5 mmol) in THF (170 ml) and H_2O (30 ml). After stirring at 20° overnight, NaCl was added until saturation and the mixture extracted with CH_2Cl_2 (50 ml, 5 times). The combined org. phase was washed with sat. aq. NaCl soln. (100 ml, 5 times), dried ($MgSO_4$), and evaporated. The oily residue was purified and separated by flash column chromatography on silica gel (200 g, CH_2Cl_2). 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 CH_2Cl_2/hexane.

2,3,5,6-Tetramethylidene-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 (CH_2Cl_2): 3400, 3040, 2990, 1610, 1600, 1460, 1440, 1380, 1240, 1190, 1080, 1000, 980. ^{1}H-NMR (80 MHz, $CDCl_3$): 5.43, 5.23, 5.11, 4.95 (4*s*, 4 CH_2=C); 5.05 (*s*, CH_2(1')); 3.4 (*s*, H–C(1), H–C(4)); 1.8 (*s*, CH_3). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 147.3, 146.9 (2*s*, C(2), C(3), C(5), C(6)); 142.4 (*s*, C(2')); 115.2 (*td*, ^1J(C,H) = 156, ^3J(C,H) = 6, CH_2(1')); 104.7, 103.1 (2*d*, ^1J(C,H) = 156, *C*H_2–C(2), *C*H_2=C(3), *C*H_2=C(5), *C*H_2=C(6)); 85.6 (*s*, C(7)); 61.7 (*d*, ^1J(C,H) = 148, C(1), C(4)); 18.6 (*qm*, ^1J(C,H) = 126, CH_3). 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 $C_{14}H_{16}O$ (200.28): C 83.96, H 8.05; found: C 83.80, H 8.03.

7-(2'-Hydroxypropan-2'-yl)-2,3,5,6-tetramethylidenebicyclo[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}H-NMR (80 MHz, $CDCl_3$): 5.30, 5.17, 5.13, 4.93 (4*s*, CH_2=C(2), CH_2=C(3), CH_2=C(5), CH_2=C(6)); 3.25 (*s*, H–C(1), H–C(4)); 1.27 (*s*, 2 Me). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 148.0, 147.9 (2*s*, C(2), C(3), C(5), C(6)); 104.2, 104.0 (2*t*, ^1J(C,H) = 160, CH_2=C); 87.2 (*s*, C(7)); 74.3 (*s*, C(2′)); 60.9 (*d*, ^1J(C,H) = 158, C(1), C(4)); 25.8 (*qm*, ^1J(C,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 $C_{14}H_{18}O_2$ (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 vigourously 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° (pentane). UV (isooctane): 206 (10150), 213 (9225), 258 (12300), 282 (sh, 4730). UV (CH_3CN): 260 (13800), 285 (sh, 3000), 311 (390), 327 (220): UV (95% EtOH): 219 (sh, 15400), 226 (15600), 235 (13500), 251 (sh, 9100). IR ($CHCl_3$): 3110, 3000, 2985, 2940, 2245, 1795, 1635, 1270, 1225, 1170. ^{1}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(C,H) = 160, CH_2=C); 62.4 (*d*, ^1J(C,H) = 155, C(1), C(4)). Anal. calc. for $C_{11}H_{10}O$ (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), $VO(acac)_2$ (2 mg) in C_6H_6 (1 ml) and *t*-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°. UV (isooctane): 223 (sh, 12000), 240 (9000), 245 (8000). UV (95% EtOH): 207 (16000), 223 (sh, 13500), 240 (13000), 245 (12300), 299 (6800). IR (CH_2Cl_2): 3540, 3010, 2990, 2960, 1710, 1380, 1240, 1200, 1060, 890. ^{1}H-NMR (80 MHz, $CDCl_3$): 5.4, 5.05 (2*m*, CH_2=C(2), CH_2=C(3), CH_2=C(5), CH_2=C(6)); 3.3 (*s*, OH); 3.1 (*s*, CH_2(3′)); 2.73, 2.35 (2*s*, H–C(1), H–C(4)); 1.42 (*s*, CH_3). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 147.4, 147.2, 147.1, 145.7 (4*s*, C(2), C(3), C(5), C(6)); 104.2, 103.7, 103.5 (3*t*, ^1J(C,H) = 156, CH_2=C(2), CH_2=C(3), CH_2=C(5), CH_2=C(6)); 84.4 (*s*, C(2′)); 60.9, 60.6, (2*dm*, ^1J(C,H) = 150, C(1), C(4)); 58.8 (*s*, C(7)); 56.6 (*tm*, ^1J(C,H) = 172, C(3′)); 18.6 (*q*, ^1J(C,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 $C_{14}H_{16}O_2$ (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° (dec.). UV (95% EtOH): 206 (31000), 238 (9500), 301 (1000). IR (CH_2Cl_2): 3120, 3000, 2940, 2245, 1790, 1650, 1290, 1240, 1100, 980, 900. ^{1}H-NMR (80 MHz, CD_3COCD_3): 5.62, 5.32 (2*s*, CH_2=C(9), CH_2=C(10)); 3.82 (*s*, H–C(1), H–C(8)); 3.75 (*m*, CH_2(3), CH_2(6)). ^{13}C-NMR (90.55 MHz, CD_3COCD_3): 206.5 (*s*, C(11)); 146.4 (*m*, C(9), C(10)); 137.8 (*m*, C(2), C(7)); 111.7, 111.0 (2*s*, CN); 102.2 (*t*, ^1J(C,H) = 136, CH_2=C(9), CH_2=C(10)); 57.2 (*dm*, ^1J(C,H) = 130, C(1), C(8)); 40.1 (*s*, C(4), C(5)); 31.7 (*t*, ^1J(C,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 CH_3CN/Et_2O/petroleum ether 1:1:5 yielding 30 mg (61%), beige powder. M.p. > 200°. UV (95% EtOH): 207 (43000), 220 (sh, 16000), 225 (sh, 1400), 271 (1000), 280 (9000). IR (KBr): 2990, 2920, 1520, 1435, 1350, 1300, 1250, 1130, 1050, 1000, 970. ^{1}H-NMR (80 MHz, CD_3COCD_3): 7.59 (*s*, H–C(9), H–C(10)); 4.25 (*s*, CH_2(1), CH_2(4), CH_2(5), CH_2(8)). MS (70 eV): 386 (10, M^+), 258 (100), 130 (11), 115 (7).

13,15-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-3*H*-1,2,4-triazole-3,5(4*H*)-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°. IR (KBr): 2990, 2920, 2280, 1770, 1725, 1610, 1510, 1420, 1300, 1290, 1250, 1070, 950. ^{1}H-NMR (80 MHz, CD_2COCD_3): 7.4–7.6 (*m*, H–C(2), H–C(9), Ph); 4.45 (*m*, CH_2(4), CH_2(7)); 4.25 (*s*, CH_2(11), 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. C_6H_6 (5 ml) was allowed to stand at 20° for 2 h. The solvent was evaporated and the residue recrystallized from CH_2Cl_2, 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. ^{1}H-NMR (80 MHz, CD_2Cl_2): 5.65, 5.25 (2*s*, CH_2=C(11), CH_2=C(12)); 3.85 (*s*, H–C(1)); 3.7 (*m*, CH_2(3), CH_2(6)); 3.35 (*s*, H–C(8)); 1.1, 1.05 (2*s*, 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 $C_{20}H_{16}N_4O$ (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 CH_3CN/CH_2Cl_2 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. ^{1}H-NMR (80 MHz, CD_3COCD_3): 4.15 (*s*, H–C(1)); 3.77 (*m*, H–C(8), CH_2(3), CH_2(6), CH_2(10), CH_2(13)); 1.15 (*s*, 2 Me). Anal. calc. for $C_{26}H_{16}N_8O$ (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. C_6H_6 (10 ml) was allowed to stand at 20° for 3 h. The solvent was evaporated and the residue recrystallized from CH_2Cl_2, yielding 325 mg (98%) of a 3:2 mixture **34a**/**34b** (by 360-MHz ^{1}H-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 CH_2Cl_2. 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. ^{1}H-NMR (80 MHz, CD_3COCD_3): 5.3, 5.15 (2*s*, CH_2=C(9), CH_2=C(10)); 4.95 (*s*, CH_2=C(2′)); 3.6 (*s*, CH_2(3), CH_2(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 $C_{20}H_{16}N_4O$ (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 CH_2Cl_2. 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. ^{1}H-NMR (360 MHz, CD_3COCD_3): 5.5, 5.15 (2*s*, CH_2=C(10)); 5.05 (*s*, CH_2=C(2′)); 3.55 (*s*, CH_2(3), CH_2(6)); 3.50 (*s*, H–C(1), H–C(8)); 1.85 (*s*, CH_3). 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 $C_{20}H_{16}N_4O$ (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. C_6H_6 (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, ε_{210} = 410. IR (KBr): 3580, 3440, 2980, 2960, 2260, 1480, 1260, 1200, 1070, 990, 900, 860. ^{1}H-NMR (80 MHz, CD_3COCD_3): 5.07–4.8 (*m*, CH_2=C(2′)); 3.82 (*s*, H–C(1), H–C(8)); 3.57 (*m*, CH_2(3), CH_2(6), CH_2(10), CH_2(13)); 1.77 (*s*, CH_3). MS (70 eV): 456 (8, M^+), 427 (19), 258 (100), 129 (10), 115 (30), 70 (56), 45 (90). Anal. calc. for $C_{26}H_{16}N_8O$ (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. ^{1}H-NMR (80 MHz, CD_3COCD_3): 3.67 (*m*, H–C(1), H–C(8), CH_2(3), CH_2(6), CH_2(10), CH_2(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. C_6H_6 (10 ml) was allowed to stand at 20° for 24 h. The solvent was evaporated and the residue recrystallized from acetone/Et_2O, yielding 300 mg (81%), white powder. M.p. > 230° (dec.). UV (95% EtOH): final absorption, ε_{205} = 5600. IR (KBr): 3520, 2980, 2970, 2260, 1710, 1670, 1440, 1380, 1230, 1080, 1060, 920, 900. ^{1}H-NMR (80 MHz, CD_3COCD_3): 3.6 (*m*, CH_2(3′)); 3.1 (*m*, H–C(1), CH_2(3), CH_2(6), H–C(8), CH_2(10), CH_2(13)); 1.45 (*s*, CH_3).

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