17. Face Selectivity of the *Diels-Alder* Additions of 2-Substituted 5,6-bis((*E*)-chloromethylidene)bicyclo[2.2.2]octanes[1][2])

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Summary

The preparation of 5,6-bis((*E*)-chloromethylidene)bicyclo[2.2.2]oct-2-ene (**13**), 2,3-bis((*E*)-chloromethylidene)-5*exo*,6*exo*- and -5*endo*,6*endo*-epoxybicyclo[2.2.2] octane (**14** and **15**), 5,6-bis((*E*)-chloromethylidene)-2*exo*- and -2*endo*-bicyclo[2.2.2] octanol (**16** and **17**) and 5,6-bis((*E*)-chloromethylidene)-2-bicyclo[2.2.2]octanone (**18**) are described. The face selectivity (*endo*-face *vs.* *exo*-face attack onto the exocyclic diene) of their cycloadditions to tetracyanoethylene has been determined in benzene at 20°. It is 78/22, 80/20, 60/40, 68/32, 3/97 and 30/70 for **13**, **14**, **15**, **16**, **17** and **18**, respectively.

Introduction. – The *exo*-face stereoselectivity of the 2-norbornene[4]) in its reactions with a large variety of reagents has been attributed to steric factors [3] (the *exo*-face of the π-system being less crowded than the *endo*-face), to torsional effects [4] (eclipsing of the bridgehead H-atoms or substituents with those at the olefinic C-atoms when the attack occurs onto the *endo*-face) and to electronic factors, *e.g.* nonequivalent π-orbital extension toward the *exo*-face [5]. The latter hypothesis has been substantiated by single crystal structures of norbornene [6] [7] and oxanorbornene derivatives [7] [8]. The face stereoselectivity of the *Diels-Alder* cycloadditions to cyclopentadiene annelated to norbornene has been studied first by *Alder et al.* [9]. They reported that maleic anhydride adds to cyclopenta[*b*]norbornene (=4,7-methano-4,5,6,7-tetrahydro-2*H*-indene; isodicyclopentadiene; **1**) with *exo*-face selectivity, following the *Alder-endo*-rule and giving the adduct **3** preferentially. Twenty years later, *Sugimoto et al.* found the [4+2]-cycloadditions of methyl acrylate and propynoate to **1** to be *endo*-face selective [10]. Recently, *Paquette et al.* confirmed *Sugimoto's* conclusions and reported that the *endo*-face stereoselectivity was generally preferred for the *Diels-Alder* additions of the cyclopentadiene derivatives **1**

[1]) Interaction between non-conjugated chromophores, Part 15; Part 14, see [1].

[2]) For a preliminary report, see [2].

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[4]) According to the IUPAC nomenclature 'bicyclo[2.2.1]heptane' is now called '8,9,10-trinorbornane'; for commodity reasons we use in this paper the abolished name 'norbornane'.

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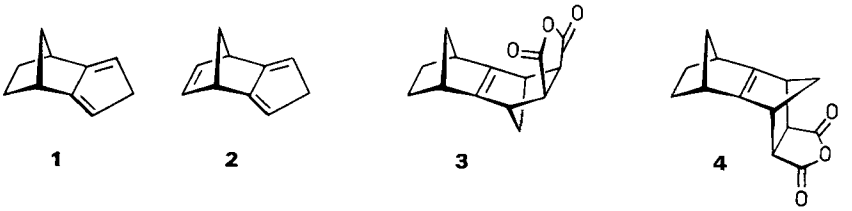
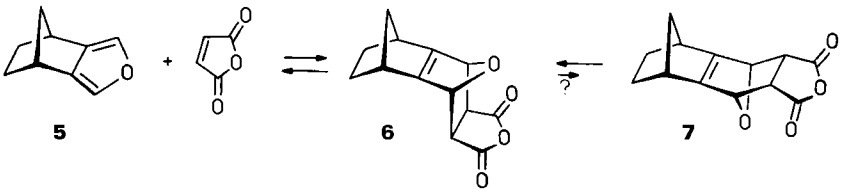


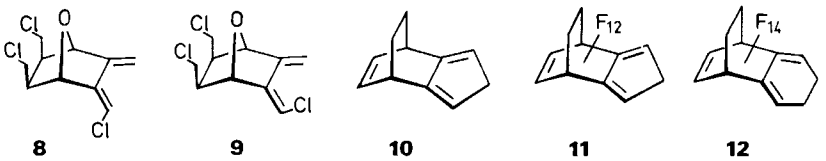
1 **2** **3** **4**

and **2** to a large variety of dienophiles including benzyne and maleic anhydride [11], in contradiction with *Alder's* report [9]. However, *Bartlett et al.* pointed out, that the *endo- vs. exo*-face selectivity in the reaction of **1** with maleic anhydride varied between 55:45 and 35:65 (giving **3** and **4**) depending upon the solvent and the temperature [6]. The photooxidations of **1** and **2** proceeded only with moderate *endo*-face selectivity [12]. *Paquette et al.* attributed the *endo*-face selectivity of the *Diels-Alder* additions of **1** and **2** to a kinetic stereoelectronic control (secondary orbital interactions between the dienophiles and the dienes).



5 **6** **7**

We reported that cycloadditions of maleic anhydride and dimethyl acetylenedicarboxylate to (2-norborneno)[*c*]furan (**5**) were highly *endo*-face selective under kinetic and thermodynamic control. The *syn*-11-oxasesquinorbornene **6** appeared to be more stable than its *anti*-isomer **7**[5]). This was attributed to a 'synergic' effect of the polarization of the double bond π-electron density on the *exo*-face of the norbornene and oxanorbornene sub-systems joined together by the same C(2),C(7) double bond [7]. Thus, the kinetic *endo*-face *Diels-Alder* selectivity of **5** was parallel to the thermodynamic stereoselectivity, in agreement with the *Bell-Evans-Polanyi* principle [13]. This might also be the case with the cyclopentadiene derivatives **1** and **2**. The first case of [4+2]-additions of dienes grafted onto a bicyclic skeleton where the face stereoselectivity was proven *not* to be controlled by the stability of the adducts was the tetracyanoethylene (ethylenetetracarbonitrile; TCE) cycloadditions to 2-((*Z*)-chloromethylidene)- and 2-((*E*)-chloromethylidene)-3-methylidene-5*exo*, 6*exo*-bis(chloromethyl)-7-oxanorbornanes (**8** and **9**) where the *exo*-face was preferred [2] [14].

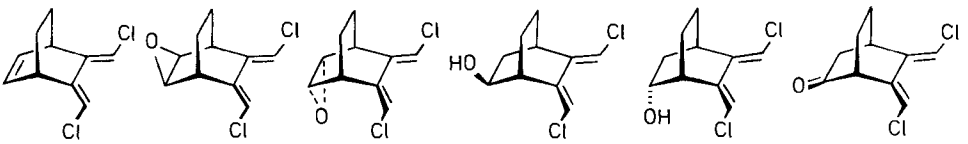


8 **9** **10** **11** **12**

[5]) The terms *syn* and *anti* refer to the relative positions of the methanes (C(12)) and the oxa-(O(11)) bridge to each other.

The cycloadditions of the cyclopentadiene **10** annelated to bicyclo[2.2.2]octa-2,5-diene were found to prefer the *exo*-face with benzyne, methyl propynoate and acetylenedicarboxylate [11]. However, the *Diels-Alder* addition of **10** to *N*-methyltriazolinedione (NMTAD) was highly *endo*-face selective [15]. *Feast et al.* found the perfluorinated derivative **11** to add to 2-butyne and propyne preferentially onto the *endo*-face [16], whereas the *exo*-face was preferred for the additions of the triene **12** to 2-butyne and dimethyl acetylenedicarboxylate [17].

All these results demonstrate that the face selectivity of the *Diels-Alder* additions of dienes grafted onto bicyclic skeletons is governed by subtile and numerous differential factors reigning on the two faces of the diene[6]). To gain more detailed informations on these factors we prepared the 5,6-bis((*E*)-chloromethylidene)bicyclo[2.2.2]oct-2-ene (**13**) and the 2-substituted 5,6-bis((*E*)-chloromethylidene)bicyclo[2.2.2]octanes **14–18**. The *exo*-face (= side of the ethano bridge $H_2C(7)$, $H_2C(8)$) and the *endo*-face (= side opposite to $H_2C(7)$, $H_2C(8)$) of these new exocyclic[7]) *s-cis*-butadienes are differentiated by minor structural features. To a first approximation, the C(2), C(3) and C(7), C(8) bridges of **14** and **16** should have similar bulk on the *endo*- and *exo*-faces, respectively[8]). This is not true for **13**, **15**, **17** and **18**. The nonbonding electrons of the polar functions in **15**, **17** and **18** may intervene and influence the face selectivity of the cycloadditions of these dienes.



13 **14** **15** **16** **17** **18**

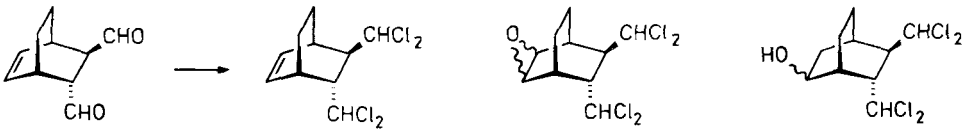
Results. – The preparation of the dichlorodienes **13–18** starts with the *Diels-Alder* addition of 1,3-cyclohexadiene to a mixture of malealdehyde and fumaraldehyde [20] yielding the *trans*-bicyclo[2.2.2]oct-5-ene-2,3-dicarbaldehyde **19**; 85%. Chlorination with PCl_5 in $CHCl_3$ [21] furnished the tetrachloride **20** (60%). Heating **20** in KOH/EtOH gave the triene **13** (91%). Epoxidation of **20** with *m*-chloroperbenzoic acid in CH_2Cl_2 yielded a mixture of the *exo*- and *endo*-epoxy derivatives **21** (90%) which eliminated two mol-equiv. of HCl upon heating in KOH/EtOH giving the epoxydienes **14** and **15** in a 9:1 product ratio (95%). The two isomers could be separated readily by column chromatography on silica gel. Nucleophilic additions to the epoxydienes **14** and **15** appeared to be slow reactions under our conditions. Hydroboration followed by oxidative workup gave a mixture of the *exo*- and *endo*-alcohols **22** (70%) that yielded the dienols **16** and **17** (95:5, 95% yield) upon treatment in KOH/EtOH. They were also separated by column chromatography on silica gel. *Collin*'s oxidation (CrO_3, pyridin, CH_2Cl_2) of **16** gave the dienone **18** (60%). Reduction of **18** with $LiAlH_4$ in THF furnished a 1:1 mixture of **16** and **17**.

[6]) For the face-selectivity of *Diels-Alder* additions of endocyclic dienes, *cf.* footnote [7]) being part of propellanes, see [18]. See also the cycloadditions of bicyclo [4.4.0]deca-2,4-dienes [19a] and 5-hydroxycyclopentadienes [19b].

[7]) An exocyclic butadiene moiety means that each double bond is in an exocyclic position on the ring skeleton.

[8]) For the purpose of an easier discussion, compounds **13–18** are numbered in the same way in the *General Part.* Systematic nomenclature is used in the *Exper. Part.*

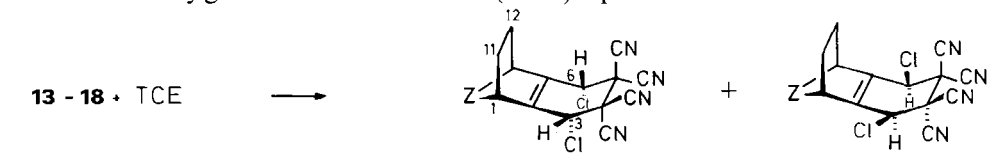
The *exo*-preference for the epoxidation and hydroboration of **20** was expected as being due to the bulk of the *endo*-dichloromethyl substituent. The *exo*- and *endo*-configurations of the epoxy group in **14** and in **15**, respectively, and of the hydroxy substituent in **16** and in **17**, respectively, was confirmed by lanthanide-induced shifts in the ^{1}H-NMR. ($Eu(dpm)_3$) and ^{13}C-NMR. ($Yb(dpm)_3$) spectra. The (*E*)-configuration of the two chloromethylidene moieties of **13–18** was expected from their mode of formation. It was confirmed by ^{13}C-NMR., and more specifically, by the analysis of the $^3J_{(C,H)}$ coupling-constants of C(5) and C(6) with the methylidene H-atoms (absence of relatively large *trans* $^3J_{(C,H)}$ [22] and comparison with the ^{13}C-NMR. spectra of the *(Z)*- and *(E)*-chlorodienes **8** and **9** [2] [14]. With **16–18**, a nuclear *Overhauser* effect (NOE) [23] was measured on *H*CCl=C(6) while irradiating *H*CCl=C(5), or *vice-versa*. Irradiation of the bridgehead H-atoms H-C(1) and H-C(4) did not give a NOE on *H*CCl=C(5) and *H*CCl=C(6) for **13–18**[8]).



19 **20** **21** **22**

A typical bathochromic shift of 10–15 nm [24] was observed in the UV. spectra of **13–18** when compared with those of the corresponding 5,6-dimethylidenebicyclo[2.2.2]octane derivatives [1].

The cycloadditions of TCE to **13–18** in benzene (20°) gave the mixtures of adducts *endo*-**23**/*exo*-**23** – *endo*-**28**/*exo*-**28**, respectively, in excellent yield (>95%). The product ratios were determined by ^{1}H-NMR. (360 MHz) of the reaction mixtures. They gave the face selectivities (± 1%) reported below.



Z=CH=CH	*endo*-**23** (78%)	*exo*-**23** (22%)
exo	*endo*-**24** (80%)	*exo*-**24** (20%)
endo	*endo*-**25** (60%)	*exo*-**25** (40%)
$CH_2CH(OH)_{exo}$	*endo*-**26** (68%)	*exo*-**26** (32%)
$CH_2CH(OH)_{endo}$	*endo*-**27** (3%)	*exo*-**27** (97%)
$CH_2C=O$	*endo*-**28** (30%)	*exo*-**28** (70%)

The major adducts *endo*-**23**–*endo*-**26**, *exo*-**27** and *exo*-**28** could be purified by fractional crystallization in CH_2Cl_2/pentane. The configuration of the Cl-atoms in **23–28** was given by NOE in their ^{1}H-NMR. spectra.

For **23–25**, 1:1 mixtures of the *endo/exo*-adducts were analyzed by FT-^{1}H-NMR. (360 MHz). A NOE was observed for H-C(3) and H-C(6) of *endo*-**23**–*endo*-**26** while irradiating the H-atoms at C(11) and C(12) (see *Fig. 1* and *2*). With *endo*-**26**, irradiation of $H_2C(10)$ or H-C(9) gave no NOE on H-C(3) and H-C(6) (*Fig. 3*). With *exo*-**27**, irradiation of $H_2C(11)$ and $H_2C(12)$ gave no NOE on H-C(3) and H-C(6), whereas irradiation of H_{endo}-C(10) produced a NOE. Similar observations were made for the pure adduct *exo*-**28**. In the case of *endo*-**28** (2:1 mixture *endo*-**28**/*exo*-**28**), a NOE on H-C(3) and H-C(6) was measured while irradiating $H_2C(11)$ and $H_2C(12)$.

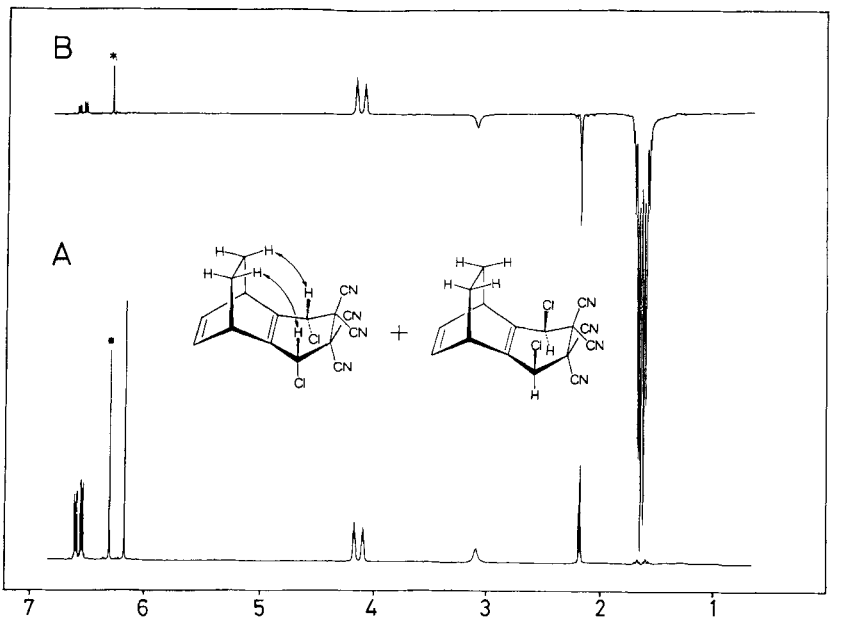


Figure 1. *FT.-^{1}H-NMR.(360 MHz, CD_3COCD_3) spectrum of a* ca. *1:1 mixture of* endo-**23**/exo-**23**. (A) During irradiation of $H_2C(11)$ and $H_2C(12)$ at 1.7 ppm; (B) spectrum A substracted by the non-irradiated spectrum. The asterisk refers to the signal of H-C(3) and H-C(6) of *endo*-**23** (the major adduct from **13** and TCE) that shows a NOE.

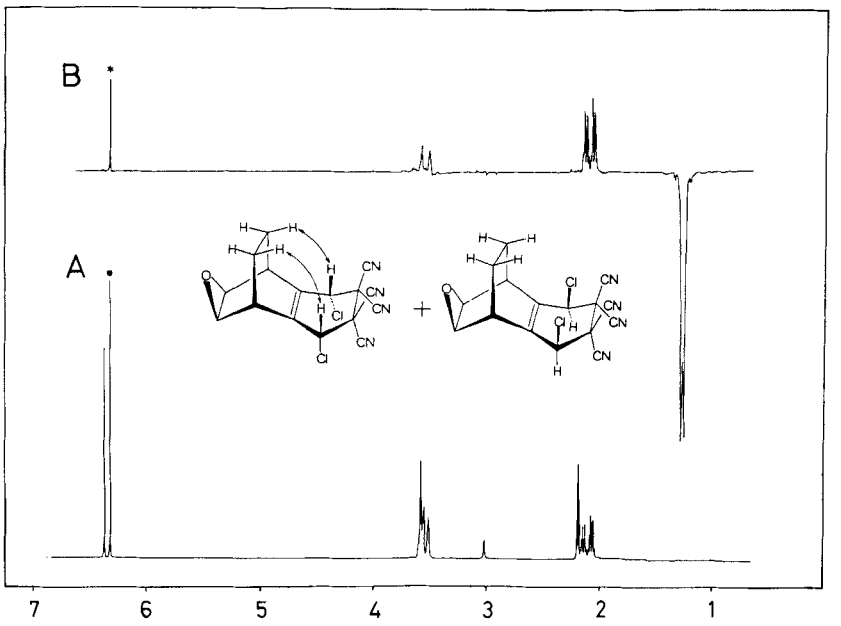


Figure 2. *FT.-^{1}H-NMR.(360 MHz, CD_3COCD_3) spectrum of a* ca. *1:1 mixture of* endo-**24**/exo-**24**. (A) During irradiation of $H_2C(11)$ and $H_2C(12)$; (B) spectrum A substracted by the non-irradiated spectrum. The asterisk refers to the signal of H-C(3) and H-C(6) of *endo*-**24** that shows a NOE.

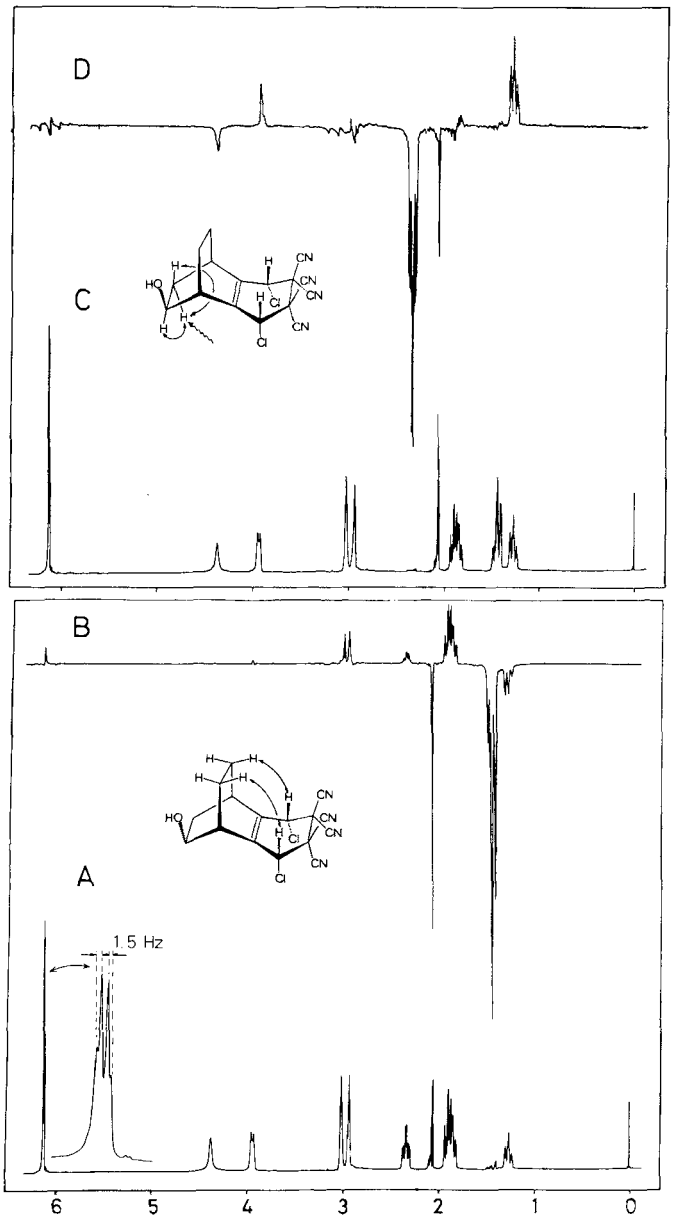


Figure 3. *FT.-^{1}H–NMR.(360 MHz, CD_3COCD_3) spectrum of pure* endo-**26**. (A) During irradiation of H-C(11) and H-C(12) opposite to the C(9), C(10) branch; (B) spectrum A substracted by the non-irradiated spectrum showing NOE at the signal of H-C(3) and H-C(6) at 6.1 ppm and at that of near protons; (C) during irradiation of H*endo*-C(10) at 2.35 ppm; (D) spectrum C substracted by the non-irradiated spectrum showing no NOE at 6.1 ppm.

Confirmation of the ^{1}H-NMR. assignments was given by *Collin*'s oxidation of the pure *exo*-hydroxy adduct *endo*-**26** yielding exclusively *endo*-**28**.

The symmetry observed in the ^{1}H- and ^{13}C-NMR. spectra of the adducts **23–25**

confirmed the stereospecificity of the $[{}_{\pi}4_s + {}_{\pi}2_s]$-cycloadditions of TCE to **13–15**. Two signals were observed for H-C(3) and H-C(6) of **26–28**. A long-range $^5J_{(H,H)}$ coupling-constant of 1.5 Hz (see *Fig. 3*) typical of a pseudoaxial/pseudoequatorial H,H-arrangement in cyclohexene derivatives [25] was observed in *endo*-**26**, *exo*-**27** and *exo*-**28**, thus confirming the stereospecificity of the *Diels-Alder* additions of TCE to **16–18**.

Discussion. – Contrary to what is known for the *Diels-Alder* adducts of the furan derivative **5** [7], we do no expect a significant difference in stability between the *endo*- and *exo*-adducts of TCE to **13–18**. The *endo*-face selectivity of the TCE addition to **13** contrasts with the *exo*-face selectivity reported for the additions of methyl propynoate and acetylenedicarboxylate to the cyclopentadiene analog **10** [11]. However, it parallels the *endo*-preference observed for the NMTAD addition to **10** [15]. It is possible that the *endo*-face selectivity of the cycloadditions of **10** [15], **11** [16] and **13** could be due to differential steric effects between the *endo*- and *exo*-faces. This steric argument is obviously not valid for the additions of **12** [17], other factors must be considered [11] [12] [15]. We postulate that the polarizability of the bridges can intervene in stabilizing the transition states of the *Diels-Alder* additions of **13–18** and other exocyclic dienes grafted onto bicyclic skeletons. We expect the unsaturated bridge in **13** (and **2** and **10–12**) and the substituted bridges in **14–18** to be more polarizable than the ethano C(7),C(8) bridge, thus favoring the dienophile to attack onto the *endo*-face. This effect will be the largest for cycloadditions involving dienophiles with the largest electronic demand. Accordingly, strong dienophiles such as TCE and NMTAD will prefer to attack onto the *endo*-face of **10–18**. In the case of the 7-oxanorbornanes **8** and **9**, the *exo*-face is preferred, perhaps because of smaller hindrance on the *exo*-face or because of the oxygen bridge (n(0) electrons) that can participate in the stabilization of the *Diels-Alder* transition state. This effect could also be present in the TCE addition to **15**, the *endo*-epoxy group stabilizing the *endo*-attack in competition with a possible steric repulsive interaction. The relatively high *exo*-face selectivity observed with the *endo*-dienol **17** could be explained by invoking a larger steric destabilization of the *endo*-attack than in the case of the *endo*-epoxy derivative **15**.

Competitive attractive polarizability effects and steric repulsive effects of the unsaturated or substituted C(2), C(3) bridge cannot explain the *exo*-face selectivity of the TCE addition to **18**. One is now tempted to invoke a third factor, for instance a repulsive dipole-dipole interaction between the carbonyl function of **18** and the cyano groups of TCE. It is also possible (although it could not be put on firm grounds experimentally by analysis of the UV./VIS. spectra recorded during the addition of TCE to **13–18**) that charge-transfer complexes implying coordination of the oxygenated functions by the dienophile (or H-bridging) could hinder the TCE attack onto the *endo*-face. If such an hypothesis should be valid for the TCE addition to **17** and **18** we must invoke that the epoxy group of **15** and the etheral bridges of **8** and **9** give weaker complexes with TCE than the OH substituent in **17** (H-bonding ?).

The face selectivity of the cycloadditions of other dienophiles than TCE should be analyzed to substantiate the above hypotheses. Preliminary results with maleic anhydride showed that the dichlorobutadienes **13–18** are not suited for such a study because their adducts loose HCl too easily, giving aromatized products that have

lost the stereochemical information of the cycloadditions. We have found that the Cl-atoms in **13** can be replaced stereoselectively by D-atoms. The cycloadditions of 5,6-bis(deuteriomethylidene)bicyclo[2.2.2]oct-2-ene and its derivatives are now under study and will be reported elsewhere. For the moment, we must admit our inability to give a simple, general and predictive rationale for the face selectivity of the *Diels-Alder* additions to dienes grafted onto bicyclic skeletons. Predictions based on the analysis of the shapes and energies of the MO's of the dienes **1**, **2**, **5** and **10–18** and various dienophiles were rather confusing in our hands because the calculated subHOMO's were numerous and their shapes were not independent upon the calculation techniques, and furthermore, the usual PMO approaches [11] became difficult to apply with non-symmetrical dienes such as **16–18**.

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Experimental Part

General remarks. See [26]. *Synthesis of fumaraldehyde/malealdehyde.* At 40–45°, 2,5-dimethoxy-2,5-dihydrofuran (65 g, 0,5 mol) was stirred for 12 h in CH_3COOH/H_2O 2:5 (200 ml). After removal of CH_3COOH and H_2O i.V., the residue was distilled (12 Torr) yielding 31 g (72%) of slightly yellow liquid that was used immediately, b.p. 52–60°/12 Torr.

Synthesis of trans-*bicyclo[2.2.2]oct-5-ene-2,3-dicarbaldehyde* (**19**). Cyclohexa-1,3-diene (20 g, 0.25 mol) and fumaraldehyde/malealdehyde (see above; 20 g, 0.25 mol) were heated under reflux in anh. benzene (80 ml) for 20 h. The mixture was distilled i.V. yielding 35 g (85%) of **19**, b.p. 132–133°, colorless liquid. – ^{1}H-NMR ($CDCl_3$): 9.7 (*s*, 1 H); 9.5 (*s*, 1 H); 6.6–6.0 (*m*, 2 H); 3.4–2.9 (*m*, 4 H); 2.0–1.0 (*m*, 4 H).

Synthesis of trans-*5,6-bis(dichloromethyl)bicyclo[2.2.2]oct-2-ene* (**20**). The dialdehyde **19** (27,3 g, 0,17 mol) in $CHCl_3$ (90 ml) was added dropwise to a stirred suspension of PCl_5 (38,5 g, 0,185 mol) in $CHCl_3$ (170 ml). The mixture was stirred at RT. for 20 h. After evaporation of the solvent i.V., the residue was dissolved in Et_2O (150 ml) and poured into ice/water (300 g). The mixture was immediately neutralized with sat. Na_2CO_3 solution. The aq. phase was extracted with ether (3 times 50 ml). The etheral extracts were combined and dried ($MgSO_4$). After evaporation of the solvent i.V., the residue was purified on a short column of silica gel (350 g, hexane/$CHCl_3$ 1:1) yielding 28 g (60%) of colorless oil. – IR. (film): 3060, 2970, 2880, 1470,1450, 1375, 1290, 1230, 1170, 930, 920, 895, 885, 870, 835, 750, 710. – ^{1}H-NMR. ($CDCl_3$): 6.4 (*m*, 2 H); 6.0–5.7 (*d* × *d*, 2 H); 3.1 (*m*, 2 H); 2.2–1.0 (*m*, 6 H). – MS. (70 eV): 278 (1.2), 276 (5), 275 (10), 272 (8), 241 (3), 239 (8), 237 (8), 203 (11), 201 (18), 191 (15), 189 (23), 167 (7), 165 (17), 161 (10), 155 (8), 153 (24), 129 (30), 127 (45), 125 (100), 117 (35), 115 (45), 103 (20), 102 (12), 101 (12), 99 (13), 91 (53), 89 (22), 87 (25), 85 (40), 83 (38).

$C_{10}H_{12}Cl_4$ (274.01) Calc. C 43.83 H 4.41% Found C 43.63 H 4.51%

Synthesis of 2endo, 3exo-*bis(dichloromethyl)*-5exo, 6exo- *and* -5endo, 6endo-*epoxybicyclo[2.2.2]octanes* (**21**). The tetrachloride **20** (5 g, 18 mmol) in anh. CH_2Cl_2 (20 ml) was added to a solution of *m*-chloroperbenzoic acid (10.2 g, 57 mmol) in anh. CH_2Cl_2 (120 ml). After heating under reflux for 3 days, the mixture was washed with aq. 10% K_2CO_3-solution (3 times 50 ml), then with water. After drying ($MgSO_4$) the solvent was evaporated i.V. yielding 4.7 g (90%) of viscous oil. – IR. (film): 3020, 2960, 2920, 2880, 1795, 1770, 1730, 1470, 1450, 1410, 1360, 1340, 1300, 1290, 1260, 1245, 1230, 1215, 1170, 1010, 960, 940, 920, 910, 870, 845, 800, 780, 740. – ^{1}H-NMR. ($CDCl_3$): 6.25–5.75 (*m*, 2 H); 3.65–3.25 (*m*, 2 H); 2.8 (*m*, 2 H); 2.4–2.15 (*m*, 2 H); 2.1–1.0 (*m*, 4 H). – MS. (70 eV): 294 (0.5), 292 (3), 290 (7), 288 (4.5), 257 (5), 255 (15), 253 (16), 221 (7), 219 (20), 217 (39), 207 (17), 205 (19), 191 (12), 189 (23), 187 (21), 153 (49), 151 (47), 141 (71), 139 (89), 127 (69), 125 (83), 117 (100), 115 (80), 113 (72), 111 (71), 105 (89), 91 (95).

$C_{10}H_{12}Cl_4O$ (290.02) Calc. C 41.41 H 4.17% Found C 41.45 H 4.31%

Synthesis of 5exo, 6endo-*bis(dichloromethyl)*-2exo- *and* -2endo-*bicyclo[2.2.2]octanol* (**22**). Freshly distilled $BF_3 \cdot Et_2O$ (5 g, 35 mmol) was added dropwise under N_2 at 0° to a stirred suspension of **20** (5 g,

18 mmol) and $NaBH_4$ (1.2 g, 32 mmol) in anh. THF (50 ml). The mixture was stirred at RT. for 15 h. After cooling to 0°, water (10 ml) was added dropwise, then 3N KOH (20 ml) and 30% H_2O_2-solution (20 ml). After stirring at RT. for 24 h, the precipitate was filtered off on silica gel (10 g) and extracted with $CHCl_3$ (3 times 50 ml). The organic solution was washed with water (3 times 50 ml), dried ($MgSO_4$) and evaporated i.V. yielding 3.7 (70%) of colorless, viscous liquid. – IR. (film): 3600, 3370, 2950, 2830, 1470, 1455, 1300, 1280, 1235, 1140, 1115, 1100, 1080, 1010, 935, 900, 890, 875, 855, 750. – ^{1}H-NMR. ($CDCl_3$): 6.05–5.75 (*m*, 2 H); 4.05–3.8 (*m*, 1 H); 2.5–2.15 (*m*, 2 H); 2.1–1.0 (*m*, 9 H). – MS. (70 eV): 296 (1.1), 294 (6), 292 (11), 290 (8.8), 278 (3), 276 (9), 274 (14), 272 (11), 259 (2), 257 (5), 255 (7), 221 (15), 219 (18), 203 (14), 201 (16), 191 (30), 189 (47), 167 (10), 165 (19), 163 (18), 161 (19), 155 (38), 153 (91), 135 (34), 129 (37), 127 (61), 125 (59), 117 (58), 91 (100).

*Synthesis of 5,6-bis((*E*)-chloromethylidene)bicyclo[2.2.2]oct-2-ene* (**13**). Powdered KOH (10.5 g, 0.19 mol) was added to a solution of **20** (17 g, 0.062 mol) in abs. EtOH (120 ml). The mixture was heated under reflux for 24 h. After cooling to RT., water (70 ml) was added and the mixture extracted with ether (5 times 50 ml). After drying ($MgSO_4$) and evaporation i.V., the residue was purified by filtration on silica gel (50 g, hexane/$CHCl_3$ 1:1) yielding 11.4 g (91%) of colorless liquid, b.p. 117°/12 Torr. – UV. (isooctane): 261 (11200). UV. (95% EtOH): 261 (11000). – IR. (film): 3070, 2940, 2280, 1630, 1460, 1360, 1320, 1280, 1105, 925, 780, 750, 690. – ^{1}H-NMR. ($CDCl_3$): 6.3 (*m*, 2 H); 6.15 (*s*, 2 H); 3.95 (*m*, 2 H); 1.80–1.25 (*m*, 4 H). – ^{13}C-NMR. ($CDCl_3$): 140.2 (br.*s*, C(5), C(6)); 133.0 (*d*, J=170, C(2), C(3)); 107.1 (*d*, J=194, C=C(5), C=C(6)); 34.9 (*d*, J=141, C(1), C(4)); 23.7 (*t*, J=134, C(7), C(8)). – MS. (70 eV): 204 (3), 202 (18), 200 (27), 176 (10), 174 (70), 172 (100), 139 (30), 137 (90), 129 (17), 128 (8), 127 (10), 105 (7), 102 (27), 101 (21).

$C_{10}H_{10}Cl_2$ (201.086) Calc. C 59.72 H 5.01% Found C 59.69 H 4.94%

*Synthesis of 2,3-bis((*E*)-chloromethylidene)-5*exo,*6*exo- *and -5*endo,*6*endo-*epoxybicyclo[2.2.2]octane* (**14** and **15**). Powdered KOH (3,1 g, 56 mmol) was added to a solution of **21** (5 g, 17 mmol) in abs. EtOH (50 ml). The mixture was heated under reflux for 24 h. After cooling to RT., water (20 ml) was added and the mixture was extracted with ether (3 times 50 ml) after saturation of the aq. layer with NaCl. The ethereal extract was dried ($MgSO_4$) and evaporated i.V. A 9:1 mixture of **14**/**15** was obtained (3.5 g, 95%) which was separated by column chromatography on silica gel (AcOEt/hexane 1:2). The first fraction contained 3.1 g (89%) of **14**, white crystals, m.p. 67–68° (hexane). – UV. (isooctane): 263 (10000). UV. (95% EtOH): 263 (10100). – IR. (KBr): 3080, 3020, 2980, 2950, 2910, 2870, 1670, 1650, 1460, 1405, 1315, 1280, 1130, 945, 920, 850, 790, 750. – ^{1}H-NMR. ($CDCl_3$)[9]: 6.4 (*s*, HC=C(2), HC=C(3)[14]); 3.55 (*m*, H-C(1), H-C(4)[36.3]); 3.25 (*m*, H-C(5), H-C(6)[100]); 1.9 (*m*, H-C(7) and H-C(8) *syn* to epoxy)[51]); 1.25 (*m*, H-C(7) and H-C(8) *anti* to epoxy)[27.3]). – ^{13}C-NMR. ($CDCl_3$): 138.7 (br.*s*, C(2), C(3)); 110.9 (*d*, J=194, C=C(2), C=C(3)); 51.7 (*d*, J=188, C(5), C(6)); 33.3 (*d*, J=141, C(1), C(4)); 21.9 (*t*, J=134, C(7), C(8)). – MS. (70 eV): 220 (9), 218 (37), 216 (58), 183 (4), 181 (15), 174 (3), 172 (5), 167 (5), 165 (3), 163 (7), 161 (7), 159 (9), 155 (5), 154 (8), 153 (12), 151 (19), 149 (8), 145 (33), 139 (97), 138 (7), 137 (8), 131 (9), 128 (17), 127 (32), 125 (37), 118 (16), 117 (87), 116 (39), 115 (100), 103 (27), 102 (15), 101 (15), 99 (10), 91 (30), 89 (24), 77 (32), 75 (20), 73 (8).

$C_{10}H_{10}Cl_2O$ (217.086) Calc. C 55.32 H 4.64% Found C 55.28 H 4.77%

The second fraction of the above chromatography contained 0.4 g (11%) of **15**, colorless crystals, m.p. 80–81°. – UV. (isooctane): 264 (10200). UV. (95% EtOH): 264 (9800). – IR. (KBr): 3090, 3040, 2980, 2960, 2920, 2880, 1670, 1470, 1420, 1350, 1235, 1165, 1140, 1030, 960, 925, 910, 865, 845, 810, 730. – ^{1}H-NMR. ($CDCl_3$)[9]: 6.3 (*s*, HC=C(2), HC=C(3)[23]); 3.65 (*m*, H-C(1), H-C(4)[48.3]); 3.4 (*m*, H-C(5), H-C(6)[100]); 1.75 (*m*, H-C(7) and H-C(8) *syn* to epoxy)[27]); 1.6 (*m*, H-C(7) and H-C(8) *anti* to epoxy)[26.4]). – ^{13}C-NMR. ($CDCl_3$): 137.0 (br.*s*, C(2), C(3)); 109.9 (*d*, J=194, C=C(2), C=C(3)); 50.2 (*d*, J=185, C(5), C(6)); 32.3 (*d*, J=141, C(1), C(4)); 21.4 (*t*, J=134, C(7), C(8)). – MS. (70 eV): 220 (8), 218 (36), 216 (56), 183 (6), 181 (19), 151 (28), 149 (60), 145 (27), 139 (38), 137 (25), 127 (36), 125 (45), 117 (87), 115 (100).

$C_{10}H_{10}Cl_2O$ (217.086) Calc. C 55.32 H 4.64% Found C 55.51 H 4.62%

*Synthesis of 5,6-bis((*E*)-chloromethylidene)-2*exo-*bicyclo[2.2.2]octanol* (**16**). Powdered KOH (3.1 g, 56 mmol) was added to a solution of **22** (5 g, 17 mmol) in abs. EtOH (50 ml). The mixture was heated un-

[9]) The relative induced shifts by $Eu(dpm)_3$ are given in brackets.

der reflux for 24 h. After cooling to RT., water (20 ml) was added and the mixture was extracted with ether (3 times 50 ml) after saturation of the aq. layer with NaCl. The ethereal extract was dried ($MgSO_4$) and evaporated i.V. yielding 3.5 g (95%) of a 95:5 mixture of **16**/**17**. After separation by column chromatography on silica gel (AcOEt/hexane 1:2), 3.1 g (89%) of **16** were obtained as pure, colorless crystals, m.p. 82–83°. – UV. (isooctane): 260 (9600). – UV. (95% EtOH): 260 (9200). – IR (KBr): 3300, 3080, 2950, 2860, 1625, 1455, 1440, 1270, 1050, 1010, 930, 900, 820, 780, 730. – ^{1}H-NMR. ($CDCl_3$)[9]): 6.25 (*s*, HC=C(6)[10.8]); 6.15 (*s*, HC=C(5)[8.4]); 3.95 (*m*, H-C(2)[85]); 3.1 (*m*, H-C(1), H-C(4)); 2.5 (*s*, HO[100]); 2.25–1.0 (*m*, H_2C(3), H_2C(7), H_2C(8)). – ^{13}C-NMR. ($CDCl_3$)[10]): 141.1 (br.*s*, C(5)[17.9]); 139.6 (br.*s*, C(6)[21.1]); 110.5 (*d*, *J*=194, *C*=C(6)[9.8]); 108.9 (*d*, *J*=194, *C*=C(5)[8.7]); 67.0 (*d*, *J*=152, C(2)[100]); 37.5 (*d*, *J*=137, C(1)[44]); 35.1 (*t*, *J*=136, C(3)[44.1]); 30.4 (*d*, *J*=138, C(4)[24]); 24.1 (*t*, *J*=134, C(7)[24.7]); 16.8 (*t*, *J*=134, C(8)[31.5]). – MS. (70 eV): 222 (5), 220 (32), 218 (46), 187 (1), 185 (6), 183 (16), 178 (18), 176 (38), 174 (22), 172 (13), 167 (12), 165 (33), 159 (8), 154 (19), 152 (16), 147 (29), 141 (41), 140 (22), 139 (100), 138 (30), 129 (37), 128 (13), 127 (43), 125 (74), 119 (23), 117 (14), 115 (19), 105 (18), 104 (22), 103 (98), 102 (19), 101 (14), 100 (11), 91 (36), 89 (14), 77 (50).

$C_{10}H_{12}Cl_2O$ (219.10) Calc. C 54.81 H 5.52% Found C 54.87 H 5.53%

*Synthesis of 5,6-bis((*E*)-chloromethylidene)-2-bicyclo[2.2.2]octanone* (**18**). CrO_3 (12.5, 0,125 mol) was added in small portions under N_2 to a stirred solution of anh. pyridin (20 g, 0.25 mol) in anh. CH_2Cl_2 (125 ml) maintained at 0°. After stirring at 20° for 10 min, **16** (2 g, 9 mmol) in anh. CH_2Cl_2 (5 ml) was added dropwise. The mixture was stirred at 20° for 3 h. The precipitate was filtered off on silica gel (20 g) and washed with CH_2Cl_2. The solvent was concentrated i.V. to 20 ml and ether (100 ml) was added. The organic solution was washed successively with 1N HCl (50 ml), aq. $NaHCO_3$-solution and water. After drying ($MgSO_4$), the solvent was evaporated i.V. The crude **18** was purified on a column of silica gel (30 g, AcOEt/Hexane 1:2) yielding 1.2 (60%) of white crystals, m.p. 76–77° (hexane). – UV. (isooctane): 265 (8400), 304 (300). – UV. (95% EtOH): 265 (8500), 298 (280). – IR. (KBr): 3080, 2950, 2910, 2880, 1725, 1620, 1210, 1090, 900, 770. – ^{1}H-NMR. ($CDCl_3$[9]): 6.35 (*s*, HC=C(5)[17.5]); 6.3 (*s*, HC=C(6)[20]); 3.75 (*m*, H-C(4)[29]); 3.5 (*m*, H-C(1)[100]); 2.35 (*d*, H_2C(3)[96]); 1.9 (*m*, H_2C(7), H_2C(8)). – ^{13}C-NMR. $CDCl_3$)[10]): 208.8 (br.*s*, C(2)[100]); 139.1 (br.*s*, C(5)[15.4]); 134.6 (br.*s*, C(6)[19]); 112.7 (*d*, *J*=194, *C*=C(6)[10.8]); 110.4 (*d*, *J*=194, *C*=C(5)[9.2]); 47.9 (*d*, *J*=145, C(1)[45]); 42.8 (*t*, *J*=134, C(3)[45.1]); 31.9 (*d*, *J*=139, C(4)[20.9]); 23.4 (*t*, *J*=134, C (7)[15.6]); 22.4 (*t*, *J*=134, C(8)[18.1]). – MS. (70 eV): 220 (5), 218 (26), 216 (40), 185 (0.5), 183 (3.5), 181 (9.5), 176 (16), 174 (67), 172 (100), 163 (1.5), 161 (4.4), 159 (6), 141 (17), 139 (51), 137 (15), 127 (10), 125 (27), 117 (18), 115 (16), 104 (11), 103 (49), 102 (9), 91 (15), 89 (9), 77 (24).

$C_{10}H_{10}Cl_2O$ (217.085) Calc. C 55.32 H 4.64% Found C 55.38 H 4.88%

*Synthesis of 5,6-bis((*E*)-chloromethylidene)-2*endo-*bicyclo[2.2.2]octanol* (**17**). The ketone **18** (1 g, 4.6 mmol) was added to a stirred suspension of $LiAlH_4$ (0.35 g, 9.2 mmol) in anh. THF (20 ml). After stirring at 20° for 1 h, water (1 ml) was added and the precipatate was filtered off. The solvent was evaporated i.V. to dryness and the residue was triturated with pentane (50 ml). The extract was dried ($MgSO_4$) and evaporated i.V.: 0.95 g (95%) of **16**/**17** (1:1) which were separated by column chromatography on silica gel (AcOEt/hexane 1:2). The first fraction contained 0.45 g of **16**, the second 0.4 g of **17**. The latter was obtained pure after recrystallization from pentane: 0.39 g (39%), white crystals, m.p. 77–78°. – UV. (isooctane): 260 (9300). UV. (95% EtOH): 260 (9800). – IR. (KBr): 3560, 3380, 3080, 2950, 2880, 1630, 1465, 1450, 1265, 1075, 1050, 965, 910, 810, 785, 730. – ^{1}H-NMR. ($CDCl_3$): 6.4 (br.*s*, HC=C(6)); 6.2 (br.*s*, HC=C(5)); 4.05 (*m*, H-C(2)); 3.15 (*m*, H-C(1), H-C(4)); 2.2 (*m*, H_{exo}-C(3)); 1.8 (br.*s*, HO); 1.5 (*m*, H_2C(7), H_2C(8)); 1.2 (*m*, H_{endo}-C(3)). – ^{13}C-NMR. ($CDCl_3$): 141.1 (br.*s*, C(5)); 137.6 (br.*s*, C(6)); 112.4 (*d*, *J*=194, *C*=C(6)); 108.7 (*d*, *J*=194, *C*=C(5)); 68.7 (*d*, *J*=148, C(2)); 37.8 (*d*, *J*=140, C(1)); 36.8 (*t*, *J*=135, C(3)); 29.7 (*d*, *J*=137, C(4)); 23.1 (*t*, *J*=131, C(7)); 21.4 (*t*, *J*=131, C(8)). – MS. (70 eV): 222 (7), 220 (33), 218 (48), 185 (6), 183 (16), 167 (10), 165 (38), 154 (17), 152 (18), 147 (33), 141 (40), 140 (23), 139 (100), 138 (27), 129 (38), 127 (42), 125 (80), 119 (25), 117 (16), 115 (20), 105 (19), 104 (24), 103 (99), 102 (21), 101 (16), 91 (58), 77 (41).

$C_{10}H_{12}Cl_2O$ (219.10) Calc. C 54.81 H 5.52% Found C 55.00 H 5.58%

Diels-Alder *adducts of TCE to* **13–18**, *synthesis of* endo-**23**–endo-**26**, exo-**27** *and* exo-**28**. Each diene **13–18** (1–5 mmol) and TCE (1 mol-equiv., 1–5 mmol) in anh. benzene (3–15 ml) were stirred at 20° for

[10]) The relative induced shifts by $Yb(dpm)_3$ are given in brackets.

24 h. After evaporation of the solvent, the crude adduct (>95%) was crystallized from CH_2Cl_2/pentane 9:1 until the major isomer was obtained in pure form.

*3*endo,*6*endo-*Dichlorotricyclo[6.2.2.O^{2,7}]dodeca-2(7),9-diene-4,4,5,5-tetracarbonitrile* (*endo*-**23**). Yield 55%, colorless crystals, m.p. 182–183°. – UV. (95% EtOH): 216 (6500). – IR. (KBr): 3080, 3000, 2960, 2940, 2900, 2880, 2260, 1660, 1610, 1470, 810, 765. – ^{1}H-NMR. (CD_3COCD_3): 6.55 (*m*, 2 H); 6.3 (*s*, 2 H); 4.15 (*m*, 2 H); 1.6 (*m*, 4 H). – MS. (70 eV): 330 (0.6), 329 (0.2), 328 (1), 302 (4), 301 (1), 300 (7), 293 (3), 267 (3), 266 (2), 265 (10), 240 (1), 238 (2.5), 231 (1), 230 (5), 229 (3), 205 (2), 204 (7), 203 (8), 202 (6), 201 (2), 200 (4), 190 (2), 176 (17), 174 (61), 172 (100), 167 (3), 166 (8), 165 (12), 152 (3), 151 (4), 150 (5), 140 (7), 139 (6), 137 (11), 115 (2), 113 (1), 102 (4), 101 (5), 100 (6).

$C_{16}H_{10}Cl_2N_4$ (329.189) Calc. C 58.37 H 3.06% Found C 58.07 H 3.24%

*3*exo,*6*exo-*Dichlorotricyclo[6.2.2.O^{2,7}]dodeca-2(7),9-diene-4,4,5,5-tetracarbonitrile* (*exo*-**23**). – ^{1}H-NMR. (CD_3COCD_3): 6.55 (*m*, 2 H); 6.15 (*s*, 2 H); 4.05 (*m*, 2 H); 1.6 (*m*, 4 H).

*3*endo,*6*endo-*Dichloro-9*exo-*10*exo-*epoxytricyclo[6.2.2.O^{2,7}]dodec-2(7)-ene-4,4,5,5-tetracarbonitrile* (*endo*-**24**). Yield 60%, colorless crystals, m.p. 146–147° (dec.). – IR. (KBr.): 3050, 3000, 2960, 2940, 2920, 2880, 2260, 1470, 1415, 1290, 1265, 1240, 1165, 1090, 1010, 855, 800. – ^{1}H-NMR. (CD_3COCD_3): 6.3 (*s*, 2 H); 3.6 (*m*, 4 H); 2.15–2.0 (*m*, 2 H); 1.25 (*m*, 2 H). – MS. (70 eV): 311 (10), 310 (6), 309 (29), 291 (8), 281 (17), 279 (13), 273 (26), 267 (8), 266 (7), 265 (15), 256 (18), 255 (35), 254 (12), 253 (10), 252 (14), 246 (28), 245 (61), 244 (19), 243 (14), 231 (35), 229 (16), 228 (22), 227 (21), 221 (27), 220 (20), 219 (28), 218 (85), 217 (46), 216 (35), 213 (21), 204 (42), 203 (40), 202 (22), 197 (55), 193 (72), 192 (66), 191 (100), 190 (32), 189 (30), 181 (41), 180 (37), 179 (81), 178 (33), 177 (30), 176 (24), 169 (45), 168 (33), 167 (37), 165 (66), 140 (55), 117 (49), 115 (70).

$C_{16}H_{10}Cl_2N_4O$ (345.18) Calc. C 55.66 H 2.92% Found C 55.58 H 3.04%

*3*exo,*6*exo-*Dichloro-9*exo-*10*exo-*epoxytricyclo[6.2.2.O^{2,7}]dodec-2(7)-ene-4,4,5,5-tetracarbonitrile* (*exo*-**24**). – ^{1}H-NMR. (CD_3COCD_3): 6.35 (*s*, 2 H); 3.5–3.6 (*m*, 4 H); 2.15–2.0 (*m*, 2 H); 1.25 (*m*, 2 H).

*3*endo,*6*endo-*Dichloro-9*endo,*10*endo-*epoxytricyclo[6.2.2.O^{2,7}]dodec-2(7)-ene-4,4,5,5-tetracarbonitrile* (*endo*-**25**). Yield 40%, colorless crystals, m.p. 141–142° (dec). – IR. (KBr): 3040, 3000, 2960, 2940, 2920, 2880, 2260, 1640, 1465, 1410, 1360, 1290, 1260, 1240, 1160, 1140, 1085, 1055, 1005, 940, 930, 850, 815, 800, 785, 760, 710. – ^{1}H-NMR. (CD_3COCD_3): 6.0 (*s*, 2 H); 3.4 (*m*, 4 H); 1.8 (*m*, 2 H); 1.45 (*m*, 2H). – MS. (70 eV): 311 (9), 309 (20), 273 (25), 255 (42), 245 (61), 231 (47), 218 (85), 217 (49), 204 (45), 203 (50), 197 (60), 193 (80), 192 (65), 191 (100), 190 (44), 181 (52), 180 (53), 179 (91), 178 (49), 177 (34), 165 (75), 153 (55), 140 (76), 127 (60), 125 (65), 117 (91), 115 (97), 103 (53), 102 (47), 101 (45), 100 (55), 91 (64).

$C_{16}H_{10}Cl_2N_4O$ (345.18) Calc. C 55.66 H 2.92% Found C 55.64 H 2.82%

*3*exo,*6*exo-*Dichloro-9*endo,*10*endo-*epoxytricyclo[6.2.2.O^{2,7}]dodec-2(7)-ene-4,4,5,5-tetracarbonitrile* (*exo*-**25**). – ^{1}H-NMR. (CD_3COCD_3): 5.95 (*s*, 2 H); 3.4 (*m*, 4 H); 1.8 (*m*, 2H); 1.45 (*m*, 2H).

*3*endo,*6*endo-*Dichloro-9*exo-*hydroxytricyclo[6.2.2.O^{2,7}]dodec-2(7)-ene-4,4,5,5-tetracarbonitrile* (*endo*-**26**). Yield 39%, colorless crystals, m.p. 175–176° (dec.). – IR. (KBr): 3570, 3390, 2940, 2880, 2260, 1465, 1445, 1310, 1280, 1250, 1230, 1170, 1145, 1045, 1000, 955, 935, 790, 755, 710. – ^{1}H-NMR. (CD_3COCD_3): 6.115 and 6.10 (2 *d*, *J*=1.5 each, H-C(3), H-C(6)); 4.3 (br.*s*, 1 H); 3.95 (*m*, 1 H); 3.03 (*m*, 1 H); 2.95 (*m*, 1 H); 2.3 (*m*, 1 H); 1.9 (*m*, 2 H); 1.4 (*m*, 2 H); 1.25 (*m*, 1 H). – MS. (70 eV): 304 (13), 302 (15), 231 (37), 206 (15), 205 (14), 204 (21), 179 (40), 178 (46), 176 (48), 174 (100), 165 (24), 149 (31), 139 (38), 128 (55), 111 (47), 109 (39), 97 (72), 95 (79), 91 (28).

$C_{16}H_{12}Cl_2N_4O$ (347.2) Calc. C 55.35 H 3.48% Found C 55.21 H 3.53%

*3*exo,*6*exo-*Dichloro-9*exo-*hydroxytricyclo[6.2.2.O^{2,7}]dodec-2(7)-ene-4,4,5,5-tetracarbonitrile* (*exo*-**26**). – ^{1}H-NMR. (CD_3COCD_3): 5.915 and 5.90 (2 *d*, *J*=1.5 each, H-C(3), H-C(6)); 4.3 (br.*s*, 1 H); 3.95 (*m*, 1 H); 3.03 (*m*, 1 H); 2.95 (*m*, 1 H); 2.3 (*m*, 1 H); 1.9 (*m*, 2 H); 1.4 (*m*, 2 H); 1.25 (*m*, 1 H).

*3*exo,*6*exo-*Dichloro-9*endo-*hydroxytricyclo[6.2.2.O^{2,7}]dodec-2(7)-ene-4,4,5,5-tetracarbonitrile* (*exo*-**27**). Yield 90%, colorless crystals, m.p. 197–198° (dec.). – IR. (KBr): 3580, 3390, 2990, 2960, 2930, 2880, 2260, 1470, 1450, 1440, 1350, 1285, 1245, 1190, 1170, 1150, 1070, 1035, 970, 900, 870, 790, 760. – ^{1}H-NMR. (CD_3COCD_3): 6.12 and 5.75 (2 *d*, *J*=1.5 each, H-C(3), H-C(6)); 4,2 (*m*, 1 H); 4.05 (br.*s*, 1 H); 3.05 (*m*, 1 H); 2.95 (*m*, 1 H); 2.2 (*m*, 1 H); 1.75–1.55 (*m*, 2 H); 1.5–1.4 (*m*, 2 H); 1.3 (*m*, 1 H). – MS. (70 eV):

304 (7), 302 (12), 269 (4), 268 (6), 267 (10), 231 (31), 213 (8), 204 (19), 179 (37), 178 (43), 176 (61), 174 (100), 165 (19), 139 (40), 128 (15), 127 (17), 125 (23), 97 (58), 95 (30), 91 (25).

$C_{16}H_{12}Cl_2N_4O$ (347.2) Calc. C 55.35 H 3.48% Found C 55.41 H 3.58%

*3*endo,*6*endo-*Dichloro-9*endo-*hydroxytricyclo[6.2.2.O^{2,7}]dodec-2(7)-ene-4,4,5,5-tetracarbonitrile* (*endo*-**27**). – ^{1}H-NMR. (CD_3COCD_3): 6.08 and 5.98 (2 *d*, *J* = 1.5 each, H-C(3), H-C(6)); 4.2 (*m*, 1 H); 4.05 (br.*s*, 1 H); 3.05 (*m*, 1 H); 2.95 (*m*, 1 H); 2.2 (*m*, 1 H); 1.75–1.55 (*m*, 2 H); 1.5–1.4 (*m*, 2 H); 1.3 (*m*, 1 H).

*3*exo,*6*exo-*Dichloro-9-oxotricyclo[6.2.2.O^{2,7}]dodec-2(7)-ene-4,4,5,5-tetracarbonitrile* (*exo*-**28**). Yield 40%, colorless crystals, m.p. 224–225°. – UV. (95% EtOH): 300 (400), 215 (6000). – IR. (KBr): 2950, 2920, 2880, 2250, 1725, 1400, 1300, 1150, 1090, 975, 915, 790, 755, 705, 665. – ^{1}H-NMR. (CD_3COCD_3): 6.24 and 6.22 (2 *d*, *J* = 1.5 each, H-C(3), H-C(6)); 3.47 (*m*, 2 H); 2.3–2.25 (*m*, 2 H); 2.2–2.0 (*m*, 2 H); 1.9–1.65 (*m*, 2 H). – MS. (70 eV): 344 (4), 310 (8), 309 (9), 308 (18), 304 (10), 302 (14), 281 (5), 267 (18), 265 (15), 253 (12), 240 (16), 232 (20), 231 (46), 204 (27), 199 (23), 191 (25), 179 (35), 178 (36), 176 (69), 174 (100), 165 (36), 155 (49), 154 (37), 153 (30), 152 (34), 141 (62), 139 (59), 129 (45), 128 (48), 127 (36), 125 (34), 115 (55), 103 (41), 101 (48), 91 (61).

$C_{16}H_{10}Cl_2N_4O$ (345.19) Calc. C 55.67 H 2.92% Found C 55.60 H 2.84%

*3*endo-*6*endo-*Dichloro-9-oxotricyclo[6.2.2.O^{2,7}]dodec-2(7)-ene-4,4,5,5-tetracarbonitrile* (*endo*-**28**). – ^{1}H-NMR. (CD_3COCD_3): 6.3 and 6.18 (2 *d*, *J* = 1.5 each, H-C(3), H-C(6)); 3.55 (*m*, 2 H); 3.4 (*m*, 2 H); 2.4 (*m*, 2 H); 2.2–2.0 (*m*, 2 H); 1.9–1.65 (*m*, 2 H).

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