124. Face Selectivity of the *Diels-Alder* Reaction of 5,6-Bis((D)methylidene)-2-bicyclo[2.2.2]octene[1])

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Summary

The face selectivity (*endo*-face *vs.* *exo*-face attack onto the exocyclic s-*cis*-butadiene moiety) of the [4+2]cycloadditions of 5,6-bis((D)methylidene)-2-bicyclo-[2.2.2]octene (**11**) to strong dienophiles has been determined in benzene at 25°. It is *ca.* 95/5, 75/5, 70/30, 60/40 and 50/50 for *N*-phenyltriazolinedione (NPTAD), tetracyanoethylene (TCE), dimethyl acetylenedicarboxylate (DMAD), maleic anhydride (MA) and singlet oxygen ($^1O_2$), respectively. The *endo*-face preference is probably due to a participation of the homoconjugated double bond at C(2), C(3) which makes the etheno bridge more polarizable than the ethano bridge in **11**. The absence of face selectivity with $^1O_2$ is consistent with an entropy-controlled mechanism involving the intermediacy of an exciplex.

Introduction. – Face selectivity can be observed for reactions of a π-function attached to a skeleton which is not symmetrical with respect to the 'π-plane' of this function[4]). The face selectivity of the *Diels-Alder* additions of 4,7-methano-4,5,6,7-tetrahydro-2*H*-indene (**1**) was first studied by *Alder et al.* [25], later by *Sugimoto et al.* [26], and more recently by *Paquette et al.* [27]. Several strong dienophiles were found to add to **1** preferentially onto its *endo*-face. This was attributed by *Paquette & Gleiter* [27] to a kinetic stereoelectronic factor. The shape of the subHOMO's of **1** and of analogous dienes grafted onto the trinorbornane skeleton suggested a

[1]) Interaction between non-conjugated chromophores, Part 20; Part 19, see [1]; Part 18, see [2].

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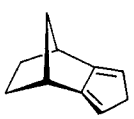
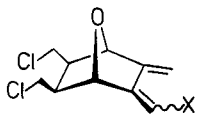
[4]) See for instance the nucleophilic additions to cyclohexanones [3-6], the hydroboration of methylidenecyclohexanes [7], the electrophilic additions [8-10] and cycloadditions [11] of bicyclo-[2.2.1]hept-2-enes and of 7-isopropylidenebenzo[*b*]bicyclo[2.2.1]hepta-2,5-dienes [12], the electrophilic additions to aryl-substituted 7-isopropylidenebenzo[*b*]bicyclo[2.2.1]hept-2-enes [13], 7-isopropylidenebicyclo[2.2.1]hept-2-enes [14], aryl-substituted benzo[*b*]bicyclo[2.2.2]octa-2,5-dienes [15] and to 8-methylidene-*endo*-tricyclo[3.2.1.$0^{2,4}$]octanes [16] [17], the electrophilic attacks onto bicyclo[4.3.1]decatetraenyl anion [18], the 4,7-methano-4,5,6,7-tetrahydroindenyl anion [19] and the 2-bicyclo[2.2.1]hept-5-enyl anions [20], the *Diels-Alder* additions of chiral dienophiles [21], the nitrile oxide cycloadditions to chiral olefins [22], the stereoselective keto-enol tautomerism in monocyclic and bicyclic ketones [23], and the reactions of chiral enolates [24].

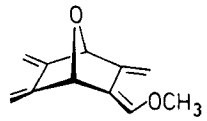
stronger repulsive interaction between the diene and dienophile for the *exo*- than for the *endo*-attack. *Bartlett et al.* reported, however, that the feeble face selectivity for the cycloadditions of maleic anhydride (MA) to **1** can be reversed by changing the solvent [28]. When applied to the *Diels-Alder* additions of the furan derivative **2** (*endo*-face preferred under conditions of kinetic and thermodynamic control) [29] and of the exocyclic dienes **3** (X = Cl ((*E*) and (*Z*) isomer), OCH_3 ((*E*) isomer) and **4** (*exo*-face preferred) [30], the PMO approach proposed by *Paquette & Gleiter* gave predictions at variance with the face selectivities observed [31]. Furthermore, the shape of the numerous subHOMO's that should be considered in this type of analysis were, in our hands [31], dependent upon the calculation technique (*ab initio* STO 3G, MNDO, MINDO/3, EHT) and upon small variations in the geometry of the dienes.

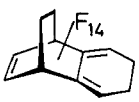
Although we do not exclude *a priori* that a 'well-adapted' MO technique might give diene subHOMO's whose shapes correlate the face selectivities of their cycloadditions, we think that several factors can intervene and be made responsible for the observed face selectivities. One can cite (1) differential steric effects (repulsive or attractive [32]), (2) differential dipole effect (repulsive or attractive) [33] [34], (3) differential attractive polarizability effects [33], (4) coordination of the dienophile with a substituent or a function of the bicyclic framework (entropy or/and enthalpy effects) [30], (5) non-equivalent extension of the π-electron densities [26] (π-anisotropy [35]), and (6) differences in the exothermicities of the *endo- vs. exo*-face additions [29] (assuming validity of the *Dimroth* [36] and *Bell-Evans-Polanyi* principle [37])[5]). Any or all of the six factors listed above, plus others, might intervene or not, depending upon the type of the dienes and the dienophiles involved.

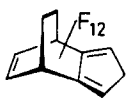
Feast et al. found the perfluorinated triene **5** to add to 2-butyne and dimethyl acetylenedicarboxylate (DMAD) preferentially onto the *exo*-face (= side of the ethano bridge) [40], whereas the *endo*-face (= side opposite to the ethano bridge) was preferred for the additions of 2-butyne and propyne to the triene **6** [41].

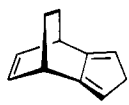


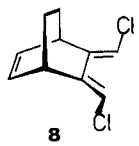


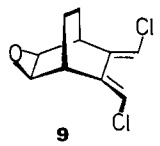


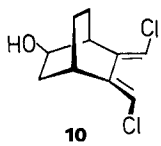










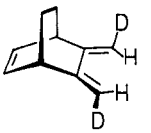


[5]) Volumes of activation suggest that *Diels-Alder* transition states are in fact product-like [38] rather than reactant-like as usually assumed [39].

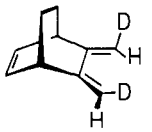
Paquette et al. [27a] reported that dehydrobenzene, DMAD and methyl propynoate add preferentially onto the *exo*-face of the cyclopentadiene derivative **7**, whereas *N*-phenyltriazolinedione (NPTAD) prefers the *endo* face [42]. We found that tetracyanoethylene (TCE) cycloadditions to the dichlorodienes **8**, **9** [43] and **10** were *endo*-face-selective, and we attributed tentatively the stereoselectivity to a differential attractive polarizability factor (factor (3) [33]). The unsaturated bridge in **5**–**8** is more polarizable than the saturated ethano bridge. The *exo*-face selectivity observed for some cycloadditions of **5** and **7** might be attributed to the competitive intervention of other factors, *e.g.* factors (2) and (6) (see above).

If one wishes to understand the origin of the *Diels-Alder* face selectivity of a diene grafted onto the bicyclo[2.2.2]octane skeleton whose two faces are made non-equivalent by unsaturation of one of the bridges, one has to strip down the stereochemical markers which substitute the diene in a way that allows one to reduce the number of the possible factors that may intervene. With the dideuterated diene **11** at least factors (2) and (6) can be excluded. We show in the following that strong dienophiles such as NPTAD, TCE and DMAD prefer to add onto the *endo*-face of **11**. Contrastingly, $^1O_2$-addition to **11** is not face-selective.

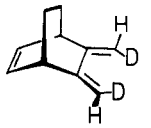
Results. – The reduction of 5,6-bis((*E*)-chloromethylidene)-2-bicyclo[2.2.2]-octene (**8**) [33] with the Zn/Cu couple in D_2O/THF 4:30 [44] furnished a mixture of the dideuterated dienes **11A**, **11B** and **11C** in a good yield (90%). As in the case of (*E*,*E*)-1,4-dichlorobutadiene, deuteration occured with partial retention of configuration [44]. The ^{1}H-NMR. spectrum of **11** showed two singlets at 5.1 and 4.8 ppm, with a peak area ratio of 4:1. They correspond to the H-atoms of the (*E*)- and (*Z*)-configurated (D)methylidene groups, respectively, as confirmed by



11A (*E*,*E*)

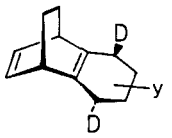


11B (*Z*,*E*)

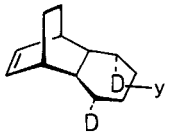


11C (*Z*,*Z*)

K



L



M

11A attacked onto *exo*-face ⟶ **K**
11A attacked onto *endo*-face ⟶ **M**
11C attacked onto *exo*-face ⟶ **M**
11C attacked onto *endo*-face ⟶ **K**
11B gives only **L**

nuclear-*Overhauser*-effect (NOE) measurements while irradiating the bridgehead protons H–C(1) and H–C(4). When the epoxydiene **9** was treated with Zn/Cu in D_2O/THF, the epoxide ring was reduced competitively [45] with the dichlorodiene giving **11** with a lower stereoselectivity ((*E*)- to (*Z*)-configurated (D)methylidene groups 3:2) than from the reaction **8** → **11**.

The *Diels-Alder* reaction of a mixture of **11A/11B/11C** with any dienophile gives a mixture of adducts **K**, **L** and **M**. If one defines x = *exo*-face selectivity ($1-x$ = *endo*-face selectivity) of the addition, s = proportion of (*E*)-configurated (D)methylidene groups in **11** ($s=a+b/2$, and $1-s=c+b/2$, with a, b and c = proportions of dienes **11A**, **11B** and **11C**, respectively) and t = degree of deuteration of the *exo*-positions in the allylic methylene groups in the adducts **K/L/M**, one can write (assuming suprafacial-suprafacial stereospecific cycloadditions [33]):

$$t = ax + (b/2)x + (b/2)(1-x) + c(1-x)$$
$$= x(a+b/2) + (1-x)(c+b/2)$$
$$= sx + (1-s)(1-x)$$

This gives *Equation 1:*

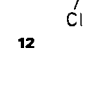
$$x = \frac{t+s-1}{2s-1} \tag{1}$$

which allows to evaluate the face selectivity of the cycloadditions of **11** as long as the ratio of (*E*)- to (*Z*)-configurated (D)methylidene groups in **11** differs from 1:1. The product ratios of **11A/11B/11C** does not have to be determined[6]) (see *Eqn. 1*).

The *Diels-Alder* additions of **11** to NPTAD, TCE and DMAD (benzene, 25°) were nearly quantitative and gave the corresponding adducts **14–16** (isolated yield >95%) whose structures were given by their spectral data. The deuterium content was better than 1.96 deuterium atoms (by ^{1}H-NMR. and mass spectroscopy).

With maleic anhydride (MA), a $60\pm3:40\pm3$ mixture of the isomeric adducts **17/18** was formed (determined by ^{1}H- and ^{13}C-NMR. spectroscopy). The major component **17** was obtained pure by fractional crystallization from ethyl acetate. The ^{1}H-NMR. characteristics of the minor isomer **18** were derived from the spectrum of the mixture **17/18**. The structure of **17** was given by the ^{1}H-NMR. spectrum of the unlabelled compound (relatively large $^3J_{H,H}$ (=4.4 Hz) and $^4J_{H,H}$ (=1.9 Hz) between the H_{endo} at C(3),C(6) and C(4),C(5) and smaller coupling constants between the H_{exo} at C(3),C(6) and the H_{endo} at C(4),C(5): $^3J_{H,H}=2.0$ Hz, $^4J_{H,H}<0.2$ Hz) and with the help of double irradiation experiments. Irradiation of the

[6]) The ^{1}H-NMR. spectra of **K**, **L** and **M** should display different signals for their allylic methylene groups because of the expected different $^5J_{H,H}$ homoallylic coupling constants of the *'trans'* (**L**) and *'cis'* (**K**, **M**) proton pairs [46]. Thus, in principle the analysis of the shape of the methylene multiplets of **K**, **L** and **M** should allow one to determine their ratio. This was not possible with the adducts studied here because of the H,D coupling constants that broadened the ^{1}H-NMR. signals. Nevertheless, by assuming that the stereoselectivity (retention/inversion = r/i) for the monodeuteration of **8** into **12**+**13** ([12]/[13] = r/i) is the same as that for the deuterations of **12** and **13** into **11**, one calculates product ratios of 64:32:4 for **11A/11B/11C** ($r^2+ri=4$, $i^2+ri=1$). Control experiments confirmed that **11A**, **11B** and **11C** were stable under the conditions of their formation (no *cis/trans*-isomerization of the deuterium label).



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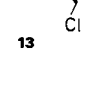

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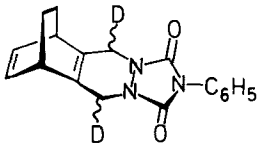
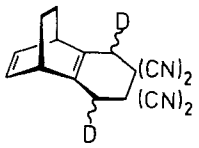
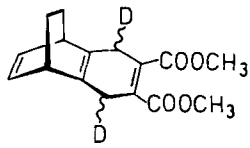


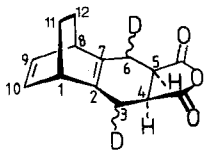
14 ($t = 0.23 \pm 0.02$) ($x = 0.05 \pm 0.03$)



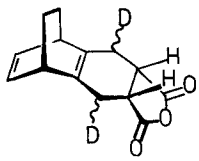
15 ($t = 0.35 \pm 0.03$) ($x = 0.25 \pm 0.05$)



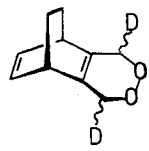
16 ($t = 0.38 \pm 0.03$) ($x = 0.30 \pm 0.05$)



17 ($t = 0.40 \pm 0.03$) ($x = 0.40 \pm 0.05$)



18 ($t = 0.40 \pm 0.03$) ($x = 0.40 \pm 0.05$)



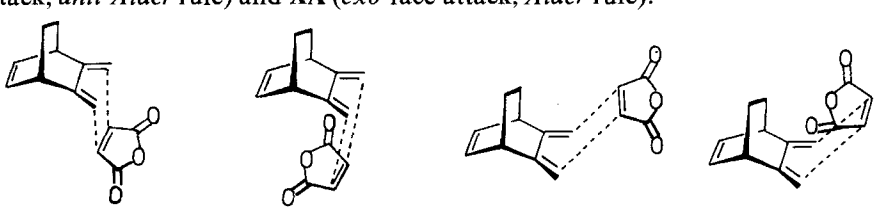
19 ($t = 0.50 \pm 0.03$) ($x = 0.50 \pm 0.05$)

signal at 2.5 ppm (H_{endo}–C(3), H_{endo}–C(6)) led to strong NOE's at 2.65 (H_{exo}–C(3), H_{exo}–C(6)) and 3.30 ppm (H–C(4), H–C(5)), thus confirming the *endo*-position of the H-atoms at C(4) and C(5). The structure of **17** has also been confirmed by single-crystal X-ray diffraction studies [47].

Sensitized photo-oxidation (5, 10, 15, 20-tetraphenylporphin (TPP), CH_2Cl_2, iodine lamp, 20°) of **11** yielded the corresponding endoperoxide **19**.

The 360-MHz-^{1}H-NMR. spectra displayed well-separated signals for the *exo* and *endo*-allylic-methylene protons in the adducts **14–19** whose attributions were based on NOE measurements. Irradiation of the signals of the ethano bridge protons led to the observation of NOE's for the *exo*- but not for the *endo*-proton signals (see [33] for examples). Careful integration of these signals gave the deuteration degrees t and the *exo*-face selectivities x (for $s = 0.8$) indicated above with formulae **14–19**.

Except for the photo-oxidation of **11**, for which no face selectivity was observed, the *Diels-Alder* additions reported here were all preferentially *endo*-face selective. The stronger the dienophile or the faster the reaction, the more *endo*-selective was its cycloaddition to **11**. In the case of the reaction of **11** + MA, the following proportions have been established for the four possible transition states, *i.e.*: **NAA** (*endo*-face attack, *anti-Alder* rule), **NA** (*endo*-face attack, *Alder* rule), **XAA** (*exo*-face attack, *anti-Alder* rule) and **XA** (*exo*-face attack, *Alder* rule):



It is interesting to note that the reactions following the *'Alder* rule' show no face selectivity whereas the *'anti-Alder* rule' additions are *endo*-face selective.

Discussion. – The *exo*-face of the s-*cis*-butadiene moiety in **11** is not expected to be severely more crowded than its *endo*-face. If it were the case and if a repulsive steric factor (1) should influence the face selectivity of our cycloadditions, we would have expected a larger *endo*-face selectivity for the addition of MA following the *Alder* rule (steric repulsion being overwhelmed by secondary orbital interactions, *i.e.* attractive polarizability effect) than for the addition that does not follow it. The steric demand in the transition states of the TCE cycloadditions is expected to be larger than that for the DMAD additions. Again, if a differential steric factor (1) should play a dominant role, we would not have expected similar *endo*-face selectivities for these reactions. Furthermore, steric factors alone cannot explain the larger selectivity observed with NPTAD than with MA.

Preliminary X-ray diffraction studies on derivatives of **11** [47] showed that a diene grafted – with each double bond in an exocyclic position – onto the 2-bicyclo-[2.2.2]octene system does not deviate from planarity (the plane of the diene function makes an angle of *ca.* 180° with that containing carbon atoms C(4), C(5), C(6), C(1) thus excluding a polarization of the π-electron density toward one of the face of the s-*cis*-butadiene moiety (factor (5)). The observation that the most electrophilic dienophile (the one with the largest electron affinity [39]) adds with the highest *endo*-face selectivity is in agreement with the hypothesis of a differential polarizability factor (3) (assistance of the endocyclic double bond to the stabilization of the *Diels-Alder* transition state) or/and with the intervention of a preassociation of the dienophile and **11** involving the endocyclic double bond.

$^1O_2$ has often been considered as a 'super' dienophile that gives [4+2] cycloadducts with activation enthalpies approaching zero [48]. The lack of face selectivity in the photo-oxidation of **11** is consistent with the formation of an exciplex or encounter complex [49] on which the bicyclic skeleton has no influence. Under these conditions, and since steric factors are rather small, the two faces of the exocyclic diene moiety in **11** have nearly the same probability to interact with $^1O_2$ and yield the endoperoxide **19**. In this context, it is interesting to note the feeble face selectivities reported for the photo-oxidation of the cyclopentadienes annulated to bicyclo[2.2.1]hept-2-ene (**1**) and bicyclo[2.2.2]hepta-2,5-diene systems [50] compared with the high *endo*-face selectivity observed for the *Diels-Alder* additions of these derivatives to strong dienophiles [26] [27].

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Experimental Part

General Remarks. See [33] [51]. The ^{1}H-NMR.-signal integrations were taken for at least two samples prepared independently. They were repeated at least 10 times for various settings of the *Bruker WH 360 MHz* spectrometer and were evaluated by the spectrometer integrator and also by using the 'xeroxing-cutting' technique. The deviations given for the peak ratios correspond to the maximum deviation measured with respect to the given mean value.

Preparation of zinc-copper couple. A solution of $CuCl_2$ (0.44 g) in 5% HCl (22 ml) was added dropwise and under N_2 to a vigourously stirred suspension of Zn powder (6.5 g, 0.1 mol) in H_2O (10 ml). After the end of H_2 evolution, the suspension was filtered under N_2, and the precipitate was washed successively with D_2O (10 ml, 2 times), anh. acetone (10 ml) and anh. Et_2O (10 ml). The black powder was transferred into a round bottom flask under Ar, and was heated to 100° under reduced pressure (1 Torr) for 1 h.

5,6-Bis((D)methylidene)-2-bicyclo[2.2.2]octene (**11**). The 5,6-bis((*E*)-chloromethylidene)-2-bicyclo-[2.2.2]octene [33] (**8**, 1 g, 5 mmol) was added to a stirred suspension of Zn-Cu couple (3 g) in anh. THF (30 ml) and D_2O (4 ml). The mixture was heated under reflux for 24 h. After cooling to 20°, the precipitate was eliminated by filtration and the solution concentrated to 5 ml by evaporation *i.v.* After addition of pentane (50 ml) and drying ($MgSO_4$), the solvent was evaporated *i.v.* and the residue distilled (bulb-to-bulb distillation, *Büchi* 'Kugelrohr') yielding 0.6 g (90%) of a colourless liquid, b.p. 68°/12 Torr. – ^{1}H-NMR. ($CDCl_3$): 6.17 (*m*, 2 H); 5.1 (*s*, 1.6 H); 4.8 (*s*, 0.4 H); 3.15 (*m*, 2 H); 1.2–1.7 (*m*, 4 H). – MS. (70 eV): 134 (22.3), 133 (0.4), 132 (0.4), 130 (1.4), 129 (1.0), 107 (9.2), 106 (100), 105 (27), 104 (4.4), 103 (1.6), 102 (0.4), 101 (0.1). The other spectral data were similar to those reported for the undeuterated triene, see [52].

Diels-Alder *adduct of NPTAD to* **11**: *6-phenyl-4,6,8-triaza(3,9-D_2)tetracyclo[9.2.2.0^{2,10}.0^{4,8}]pentadeca-2(10),12-diene-5,7-dione* (**14**). The triene **11** (0.1 g, 0.75 mmol) and NPTAD (0.13 g, 0.74 mmol) were mixed in anh. benzene (10 ml) and allowed to stand at 20° for 5 min. The solvent was evaporated *i.v.* and the residue recrystallized from AcOEt/pentane 1:3 yielding 0.22 g (96%) of colourless crystals, m.p. 186–187°. – IR. (KBr): 3060, 2970, 2960, 2880, 1780, 1700, 1600, 1500, 1430, 1310, 1150, 770. – ^{1}H-NMR. ($(CD_3)_2CO$): 7.5 (*m*, 5 H); 6.4 (*m*, 2 H); 4.2 (br. *s*, 1.54 H, H_{exo}–C(3),H_{exo}–C(9)); 4.15 (br. *s*, 0.46 H, H_{endo}–C(3),H_{endo}–C(9)); 3.6 (*m*, 2 H); 1.4 (*m*, 4 H). – MS. (70 eV): 309 (81), 308 (< 1), 281 (59), 205 (22), 149 (68), 137 (24), 133 (25), 125 (51), 123 (52), 119 (48), 111 (70), 109 (67), 105 (82), 97 (100), 95 (84).

Diels-Alder *adduct of TCE to* **11**: *(3,6-D_2)tricyclo[6.2.2.0^{2,7}]dodeca-2(7),9-diene-4,4,5,5-tetracarbonitrile* (**15**). A mixture of triene **11** (0.1 g, 0.75 mmol) and freshly sublimed TCE (0.096 g, 0.75 mmol) in anh. benzene (2 ml) was stirred at 20° for 1 h. After evaporation of the solvent *i.v.*, the residue was recrystallized from pentane/CH_2Cl_2 1:9 yielding 0.187 g (95%), white powder, m.p. 165–166°. – IR. (KBr): 3060, 2960, 2880, 2260, 1610, 1465, 1450, 1260, 1110, 880, 830, 720. – ^{1}H-NMR. ($(CD_3)_2CO$): 6.35 (*m*, 2 H); 3.6 (*m*, 2 H); 3.5 (br. *s*, 1.3 H, H_{exo}–C(3),H_{exo}–C(6)); 3.42 (br. *s*, 0.7 H, H_{endo}–C(3),-H_{endo}–C(6)); 1.4 (*m*, 4 H). – MS. (70 eV): 262 (10), 261 (0.2), 260 (0.2), 235 (21), 234 (82), 233 (27), 232 (12), 208 (8), 207 (10), 206 (9), 205 (6), 181 (15), 180 (13), 179 (12), 155 (18), 156 (17), 155 (15), 107 (28), 106 (100), 105 (36).

Diels-Alder *adduct of DMAD to* **11**: *dimethyl (3,6-D_2)tricyclo[6.2.2.0^{2,7}]dodeca-2(7),4,9-triene-4,5-dicarboxylate* (**16**). A mixture of freshly distilled DMAD (0.106 g, 0.75 mmol) and **11** (0.1 g, 0.75 mmol) in Et_2O (3 ml) was stirred at 20° for 48 h. After evaporation of the solvent, the residue was recrystallized from AcOEt/pentane 1:3 yielding 0.196 g (95%) of colourless crystals, m.p. 64–65°. – IR. (KBr): 3080, 3060, 3010, 2960, 2940, 2880, 1730, 1645, 1450, 1440, 1430, 1330, 1270, 1160, 1070, 695. – ^{1}H-NMR. ($(CD_3)_2CO$): 6.3 (*m*, 2 H); 3.7 (*s*, 6 H); 3.4 (*m*, 2 H); 3.1 (*m*, 0.76 H, H_{endo}–C(3),H_{endo}–C(6)); 3.0 (*m*, 1.24 H, H_{exo}–C(3),H_{exo}–C(6)); 1.3 (*m*, 4 H). – MS. (70 eV): 276 (9), 275 (< 0.1), 245 (28), 244 (36), 243 (21), 217 (18), 216 (98), 215 (100), 214 (51), 213 (10), 189 (12), 158 (8), 157 (31), 156 (25), 130 (62), 129 (52), 128 (38), 105 (18), 97 (21), 95 (20); see [53] for the unlabelled adduct.

Diels-Alder *adducts of MA to* **11**: *(3,6-D_2)tricyclo[6.2.2.0^{2,7}]dodeca-2(7),9-diene-4,5-dicarboxylic anhydride* (**17**/**18**). A mixture of freshly sublimed MA (0.75 g, 0.76 mmol) and **11** (0.1 g, 0.75 mmol) in anh. benzene (2 ml) was stirred at 40° for 15 h. Evaporation of the solvent gave crude **17**/**18** (0.167 g, 97%). Three recrystallization from AcOEt yielded 0.052 g (30%) of pure **17**, colourless crystals,

m.p. 147–148°. – IR. (KBr): 3070, 2980, 2960, 2880, 1840, 1770, 1710, 1600, 1420, 1340, 1315, 1225, 1195, 1070, 1005, 990, 935, 915, 840, 725, 700. – ^{1}H-NMR. ($CDCl_3$): 6.27 (*m*, 2 H); 3.40 (*m*, 2 H); 3.30 (*m*, 2 H); 2.65 (br. *s*, 1.2 H, H_{exo}–C(3),H_{exo}–C(6)); 2.50 (*m*, 0.8 H, H_{endo}–C(3),H_{endo}–C(6)); 1.2 (*m*, 4 H). – MS. (70 eV): 232 (9), 231 (<0.1), 230 (<0.1), 205 (7), 204 (46), 203 (6), 178 (10), 174 (100), 159 (7), 158 (6), 157 (6), 133 (41), 132 (91), 131 (71), 107 (34), 109 (29).

The 360-MHz-^{1}H-NMR. of the 3:2 mixture of **17/18** showed the following signals attributed to **18**: 6.31 (*m*); 3.42 (*m*); 3.33 (*m*); 2.60 (br. *s*, 0.8 H, H_{endo}–C(3),H_{endo}–C(6)); 2.55 (*m*, 1.2 H, H_{exo}–C(3),H_{exo}–C(6)); 1.25 (*m*, 4 H).

The undeuterated adduct **17** was obtained according to the same procedure, using unlabelled **11** [52]. – ^{1}H-NMR. (360 MHz, $CDCl_3$): 6.27 (*d*×*d*, *J* = 4.4, 2.8, 2 H); 3.40 (*t*×*d*×*d*×*d*, *J* = 3.0, 4.4, 2.8, 1.2, 2 H); 3.30 (*m*, *J* = 4.4, 2.0, 1.9, 2 H, H_{endo}–C(4),H_{endo}–C(5)); 2.65 (*d*×*m*, *J* = 15.6, 2.0, 2 H, H_{exo}–C(3),H_{exo}–C(6)); 2.50 (*d*×*m*, *J* = 15.6, 4.4, 1.9, 2 H, H_{endo}–C(3),H_{endo}–C(6)); 1.2 (*m*, 4 H).

$C_{14}H_{14}O_3$ (230.264) Calc. C 73.03 H 6.13% Found C 73.08 H 6.08%

4,5-Dioxa(3,6-D$_2$)tricyclo[6.2.2.0^{2,7}]dodeca-2(7),9-diene (**19**). A solution of **11** (0.5 g, 3.7 mmol) in CH_2Cl_2 (200 ml) containing 5,10,15,20-tetraphenylporphin (15 mg, 0.025 mmol) was continuously saturated with O_2 and irradiated with a iodine lamp (*Phillips*, 24 V/10 A) in a pyrex vessel (20°) for 1 h. After solvent evaporation *i.v.*, the residue was purified by column chromatography on silica gel ($CHCl_3$/hexane 1:1) yielding 0.3 g (48%) of a colourless oil. – IR. ($CHCl_3$): 2990, 2920, 2880, 1580, 1465, 1380, 1345, 1260, 1150, 1120, 1030, 990, 900. – ^{1}H-NMR. ($(CD_3)_2CO$): 6.45 (*d*×*d*, 2 H); 4.68 (*m*, 1 H); 4.62 (*m*, 1 H); 3.6 (*m*, 2 H); 1.45 (*m*, 4 H). – MS. (70 eV): 166 (18), 165 (<0.5), 164 (<0.5), 138 (18), 135 (6), 134 (13), 122 (11), 120 (13), 119 (12), 108 (12), 107 (99), 106 (42), 105 (16), 104 (12), 103 (8), 93 (32), 92 (67), 91 (62), 81 (10), 80 (63), 79 (100).

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