82. Face Selectivity of the *Diels-Alder* Additions of Exocyclic Dienes Grafted onto 7-Oxabicyclo[2.2.1]heptanes[1][2])

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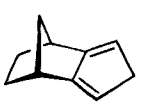
Summary

Stereoselective syntheses of 2*exo*,3*exo*-bis(chloromethyl)-5-[(*Z*)-chloromethylidene]- (**9**), 2*exo*,3*exo*-bis(chloromethyl)-5-[(*E*)-chloromethylidene]- (**10**) and 2*exo*,3*exo*-bis(chloromethyl)-5-[(*E*)-methoxymethylidene]-6-methylidene-7-oxabicyclo[2.2.1]heptane (**13**) are presented. Double elimination of HCl from **9**, **10** and **13** yielded 2-[(*Z*)-chloromethylidene]- (**14**), 2-[(*E*)-chloromethylidene]- (**15**) and 2-[(*E*)-methoxymethylidene]-3,5,6-trimethylidene-7-oxabicyclo[2.2.1]heptane (**18**), respectively, without loss of the olefin configuration. Ethylene tetracarbonitrile (TCE) and *N*-phenyltriazolinedione (NPTAD) added to these new exocyclic dienes and tetraenes preferentially onto their *exo*-face. The same face selectivity was observed for the cycloadditions of TCE to the (*Z*)- and (*E*)-chlorodienes **9** and **10**, thus realizing a case where the kinetic stereoselectivity of the additions is proven not to be governed by the stability of the adducts. The *exo*-face selectivity of the *Diels-Alder* additions of dienes grafted onto 7-oxabicyclo[2.2.1]heptanes contrasts with the *endo*-face selectivity reported for a large number of cycloadditions of dienes grafted onto bicyclo[2.2.1]heptane skeletons.

Introduction. – The face stereoselectivity of the *Diels-Alder* cycloadditions to cyclopentadiene annelated to 2-bicyclo[2.2.1]heptene (=norbornene) has been studied first by *Alder et al.* [3]. They reported that maleic anhydride adds to cyclo-



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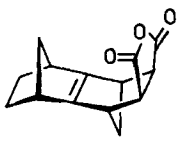

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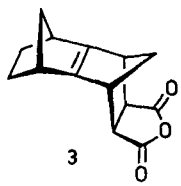

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[1]) Interaction between non-conjugated chromophores, Part 16; Part 15, see [1]. An exocyclic butadiene moiety means that each double bond is in an exocyclic position on the ring skeleton.

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

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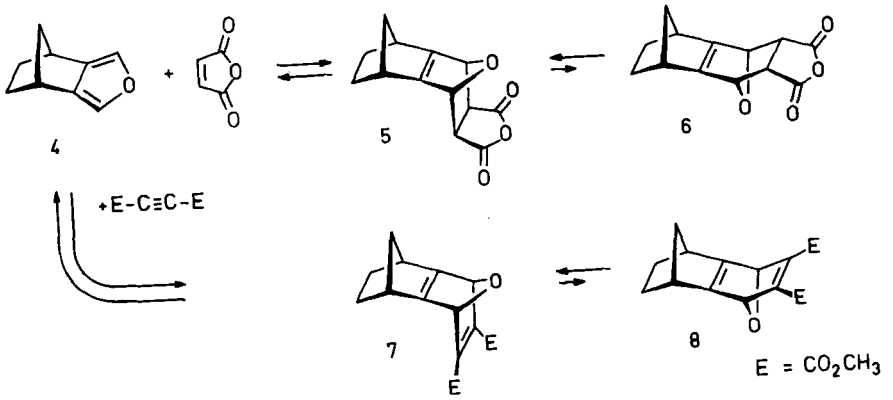

penta[*b*]norbornene (= 4,7-methano-4,5,6,7-tetrahydro-2*H*-indene **1**) preferentially onto the *exo*-face giving **2**. Twenty years later, *Sugimoto et al.* found methyl acrylate and methyl propynoate to add to **1** with *endo*-face selectivity [4]. Recently, *Paquette et al.* confirmed *Sugimoto's* conclusions in contradiction with *Alder*'s report [5]. *Bartlett et al.* pointed out, however, that the *endo-vs. exo*-face selectivity in the reaction of **1** with maleic anhydride varied between 55:45 and 35:65 (giving **2** and **3**) depending upon the solvent and the temperature [6]. *Paquette et al.* attributed the *endo*-face selectivity of the cycloadditions of **1** to a kinetic stereoelectronic control involving secondary orbital interactions between the dienes and dienophiles [5].

We reported that the additions of maleic anhydride and dimethyl acetylenedicarboxylate to (2-norborneno)[*c*]furan (**4**) were highly *endo*-face selective under kinetic and thermodynamic control. The *syn*-11-oxasesquinorbornenes **5** and **7** appeared to the more stable than their *anti*-isomer **6** and **8** [2] [7][4]). This was attributed [7] to a 'synergic' effect of the polarization of the double bond π-electron density in the *exo*-face of the 2-bicyclo[2.2.1]heptene and 7-oxabicyclo[2.2.1]hept-2-ene subsystems joined together by the same C(2),C(7) double bond [6] [8]. Thus, the kinetic *endo*-face *Diels-Alder* selectivity of **4** was parallel to the thermodynamic stereoselectivity, in agreement with the *Bell-Evans-Polanyi* principle [9]. This might also be the case with at least some of the additions of **1**. To our knowledge, there has been until now no case of diene grafted onto a bicyclic skeleton [5–7] [10] where the kinetic face selectivity of its cycloadditions had been proven *not* to be governed by the stability of the adducts.

We have prepared stereospecifically substituted exocyclic *s-cis*-butadienes[1]) grafted onto 7-oxabicyclo[2.2.1]heptanes (**9–18**). We report the *exo*-face selectivity of the additions of ethylenetetracarbonitrile (TCE, tetracyanoethylene) to the dienes **9**, **10**, and **13** and to the tetraene **18**. The addition of *N*-phenyltriazolinedione (NPTAD) occurred also preferentially on the *exo*-face of the (*E*)-methoxydiene **13**.

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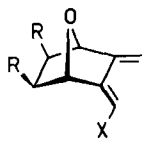
[4]) The name 'sesquinorbornene' is generally used for 1,4:5,8-dimethano-1,2,3,4,5,6,7,8-octahydronaphthalene [5] [6]. We use the IUPAC numbering derived from tetracyclo[6.2.1.$1^{3,6}$.$0^{2,7}$]dodec-2(7)-ene. The prefixes *syn* and *anti* refer to the relative position of the methano bridges (C(11) and C(12) or O(12)) with respect to each other.

Synthesis of substituted exocyclic dienes and tetraenes. – The synthesis of 2*exo*, 3*exo*, 5*exo*, 6*exo*-tetrakis(chloromethyl)-7-oxabicyclo[2.2.1]heptane (**19**) has been described previously [11]. Quadruple elimination of HCl led to the tetraene **20** [11], a useful synthon for the preparation of polycyclic, polyfunctional systems including the anthracyclines [12]. Under controlled conditions, double elimination of HCl giving the conjugated diene **21** can be achieved [13]. In order to generate substituted dienes such as **9**–**13** we considered the classical technique that starts with the addition of XY to the diene **21** followed by the elimination of HX or HY.

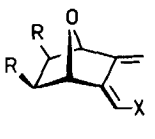
When heated with an excess of ICl [14], **21** furnished the tetrachloride **22** in low yield (*ca.* 10%) together with several unidentified products, including polymers. Direct chlorination with chlorine [15] or $SbCl_5$ [16] were even less successful. The diene **21** added one equivalent of bromine in CCl_4 at 0° and gave the dibromide **23** in moderate yield (37%). The bromine atoms of the latter were readily displaced by methanol (THF, K_2CO_3) to give **24** (85%) or by acetic acid (AcOH/AcOK) yielding **25** (80%). Attempts to eliminate AcOH from **25** thermally (gas phase or in the presence of $Pd(OAc)_2/Ph_3P$ [17]) failed to give the expected acetoxydienes.

Elimination of one equivalent of HBr from **23** could be achieved by heating **23** in DMF in the presence of an excess of CsF [18] or by treatment in THF with potassium *t*-butoxide (*t*-BuOH) at 20° (5 min). Under these conditions, 1:1 mixtures of the (*Z*)- and (*E*)-bromodienes **11** and **12**, respectively, were obtained. These compounds were unstable and could not be purified by the usual preparative techniques. Polymerization was fast even in highly diluted solutions.

Monoepoxidation of the diene **21** (*m*-chloroperbenzoic acid/CH_2Cl_2) gave a mixture of the *exo*/*endo*-monoepoxides **26**. When treated with $SOCl_2$ and pyridine in $CHCl_3$ (60°, 2 h), **26** was chlorinated to **22** in a relatively good yield (75–80%). Selective elimination of one equivalent of HCl (*t*-BuOK, THF, 20°, 1 h) yielded a



X = Cl **9**
X = Br **11**
X = OCH_3



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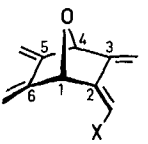
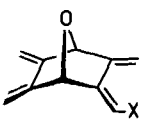
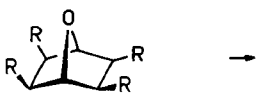
12
13



14
16



15
17
18
X = H **20**



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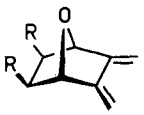

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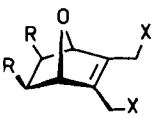
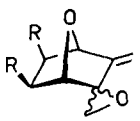
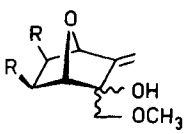


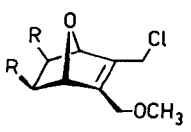
X = Cl **22**
X = Br **23**
X = OCH_3 **24**
X = OAc **25**



26



27



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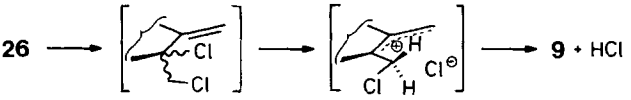
R = $ClCH_2$

1:1 mixture of the (*Z*)- and (*E*)-chlorodienes **9** and **10**, respectively. Pure **9** was obtained directly by treatment of the epoxides **26** with $SOCl_2$ in $CHCl_3$ (without pyridine, 60°, 2 h).

Methanolysis (MeONa, MeOH, 25°, 5 h) of **26** yielded the alcohols **27** (94%) that furnished the oxanorbornene **28** (77%) upon treatment with $SOCl_2$/pyridine (CCl_4, 60°, 30 min). Selective elimination of one equivalent of MeOH or HCl from **28** (*t*-BuOK, THF, 20°, 1 h) gave a 21:29 mixture of the (*E*)-chlorodiene **10** and (*E*)-methoxydiene **13**, respectively, with no detectable amount of the (*Z*)-isomers. These compounds were easily separated and purified by column chromatography on silica gel.

The stereoselectivity of the reaction **26** + $SOCl_2$ → **9** contrasts with that of the eliminations **28** → **10** + MeOH and **28** → **13** + HCl. The treatment of the epoxides **26** with $SOCl_2$ generates probably 1,2-dichloro intermediates that can undergo a *E*1 elimination of HCl generating the most stable chlorodiene **9**. It is possible also that the (*E*)-isomer **10**, if generated, undergoes isomerization to **9** under the above acidic conditions. We found that **10** could be isomerized to **9** by heating (120°) in chlorobenzene in the presence of iodine. Equilibrium could not be reached because **9** was decomposed faster than **10** under these conditions.



In the cases of **28** → **10** and **28** → **13**, the less stable (*E*)-olefins are generated. This suggests reactions under kinetic control that imply the assistance by the OMe group and Cl-atom. It is conceivable to admit coordination of the potassium ion by these functions, as shown below. With **22** and **23**, the coordination of the potassium cation is weaker than with **28** (absence of MeO group), thus leading to a loss of the (*E*)-selectivity in the elimination of HCl and HBr, respectively[5]).

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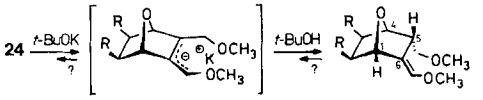
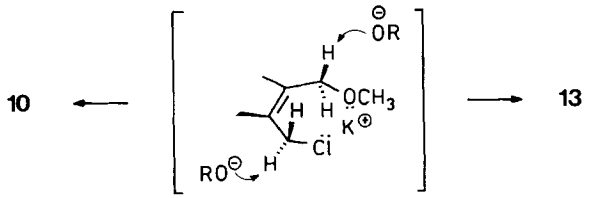
[5]) In the presence of one equivalent of *t*-BuOK in THF at 20° (2 h) the double methoxyallylic derivative **24** was isomerized *stereospecifically* into 2*exo*,3*exo*-bis(chloromethyl)-5*endo*-methoxymethyl-6-[(*E*)-methoxymethylidene]-7-oxabicyclo[2.2.1]heptane (**ii**).

The (*E*)-olefin **ii** was stable under the above conditions, it did not equilibrate with **24**, its (*Z*)-isomer or 5*exo*-methoxymethyl-substituted analogs. The structure of **ii** was established by its ^{1}H-NMR. (80 MHz) spectrum that showed a typical vicinal coupling (J = 4 Hz) between H–C(4) and H*exo*–C(5) and an allylic coupling (J = 2 Hz) between H–C(5) and *H*C(OMe)=C(6). Irradiation of the signal at 6.15 ppm (*H*C(OMe)=C(6)) led to the observation of a nuclear *Overhauser* effect (NOE) of 12% at the signal (δ = 4,85 ppm) of H–C(1).

The facile rearrangement **24** → **ii** confirms the hypothesis of the coordination of the potassium cation by the allylic methoxy groups. Contrary to what was observed with **28**, elimination of MeOH did not occur, even under 'forcing' conditions (excess of *t*-BuOK, heating). This could be attributed to the better solvation of K^+ by the CH_3OCH_2- *vs.* $ClCH_2$-groups, thus making the hypothetical intermediate **i** 'overstabilized' and the elimination of MeOK too difficult.





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When treated with an excess of *t*-BuOK in THF, the dienes **9–13** gave the corresponding exocyclic tetraenes **14–18**, respectively. The bromo derivatives **16** and **17** could not be obtained in a pure form because they polymerized rapidly at room temperature.

Structure of the exocyclic dienes and tetraenes. – The structure of the new olefins **9–18** was determined by their mode of formation, by their additions to strong dienophiles (see below), by elemental analysis, by their spectral data and by comparison of them with those of **20** and **21** and other exocyclic dienes [19] [20]. The UV. spectra of the dienes **9**, **10**, **13** and **21** are reproduced in *Figure 1*, those of

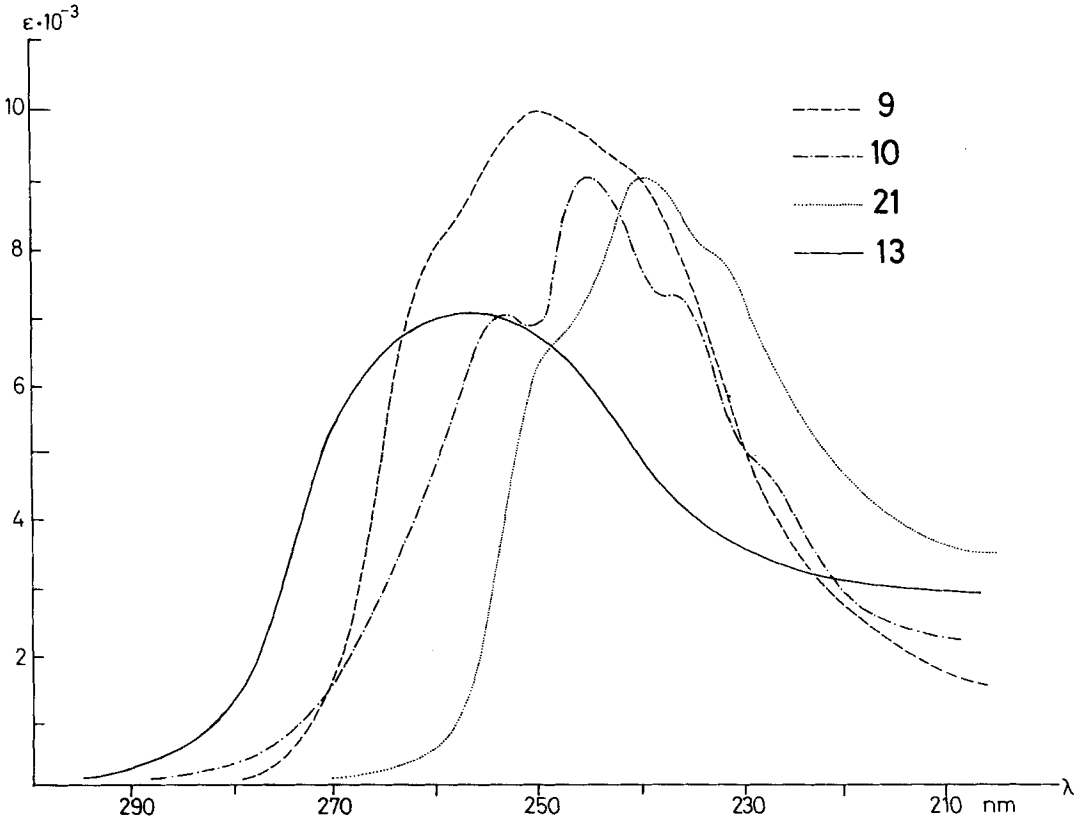


Fig. 1. *UV. absorption spectra of dienes* **9**, **10**, **13** *and* **21** *in EtOH/H₂O 95:5*

the tetraenes **14**, **15**, **18** and **20** in *Figure 2*. As expected, the substitution of the *s-cis*-butadiene **21** by a Cl-atom induces a bathochromic shift [21]. It is larger (10 nm) in the case of the (*Z*)-chlorodiene **9** than for the (*E*)-isomer **10** (5 nm). This is probably due to out-of-plane deformation in the latter diene because of repulsive interactions between the Cl- and an H-atom of the diene moiety of **10**.

Similar effects were also observed when comparing the UV. spectra of the chlorotetraenes **14** (+6 nm) and **15** (+3 nm) with that of **20** (λ_{max}=228 nm, see *Fig. 2*). The relatively large bathochromic shift observed for the methoxy substituent effect when comparing the (*E*)-olefins **13** *vs.* **21** (+18 nm) and **18** *vs.* **20** (+7 nm) suggests that the out-of-plane deformation of the (*E*)-methoxydienes **13** and **18** is smaller than that in the (*E*)-chlorodienes **10** and **15**, in agreement with the smaller bulk of the O- *vs.* Cl-atom [22]. The smaller substituent effects observed in the case of the tetraenes **14**, **15** and **18** compared with those in the dienes **9**, **10** and **13**,

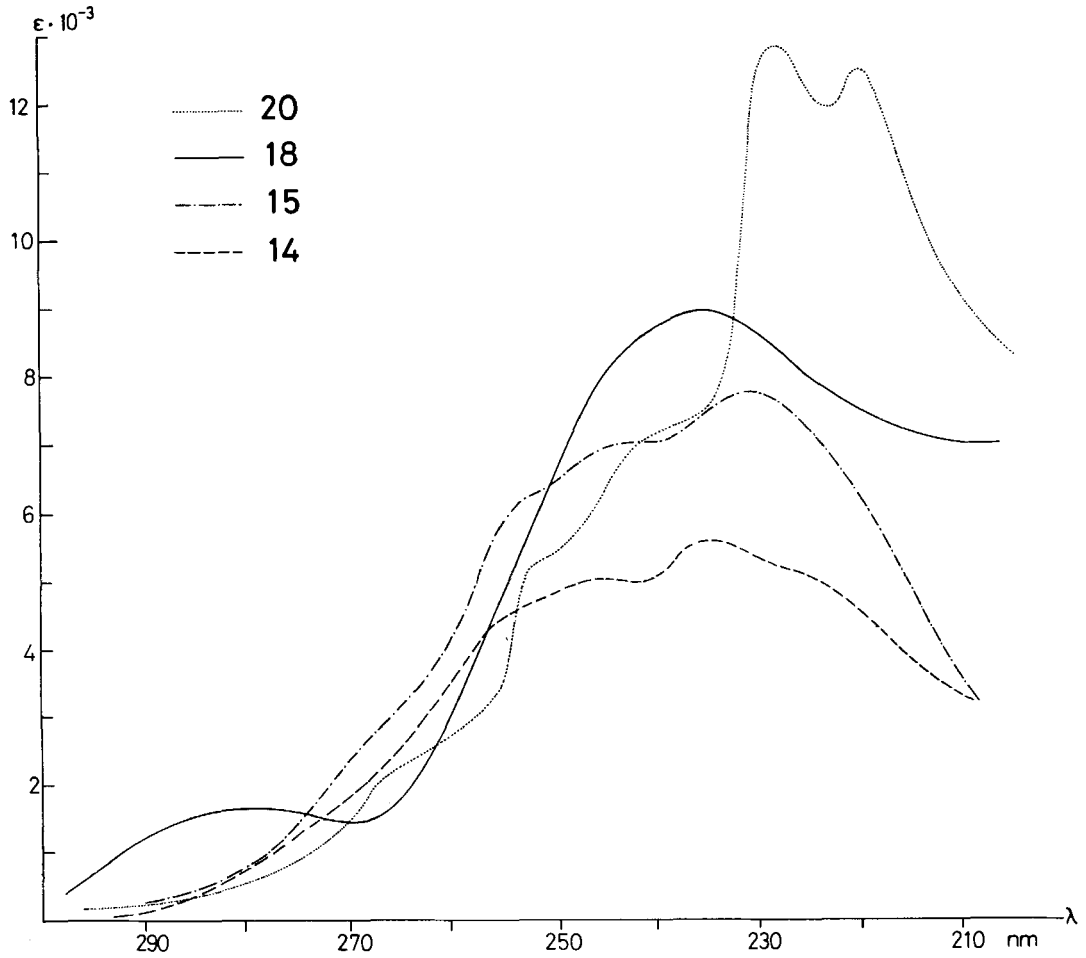


Fig. 2. *UV. absorption spectra of tetraenes* **14**, **15**, **18** *and* **20** *in EtOH/H_2O 95:5*

Table 1. *^{13}C-NMR. data of the dienes* **21**, **9**, **10** *and* **13**, *tetraenes* **14**, **15**, **18** *and* **20**, *and oxanorbornenes* **22**–**25** *and* **28**. Chemical shifts in ppm (±0.1 ppm; $\delta_{TMS} = 0.0$ ppm, $CDCl_3$ as solvent and deuterium lock); ^1J(C,H) in Hz (± 1 Hz, otherwise indicated).

Chemical shifts of	C(1)	C(2)	*C* at C(2)	C(3)	*C* at C(3)	C(4)	C(5)	*C* at C(5)	C(6)	*C* at C(6)	others
21[6])	84.8 *d*×*m*, *J* = 156	146.4 br. *s*	102.3 *t*, *J* = 161	146.4 br. *s*	102.3 *t*; *J* = 161	84.8 *d*×*m*, *J* = 156	49.5 *d*×*m*, *J* = 140	42.5 *t*×*m*, *J* = 149	49.5 *d*×*m*, *J* = 140	42.5 *t*×*m*, *J* = 149	-
9[6])	82.1	141.0 br. *s*	109.8 *d*, *J* = 197	144.9 br. *s*	102.2 *t*, *J* = 160	85.0 *d*×*m*, *J* = 160 ± 5	49.3[b]) *d*×*m*, *J* = 138	42.3 *t*×*m*, *J* = 150	48.3[b]) *d*×*m*, *J* = 138	42.1 *t*×*m*, *J* = 150	-
10[6])	84.3[a]) *d*×*m*, *J* = 158 ± 5	138.8 br. *s*	112.4 *d*, *J* = 196	144.7 br. *s*	110.4 *d*×*d*, *J* = 157 and 163	85.6[a]) *d*×*m*, *J* = 164 ± 5	49.3 *d*×*m*, *J* = 140	42.2 *t*×*m*, *J* = 152	49.3 *d*×*m*, *J* = 140	42.2 *t*×*m*, *J* = 152	-
13[6])	82.3 *d*×*m*, *J* = 162	117.5 br. *s*	142.7 *d*, *J* = 176	145.3 br. *s*	105.0 *d*×*d*, *J* = 157 and 164	85.5 *d*×*m*, *J* = 166	50.6[b]) *d*×*m*, *J* = 138	42.7 *t*×*m*, *J* = 152	49.5[b]) *d*×*m*, *J* = 141	42.7 *t*×*m*, *J* = 152	60.6 *qa*×*d*, *J* = 144 and 6
14	86.3[a]) *d*×*m*, *J* = 159 ± 5	140.6 br. *s*	110.3 *d*, *J* = 196	144.0 br. *s*	102.6 *t*, *J* = 160	82.9[a]) *d*×*m*, *J* = 168 ± 5	144.8[b]) br. *s*	103.2[c]) *t*, *J* = 160	145.6[b]) br. *s*	103.3[c]) *t*, *J* = 160	-
15	86.8[a]) *d*×*m*, *J* = 158 ± 5	144.8 br. *s*	112.8 *d*, *J* = 197	145.5 br. *s*	110.7 *d*×*d*, *J* = 157 and 163	85.2[a]) *d*×*m*, *J* = 158 ± 5	145.5[b]) br. *s*	103.1 *t*, *J* = 160	146.0[b]) br. *s*	103.1 *t*, *J* = 160	-
18	86.7[a]) *d*×*m*, *J* = 160	117.2 br. *s*	143.1 *d*, *J* = 175	146.7[b]) br. *s*	105.4 *d*×*d*, *J* = 157 and 163	83.4[a]) *d*×*m*, *J* = 160	146.6[b]) br. *s*	100.9 *t*, *J* = 160	146.2[b]) br. *s*	102.2 *t*, *J* = 160	60.5 *qa*×*d*, *J* = 144 and 6
20[d])	85.6 *d*×*m*, *J* = 163	145.7 br. *s*	102.7 *t*, *J* = 160	145.7 br. *s*	102.7 *t*, *J* = 160	85.6 *d*×*m*, *J* = 163	145.7 br. *s*	102.7 *t*, *J* = 160	145.7 br. *s*	102.7 *t*, *J* = 160	-
22	84.3 *d*×*m*, *J* = 165	141.3 br. *s*	35.4 *t*, *J* = 152	141.3 br. *s*	35.4 *t*, *J* = 152	84.3 *d*×*m*, *J* = 165	45.9 *d*×*m*, *J* = 141	43.5 *t*×*m*, *J* = 148	45.9 *d*×*m*, *J* = 141	43.5 *t*×*m*, *J* = 148	-
23	84.8 *d*×*m*, *J* = 166	141.7 br. *s*	21.3 *t*, *J* = 154	141.7 br. *s*	21.3 *t*, *J* = 154	84.8 *d*×*m*, *J* = 166	46.2 *d*×*m*, *J* = 139	43.5 *t*×*m*, *J* = 150	46.2 *d*×*m*, *J* = 139	43.5 *t*×*m*, *J* = 150	-
24	83.6 *d*×*m*, *J* = 162	141.5 br. *s*	65.5 *t*×*qa*, *J* = 141 and 5.5	141.5 br. *s*	65.5 *t*×*qa*, *J* = 141 and 5.5	83.6 *d*×*m*, *J* = 162	45.5 *d*×*m*, *J* = 139	43.7 *t*×*m*, *J* = 146	45.5 *d*×*m*, *J* = 139	43.7 *t*×*m*, *J* = 146	58.2 *qa*×*t*, *J* = 141 and 4
25	83.5 *d*×*m*, *J* = 165	140.2 br. *s*	57.2 *t*, *J* = 149	140.2 br. *s*	57.2 *t*, *J* = 149	83.5 *d*×*m*, *J* = 165	45.3 *d*×*m*, *J* = 137	43.5 *t*×*m*, *J* = 150	45.3 *d*×*m*, *J* = 137	43.5 *t*×*m*, *J* = 150	170.2; 20.9 br. *s* *qa*, *J* = 130
28[6])	84.1[a]) *d*×*m*, *J* = 157	143.1[b]) br. *s*	65.8 *t*×*qa*, and 5.0	139.4[b]) br. *s*	36.3 *t*, *J* = 152	83.6[a]) *d*×*m*, *J* = 159	45.9[c]) *d*×*m*, *J* = 135	43.6 *t*×*m*, *J* = 148	45.4[c]) *d*×*m*, *J* = 136	43.6 *t*×*m*, *J* = 148	58.5 *qa*×*t*, *J* = 144 and 6.0

[a]) [b]) [c]) Pairs of signals whose attributions can be interconverted.

[d]) Long-range coupling constants ^3J(C(1),H–C(4)) = 6 Hz, ^3J(C(1),*H*CH=C(2) *cis* to C(1),C(2)) = 6 Hz, ^3J(C(1),HC*H*=C(2) *trans* to C(1),C(2)) = 12 Hz.

respectively, must be attributed to the complex nature of the electronic spectra of the tetraenes (superposition of at least two transitions).

^{1}H- and ^{13}C-NMR. spectra (s. *Table 1*) allowed to distinguish between the (*E*)- and (*Z*)-configurated exocyclic dienes.

Irradiation of the proton signal of the HC(C1)=C(2) group in the (*Z*)-isomers **9**[6]) and **14** led to significant NOE's [23] on the signals of the *H*CH=C(3) *cis* to the C(2),C(3)-bond. No such NOE was

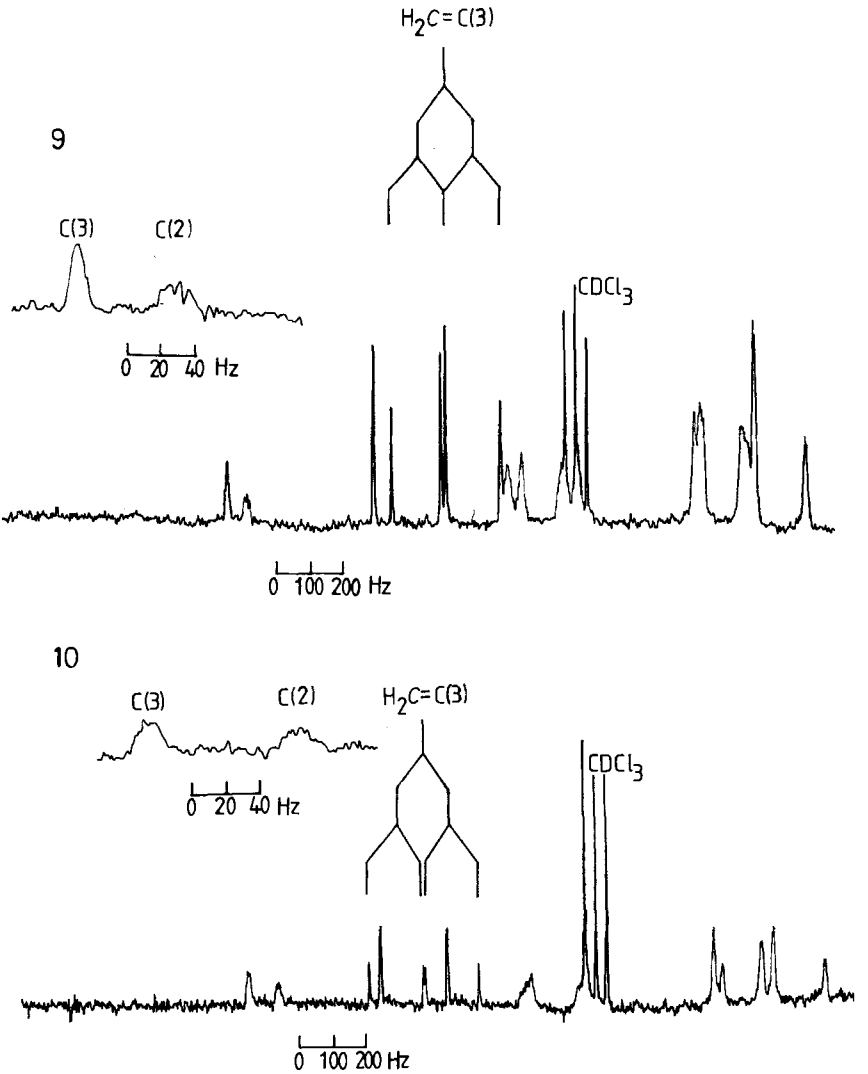
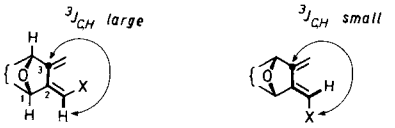


Fig. 3. *Proton-coupled ^{13}C-NMR.* (15.08 MHz, $CDCl_3$) *spectra of dienes* **9** *and* **10**[6])

[6]) For the purpose of an easier discussion compounds **9**–**28** are all numbered in the same way. Systematic numbering of **9**, **10**, **13**, **21**, **26**, and **28** is given in the *Exper. Part.*

observed for the (*E*)-isomers **10**[6]), **13**[6]), **15** and **18**. The *H*CH=C(3) *cis* to C(2),C(3) in **10** and **15** were more deshielded ($\delta > 6$ ppm) than in **9** and **14** ($\delta = 5$–5.5 ppm), respectively, in accordance with the position of the Cl-atom.

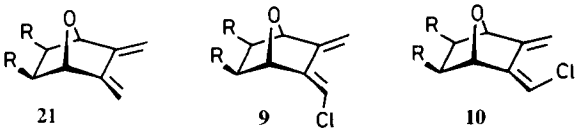
Long-range C,H-couplings ^3J(C,H) in olefins are larger for *trans*- than for *cis*-alignments [24]. Consequently, the ^{13}C-resonance of C(3) is expected to be more decoupled in the (*E*)-configurated exocyclic dienes (*e.g.* **10**) than in the (*Z*)-isomers (*e.g.* **9**), as observed (s. *Fig. 3*). The steric repulsion between the Cl- or MeO-substituents and the *H*CH=C(3) in the (*E*)-olefins **10**, **13**, **15** and **18** renders the ^1J(C,H) significantly different for the two H-atoms of the CH_2=C(3) group [25], thus leading to a $d \times d$ for the CH_2=C(3) signal (s. *Table 1*). A triplet is observed instead for this C-atom in the (*Z*)-isomers **9** and **14** (s. *Fig. 3*, *Table 1*).



'(*E*)-olefins' '(*Z*)-olefins'

Reactivity and face selectivity of the *Diels-Alder* additions. – The stereoselectivity of the additions of TCE to the dienes **9**, **10**, **13** and tetraene **18** and of *N*-phenyltriazolinedione (NPTAD) to **13** are reported in *Table 2*. In all five reactions the *exo*-face was preferred in contrast with the *endo*-face selectivity reported for the *Diels-Alder* additions of cyclopentadiene [4] [5] and furan [2] [7] annulated to bicyclo-[2.2.1]heptane systems.

As expected for a *s-cis*-butadiene substituted by an electron-rich substituent, TCE added faster to the methoxydiene than to the non-substituted diene moiety of the tetraene **18**, giving the monoadducts **33** and **34** in good yield (85%) in the presence of one equivalent of the dienophile. Confirming the above results, TCE added to **13** about 10–50 times faster than to **21**. Preliminary kinetic measurements[7]) showed the chlorodienes **9** and **10** to be less reactive toward TCE than **21**. Confirming these results, the chlorotetraenes **14** and **15** added TCE selectively onto the non-substituted diene moiety (in the presence of one equivalent of dienophile) giving the corresponding adducts **37** and **38**. The much lower reactivity of **10**



21 **9** **10**

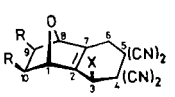
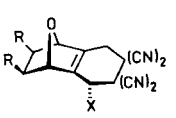
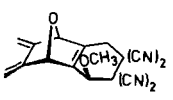
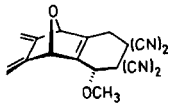
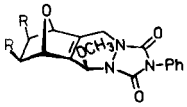
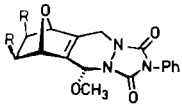
TCE/C_6H_5Cl/60°: $k^{II} \approx 16 \cdot 10^{-5}$ mol^{-1}s^{-1} $k^{II} \approx 3.8 \cdot 10^{-5}$ mol^{-1}s^{-1}

TCE/C_6H_5Cl/130°: $k^{II} \approx 1.1 \cdot 10^{-2}$ mol^{-1}s^{-1} $k^{II} = 1.5 \cdot 10^{-5}$ mol^{-1}s^{-1}

37 **38**

[7]) By GLC. measurement of the disparition of the dienes (mixture of dienes **9**, **10** and **21**; internal standard: tetradecane).

Table 2. *Face selectivity of the* Diels-Alder *additions of TCE to* **9**, **10**, **13** *and* **18**, *and of NPTAD to* **13** (R = $ClCH_2$)

Reaction	Solvent	Temperature	Adduct ratio[a])			Conversion percentage of the diene	Isolated yield of the adducts
9 + TCE	acetone	60°	85:15	**29/30**	X = Cl	> 95%	90%
	o-$C_6H_4Cl_2$	180°	70:30	**29/30**	R = $ClCH_2$	> 95%	78%
10 + TCE	acetone	130°	20:80	**29/30**		10%[b])	8%
	C_6H_5Cl	130°	20:80	**29/30**		10%	~ 5%
	o-$C_6H_4Cl_2$	180°	20:80	**29/30**		> 45%	30%
13 + TCE	acetone	20°	< 3:> 97	**31/32**	X = OMe	> 90%	85%[c])
	benzene	20°	< 3:> 97	**31/32**	R = $ClCH_2$	> 90%	85%[c])
							
18 + TCE	acetone	20°	15:85	**33/34**		> 95%	85%
	benzene	20°	15:85	**33/34**		> 95%	85%
							
13 + NPTAD	benzene	20°	< 3:> 97	**35/36**	R = $ClCH_2$	> 95%	70%[c])
	$CHCl_2$	20°	< 3:> 97	**35/36**		> 95%	75%

[a]) By 360-MHz-^{1}H-NMR. of the reaction mixtures, before isolation of the adducts, ± 10%.

[b]) Low conversion-percentage was necessary to make the isolation of the adducts easy. The latter and the starting diene decomposed competitively under the conditions of the cycloadditions.

[c]) This relatively low isolated yield is due to the competitive polymerization of the starting diene. The ^{1}H-NMR. spectrum of the reaction mixture did not show any signals that could correspond to the minor isomeric adduct.

compared with that of **9** (rate ratio *ca.* 1/730 at 130°, chlorobenzene) can be attributed to the out-of-plane deformation of the (*E*)-chlorodiene **10**, in agreement with the UV. spectra of these compounds (s. above). It has been shown that the larger is the 1,4-distance between the diene C-atoms interacting with a dienophile, the lower is the *Diels-Alder* reactivity [27]. It is plausible also, that the Cl,H-repulsions in the diene moiety of **10** makes the 1,4-distance between the methylidene C-atoms larger in **10** than in **9** and **21**, thus explaining the lower reactivity of **10** *vs.* **9**.

A large reactivity difference between **9** and **10** was also observed for their cycloadditions to NPTAD. While the (*Z*)-chlorodiene **9** could be titrated by a dilute solution of NPTAD at 20°, a 1:1 mixture of **10** and NPTAD in CH_2Cl_2 (~ 0.5 M) was decolorized after 20–30 minutes only (20°). The face selectivity of these cycloadditions could not be established since the corresponding adducts were not stable at 20°, they rearranged quantitatively into the same salt whose structure is under

investigation[8]). The adducts **29**, **30**, **32–34** and **36** *(Table 2)* were not isomerized under the conditions of their formation.

The additions of maleic anhydride and benzoquinone to **9** and **13** were relatively slow reactions. The corresponding *Diels-Alder* adducts were unstable under the conditions of their formation; they underwent competitive eliminations of HCl and MeOH, respectively *(retro-Michael)*.

Discussions. – Because we have observed the same *exo*-face selectivity for the TCE additions to **9** and **10** (within experimental errors), these two reactions represent the first case where the kinetic *Diels-Alder* face selectivity is demonstrated *not* to be controlled by the stability of the adducts. In our view, the following factors must be considered in trying to approach an explanation of the observed stereoselectivities: *1)* the steric hindrance to the attack of the dienophile is larger in the *endo*-face than in the *exo*-face [28], *2)* differential dipole and *3)* polarizability effects of the O(7)- and C(5),C(6)-bridges[6]) on the stability of the *Diels-Alder* transition states, *4)* non-equivalent extension of the π-electron densities (π-anisotropy) [29] due to skeleton-diene and O(7)-diene interactions, and *5)* coordination (formation of charge-transfer complexes) of the dienophiles by the O(7)-atom (entropy and/or enthalpy effects).

Factors 2–4 could be apprehended, in part at least, by MO calculations as suggested by *Paquette et al.* [5] and *Houk et al.* [29b]. Predictions based on the analysis of the shapes and energies of the MO's of our exocyclic dienes and of various dienophiles were rather confusing in our hands because the subHOMO's were numerous and their shapes were not independent upon the calculation techniques [30]. Furthermore, the usual qualitative PMO approaches [5] [31] became difficult to apply with our non-symmetrical dienes and tetraenes.

The *exo*-face selectivities observed here could be attributed to the steric *factor 1*. Such a hypothesis should also apply to the cycloadditions of cyclopentadiene and furan annelated to bicyclo[2.2.1]heptane skeletons [5–7]. Since *endo*-face selectivity was generally observed in the latter cases, we must invoke, for our additions, the formation of 7-oxabicyclo[2.2.1]heptane-dienophile charge-transfer complexes *(factor 5)*. The ethereal bridge could 'assist' the cycloaddition onto the *exo*-face.

Structures of the *Diels-Alder* adducts. – ^{1}H-NMR. (360 MHz) spectra *(Table 3)* established the configuration of the substituted (Cl, MeO)[9]) cyclohexene-3,3,4,4-tetracarbonitrile moiety of **29**, **30**, **32–34** and of the 1,2,3,6-tetrahydropyridazine-1,2-dicarboxylate moiety of **36**. The proton-signal attributions were confirmed by double irradiation experiments.

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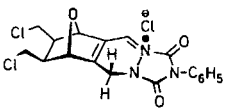
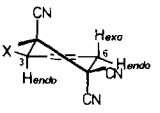
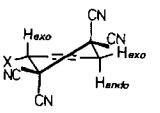
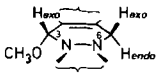
[8]) Preminary spectral data suggest the following structure for this salt:



[9]) We design by *endo* and *exo* the positions at C(3) and C(6) that are *anti* and *syn*, respectively, to the O-bridge of the 11-oxatricyclo[6.2.1.$0^{2,7}$]undec-2(7)-enes (see *Table 2*).

Table 3. *^{1}H-NMR.* (360 MHz) *of the* Diels-Alder *adducts* **29**, **30**, **32–34** *and* **36**. Chemical shifts in ppm (±0.01 ppm; $\delta_{TMS} = 0.0$ ppm, $J(H,H) \pm 0.1$ Hz, FT.-mode, 32768 points, spectrum width 3000 to 3500 Hz, atom numbering, see *Table 2*).

Chemical shifts of								
	29 X = Cl		**33** X = OMe	**30** X = Cl		**32** X = OMe	**34**	**36**
H–C(1)	4.96[a])	5.17[b])	5.33[b])	4.95[a])	5.22[b])	5.17	5.35[b])	5.0
H–(3)		5.14	4.47		5.42	4.85	4.89	5.90
H*endo*–C(6)		3.25	3.05		3.26	3.19	3.10	4.5
H*exo*–C(6)		3.58	3.49		3.54	3.45	3.41	4.4
H–C(8)	4.98	5.09	5.10	5.02	5.03	4.98	5.10	4.90
H*endo*–C(9)		2.20	–		2.21	2.45	–	} 2.3
H*endo*–C(10)		2.18	–		2.19	2.24	–	
$CH_2C(9)$ $CH_2C(10)$		3.7, 3.5	5.45, 5.20		3.7, 3.4	3.72, 3.47	5.46, 5.44 5.21, 5.20	3.5
CH_3O–C(3)		–	3.80		–	3.88	3.88	3.6[c])
$^2J_{Hendo-C(6),Hexo-C(6)}$		18.6	17.8		18.9	19.0	18.4	17
$^5J_{H-C(3),Hendo-C(6)}$		1.8	1.6		3.7	3.0	3.1	0.5
$^5J_{H-C(3),Hexo-C(6)}$		3.7	3.0		2.5	1.5	2.4	2.0
$^5J_{H-C(3),H-C(8)}$		< 0.2	< 0.2		1.1	1.2	1.2	1.3
$^5J_{Hendo-C(6),H-C(1)}$		< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
$^5J_{Hexo-C(6),H-C(1)}$		1.1	1.4	1.2	1.2	1.2	1.3	1.3
$^4J_{H-C(1),H-C(8)}$		1.1	~ 1.0		1.1	1.1	~ 1.0	1.0
$^4J_{Hexo-C(6),H-C(8)}$		0.5	~ 0.4		0.5	0.4	0.5	< 0.2
$^4J_{H-C(3),H-C(1)}$		0.5	0.5		< 0.2	0.5	< 0.2	< 0.2

[a]) In CD_3COCD_3. [b]) In $CDCl_3$. [c]) Moreover, *m* at 7.4 (5 H, arom.).

With **29** in $CDCl_3$, a NOE [23] of *ca.* 20% was recorded at 5.14 ppm (H–C(3)) when irradiating the signal of H*endo*–C(10) at 2.18 ppm. Contrastingly, no such effect was observed for the signals of H–C(3) in **30**, **32** and **36** when irradiating H–C(9)/H–C(10), thus establishing unambiguously the *exo*-position of the chloro-substituent in **29** and the *endo*-position of the chloro- and methoxy-substituents in **30**, **32** and **36**, respectively. Irradiation of H*endo*–C(9) of **36** led to the observation of a 10-20% NOE at H*endo*–C(6) and at bridgehead proton H–C(8); irradiation of H–C(9) and H–C(10) of **29**, **30** and **32** led to a NOE of *ca.* 10% on the bridgehead protons H–C(8) and H–C(1), respectively, thus confirming their signal assignments. Similarly, irradiation of H*endo*–C(6) gave NOE's for H*endo*–C(9). The H*exo*–C(6) of **29**, **30**, and **32–34** was more deshielded than H*endo*–C(6). In the case of **36**, the opposite was observed *(Tab. 3)*.

Long-range homoallylic $^5J(H,H)$ coupling constants [32] between the cyclohexene protons H–C(3) and H–C(6) confirmed the proposed structures, the signal assignments and the half-chair conformation [33] for **29**, **30**, and **32–34**, with the Cl- or MeO-substituent preferring the pseudo-equatorial position [34]. Because of the triazolidinedione annelation, the conformation of the cyclohexene of **36** may deviate significantly from that of a half-chair [35], thus explaining the somewhat different ^{1}H-NMR. characteristics observed for this compound when compared with those of **29**, **30**, and **32–34** *(Table 3)*.

Interestingly, homoallylic coupling constants $^5J(H,H) = 1.1$–1.4 Hz were observed between H–C(1) and H*exo*–C(6) for all our adducts. Contrastingly, the coupling constants between H–C(1) and H*endo*–C(6) were smaller than 0.2 Hz (s. *Table 3*). This difference between the homoallylic coupling constants of H*exo* and H*endo* of the cyclohexene ring realizes another analytical tool that allows to recognize the configuration of the H–C(3) hydrogen atoms. Indeed, in **29** and **33**, ^5J(H*endo*–C(3),H–C(8)) is < 0.2 Hz, whereas in **30**, **32**, **34** and **36** ^5J(H*exo*–C(3), H–C(8)) = 1.1–1.3 Hz (*Table 3, Fig. 4* and *5*).

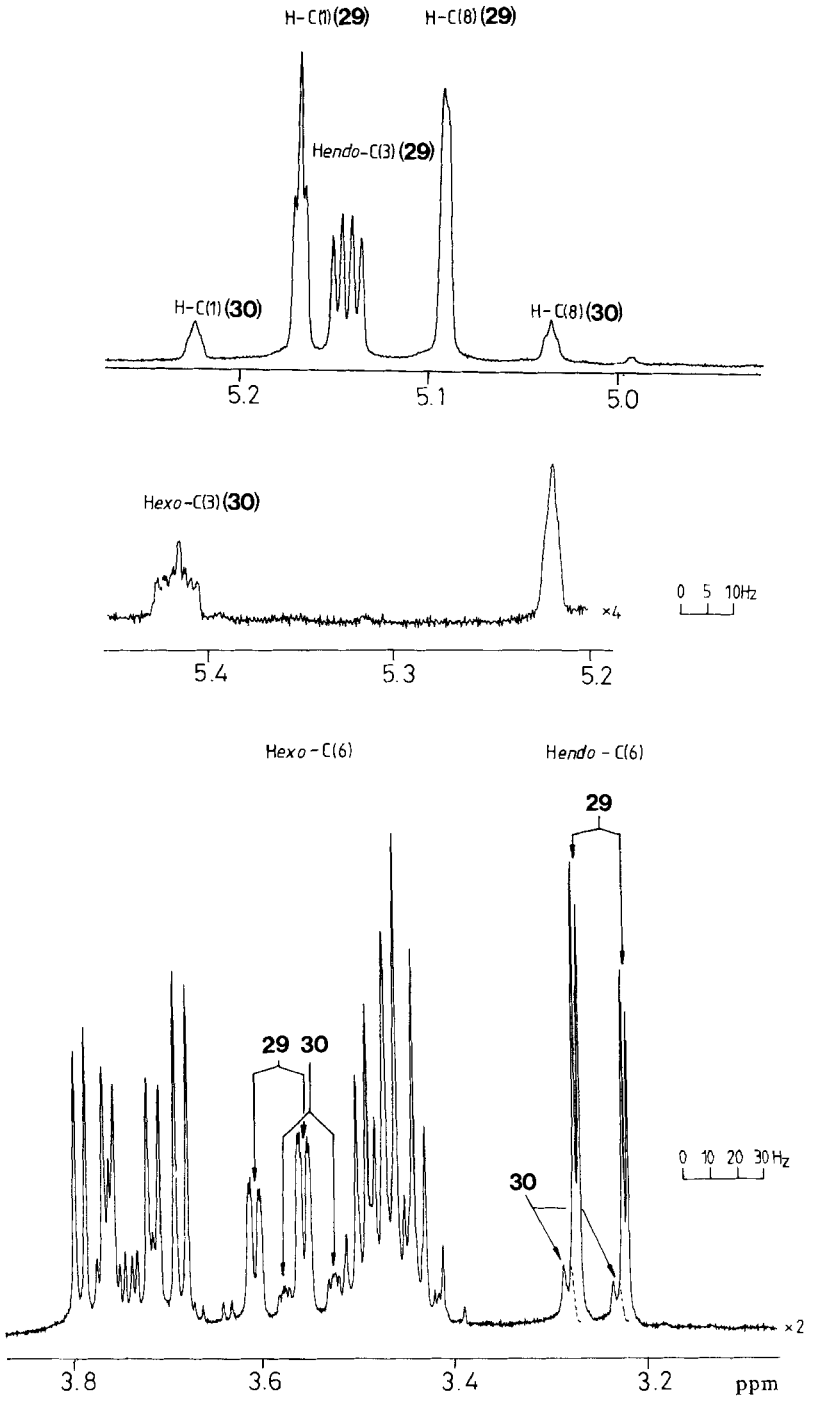


Fig. 4. *^{1}H-NMR.* (360 MHz, $CDCl_3$) *spectrum of the reaction mixture* **9** + *TCE* → **29/30** (85 : 15)

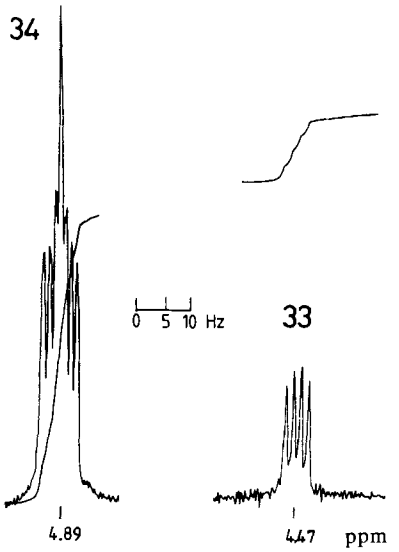


Fig. 5. *Partial ^1H-NMR.* (360 MHz, $CDCl_3$) *spectrum of the reaction mixture* **18** + *TCE* → **33/34** (15:85). The signals of H–C(3) are shown (compare with those of **29** and **30**, *Fig. 4*).

The configuration of the adducts **33** and **34** was based on this criterium (there are no *Hendo*–C(9)/*Hendo*–C(10) protons that can be irradiated to observe NOE's at the H–C(3)/H–C(6) signals) and by comparison of the other ^{1}H-NMR. characteristics with those of **29** and **30** *(Fig. 4* and *5, Table 3)*. It was confirmed by double elimination of HCl (*t*-BuOK, THF, 25°) from **32** that gave **34** together with decomposed products arising probably from the competitive elimination of MeOH and HCN. No trace of **33** could be detected in the reaction mixture.

Conclusion. – Exocyclic dienes grafted onto 7-oxabicyclo[2.2.1]heptanes add strong dienophiles preferentially onto their *exo*-face, in contrast with the *endo*-face selectivity observed generally for the cycloadditions of cyclopentadiene and furan annelated to bicyclo[2.2.1]heptanes. The TCE-additions to the (*Z*)- and (*E*)-chloro-dienes **9** and **10**, respectively, showing the same face selectivity[10]), realize the first case where the kinetic stereoselectivity is proven *not* to be governed by the stability of the adducts. Numerous factors can intervene and command the intriguing face selectivity of these reactions. More experimental results are required to approach a general predictive model. The stereoselective syntheses of new exocyclic dienes and tetraenes have been developped. These compounds should become useful synthetic intermediates because of their stereoselective *Diels-Alder* additions[11]).

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[10]) It should be noted that there is no prerequisite for the same kinetic face selectivity in the cyclo-additions and other reactions of (*E*)- and (*Z*)-chloro- and methoxy-*s-cis*-butadienes grafted onto bicyclic skeletons, eventhough the reactions should have the same exothermicity.

[11]) See for instance the stereoselective addition of benzoquinone to **20** [8].

Experimental Part

General remarks [12b]. The exact molecular masses have been measured with a *Micromass Ltd.* ZAB-2F instrument; we thank Dr. *D. Stahl* and Prof. *T. Gäumann* for these measurements.

Synthesis of 2exo,3exo-bis(chloromethyl)-5,6-dimethylidene-7-oxabicyclo[2.2.1]heptane (**21**). Solid *t*-BuOK (8 g, 70 mmol) was added portionwise to a stirred solution of *2exo,3exo,5exo,6exo-tetrakis(chloromethyl)-7-oxanorbornene* (**19**) [11] (10 g, 34 mmol) in anh. THF (45 ml) maintained at 0°. After stirring at 0° for 30 min, the mixture was allowed to warm to r.t. and stirred for 12 h. After the slow addition of water (100 ml), the mixture was extracted with pentane (50 ml), then with pentane/CH_2Cl_2 2:1 (2 times 75 ml). The organic phases were united and washed with water (6 times 50 ml), decolorized with charcoal and dried ($MgSO_4$). After removal of the solvent *i.v.*, the residue was stirred with pentane (120 ml) for 2 h at r.t. The unreacted **19** (0.8 g) was filtered off. By evaporation of the pentane, pure **21** was obtained: 6.5 g (87%), colorless crystals, soluble in chlorinated solvents, m.p. 81–82° (pentane). – UV. (EtOH/H_2O 95:5): 240 (9000). – IR. (CH_2Cl_2): 3060, 2990, 2970, 1800, 1650, 1450, 1260, 1000, 900. – ^{1}H-NMR. ($CDCl_3$)[6]): 5.45 (*s*, 2 H, *H*CH=C(5) *cis* to C(4),C(5) and *H*CH=C(6) *cis* to C(4),C(5)); 5.20 (*s*, 2 H, HC*H*–C(5) *trans* to C(4),C(5) and HC*H*=C(6) *trans* to C(4),C(5) (confirmed by lanthanide-induced shift experiments using Eu(thd)$_3$)); 4.95 (*s*, H–C(1) and H–C(4)); 3.7 (*m*, 4 H, 2 $ClCH_2$); 2.51 (*m*, H–C(2) and H–C(3)). – ^{13}C-NMR.: s. *Table 1.* – MS. (70 eV): 222 (0.5), 220 (2), 218 (4), 185 (38), 183 (11), 169 (20), 171 (7), 149 (14), 147 (19), 129 (30), 119 (43), 105 (27), 94 (100), 91 (76), 79 (19), 66 (24), 65 (43), 53 (14), 51 (16).

$C_{10}H_{12}Cl_2O$ (219.11) Calc. C 54.81 H 5.52 Cl 32.36% Found C 54.89 H 5.53 Cl 32.57%

Synthesis of 2exo,3exo-bis(chloromethyl)-5exo,5endo- and 5exo,5endo-(epoxymethano)-6-methylidene-7-oxabicyclo[2.2.1]heptanes (**26**). *m*-Chloroperbenzoic acid (2 g, 11.5 mmol) was added portionwise to a stirred solution of **21** (2.4 g, 11 mmol) in CH_2Cl_2 at r.t. The mixture became viscous; vigorous stirring was maintained for 12 h at r.t. The precipitated benzoic acid was filtered off and washed with cold CH_2Cl_2. The organic solution was washed with aq. Na_2CO_3-solution (10%, 30 ml), then with water (30 ml) and dried ($MgSO_4$). After evaporation of the solvent *i.v.*, 2.2 g (86%) of **26** was obtained as a viscous, colorless oil.

Synthesis of 5exo,6exo-bis(chloromethyl)-2-methoxymethyl-3-methylidene-7-oxabicyclo[2.2.1]heptan-2exo- and -2endo-ol (**27**). The mixture **26** obtained above (1.7 g, 6.5 mmol) was added to a stirred solution of MeONa in abs. MeOH (obtained by dissolving metallic Na (5.1 g, 0.22 mol) in abs. MeOH (170 ml)) at r.t. After stirring at r.t. for 5 h, water (250 ml) was added slowly. The mixture was extracted with CH_2Cl_2 (3 times, 150 ml). The organic extract was washed with water (3 times 200 ml), then with 5% HCl-solution (100 ml) and finally with a sat. $NaHCO_3$-solution (100 ml). After drying ($MgSO_4$), the solvent was evaporated *i.v.* yielding 1.6 g (83%) of **27** as a viscous, colorless oil, pure enough for the following steps.

Synthesis of 2,3,5exo,6exo-tetrakis(chloromethyl)-7-oxabicyclo[2.2.1]hept-2-ene (**22**). Freshly distilled $SOCl_2$ (0.212 g, 1.8 mmol) and anh. pyridine (0.14 g, 1.8 mmol) were added successively to a stirred solution of **27** (0.28 g, 1.2 mmol) in anh. $CHCl_3$ (7 ml) at r.t. The mixture was stirred at 60° for 2 h and then allowed to cool to r.t. After the addition of ether (20 ml), water (20 ml) was added dropwise (destruction of the excess of $SOCl_2$). The ethereal solution was separated and washed successively with 0.1N HCl (20 ml), with sat. aq. $NaHCO_3$-solution (20 ml) and with water (20 ml). After drying ($MgSO_4$), the solvent was evaporated *i.v.* The crude **22** (0.28 g) was recrystallized from CCl_4 (2 ml) yielding 0.23 g (66%) of white crystals, m.p. 82–83°. – IR. (KBr): 3020, 2970, 2860, 1445, 1285, 1270, 1250, 1010, 950, 910, 850, 820, 770, 710, 685. – ^{1}H-NMR. ($CDCl_3$): 5.03 (*s*, H–C(1) and H–C(4)); 4.3 (*s*, 4 H, $ClCH_2$–C(2) and $ClCH_2$–C(3)); 3.65 (*m*, 4 H, $ClCH_2$–C(5) and $ClCH_2$–C(6)); 2.4 (*m*, H–C(5) and H–C(6)). – ^{13}C-NMR. ($CDCl_3$): s. *Table 2.* – MS. (70 eV): 168 (5), 166 (46), 164 (71, $M^+ - ClCH_2–CH=CH–CH_2Cl$), 131 (7), 129 (100), 91 (23), 77 (23), 65 (58), 52 (29), 49 (27).

$C_{10}H_{12}Cl_4O$ (290.018) Calc. C 41.41 H 4.17% Found C 41.51 H 4.12%

Synthesis of 2,3-bis(bromomethyl)-5exo,6exo-bis(chloromethyl)-7-oxabicyclo[2.2.1]hept-2-ene (**23**). Bromine (1.5 g, 9.4 mmol) was added at once to a stirred solution of **21** (1.6 g, 7.3 mmol) in CCl_4 (10 ml) at r.t. After 5 min, a precipitate was formed. It was redissolved by the addition of CH_2Cl_2 (20 ml). Finely pulverized $Na_2S_2O_3$ (15 g) was added to the deep-orange solution and stirred vigourously at r.t. for 30 min. The solution became slightly yellow. The precipitate was filtered off and washed with CH_2Cl_2

(2 times 15 ml). After drying ($MgSO_4$), the solvent was evaporated *i.v.* The residue was recrystallized from CCl_4 (15 ml) yielding 1.1 g (40%) of **23**, colorless crystals, soluble in chlorinated solvents, THF and AcOH, m.p. 95–96°. – IR. (CH_2Cl_2): 3050, 2960, 2990, 2860, 1460, 1440, 1210, 1195, 1100, 900, 800, 770, 630. – ^{1}H-NMR. ($CDCl_3$): 4.88 (*s*, H–C(1) and H–C(4)); 4.05 (*s*, 4 H, 2 $BrCH_2$); 3.63 (*m*, 4 H, 2 $ClCH_2$); 2.43 (*m*, 2 H, H–C(5) and H–C(6)). – ^{13}C-NMR.: s. *Table 1.* – MS. (70 eV): 301 (0.6), 299 (2.1), 297 (1.3, $M^+ - Br$), 256 (3), 254 (5), 252 (3), 221 (4), 177 (14), 175 (25), 174 (25), 149 (27), 119 (40), 91 (81), 94 (63), 85 (70), 83 (100), 77 (51), 65 (67).

$C_{10}H_{12}Br_2Cl_2O$	Calc.	C 31.69	H 3.19	Br + Cl 65.14%
(378.92)	Found	,, 31.80	,, 3.40	,, 64.97%

Synthesis of 5exo,6exo-*bis(chloromethyl)-2,3-bis(methoxymethyl)-7-oxabicyclo[2.2.1]hept-2-ene* (**24**). Anh. K_2CO_3 (0.6 g) was added to a solution of **22** (0.38 g, 1 mmol) in anh. MeOH/THF 2:1 (15 ml). The suspension was stirred at r.t. for 12 h. After evaporation of the solvent *i.v.*, the residue was stirred with $CHCl_3$ (30 ml) at r.t. for 15 min. The solid was filtered off and washed with $CHCl_3$ (10 ml). After drying ($MgSO_4$), the solvent was evaporated *i.v.* and the oily residue recrystallized from ether/petrol ether 8:1 (10 ml) yielding 0.215 g (76%) of **24**, colorless crystals, m.p. 58–59°. – IR. (KBr): 3010, 2960, 2940, 2900, 2890, 2860, 2840, 1450, 1390, 1290, 1250, 1190, 1090, 1070, 1005, 940, 900, 720. – ^{1}H-NMR. ($CDCl_3$): 4.85 (*s*, 2 H, H–C(1) and H–C(4)); 4.1 (*s*, 4 H, 2 CH_3OCH_2); 3.65 (*m*, 4 H, 2 $ClCH_2$); 3.35 (*s*, 6 H, 2 CH_3O); 2.20 (*m*, 2 H, H–C(5) and H–C(6)). – ^{13}C-NMR.: s. *Table 1.* – MS. (70 eV): 247 (0.3), 245 (0.8, $M^+ - Cl$), 171 (4), 169 (10), 156 (5), 124 (100), 95 (25), 94 (25), 77 (17), 67 (19), 53 (22), 45 (64).

$C_{12}H_{18}Cl_2O_3$ (281.182) Calc. C 51.25 H 6.45% Found C 51.19 H 6.50%

Synthesis of 5exo,6exo-*bis(chloromethyl)-7-oxabicyclo[2.2.1]hept-2-ene-2,3-dimethyl diacetate* (**25**). The dibromide **23** (0.63 g, 1.66 mmol), anh. AcONa (1.24 g, 15.1 mmol) and anh. AcOH (10 ml) were stirred at 100° for 12 h. After cooling to r.t., water (30 ml) was added. The mixture was extracted with ether (3 times 30 ml). The ethereal extract was washed successively with water (5 times 50 ml) and a sat. aq. $NaHCO_3$-solution (5 times 50 ml). The organic phase was decolorized with charcoal, dried ($MgSO_4$) and evaporated *i.v.* yielding 0,49 (87%) of **25**, colorless crystals, m.p. 83–84° (ether). – IR. (KBr): 3000, 2950, 1750, 1740, 1390, 1370, 1290, 1240, 1220, 1025, 970, 940, 910, 820, 720. – ^{1}H-NMR. ($CDCl_3$): 4.90 (*s*, 2 H, H–C(1) and H–C(4)); 4.80 (*s*, 4 H, H_2C–C(2) and H_2C–C(3)); 3.6 (*m*, 4 H, 2 $ClCH_2$); 2.2 (*m*, 2 H, H–C(5) and H–C(6)); 2.1 (*s*, 6 H, 2 CH_3COO). – ^{13}C-NMR.: s. *Table 1.* – MS. (70 eV): 243 (0.5), 241 (1.5, $M^+ - Cl - OAc$), 212 (8), 183 (5), 181 (11), 152 (63), 110 (84), 81 (9), 77 (7), 65 (8), 59 (11), 43 (100).

$C_{14}H_{18}Cl_2O_5$ (337.204) Calc. C 49.93 H 5.43% Found C 49.87 H 5.38%

Synthesis of 2,5exo,6exo-*tris(chloromethyl)-3-methoxymethyl-7-oxabicyclo[2.2.1]hept-2-ene* (**28**). Freshly distilled $SOCl_2$ (3 ml, 40 mmol) and anh. pyridine (1.2 ml, 15 mmol) were added successively to a solution of the alcohols **27** (1.44 g, 5.4 mmol) in CCl_4 (18 ml). The mixture was stirred at 60° for 30 min. After the disparition of **27** (control by TLC., AcOEt/petroleum ether 3:7), the mixture was cooled to r.t., and water (30 ml) was added dropwise (a good reflux condenser is required, evolution of SO_2 + HCl). The organic phase was separated and the aqueous layer extracted with $CHCl_3$ (30 ml). The organic extracts were united and washed successively with water (3 times 50 ml) and sat. aq. $NaHCO_3$-solution (2 times 50 ml). After decolorizing with charcoal and drying ($MgSO_4$), the solvent was evaporated *i.v.* yielding 1.2 g (77%) of slightly yellow oil used directly for the preparation of the dienes **10** and **13**. Pure **28** was obtained by chromatography on a column of silica gel (50 g, 70–230 mesh, AcOEt/petroleum ether 3:7); **28** could not be crystallized. – IR. (CH_2Cl_2): 3010, 2970, 2940, 2480, 1900, 1450, 1290, 1250, 1190, 1100, 860, 810, 680. – ^{1}H-NMR. ($CDCl_3$)[6]: 4.98 (*s*, 1 H, H–C(1)); 4.90 (*s*, 1 H, H–C(4)); 4.35 (*s*, 2 H, H_2C–C(3)); 4.13 (*s*, 2 H, H_2C–C(2)); 3.38 (*s*, 3 H, CH_3O); 3.60 (*m*, 4 H, H_2C–C(5) and H_2C–C(6)); 2.30 (*m*, 2 H, H–C(5) and H–C(6)). – ^{13}C-NMR.: s. *Table 1.* – MS. (70 eV): 253 (0.3), 251 (0.9), 249 (1.0, $M^+ - MeOH$), 171 (4), 169 (9), 162 (11), 160 (29), 130 (60), 128 (100), 95 (50), 65 (42), 53 (29), 45 (66).

$C_{11}H_{19}Cl_3O_2$ (285.598) Calc. C 46.26 H 5.29 Cl 37.24% Found C 46.10 H 5.55 Cl 36.98%

Synthesis of 2exo,3exo-*bis(chloromethyl)-5-[(Z)-chloromethylidene]-6-methylidene-7-oxabicyclo-[2.2.1]heptane* (**9**). Freshly distilled $SOCl_2$ (1.2 ml, 16.5 mmol) was added to a solution of **26** (1 g,

4.25 mmol) in $CHCl_3$ (20 ml). The mixture was stirred at 60° for 2 h. Strict control of the temp. is necessary. After allowing to cool to r.t., water (20 ml) was added dropwise (a good reflux condenser is required). After addition of ether (50 ml) and vigorous shaking for 2 min, the organic phase was separated and washed with water (50 ml), then with a sat. aq. $NaHCO_3$-solution (3 times 50 ml). After drying ($MgSO_4$), the solvent was evaporated *i.v.* The residue was purified by column chromatography on silica gel (50 g, 70–230 mesh, AcOEt/petroleum ether 1:7). The first fraction contained **9** (95–97%) contaminated by its (*E*)-isomer **10** (3–5%). The former was crystallized from hexane (12 ml) yielding 0.26 g (24%) of **9**, white crystals, m.p. 63–64°. – UV. ($EtOH/H_2O$ 95:5): 260 *S* (8000), 250 (10000), 242 *S* (9100), *cf. Figure 1.* – IR. (KBr): 3070, 3010, 1800, 1685, 1645, 1285, 1000, 910, 890, 845, 830, 810, 800, 770, 705. – ^{1}H-NMR.[6]) (CD_3COCD_3): 6.7 (*s*, 1 H, HC(Cl)=C(5)); 5.4 (*s*, 1 H, *H*CH=C(6) *cis* to C(5),C(6)); 5.25 (*s*, 1 H, H–C(4)); 5.18 (*s*, 1 H, HC*H*=C(6) *trans* to C(5),C(6)); 4.95 (br. *s*, H–C(1)); 3.75 (*m*, 4 H, 2 $ClCH_2$); 2.55 (*m*, 2 H, H–C(5) and H–C(6)). – ^{13}C-NMR.: s. *Table 1.* – MS. (70 eV): 256 (2.1), 254 (2.5), 252 (2.6, M^+), 221 (1.8), 219 (10), 217 (15), 183 (4), 181 (25), 163 (14), 153 (20), 117 (39), 115 (30), 128 (100), 130 (35), 91 (32), 66 (48).

$C_{10}H_{11}Cl_3O$ (253.556) Calc. C 47.37 H 4.37 Cl 41.94% Found C 47.46 H 4.35 Cl 42.06%

*Synthesis of 2*exo,*3*exo-*bis(chloromethyl)-5-[(*E*)-chloromethylidene]-6-methylidene-7-oxabicyclo-[2.2.1]heptane* (**10**). Solide *t*-BuOK (0.6 g, 5.4 mmol) was added portionwise to a stirred solution of the **28** (1.4 g, 4.9 mmol) in THF (28 ml) cooled to 0°. The mixture was stirred at r.t. for 1 h. After addition of water (50 ml), the mixture was extracted with CH_2Cl_2/ether 1:2 (3 times 60 ml). The organic extract was dried ($MgSO_4$) and evaporated *i.v.* The oily residue was purified by column chromatography on silica gel (80 g, 70–230 mesh, AcOEt/petroleum ether 1:7). The first fraction contained **10**. It was recrystallized from hexane yielding 0.26 g (20%) of white crystals, m.p. 84–85°. – UV. (hexane): 254 *S* (7000), 245 (9000), 237 *S* (7300, *cf. Fig. 1*); identical spectrum in ethanol/H_2O 95:5. – IR. (KBr): 3080, 3020, 2960, 1850, 1650, 1640, 1450, 1290, 1250, 1200, 1120, 1000, 970, 910, 900, 800, 770, 700, 630. – ^{1}H-NMR. (CD_3COCD_3)[6]): 6.60 (*s*, 1 H, HC(C1)=C(5)); 6.03 (*s*, 1 H, *H*CH=C(6) *cis* to C(5),C(6)); 5.48 (*s*, 1 H, HC*H*=C(6) *trans* to C(5),C(6)); 4.95 and 4.90 (2 *s*, 2 H, H–C(1) and H–C(4)); 3.75 (m, 4 H, 2 $ClCH_2$); 2.55 (m, 2 H, H–C(2) and H–C(3)). – ^{13}C-NMR.: s. Table 1. – MS. (70 eV): 256 (1), 254 (2.4), 252 (2.8, M^+), 221 (3), 219 (14), 217 (21), 183 (15), 181 (26), 153 (25), 128 (100), 130 (30), 118 (66), 91 (54), 66 (55).

$C_{10}H_{11}Cl_3O$ (253.556) Calc. C 47.37 H 4.37 Cl 41.94% Found C 47.41 H 4.51 Cl 41.94%

*Synthesis of 2*exo,*3*exo-*bis(chloromethyl)-5-[(*E*)-methoxymethylidene]-6-methylidene-7-oxabicyclo-[2.2.1]heptane* (**13**). The second fraction of the above chromatography contained the diene **13**. Yield: 0.35 g (29%), white crystals, m.p. 88–89°; polymerized readily in the air and in solution, even at low temperature. It can be stored as crystals at –20°, in the absence of air. – UV. ($EtOH/H_2O$ 95:5): 258 (7000). – IR. (KBr): 3005, 2880, 2870, 2220, 1685, 1450, 1250, 1155, 1125, 980, 810. – ^{1}H-NMR. ($CDCl_3$)[6]): 6.35 (*s*, 1 H, HC(MeO)=C(5)); 5.45 (*s*, 1 H, *H*CH=C(6) *cis* to C(5),C(6)); 5.18 (*s*, 1 H, HC*H*=C(6) *trans* to C(5),C(6)); 480 and 4.75 (2 br. *s*, 2 H, H–C(1) and H–C(4)); 3.8 (*s*, 3 H, CH_3O); 3.6 (*m*, 4 H, 2 $ClCH_2$); 2.5 (*m*, 2 H, H–C(2) and H–C(3)). – ^{13}C-NMR.: s. *Table 1.* – MS. (70 eV): 252 (0.2), 250 (0.8), 248 (1.8, M^+), 215 (3), 213 (8), 117 (95), 115 (67), 91 (100), 77 (83), 66 (63).

$C_{11}H_{14}Cl_2O_2$ (249.139) Calc. C 53.03 H 5.66 Cl 28.46% Found C 52.85 H 4.49 Cl 28.45%

*Synthesis of 2-[(Z)-bromomethylidene]- and 2-[(E)-bromomethylidene]-5*exo,*6*exo-*bis(chloromethyl)-3-methylidene-7-oxabicyclo[2.2.1]heptane* (**11/12**). Solid *t*-BuOK (0.12 g, 1.1 mmol) was added at once to a stirred solution of **23** (0.38 g, 1 mmol) in THF (10 ml) at r.t. After stirring at r.t. for 5 min, water (15 ml) was added and the mixture extracted with pentane/CH_2Cl_2 2:1 (3 times 15 ml). The organic extract was washed with water (6 times 30 ml) and dried ($MgSO_4$). After evaporation of the solvent *i.v.* a 1:1 mixture of **11/12** was obtained: 0.28 g (90%) of instable oil that polymerizes readily in the air. – ^{1}H-NMR. ($CDCl_3$): 6.4 (br. *s*, 2 H, HC(Br)=C(2)); 6.15 (br. *s*, *H*CH=C(3) *cis* to C(2),C(3) of **12**); 5.3, 5.15, 5.10, 4.90 and 4.85 (5 br. *s*, 7 H); 3.75 (*m*, 8 H, $ClCH_2$–C(5) and $ClCH_2$–C(6)); 2.50 (*m*, 4 H, H–C(5) and H–C(6)). – ^{13}C-NMR. ($CDCl_3$): 145.54, 143.89, 141.37, 109.83, 102.50, 100.18, 97.93, 85.60, 85.46, 84.07, 83.80, 49.32, 48.92, 48.06, 41.96, 41.7. – GC./MS. (70 eV): **11**: 300 (5), 298 (11), 296 (7, M^+), 265 (6), 263 (21), 261 (18), 217 (20), 209 (20), 181 (18), 173 (97), 171 (100), 145 (40), 117 (99), 91 (76), 77 (51). **12**: 300 (5), 298 (12), 296 (8, M^+), 265 (6), 263 (20), 261 (18), 217 (18), 209 (21), 181 (18), 173 (93), 171 (97), 145 (40), 117 (100), 91 (76), 77 (45).

Synthesis of 2-[(Z)-chloromethylidene]-3,5,6-trimethylidene-7-oxabicyclo[2.2.1]heptane (**14**). Solid *t*-BuOK (1.2 g, 10 mmol) was added portionwise to a stirred solution of **9** (0.5 g, 1.97 mmol) in anh. THF (10 ml) at 0°. After stirring at r.t. for 8 h, water was added (30 ml) and the mixture extracted with pentane (3 times 30 ml). The organic extract was washed with water (6 times 20 ml), decolorized (charcoal) and dried ($MgSO_4$). After evaporation of the solvent *i.v.*, **14** was obtained as an oil pure enough for the *Diels-Alder* additions. Yield: 0.32 g (90%). Crystallization from hexane (10 ml, −20°) gave 0.22 g (62%) of white needles, soluble in the usual organic solvents, m.p. 46–47°. – UV. (hexane): 234 (5600), 246 (5000), s. *Figure 2.* – IR. (KBr): 3080, 1660, 1630, 1430, 1415, 1290, 970, 920, 890, 840, 810, 800, 780, 700. – ^{1}H-NMR. ($CDCl_3$): 6.35 (*s*, 1 H, HC(C1)=C(2)); 5.5 (*s*, 1 H, H–C(1)); 5.35, 5.25, 5.15, 5.20 and 5.10 (*s*, 7 H, 3 CH_2=C and H–C(4)). – ^{13}C-NMR.: s. *Table 1.* – MS. (70 eV): 182 (5), 180 (15, M^+), 154 (13), 152 (4), 145 (27), 115 (100), 91 (43), 63 (87), 51 (90).

Synthesis of 2-[(E)-chloromethylidene]-3,5,6-trimethylidene-7-oxabicyclo[2.2.1]heptane (**15**). Same procedure as above, starting with **10**. Yield: 76%, white crystals, m.p. 51–52° (hexane). – UV. (hexane): 231 (7800), 242 *S* (7100), 250 *S* (6400), s. *Figure 2.* – IR. (KBr): 3080, 1780, 1650, 1300, 1240, 1140, 1090, 980, 880, 800, 790, 740. – ^{1}H-NMR. ($CDCl_3$): 6.40 (*s*, 1 H, HC(C1)=C(2)); 6.05 (*s*, 1 H, *H*CH=C(3) *cis* to C(2),C(3)); 5.50 (*s*, 1 H, HC*H*=C(3) *trans* to C(2),C(3)); 5.35, 5.20, 5.15, 5.10 and 5.0 (*s*, 6 H, H_2C=C(5), H_2C=C(6), H–C(1) and H–C(4)). – ^{13}C-NMR.: s. *Table 1.* – MS. (70 eV): 183 (2), 180 (9, M^+), 154 (3), 152 (10), 145 (9), 115 (100), 91 (36), 65 (23), 63 (31), 51 (36).

Synthesis of 2-[(Z)-bromomethylidene]- and 2-[(E)-bromomethylidene]-3,5,6-trimethylidene-7-oxabicyclo[2.2.1]heptane (**16/17**). Solid *t*-BuOK (1.2 g, 10.1 mmol) was added portionwise to a stirred solution of **11/12** (0.6 g, 2 mmol) in anh. THF (10 ml) at 0°. After stirring at r.t. for 8 h, water (30 ml) was added. The mixture was extracted with CH_2Cl_2/pentane 1:2 (3 times 30 ml), and the organic extract was washed with water (6 times 20 ml), decolorized (charcoal) and dried ($MgSO_4$). The mixture **16/17** was polymerized readily in this solution. All attempts to isolate these compounds by prep. chromatography (GC., elution) failed. – ^{1}H-NMR. ($CDCl_3$, **16/17**): 6.5 (*s*, HC(Br)=C(2) of **16** and **17**); 6.2, 5.4, 5.35, 5.3, 5.15, 5.10 and 5.05 (7 *s*, CH_2=C, H–C(1) and H–C(4) of **16** and **17**). – GC./MS. (70 eV; *OV 17* 3%, 160°, isotherm) gave for **16** or **17**: 226 (8), 224 (7, M^+), 198 (5), 196 (5), 145 (44), 115 (100), 91 (53), 65 (35), 63 (49), 51 (50), 39 (44); for **17** or **16**: 226 (7), 224 (7, M^+), 198 (4), 196 (3), 145 (53), 115 (100), 91 (57), 65 (34), 63 (46), 51 (46), 39 (46).

Synthesis of 2-[(E)-methoxymethylidene]-3,5,6-trimethylidene-7-oxabicyclo[2.2.1]heptane (**18**). Solid *t*-BuOK (0.6 g, 5 mmol) was added portionwise to a stirred solution of **13** (0.25 g, 1 mmol) in anh. THF (3 ml) at 0°. After stirring at r.t. for 8 h, water (10 ml) was added, and the mixture was extracted with ether/pentane 1:1 (3 times 10 ml). The organic extract was washed with ice-water (6 times 20 ml) and dried ($MgSO_4$). After evaporation of the solvent *i.v.*, **18** was obtained as a viscous oil that could not be crystallized. In solution, **18** was more stable than **13**. Yield: 73%. – UV. (95% EtOH): 235 (9000), 282 (1700), s. *Figure 2.* – IR. (film): 3080, 1680, 1450, 1430, 1260, 1240, 1210, 1140, 1120, 980, 960, 885, 810, 770. – ^{1}H-NMR. ($CDCl_3$): 6.35 (*s*, 1 H, HC(MeO)=C(2)); 5.4 (*s*, 1 H, *H*CH=C(3) *cis* to C(2),C(3)); 5.30, 5.25, 5.20, 5.05 and 4.95 (5 *s*, 7 H, H–C(1), H–C(4), HC*H*=C(3) *trans* to C(2),C(3), H_2C=C(5) and H_2C=C(6)). – ^{13}C-NMR.: s. *Table 1.* – MS. (70 eV): 176 (2, M^+), 161 (2), 133 (9), 115 (38), 104 (49), 102 (43), 91 (49), 79 (64), 77 (100), 51 (92), 39 (80).

Synthesis of 3exo-*chloro*-9exo,10exo-*bis(chloromethyl)-11-oxatricyclo[6.2.1.0^{2,7}]undec-2(7)-ene-4,4,5,5-tetracarbonitrile* (**29**). A solution of **9** (250 mg, 0.98 mmol) and TCE (260 mg, 2 mmol) in anh. acetone (1.2 ml) was heated in a sealed pyrex tube under stirring to 130° for 2 h. After cooling r.t., the mixture **29/30** (85:15) was rapidly filtered through SiO_2 (10 g, AcOEt) and the solvent evaporated *i.v.* The residue was dissolved in warm $CHCl_3$ (5 ml, 60°). After slow cooling to r.t., a precipitate was formed and collected (0.34 g, 92% of **29/30** 85:15). Three recrystallizations in $CHCl_3$/hexane 4:1 (6 ml, then 3 ml and 3 ml) yielded 0.027 g (8%) of pure **29**, colorless crystals, soluble in acetone, insoluble in the usual organic solvents, m.p. 212–213°. – IR. (KBr): 3080, 2890, 2880, 2260, 1670, 1440, 1295, 1280, 1250, 910, 860, 770, 720, 620. – ^{1}H-NMR.: s. *Table 3.* – MS. (70 eV): 258 (39), 256 (100, M^+ − $ClCH_2$–CH=CH–CH_2Cl), 221 (36), 195 (21), 166 (3), 139 (3), 128 (25), 130 (7), 75 (4), 53 (5).

$C_{16}H_{11}Cl_3N_4O$ (381.65) Calc. C 50.35 H 2.91 Cl 27.87% Found C 50.51 H 3.07 Cl 28.12%

Synthesis of 3endo-*chloro*-9exo,10exo-*bis(chloromethyl)-11-oxatricyclo[6.2.1.0^{2,7}]undec-2(7)-ene-4,4,5,5-tetracarbonitrile* (**30**). A solution of **10** (0.25 g, 0.98 mmol) and TCE (0.26 g, 2 mmol) in chlorobenzene (5 ml) was stirred at 130° for 12 h (*ca.* 15% conversion of **10**). After evaporation of the solvent, the residue was purified by column chromatography on silica gel (AcOEt/petroleum ether 2:7). A fraction was collected

that contained a 4:1 mixture of **30/29**. They could not be separated. After solvent evaporation, a slightly yellow oil was obtained. Yield: 0.02 g (8%). – ^{1}H-NMR.: s. *Table 3.*

Synthesis of 9exo, *10*exo-*bis(chloromethyl)-3*endo-*methoxy-11-oxatricyclo[6.2.1.0^{2,7}]undec-2(7)-ene-4,4,5,5-tetracarbonitrile* (**32**). A solution of **13** (0.25 g, 1 mmol) and TCE (0.13 g, 1 mmol) in anh. benzene (13 ml) was stirred at r.t. for 30 min. The precipitate was collected, dissolved in $CHCl_3$ and filtered rapidly through silica gel (10 g, AcOEt/petroleum ether 3:7). After evaporation of the solvent *i.v.* and recrystallization from $CHCl_3$/hexane 4:1, 0,325 g (85%) of colorless, small crystals were obtained (insoluble in C_6H_6, toluene, methanol; soluble in acetone and chlorinated solvents), m.p. 238–239°. – IR. (KBr): 3080, 2980, 2260, 1720, 1450, 1290, 1255, 1210, 1100, 1070, 1010, 980, 950, 910, 860, 815, 770, 730, 690, 630. – ^{1}H-NMR.: s. *Table 3.* – MS. (70 eV): 252 (4, $M^+ - ClCH_2-CH=CH-CH_2Cl$), 141 (1), 140 (2), 124 (100), 109 (7), 95 (17), 98 (8), 88 (8), 77 (5), 66 (2), 65 (1), 53 (8).

$C_{17}H_{14}Cl_2N_4O_2$ (377.231) Calc. C 54.11 H 3.71 N 14.85% Found C 53.85 H 3.83 N 14.60%

Synthesis of 3endo-*methoxy-9,10-dimethylidene-11-oxatricyclo[6.2.1.0^{2,7}]undec-2(7)-ene-4,4,5,5-tetracarbonitrile* (**34**). A solution of **18** (0.08 g, 0.45 mmol) and TCE (0.06 g, 0.47 mmol) in anh. benzene (1 ml) was stirred at r.t. for 1 h. The precipitate, 0.105 g (85%) of **33/34** (15:85), was collected and washed with cold benzene (2 times 2 ml). The major adduct **34** was obtained pure after 3 recrystallizations from CCl_4 (2 ml, then 1 and 1 ml): 0.012 g (8%), colorless crystals, m.p. 174–175°. – UV. (EtOH/H_2O 95:5): 226 (5600). – IR. (KBr): 3080, 2970, 2950, 2240, 1670, 1440, 1370, 1260, 1140, 1100, 980, 900, 860, 770. – ^{1}H-NMR.: s. *Table 3.* – MS. (70 eV): 304 (6, M^+), 175 (7), 246 (8), 216 (6), 147 (18), 124 (25), 96 (18), 94 (20), 91 (17), 83 (20), 80 (18), 77 (13), 71 (24), 52 (100). HR.-MS. for $C_{17}H_{12}O_2N_4$: Calc. 304.09901, Found 304.09994 ($\Delta M/M = 3$ ppm).

Synthesis 3exo-*methoxy-9,10-dimethylidene-11-oxatricyclo[6.2.1.0^{2,7}]undec-2(7)-ene-4,4,5,5-tetracarbonitrile* (**33**). The minor adduct in the above reaction could not be isolated in a pure state. Its ^{1}H-NMR. was obtained from the spectrum of the crude mixture **33/34** (15:85).

Synthesis of 9exo, *10*exo-*bis(chloromethyl)-3*endo-*methoxy*-N-*phenyl-4,5-diaza-11-oxatricyclo-[6.2.1.0^{2,7}]undec-2(7)-ene-4,5-dicarboximide* (**36**). *N*-Phenyltriazolinedione (0.037 g, 0.2 mmol, NPTAD) in anh. benzene (2 ml) was added portionwise to a stirred solution of **13** (0.05 g, 0.2 mmol) in anh. benzene (1 ml). The disappearance of the red color of NPTAD was instantaneous. After evaporation of the solvent *i.v.*, the crude adduct was recrystallized from benzene/hexane 9:1 yielding 0.064 g (75%) of colorless crystals, m.p. 185–186°. – UV. (CH_3CN): 215 (15000). – IR. (KBr): 2280, 1830, 1770, 1725, 1610, 1510, 1500, 1420, 1370, 1290, 1280, 1230, 1140, 1070, 950, 770, 730. – ^{1}H-NMR.: s. *Table 3.*

*Synthesis of 9-[(*Z*)-chloromethylidene]-10-methylidene-11-oxatricyclo[6.2.1.0^{2,7}]undec-2(7)-ene-4,4,5,5-tetracarbonitrile* (**37**). A solution of **14** (0.08 g, 0.3 mmol) and TCE (0.115 g, 0.9 mmol) in anh. benzene (3,5 ml) was stirred under N_2 at 70° for 6 h. After evaporation of the solvent *i.v.*, the crude adduct was purified by column chromatography on silica gel (8 g, AcOEt/petroleum ether 2:7). A fraction containing 0.098 g of **37** was obtained as a yellowish oil that was crystallized from $CHCl_3$/hexane 9:1 (4 ml) yielding 0.067 g (58%) of white needles, m.p. 210° (dec.). – UV. (EtOH/H_2O 95:5): 213 (8900), 232 *S* (7500), 243 *S* (5900). – IR. (KBr): 3080, 2690, 2260, 1820, 1660, 1640, 1440, 1300, 1240, 1140, 1070, 990, 860, 790. – ^{1}H-NMR. (CD_3COCD_3): 6.7 (*s*, 1 H, HC(C1)=C(9)); 5.7 (br. *s*, 1 H, H–C(8)); 5.5 (br. *s*, *H*CH=C(10) *trans* to C(9),C(10)); 5.4 (br. *s*, 1 H, H–C(1)); 5.3 (br. *s*, 1 H, HC*H*=C(10) *cis* to C(9),C(10)); 3.8 (*d*×*m*, 2 H, $J = 18$, H*exo*–C(3) and H*exo*–C(6)); 3.4 (*d*×*m*, 2 H, $J = 18$, H*endo*–C(3) and H*endo*–C(6)). – MS. (70 eV): 310 (2), 308 (5, M^+), 282 (1), 281 (2), 280 (3), 279 (5), 273 (3), 245 (7), 218 (4), 191 (5), 115 (10), 88 (30), 86 (100), 52 (75).

$C_{16}H_9ClN_4O$ (308.728) Calc. C 62.22 H 2.94 N 18.15% Found C 62.03 H 2.99 N 17.93%

*Synthesis of 9-[(*E*)-chloromethylidene]-10-methylidene-11-oxatricyclo[6.2.1.0^{2,7}]undec-2(7)-ene-4,4,5,5-tetracarbonitrile* (**38**). Same procedure as for the preparation of **37**, using **15** (0.08 g, 0.3 mmol): 0.087 g (76%) of **38**, white crystals, m.p. 170° (dec.). – UV. (EtOH/H_2O 95:5): 231 (8600), 228 (8100), 236 (6800), 245 (5600). – IR. (KBr): 3080, 3020, 2960, 2260, 1650, 1440, 1290, 1240, 1140, 980, 900, 860, 800, 760, 720. – ^{1}H-NMR. ($CDCl_3$): 6.7 (br. *s*, 1 H, HC(C1)=C(9)); 5.9 (br. *s*, 1 H, *H*CH=C(10) *cis* to C(9),C(10)); 5.5 (br. *s*, 1 H, HC*H*=C(10) *trans* to C(9),C(10)); 5.40 and 5.35 (br. *s*, 2 H, H–C(1) and H–C(8)); 3.8 (*d*×*m*, 2 H, $J = 18$, H*exo*–C(3) and H*exo*–C(6)); 3.40 (*d*×*m*, 2 H, $J = 18$, H*endo*–C(3) and H*endo*–C(6)). – MS. (70 eV): 310 (4), 308 (12, M^+), 282 (3), 281 (6), 280 (9), 279 (18), 273 (5), 254 (9), 218 (4), 191 (7), 115 (10), 88 (30), 86 (100), 57 (25), 52 (30).

$C_{16}H_9ClN_4O$ (308.728) Calc. C 62.22 H 2.94 N 18.15% Found C 62.08 H 3.11 N 18.13%

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