16. Regioselectivity of the *Diels-Alder* Additions of 2-Substituted 5,6-Dimethylidenenorbornanes and -bicyclo[2.2.2]octanes[1])[2])

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(23. X. 81)

Summary

The cycloadditions of methyl propynoate and methyl vinyl ketone to 5,6-dimethylidene-2-norbornanone (**6**) are *'para'*-regioselective[5]). A smaller *'para'*-regioselectivity is observed for the addition of methyl propynoate to 5,6-dimethylidene-2-bicyclo[2.2.2]octanone (**10**). No regioselectivity is observed with 5,6-dimethylidene-2*exo*-norbornyl alcohol (**3**), acetate (**5**) and 5,6-dimethylidene-2*exo*-bicyclo[2.2.2]octanol (**9**). PMO arguments based on the shape of the HOMO's and subHOMO's of the dienes allow to rationalize these observations. Unpredictable *'para'*- or *'meta'*-regioselectivities are found for the *Diels-Alder* additions of 5,6-dimethylidene-2*endo*-norbornyl alcohol (**2**), acetate (**4**) and 5,6-dimethylidene-2*endo*-bicyclo[2.2.2]octanol (**8**). The carbonyl group of β,γ-unsaturated ketones such as **6** and **10** can act as an electron donating homoconjugated substituent. The $n(CO) \leftrightarrow \sigma[C(1),C(2)] \leftrightarrow \pi[C(5),C(6)]$ hyperconjugative interaction can override the usual electron-withdrawing effect of this function.

Introduction. – The *Diels-Alder* reactivity of an exocyclic *s-cis*-butadiene[6]) grafted onto norbornane [2] [3] and bicyclo[2.2.2]octane [1] [4] skeletons (s. **1** and **7**, resp.) can be affected by remote substitution of the bicyclic systems. The carbonyl group in 5,6-dimethylidene-2-norbornanone (**6**) and in 5,6-dimethylidene-2-bicyclo[2.2.2]octanone (**10**) causes a significant rate retardation effect on the cycloadditions of the diene to strong dienophiles. We report now on the regioselectivity of the *Diels-Alder* additions of the homoconjugated dienones **6** and **10**, and of the related *endo*- and *exo*-alcohols **2, 8, 3** and **9**, and acetates **4** and **5**.

Since our exocyclic dienes are grafted onto rigid bicyclic skeletons, geometry and steric factors should not play a dominant role in determining the regioselectivity

[1]) Interaction between non-conjugated chromophores, Part 14; Part 13, see [1]. According to the IUPAC nomenclature 'bicyclo[2.2.1]heptane' is now called '8,9,10-trinorbornane'; for commodity reasons we use in this paper the abolished name 'norbornane'.

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

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[5]) "Para" *(p)* designs in this paper the 4,9-disubstituted tricyclo[6.2.1.$0^{2,7}$]undecane- and 4,9-disubstituted tricyclo[6.2.2.$0^{2,7}$]dodecane derivatives, "meta" *(m)* designs the corresponding 4,10-disubstituted compounds.

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

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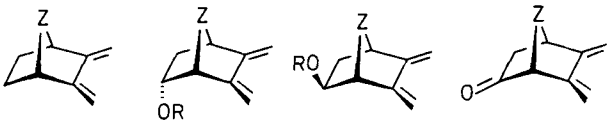
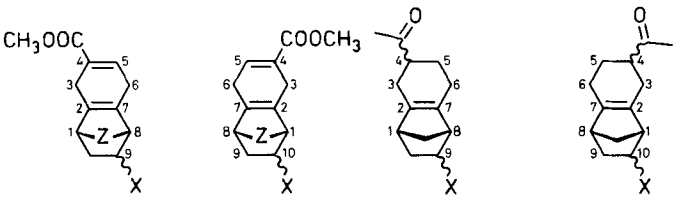


$Z=CH_2$:	**1**	**2** (R = H) **4** (R = Ac)	**3** (R = H) **5** (R = Ac)	**6**
$Z=CH_2-CH_2$:	**7**	**8** (R = H)	**9** (R = H)	**10**

of their cycloadditions. The dienes are differentiated by remote substitution only. Therefore, dipole-dipole (hard) and charge-transfer (soft) interactions [5] between the cycloaddends should be responsible for the regioselectivities. Perturbational MO arguments [6] will be presented that allow partial rationalization of our observations. Particularly interesting is the finding that a homoconjugated carbonyl group can act as an electron-donating group rather than an electron-withdrawing substituent (as expected from the observation of a rate-retardation effect when comparing the *Diels-Alder* reactivities of **6** and **10** *vs.* those of **1** and **7**, respectively) in the cycloaddition of 5,6-dimethylidene-2-norbornanone (**6**) to methyl propynoate (MP) and methyl vinyl ketone (MVK). This effect is less important with the bicyclo[2.2.2]octanone analog **10** where it is counterbalanced by the 'normal' electron-withdrawing effect.

Results. – The dienes **1–6** and **8–10** were heated with a 6–7fold excess of degassed methyl propynoate in sealed pyrex tubes to 80° for 5–20 h. After removal of the excess of the dienophile *in vacuo*, the corresponding adducts *p*-**11**/*m*-**11** – *p*-**19**/*m*-**19**[5]), respectively, were distilled (yield: 92–97%) and analyzed by ^{13}C-NMR. The regioselectivities *'para'/'meta' ('p'/'m')* are reported in *Table 1* together with those observed for the additions of methyl vinyl ketone to **2–6** yielding the corresponding adducts **20–24**.



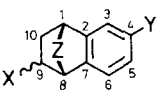
		'p'	*'m'*	*'p'*	*'m'*
$Z=CH_2$	$X=OH_{endo}$	*p*-**11**	*m*-**11**	*p*-**20**	*m*-**20**
	OH_{exo}	*p*-**12**	*m*-**12**	*p*-**21**	*m*-**21**
	OAc_{endo}	*p*-**13**	*m*-**13**	*p*-**22**	*m*-**22**
	OAc_{exo}	*p*-**14**	*m*-**14**	*p*-**23**	*m*-**23**
	OXO	*p*-**15**	*m*-**15**	*p*-**24**	*m*-**24**
	H	**16**			
$Z=CH_2CH_2$	$X=OH_{endo}$	*p*-**17**	*m*-**17**		
	OH_{exo}	*p*-**18**	*m*-**18**		
	OXO	*p*-**19**	*m*-**19**		

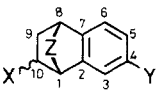
The regioisomers *p*-**11**/*m*-**11** – *p*-**15**/*m*-**15** were recognized by comparing the ^{13}C-NMR. chemical shifts of the olefinic C-atoms C(2) and C(7) with those calculated for 9- and 10-substituted methyl tricyclo[6.2.1.$0^{2,7}$]undeca-2(7),4-diene-4-carbox-

Table 1. *Regioselectivities of the* Diels-Alder *additions of 2-substituted 5,6-dimethylidenenorbornanes* **2–6** *and bicyclo[2.2.2]octanes* **8–10** *at 80°*

Diene	Adducts with $H-C\equiv C-COOCH_3$ *p/m*[a])	Adducts with $H_2C=CHCOCH_3$ *p/m*[a])
2	33/67 (35/65[b]))	64/36 (58/42[c]))
3	49/51 (50/50[b]))	46/54 (38/62[c]))
4	68/32 (68/32[b]))	36/64 (37/63[c]))
5	49/51 (47/53[b]))	40/60 (47/53[c]))
6	75/25 (73/27[b]))	75/25 (73/27[c]))
8	45/55 (45/55[b]))	
9	50/50	
10	56/44	

[a]) Given in % (±2%), by ^{13}C-NMR.
[b]) After aromatization with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ).
[c]) After aromatization with sulfur.





			Y = $COOCH_3$	Y = $COCH_3$	Y = CH_2OH	Y = $COOCH_3$	Y = $COCH_3$	Y = CH_2OH
$Z=CH_2$	X =	OH_{endo}	*p*-**25**	*p*-**31**	*p*-**37**	*m*-**25**	*m*-**31**	*m*-**37**
		OH_{exo}	*p*-**26**	*p*-**32**		*m*-**26**	*m*-**32**	
		OAc_{endo}	*p*-**27**	*p*-**33**		*m*-**27**	*m*-**33**	
		OAc_{exo}	*p*-**28**	*p*-**34**		*m*-**28**	*m*-**34**	
		OXO	*p*-**29**	*p*-**35**		*m*-**29**	*m*-**35**	
		H	**30**					
$Z=CH_2CH_2$		OH_{endo}	*p*-**36**			*m*-**36**		

ylates, assuming γ- and δ-substituent effects similar to those reported for 2-substituted 5-norbornenes [7]. The model compound **16** was obtained by addition of methyl propynoate to the diene **1** (see *Table 2*).

Treatment of the adducts **11–16** with 1.2 mol-equiv. of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) [8] in benzene (20°) for *ca.* 6 h gave the corresponding benzonorbornenes **25–30** in excellent yield (95–98%). No regioselectivity was observed during the aromatization. The aromatic C-atoms in the ^{13}C-NMR. spectra of **25–29** could be assigned unequivocally by analysis of the proton-coupled spectra ($^3J(C,H) = 7–10$ Hz [9]). The *'p'*-regioisomers displayed a larger chemical shift difference $\delta(C(7))-\delta(C(2))$ than the *'m'*-isomers because of the cumulative γ (negative) and δ (positive) substituent effects due to the X and ester groups (see *Table 2*). The signal attribution as well as the structures of **11, 12, 15, 16, 26** and **37** (obtained by $LiAlH_4$ reduction of **25**) were confirmed by the relative shifts induced by $Yb(dpm)_3$ (see *Table 2*).

Treatment of the ketones **15** with $NaBH_4$ in THF gave directly the aromatized alcohols *p*-**25**/*m*-**25** in a 75:25 ratio, contrasting with the 35:65 product ratio observed by DDQ oxidation of **11**. These experiments confirmed the ^{13}C-NMR. test used here for assigning the regioselectivities of our cycloadditions (see *Table 1*).

The distinction between the *'p'*- and *'m'*-regioisomers **17–19** of the bicyclo[2.2.2]octane series was based on the ^{13}C-NMR. spectra using the same chemical shift test developed for the norbornane series.

Table 2. *^{13}C-NMR. data of the adducts* **11–19** *and of the aromatized derivatives* **25–37**. Chemical shifts in ppm (±0.1 ppm, $\delta_{TMS}=0.0$ ppm, $CDCl_3$ as solvent and deuterium lock), $^1J_{CH}$ in Hz (±1 Hz). In parenthesis: relative induced shift by added $Yb(dpm)_3$.

	Chemical shifts of													
	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	C(11)	C(12)	others	
p-**11**	44.2 *d*, *J*=146 (25.7)	138.2 br. *s* (30.2)	23.8 *t*, *J*=130 (18.1)	127.8 br. *s* (14.8)	137.4 *d*, *J*=160 (12.0)	28.5 *t*, *J*=130 (22.9)	131.6 br. *s* (37.4)	49.7 *d*, *J*=146 (39.3)	73.5 *d*, *J*=150 (100)	35.7 *t*, *J*=136 (45.3)	45.6 *t*, *J*=134 (20.5)	–	167.1 br. *s* (18.5)	50.7 *qa*, *J*=147 (6.2)
p-**12**	43.0 *d*, *J*=148	141.0 br. *s* (19.0)	24.3 *t*, *J*=130 (15.4)	128.0 br. *s*	136.9 *d*, *J*=160 (11.5)	25.9 *t*, *J*=130 (12.3)	132.3 br. *s* (21.7)	51.9 *d*, *J*=148 (44.3)	72.3 *d*, *J*=151 (100)	37.4 *t*, *J*=134	43.0 *t*, *J*=134	–	167.3 br. *s*	51.1 *qa*, *J*=147
p-**13**	43.9 *d*, *J*=147	138.9 br. *s*	23.9 *t*, *J*=131	128.0 br. *s*	137.0 *d*, *J*=162	28.1 *t*, *J*=131	131.6 br. *s*	47.4 *d*, *J*=148	76.6 *d*, *J*=154	33.6 *t*, *J*=137	45.3 *t*, *J*=134	–	167.0 br. *s*	51.0 *qa*, *J*=146
p-**14**	43.1 *d*, *J*=146	142.3 br. *s*	24.5 *t*, *J*=130	128.1 br. *s*	136.9 *d*, *J*=159	26.1 *t*, *J*=130	131.7 br. *s*	49.3 *d*, *J*=146	75.2 *d*, *J*=156	35.2 *t*, *J*=138	43.9 *t*, *J*=133	–	167.2 br. *s*	51.3 *qa*, *J*=147
p-**15**	41.6 *d*, *J*=155 (9.2)	144.9 br. *s* (14.6)	25.2 *t*, *J*=132 (26.6)	127.5 br. *s* (44.1)	136.0 *d*, *J*=160 (26.6)	25.9 *t*, *J*=131 (13.1)	129.4 br. *s* (14.9)	57.4 *d*, *J*=155 (16.7)	212.8 br. *s* (39.6)	36.1 *t*, *J*=135 (15.6)	47.6 *t*, *J*=135 (9.2)	–	166.6 br. *s* (100)	51.1 *qa*, *J*=147 (34.3)
p-**16**	44.4 *d*, *J*=145 (2.8)	136.8 br. *s* (8.6)	24.1 *t*, *J*=131 (22.8)	128.6 br. *s* (43.3)	137.5 *d*, *J*=160 (25.6)	25.7 *t*, *J*=131 (8.6)	134.5 br. *s* (6.4)	43.9 *d*, *J*=145 (2.8)	25.5 *t*, *J*=134 (2.0)	25.5 *t*, *J*=134 (2.0)	46.3 *t*, *J*=133 (2.2)	–	166.6 br. *s* (100)	51.2 *qa*, *J*=147 (34.8)
p-**17**	33.9 *d*	132.2 br. *s*	27.2 *t*	127.7 br. *s*	137.1 *d*	31.1 *t*	124.4 br. *s*	41.3 *d*	69.3 *d*	38.6 *t*	24.3 *t*	22.0 *t*	167.4 br. *s*	51.3 *qa*
p-**18**	34.0 *d*, *J*=137	134.0 br. *s*	27.0 *t*, *J*=130	128.0 br. *s*	137.1 *d*, *J*=160	28.9 *t*, *J*=130	128.6 br. *s*	41.0 *d*, *J*=137	68.8 *d*, *J*=147	35.4 *t*, *J*=131	25.8 *t*, *J*=130	17.3 *t*, *J*=130	167.2 br. *s*	51.1 *qa*, *J*=147
p-**19**	35.8 *d*, *J*=137	136.5 br. *s*	27.1 *t*, *J*=131	127.7 br. *s*	136.0 *d*, *J*=160	28.7 *t*, *J*=131	125.5 br. *s*	53.3 *d*, *J*=141	211.4 br. *s*	40.1 *t*, *J*=134	24.1 *t*, *J*=133	22.4 *t*, *J*=133	166.6 br. *s*	51.1 *qa*, *J*=147
m-**11**	50.2 *d*, *J*=146 (40.3)	133.7 br. *s* (33.0)	26.9 *t*, *J*=130 (22.1)	128.3 br. *s* (14.2)	136.8 *d*, *J*=160 (12.0)	25.4 *t*, *J*=130 (14.3)	136.1 br. *s* (25.7)	43.8 *d*, *J*=146 (22.5)	35.7 *t*, *J*=136 (40.3)	73.5 *d*, *J*=150 (91.7)	45.6 *t*, *J*=134 (20.5)	–	167.1 br. *s* (12.7)	50.7 *qa*, *J*=147 (5.3)
m-**12**	52.4 *d*, *J*=148 (39.5)	134.4 br. *s* (20.1)	24.3 *t*, *J*=130 (13.5)	128.0 br. *s*	137.1 *d*, *J*=160 (10.3)	25.9 *t*, *J*=130 (10.3)	138.9 br. *s* (17.4)	42.6 *d*, *J*=148	37.4 *t*, *J*=134	72.3 *d*, *J*=151 (90.8)	43.0 *t*, *J*=134	–	166.9 br. *s*	51.1 *qa*, *J*=147

Table 2 (continued)

	Chemical shifts of													
	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	C(11)	C(12)	others	
m-**13**	47.9 *d*, *J* = 148	133.8 br. *s*	26.4 *t*, *J* = 131	128.3 br. *s*	136.7 *d*, *J* = 162	25.5 *t*, *J* = 131	137.0 br. *s*	43.5 *d*, *J* = 147	33.6 *t*, *J* = 137	76.6 *d*, *J* = 154	45.3 *t*, *J* = 134	–	167.0 br. *s*	51.0 *qa*, *J* = 146
m-**14**	49.7 *d*, *J* = 146	133.9 br. *s*	24.4 *t*, *J* = 130	128.3 br. *s*	136.7 *d*, *J* = 159	25.9 *t*, *J* = 130	140.0 br. *s*	42.7 *d*, *J* = 146	35.4 *t*, *J* = 138	75.2 *d*, *J* = 156	43.9 *t*, *J* = 133	–	167.2 br. *s*	51.3 *qa*, *J* = 147
m-**15**	57.8 *d*, *J* = 155 (17.1)	131.6 br. *s* (13.1)	24.3 *t*, *J* = 132 (21.2)	127.7 br. *s* (37.6)	135.8 *d*, *J* = 160 (22.5)	26.6 *t*, *J* = 131 (8.4)	142.8 br. *s* (11.1)	41.2 *d*, *J* = 155 (9.4)	36.1 *t*, *J* = 135 (15.6)	212.8 br. *s* (39.6)	47.6 *t*, *J* = 135 (9.2)	–	166.6 br. *s* (77.9)	51.1 *qa*, *J* = 147 (27.0)
m-**17**	41.8 *d*	126.4 br. *s*	29.2 *t*	128.2 br. *s*	137.1 *d*	29.1 *t*	129.2 br. *s*	33.4 *d*	38.6 *t*	69.3 *d*	24.3 *t*	22.0 *t*	167.4 br. *s*	51.3 *qa*
m-**18**	41.5 *d*, *J* = 137	130.6 br. *s*	27.0 *t*, *J* = 130	128.0 br. *s*	137.1 *d*, *J* = 160	28.9 *t*, *J* = 130	132.0 br. *s*	33.6 *d*, *J* = 137	35.4 *t*, *J* = 131	68.8 *d*, *J* = 147	25.8 *t*, *J* = 130	17.3 *t*, *J* = 130	167.2 br. *s*	51.1 *qa*, *J* = 147
m-**19**	51.7 *d*, *J* = 141	127.5 br. *s*	26.9 *t*, *J* = 131	127.7 br. *s*	136.0 *d*, *J* = 160	28.8 *t*, *J* = 131	134.5 br. *s*	35.3 *d*, *J* = 137	40.1 *t*, *J* = 134	211.4 br. *s*	24.1 *t*, *J* = 133	22.4 *t*, *J* = 133	166.6 br. *s*	51.1 *qa*, *J* = 147
p-**25**	43.3 *d*	148.9 br. *s*	120.9 *d*	127.4 br. *s*	127.8 *t*	123.6 *d*	147.9 br. *s*	50.1 *d*	70.7 *d*	37.8 *t*	47.8 *t*	–	167.1 br. *s*	51.4 *qa*
p-**26**	42.5 *d*, *J* = 147 (22.2)	149.6 br. *s* (17.2)	121.3 *d*, *J* = 163 (14.7)	127.7 br. *s* (16.4)	127.7 *d*, *J* = 163 (11.0)	121.6 *d*, *J* = 163 (9.9)	150.2 br. *s* (20.4)	52.1 *d*, *J* = 148 (42.6)	72.5 *d*, *J* = 151 (100)	38.9 *t*, *J* = 135 (39.9)	45.6 *t*, *J* = 137 (28.9)	–	167.3 br. *s* (21.9)	51.7 *qa*, *J* = 147 (10.9)
p-**27**	42.9 *d*, *J* = 148	148.1 br. *s*	121.2 *d*, *J* = 163	128.0 br. *s*	127.6 *d*, *J* = 163	122.9 *d*, *J* = 162	148.1 br. *s*	47.8 *d*, *J* = 152	73.5 *d*, *J* = 156	35.1 *t*, *J* = 136	47.6 *t*, *J* = 136	–	167.1 br. *s*	51.5 *qa*, *J* = 147
p-**28**	42.2 *d*, *J* = 148	149.3 br. *s*	121.3 *d*, *J* = 163	128.3 br. *s*	127.8 *d*, *J* = 163	122.1 *d*, *J* = 162	148.6 br. *s*	49.1 *d*, *J* = 148	75.0 *d*, *J* = 159	36.6 *t*, *J* = 136	46.3 *t*, *J* = 137	–	166.8 br. *s*	51.5 *qa*, *J* = 148
p-**29**	41.4 *d*, *J* = 152	148.6 br. *s*	122.3 *d*, *J* = 164	129.4 br. *s*	128.6 *d*, *J* = 164	123.1 *d*, *J* = 164	145.0 br. *s*	58.7 *d*, *J* = 154	211.6 br. *s*	39.6 *t*, *J* = 136	50.6 *t*, *J* = 136	–	166.6 br. *s*	51.8 *qa*, *J* = 148
30	43.3 *d*, *J* = 148	148.2 br. *s*	121.3 *d*, *J* = 162	127.5 br. *s*	127.7 *d*, *J* = 162	120.1 *d*, *J* = 161	153.6 br. *s*	43.6 *d*, *J* = 148	26.3 *t*, *J* = 135	26.5 *t*, *J* = 135	49.0 *t*, *J* = 134.5	–	167.4 br. *s*	51.5 *qa*, *J* = 147
p-**31**	43.6	149.5	119.9	135.9	126.8	123.9	148.1	50.4	71.1	38.4	48.0	–	199.4	26.3
p-**32**	42.6	149.9	120.0	135.6	126.9	121.8	150.5	52.4	72.8	39.2	45.7	–	198.2	26.4

p-**33**	43.1	148.5	120.0	135.8	126.8	123.2	148.5	47.8	73.6	35.3	47.8	–	198.2 26.4	170.8 20.7
p-**34**	42.2	149.5	119.8	135.7	126.8	122.1	148.8	49.0	74.0	36.5	46.1	–	197.4 26.1	170.2 20.8
p-**35**	41.2	148.7	120.6	136.2	127.4	122.8	145.0	57.8	211.3	39.4	50.3	–	197.1	26.1
p-**36**	34.1 *d*	144.4 br. *s*	124.5 *d*	128.4 br. *s*	127.8 *d*	126.5 *d*	143.9 br. *s*	42.1 *d*	69.4 *d*	38.8 *t*	24.2 *t*	22.3 *t*	167.3 br. *s*	51.8 *qa*
p-**37**	43.5 *d*, *J* = 144 (29.0)	149.5 br. *s* (36.6)	119.5 *d*, *J* = 159 (39.6)	139.3 br. *s* (51.5)	124.4 *d*, *J* = 159 (36.3)	123.9 *d*, *J* = 159 (34.7)	141.0 br. *s* (42.7)	49.9 *d*, *J* = 148 (46.8)	71.3 *d*, *J* = 153 (100)	38.6 *t*, *J* = 136 (45.9)	47.7 *t*, *J* = 135 (25.1)	–	64.9	
m-**25**	49.7 *d*	142.3 br. *s*	124.6 *d*	127.4 br. *s*	128.3 *d*	119.8 *d*	154.3 br. *s*	43.6 *d*	37.8 *t*	70.7 *d*	47.8 *t*	–	167.1 br. *s*	51.4 *qa*
m-**26**	51.7 *d*, *J* = 148 (38.3)	144.8 br. *s* (18.8)	122.7 *d*, *J* = 162 (11.8)	127.2 br. *s* (13.2)	128.3 *d*, *J* = 162 (9.4)	120.3 *d*, *J* = 161 (9.0)	155.1 br. *s* (15.6)	42.8 *d*, *J* = 147 (21.5)	38.6 *t*, *J* = 135 (38.1)	72.5 *d*, *J* = 151 (94.1)	45.6 *t*, *J* = 137 (28.9)	–	167.3 br. *s* (17.3)	51.7 *qa*, *J* = 147 (7.9)
m-**27**	47.2 *d*, *J* = 152	142.9 br. *s*	124.1 *d*, *J* = 162	127.5 br. *s*	128.3 *d*, *J* = 163	120.0 *d*, *J* = 161	153.5 br. *s*	43.2 *d*, *J* = 148	35.1 *t*, *J* = 136	73.5 *d*, *J* = 156	47.6 *t*, *J* = 136	–	167.1 br. *s*	51.5 *qa*, *J* = 147
m-**28**	48.7 *d*, *J* = 148	143.4 br. *s*	123.2 *d*, *J* = 163	127.8 br. *s*	128.6 *d*, *J* = 163	120.3 *d*, *J* = 162	154.6 br. *s*	42.5 *d*, *J* = 148	36.4 *t*, *J* = 136	75.0 *d*, *J* = 159	46.3 *t*, *J* = 137	–	166.8 br. *s*	51.5 *qa*, *J* = 148
m-**29**	57.5 *d*, *J* = 154	140.1 br. *s*	124.3 *d*, *J* = 164	128.8 br. *s*	129.4 *d*, *J* = 164	121.2 *d*, *J* = 163	153.6 br. *s*	41.6 *d*, *J* = 152	39.5 *t*, *J* = 136	211.6 br. *s*	50.4 *t*, *J* = 134.5	–	166.6 br. *s*	51.8 *qa*, *J* = 148
m-**31**	50.0	142.6	123.6	135.4	127.7	120.3	154.9	43.8	38.4	71.1	48.0	–	199.4	26.3
m-**32**	52.0	145.1	121.4	135.2	127.5	120.4	155.5	42.9	38.8	72.8	45.7	–	198.2	26.4
m-**33**	47.5	143.0	122.9	135.4	127.6	120.3	153.9	43.3	35.3	73.6	47.8	–	198.2 26.4	170.8 20.7
m-**34**	48.6	143.6	121.8	135.2	127.5	120.3	154.7	42.4	36.3	74.8	46.1	–	197.2 26.1	170.2 20.8
m-**35**	57.2	140.2	122.6	135.8	128.0	121.2	153.6	41.4	39.1	211.3	50.0	–	196.8	26.1
m-**36**	42.3 *d*	138.8 br. *s*	127.5 *d*	128.4 br. *s*	127.8 *d*	123.5 *d*	149.4 br. *s*	34.3 *d*	39.0 *t*	69.4 *d*	24.2 *t*	22.3 *t*	167.3 br. *s*	51.8 *qa*
m-**37**	50.1 (39.9)	142.1 (37.5)	123.1 (38.0)	138.4 (42.8)	125.4 (29.6)	120.2 (22.1)	148.5 (28.4)	43.4 (23.4)	38.6 (38.2)	71.3 (84.0)	48.8 (20.9)	–	65.1 (78.2)	

Cycloadditions with methyl vinyl ketone gave mixtures of 4 stereoisomers. The stereoselectivities could not be determined unambigously. They were not very important, except in the case of the reaction of the *endo*-alcohol **2**. The regioselectivities *'p'/'m'* were determined again by analysis of the ^{13}C-NMR. chemical shifts of C(2) and C(7) of the adducts **20–24** (see *Table 3*). They were confirmed by the more facile analysis of the ^{13}C-NMR. spectra of the aromatized compounds **31–35** (see *Table 2*) obtained upon heating (400°, 1–3 min) the adduct mixtures **20–24** with an excess of sulfur [10] (yield 50–80%).

Table 3. *^{13}C-NMR. characteristics of the adduct mixtures* **20–24** ($CDCl_3$, $\delta_{TMS} = 0.0$ ppm). In paranthesis: sum of the relative intensities of the C(2) and C(7) signal.

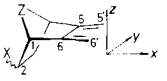
	'p' isomer			*'m'* isomer		
	δ(C(2))	δ(C(7))		δ(C(2))	δ(C(7))	
20	139.1	135.7	(64%)	133.4	141.1	(36%)
21	141.0	136.7	(31%)	134.4	143.4	(37%)
	141.9	135.7	(15%)	135.4	142.4	(17%)
22	139.1	136.4	(24%)	134.2	141.3	(51%)
	140.0	135.8	(12%)	135.3	140.6	(13%)
23	142.4	136.0	(27%)	133.9	144.7	(42%)
	143.4	135.1	(13%)	134.8	143.7	(18%)
24	145.5	133.7	(64%)	131.6	147.6	(19%)
	146.6	132.6	(11%)	132.5	146.9	(6%)

Discussion. – To a first approximation, geometry factors and steric factors should not play a dominant role in determining the regioselectivity of the cycloadditions of **2–6** and **8–10** because the exocyclic *s-cis*-butadienes are grafted onto rigid skeletons. Moreover, the dienes are differentiated by remote substitution only. If dipole-dipole (hard) interactions between the dienes and dienophiles should dominate, the *'p'*-regioselectivity would have been expected for all the cycloadditions reported here! This is not the case, showing that other factors intervene.

Perturbational molecular orbital theory (PMO [5] [6]) has been applied to interpret *Diels-Alder* reactivity. According to this theory and to a first approximation, the shape of the frontier orbitals (FMO) of the dienes and dienophiles should enable us to predict the regioselectivity of their cycloadditions. The coefficients (c_i) at the C-atoms C(α) and C(β) of the HOMO of MP and MVK are similar, moreover, the coefficients at the carbonyl centers are relatively small (1,3-interactions between the MO's of the cycloaddends reaching the geometries of the *Diels-Alder* transition state cannot be neglected *a priori*). This suggests that the HOMO (dienophile) – LUMO (diene) interaction should not be important in determining the regioselectivity. A dominant role is played probably by the LUMO (dienophile)/HOMO (diene) interaction. Accordingly, one predicts from the c_i reported in *Table 4* that the dienone **6** must give the highest *'p'*-regioselectivity (the highest overlap is realized between C(6') of **6** and C(β) of MP and MVK), whereas the other dienes **2–5** and **8–10** should give a smaller *'p'*-or no regioselectivity. Our results are in agreement with these predictions for **6** and MP, and **6** and MVK. In the other cases, the regioselectivities are insignificant (**3, 5, 8–10**) or contradicting (see *Table 1*). The cycloaddition of the *en-*

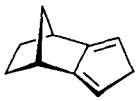
do-alcohol **2** is *'m'*-selective with MP and *'p'*-selective with MVK. The opposite is observed for the additions of the *endo*-acetate **4**. This demonstrates that simple FMO theory cannot be applied here. A gratuitous statement is to invoke the role played by

Table 4. *Eigenvalues (ε, eV) and eigenvectors $2p_z$ (coefficients c_i) at the olefinic C-atoms in the FMO's of the dienes* **1–10, 6-H⁺, 10-H⁺** *and dienophiles MP and MVK, obtained by the EHT [11] on MINDO/3-minimized geometries [12].* In italics: ε and c_i by the MNDO [13] technique.



	HOMO's						LUMO's				
	ε_k	c_i at C(5)	C(5')	C(6)	C(6')	Δ[a) [%]	ε_{k+1}	c_i at C(5)	C(5')	C(6)	C(6')
1	–12.4	–0.31	–0.53	0.31	0.53	0	– 8.9	0.5	–0.62	+0.5	–0.62
	– 9.2	*0.42*	*0.54*	*– 0.42*	*– 0.54*	*0*	*0.43*	*0.42*	*–0.56*	*0.42*	*–0.56*
2	–12.35	0.28	0.49	– 0.30	– 0.53	+ 3.9	– 8.35	–0.5	0.62	– 0.5	0.61
	– 9.13	*–0.42*	*–0.537*	*0.43*	*0.544*	*+ 0.7*	*0.44*	*–0.41*	*0.56*	*– 0.42*	*0.56*
3	–12.37	–0.29	–0.5	+0.31	+0.54	+ 3.8	– 8.87	–0.5	0.61	– 0.49	0.61
	– 9.24	*0.426*	*0.5404*	*– 0.42*	*– 0.5393*	*– 0.1*	*+0.33*	*–0.41*	*0.55*	*– 0.43*	*0.56*
4	–12.36	–0.3	–0.51	0.31	0.53	+ 1.9	– 8.87	–0.49	0.60	– 0.49	0.61
	– 9.22	*–0.42*	*–0.538*	*0.43*	*0.544*	*+ 0.6*	*0.35*	*0.42*	*–0.56*	*0.42*	*–0.56*
5	–12.37	–0.29	–0.51	0.30	0.53	+ 1.9	– 8.88	–0.5	0.61	– 0.49	0.61
	– 9.27	*–0.43*	*–0.542*	*0.43*	*0.537*	*– 0.5*	*0.31*	*–0.41*	*0.55*	*– 0.43*	*0.56*
6	–12.32	–0.23	–0.43	0.29	0.53	+10.4	– 9.1	–0.24	0.3	– 0.3	0.4
	– 9.41	*–0.41*	*–0.519*	*0.43*	*0.542*	*+ 2.1*	*0.14*	*0.4*	*–0.54*	*0.41*	*–0.56*
	– 7.13[b])	–0.355[b])	–0.485[b])	0.388[b])	0.525[b])	+ 4[b])	6.41[b])	0.43[b])	–0.58[b])	0.45[b])	–0.61[b])
7	–12.3	0.29	0.53	– 0.29	– 0.53	0	– 8.9	–0.5	0.6	– 0.5	0.6
	– 9.1	*0.42*	*0.54*	*– 0.42*	*– 0.54*	*0*	*0.4*	*0.41*	*–0.56*	*0.41*	*–0.56*
8	*– 9.09*	*–0.418*	*–0.539*	*0.422*	*0.545*	*+ 0.6*	*0.39*	*0.416*	*0.558*	*0.42*	*–0.56*
9	*– 9.18*	*0.424*	*0.544*	*– 0.42*	*– 0.540*	*– 0.4*	*0.31*	*–0.41*	*0.556*	*– 0.42*	*0.56*
10	–12.26	–0.23	–0.44	0.37	0.52	+ 8.3	– 9.26	–0.28	0.38	– 0.32	0.44
	– 9.37	*0.41*	*0.526*	*– 0.426*	*– 0.539*	*1.1*	*0.1*	*–0.40*	*0.545*	*– 0.41*	*0.566*
	– 6.98[b])	0.36[b])	–0.497[b])	0.38[b])	0.523[b])	2.5[b])	6.38[b])	–0.45[b])	0.61[b])	– 0.43[b])	0.58[b])
6-H⁺	–12.4	–0.29	–0.5	0.32	0.55	+ 4.7	– 8.8	0.49	–0.58	0.42	–0.5
	–13.1	*–0.52*	*–0.54*	*0.41*	*0.48*	*– 5.9*	*– 3.6*	*0.28*	*–0.47*	*0.43*	*–0.62*
10-H⁺	–12.29	0.26	0.498	0.3	0.54	+ 4.1	– 9.3	0.22	–0.31	0.27	–0.40
	–12.96	*0.5*	*0.55*	*– 0.41*	*– 0.486*	*– 6.1*	*– 3.5*	*0.29*	*–0.49*	*0.44*	*–0.63*

a) $\Delta = ([c_i(6')] - [c_i(5')]/([c_i(6')] + [c_i(5')])$; a positive value predicts *'p'*-regioselectivity with MP and MVK.
b) By *ab initio* STO 3G [14] on minimized MNDO geometry.



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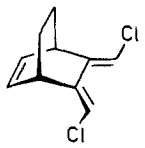
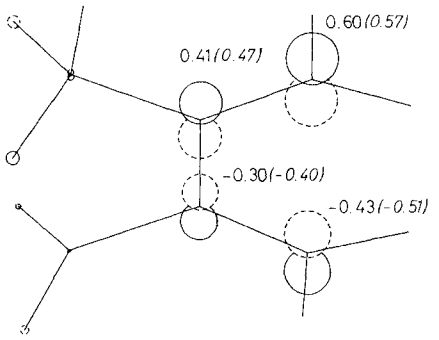


39

secondary MO interactions [15]. We did not find an explanation to our observations (opposite regioselectivities with MP and MVK) by analyzing the shapes of the subjacent FMO's of the alcohol- and acetate-diene derivatives.

The *Diels-Alder* additions to dienes such as **38** [16] and **39** [17] can be 'face'-selective, the dienophile prefering to attack onto the *endo*-face of the bicyclic system. If this is true in our cycloadditions, the *endo*-substituent in **2**, **4** and **8** can perturb the attack of the dienophile. From our results, these perturbations can be attractive (hydrogen bridging OH. . .ester group, charge transfer AcO. . .C=O, leading to *'m'*-regioselectivity) or repulsive (steric effects between the *endo* substituent of the diene and the ester group of MP or acetyl group of MVK leading to *'p'*-regioselectivity). At this moment, it is not possible to predict the *Diels-Alder* regioselectivities of dienes such as **2**, **4** and **8**.

The HOMO of *s-cis*-2-formyl-3-methylbutadiene (= 3-methyl-2-methylidenebutanal, **40**) is reproduced in *Figure 1*. As expected from a naive valence-bond model, the smallest coefficients c_i are calculated at the olefinic center directly substituted by the electron-withdrawing substituent (CHO).



40

Fig. 1. *HOMO of* s-cis-*2-formyl-3-methylbutadiene* (**40**) *as calculated by the EHT and MNDO* (in italic) *techniques* (MNDO-minimized geometry with the constraint of all C- and O-atoms coplanar; MO drawing program [26]).

If the dienones **6** and **10** could be considered as homoconjugative derivatives of **40**, the polarization of the HOMO of the diene moiety would be expected opposite to that calculated by the EHT, MNDO and *ab initio* STO 3G techniques *(Table 4)*. Thus, the carbonyl group appears to act as an electron-donating rather than an electron-withdrawing substituent according to the calculated shapes of the HOMO's of **6** and **10** *(Table 4, Fig. 2)*. The non-bonding n(CO)-electrons interact with the π-system at C(5) and C(6) *via* the σ[C(1),C(2)]-bond as illustrated in *Fig. 2*. This

effect is also calculated for the simpler diene **41**, the polarization of the HOMO's being the largest when the σ[C(1),C(2)]-bond is perpendicular to the π-plane of the diene (leading to a maximum π,σ-overlap, see *Fig. 3*).

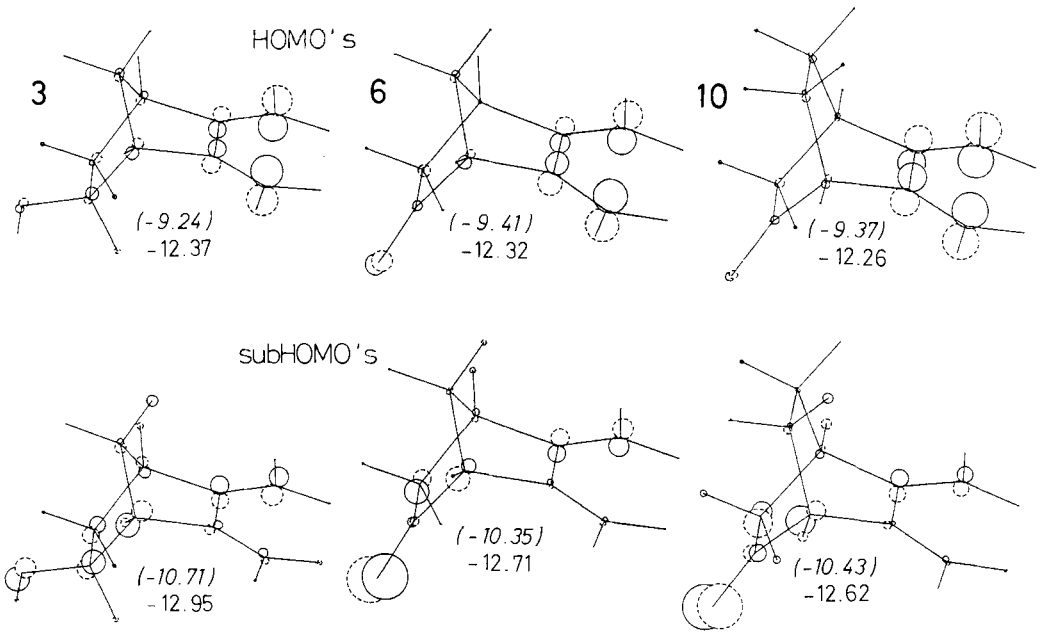
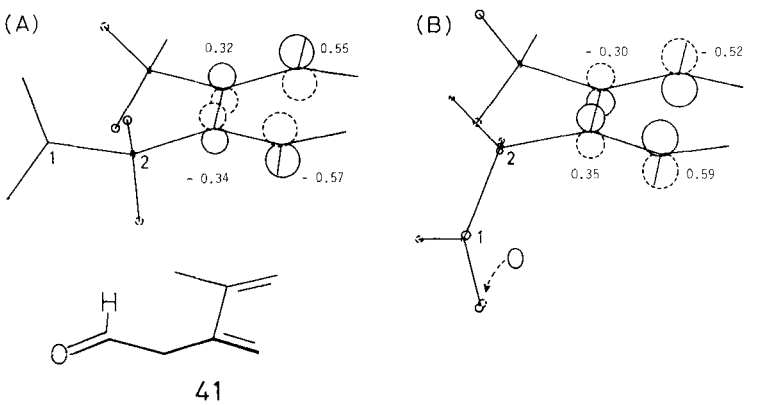


Fig. 2. *Shapes and eigenvalues (eV) of the HOMO's and subHOMO's of the alcohol* **3** *and the ketones* **6** *and* **10** (MNDO-minimized geometries). Eigenvalues by the EHT and MNDO (in italic) techniques, see *Table 4.*



41

Fig. 3. *HOMO of 3-methylidene-4-methyl-4-pentenal* (**41**) *in the* s-cis-*conformation.* (A) σ[C(1),C(2)] is coplanar with the π-plane of the diene, (B) σ[C(1),C(2)] is in a plane perpendicular to the π-plane of the diene (MNDO-minimized geometries with no other constraints than those indicated; N. B.: the coefficients (MNDO) at the O-atom and at C(1) and C(2) in (B) vanish in (A)).

42 **43**

By protonation of the CO-group, the polarization of the diene HOMO's in **6–H**$^+$ and **10–H**$^+$ is dramatically reduced[7]) *(Table 4)*, confirming the intervention of the n(CO)↔σ[C(1),C(2)]↔π[C(5),C(6)] interaction in **6** and **10**. The latter is related to the 'frangomeric effect' and to the *Grob* fragmentation [19]. It is responsible for making the 6-oxo-2-norbornyl cation **42** more stable than the 5-oxo-isomer **43** [20].

Obviously, the HOMO's alone cannot describe all the properties of our dienes[8]); the subMO's should also be considered. In the case of **6** and **10**, the subHOMO's *(Fig. 2)* are (n(CO),σ,π)-delocalized with significant p_z-coefficients at the olefinic C-atoms, but contrary to the HOMO's they are larger at C(5) and C(5') than at C(6) and C(6') and could favor the formation of the *'m'*-isomers. Similar, but smaller effects are also calculated for the HOMO's and subHOMO's of the alcohols **2**, **3**, **8** and **9** *(Table 4, Fig. 2)*.

If simple PMO arguments should rationalize the regioselectivity of the *Diels-Alder* additions of MP and MVK to our dienes, it appears that the LUMO (dienophile)/HOMO (**6**) interaction commands the *'p'*-regioselectivity and overweights the *'m'*-orientation effect of the LUMO (dienophile)/subHOMO (**6**) interaction. It is interesting to note, that the 'inverse polarization' is significantly larger for the HOMO of **6** than for that of **10**. This is probably due to the enhanced polarizability (because of the higher strain and specific electronic features [22]) of the norbornane skeleton compared with that of the bicyclo[2.2.2]octane system. The better σ[C(1),C(2)], pC(6) alignment in **6** than in **10** (because of smaller C(2),C(1),C(6) bond angle in **6** than in **10**) may also play a role [1]. Accordingly and invoking the competitive LUMO (dienophile)/HOMO and subHOMO (diene) interactions, the PMO theory predicts a larger *'p'-Diels-Alder* regioselectivity for **6** than for **10**, as observed.

Conclusion. – The *Diels-Alder* regioselectivities of 2-*exo*-substituted 5,6-dimethylidenenorbornanes and bicyclo[2.2.2]octanes are insignificant. *'p'*- or *'m'*-regioselectivities can be observed for *endo*-isomers. It cannot be predicted by invoking

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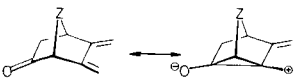
[7]) In the presence of anhydrous $ZnCl_2$, the regioselectivity of the additions of MP or MVK to **6** or **10** is not improved, probably because the enhanced *'p'*-regioselectivity expected by *Lewis* acid coordination of the dienophile [18] must compete with a loss of the polarization of the diene HOMO's upon $ZnCl_2$-complexation of the homoconjugated ketone.

[8]) For instance the ^{13}C-NMR. characteristics of **6** [21] and **10** [1], as well as their *Diels-Alder* reactivity toward tetracyanoethylene [1] are better explained by considering the electron-withdrawing effect of the carbonyl function:



PMO arguments. The 5,6-dimethylidene-2-norbornanone (**6**) adds to strong dienophiles with relatively good *'p'*-regioselectivity, as predicted by FMO theory. In this case, the carbonyl group acts as an electron-donating substituent. The hyperconjugative n(CO)/σ[C(1),C(2)]/π[C(5),C(6)] interaction overrides the usual electron-withdrawing effect (π^*(CO)/π[C(5),C(6)] interactions) of this function.

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Experimental Part

General remarks. See [1]. *Preparation of the dienes.* See [1] for **8–10**, [23] for **2**, **4** and **5**, and [24] for **3** and **6**.

1. *Adduct mixture* **11–19** *with methyl propynoate (MP).* Each diene **1–6**, and **8–10** (6 mmol) was mixed without solvent with MP (36 mmol, 3 g, freshly distilled) in a pyrex tube. After careful degassing on a vacuum line, the tube was sealed i. V. and heated in an oil bath to 80° for 5 h (**8–10**) or 15–20 h (**1–6**). After cooling, the tube was opened, and the mixture separated by distillation i. V. – ^{13}C-NMR.: see *Table 2.*

*Methyl 9*endo- *and 10*endo-*hydroxytricyclo[6.2.1.0^{2,7}]undeca-2(7),4-diene-4-carboxylate* (*p*-**11**/*m*-**11**). Yield 78%, oil. – IR (film): 3220, 2980, 1730, 1450, 1270, 740. – ^{1}H-NMR. (60 MHz, $CDCl_3$): 7.0 (*m*, 1 H); 4.6 (*m*, 1 H); 3.8 (*s*, 3 H); 3.0 (br. *s*, 4 H); 2.8 (br. *s*, 1 H); 2.6 (br. *s*, 2 H); 2.0–1.0 (*m*, 4 H). – MS. (70 eV): 220 (5), 176 (32), 161 (12), 143 (16), 136 (45), 129 (16), 117 (100), 115 (68), 105 (6), 91 (41), 89 (6), 77 (31).

$C_{13}H_{16}O_3$ (220.27) Calc. C 70.89 H 7.32% Found C 70.73 H 7.41%

*Methyl 9*exo- *and 10*exo-*hydroxytricyclo[6.2.1.0^{2,7}]undeca-2(7),4-diene-4-carboxylate* (*p*-**12**/*m*-**12**). Yield 92%, oil – IR. (film): 3220, 2980, 1720, 1450, 1270, 740. – ^{1}H-NMR. ($CDCl_3$): 7.0 (*m*, 1 H); 3.8 (*m*, 5 H); 2.9 (*m*, 4 H); 2.6 (*m*, 2 H); 2.0–1.0 (*m*, 4 H). – MS. (70 eV): 220 (8), 189 (9), 176 (58), 161 (21), 143 (25), 129 (23), 117 (100), 115 (65), 105 (8), 91 (34), 77 (19).

$C_{13}H_{16}O_3$ (220.27) Calc. C 70.89 H 7.32% Found C 71.03 H 7.32%

*Methyl 9*endo- *and 10*endo-*acetoxytricyclo[6.2.1.0^{2,7}]undeca-2(7),4-diene-4-carboxylate* (*p*-**13**/*m*-**13**). Yield 87%.

$C_{15}H_{18}O_4$ (262.31) Calc. C 68.68 H 6.92% Found C 68.84 H 6.87%

*Methyl 9*exo- *and 10*exo-*acetoxytricyclo[6.2.1.0^{2,7}]undeca-2(7),4-diene-4-carboxylate* (*p*-**14**/*m*-**14**). Yield 88%.

$C_{15}H_{18}O_4$ (262.31) Calc. C 68.68 H 6.92% Found C 68.69 H 6.84%

Methyl 9- and 10-oxotricyclo[6.2.1.0^{2,7}]undeca-2(7),4-diene-4-carboxylate (*p*-**15**/*m*-**15**). Yield 97%, oil. – IR. (film): 2970, 1750, 1640, 1260, 1150, 1090, 720. – ^{1}H-NMR. ($CDCl_3$): 7.0 (*m*, 1 H); 3.8 (*s*, 3 H); 3.0 (*m*, 6 H); 2.1–1.9 (*m*, 4 H). – MS. (70 eV): 218 (16), 187 (13), 176 (72), 175 (50), 174 (40), 161 (24), 143 (18), 129 (42), 128 (40), 127 (23), 117 (100), 115 (83), 103 (9), 91 (42), 89 (13), 77 (18).

$C_{13}H_{14}O_3$ (218.25) Calc. C 71.54 H 6.46% Found C 71.28 H 6.62%

Methyl tricyclo[6.2.1.0^{2,7}]undeca-2(7),4-diene-4-carboxylate (**16**). Yield 95%, oil. – UV. (EtOH): 247 (2280), 210 *S* (9900). – UV. (isooctane): 251 (1750), 244 (2200), 210 (9750). – IR. (film): 2960, 2920, 2880, 1720, 1685, 1640, 1440, 1380, 1290, 1250, 1130, 1085, 1050, 940, 720. – ^{1}H-NMR. ($CDCl_3$): 7.0 (*m*, 1 H); 3.8 (*s*, 3 H); 3.0 (*m*, 4 H); 2.7 (*m*, 2 H); 1.8–0.8 (*m*, 6 H). – MS. (70 eV): 204 (3), 176 (3), 175 (4), 174 (6), 145 (2), 143 (4), 117 (7), 71 (3), 69 (4), 32 (95), 28 (100).

$C_{13}H_{16}O_2$ (204.27) Calc. C 76.44 H 7.90% Found C 76.60 H 7.94%

*Methyl 9*endo- *and 10*endo-*hydroxytricyclo[6.2.2.0^{2,7}]dodeca-2(7),4-diene-4-carboxylate* (*p*-**17**/*m*-**17**). Yield 90%, oil. – IR. (film): 3600, 3440, 3000, 2950, 2875, 1715, 1650, 1440, 1260, 1000. – ^{1}H-NMR. ($CDCl_3$): 7.0 (*m*, 1 H); 3.95 (*m*, 1 H); 3.75 (br. *s*, 3 H); 3.1 (*m*, 4 H); 2.3 (*m*, 2 H); 2.0–1.0 (*m*, 6 H). – MS. (70 eV): 234 (11), 215 (5), 203 (7), 190 (80), 157 (20), 131 (100), 130 (43), 129 (68), 128 (41), 115 (40), 105 (16), 91 (38).

$C_{14}H_{18}O_3$ (234.30) Calc. C 71.77 H 7.74% Found C 71.98 H 7.69%

*Methyl 9*exo- *and 10*exo-*hydroxytricyclo[6.2.2.0^{2,7}]dodeca-2(7),4-diene-4-carboxylate* (*p*-**18**/*m*-**18**). Yield 88%, oil. – IR. (film): 3430, 2950, 2860, 2820, 1750, 1650, 1430, 1260, 1070, 1050, 1000, 940, 720. – ^{1}H-NMR. ($CDCl_3$): 7.0 (*m*, 1 H); 3.85 (*m*, 1 H); 3.75 (br. *s*, 3 H); 2.9 (br. *s*, 4 H); 2.25 (*m*, 2 H); 2.1–1.0 (*m*, 6 H). – MS. (70 eV): 234 (9), 215 (4), 203 (6), 190 (78), 186 (15), 159 (8), 158 (10), 157 (17), 131 (100), 130 (40), 129 (61), 128 (38), 115 (32), 105 (11), 103 (9), 91 (30).

$C_{14}H_{18}O_3$ (234.30) Calc. C 71.77 H 7.74% Found C 72.01 H 7.81%

Methyl 9- and 10-oxotricyclo[6.2.2.0^{2,7}]dodeca-2(7),4-diene-4-carboxylate (*p*-**19**/*m*-**19**). Yield 90%, oil. – IR. (film): 2950, 2880, 1760, 1650, 1440, 1280, 1090, 1070, 760, 730. – ^{1}H-NMR. ($CDCl_3$): 7.05 (*m*, 1 H); 3.75 (br. *s*, 3 H); 3.05 (br. *s*, 4 H); 2.9 (*m*, 1 H); 2.75 (*m*, 1 H); 2.1 (*d* × *m*, 2 H); 2.0–1.5 (*m*, 4 H). – MS. (70 eV): 232 (44), 201 (15), 200 (10), 199 (9), 191 (25), 190 (96), 189 (30), 188 (40), 186 (37), 157 (31), 131 (100), 130 (45), 129 (90), 128 (43), 115 (45), 91 (79).

$C_{14}H_{16}O_3$ (232.28) Calc. C 72.39 H 6.94% Found C 72.21 H 6.99%

2. *Adduct mixtures* **20–24** *with methyl vinyl ketone (MVK).* Each diene **2–6** (6 mmol) was heated for 12 h to 80° with MVK (2.5 g, 36 mmol, freshly distilled) and hydroquinone (10 mg), without solvent and under N_2. The mixture was evaporated i. V. and separated by column chromatography on silica gel (Hexane/AcOEt 4:1). The crude adducts were purified by bulb-to-bulb distillation, (*Büchi*). – Partial ^{13}C-NMR.: see *Table 3.*

*9*endo- *and 10*endo-*hydroxytricyclo[6.2.1.0^{2,7}]undec-2(7)-en-4-yl methyl ketone* (*p*-**20**/*m*-**20**). Yield 70%, oil.

$C_{13}H_{18}O_2$ (206.29) Calc. C 75.69 H 8.80% Found C 75.72 H 8.85%

*9*exo- *and 10*exo-*hydroxytricyclo[6.2.1.0^{2,7}]undec-2(7)-en-4-yl methyl ketone* (*p*-**21**/*m*-**21**). Yield 89%, oil.

$C_{13}H_{18}O_2$ (206.29) Calc. C 75.69 H 8.80% Found C 75.77 H 8.89%

*9*endo- *and 10*endo-*acetoxytricyclo[6.2.1.0^{2,7}]undec-2(7)-en-4-yl methyl ketone* (*p*-**22**/*m*-**22**). Yield: 70%, oil.

$C_{15}H_{20}O_3$ (248.32) Calc. C 72.55 H 8.11% Found C 72.66 H 8.19%

*9*exo- *and 10*exo-*acetoxytricyclo[6.2.1.0^{2,7}]undec-2(7)-en-4-yl methyl ketone* (*p*-**23**/*m*-**23**). Yield 82%, oil.

$C_{15}H_{20}O_3$ (248.32) Calc. C 72.55 H 8.11% Found C 72.51 H 8.05%

9- and 10-oxotricyclo[6.2.1.0^{2,7}]undec-2(7)-en-4-yl methyl ketone (*p*-**24**/*m*-**24**). Yield: 85%, oil.

$C_{13}H_{16}O_2$ (204.27) Calc. C 76.44 H 7.90% Found C 76.39 H 7.83%

3. *Aromatization of the adducts* **11–17,** *preparation of the methyl benzoates* **25–30** *and* **36**. Each adduct **11–17** (4 mmol; *m*/*p*-mixture) was mixed with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (1 g, 4.4 mmol) and benzene (6 ml) and stirred at RT. for 6 h or heated under reflux for 2 h. After cooling to RT., the precipitate was filtered off and washed with benzene (2 times 5 ml). The benzene solution was washed with water (3 times 15 ml) and dried ($MgSO_4$). The alcohols **11** and **12** were partially oxidized (5–10%) to the ketones **29** under these conditions. After evaporation of the solvent i. V., the residue was purified by column chromatography on silica gel ($CHCl_3$/Acetone 95:5). – ^{13}C-NMR. of **25–30** and **36**: see *Table 2.*

*Methyl 9*endo- *and 10*endo-*hydroxytricyclo[6.2.1.0^{2,7}]undeca-2,4,6-triene-4-carboxylate* (*p*-**25**/*m*-**25**). Yield 95%, oil. – IR. (film): 3450, 2990, 2896, 1720, 1630, 1600, 1450, 1275, 1200, 1100, 1050, 770, 740. – ^{1}H-NMR. ($CDCl_3$): 8.0–7.2 (*m*, 3 H); 4.5 (*m*, 1 H); 3.7 (br. *s*, 3 H); 3.6 (br. *s*, 1 H); 2.5 (*m*, 2 H); 2.0–1.0 (*m*, 4 H). – MS. (70 eV): 218 (7), 174 (21), 143 (9), 138 (16), 129 (9), 115 (21), 105 (21), 94 (80), 91 (33), 86 (18), 84 (29), 79 (100), 77 (31).

$C_{13}H_{14}O_3$ (218.25) Calc. C 71.54 H 6.46% Found C 71.66 H 6.42%

*Methyl 9*exo- *and 10*exo-*hydroxytricyclo[6.2.1.0^{2,7}]undeca-2,4,6-triene-4-carboxylate* (*p*-**26**/*m*-**26**). Yield 96%, oil.

$C_{13}H_{14}O_3$ (218.25) Calc. C 71.54 H 6.46% Found C 71.68 H 6.48%

*Methyl 9*endo- *and 10*endo-*acetoxytricyclo[6.2.1.0^{2,7}]undeca-2,4,6-triene-4-carboxylate* (*p*-**27**/*m*-**27**). Yield 98%, oil.

$C_{15}H_{16}O_4$ (260.29) Calc. C 69.22 H 6.20% Found C 69.39 H 6.26%

*Methyl 9*exo- *and 10*exo-*acetoxytricyclo[6.2.1.0^{2,7}]undeca-2,4,6-triene-4-carboxylate* (*p*-**28**/*m*-**28**). Yield: 98%, oil.

$C_{15}H_{16}O_4$ (260.29) Calc. C 69.22 H 6.20% Found C 69.32 H 6.25%

Methyl 9- and 10-oxotricyclo[6.2.1.0^{2,7}]undeca-2,4,6-triene-4-carboxylate (*p*-**29**/*m*-**29**). Yield 96%, oil.

Methyl tricyclo[6.2.1.0^{2,7}]undeca-2,4,6-triene-4-carboxylate (**30**). Yield 95%, oil. – UV. (EtOH): 286 (1480), 277 (1750), 247 (12350), 213 *S* (22000), 206 (31500). – UV. (isooctane): 286 (1360), 276 (1450), 250 *S* (10100), 243 (12500), 206 (37500). – IR. (film): 2890, 2260, 2040, 1725, 1440, 1320, 1270, 1190, 1160, 1090, 760. – ^{1}H-NMR. ($CDCl_3$): 7.9 (*m*, 2 H); 7.3 (*s*, 1 H); 3.9 (*s*, 3 H); 3.4 (*m*, 2 H); 2.0–1.0 (*m*, 6 H). – MS. (70 eV): 202 (6), 174 (11), 149 (2), 143 (6), 128 (4), 115 (10), 83 (2), 71 (2), 69 (3), 57 (4), 44 (4), 32 (100).

$C_{13}H_{14}O_2$ (202.25) Calc. C 77.20 H 6.98% Found C 77.15 H 7.05%

*Methyl 9*endo- *and 10*endo-*hydroxytricyclo[6.2.2.0^{2,7}]dodeca-2,4,6-triene-4-carboxylate* (*p*-**36**/*m*-**36**). Yield 94%, oil. – ^{1}H-NMR. ($CDCl_3$): 8.0–7.2 (*m*, 3 H); 3.9 (*m*, 1 H); 3.8 (br. *s*, 3 H); 2.4 (*m*, 2 H); 2.0–1.0 (*m*, 7 H). – IR. (film): 3450, 2990, 2880, 1720, 1640, 1450, 1275, 1210, 1050, 780, 720. – MS. (70 eV): 232 (24), 213 (7), 201 (35), 100 (34), 188 (60), 157 (19), 129 (100), 113 (47), 105 (17), 91 (77).

$C_{14}H_{16}O_3$ (232.26) Calc. C 72.39 H 6.94% Found C 72.17 H 6.71%

4. *Aromatization of the adducts* **20–24**, *preparation of the acetophenones* **31–35**. Each adduct **20–24** (4 mmol; *m*/*p*-mixture) was mixed with sulfur (powder, 0.64 g; 20 mmol) and heated to 400–450° for 1–3 min (H_2S-evolution). After cooling to RT. the mixture was triturated with $CHCl_3$. The organic extract was filtered through a short column of silica gel (hexane/AcOEt 1:1). After evaporation of the solvent, the crude product was purified by bulb-to-bulb distillation i. V. *(Büchi)*. – ^{13}C-NMR.: see *Table 2*.

*9*endo- *and 10*endo-*Hydroxytricyclo[6.2.1.0^{2,7}]undeca-2,4,6-trien-4-yl methyl ketone* (*p*-**31**/*m*-**31**). Yield 45%.

*9*exo- *and 10*exo-*Hydroxytricyclo[6.2.1.0^{2,7}]undeca-2,4,6-trien-4-yl methyl ketone* (*p*-**32**/*m*-**32**). Yield 47%.

*9*endo- *and 10*endo-*Acetoxytricyclo[6.2.1.0^{2,7}]undeca-2,4,6-trien-4-yl methyl ketone* (*p*-**33**/*m*-**33**). Yield 75%.

*9*exo- *and 10*exo-*Acetoxytricyclo[6.2.1.0^{2,7}]undeca-2,4,6-trien-4-yl methyl ketone* (*p*-**34**/*m*-**34**). Yield 74%.

9- and 10-Oxotricyclo[6.2.1.0^{2,7}]undeca-2,4,6-trien-4-yl methyl ketone (*p*-**35**/*m*-**35**). Yield 80%.

Reduction and oxidation of the ketoesters **15** *to the hydroxybenzoates* p-**25**/m-**25**[8]). The adducts **15** (1.6 g, 8 mmol) in THF (40 ml) and $NaBH_4$ (0.15 g, 4 mmol) were heated under reflux for 24 h. After cooling to RT., 2N H_2SO_4 (20 ml) was added slowly under stirring. The precipitate was filtered off and washed with ether (4 times 10 ml). The organic extract was dried ($MgSO_4$) and evaporated i. V. The crude **25** (+ *ca.* 10% **11**) was purified by column chromatography on silica gel (hexane/AcOEt 1:1): 1 g (60%) of **25**.

5. *Reduction of the aromatized adducts* p-**25**/m-**25** *to 9*endo- *and 10*endo-*hydroxytricyclo [6.2.1.0^{2,7}]undeca-2,4,6-trien-4-methanol* (*p*-**37**/*m*-**37**). The adducts **25** (250 mg, 1.14 mmol) in THF (5 ml) and $LiAlH_4$ (30 mg, 0.8 mmol) were heated under reflux for 1 h. After cooling to RT., H_2O (2 ml) was added slowly under stirring. After filtration, the solution was diluted with Et_2O (20 ml), washed with H_2O (2 times 10 ml), dried ($MgSO_4$) and evaporated i. V. The crude **37** was purified by chromatography on silica gel (hexane/AcOEt 1:1) yielding 153 mg (70%) of oil.

$C_{12}H_{14}O_2$ (190.24) Calc. C 75.76 H 7.42% Found C 75.90 H 7.50%

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[8]) Dehydrogenation of 1,4-cyclohexadiene derivatives by hydrides has been reported before [25].

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