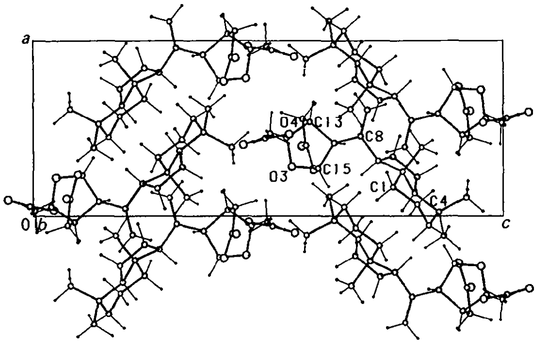

Fig. 2. Crystal packing projected on the *ac* plane.

The cyclohexane is in a nearly ideal chair conformation with C1 and C4 displaced 0.681 (3) and 0.651 (3) Å in opposite directions from the best plane through the remaining endocyclic C atoms. The puckering parameters (Cremer & Pople, 1975) are: $Q = 0.560\ (6)$ Å, $\theta = 3.7\ (7)°$. The *trans*-fused pentacyclic ring adopts an envelope C_s conformation with apex at C10, which is 0.750 (4) Å out of the mean plane passing through the other four atoms. In the oxabicyclic system, the furanoid ring is in a distorted twist form with C13 and C14 out of the plane defined by the remaining ring atoms, at distances of 0.219 (4) and 0.521 (3) Å, respectively. The δ-lactone can be described as a half-boat form with C14 0.915 (3) Å out of the best plane of the remaining atoms. The axial acetoxy group is strictly planar with O5 *cis* to C16.

Fig. 2 shows the molecular packing which is governed by normal van der Waals interactions.

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Pyramidalization in a Tetracyclic Perpendicular Diene Derivative

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Abstract. *endo,exo*-11,11-Dimethoxy-12-methylenetetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-9-ene (1), $C_{15}H_{20}O_2$, $M_r = 232.32$, monoclinic, $P2/n$, $a = 19.362\ (1)$, $b = 6.703\ (1)$, $c = 20.011\ (1)$ Å, $\beta = 109.656\ (4)°$, $V = 2445.59$ Å^3, $Z = 8$, $D_x = 1.262$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1.54056$ Å, $\mu = 6.088$ cm^{-1}, $F(000) = 1008$, $T = 148$ K, $R = 0.0483$ and $wR = 0.0494$ for 4648 unique reflections. The molecule contains a methylenenorbornyl unit fused to a substituted norbornene. The

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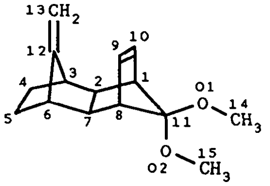
ring C atom of the exocyclic double bond is significantly pyramidalized. Possible explanations of this deformation include polarization of the π system and π–π electronic repulsions at the methylene C atom.

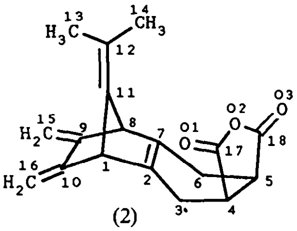
Introduction. There has been considerable recent research activity focusing on synthetic, spectroscopic, chemical and theoretical aspects of molecules having C=C double bonds with pyramidalized C atoms (Borden, 1989; Haddon, 1990; Luef & Keese, 1991). Much of this work concerned tetrasubstituted and/or endocyclic double bonds (*e.g.* sesquinorbornenes), while deformations of other types of double bonds have only been partially explored (Luef & Keese, 1991).

An interesting case with three different types of C=C double bonds is structure (2) (Pinkerton, Schwarzenbach, Birbaum, Carrupt, Schwager & Vogel, 1984). The C(2)=C(7), C(11)=C(12) and C(16)=C(10)—C(9)=C(15) π bonds each experience non-equivalent facial symmetry. In the low-temperature X-ray crystal structure of (2) the C(2)—C(3) or C(7)—C(6) bond is bent downward (*endo* direction) 13–14° relative to the C(1)—C(2)—C(7)—C(8) least-squares plane. This type of π-bond bending is well known (Houk, 1983; Watson, Kashyap & Plummer, 1991).

Neither the C(11) nor the C(12) atom of the exocyclic isopropylidene group in (2) is apparently nonplanar. Pyramidalizations at C(9) and C(10) were likewise too small to be considered significant. Possible reasons for the near planarity of C(9) and C(10) have been discussed (Houk, 1983).



(1)



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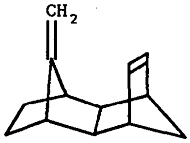

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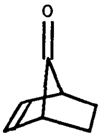

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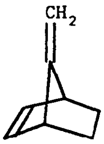

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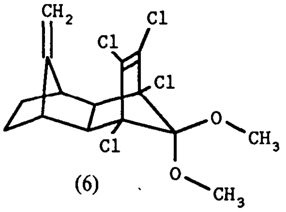

(6)

The study of (2) and similar molecules led us to investigate the structural system (3) that might have significant C-atom pyramidalization in the exocyclic double bond. Hydrocarbon (3) is known (Lap & Paddon-Row, 1979), and peaks were observed at 8.26 and 9.5 eV in its UV photoelectron spectrum (Gleiter, Jähne, Allred & Lloyd, 1992), which are consistent with through-space π–π interaction. It seemed likely that this electronic effect would result in deformations of the double bonds.

Hydrocarbon (3) is a liquid at 268 K and it polymerizes slowly at room temperature. The dimethoxy derivative (1) was therefore synthesized and its structure was determined by X-ray diffraction.

Experimental. 7-Norbornenone (bicyclo[2.2.1]hept-2-en-7-one), (4), was made by the standard method (Gassman & Marshall, 1973). 7-Methylenenorbornene (5) has been made *via* a Wittig reaction of (4) with methylenetriphenylphosphorane (Adam, Lucchini, Pasquato, Peters, Peters & von Schnering, 1986). The yield of (5) was improved to 90% by generating methylenetriphenylphosphorane from methyltriphenylphosphonium bromide with sodium amide in the high boiling polyether solvent tetraglyme under dry nitrogen. After filtration of the insoluble salts, (4) was added, and the product (5) was distilled out under vacuum. Diels–Alder reaction of (5) and dimethoxytetrachlorocyclopentadiene in hexane at 393 K afforded (6) in 88% yield. Crude (6) was chromatographed on alumina (ether), recrystallized (ether/pentane), and vacuum sublimed: m.p. 376–378 K; ^{1}H NMR (90 MHz, acetone-d_6) δ 1.20–1.93 (*m*, 4H), 2.33 (*m*, 2H), 2.675 (*s*, 2H), 3.47 (*s*, 3H), 3.58 (*s*, 3H), 4.58 (*s*, 2H, $C{=}CH_2$). Compound (6) was dechlorinated with sodium in refluxing ethanol (Lap & Paddon-Row, 1979) to yield (1) which was purified by short-path vacuum distillation (90%, b.p. 344–346 K, 6.67 Pa). The oil crystallized on cooling. Recrystallization at 273 K from pentane gave white crystals of (1): m.p. 304–306 K; ^{1}H NMR (300 MHz, acetone-d_6) δ 1.09–1.28 (*m*, 2H), 1.30–1.44 (*m*, 2H), 1.98–2.09 (*m*, 2H), 2.10–2.21 (*m*, 2H), 2.70–2.83 (*m*, 2H), 2.95 (*s*, 3H), 3.08 (*s*, 3H), 4.23 (*s*, 2H, $C{=}CH_2$), 5.61 (*t*, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, acetone-d_6) δ 29.78, 42.14, 46.05, 49.00, 49.38, 51.83, 98.05 [C(13)], 121.01 [C(11)], 132.21 [C(9), C(10)], 161.27 [C(12)].

A crystal of (1) suitable for X-ray structure analysis was obtained by vacuum sublimation (dimensions 0.21 × 0.18 × 0.12 mm). Intensity data were collected at low temperature (148 K) on an Enraf–Nonius CAD-4 diffractometer using the $\theta/2\theta$ scan technique (4–130°). Lattice parameters were calculated from least-squares refinement of 25 reflections in the range $20 \leq 2\theta \leq 30°$. An empirical absorption correction was applied (minimum transmission 88.03%, maximum transmission 99.95%). The maximum value of $\sin\theta/\lambda$ was 0.588 Å^{-1}. A total of 4702 reflections were measured ($0 \leq h \leq 22$, $0 \leq k \leq 7$ and $-23 \leq l \leq 23$), with 4648 unique ($R_{\text{int}} = 0.011$), and 3647 with $I \geq 3\sigma(I)$ in the final cycle of refinement. Standard reflections showed variations in intensity of less than 3%, and no decay correction was applied. The structure was solved and refined using the direct method *SDP* package (Enraf–Nonius, 1979). F magnitudes were used in the least-squares refinement. H atoms were located and refined with fixed isotropic thermal parameters. The number of parameters refined in the final cycle was 308 (C and O anisotropic, unit weighting) yielding $R = 0.0483$, $wR = 0.0494$, $S = 2.311$, $(\Delta/\sigma)_{\max} = 0.001$. The highest peak in the final difference map was 0.891 e Å^{-3}. An isotropic secondary-extinction correction had a value of 1.797×10^{-6}. Atomic scattering factors f' and f'' were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). There were two independent molecules in the asymmetric unit. Table 1 lists the atomic positional parameters while Table 2 gives bond lengths and bond angles for one of the molecules.*

Discussion. *ORTEP* (Johnson, 1965) and *PLUTO* (Motherwell & Clegg, 1983) side view drawings of one of the molecules are shown in Figs. 1 and 2, respectively. Bond lengths and bond angles are similar to those of other systems with norbornyl skeletons fused across a common single bond (Bartlett, Combs, Le, Watson, Galloy & Kimura, 1982). Differences between the corresponding bond lengths and bond angles in the tetracyclic hydrocarbon framework are ≤0.008 Å and ≤0.7°, respectively, for the two independent molecules. Differences of 0.014 Å in the O(2)—C(15) bond length and 1.5° in the O(1)—C(11)—C(1) angle at C(11) reflect somewhat different CH_3—O— conformations in the two independent molecules. There are no non-hydrogen intermolecular contact distances ≤3.5 Å.

Table 1. *Atomic coordinates and isotropic or equivalent isotropic thermal parameters* (Å^2)

C and O atoms were refined anisotropically, for which $B_{\text{eq}} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$. H atoms were refined with fixed isotropic thermal parameters.

	x	y	z	$B_{\text{iso}}/B_{\text{eq}}$
O(1)	0.56011 (7)	0.2701 (2)	0.52507 (7)	1.61 (3)
O(2)	0.65126 (7)	0.4793 (2)	0.59396 (7)	1.58 (3)
C(1)	0.6045 (1)	0.5189 (3)	0.4611 (1)	1.40 (4)
C(2)	0.6808 (1)	0.6214 (3)	0.4770 (1)	1.41 (4)
C(3)	0.7067 (1)	0.6888 (3)	0.4153 (1)	1.66 (4)
C(4)	0.7803 (1)	0.8018 (4)	0.4509 (1)	2.12 (5)
C(5)	0.8351 (1)	0.6301 (4)	0.4862 (1)	2.16 (5)
C(6)	0.7868 (1)	0.4399 (3)	0.4671 (1)	1.72 (4)
C(7)	0.7363 (1)	0.4491 (3)	0.5126 (1)	1.46 (4)
C(8)	0.6851 (1)	0.2696 (3)	0.5113 (1)	1.51 (4)
C(9)	0.6439 (1)	0.2138 (3)	0.4349 (1)	1.77 (4)
C(10)	0.5966 (1)	0.3588 (3)	0.4060 (1)	1.66 (4)
C(11)	0.6225 (1)	0.3820 (3)	0.5278 (1)	1.34 (4)
C(12)	0.7375 (1)	0.5018 (3)	0.3940 (1)	1.70 (4)
C(13)	0.7330 (1)	0.4349 (4)	0.3303 (1)	2.33 (5)
C(14)	0.5760 (1)	0.0982 (4)	0.5701 (1)	2.14 (5)
C(15)	0.5969 (1)	0.5856 (4)	0.6144 (1)	1.88 (4)
H(1)	0.562 (2)	0.615 (6)	0.454 (2)	4.0
H(3)	0.670 (2)	0.762 (6)	0.377 (2)	4.0
H(6)	0.814 (2)	0.309 (6)	0.471 (2)	4.0
H(8)	0.710 (2)	0.159 (6)	0.545 (2)	4.0
H(9)	0.655 (2)	0.095 (6)	0.410 (2)	4.0
H(10)	0.564 (2)	0.370 (6)	0.355 (2)	4.0
H(13a)	0.762 (2)	0.319 (6)	0.328 (2)	4.0
H(13b)	0.701 (2)	0.501 (6)	0.284 (2)	4.0

Table 2. *Bond distances* (Å) *and bond angles* (°)

C(1)—C(2)	1.562 (2)	C(1)—C(10)	1.510 (2)
C(1)—C(11)	1.559 (2)	C(2)—C(3)	1.549 (2)
C(2)—C(7)	1.576 (2)	C(3)—C(4)	1.558 (2)
C(3)—C(12)	1.509 (2)	C(4)—C(5)	1.563 (2)
C(5)—C(6)	1.551 (2)	C(6)—C(7)	1.546 (2)
C(6)—C(12)	1.510 (2)	C(7)—C(8)	1.553 (2)
C(8)—C(9)	1.514 (2)	C(8)—C(11)	1.554 (2)
C(9)—C(10)	1.328 (2)	C(11)—O(1)	1.407 (2)
C(11)—O(2)	1.411 (2)	C(12)—C(13)	1.327 (2)
C(14)—O(1)	1.432 (2)	C(15)—O(2)	1.440 (2)

C(11)—O(1)—C(14)	113.9 (1)	C(11)—O(2)—C(15)	113.6 (1)
C(2)—C(1)—C(10)	108.5 (1)	C(2)—C(1)—C(11)	99.3 (1)
C(10)—C(1)—C(11)	98.4 (1)	C(1)—C(2)—C(3)	120.3 (1)
C(1)—C(2)—C(7)	102.9 (1)	C(3)—C(2)—C(7)	102.7 (1)
C(2)—C(3)—C(4)	105.6 (1)	C(2)—C(3)—C(12)	104.3 (1)
C(4)—C(3)—C(12)	98.4 (1)	C(3)—C(4)—C(5)	103.0 (1)
C(4)—C(5)—C(6)	103.5 (1)	C(5)—C(6)—C(7)	105.7 (1)
C(5)—C(6)—C(12)	98.3 (1)	C(7)—C(6)—C(12)	103.9 (1)
C(2)—C(7)—C(6)	103.5 (1)	C(2)—C(7)—C(8)	103.1 (1)
C(6)—C(7)—C(8)	119.1 (1)	C(7)—C(8)—C(9)	108.9 (1)
C(7)—C(8)—C(11)	99.2 (1)	C(9)—C(8)—C(11)	98.6 (1)
C(8)—C(9)—C(10)	108.2 (1)	C(1)—C(10)—C(9)	108.4 (1)
O(1)—C(11)—O(2)	110.3 (1)	O(1)—C(11)—C(1)	109.7 (1)
O(2)—C(11)—C(1)	115.8 (1)	O(1)—C(11)—C(8)	117.0 (1)
O(2)—C(11)—C(8)	109.5 (1)	C(1)—C(11)—C(8)	94.0 (1)
C(3)—C(12)—C(6)	97.9 (1)	C(3)—C(12)—C(13)	130.3 (1)
C(6)—C(12)—C(13)	130.7 (1)		

Analysis of least-squares planes and torsion angles showed that twisting of the tetracylic hydrocarbon framework is small. Excluding the ketal group, a single molecule contains an approximate non-crystallographic mirror plane. Differences between symmetry related pairs of bond lengths and bond angles in the tetracyclic hydrocarbon framework were ≤0.009 Å and ≤0.8°, respectively, except for angles C(1)—C(2)—C(3) and C(6)—C(7)—C(8) where the difference is 1.2°.

The most interesting feature of the structure (revealed in Fig. 2) is the pyramidalized C(12) atom. The C(13) atom lies 0.194 (2) Å out of the C(3)—C(12)—C(6) plane, and the pyramidalization angle (Borden, 1989) is 8.41°. The analogous parameters

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* Complete lists of atomic coordinates, bond distances, bond angles, least-squares planes, torsion angles, thermal parameters and structure factors, and a cell packing diagram have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55350 (42 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH0596]

for the second molecule are 0.164 (2) Å and 7.12°, respectively.

The angle between the H(9)—C(9)—C(10)—H(10) and C(8)—C(9)—C(10)—C(1) least-squares planes is 6°. Although this value is not statistically significant, it is in the same direction (*endo*) and is near the accurate measurement of 7.4° for a pyramidalized double bond in a simple norbornene derivative (Ermer, Bell & Mason, 1990).

It is unlikely that pyramidalization at C(12) is caused by relief of the usual type of angle strain because the C(3)—C(12)—C(13) and C(6)—C(12)—C(13) bond angles are much larger than 100° (Borden, 1989). Nor is it a result of alleviation of torsional (eclipsing) repulsions because C(12) has no substituents that can interact sterically with H(3) or H(6).

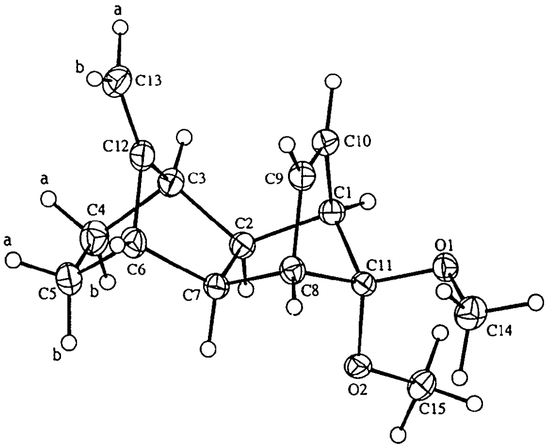


Fig. 1. *ORTEP* (Johnson, 1965) drawing of one of the two independent molecules of (1) with thermal ellipsoids at the 30% probability level and spherical H atoms of arbitrary size.

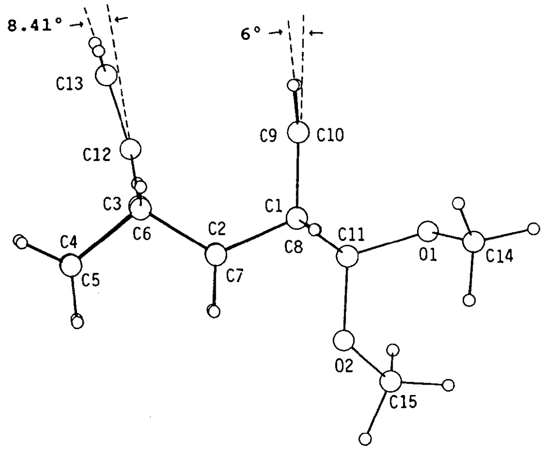
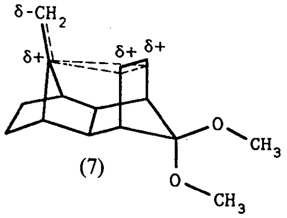


Fig. 2. *PLUTO* (Motherwell & Clegg, 1983) side view looking down the C(7)—C(2) and C(5)—C(4) bonds.

NMR data suggest that the π system is somewhat polar, *i.e.* it may have partial homocyclopropenyl carbocation character (Winstein & Hansen, 1960), as in structure (7). The C(9)···C(12) and C(10)···C(12) distances [2.946 (2) and 2.977 (2) Å, respectively] are consistent with π–π repulsion in (1), which would be mitigated by electron transfer from the C(9)=C(10) double bond towards C(13). If the C(12) atom were rehybridized towards sp^3 it could better accommodate bond angle compression between C(3)—C(12), C(6)—C(12), C(12)=C(13), and partial σ bonds from C(12) to C(9) and C(10).



(7)

Alternatively, π–π electronic and other steric repulsions between C(13) and the C(9)=C(10) bridge could cause the C(13) atom to bend away, since C(9)···C(13) and C(10)···C(13) distances [3.463 (2) and 3.497 (2) Å] are near van der Waals contacts (Bondi, 1964). *Ab initio* calculations are needed to investigate these possibilities.

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Functionalized Hydrocarbons with Condensed Ring Skeletons. XII.* A Methyltricyclo[8.4.0.0^{2,7}]tetradec-8-ene and a Vinylcyclododeca-3,9-diene, Products from Competing Intramolecular Diels–Alder Cycloadditions

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Abstract. (III) Tetramethyl 1,10-*trans*-1,2-*cisoid*-2,7-*trans*-1-methyltricyclo[8.4.0.0^{2,7}]tetradec-8-ene-5,5,-12,12-tetracarboxylate, $C_{23}H_{32}O_8$, $M_r = 436.50$, tetragonal, $P4_2/mbc$, $a = 13.1959\,(8)$, $c = 26.6986\,(11)$ Å, $V = 4648.3\,(2)$ Å^3, $Z = 8$, $D_x = 1.247$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1.54056$ Å, $\mu = 0.74$ mm^{-1}, $F(000) = 1872.0$, $T = 293$ K, final $R = 0.063$ for 2950 observed reflections. (IV) Tetramethyl (3*E*,9*Z*)-9-methyl-2-vinylcyclododeca-3,9-diene-1,1,-6,6-tetracarboxylate, $C_{23}H_{32}O_8$, $M_r = 436.50$, monoclinic, $P2_1/n$, $a = 12.767\,(5)$, $b = 10.199\,(3)$, $c = 19.175\,(3)$ Å, $\beta = 109.21\,(2)^\circ$, $V = 2357$ Å^3, $Z = 4$, $D_x = 1.230$ Mg m^{-3}, $\lambda(\mathrm{Cu}K\alpha) = 1.54056$ Å, $\mu = 0.73$ mm^{-1}, $F(000) = 936.0$, $T = 293$ K, final $R = 0.046$ for 2644 observed reflections. Structure (III) consists of three angularly fused six-membered rings *A*, *B* and *C*. The relative stereochemistry is *trans* for the *AB* ring junction, *syn* between the methyl group on C(1) and the C(2) proton and *trans* for the *BC* ring junction (abbreviated to TST). The double bonds $\Delta^{1,2}$, $\Delta^{7,8}$ and $\Delta^{9,10}$ in the allylic chloride precursor tetramethyl 14-chloro-5-methyltetradeca-4,10,12-triene-1,1,8,8-tetracarboxylate (I) and the corresponding double bonds in the cyclization product (IV) are *cis*, *trans* and *trans*. The cyclization of the *cis–trans–trans* allylic chloride (I) can produce two different compounds from competing S_N2 and S_N2' intramolecular substitution reactions. The S_N2 displacement produces a reactive 14-membered ring (II) which rapidly undergoes Diels–Alder cycloaddition to tricyclic compound (III), while the S_N2' reaction produces a final stable vinylic 12-membered ring (IV).

Introduction. The intramolecular version of the Diels–Alder cycloaddition reaction has attracted considerable interest in the past 20 years. The reasons for this are that this reaction provides better regio- and stereocontrol as well as, for most cases, increased reactivity over the corresponding intermolecular process. Recent communications from these laboratories (Baettig, Dallaire, Pitteloud & Deslongchamps, 1987; Baettig, Marinier, Pitteloud & Deslongchamps, 1987; Bérubé & Deslongchamps, 1987; Lamothe, Ndibwami & Deslongchamps, 1988*a*) showed that selectivity and reactivity can be further improved when the diene and the dienophile are held together by two chains of atoms. One of these papers reported a general study of transannular

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* Part XI: Drouin, Michel-Dewez & Michel (1993).
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