Stereoselectivity and Stereospecificity in Electron Deficient Diene Cycloadditions with Norbornadiene and 7-t-Butoxynorbornadiene: Results and MINDO/2 Theoretical Study[1]

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Unlike norbornadiene, which reacts stereospecifically with cyclopentadiene and cyclopentadienone derivatives in inverse electron demand [$_{\pi}4_s + {}_{\pi}2_s$] cycloadditions (giving the *endo-exo*-series of adducts), 7-t-butoxynorbornadiene exhibits stereoselectivity for the *endo-syn*-mode in similar cycloadditions, giving an *anti*-t-butoxy *endo-endo*-adduct as the major (periselective) component of the product mixtures. MINDO/2 Calculations indicate that the olefinic site of addition *syn* to the bridge alkoxy group is the HOMO (as required by qualitative cycloaddition theory), and also that the π orbital coefficients are larger than in norbornadiene. ^{1}H and ^{13}C n.m.r. data for the various adducts are tabulated and mass spectral data are also recorded.

It is recorded [2] that contrary to expectation based on the lack of ' activating ' substituents, Diels–Alder adduction of hexachlorocyclopentadiene and norbornadiene occurs under remarkably mild conditions giving more or less stereospecifically the pesticidally active *endo-exo*-adduct (1) (aldrin). In contrast, the addition of cyclopentadiene to 1,2,3,4,7,7-hexachloronorbornadiene [3] and its simple derivatives [4] exhibits *endo-endo*-stereospecificity giving analogues of adduct (2) (isodrin).[5] Precise product composition data for these cycloadditions is however scanty (stereospecificity is under investigation [5]) and little if anything is known about the effect of a single norbornadiene bridge methylene substituent either in respect of rate of cyclo-addition, or of effect on the stereochemical course of the reaction,† the effect of variations in the previously more readily accessible diene component having attracted much more attention.[7,8] Interestingly for example halogenated cyclopentadienone acetals (3) and (4) [8a,b] and cyclopentadienones such as tetracyclone (23) [7] all parallel the behaviour of hexachlorocyclopentadiene and its derivatives in giving apparently exclusively *endo-exo*-adducts when heated with norbornadiene [whilst phencyclone (24) reacts with norbornadiene at 25° [9]]. Stereospecific *endo-exo*-addition is also observed in reactions of hexachlorocyclopentadiene, and acetals (3) and (4) with 2,3-diazanorbornene derivatives.[8c] On the other hand *endo-endo*-adducts analogous to isodrin (2) [*e.g.* compound (20)] result [10] (albeit in small yield) from heating unstable 1,2,3,4-tetrachloronorbornadien-7-one acetals with cyclopentadiene [11] or dienone acetal (4).[11] More accurately we have now found that adduction of norbornadiene with acetal (3) is 98.5% stereospecific for *endo-exo*-compound (21), but only *ca.* 94% stereoselective for analogue (22), reaction with acetal (4) giving in addition up to *ca.* 6% *endo-endo*-adduct (20) (and perhaps constituting a less wasteful overall synthesis of the latter adduct!); the difference here is a small one, and could well be steric in origin.

Put into the simplest terms the stereochemical features

† Hexachlorocyclopentadiene forms an *endo-exo* adduct with 7-benzoyloxynorbornadiene (13) [6a] but an *endo-endo*-adduct is the major product; [6b] the 7-acetoxy analogue forms three adducts.[5]

[1] Preliminary account, K. Mackenzie, *Tetrahedron Letters*, 1974, 1203.

[2] S. B. Soloway, *J. Amer. Chem. Soc.*, 1952, **74**, 1027; *cf.* U.S.P. 2,635,977; C. W. Bird, R. C. Cookson, and E. Crundwell, *J. Chem. Soc.*, 1961, 4809.

[3] S. B. Soloway, A. M. Damiana, J. W. Sims, H. Bluestone, and R. E. Lidov, *J. Amer. Chem. Soc.*, 1960, **82**, 5377; *cf.* U.S.P. 2,676,132; 2,717,851.

[4] K. Mackenzie, *J. Chem. Soc.*, 1962, 457.

[5] D. Wege, personal communication.

[6] (*a*) C. T. Bedford and R. K. Harrod, *J.C.S. Chem. Comm.*, 1972, 735; (*b*) M. A. Battiste, personal communication.

[7] *Cf.* D. W. Jones, *J.C.S. Chem. Comm.*, 1973, 421; W. H. Dietsche, *Tetrahedron Letters*, 1966, 201.

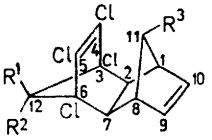
[8] (*a*) K. Mackenzie, *J. Chem. Soc.*, 1960, 473; (*b*) K. Mackenzie and W. P. Lay, *Tetrahedron Letters*, 1970, 3241; *cf.* R. Wege, R. McColloch, and A. R. Rye, *ibid.*, 1969, 5231; (*c*) K. Mackenzie, W. P. Lay, and J. R. Telford, *J. Chem. Soc.* (*C*), 1971, 3199.

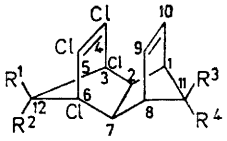
[9] K. Mackenzie, unpublished observation; *cf.* ref. 8*a*.

[10] E. Lund and K. Mackenzie, unpublished observations; E. Lund, B.Sc. Dissertation, University of Bristol, 1965.

[11] R. J. Stedman and L. S. Miller, *J. Org. Chem.*, 1967, **32**, 35.

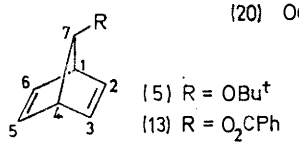
of these cycloadditions can be superficially understood on the grounds of (i) avoidance of unfavourable transition state eclipsing interactions between incipient ring-junction and bridgehead substituents favouring *endo-exo*-addition (in analogy to the stereospecific discharge of



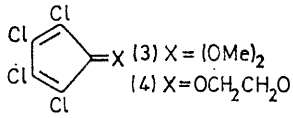


	$R^{1,2}$	R^3
(1)	Cl	H
(8)	OMe	OBu^t
(11)	OCH_2CH_2O	OBu^t
(15)	OMe	O_2CPh
(18)	Cl	OBu^t
(21)	OMe	H
(22)	OCH_2CH_2O	H

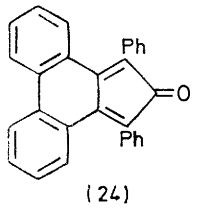
	$R^{1,2}$	R^3	R^4	
(2)	Cl	H	H	
(7)	OMe	OBu^t	H	(*i.e. syn*)
(6)	OMe	H	OBu^t	(*i.e. anti*)
(9)	OCH_2CH_2O	H	OBu^t	
(10)	OCH_2CH_2O	OBu^t	H	
(14)	OMe	H	O_2CPh	
(17)	Cl	OBu^t	H	
(16)	Cl	H	OBu^t	
(19)	OMe	H	H	
(20)	OCH_2CH_2O	H	H	



(5) R = OBu^t
(13) R = O_2CPh



(3) X = $(OMe)_2$
(4) X = OCH_2CH_2O



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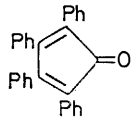
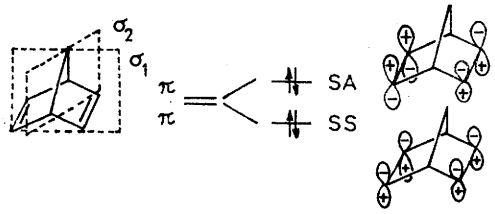


(23)

norbornyl cation at the *exo*-face [12]); and (ii) where *exo*-approach at the dienophile is inhibited by steric effects due to bridge methylene substituents, *endo*-addition supervening–eclipsing interactions notwithstanding. Such arguments neglect electronic effects, but steric and electronic factors must obviously be finely balanced having regard to the facility with which *endo-exo*-addition occurs with norbornadiene,[2] contrary to expectation from recent theoretical developments (see below), and the spontaneous exothermicity of the *endo-endo*-addition of cyclopentadiene and hexachloronorbornadiene [3] (which is however a more ' normal ', *i.e.* relatively electron deficient dienophile).

From a molecular orbital point of view, that reactions involving additions of electron deficient enophiles as diverse as hexachlorocyclopentadiene and arylated cyclopentadienones to norbornadiene *do* occur readily most likely follows from the marked quantum mechanical splitting of the degeneracy of the norbornadiene π bond system; this gives rise to two MOs of rather different energies as a result of symmetric (SS) and antisymmetric (SA) π bond combinations; the calculated [13] level separation is 0.43 eV but the experimental [14a] value is about twice as large (0.86 eV), representing an exaltation of the HOMO of *ca.* 0.5 eV compared to the estimated ' unperturbed ' level (*ca.* −9.1 eV).[14b]



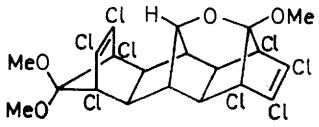
A necessary transition state requirement for easy *inverse* electron demand $[{}_{\pi}4_s + {}_{\pi}2_s]$ cycloaddition [15] is strong interaction of the *dienophile* HOMO with the inductively lowered *diene* LVMO; evidently this condition is met in reactions of norbornadiene with hexachlorocyclopentadiene and cyclopentadienones by the relative raising of the dienophile HOMO. Further, from the point of view of primary and secondary MO interactions,[16] *endo-endo*-addition would be expected to be the predominant, if not exclusive, mode of reaction, pointing to the decisive effect of torsional (and perhaps other unknown factors) in steering addition to the *exo*-face of the dienophile. The question naturally arises as to how remote ' non-conjugated ' substituents in the dienophile might effect the stereochemistry of similar cycloadditions and how such effects might be utilised for the synthesis of specific stereoisomers.

In preliminary work directed *e.g.* to the possible synthesis and fragmentation of *endo-cis*-3,4,5,6-tetrachlorotricyclo[6.2.1.$0^{2,7}$]undeca-3,5,9-triene and related compounds for comparison with the known *exo-cis*-isomer,[8,17] we investigated additions of dienone acetal (3) with 7-t-butoxynorbornadiene (5).[18] Heating the components in sealed tubes [$\gtrsim$120—130°; 48 h,* excess of (3)] gives a good overall product yield from which the isomeric *anti*- and *syn*-t-butoxy *endo-endo*-adducts (6) and (7) are separated by column chromatography, together with the *syn*-t-butoxy *endo-exo*-adduct (8) in the ratio 3.2 : 1.8 : 1.0. Clearly steric factors preclude formation of any appreciable amounts of the corresponding *anti*-t-butoxy *endo-exo*-compound, and bisadducts are virtually absent, although *traces* of a compound $C_{20}H_{16}Cl_8O_4$ arise from forced reaction of adduct (8) and dieneone acetal

* While this paper was in the press R. K. Lustgarten and H. G. Richey (*J. Amer. Chem. Soc.*, 1974, **96**, 6393) reported kinetic data for the unimolecular isomerisation of 7-t-butoxynorbornadiene into t-butoxytropilidene. The half-life calculated from these data is 77 h at 127°.

[12] P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1967, **89**, 701.
[13] R. Hoffmann, *J. Amer. Chem. Soc.*, 1970, **92**, 706.
[14] (*a*) E. Heilbronner, *Helv. Chim. Acta*, 1970, **53**, 1645; A. Y. Yencha and D. A. Demeo, *J. Chem. Phys.*, 1970, **53**, 4536; (*b*) P. Bischoff and E. Heilbronner, *Helv. Chim. Acta*, 1970 53 1677.
[15] R. Sustmann, *Tetrahedron Letters*, 1971, 2721; *cf. ibid.*, p. 2719.
[16] R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, 1965, **87**, 4388.
[17] A related synthesis has been achieved, A. R. Rye, Ph.D. Dissertation, University of W. Australia, 1973.
[18] P. R. Story, *J. Org. Chem.*, 1961, **26**, 287.

(3), whose ^{1}H n.m.r. and mass spectral characteristics are consistent with it being structure (8a), formed by an *exo-exo*-addition, followed by elimination (or *vice versa*).[19]



(8a)

The major stereoisomeric adducts are readily distinguished by a small or zero $^3J_{1,2}$ coupling constant in the *endo-exo*-adduct (due to the perpendicular dihedral,[8b,c] H-2 and -7 appearing as a sharp singlet). By contrast are summarised in Table 1. Fortunately the various isomers have sufficiently well differentiated signals to enable product mixture compositions to be reliably estimated from signal integration (as confirmed by product separations).

The gross structural features of the adducts are also readily recognised in the ^{13}C n.m.r. data (Table 2) which do not, unfortunately, enable a ready distinction between the 1,8 and 2,7 (bridgehead and ring junction) carbons, although the relevant signals appear to be subject to marked chemical shift differences as between isomers.

Similar *anti*- and *syn*-t-butoxy *endo-endo*-adducts (9) and (10) and an *endo-exo-adduct* (11) are isolated from the mixture of at least five compounds (including an

TABLE 1

^{1}H N.m.r. chemical shifts (τ) [a] for stereoisomeric adducts

	9,10-vinyl	1,8-bridgehead	2,7-ring junction	11 or CHO	12-$(OR)_2$	OBu^t
(1) [20]	3.68 (t)	7.11 (t)	7.28 (s)	8.41, 8.69 (dd)		
(2) [20]	3.93 (t)	6.97 (sextet)	6.61 (t)	8.21, 8.47 (dd)		
(6)	4.10 (t)	7.34 (sextet)	6.63 (t)	6.56 (t)	6.35, 6.48 (s)	8.84 (s)
(7)	4.06br (s)	7.06 (heptet)	6.92 (q)	6.18br (s)	6.38, 6.50 (s)	8.88 (s)
(8)	3.91 (quintet)	7.23 (q)	7.54 (s)	5.84br (s)	6.54, 6.56 (s)	8.91 (s)
(9)	4.14 (t)	7.34 (m)	6.68 (t)	6.59 (t)	5.81 (m)	8.86 (s)
(10)	4.07br (s)	7.04 (m)	6.92 (t)	6.20br (s)	5.80 (m)	8.88 (s)
(11) [b]	3.83 (m)	7.11 (t)	7.47 (s)	Obscured	5.8 (m)	8.86 (s)
(14)	4.00 (t)	6.89 (sextet)	6.58 (t)	5.29 (t)	6.37, 6.49 (s)	2—2.5 (Ph)
(15)	4.12br (s)	6.73 (s)	6.69 (m)	5.11br (s)	6.38, 6.50 (s)	2—2.6 (Ph)
(16)	4.06 (t)	7.25 (sextet)	6.45 (t)	6.4 (obscured)		8.85 (s)
(17)	4.00 (quintet)	6.98 (sextet)	6.71 (t)	6.16br (s)		8.86 (s)
(18) [b]	3.79br (s)	7.07 (m)	7.30 (s)	5.73br (s)		8.86 (s)
(19) [b]	4.07 (t)	7.10 (m)	6.81 (t)	Obscured	6.36, 6.47 (s)	
(20) [10,11]	4.04 (t)	7.05 (m)	6.84 (t)	8.26, 8.45 (dd)	5.83 (m)	
(21)	3.69 (t)	7.16 (quintet)	7.43 (s)	8.44, 8.75 (dd)	6.42, 6.46 (s)	
(22)	3.75 (t)	7.17 (quintet)	7.47 (s)	8.48, 8.78 (dd)	5.83 (m)	
(25)	5.85 (t)	6.93 (m)	6.14 (t)	6.73 (t)	[1.2—3.1 (Ar)]	8.77 (s)
(26)	5.79br (s)	6.68 (m)	6.43 (t)	5.92br (s)	[1.2—3.1 (Ar)]	8.87 (s)
(27)	3.61br (s)	6.94 (m)	6.99 (s)	7.47br (s)	[1.2—3.1 (Ar)]	10.18 (s)

[a] Solvent $CDCl_3$; internal reference Me_4Si. [b] Component in binary mixture. All signals, unless obscured, show the correct relative intensity.

TABLE 2

^{13}C N.m.r. chemical shifts [a] for selected stereoisomers

	1,8/2,7	3,6	4,5	9,10	11	12	MeO, MeO	13	14
(6)	46.53, 51.21	88.76	116.9	128.3	76.57	128.3	51.45, 52.42	74.02	28.15
(7)	48.35, 48.84	91.80	115.6	126.6	76.69	127.5	51.45, 52.54	73.65	28.09
(8)	54.60, 46.17	80.33	115.1	135.6	75.78	130.6	51.45, 52.42	73.59	28.51
(16)	51.51, 47.14	89.43	102.02	128.44	74.30	129.90		80.03	28.09
(17)	48.84, 48.84	92.28	105.99	126.99	74.08	129.59		80.03	28.09
(18)	54.60, 46.41	80.45	105.45	135.90	74.14	132.45		79.48	28.58
(21)	40.23, 40.41	76.20	115.3	140.76	54.30	128.74	51.34, 52.36		

[a] P.p.m. downfield from Me_4Si in $CDCl_3$.

this signal characteristically appears as a 'triplet' or 'quartet' in the various *endo-endo*-adducts,[20] and in addition is deshielded by proximate chlorine atoms or alkoxy-groups (τ 0.2—0.3). In conjunction with evidence for long range ^4J W type vinyl–*anti*-bridge methylene proton spin coupling (*e.g.* loss of resolution in the vinyl signal) bridge substituent stereochemistry may thus also be deduced. On the other hand the bridgehead H-1–H-8 resonance invariably appears as a complex multiplet in all stereoisomers (its width is of some structurally diagnostic value). Relevant ^{1}H n.m.r. chemical shifts

acetal Diels–Alder dimer and a bisadduct) which result from heating the rather more reactive [21] dienone cyclic acetal (4) with norbornadienyl ether (5). The addition of hexachlorocyclopentadiene to dienophile (5) however parallels that of dienone acetal (3), with a roughly similar product distribution for the *endo-exo*- (18) and *endo-endo*-adducts (16) and (17) (see Table 3). It is noticeable that in each of these cycloadditions, contrary to expectation based on the grounds of incipient ring junction hydrogen–Bu^tO group steric opposition, the major product is the *anti*-t-butoxy *endo-endo*-adduct. This im-

[19] W. P. Lay and K. Mackenzie, unpublished observations.

[20] *Cf.* A. P. Marchand and H. E. Rose, *J. Amer. Chem. Soc.*, 1968, **90**, 3724.

[21] K. MacKenzie, *J. Chem. Soc., Supplement I*, 1964, 5710; Wen-Hsuan Chang, *Chem. and Ind.*, 1964, 709; *J. Chem. Soc.*, 1965, 4744.

plies a faster *endo*-addition at the dienophilic site *syn* to the dienophile bridge substituent for the reactions can (reasonably) be assumed essentially kinetically controlled since *e.g.* compound (16) is thermally stable under the reaction conditions. The effect is even more marked for

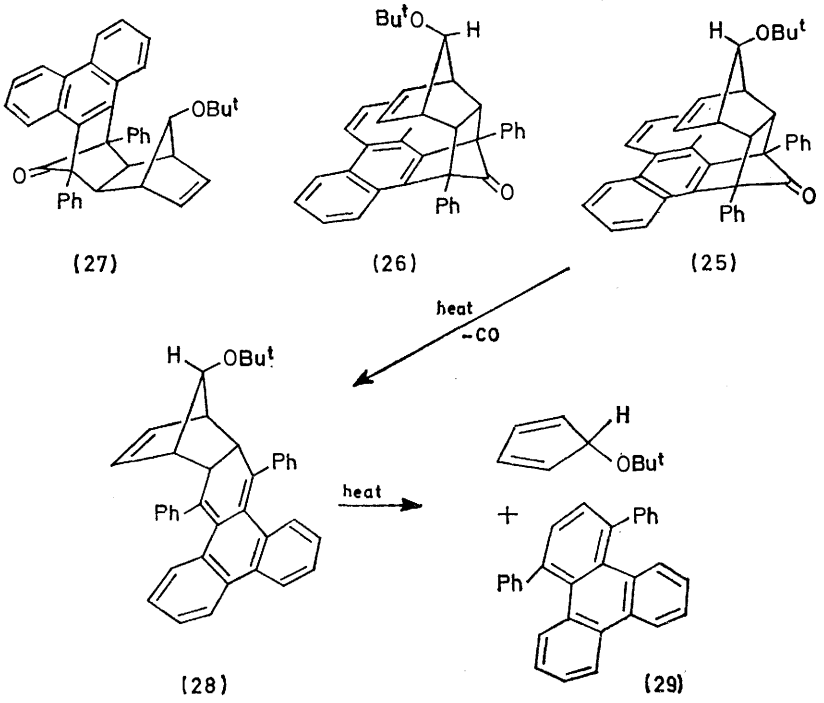
TABLE 3
Stereoisomeric product ratios for diene additions to 7-t-butoxynorbornadiene

endo-endo-anti-Bu^{t}O			*endo-endo-syn*-Bu^{t}O			*endo-exo*		
(6)	3.2	(53%)	(7)	1.8	(30%)	(8)	1.0	(17%)
(9)	3.4	(50%)	(10)	2.4	(35%)	(11)	1.0	(15%)
(16)	3.8	(61%)	(17)	1.4	(23%)	(18)	1.0	(16%)
(25)	10.3	(70%)	(26)	3.5	(23%)	(27)	1.0	(7%)

addition of phencyclone [22] (24) to dienophile (5), *endo-endo-anti*-adduct (25) comprising 70% of the total product. The isomeric adducts are again readily distinguished by their ^{1}H n.m.r. spectra, a point of interest

7-Benzoyloxynorbornadiene (13) also forms an *endo-endo*-adduct (14) with acetal (3) in addition to an *endo-exo*-adduct (15). It is likely that adduct (14) is also formed by *endo-syn*-addition. A similar mixture of products has been reported for reaction of hexachlorocyclopentadiene with dienophile (13) (*cf.* ref. 6).

A simplified qualitative frontier-orbital interpretation of the preference for faster *endo-syn*-addition of electron deficient dienes to dienophile (5) might be that localised dienophile π-bond–oxygen σ-type lone pair interaction leads to a relative raising of the *syn*-π-bond energy thus making it the HOMO for the molecule, as required for ready reaction. The lifting of the degeneracy of the π orbitals would of course imply a reduction in their interaction so that the two π-bonds behave more or less independently. It is tempting to ascribe the preference for *endo-anti*- over *exo*-addition however to secondary



being the strong shielding of the vinylic proton signals in the *endo-endo*-adducts (25) and (26) (τ 5.83 and 5.80) due to the proximate aromatic ring current. In the former compound the vinyl proton is as usual well resolved, but ^4J coupling to the H–C–OBu^t group results in a broad singlet for the vinyl proton signal at τ 5.80 in adduct (26). For *endo-exo*-adduct (27) the vinyl signal appears at the more normal position, τ 3.61br (s), but the bridge methylene and Bu^t groups are noticeably shielded, τ 7.47br (s) and 10.18 (s), respectively. The gross structure of *e.g.* adduct (25) is confirmed by its thermolysis (220°) giving diphenyltriphenylene (29), resulting from decarbonylation, and cycloreversion [8a,c] of the intermediate 4,5-(*o*,*o*′-biphenyldiyl)tricycloundecatriene (28).

orbital interactions involving the diene LVMO and dienophile HOMO [16] but this view is invalid if the π-orbitals of the dienophile do not interact in a simple way.

The photoelectron spectrum of norbornadienyl ether (5) shows major transitions from energy levels at −8.55, −9.03, and −9.40 eV. In comparison with the parent molecule (π −8.69 and π −9.55 eV [13,14]) and assuming that the transition at −8.55 eV is due to excitation of oxygen 2*p* electrons,* the data showed only that the HOMO for ether (5) is relatively lower than for norbornadiene. In order to rationalise the chemical behaviour

* Estimated at *ca.* −8.7 eV from published data.[23]

[22] W. Dilthey, I. ter Horst, and W. Schommer, *J. prakt. Chem.*, 1935, **143**, 189.
[23] D. W. Turner, *Adv. Phys. Org. Chem.*, 1966, **4**, 31.

and photoelectron spectrum of norbornadienyl ether (5) we have carried out MINDO/2 [24] calculations on norbornadiene and the 7-methoxy-derivative (which is taken to be a reasonable, simplified model). For both compounds the double bonds are fixed at 1.34 Å and a plane of symmetry is preserved through C-7 bisecting the olefinic bonds C-2–C-3 (*syn* to the methoxy-group) and C-5–C-6.[25] * The calculated ionisation potentials for norbornadiene and the 7-methoxy-derivative are then 9.31 and 9.34 eV. However the orbital manifold for norbornadiene is as expected for through space splitting of the degeneracy, the a_1 level (−9.51 eV) being 0.2 eV more stable than the b_2 level. The orbital manifold for 7-methoxynorbornadiene is rather different however, the 7-substituent removing the degeneracy of the π levels; in fact the HOMO of the molecule *is* largely $\pi_{2,3}$ with some C-1–C-4–C-7 p_z admixed; $\pi_{5,6}$ occurs at −9.44 eV. The virtual orbitals for 7-norbornadienyl methyl ether and norbornadiene appear to be little different so it is expected that both compounds and analogues of the methyl ether should react with electron rich species in a similar way.

$[_{\pi}4_s + {}_{\pi}2_s]$ Cycloaddition with dienophile (5) and electron deficient dienes is now partly rationalised by the observation that $\pi_{2,3}$ *is* the HOMO of the molecule. In addition *endo-syn*-approach is favoured for the 7-alkoxynorbornadienes due to the larger orbital coefficients at the $\pi_{2,3}$ bond (0.55 for 7-methoxynorbornadiene compared to 0.47 in norbornadiene), ensuring better orbital overlap in the transition state, a necessary concomitant for energy lowering.[27] It is however surprising that *endo-syn* $\pi_{2,3}$- diene addition is not the *exclusive* reaction; very likely the expected steric factor partially offsets increased transition state stabilisation arising from HOMO (olefin)–LVMO (diene) interaction, mitigating the significance of the lower ground state $\pi_{5,6}$- energy for the alternative addition modes. On a scale including *trans*-but-2-ene, ethylene, and maleic anhydride, for comparison, the π energy difference here is actually rather modest (*ca.* 8.5 kcal mol^{-1}), and in the light of this the selectivity observed is informative.

Interestingly the calculations show that the 7-methylene group in 7-methoxynorbornadiene is deflected *ca.* 1.5° away from the vertical plane through C-1–C-4 towards $\pi_{5,6}$, and the geometrical situation resembles that in the 7-norbornadienyl or 7-norbornenyl anion where there is likely to be repulsion between the electron pair at the bridge and the *syn* π-orbital.[28,†]

Further chemistry with the various adducts of 7-t-butoxynorbornadiene described here is in hand.

EXPERIMENTAL

Column and preparative t.l.c. chromatography were carried out using silica gel with 50% dichloromethane–light petroleum (b.p. 40—60° or 60—80°) as eluant unless otherwise stated. ^{1}H N.m.r. data were obtained with a Varian HA 100 instrument for solutions in deuteriochloroform with tetramethylsilane as internal standard. ^{13}C Resonance data were obtained with a JEOL PFT 100 machine and refer to solutions in deuteriochloroform, as concomitant standard, *downfield* chemical shifts being computed relative to tetramethylsilane. I.r. data were determined with a Perkin-Elmer PE257 instrument. The photoelectron spectrum of 7-t-butoxynorbornadiene was obtained by Dr. K. MacNiel using a Perkin-Elmer PS16 photoelectron spectrometer and MINDO/2 calculations (Dr. B. Astin) were performed using an ICL 470 computer. Mass spectra were determined using a GEC-AEI MS902 mass spectrometer with Linc-8 computer readout.

General Procedure for making Adducts with Acetals (3) *and* (4), *and with Hexachlorocyclopentadiene.*—Tetrachlorocyclopentadienone acetals (3) and (4) and 5-t-butoxynorbornadiene (5) were made by the published procedures.[18,21,29] In a typical experiment (a) t-butoxynorbornadiene (5) (3.28 g, 0.02 mol) was heated with tetrachlorocyclopentadienone dimethyl acetal (3) (5.28 g, 0.02 mol) diluted with carbon tetrachloride (1 ml) in a sealed tube for 7 days at 100—110°. Excess of diene (3) was removed *in vacuo*, and the composition of the gummy product estimated by ^{1}H n.m.r. signal integration (Table 3) using the correlations obtained for the three isomers separately prepared as follows. (b) Dienone acetal (3) (31.7 g; 20% excess) was heated in a sealed tube with the diene (5) (16.4 g) at 90—100° for 3 days. The product was distilled to remove lower boiling material and the residue recrystallised from ethanol to give endo-exo-11-syn-*t-butoxy*-3,4,5,6-*tetrachloro*-12,12-*dimethoxytetracyclo*-[6.2.1.1.^{3,6}0^{2,7}]*dodeca*-4,9-*diene* (8) (2.8 g), m.p. 196—197° (from ethanol), ^{1}H and ^{13}C n.m.r., Tables 1 and 2 (Found: C, 50.6; H, 5.25. $C_{18}H_{22}Cl_4O_3$ requires C, 50.5; H, 5.2%), *m/e* 426 ($M^{+\cdot}$, weak), 391 (M − Cl$^{+\cdot}$), 262, 253 (RDA − Cl$^{+\cdot}$), 207 (RDA − Cl − $C_2H_6O^{+\cdot}$).

The recrystallisation residues from a number of such experiments were evaporated and the viscous product distilled at 170° and 0.6—0.8 mmHg. The pale yellow oily product solidified; since t.l.c. indicated compound (8) and two other components, 1 g of this solid was chromatographed on silica gel (45 g), giving *endo-endo*-11-*anti*-t-butoxy-3,4,5,6-tetrachloro-12,12-dimethoxytetracyclo[6.2.1.1.^{3,6}0^{2,7}]dodeca-4,9-*diene* (6) (527 mg), m.p. 116—117° (lit.,[17] 116.5°), and endo-endo-11-syn-*t-butoxy*-3,4,5,6-*tetrachloro*-12,12-*dimethoxytetracyclo*[6.2.1.1.^{3,6}0^{2,7}]*dodeca*-4,9-*diene* (7) (350 mg), m.p. 124—125° (from light petroleum), ^{1}H and ^{13}C n.m.r.,

* The calculated geometry of norbornadiene is in substantial agreement with that calculated by Dewar using MINDO/2 with the Simplex optimisation method; [26] in addition the heat of formation is in good agreement, *e.g.*, ΔH_f = +31.6 kcal mol^{-1} compared with [26] +29.4 kcal mol^{-1}. 7-Methoxynorbornadiene is substantially more stable, ΔH_f −21.6 kcal mol^{-1}.

† We have become aware since the preparation of this paper of a complementary study of the addition of azoalkanes to 7-substituted norbornadienes published since our preliminary report [1] (M. Franck-Neumann and M. Sadrati, *Angew. Chem. Internat. Edn.*, 1974, **13**, 606) and which arrives at similar conclusions to ours with regard to the stereo-electronic structure of 7-butoxynorbornadiene.

[24] (*a*) M. J. S. Dewar and E. Haselbach, *J. Amer. Chem. Soc.*, 1970, **92**, 590; (*b*) N. Bodor, M. J. S. Dewar, D. Harget, and E. Haselbach, *ibid.*, p. 3854.
[25] M. J. D. Powell, *Computer J.*, 1965, **7**, 303.
[26] M. J. S. Dewar and W. W. Schoeller, *Tetrahedron*, 1971, **27**, 4401.
[27] L. W. Hall and W. C. Herndon, *Tetrahedron Letters*, 1967, 3095.
[28] *Cf.* R. R. Sauers and R. M. Hawthorne, *J. Org. Chem.*, 1964, **29**, 1686.
[29] J. S. Newcomber and E. T. McBee, *J. Amer. Chem. Soc.*, 1949, **71**, 946.

Tables 1 and 2. The mass spectrum is closely similar to that of compound (8).

In experiments similar to (a) above hexachlorocyclopentadiene (5.50 g, 0.02 mol) diluted with carbon tetrachloride (1 ml) was heated in a sealed tube at *ca.* 120° for 48 h with t-butoxynorbornadiene (3.28 g, 0.02 mol). Volatile materials were removed by distillation *in vacuo* and a portion of the crude product (3 g, 50%) was chromatographed to give two main fractions: (i) (1.75 g) recrystallised from methanol giving endo-endo-11-anti-*t-butoxy*-3,4,5,6,12,12-*hexachlorotetracyclo*[6.2.1.1.^{3,6}0^{2,7}]*dodeca*-4,9-*diene* (16) (1.00 g), m.p. 110.5—111.5°, ^{1}H and ^{13}C n.m.r., Tables 1 and 2 (Found: C, 43.7; H, 3.9. $C_{16}H_{16}Cl_6O$ requires C, 43.97; H, 3.7%), *m/e* 435.930 (calc. for $C_{16}H_{16}{}^{37}Cl^{35}Cl_5O$ 435.930), 434 ($M^{+\cdot}$, weak), 419, 399 (M — $Cl^{+\cdot}$), 398 (M — $HCl^{+\cdot}$), 378, 342, 270 ($C_5Cl_6^{+\cdot}$, RDA), 261, 235 (RDA — $Cl^{+\cdot}$), and 243; and (ii) a mixture (1 g) of compound (17) with isomer (18) (^{1}H n.m.r.) which when rechromatographed and the crude first fraction (589 mg) recrystallised from light petroleum (b.p. 60—80°) gave endo-endo-11-syn-*t-butoxy*-3,4,5,6,12,12-*hexachlorotetracyclo*[6.2.1.1.^{3,6}0^{2,7}]*dodeca*-4,9-*diene* (17) (300 mg), m.p. 132—133° (after further recrystallisation), ^{1}H and ^{13}C n.m.r., Tables 1 and 2, identical mass spectral fragment ions to those from adduct (16). Further chromatography and crystallisation of later fractions gave a binary mixture of compounds (17) and (18) enriched in the *syn*-isomer (18) (^{1}H and ^{13}C n.m.r., g.l.c.*). The mass spectrum is similar to those of compounds (16) and (17) with identical fragment ions but *m/e* 359 is prominent due to a contaminant. The composition of the remaining original crude mixture was determined by ^{1}H n.m.r. integration.

In an experiment similar to (a) above, tetrachlorocyclopentadienone ethylene acetal (4) (10.48 g, 0.04 mol) was heated with t-butoxynorbornadiene (5) (3.28 g, 0.02 mol) diluted with carbon tetrachloride (1.0 ml) in a sealed tube for 4 days at 100°. The crude product which had solidified was washed out with methylene chloride, insoluble material being separated off (2.3 g), and evaporation of the solution afforded a viscous syrup (11.7 g).

Chromatography, partial separation, and ^{1}H n.m.r. monitoring indicated the presence of *endo-endo*-adduct (9) in the ratio 1 : 1 with a bisadduct, τ *ca.* 5.84 [$(OCH_2)_2$], 6.59 (m, ring junction), 7.23 (s, ring junction), and 7.55 (m, bridgehead), in early fractions, *endo-endo*-adduct (10) in intermediate fractions, and *endo-exo*-adduct (11) mixed with adduct (10) in later fractions, whilst crystals of the acetal dimer separated from the earlier prepared crude product solution. Manipulation of the intermediate fraction from crude mixture (2.1 g) gave endo-endo-11-syn-*t-butoxy*-3,4,5,6-*tetrachloro*-12,12-*ethylenedioxytetracyclo*[6.2.1.1.^{3,6}0^{2,7}]*dodeca*-4,9-*diene* (10) (328 mg), m.p. 143—144°, ^{1}H n.m.r., Table 1, *m/e* 424 ($M^{+\cdot}$), 389 (M — $Cl^{+\cdot}$), 333, 260 ($RDA^{+\cdot}$), 251 (RDA — $Cl^{+\cdot}$), 207 (RDA — Cl — $C_2H_4O^{+\cdot}$), *cf.* adduct (8). Fractional crystallisation from light petroleum (b.p. 60—80°) of the mixed product from the early eluates gave endo-endo-11-anti-*t-butoxy*-3,4,5,6-*tetrachloro*-12,12-*ethylenedioxytetracyclo*[6.2.1.1.^{3,6}0^{2,7}]*dodeca*-4,9-*diene* (9) (360 mg), m.p. 134.5°—135.5°, ^{1}H n.m.r., Table 1 (Found: C, 50.3; H, 4.7. $C_{18}H_{20}Cl_4O_3$ requires C, 50.7; H, 4.7%). The mass spectrum shows identical fragment ions to those of adduct (10). The fractional crystallisation also afforded bisadduct (360 mg), m.p. 286°.

The *endo-exo*-adduct (11) accumulated in later fractions [^{1}H n.m.r. (Table 1) and identical fragmentation patterns to that of adduct (10)], but was not purified. The relative composition of the mixture was determined as before by ^{1}H n.m.r. signal integration.

Reaction of Phencyclone (24) *with t-Butoxynorbornadiene.*—Phencyclone [22] (192 mg, 0.5 mmol) was heated with t-butoxynorbornadiene (5) (123 mg, 0.75 mmol) in dry benzene (5 ml) at the b.p. under nitrogen for 4.5 h, after which the colour had faded to a pale green. Solvent and excess of diene (5) were removed *in vacuo*, giving a crude product (400 mg) containing the three isomeric adducts (25)—(27) (^{1}H n.m.r. indicated the ratio 10.4 : 4 : 1). Preparative t.l.c. (7 × 0.1 mm × 20 × 20 cm plates) separated the components from the mixture (210 mg) into (i) endo-endo-4,5-(o,o′′-*biphenyldiyl*)-11-anti-*t-butoxy*-3,6-*diphenyltetracyclo*-[6.2.1.1.^{3,6}0^{2,7}]*dodeca*-4,9-*dien*-12-*one* (25) (103 mg), m.p. 222° (vigorous decomp.), ^{1}H n.m.r., Table 1, $\nu_{max.}$ 1 780vs cm^{-1} (bridged ring CO) (Found: C, 88.15; H, 6.25. $C_{40}H_{34}O_2$ requires C, 87.9; H, 6.25%), *m/e* 546 ($M^{+\cdot}$), 518 (M — $CO^{+\cdot}$), 490 (M — $C_4H_8^{+\cdot}$), 382 ($RDA^{+\cdot}$), 381, (RDA — $H^{+\cdot}$), 380 ($RDA^{+\cdot}$), 379, 363 354 (RDA — CO), 303, and 302; (ii) endo-endo-11-syn-*t-butoxy*-isomer (26) (35 mg), m.p. 224° (vigorous decomp.), ^{1}H n.m.r., Table 1, identical mass spectral fragment ions to those of compound (25), with similar abundances; and (iii) endo-exo-4,5-(o,o′-*biphenyldiyl*)-11-syn-*t-butoxy*-3,6-*diphenyltetracyclo*-[6.2.1.1.^{3,6}0^{2,7}]*dodeca*-4,9-*dien*-12-*one* (27) (10 mg), m.p. 245° (vigorous decomp.), ^{1}H n.m.r., Table 1, identical mass spectral fragment ions to those of compound (25), with similar abundances.

Thermolysis of Adduct (25).—The adduct (20 mg) was heated at 220—230° in a small fusion tube for 10 min and the crude orange glass which resulted on cooling recrystallised from dichloromethane–light petroleum (b.p. 60—80°) to give diphenyltriphenylene [8a] (*ca.* 10 mg), m.p. and mixed m.p. 221—222 and 223—224°. The product had identical R_F and fluorescence characteristics on t.l.c. with those of an authentic sample.

Addition of Cyclopentadienone Acetals (3) *and* (4) *to Norbornadiene.*—The procedure was as described in ref. 8*a*. In addition, the crystallisation residues after separation of adducts (21) and (22) were evaporated and column chromatographed, the fractions being monitored by t.l.c. ^{1}H N.m.r. spectra of the resulting fractions indicated formation of 6.5 ± 0.5% *endo-endo*-adduct [10,11] (20) from reaction of acetal (4) with norbornadiene, in addition to *endo-exo-adduct* (22), m.p. 105—106°, ^{1}H n.m.r., Table 1; and 1—1.5% *endo-endo*-adduct (19) in addition to *endo-exo*-adduct [8a,b] (21), m.p. 117—118.5°, formed in the reaction of acetal (3) with norbornadiene.

Addition of Cyclopentadienone Acetal (3) *to* 7-*Benzoyloxynorbornadiene.*—7-Benzoyloxynorbornadiene † (2.12 g, 0.01 mol) in carbon tetrachloride (1 ml) was heated with tetrachlorocyclopentadienone acetal (3) (5.28 g, 0.02 mol) at 120° for 24 h in a sealed tube; excess of acetal was removed by distillation *in vacuo*. The crude product which contained two components (t.l.c.) was recrystallised from dichloromethane–light petroleum (b.p. 60—80°) giving endo-exo-11-syn-*benzoyloxy*-3,4,5,6-*tetrachloro*-12,12-*dimethoxytetracyclo*-[6.2.1.1.^{3,6}0^{2,7}]*dodeca*-4,9-*diene* (15) (600 mg), m.p. 185—186° (after further recrystallisation from methanol), ^{1}H n.m.r., Table 1 (Found: C, 53.25; H, 3.7. $C_{21}H_{18}Cl_4O_4$ requires C, 52.95; H, 3.8%). Chromatography of one-third

* Perkin-Elmer F11 ECD instrument operated with OV17 columns, 190—240°, N_2.

† We thank Professor M. A. Battiste for a sample of this compound.

of the crystallisation residues gave further *endo-exo*-adduct (15) (170 mg) and in addition the *endo-endo*-11-*anti*(?)-benzoyloxy-isomer (14) (422 mg) (≡ total 1.266 g), m.p. 154—155° [ratio of (14) to (15) 1.1 : 1 by ^{1}H n.m.r. and g.l.c.*]. The products had identical fragment ions with similar abundances at *m/e* 474 ($M^{+\cdot}$, weak), 439 ($M - Cl^{+\cdot}$), 405, 403 ($M - HCl_2^{+\cdot}$), 369 ($M - Cl_3^{+\cdot}$?), 317, 253 (RDA — $Cl^{+\cdot}$), and 207 (RDA — Cl — $C_2H_6O^{+\cdot}$) [*cf.* adducts (8) and (10)].

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* Same footnote as on page 1009.