Kinetic and thermodynamic control in the formation of stereoisomeric 1:1 ($4\pi + 2\pi$) thermal cycloadducts of furans with hexachloronorbornadienes

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The thermally, relatively stable, main product of the reaction of furan with dienophile 5a has been found to belong unambiguously to the *endo–exo* series of stereoisomeric adducts analogous to aldrin (*endo–exo*-3,4,5,6,11,11-hexachlorotetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-diene) 8. Also, the *endo–endo* isomeric adduct 16 has been found to comprise a minor component of the total products. In similar reactions of 2-methyl-, 2-ethyl- and 2,5-dimethyl-furan with 5a, it is shown that the respective *endo–endo* adducts 21, 23 and 25 are important reaction products and that the thermally unstable *endo–endo* adduct 25 predominates ($\geqslant 6:1$) over its *endo–exo* isomer 26 in the early phases of reaction, its abundance falling with heating time. The reactions of especially the alkylated furans with 5a provide useful sources of compounds ('oxaisodrins') having the skeletal features of isodrin *endo–endo*-3,4,5,6,11,11-hexachlorotetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-diene 1 otherwise not easily accessible.

Introduction

In connection with our interest in the synthesis and reactivity of compounds which have face-proximate π-bonds,[1] typified by structures containing the skeletal features of the former insecticide isodrin **1**,[2] we have investigated the products of reaction of furan **2**, 2-methyl- and 2-ethyl-furans **3a,b** and 2,5-dimethylfuran **4** with 1,2,3,4,7,7-hexachloronorborna-2,5-diene **5a** ('nbd-Cl_6'). The patent literature discloses the formation and composition of single adducts of **5a** with a variety of furanoid dienes,[3] but no evidence is available as to the stereochemistry of the monoadducts formed in these ($4\pi + 2\pi$) thermal cycloadditions, giving putative analogues of isodrin. *endo–endo* Adduct, isodrin **1**, is the sole monoadduct isolated from the spontaneous, exothermic reaction of **5a** with cyclopentadiene **6** at ambient pressure,[2b] and finds analogy in the similar *endo–endo* cycloaddition of **6** with 2-alkoxy-1,3,4,7,7-pentachloronorborna-2,5-dienes **5b**,[4] and in the stereochemically identical reaction of **6** with 1,2,3,4-tetrachloronorborna-2,5-dien-7-one acetals **5c**.[1b,5]

These stereospecific *endo–endo* cycloadditions could be considered to be perfect examples of frontier-orbital, HOMO–LUMO (where HOMO is the highest occupied molecular orbital and LUMO is the lowest unoccupied molecular orbital) controlled processes, with stereochemically imposed favourable non-bonding secondary orbital interactions[6a] between the relevant, *e.g.* ($\pi_1^* + \pi_2^*$), combination of orbitals of **5a** (LUMO) and **6** (HOMO) leading to transition state stabilisation [*cf.* Fig. 1A, TS_2^c] when *exo* approach of the diene **6** is sterically inhibited by the 7-substituents of the norbornadiene. The stereochemical outcome here is in stark contrast to $\geqslant 96\%$ stereoselectivity for the *exo*-addition of electron-deficient dienes, *e.g.* the reaction of hexachlorocyclopentadiene **7** with norborna-2,5-diene **5d** gives the *exo–endo* isomer of **1**, aldrin **8**, and in the analogous reaction of **5d** with tetrachlorocyclopentadienone ketals **9** and **10**, aldrin analogues **11** and **12** are given.‡[,7] With the replacement of a single bridge-methylene H with an electronegative substituent, *e.g.* **5e**, the stereochemical outcome of cycloaddition reactions with electron-deficient dienes, *e.g.* **7** and **9**, is different again: mixtures of *endo–endo* adducts **13** and **14** and *endo–exo* isomers **15** result, the main isodrin-like product **13** (*ca.* 50%) derived from *endo* addition *syn* to the 7-substituent.§[,7b,8] The simplest rationale for the observed stereochemical behaviour of norbornadienes **5a–c** in their reactions with cyclopentadiene lies in the combined effect of a favourable secondary non-bonding dienophile LUMO–diene HOMO interaction and a preference for the CH_2 group in cyclopentadiene **6** to be *exo* to the reaction zone, as depicted in Fig. 1A, TS_2^c. The exothermicity observed in the reaction of nbd-Cl_6 **5a** with cyclopentadiene **6** additionally implies a reactant-like transition state. For the parent norbornadiene, **5d**, there is theoretical and experimental evidence for *endo*-directional pyramidalisation at the sp^2 receptor carbons,[10] with an increased π-orbital coefficient at the *exo*-face, together with more favourable torsional effects, favouring *exo*-addition, as is observed. For 7-substituted norbornadienes (**5e**, *e.g.* $R^2 = Bu^tO$), an oxygen lone-pair–proximate π-bond interaction raises the π-energy, making the HOMO largely π_1, as indicated by MINDO-2 calculations;[8,9] since *exo*-addition is clearly impossible *syn* to the substituent,¶ *endo* addition supervenes, despite evidence for a larger π-coefficient in the *exo*-direction. Consequently in the presence of an electron-withdrawing 7-substituent, π_2 is lowered in energy, consistent with the minor product (*ca.* 25%) arising from *exo*-cycloaddition at this site.[8]

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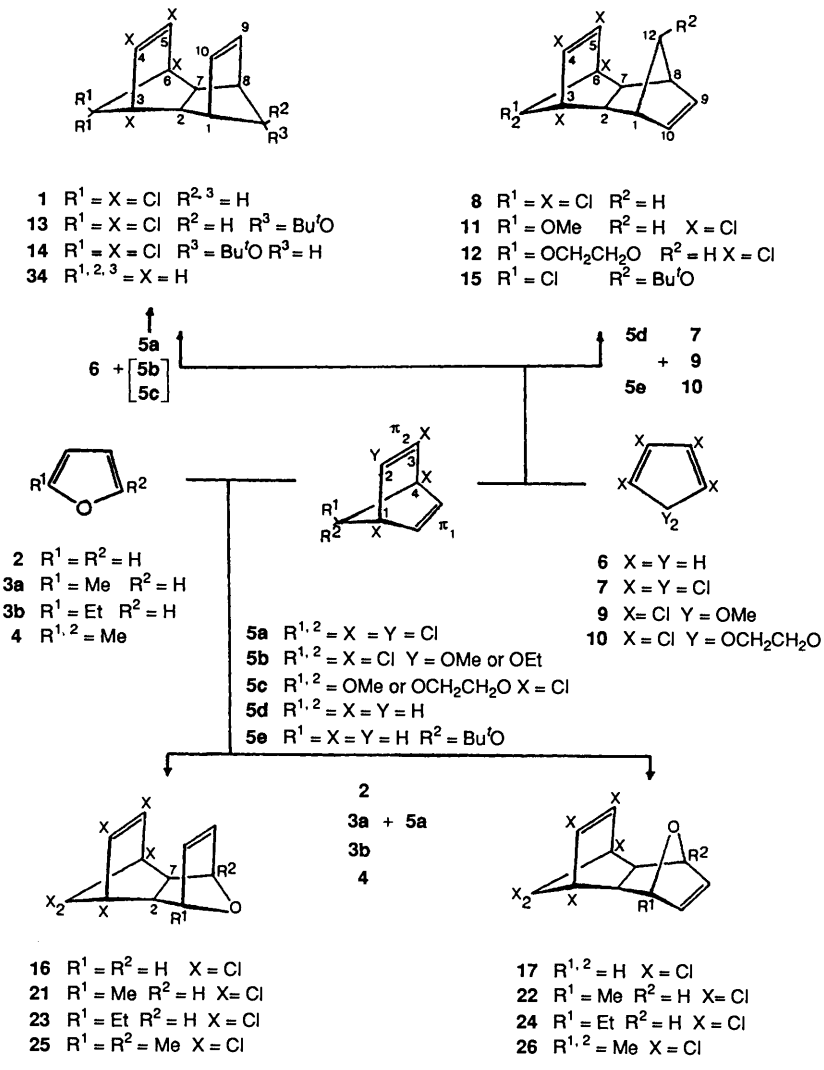
‡ Stereoselectivity for *endo–exo* adducts analogous to **8** is, however, attenuated in the cycloaddition of norborna-2,5-diene **5d** with halogenated acetals like **9**, when vinylic chlorine is replaced by OMe; with 1,4-dichloro-2,3,5,5-tetramethoxycyclopentadiene, significant amounts (*ca.* 13%) of *endo–endo* adducts having isodrin-like stereochemistry arise from the reaction with **5d**.[1b]

§ For a more complete study of 7-substituent effects of norborna-2,5-diene, see work by Houk and co-workers[9] who have shown that 7-alkoxynorborna-2,5-dienes are exceptional in their behaviour.

¶ Under forcing conditions, the minor *endo–exo* adduct **15** reacts with acetal **9**, apparently by eliminative-coupling of H–C^7–OBu^t with MeO–C–OMe→C^7–O–C–OMe, followed by diene addition at the unsubstituted dienophilic site.[11]



Scheme 1

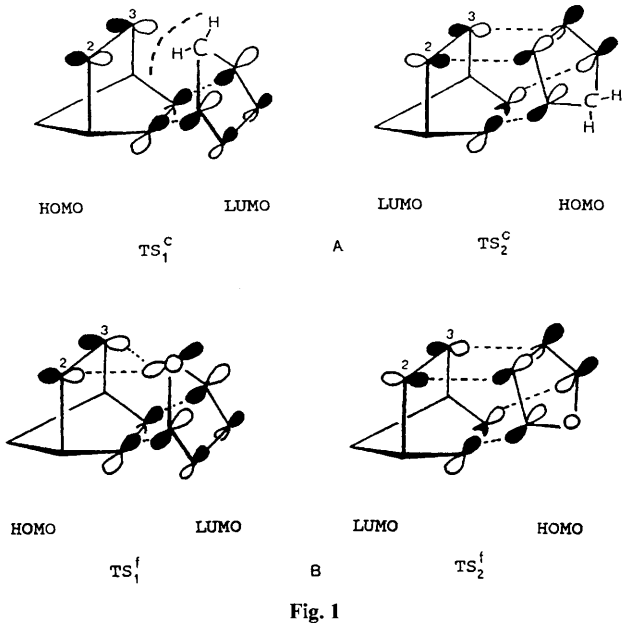


Fig. 1

From these results it is clear that interlocking steric and electronic effects control the stereochemical outcome in cycloalkadiene additions to norbornadiene and its derivatives and similar effects may be expected to become evident when the diene contains an oxygen atom, such as in furan derivatives.

Results and discussion

Reaction of furan 2 with 1,2,3,4,7,7-hexachloronorborna-2,5-diene 5a

A number of factors need to be considered in order to decide the most likely outcome of furan–nbd-Cl_6 **5a** addition, and consequently give indications for corroborative experiments. (*i*) Furans have aromatic character (π^4 and $O2p^2$) and are likely to be much less reactive than cyclopentadiene (or other cycloalka-1,3-dienes[12]) in cycloaddition reactions with **5a**. Transition states are then likely to be shifted to a product-like geometry. Since calculated strain energies[13] for *endo–endo* adduct **16** (E_s = 85.97 kcal mol^{-1})‖ and its *endo–exo* isomer **17** (E_s = 77.69 kcal mol^{-1}) differ significantly (ΔE_s = 8.3 kcal mol^{-1}), together with the fact that heating is required for significant reaction, *endo–exo* addition giving mainly adduct **17** appears most likely. (*ii*) (4π + 2π) Thermal cycloadducts of furans are well known to be thermally unstable** and the possibility of

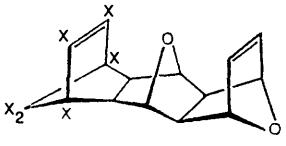
‖ 1 cal = 4.184 J; for relevant thermochemical and structural information see Table 4.

** The Alder–Rickert cycloreversion of furan adducts of dimethyl acetylenedicarboxylate (MAD) is an early example;[14a] other important examples are found with 2-methylfuran–maleic anhydride addition and KIE studies pointing to concertedness.[14b] The general complexity and time–temperature dependence of products observed in reactions of MAD with furan have also been noted.[14c] A bis-adduct of MAD with furan (at the methoxycarbonylated dienophilic site in the mono-adduct) undergoes cycloreversion at 70 °C with $k_1 = 10^{-4}$ s^{-1}.[14d]

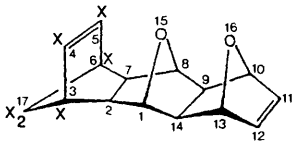
equilibration **16**–**17** arises. (*iii*) Notwithstanding the marginal preference argued above for formation of **17**, if any additional effect operates, leading to a relative lowering of the TS_2^f energy (Fig. 1B) and delivering *endo–endo* adduct **16** as the product of kinetic control, product composition may become time–temperature dependent. (*iv*) O in furan is less sterically demanding than CH_2 in cyclopentadiene††[15a] (*cf.* Fig. 1A, TS_1^s) and O in furan has a larger π-component than does CH_2 in cyclopentadiene.[16] If HOMO diene–LUMO dienophile (and *vice versa*) interactions control the products observed, the effect on oxygen of a significantly interacting π-component could be important. This type of interaction is made potentially more important when it is seen[16] that the orbital coefficients at the non-bonding sp^2 C atoms in both furan and cyclopentadiene are attenuated compared with those on the sp^2 C atoms involved in σ-bond formation and compared with the O π-component. A reduced carbon-framework secondary π–π interaction compared with a relatively larger dienophile HOMO ($\pi_1 - \pi_2$)–diene LUMO interaction, involving a suitably phased O π-component could favour TS_1^f rather than TS_2^f. Thus, both product strain energy differences and electronic effects in the transition state strongly suggest that the furan–nbd-Cl_6 adduct described in the literature[3a] has *endo–exo* stereochemistry, **17**. Nevertheless, experimental structural verification is clearly required.

Experimental observations. Reaction of furan 2 with nbd-Cl_6 5a

In an attempted preparation of the furan–1,2,3,4,7,7-hexachloronorborna-2,5-diene adduct using the patented procedure,[3a] by dropwise addition of furan into hot nbd-Cl_6, no identifiable adduct was isolated, possibly due to the small scale procedure adopted. However, when nbd-Cl_6 was heated with an approximately three-fold molar excess of furan in a sealed tube at 160 ± 5 °C for 4 h and the solid products Soxhlet-extracted from the polymeric product, then partially resolved by preparative TLC, three fractions were isolated: (*i*) a mixture of adducts **16** and **17** in a 1 : 4 ratio (40%); (*ii*) a bis-furan adduct assigned the *endo–exo–exo–endo* structure **18** on the basis of ^1H NMR spectroscopy, (20%), mp 103–105 °C; and (*iii*) the *endo–exo–exo–exo* isomer of **18**, **19** (20%), mp 242–245 °C. The yields



18 X = Cl



19 X = Cl

of these products varied considerably in several experiments and during the work-up procedure, which involved hot petroleum extraction, the mixture appeared to equilibrate towards the bis-adduct **18**. Subsequently, a pure sample of adduct **17** was isolated, mp 139–141 °C (lit.,[3a] mp 139 °C). Adduct **16** was so scarce in some preparations as to be almost undetectable, suggesting its thermal instability. Good but indecisive evidence for the structure of **17** having *endo–exo* stereochemistry is the absence of bridgehead–ring-junction ^3J spin coupling (1, 8-H–2, 7-H) on account of the torsion angle H_1–H_2 *ca.* 90° in this isomer, with 2, 7-H at δ 2.79 a sharp singlet. By contrast, the minor isomer, the *endo–endo* adduct **16** exhibits 2, 7-H as a multiplet signal at δ 3.56 (deshielded by proximate bridge O), reflecting a reduced H_1–H_2 torsion angle (*ca.* 40°). However, we have occasionally seen expected vicinal ^3J couplings vanish owing to the presence of an electronegative substituent (*e.g.* O on C-1) on at least one of the proton-bearing C atoms. To place the stereochemistry on a more secure basis

†† For a discussion of *exo* and *endo* selectivity in (4 + 2)π cycloadditions, see Jones and Wife.[15b]

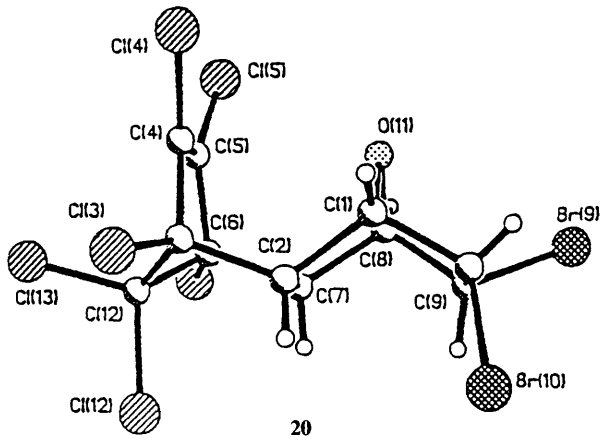


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Fig. 2

we sought chemical and other evidence. A sample of the mixed adducts **16** and **17** (containing very little **16**) exposed to C_5H_5NH Br_3–HOAc at 20 °C gave a single unsaturated dibromide in 88% isolated yield mp 204–206 °C, [ν_{max} 1606 cm^{-1}, (ClC=CCl)]. It is well known (and is one of several reasons for our interest in such structures[1a,4]) that compounds containing the structural elements characteristic of isodrin **1** undergo transannular π–π cyclisation when subjected to electrophilic reagents,[17] and do not form simple 1,2-dibromo-adducts. The dibromide also contains a *trans*-CHBr–CHBr-element, as shown by NMR spectroscopy [δ 4.78 (1 H, d, *endo*-9-H) and δ 4.45 (1 H, q, *exo*-10-H)], and is consistent with structure **20** for the dibromide. Well formed crystals of the dibromide, suitable for single-crystal X-ray crystallographic analysis, were obtained, with the resulting structure depicted in Fig. 2,[18] unambiguously defining the major product of reaction of nbd-Cl_6 with furan as the *endo–exo* adduct **17**. To account in the simplest terms for this result, a lowered E_s for **17** compared with the thermally unstable isomer **16** ensures its predominance, but leaves open the question as to whether it is also the kinetic product resulting from a more important stabilising secondary orbital interaction as depicted in TS_1^f. The fact that a little **16** is actually formed (*ca.* 10%) is evidence nevertheless for the orbital coupling depicted as leading to TS_2^f and invites examination of whether product composition can be modulated by using suitably substituted furans. If so, there arises the potential to identify kinetic and thermodynamic products with certainty, so illuminating relative transition state energies for the alternative cycloaddition modes.

Reaction of 2-methyl- and 2-ethyl-furan with nbd-Cl_6 5a

Although molecular modelling (MM) calculations indicate greater strain energy generally for the *endo–endo* series of adducts compared with their *endo–exo* stereoisomers, MOPAC[19] calculations suggested that in the transition state for *endo–endo* addition of 2-methylfuran to **5a**, the incipient bridgehead C-1-Me and C-3-Cl groups are slightly less congested than in the *endo–exo* addition mode. This encouraged an investigation of 2-methyl-and 2-ethyl-furans (**3a** and **3b**) as dienes in reaction with nbd-Cl_6 **5a**. Molecular modelling calculations indicate that the strain energies of the potential products from **3a**, adducts **21** and **22**, are 84.58 and 76.98 kcal mol^{-1}, respectively, a slightly smaller difference (ΔE_s = 7.60 kcal mol^{-1}) than for **16** and **17** (8.28 kcal mol^{-1}). In addition, the π-donor properties of alkyl groups are expected to increase the reactivity of **3** and **4** towards the relatively electron-deficient dienophile **5a**. There are thus good grounds for expecting a shift in product composition towards more of the *endo–endo* adduct **21**, not least that 2-Me in furan **3a** will enhance the π-orbital coefficient at C-5, leading to an earlier

Table 1 Variation of product composition with time and temperature for the reaction of 2,5-dimethylfuran **4** (5.95 mol dm^{-3}) with 1,2,3,4,7,7-hexachloronorborna-2,5-diene **5a** (2.01 mol dm^{-3}) assayed by ^1H NMR signal intensities for adducts **25** and **26**

T/°C	t/h	Ratio 25:26	Total (%), 25 + 26
135	66	0.33	66
135	20	1.0	64
135	1.5	6.0	31
110	20	2.0	61

transition state, reducing still further the product strain energy difference factor compared with **16** and **17**.

Samples of mixed products were isolated by the methodology described above, but employing lower temperatures with longer reaction times (135 °C, up to 20 h) for the addition of 2-methylfuran **3a** to nbd-Cl_6 **5a**. This strategy delivered products containing a 1:1 ratio of adducts **21** and **22**, again distinguishable from the presence of 7-H–8-H NMR spin-coupling in the *endo–endo* isomer **21** and its absence in the *endo–exo* isomer **22**. The two isomers were resolved by preparative TLC giving the *endo–endo* compound **21** (31%), mp 172–173 °C, and *endo–exo* isomer **22** (31%), mp 149–150 °C. For the former, the 2,7-H NMR signals appear at δ 3.22 (d) and 3.68 (dd), deshielded by the bridge O atom compared with these signals in the *endo–exo* isomer, δ 2.84 (d) and 2.90 (d). Exposure of *endo–endo* compound **21** to tetrachlorothiophene 1,1-dioxide (TCTD) gave triene **21A**, mp 169–171 °C, resolidifying and melting at 233–235 °C (see Experimental section). The two isomers are thus unambiguously identified by thermal ($4\sigma + 2\pi$) dyotropy[1b] in the derivative **21A** (→**21B**, mp 233–235 °C). (Notably, no products of bis-furan addition were observed under these conditions, despite the higher reactivity at the dienophilic site in these oxygenated norbornene systems, as reported below.) Identical results were obtained when 2-ethylfuran **3b** was substituted for **3a** in sealed tube reactions with nbd-Cl_6 **5a** at 110 °C for 20 h; the *endo–endo* and *endo–exo* homologues of **21** and **22**, **23** and **24** were delivered in a 1:1 ratio, the isomers being distinguishable again by the presence of 7-H–8-H spin coupling, or its absence, respectively. The two isomers were resolved as above into the *endo–endo* adduct **23** (41%), mp 181.2–181.4 °C and *endo–exo* adduct **24** (39%), a viscous gum. *endo–endo* Compound **23** yielded the dyotropically active triene **23A** when exposed to TCTD (1 mol, 61 °C, 20 h) having the double mp characteristic of compounds of this class,[1b,20] mp 149–150 °C, resolidifying (**23A**→**23B**) and finally melting at 226–227 °C.

Reaction of 2,5-dimethylfuran with nbd-Cl_6 5a

The remarkable switch in product composition observed in the reaction of nbd-Cl_6 with 2-methylfuran **3a** and its Et-analogue **3b** compared with furan **2** prompted a more careful analysis of the reaction of 2,5-dimethylfuran with dienophile **5a**, facilitated by the three very sharp singlet NMR signals in the two isomeric adducts, *endo–endo* compound **25** and *endo–exo* counterpart **26**, appearing at δ 1.6, 3.35 and 6.18 in **25** and at δ 1.65, 2.98 and 6.25 in **26** (assigned to CH_3, 2, 7-H and 9,10-H, respectively). A series of reactions was conducted in which time and temperature were varied and the composition monitored by NMR spectroscopy affording the following results (Table 1), useful in designing experiments to optimise yields of adduct **25**.

Clearly, decreasing reaction temperature and exposure time favours the *endo–endo* adduct **25** confirming it as the thermally unstable kinetic product, forming at a rate six times or more greater in the initial stages of reaction at 135 °C. Thermally stable under the reaction conditions, as independently demonstrated, thermodynamic product *endo–exo* isomer **26** accumulates with time, as **25** cyclo-reverts to the reactants.

Table 2 Thermal decay of *endo–endo* adduct **25** at 110 °C showing unimolecular behaviour

t/h at 110 °C	Ratio 25:26	$k_1/10^6$ s^{-1}
0	4.8	—
20.25	4.2	1.8
46	3.1	2.6
70	2.8	2.1
88	2.5	2.1

This hypothesis was further verified by heating a mixture of the two stereoisomers **25** and **26** in 4.8:1 initial ratio [0.152 mol dm^{-3} in $(Cl_2C{=}C)_2$] at 110 ± 0.1 °C monitoring the characteristic NMR singlet signals for each isomer under conditions where readdition of addenda released by cycloreversion of **25** is expected to be very slow. The results are shown in Table 2.

The data in Table 2 provide a fair estimate for k_1, the unimolecular rate-constant for cycloreversion of adduct **25** as $(2.15 \pm 0.40) \times 10^{-6}$ s^{-1} at 110 °C. From the data in Table 1, k_2 for addition of **4** to nbd-Cl_6 giving **25** is roughly 10^{-5} dm^3 mol^{-1} s^{-1} at 135 °C, whilst k_2 for the thermodynamic product **26** is roughly an order of magnitude smaller (10^{-6} dm^3 mol^{-1} s^{-1}) than for the kinetic addition. Clearly here $E_a/TS_2^f < E_a/TS_1^f$ and probably this holds in general.

Mixtures of the two isomers **25** and **26** were resolved by preparative TLC (as above) giving *endo–endo* adduct **25**, mp 148–149 °C (equilibration with **26**?) and its *endo–exo* isomer **26**, mp 149–149.5 °C. Annulation of both isomers using TCTD (1 mol, 61 °C) gave from **25** the dyotropically active triene **25A**, whose transparent crystals become opaque when heated (at 160–170 °C, **25A**→**25B**)‡‡ and finally melt at 305–307 °C; and from **26** triene **26A** which is thermally stable up to its mp, 175–176.5 °C.

Reactivity of furan adducts of 1,2,3,4,7,7-hexachloronorborna-2,5-diene 5a

The isolation of the bis-adducts **18** and **19** in 40% yield from the products of addition of furan **2** to nbd-Cl_6 suggests that the dienophilic π-face in adduct **17** is unusually reactive towards dienes compared with the electron-deficient dienophile **5a**. In the expectation of a higher lying HOMO for CH=CH in **17** (compared with norbornene derivatives, for example), the use of an electron-deficient diene (low lying LUMO)[6b] in a simple experiment to illustrate the enhanced reactivity of the oxanorbornene system invited itself. Aldrin **8**, 'oxaaldrin' **17** and the bis-adduct **19** were heated with phencyclone (1,3-diphenyl-2*H*-cyclopenta[l]phenanthren-2-one) **27** under identical conditions in toluene (110 °C, N_2) and the time for completion of the self-indicating reaction (intense green colour→pale yellow) was noted. The reaction completion times and rate constants k_2 are shown in Table 3. (The corresponding 1:1 adducts **28**, **29** and **30**, formed irreversibly, were isolated in high yield.) The notable enhancement in reactivity of the oxygen-bridged compounds compared with aldrin **8** is clear evidence for the effect invoked to rationalise the change in stereochemical mode and the regioselectivity seen in the reaction of 7-alkoxynorbonadienes with electrophilic dienes (including **27**[8]).[9] The O(n)–π interaction§§ in *e.g.* **17** bring HOMO (dienophile) and LUMO (diene) into closer energetic

‡‡ X-Ray crystal structures of the dyotropic isomers **25A** and **25B**, and also that of **21B** will be reported separately, together with molecular model calculated geometries and kinetic characteristics of the trienes **21A**, **25A** and other related compounds.

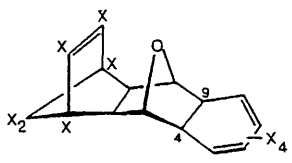
§§ There is evidence from photoelectron spectroscopy for O(n)–π interactions in compounds containing structural elements similar to those in *e.g.* **17**, **19**.[21]

Table 3 Relative reactivities of adducts **8**, **17** and **19** (0.012 mol dm^{-3}) at 110 °C towards phencyclone, **27** (0.010 mol dm^{-3}). $\{k_2 = 1/t [x/a(a - x)]$, $x = 0.01$ mol $dm^{-3}\}$

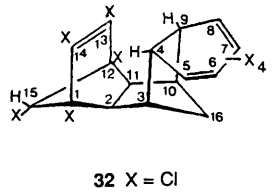
Dienophile	Completion time, $t/10^3$ s	$k_2/10^{-3}$ dm^3 mol^{-1} s^{-1}	Rel. rate
Aldrin **8** (→**28**)	144	2.89	1
Oxaaldrin **17** (→**29**)	6	69.60	24
Bis-adduct **19** (→**30**)	4	104.00	36

proximity lowering the transition state energy. In the absence of any steric impediment imposed by the bridge, *endo*-diene–*exo*-dienophile addition is expected, as shown by the stereochemical features of the products from further cycloadditions (see below). (The high insolubility of the phencyclone adducts precluded stereochemical analysis for these particular compounds.)

Further confirming the neighbouring oxygen effect, exposure of adduct **17** to the strongly electrophilic diene TCTD (1 mol, $CHCl_3$, 25 °C) resulted in complete reaction after *ca.* 12 h giving the triene-system **31**. By contrast, isodrin analogue **32** is formed



31 X = Cl



32 X = Cl

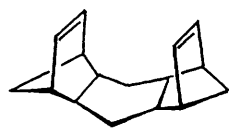
ca. 10–15-fold more slowly at 61 °C, at roughly 10^{-2} relative to the rate at 25 °C, compared with **17**.¶¶ These results show that the neighbouring oxygen effect can translate into a 10–100-fold kinetic enhancement depending on the diene reactivity. (TCTD is reactive enough to combine with ethene at 25 °C.)[22] The triene system **31** is thermally stable in the temperature range associated with dyotropy in *endo–endo–exo* analogues, *e.g.* **32**, for which the hydrogen-transfer process has been closely investigated.[20]

Bis-adduct **19** also reacted rapidly with TCTD, in contrast to the reaction of its isomer **18**, whose reactivity is more similar to that of isodrin-analogues, (→**32**), perhaps a manifestation of laticyclic conjugation of ClC=CCl with CH=CH mediated by the O-bridge, with a consequent weaker enhancement of HOMO energy compared with that in **17** and **19**.

Further cycloadditions of 17 and 19. Potentially useful polycyclics

Some indication of the potential for further studies of compounds easily derivable by cycloaddition of the *endo–exo* adduct **17** and its analogues is the observation that for the bis-adduct of norbornadiene **5d** and cyclopentadiene, **33**, CH_2 bridge-mediated π–π interaction has been demonstrated. The (π + π) and (π − π) combination molecular orbitals have ΔE_π 0.52 eV,[23] a significant interaction (if considerably smaller than in hexadechloroisodrin **34** with much closer π–π proximity).[20,24] Clearly, for the pentacyclic diene **35** lacking the CH_2 bridge no π–π interaction is expected, but if C=O, O and S bridges can be introduced, as in compounds **36** and **37**, analogous to **33**, similar effects might be observed.[23] We have therefore investigated the reactions of adduct **17** with inverse-electron demanding dienes **7** and **9**. Sealed-tube reactions of **17** with hexachlorocyclopentadiene **7** and tetrachlorocyclopentadienone dimethyl acetal **9** (130 ± 10 °C/24 h), deliver *exo–endo* adducts **36** (82%, mp > 360 °C) and **37** (66%, mp 240–242 °C) stereochemically recognisable from the very simple ^1H NMR spectra, two sharp singlets for ring-junction and bridgehead protons at δ 2.93 and 4.56, respectively, for **36** and three sharp singlets at δ 2.65, 2.83 and 4.43 for **37** having two different ring-junction environments. The bis-furan adduct **19** on reaction with hexachlorocyclopentadiene similarly gave the symmetrical octacyclic compound **38** (78%, mp 360 °C decomp.) stereochemically characterised by the appearance of three sharp NMR singlets at δ 1.95, 2.88 (different ring-junction proton types) and 4.50 (identical sets of bridgehead protons). In principle it should be possible to dechlorinate these poly-adducts[25] providing compounds suitable for PES investigation of laticyclic conjugation effects.

33



35

It should also be pointed out that other routes to oxygen-bridged compounds having isodrin-like stereochemistry (*viz.* **16**, **21**, **23** and **25**) are somewhat lengthy, involving 5–6 steps.[26a,b] The two routes potentially available to the required intermediate 3,4-furanonorbornene as a source of oxaisodrin **16** failed when a cyclic peroxide analogous to that previously described[26a] proved unstable to further manipulation; in the alternative procedure[26b] a key step, formylation at the α-position in norbornen-2-one proved, surprisingly, to be a stumbling block.

Reaction of norbornadiene and 1,2,3,4,7,7-hexachloronorborna-2,5-diene with hyperreactive isobenzofurans

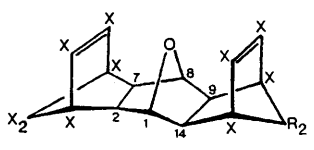
Isobenzofuran and its derivatives are known to be exceptionally reactive towards electrophilic dienophiles. For example, the relative rate of reaction of isobenzofuran with maleic anhydride[27] compared with buta-1,3-diene is 10^6. Since highly reactive components in cycloaddition reactions frequently deliver exclusively products of kinetic control, it seemed of interest to examine the reaction of hexachloronorbornadiene with representative isobenzofurans for comparison with the behaviour of the less reactive furans **2**–**4**. In fact, hexachloronorborna-2,5-diene **5a** is also very efficiently captured by diphenylisobenzofuran **39a** in boiling toluene. Although *endo* addition at the dienophile component **5a** is clearly expected, the spectroscopic properties of the single adduct formed (mp 295–297 °C) would not allow differentiation between the *endo–exo* adduct **40** and stereoisomer **41**, the *endo–endo* compound.

In an attempt to throw light on the problem, the reaction of

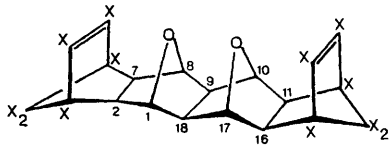
¶¶ A steric retardation associated with motion of the –CH=CH–Hs in the *endo* direction might also be invoked. However, such effects are not large[12] and will be attenuated in an exothermic (reactant-like transition state) process such as experienced with additions of TCTD.

Table 4 Heats of formation ΔH_f, strain, E_s and π-energies E_π with π–π proximity d_{cc} in *endo–endo* isomers

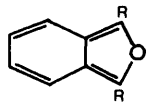
endo–endo Adducts	ΔH_f/kcal mol^{-1}	E_s/kcal mol^{-1}	E_π/kcal mol^{-1}	d_{cc}/Å	*endo–exo* Adducts	ΔH_f/kcal mol^{-1}	E_s/kcal mol^{-1}	E_π/kcal mol^{-1}	ΔE_s/kcal mol^{-1}	$\Delta\Delta H_f$/kcal mol^{-1} (nn-nx)
16	7.938	85.97	−171.785	2.863	**17**	−0.350	77.685	−171.630	8.285	+8.288
21	−3.003	84.567	−171.841	2.857	**22**	−10.611	76.976	−171.874	7.591	−7.608
25	−13.993	83.113	−171.885	2.851	**26**	−20.559	76.632	−172.274	6.481	−6.566



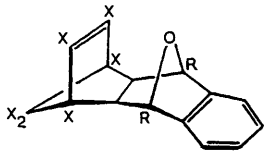
36 R = X = Cl
37 R = OMe X = Cl



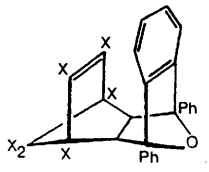
38 X = Cl



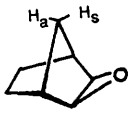
39a R = Ph
39b R = H



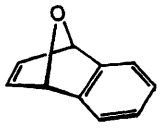
40 R = Ph X = Cl
46 R = H X = Cl



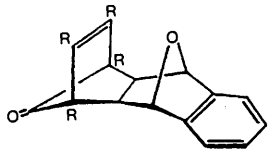
41 X = Cl



43



44



45

39a with norbornadiene, first reported by Cava and Scheel,[28a] was repeated. With a 1:1 ratio of reactants, a single mono-adduct, identical to that reported, mp 210–212 °C, was isolated. Cava and Scheel assigned *exo–exo* stereochemistry to this adduct **42** on the basis of the very different NMR δ values for CH_2-bridge protons H-*syn* and H-*anti* relative to the O bridge, which appear at δ 0.93 (deshielded by O) and δ 2.63, respectively. Tori *et al.*[28b] had earlier demonstrated the same effect in norbornene oxide **43**. In our work we further corroborated Cava's findings but identified also a long-range 1.3 Hz coupling in the ring-junction proton signal. A 2D COSY spectrum correlated this with the H-*anti* signal at δ 0.93 ('W'-type ^4J coupling). On this basis and from the report that 1,3-bis-arylbenzofurans generally form more stable products by *exo*-addition than by the *endo* mode,[29] the most likely structure for the hexachloro analogue is as shown in **40**. Further insight into the structures of these cycloadducts of **5a** and their mode of formation is potentially accessible by using unsubstituted isobenzofuran **39b**.

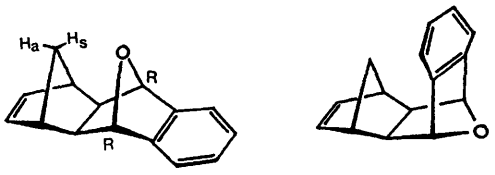
At least four routes to isobenzofuran **39b** are known, based on thermal cycloreversions.[30a–c] The most convenient route is from the tetracyclone adduct **45** (R = Ph) of 7-oxa-2,3-benzonorborna-2,5-diene **44**. This compound undergoes sequential decarbonylation and cycloreversion under mild thermal conditions,[30a] of a type we have earlier described as a potential source of isoindene derivatives.[7a,31] When contacted with **45** in boiling toluene, nbd-Cl_6 delivers a single adduct, unambiguously the *endo–exo* compound **46** (80%, mp 130–132 °C). The ring-junction protons (7, 2-H) appear as a sharp singlet at δ 2.89 and are deshielded compared with these protons in adduct **42**, a consequence of the proximate CCl_2 bridge, whilst the bridgehead protons (8, 1-H) also appear as a sharp singlet at δ 5.31 due to the H_1–H_2 torsion angle being *ca.* 90°.

Finally, we re-examined the addition of isobenzofuran **39b** to norbornadiene **5d** earlier reported by Jones and Kneen,[32] and besides the reported *exo–exo* and *endo–exo* adducts **47** and **48** (mps 85–87 °C, and 65–67 °C, respectively), when even an excess of **5d** is present, a bis-adduct **49** having *endo–exo–exo–exo* stereochemistry is formed, (17%, mp 235–240 °C decomp.). In this compound two different types of bridgehead proton give rise to singlet and multiplet signals corresponding to *exo*- and *endo*-addition with respect to the diene **39b**, and *exo* to both π-faces of norbornadiene, as expected. The two CH_2 bridge protons have very different chemical shifts: H^1 is in the aromatic ring shielding zone and *anti* to the strongly deshielded proton H^2, (*syn* to O-15) and appears at δ −1.4. H^2 appears at δ +1.62, being deshielded by oxygen, but it is also shielded by the aromatic ring. Comparison of the chemical shifts of H-*syn* in the monoadducts **47** and **48**, where aromatic ring shielding of H-*syn* (in **47**) and oxygen deshielding of H-*syn* (in **48**) are factored out, gives an average of (2.77 + 0.68)/2 = 1.72. Thus δ 1.62 is within reasonable expectation for H^2.

The ratio of *exo–exo* adduct **47**, bis-adduct **49** and *exo–endo* adduct **48** is 3:2:1, and since clearly the bis-adduct must be derived from either of the monoadducts **47** and **48**, one or both of these compounds must be more reactive towards isobenzofuran than is norbornadiene, which is in excess. As noted above,[29] isobenzofurans generally form more stable adducts by approach to dienophilic sites in the *exo* mode (→**47**) implying that **48** is the less stable (and more reactive?) adduct, raising immediately the alternative possibilities that **49** is derived from **48**, or that **48** is formed more slowly than **47**, in order to account for the relative paucity of **48** in the reaction mixture. More experiments are required to resolve this question.

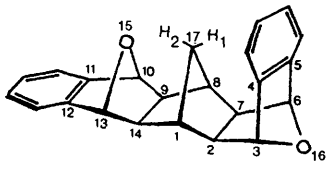
Experimental

The following apply unless otherwise indicated. NMR data refer to solutions in $CDCl_3$(Me_4Si) obtained with JEOL GX270, GX400 or GSX500 instruments; all reported signals have the correct relative intensities. *J* values are given in Hz. IR data were obtained with a Perkin-Elmer PE881 instrument and UV data with PE555/PE552 instruments. EI mass spectra were obtained with an AEI MS902 with VG Micromass facilities or with a Fisons Autospec machine; all ion clusters have the correct intrinsic halogen-isotope abundance ratios. Preparative TLC refers to 0.8 mm Merck-type $60GF_{254}$ silica gel loaded plates visualised under UV light. Light petroleum refers to the 60–80 °C bp fraction, all solvents for chromatography being routinely redistilled. Flash chromatography was carried out using Varian Mega Bond Elut silica cartidges (2 g and 10 g). Mps are uncorrected values. Combustion analysis data are the average of two consistent determinations.



42 R = Ph
47 R = H

48



49

Adduction of furan with 1,2,3,4,7,7-hexachloronorborna-2,5-diene 5a

1,2,3,4,7,7-Hexachloronorborna-2,5-diene ('nbd-Cl_6') **5a** was prepared as previously described;[2,33] small samples are conveniently purified, for example, by loading 10 g samples on to 300 g freshly activated silica (50 × 5 cm column) and eluting with light petroleum (3.25 dm^3). Evaporation of the fractions affords **5a** free of by-products.

In a typical experiment, **5a** (550 mg, 1.8 mmol) and furan **2** (400 mg, 5.9 mmol) were heated in a sealed tube at 160 ± 5 °C for 4 h. On cooling, the crude golden-yellow semi-solid product was rinsed out with CH_2Cl_2 and the solution evaporated; the resulting solid was extracted (Soxhlet thimble) with hot light petroleum for several hours and the extract then evaporated. Samples of product (150 mg) were subjected to preparative TLC (20% EtOAc–light petroleum) to give three major products; (*i*) a 1:4 mixture of *endo–endo* adduct **16** and *endo–exo* adduct **17** (43 mg, 40%, extrapolated yield); (*ii*) the *endo–exo–exo–endo* bis-furan adduct **18** (24 mg, 20%), mp 103–105 °C and (*iii*) the *endo–exo–exo–exo* adduct **19** (24 mg, 20%), mp 242–245 °C. Further preparative TLC of fraction (*i*) and recrystallisation from MeOH gave pure adduct **17**, mp 139–141 °C (lit.,[3a] mp 139 °C).

Spectroscopic data for *endo–exo*-3,4,5,6,12,12-hexachloro-11-oxatetracyclo[6.2.1.$1^{3,6}$.$0^{2,7}$]dodeca-4,9-diene **17**; δ_H 2.79 (s, 2, 7-H), 4.89 (t, 1, 8-H) and 6.49 (t, 9, 10-H,); δ_C 53.3 (C-2, 7), 76.5 (C-1, 8), 79.1 (C-3, 6), 103.9 (C-11), 128.8 (C-4, 5) and 131.1 (C-9, 10); *m/z* 364 (M^+, 9%), 329 (M − Cl^+, 14), 293 (M − HCl_2^+, 10), 261 (M − Cl − $C_4H_4O^+$, RDA,[III] 263 = 100%) and 68 ($C_4H_8O^+$, RDA, 60%). Phencyclone[34] adduct **29**. (*cf.* Table 3) (80% recovered), mp 316–317 °C (decarbonylation)[35] (Found: C, 64.35; H, 3.3. $C_{40}H_{24}Cl_6O_2$ requires C, 64.11; H, 3.23%); *m/z* 718 (M − CO^+, 100%). The adduct **29** was not sufficiently soluble in $CDCl_3$ for NMR analysis. Similarly prepared from aldrin **8**, phencyclone adduct **28** (80%), mp 335–337 °C (decarbonylation) (Found: C, 65.65; H, 3.7. $C_{41}H_{26}Cl_6O$ requires C, 65.89; H, 3.51%); *m/z* 716 (M − CO^+, 100%), 681 (M − $COCl^+$, 68%).

endo–exo Adduct **17** was converted to its *trans*-9,10-dibromo-derivative by treating **17** (190 mg, 0.52 mmol) with $C_5H_5NH^+$-Br_3^- (230 mg, 0.72 mmol) in HOAc 5 cm^3 whilst stirring (24 h, 25 °C). The adduct precipitated from solution (240 mg, 88%), mp 204–206 °C; δ_H[$(CD_3)_2SO$] 4.78 (d, *endo*-9-H), 4.51 (m, 1, 8-H), 4.45 (q, *exo*-10-H), 3.55 (q, 2, 7-H deshielded by *endo*-10-Br); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1606 vs (ClC=CCl); *m/z* 522 (M^+, 4%; 526, 20%), 487 (M − Cl^+, 4), 443 (M − Br^+, 20%; 445, 70%). For crystallographic details of the crystal structure (Fig. 2), see preliminary communication.[18] Exposure of adduct **17** (122 mg, 0.33 mmol) to tetrachlorothiophene 1,1-dioxide (TCTD)[22] (90 mg, 0.35 mmol) in CH_2Cl_2 (0.8 cm^3) for 12 h at 20 °C gave thermally stable compound **31** (165 mg, 90%), mp 279–282 °C; δ_H 4.85 (s, 9, 14-H), 3.13 (s, 2, 7-H) and 3.05 (s, 1, 8-H); *m/z* 552 (M^+), 517 (M − Cl^+), 481 (M − HCl_2^+), 68 ($C_4H_4O^+$, RDA); λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) (EtOH) 263 (3473), 274 (5278), 284 (7577), 296 (8238) and 310 (4911) *cf.* ref. 7*a*. Several attempts to obtain *endo–endo* adduct **16** in pure form were unsuccessful, perhaps due to its thermal instability. δ_H 3.56 (m, 2, 7-H), deshielded by O-11 with respect to isomer **17**), 4.97 (m, 1, 8-H) and 6.37 (t, 9, 10-H); δ_C 51.8 (C-2, 7), 78.7 (C-1, 8), 78.9 (C-3, 6), 107.2 (C-11), 129.4 (C-4, 5) and 131.7 (C-9, 10).

endo–exo–exo–endo Bis-adduct **18**, δ_H 2.40 (m, 9, 14-H, deshielded with respect to isomer **19** by O-15), 2.79 (s, 2, 7-H), 4.11 (s, 1, 8-H), 4.88 (m, 10, 13-H) and 6.26 (m, 11, 12-H); δ_C 49.4 (C-9, 14), 57.3 (C-2, 7), 72.5 (C-1, 8), 77.6 (C-3, 6), 79.1 (C-10, 13), 103.0 (C-17), 128.4 (C-4, 5) and 133.5 (C-11, 12); *m/z* 432 (M^+, 1%), 364 (M − $C_4H_4O^+$, RDA, 33), 329 (M − Cl − $C_4H_4O^+$, 37), 293 (M − HCl_2 − $C_4H_4O^+$, 14), 261 (M − Cl − $C_8H_8O_2^+$, 100) and 68 ($C_4H_4O^+$, 67). Adduct **18** was characterised as the tetrachlorocyclohexadiene annelated compound **18A**, similarly prepared as above, from **18** and tetrachlorothiophene 1,1-dioxide (TCTD), (60% purified yield) mp 320–340 °C (decomp.); δ_H 2.47 (m, AA^1XX^1, 9, 18-H), 2.85 (s, 2, 7-H), 3.25 (s, 11, 16-H), 4.37 (s, 1, 8-H) and 4.82 (m, 10, 17-H); δ_C(135° DEPT spectrum, CH = +, CH_2 = −, *q* = O) 49.6 (+, C-9, 18), 53.6 (+, C-2, 7), 56.6 (+, C-11, 16), 73.1 (+, C-1, 8), 79.2 (0, C-13, 14) and 128.6 (0, C-4, 5); *m/z* 620 (M^+, 20%), 585 (M − Cl^+, 6), 371 (M − $C_6H_2Cl_5^+$, 26), 335 (M − $C_6H_3Cl_6^+$, 15), 279 (M − $C_{14}H_{10}Cl_4O_2^+$, RDA, 100) and 68 ($C_4H_4O^+$, 40) (Found: C, 36.6; H, 1.5. $C_{19}H_{10}Cl_{10}O_2$ requires C, 36.52; H, 1.61%).

endo–exo–exo–exo Bis-furan adduct **19**, δ_H 1.85 (s, 9, 14-H), 2.82 (s, 2, 7-H), 4.51 (s, 1, 18-H), 4.93 (s, 10, 13-H) and 6.35 (s, 11, 12-H); δ_C 49.7 (C-9, 14), 56.4 (C-2, 7), 76.2 (C-1, 8), 79.4 (C-10, 13), 80.4 (C-3, 6), 102.9 (C-17), 128.5 (C-4, 5) and 137.1 (C-11, 12); *m/z* values are very similar to bis-adduct **18**. Bis-adduct **19** was characterised as its phencyclone adduct **30**, (*cf.* Table 3), mp 317–318 °C (decarbonylation) (Found: C, 64.5; H, 3.5. $C_{44}H_{28}Cl_6O_3$ requires C, 64.55; H, 3.45%); *m/z* 786 (M − CO^+, 100%).

Reactions of adduct 17 with hexachlorocyclopentadiene 7 and with tetrachlorocyclopentadienone methyl ketal 9

(*a*) Adduct **17**, (160 mg, 0.44 mmol) and C_5Cl_6 **7** (1.98 g, 7.3 mmol) were heated together in a sealed Young's pressure tube at 130 ± 10 °C (Wood's metal bath) for 24 h. On cooling, crystals separated which were collected and washed (light petroleum), then recrystallised from CH_2Cl_2 giving adduct **36**, (230 mg, 82%) mp > 360 °C (decomp.); $\delta_H(CD_2Cl_2)$ 2.93 (s, 2, 7-H and 4, 9-H) and 4.56 (s, 1, 8-H); $\delta_C(CD_2Cl_2)$ 56.7 (C-2, 7 and C-4, 9), 73.9 (C-1, 8), 79.6 (C-1, 6 and C-10, 13), 102.8 (C-16, 17) and 129.3 (C-4, 5 and C-11, 12); *m/z* 634 (M^+, 30%), 599 (M − Cl^+, 20), 364 (M − $C_5Cl_6^+$, RDA, 5), 270 ($C_5Cl_6^+$, RDA, 42), 103 (100) and 68 ($C_4H_4O^+$, RDA, 47) (Found: C, 29.9; H, 1.0. $C_{16}H_6Cl_{12}O$ requires C, 30.04; H, 0.95%).

(*b*) In a similar reaction employing adduct **17** (160 mg, 0.44 mmol) and rather less diene **9** (930 mg, 3.5 mmol), dilution of the cooled liquid product with light petroleum and scratching to induce crystallisation gave adduct **37**, (180 mg, 66%) mp 240–242 °C; δ_H 2.65 (s, 9, 14-H), 2.83 (s, 2, 7-H), 3.50 (s, OCH_3), 3.57 (s, OCH_3) and 4.43 (s, 1, 8-H); δ_C 51.6 (C-9, 14), 52.6 (C-2, 7), 56.2 and 56.4 (OCH_3), 73.0 (C-1, 8), 75.1 (C-10, 13), 79.2 (C-3, 6), 102.5 (C-17), 113.0 (C-16), 127.1 (C-11, 12) and 128.7 (C-4, 5); *m/z* 591 (M − Cl^+, 31%), 253 (100) and 68 ($C_4H_4O^+$, 2) (Found: C, 34.2; H, 1.95. $C_{18}H_{12}Cl_{10}O_3$ requires C, 34.27; H, 1.92%).

Reaction of bis-furan adduct 19 with hexachlorocyclopentadiene

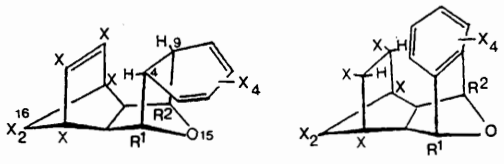
A similar reaction to that described with **17**, (*a*) above,

[III] RDA (Retro-Diels–Alder).

employing the bis-furan adduct **19** and C_5Cl_6 (excess) gave the symmetrical adduct **38**, 70%, mp 360 °C (decomp.) (from CH_2Cl_2); $\delta_H(CD_2Cl_2)$ 1.95 (s, 9, 18-H), 2.88 (s, 2, 7-H and 11, 16-H) and 4.50 (s, 1, 8-H and 10, 17-H); $\delta_C(CD_2Cl_2)$ 53.2 (C-9, 18), 56.0 (C-2, 7 and C-11, 16), 77.6 (C-1, 8 and C-10, 17), 79.7 (C-3, 6 and C-12, 15), 102.9 (C-21, 22) and 129.0 (C-4, 5 and C-13, 14); *m/z* 702 (M^+, 28%), 667 (M − Cl^+, 4), 631 (M − HCl_2^+, 6), 441 (RDA^+, 100), 68 ($C_4H_4O^+$) (Found: C, 33.9; H, 1.4. $C_{20}H_{10}Cl_{12}O_2$ requires C, 33.94; H, 1.42%).

Reaction of 2-methylfuran 3 with 1,2,3,4,7,7-hexachloronorborna-2,5-diene 5a

Dienophile **5a** (500 mg, 1.67 mmol) and 2-methylfuran **3** (411 mg, 5.01 mmol) were heated together in a Young's pressure tube for 20 h at 135 °C (Wood's metal bath). The cooled reaction mixture was diluted with 5% EtOAc–pentane (5 cm^3) and enough CH_2Cl_2 to complete solubilisation; the solution was flash-chromatographed (3% EtOAc–pentane), yielding a 1:1 mixture of adducts **21** and **22**. Preparative TLC (2.5% EtOAc–pentane) resolved this mixture into *endo–endo*-3,4,5,6,12,12-



21A R^1 = Me R^2 = H X = Cl [**21B** R^1 = Me R^2 = H X = Cl]
23A R^1 = Et R^2 = H X = Cl [**23B** R^1 = Et R^2 = H X = Cl]
25A $R^{1,2}$ = Me X = Cl [**25B** $R^{1,2}$ = Me X = Cl]

hexachloro-1-methyl-11-oxatetracyclo[6.2.1.$1^{3,6}$.$0^{2,7}$]dodeca-4,9-diene **21**, (*ca.* 200 mg, 31%) mp 172–173 °C (aq. MeOH); δ_H 1.65 (s, CH_3), 3.22 (d, *J* 9.3, 2-H), 3.68 (dd, *J* 9.3, 4.88, 7-H), 4.86 (dd, *J* 4.88, 1.71, 8-H), 6.20 (d, *J* 5.86, 10-H) and 6.33 (dd, *J* 5.9, 1.71, 9-H); *m/z* 378 (M^+, absent) 343 (M − Cl^+, 7.5%; 345, 12), 261 ($C_7H_2Cl_5^+$, RDA-Cl, 11; 263, 20) and 82 ($C_5H_6O^+$, RDA, 100) (Found: C, 38.0; H, 2.1. $C_{12}H_8Cl_6O$ requires C, 37.84; H, 2.12%). *endo–exo* Isomer **22** (*ca.* 200 mg, 31%) mp 143–145 °C; δ_H 1.75 (s, CH_3), 2.84 (d, *J* 7.08, 2-H), 2.90 (d, *J* 6.8, 7-H *cf.* 2-H, 7-H in **21**, deshielded by O-11), 4.79 (s, 8-H), 6.23 (d, *J* 5.61, 10-H) and 6.51 (d, *J* 5.62, 9-H); *m/z* values are identical to **21** with some abundance differences, *e.g.* 82 ($C_5H_6O^+$, RDA, 100%). The *endo–endo* adduct **21** was further characterised as the 9,10-(1,2,3,4-tetrachlorocyclohexadiene) annelated compound **21A**, by exposure to TCTD as described, *e.g.* for adduct **18**. **21A** (recryst. CH_2Cl_2) mp 169–172 °C, on cooling the melt set to a glass, which on reheating crystallised, finally melting at 233–235 °C (intramolecular dyotropy);[20] δ_H 1.66 (s, CH_3), 3.21 (d, *J* 11.5, 4-H), 3.28 (d, *J* 11.7, 9-H), 3.35 (d, *J* 11.5, 2-H), 3.71 (dd, *J* 11.7, 5.41, 11-H) and 4.82 (d, *J* 5.40, 10-H); *m/z* 566 (M^+, 2.6%; 570, 12), 531 (M − Cl^+, 2; 535, 9) and 261 ($C_7H_2Cl_5^+$, RDA-Cl, 94; 263, 100); λ_{max}/nm [ε_{max}/dm^3 mol^{-1} cm^{-1} (decalin)] sh262 (2618), 272 (3491), 284 (5219), 295 (6034) and 308 (3782) (Found: C, 33.8; H, 1.35. $C_{16}H_8Cl_{10}O$ requires C, 33.67; H, 1.41%).

In a similar experiment (110 °C, 20 h), substituting 2-ethylfuran for **3** and with preparative TLC resolution following flash chromatography of the *ca.* 1:1 mixture of isomeric adducts obtained (541 mg, 82%) gave *endo–exo*-3,4,5,6,12,12-hexachloro-1-ethyl-11-oxatetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-diene **24** (260 mg, 39%), mp 149–150 °C; δ_H 1.05 (t, *J* 7.32, CH_3), 2.10 (overlapping ddqs, CH_2), 2.88 (s, 7-H), 4.82 (s, 8-H), 6.29 (d, *J* 5.61, 10-H), 6.52 (d, *J* 5.61, 9-H) and 2.88 (s, 2-H overlaps 7-H) (Found: C, 39.7; H, 2.6. $C_{13}H_{10}Cl_6O$ requires C, 39.54; H, 2.55%). *endo–endo* Isomer **23** (270 mg, 41%), mp 181.2–181.4 °C; δ_H 1.05 (t, *J* 7.5, CH_3), 1.96 (dd of q, ^2J 22, ^3J 7.32, diastereotopic Hs, CH_2), 3.24 (d, *J* 9.03, 2-H), 3.68 (dd, *J* 4.88, 9.03, 7-H), 4.87 (dd, *J* 4.88, 1.95, 8-H), 6.20 (d, *J* 5.87, 10-H) and 6.33 (dd, *J* 5.85, 1.94, 9-H); *m/z* (M^+ absent), 357 (M − Cl^+, 13%; 359, 22) and 261 ($C_7H_2Cl_5^+$, RDA-Cl, 17; 263, 27), 96 ($C_6H_8O^+$, RDA, 100). *endo–endo* Adduct **23** was characterised as the 9,10-(1,2,3,4-tetrachlorocyclohexadiene)-annelated compound (**23A**) obtained by exposure of adduct (40 mg, 0.09 mmol) to TCTD (24.8 mg, 1 mol equiv.) in $CHCl_3$ (1.0 cm^3) for 20 h at 61 °C and TLC of the crude product (30% CH_2Cl_2–light petroleum) giving *endo–endo–exo*-1,5,6,7,8,12,13,14,16,16-decachloro-3-ethyl-15-oxapentacyclo[10.2.1.1^{3,10}.0^{2,11}.0^{4,9}]hexadeca-5,7,13-triene (**23A**), (13.3 mg, 54%), recrystallised from MeOH–CH_2Cl_2, mp 149–150 °C resolidifying (dyotropic H shift[20]) and remelting at 226–227 °C; δ_H 1.12 (t, *J* 7.33, CH_3), 2.40 (cm, ^3J 7.33, diastereotopic Hs, CH_2), 3.23 (d, *J* 11, 9-H), 3.45 (d, *J* 11, 4-H), 3.57 (d, *J* 11.9, 2-H), 3.66 (dd, *J* 11.72, 5.2, 11-H) and 4.84 (d, *J* 5.2, 10-H); *m/z* 556 (M^+, absent), 96 ($C_6H_8O^+$, RDA, 100%); λ_{max}/nm [ε_{max}/dm^3 mol^{-1} cm^{-1} (decalin) Shimadzu 160 data] sh266 (2184), sh278 (3223), 287 (4719), 299 (5380) and 312 (3471) (Found: C, 35.1; H, 1.7. $C_{17}H_{10}Cl_{10}O$ requires C, 34.91; H, 1.72%).

Reaction of 2,5-dimethylfuran 4 with 5a

1,2,3,4,7,7-Hexachloronorborna-2,5-diene **5a** (1.02 g, 3.4 mmol) was heated with 2,5-dimethylfuran (750 mg, 7.8 mmol) as described above, at 135 °C for *ca.* 18 h. The crude product (80% conversion to adducts) contained the isomers **25** and **26** in a 1:1 ratio after work up by preparative TLC. A series of experiments was conducted in which similar mixtures of **4** with **5a** were monitored for composition at various times and temperatures (Table 1, main text). Products from these experiments were worked up and resolved as previously described giving *endo–endo*-3,4,5,6,12,12-hexachloro-1,8-dimethyl-11-oxatetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-diene **25**, mp 148–148.6 °C (equilibration with isomer **26**?); δ_H 1.60 (s, $2CH_3$), 3.35 (s, 2, 7-H) and 6.18 (s, 9, 10-H); *m/z* 392 (M^+, scarce), 357 (M − Cl^+, 7%; 359,11), 281 (2.2), 261 ($C_7H_2Cl_5^+$, RDA-Cl, 7; 263, 11) and 96 ($C_6H_8O^+$, RDA, 96). The *endo–exo* isomer **26** had mp 149–149.2 °C; δ_H 1.65 (s, $2CH_3$), 2.98 (s, 2, 7-H), at a higher field compared with isomer **25** due to proximate O-11 in **25**) and 6.25 (s, 9, 10-H). *m/z* is similar to isomer **25**, but 392 (M^+, 3%) is more abundant. Both compounds **25** and **26** were characterised by 9,10-(1,2,3,4-tetrachlorocyclohexadiene) annelation using TCTD as previously described. From *endo–endo* isomer **25**, *endo–endo–exo*-1,5,6,7,8,12,13,14,16,16-decachloro-3,10-dimethyl-15-oxapentacyclo[10.2.1.1^{3,10}.0^{2,11}.0^{4,9}]-hexadeca-5,7,13-triene **25A**, transparent crystals became opaque at 160–170 °C (dyotropy), finally melting at 305–307 °C (decomp.) (see **25B** below); δ_H 1.65 (s, $2CH_3$), 3.35 (s, 2, 11-H), 3.88 (s, 4, 9-H allylic, 2-H, identical with **21A**); *m/z* 580 (M^+, scarce) and 545 (M − Cl^+, scarce), 282 ($C_{10}H_6Cl_4O^+$, RDA, 79%; 284, 100); λ_{max}/nm [ε_{max}/dm^3 cm^{-1} mol^{-1} (decalin)] sh277 (3095), 289 (4778), 301.5 (5949) and 313 (4327) (Found: C, 34.9; H, 1.7. $C_{17}H_{10}Cl_{10}O$ requires C, 34.91; H, 1.72%). Also isolated, (10%) the dyotropomer of **25A**, **25B**, *endo–endo*-1,5,6,7,8,12,13,14,16,16-decachloro-3,10-dimethyl-15-oxapentacyclo[10.2.1.1^{3,10}.0^{2,11}.0^{4,9}]-hexadeca-4(9),5,7-triene, mp 305–307 °C (decomp.); δ_H 2.0 (s, $2CH_3$), 3.05 (s, 2, 11-H) and 3.65 (s, 13, 14-H); *m/z* 580 (M^+, scarce), 545 (M − Cl^+, scarce), 282 ($C_{10}H_6Cl_4O^+$, RDA, 93%; 284, 100); λ/nm 290–310 absent (Found: C, 34.9; H, 1.6%). Similarly prepared from *endo–exo* compound **26**, *endo–exo–exo* isomer **26A**, of **25A**; mp 175–176 °C; δ_H 1.68 (s, $2CH_3$), 3.13 (s, 2, 11-H), 3.24 (s, 4, 9-H); *m/z* similar to **25A** with 282 ($C_{10}H_6Cl_4O^+$, RDA, 77%; 284, 100) and 96 ($C_6H_8O^+$, RDA > 100); λ_{max}/nm [ε_{max}/dm^3 mol^{-1} cm^{-1} (decalin)] 270 (1841), 282 (3594), 292 (5567) and 304 (6575).

Addition of 1,2,3,4,7,7-hexachloronorborna-2,5-diene 5a to bis-1,3-diphenylisobenzofuran 39a

A solution of **5a** (260 mg, 0.87 mmol) and 1,3-diphenylisobenzofuran **39a** (90 mg, 0.33 mmol) in toluene (5 cm^3) was heated at

110 °C for 48 h, the intense fluorescence of **39a** (365 nm, filtered Hg arc) fading with time. Removal of solvent *in vacuo* and washing of the solid product with light petroleum followed by preparative TLC (30% CH_2Cl_2–light petroleum) gave adduct **40** (believed to be the *endo–exo* isomer), (170 mg, 91%), mp 295–297 °C; δ_H 3.75 (s, 2, 7-H), 7.07 (m, Ph), 7.14 (m, Ph) and 7.73 (benzo-ring); δ_C (135 DEPT) 59.5 (+, C-2, 7), 78.7 (0, C-3, 6), 88.6 (0, C-1, 8), 106.5 (0, C-11), 5 signals 119.2–128.2 (all +, Ar-C), 129.5 and 133.2 (each 0, Ar-C quat) and 147.8 (0, C-4, 5); *m/z* 566 (M^+, 8%), 531 ($M - Cl^+$, 22) and 270 ($M - C_7H_2Cl_6^+$, RDA, 100) (Found: C, 56.6; H, 2.9. $C_{27}H_{16}Cl_6O$ requires C, 56.98; H, 2.83%).

Norborna-2,5-diene–1,3-diphenylisobenzofuran adduct

Norborna-2,5-diene **5d** (120 mg, 1.3 mmol) and **39a** (90 mg, 0.33 mmol) were heated in toluene (5 cm^3) under reflux for *ca.* 18 h. The product was isolated and purified (as for **40**) giving *exo–exo* adduct **42**,[28a] (90 mg, 70%) mp 210–212 °C; δ_H 0.94 (bd, *J* 8.4, 12-H-*syn*), 2.45 (d, *J* 1.3, 2,7-H), 2.51 (m, 3, 6-H), 2.63 (bd, *J* 8.4, 12-H-*anti*), 6.17 (t, H-4, 5), 7.03 (s) and 7.37, 7.50 and 7.70 (all m, in the ratio 4:2:4:4, Ar-H); δ_C 42.1 (t, C-12), 43.0 (d, C-3, 6), 55.9 (d, C-2, 7), 89.4 (s, C-1, 8), 118.2, 126.0, 126.2, 127.1 and 128.3 (each d, Ar-C), 137.6 (Ar-C), 140.2 (d, C-4, 5) and 150.0 (s, Ar-C); *m/z* 362 (M^+, 9%) and 270 ($M - C_7H_8^+$, RDA, 100) (Found: C, 89.4; H, 6.3. Calc. for $C_{27}H_{22}O$; C, 89.47; H, 6.12%).

Isobenzofuran precursor, 45

The *exo–exo* adduct **45** was prepared by the literature method[30a] by the reaction of tetraphenylcyclopentadienone (11.14 g, 0.029 mol) with 7-oxa-2,3-benzonorborna-2,5-diene (benzyne–furan adduct *via* $1,2\text{-}H_2NC_6H_4CO_2H + HONO + C_4H_4O$) (4.32 g, 0.03 mol) in boiling benzene, 24 h, the deep purple colour intrinsic to the dienone fading until absent. Evaporation *in vacuo* gave a solid foam, which recrystallised from $CHCl_3$–MeOH gave adduct **45**, (13.54 g, 90%) off-white crystals, mp 196–198 °C (decarbonylation) (lit.,[30a] 184–186 °C); δ_H 3.09 (s, 2, 7-H), 5.81 (s, 1, 8-H), 6.94 and 7.35 (each m, ratio 10:14, ArH); δ_C 46.7 (C-2, 7), 64.3 (C-3, 6), 81.1 (C-1, 8), 119.1, 126.7, 127.3, 127.4, 127.5, 128.3, 129.6, 129.9 (8 Ar-C), 135.1, 135.4 and 138.5 (q, Ar-C), 146.5 (q, C-4, 5) and 198.7 (CO, C-12); *m/z* 382 ($M - C_8H_6O^+$, RDA, 100%).

Reaction of 1,2,3,4,7,7-hexachloronorborna-2-5-diene 5a with isobenzofuran 39b

nbd-Cl_6, **5a**, (290 mg, 0.96 mmol) and **45** (540 mg, 1.03 mmol) in toluene (10 cm^3) was refluxed for 24 h, the solution darkening. Evaporation *in vacuo* gave a dark powdery solid (800 mg) which was divided into 200 mg portions for preparative TLC (30% CH_2Cl_2–light petroleum). A 200 mg portion resolved into 1,2,3,4-tetraphenylbenzene (81 mg, 0.21 mmol) and the *endo–exo* adduct **46**, (79 mg, 0.91 mmol, 80% extrapolated yield), mp 130–132 °C; δ_H 2.89 (s, 2, 7-H deshielded by CCl_2 bridge compared with 2, 7-H in compound **42**), 5.31 (s, 1, 8-H), 7.21 and 7.29 (each q, ratio 1:1, Ar-H); δ_C 55.1 (C-2, 7), 77.3 (C-1, 8), 79.4 (C-3, 6), 103.4 (C-12), 119.6, 127.6, 128.9 (Ar-C) and 144.9 (C-4, 5); *m/z* 414 (M^+, 25%), 379 ($M - Cl^+$, 10), 343 ($M - HCl_2^+$), 307 ($M - H_2Cl_3^+$, 11) and 118 ($M - C_7H_2Cl_6^+$, RDA, 100) (Found: C, 43.45; H, 2.0. $C_{15}H_8Cl_6O$ requires C, 43.21; H, 1.93%).

Reaction of norborna-2,5-diene with isobenzofuran 39b

Isobenzofuran progenitor **45** (5.01 g, 9.4 mmol) and an excess of norborna-2,5-diene (1.47 g, 16 mmol) in toluene (10 cm^3) was refluxed for 24 h and the solvent and excess **5d** were removed *in vacuo* to give colourless crystals (*ca.* 5.5 g). Recrystallised from CH_2Cl_2, the product, 1,2,3,4-tetraphenylbenzene (2.95 g), was identified by its mp 191 °C[7a] and ^1H NMR spectroscopy [δ_H 6.80, 6.90, 7.12 (all m) and 7.05 (s) in the ratio 2:3:5:1]. Concentration of the mother liquors gave 2.01 g solid product of which 400 mg samples were resolved by preparative TLC (as above for **46**) into four fractions: (*i*) tetraphenylbenzene, (110 mg, 0.29 mmol); (*ii*) *exo–exo* adduct **48** (110 mg, total yield 28%), mp 85–87 °C (lit.,[32] 82 °C); (*iii*) *exo–endo* adduct **47** (43 mg, total yield 10%), mp 65–67 °C (lit.,[32] 72–73 °C); and (*iv*) *endo–exo–exo–exo* bis-adduct **49** (53 mg, total yield 17%), mp 235–240 °C (decomp.).

Spectroscopic and analytical data for adducts 47,48,9,10-benzo-derivatives of the 11-oxatetracyclo[6.2.1.$1^{3,6}$.$0^{2,7}$] dodeca-4,9-diene system

exo–endo Adduct **47**: δ_H −0.98 (d, *J* 9.8, 12-H *syn* to Ar), 0.68 (d, *J* 9.8, 12-H *anti* to Ar), 2.27 (m, 2, 7-H), 2.62 (m, 3, 6-H), 5.11 (m, 1, 8-H), 6.20 (t, 4, 5-H) and 7.18 (m, Ar-H); δ_C(135° DEPT spectrum) 40.0 (+, C-2, 7), 42.0 (−, C-12), 49.2 (+, C-3, 6), 81.0 (+, C-1, 8), 120.1 and 127.0 (each +, Ar-C), 141.0 (+, C-4, 5) and 144.5 (0, Ar-C); *m/z* 210 (M^+, 35%), 144 ($M - C_5H_6^+$, RDA, 14) and 118 ($M - C_7H_8^+$, RDA, 100) (Found: C, 85.5; H, 6.9. Calc. for $C_{15}H_{14}O$: C, 85.7; H, 6.7%). *exo–exo* Adduct **48**: δ_H 1.30 (dt, *J* 8.2, 1.5, 12-H *anti* to O-11), 1.84 (d, *J* 1.3, 2, 7-H), 2.72 (bd, *J* 8.2, 12-H *syn* to O-11), 2.89 (m, 3, 6-H), 5.12 (m, 1, 8-H), 6.20 (t, 4, 5-H), 7.12 and 7.22 (each m, ratio 1:1, Ar-H); δ_C(135° DEPT spectrum) 42.9 (−, C-12). 44.3 (+, C-2, 7), 50.6 (+, C-3, 6), 81.5 (+, C-1, 8), 118.7 and 126.1 (each +, Ar-C), 139.6 (+, C-4, 5) and 147.6 (0, Ar-C); *m/z* 210 (M^+, 41%), 144 ($M - C_5H_6^+$, RDA, 14) and 118 ($M - C_7H_8^+$, RDA, 100) (Found: C, 85.9; H, 7.1%. Calc. for $C_{15}H_{14}O$: C, 85.7; 6.7%).

Bis-adduct **49**: *endo–exo–exo–exo*-4,5:11,12-dibenzo-15,16-dioxahexacyclo[6.6.1.$1^{3,6}$.$1^{10,13}$.$0^{2,7}$.$0^{9,14}$]heptadeca-4,11-diene, δ_H −1.4 (d, *J* 11.6, 17-H *syn* to O-16), 1.54 (d, *J* 1.4, 2, 7-H), 1.62 (d, *J* 11.6, 17-H-*anti*), 2.07 (bs, 9, 14-H), 2.20 (m, 1, 8-H, 5.03 (s, 10, 13-H), 5.18 (m, 3, 6-H), 7.09 and 7.15 (each m, ratio 1:3, Ar-H); δ_C(135° DEPT spectrum) 27.2 (−, C-17), 38.4 (+, C-9, 14), 49.2 (+, C-1, 8), 51.8 (+, C-2, 7), 81.2 (+, C-3, 6), 82.2 (+, C-10, 13), 118.6, 119.8, 126.2, 127.1 (all +, Ar-C), 144.4 and 146.7 (each 0, Ar-C); *m/z* 328 (M^+, 1%), 210 ($M - C_8H_6O^+$, RDA, 1) and 118 ($C_8H_6O^+$, RDA, 100) (Found: C, 83.9; 6.1. $C_{23}H_{20}O_2$ requires C, 84.12; H, 6.14%).

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