Cross and Parallel Cyclisation–Rearrangement of Face Proximate π-2*p*-*C* Cations generated in Polycyclic Olefins [1]

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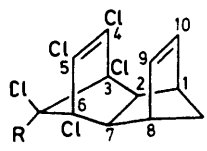
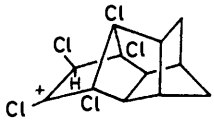
Partially dechlorinated and other derivatives of the cyclodiene pesticides have been made and their behaviour in strongly acid media investigated with a view to correlating structure with cyclisation geometry. The *X*-ray crystal structure of one key compound unambiguously indicates that in the absence of the dichloromethano-bridge characteristic of the parent pesticides aldrin and isodrin, cross rather than parallel cyclisation is preferred in strongly acid conditions. Successive *thermal* rearrangements of 1,2,3,4-tetrachlorocyclopentadiene used here in synthesis of useful model compounds is briefly discussed together with certain other acid-catalysed transformations of isodrin and dieldrin analogues. Simple Hückel MO calculations accord with experimental observation.

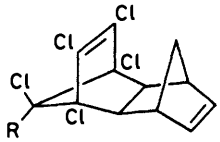
UNSATURATED compounds based on the framework of the cyclodiene pesticides provide convenient models for testing theories of chemical behaviour. We earlier [2] reported the hitherto unobserved sequential Wagner–Meerwein rearrangement of cations derived by protolysis of monodechloroaldrin (1) and stereoisomeric monodechloroisodrin (2) with previously unavailable [3] decisive ^1H n.m.r. and ^2H labelling evidence in partial confirmation of earlier mechanistic proposals featuring similar rearrangement pathways for cations derived solvolytically from analogous non-chlorinated tetracyclododecenyl arenesulphonates.[3] The initial major identical product of treating both compounds (1) and (2) with sulphuric acid is the ketone (5) reasonably presumed formed in each reaction from the same intermediate cation (A).



(2) R = H
(4) R = Cl

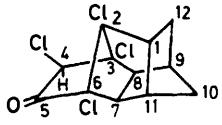


(A)



(1) R = H
(3) R = Cl

$+H_2O$
$-HCl$

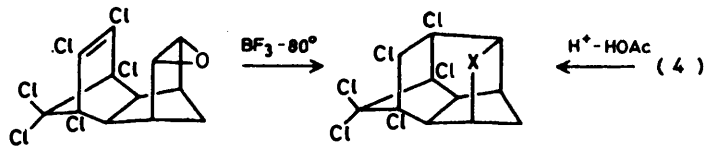


(5)

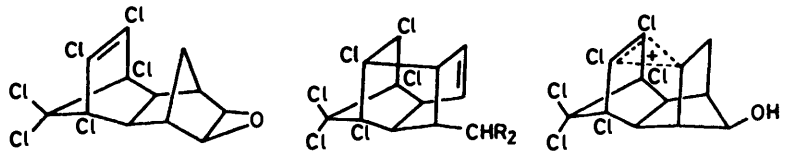
The behaviour of hexachloro-compounds isodrin (4) and its epoxide endrin (6) in cyclisation reactions with electrophilic reagents contrasts notably with that of (2) in giving only partially rearranged half-cage compounds such as (7) [(4)–H^+–HAc] [4] and (8) [(6)–BF_3–C_6H_6–80 °C] [5,†] as major products, whilst on the other hand cations solvolytically derived from 9,10-dihydro-*exo*-9-hydroxyaldrin methanesulphonate (58) showed only very limited rearrangement to *ca.* 10% of compounds analogous to those obtained from stereoisomeric isodrin-type structures.[5] Similar half-cage compounds are accessible [2] from dechloroisodrin (2) by protolysis in hydroxylic solvents, discharge by external nucleophile limiting skeletal rearrangement, but under these conditions only traces of cyclised products are produced from dechloroaldrin (1).[2] More recently it is reported [6] that *exo*-oxiran (9) (dieldrin) gives *e.g.* acetal (10) *via* an intermediate (B) similar to that which rationalizes the formation of half-cage compounds (7) and (8) in the isodrin series. From these (and other [7]) data, skeletal rearrangements in the hexachlorinated isodrin–aldrin series are restricted under appropriate conditions to the non-chlorinated ring; and cationic sites when concomitantly generated in a chlorinated environment by transannular cyclisation, whether by parallel or cross closure, are almost always discharged without further rearrangement. Few if any examples have been reported where modification of the substitution pattern as in (1) and (2) results in such a marked contrast in the behaviour of derived cations; even the pentachlorovinyl ether (11) remains true to type giving ketone (12) in concentrated acid,[8] and similarly epoxide (13) exothermically yields ketone (14) with BF_3–C_6H_6–20 °C.[8]

Wagner–Meerwein rearrangement in the halogenated

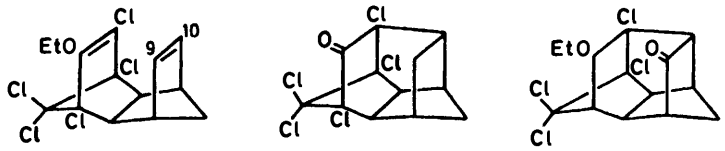
† °C = K − 273.15.



(6) (7) X = CHOAc (8) X = CO



(9) (10) R = OAc or OMe (B)



(11) (12) (14)

(13) (9,10-oxide)

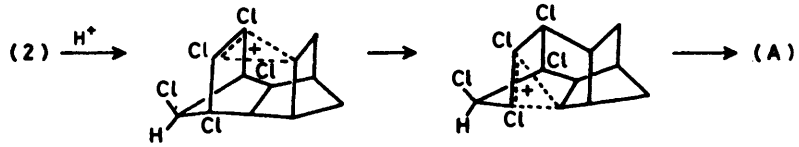
ring on protolysis of *e.g.* (2) is however concomitant only with cross cyclisation, *i.e.* C(4)–C(9) bonding rather than parallel C-5–C-9 closure characteristic of the aldrin–isodrin series [where there is one exception—in the minor product (15) (11%) isolated in the bromination of isodrin [4]]. Cross cyclisation in cations intermediate in electrophilic additions to *vinyl-unsubstituted* hydrocarbons having proximate double bonds, including hexadechloroisodrin,[4,9] can in fact now be recognised as the principal characteristic result, as seen in the examples (16) ⟶ (17),[10] (18) ⟶ (19),[11] and (20) ⟶ (21).[12,13]

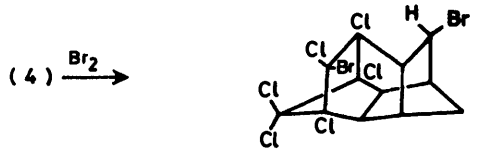
These considerations prompted us to examine the effect of changes in halogenated-ring substitution pattern in aldrin and isodrin types on the products of hydrolysis in acids with weakly nucleophilic anions; in particular, modification at the dichloromethane bridge [C(11)] proximate to the olefinic group ClC=CCl seemed of interest, *e.g.* replacing $>CCl_2$ with >CHCl and/or $>CH_2$, stereoisomeric >CHOR groups (R = H, Me, SO_2Me) and in addition replacing $>CCl_2$ in vinyl ether (11) by >CHCl for comparison with compound (2) (changes which might be expected to modify π-orbital energies, see below). The transformation of dieldrin (9) into acetal (10) and the corresponding *gem*-diacetoxy compound [6] prompts a further objective, *i.e.* whether oxygenated substituents at C(12) in isodrin types (2) and (4) has any interesting effect on their protolytic reactions.

Apart from the intrinsic chemical [2,12,14] and theoretical [15] interest in the processes discussed, diolefin cyclisation *via* cations has relevance to theories of natural product biogenesis [16] and compounds having the twist-bridged framework of pentacyclododecanones such as (5) occur in photo-products [17] and metabolites [18] of the cyclodiene pesticides.

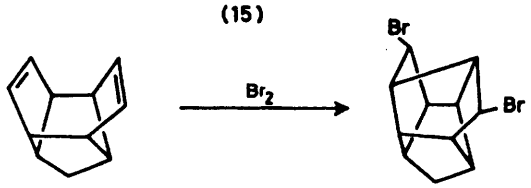
Hydride reduction of bridged ketone (22),[19] zinc debromination and chromatography of the high-yield mixed product gives *anti*- and *syn*-alcohols (23) and (24) (ratio 1 : 2.2). Stereochemistry in the isomeric alcohols follows in ^{1}H n.m.r. analysis from proximity deshielding of the ring-junction protons [2] in (23) (τ 7.31) compared with the *syn*-isomer (24) (τ 7.59) (the same effect being seen in the *trans*-9,10-dibromo-precursors); and from the fact that the sodium salt of the *syn*-isomer (24) decomposes with precipitation of sodium chloride when heated (cyclisation onto ClC=CCl and elimination) but the *anti*-isomer (23) sodium salt is quite stable under these conditions. In addition isomer (24) rapidly forms a mesylate derivative (26) (and also a tosylate) whereas *anti*-alcohol (23) reacts much more slowly with $MeSO_2Cl$–C_5H_5N (and very slowly with TsCl–C_5H_5N!); these effects are probably due to increased nucleophilicity of 11-OH in the *syn*-alcohol (π-hydrogen bonding [20]) and have a corollary in the relative effects of $Pr(fod)_3$ shift reagent in the ^{1}H n.m.r. spectra of the two alcohols: under identical conditions the *syn*-isomer, liganding more strongly, shows much larger chemical shift changes than the *anti*-alcohol.

Precedent exists [21] for the observation that neither alcohol is chlorinated with $SOCl_2$, and the survival of both mesylates (25) and (26) when strongly heated with LiCl–DMSO or $ZnCl_2$–DME illustrates the powerful inhibition of substitution (S_Ni, S_N1, or S_N2) in these systems. Both mesylates (25) and (26) are however readily hydrolysed in H_2SO_4–CCl_4 mixtures giving

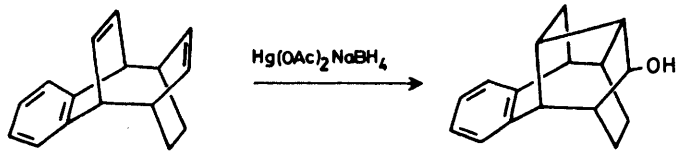




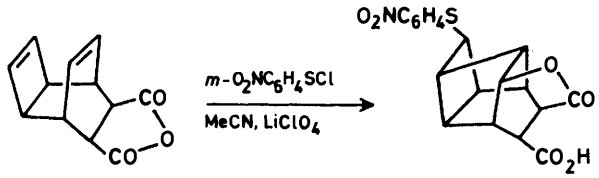
(15)



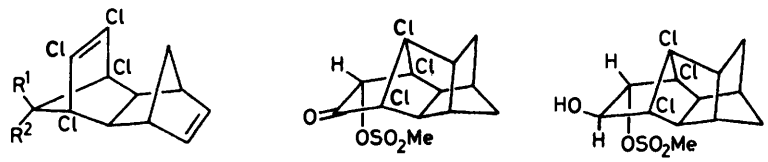
(16) (17)



(18) (19)



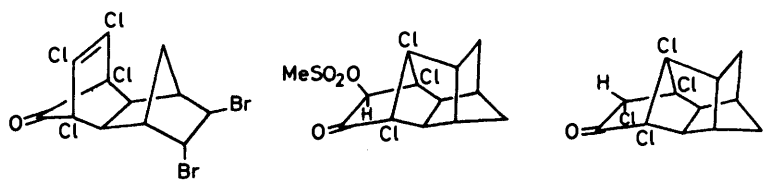
(20) (21)



(23) R^1=H, R^2=OH
(24) R^2=H, R^1=OH
(25) R^1=H, R^2=OSO_2Me
(26) R^2=H, R^1=OSO_2Me

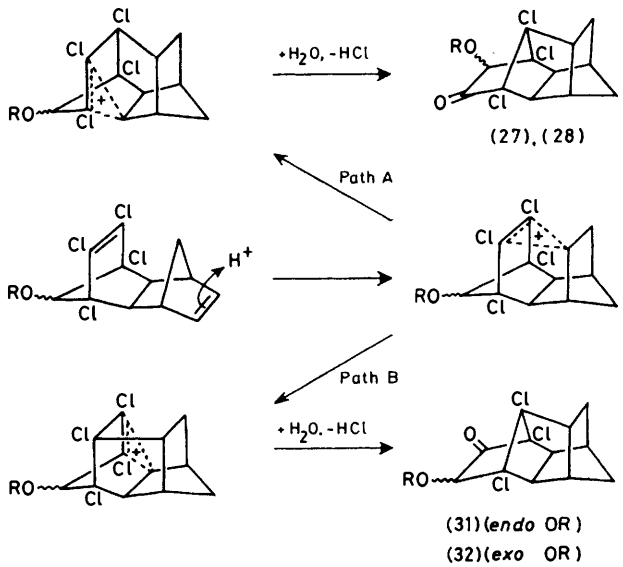
(27) (30)

C_5H_5N, 90°



(22) (28) (29)

30—50% yield of mesyloxypentacyclododecanones (27) and (28) (both having $\nu_{max.}$ *ca.* 1 780 cm^{-1}). Interestingly *exo*-mesyloxy-ketone (28), unlike chlorinated analogue (5) which epimerises giving ketone (29) on silica gel (and incorporates ^2H in weakly basic MeO^2H),[2] is unaffected by silica but is smoothly and quantitatively converted to epimer (27) by hot C_5H_5N. ^1H N.m.r. spectra of pentacyclododecanones (5) and (29) have been analysed in detail previously;[2] consistent with their formulation, both ketones (27) and (28) have spectra strongly resembling those of analogues (5) and (29),



SCHEME 1

especially *e.g.* the appearance of a highly characteristic upfield signal [τ *ca.* 8.8(q)] which appears to be unique to these systems [due to *exo*-12-H, with *endo*-12-H strongly deshielded by proximity to bridgehead Cl (τ *ca.* 7.0)]. However although framework stereochemistry deduced by n.m.r. seems secure, attempts to confirm the relative position of the CO group in *e.g.* (28) by ^2H incorporation, or hydride reduction and analysis of differential chemical shifts of assigned protons in the alcohol compared to the precursor ketone (including the use of shift reagents) proves ambiguous and fails to distinguish the structure from possible isomers (31) and (32) which would result from parallel cyclisation (path B, Scheme 1). Also the unreactivity of either of the mesyloxy-ketones (27), (28) towards nucleophilic displacement [*e.g.* by Cl^- potentially giving (5) and/or (29)] militates against chemical proof. The ambiguity has therefore been resolved by *X*-ray crystallographic determination for the diol monomesylate reduction product (30) of ketone (27), the structure being that shown in Figure 1. It is clear from these results that cross-cyclisation (path A, Scheme 1) is preferred for cations derived by protonation of both mesylates (25) and (26), at least under conditions limiting discharge by external nucleophiles.

Besides validating the cross-cyclisation pathway (A, Scheme 1) the *X*-ray analysis of (30) permits the strain imposed on the carbon skeleton by the cyclisation to be assessed (see Figure 1 and Table 1). Compound (30) contains two norbornane systems fused *endo-exo* at C(7)–C(8) and additionally linked by an *endo* bond from C(1) to bridge-carbon C(2). The C(1)–C(2) bond causes only minor perturbations of the geometry of the chlorinated norbornane system C(2)—C(8) which displays torsion angles within 10° * of those found in norbornane itself,[22] with approximately eclipsed conformations at C(4)–C(5) and C(7)–C(8). In contrast, the second norbornane system [C(1), C(7)—C(12)] is much more seriously perturbed, with a nearly eclipsed conformation at C(1)–C(11) rather than at C(1)–C(12). This permits C(1)C(2)C(3)C(8)C(9)C(12) to adopt a twist-boat conformation [endocyclic torsion angles at C(1)–C(2) and C(8)–C(9) respectively 31 and 28°] and C(1)C(2)C(6)-C(7)C(11) an envelope conformation with an unusually acute endocyclic angle of 92.7(4)° at out-of-plane C(6). Deformations of C–C–C angles to values substantially less than tetrahedral are obvious elsewhere in the molecule, most notably at bridge-carbons C(2) and C(10),

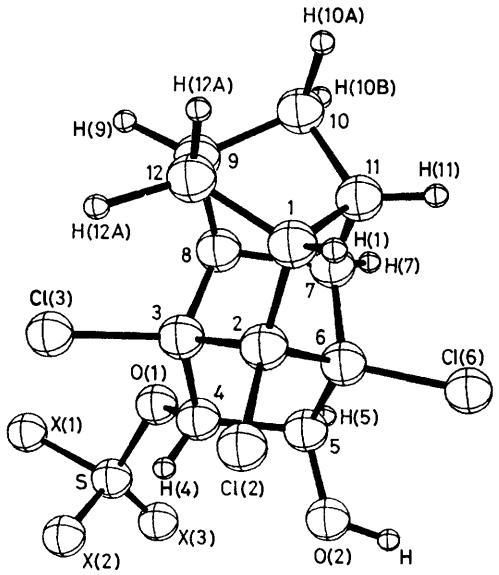


FIGURE 1 A perspective view of (30) showing the atom numbering scheme. For clarity chemical symbols for carbon atoms are omitted. X indicates disordered terminal mesylate C or O atoms. Atoms are represented by spheres of arbitrary size. H(8) is obscured by C(8)

as is the tendency for C–C–Cl angles to be greater than the tetrahedral value. Similar effects have been noticed in molecules with related cage skeletons, *e.g.* in *cis*- and *trans*-photochlordane [23] and in photoaldrin,[24] and they undoubtedly arise from the constraints imposed by ring fusion.

Compound (30) differs from other cyclodiene pesticide derivatives studied crystallographically [23] in that the chlorinated bicyclic system is *exo* rather than *endo* substituted by another ring. The closest parallel appears

* 1° = (π/180) rad.

TABLE 1

Selected distances (Å) and angles (°) in (30)

(*a*) Bond lengths

Cl(2)–C(2)	1.775(5)	C(2)–C(6)	1.535(8)
Cl(3)–C(3)	1.788(5)	C(3)–C(4)	1.531(8)
Cl(6)–C(6)	1.774(5)	C(3)–C(8)	1.521(8)
S–O(1)	1.581(6)	C(4)–C(5)	1.531(8)
S–X(1)	1.68(1)	C(5)–C(6)	1.515(8)
S–X(2)	1.14(1)	C(6)–C(7)	1.540(7)
S–X(3)	1.53(1)	C(7)–C(8)	1.589(7)
O(1)–C(4)	1.422(7)	C(7)–C(11)	1.509(8)
O(2)–C(5)	1.389(8)	C(8)–C(9)	1.559(8)
C(1)–C(2)	1.555(8)	C(9)–C(10)	1.528(9)
C(1)–C(11)	1.572(8)	C(9)–C(12)	1.543(8)
C(1)–C(12)	1.526(8)	C(10)–C(11)	1.541(9)
C(2)–C(3)	1.545(7)		

(*b*) Bond angles

S–O(1)–C(4)	118.7(4)	Cl(6)–C(6)–C(2)	115.2(4)
C(2)–C(1)–C(11)	104.3(4)	Cl(6)–C(6)–C(5)	112.8(4)
C(2)–C(1)–C(12)	108.5(4)	Cl(6)–C(6)–C(7)	113.0(3)
C(11)–C(1)–C(12)	102.8(4)	C(2)–C(6)–C(5)	110.1(4)
Cl(2)–C(2)–C(1)	114.7(4)	C(2)–C(6)–C(7)	92.7(4)
Cl(2)–C(2)–C(3)	113.8(3)	C(5)–C(6)–C(7)	111.5(4)
Cl(2)–C(2)–C(6)	116.8(4)	C(6)–C(7)–C(8)	103.8(4)
C(1)–C(2)–C(3)	111.5(4)	C(6)–C(7)–C(11)	104.6(4)
C(1)–C(2)–C(6)	105.3(4)	C(8)–C(7)–C(11)	98.6(4)
C(3)–C(2)–C(6)	92.4(4)	C(3)–C(8)–C(7)	100.0(4)
Cl(3)–C(3)–C(2)	120.6(4)	C(3)–C(8)–C(9)	113.0(4)
Cl(3)–C(3)–C(4)	106.9(4)	C(7)–C(8)–C(9)	104.9(4)
Cl(3)–C(3)–C(8)	114.4(4)	C(8)–C(9)–C(10)	100.5(4)
C(2)–C(3)–C(4)	103.7(4)	C(8)–C(9)–C(12)	108.0(4)
C(2)–C(3)–C(8)	97.5(4)	C(10)–C(9)–C(12)	99.8(5)
C(4)–C(3)–C(8)	113.4(4)	C(9)–C(10)–C(11)	94.2(5)
O(1)–C(4)–C(3)	110.7(5)	C(1)–C(11)–C(7)	99.0(4)
O(1)–C(4)–C(5)	113.8(5)	C(1)–C(11)–C(10)	106.4(5)
C(3)–C(4)–C(5)	105.1(4)	C(7)–C(11)–C(10)	99.9(4)
O(2)–C(5)–C(4)	107.7(5)	C(1)–C(12)–C(9)	98.1(5)
O(2)–C(5)–C(6)	115.8(5)	O(1)–S–X	102(1)—115(1)
C(4)–C(5)–C(6)	100.7(4)	X–S–X	101(1)—127(1)

(*c*) Torsion angles

C(12)–C(1)–C(2)–C(3)	31.4(6)
C(12)–C(1)–C(11)–C(10)	4.4(6)
C(2)–C(1)–C(12)–C(9)	−79.1(5)
C(1)–C(2)–C(3)–C(8)	40.8(5)
C(1)–C(2)–C(6)–C(7)	−46.2(4)
C(8)–C(3)–C(4)–C(5)	66.0(5)
C(4)–C(3)–C(8)–C(7)	−71.8(5)
C(3)–C(4)–C(5)–C(6)	8.1(5)
C(4)–C(5)–C(6)–C(7)	−75.5(5)
C(5)–C(6)–C(7)–C(8)	68.2(5)
C(6)–C(7)–C(8)–C(3)	4.9(5)
C(8)–C(7)–C(11)–C(1)	60.3(4)
C(3)–C(8)–C(9)–C(12)	27.8(6)
C(12)–C(9)–C(10)–C(11)	58.6(5)
C(9)–C(10)–C(11)–C(7)	64.4(5)
C(1)–C(12)–C(9)–C(8)	46.7(5)
Cl(3)–C(3)–C(4)–O(1)	69.6(5)
O(1)–C(4)–C(5)–O(2)	−108.8(5)
O(2)–C(5)–C(6)–Cl(6)	40.2(6)

to be with photoaldrin [24] which differs from (30) in having a double bond at C(4)–C(5) and perchlorination at C(1) and at C(9)—C(12), rather than at C(2), C(3), and C(6) but which has otherwise an identical carbon skeleton and broadly similar ring conformations.* Skeletal bond lengths in (30) and photoaldrin also show comparable distortions. Thus the longest C–C bonds in both molecules are the eclipsed bonds C(7)–C(8) and C(1)–C(11). Indeed, the latter bond in photoaldrin is one of the longest C–C bonds known [1.620(5) Å], its greater length compared with the corresponding bond in (30) [C(1)–C(11) 1.572(8) Å] reflecting presumably the additional effect of eclipsed chlorine rather than hydrogen atoms. Interestingly, the shortest C–C bond in both molecules is C(7)–C(11) [1.509(8) in (30), 1.514(6) Å in photoaldrin] which connects the two long eclipsed C–C bonds.

The alcohols (23) and (24) are mainly degraded by H_2SO–CCl_4 but both give small amounts of recognisable hydrolysis products, a pentacyclododecanone (34) [$\nu_{max.}$ 1 780vs cm^{-1} with τ 5.38 (CHCl)], an isomer of (29) (8—10% yield), and an aldehyde [$\nu_{max.}$ 1 720 and 1 620 cm^{-1} (CHO, ClC=CCl), τ − 0.28 (CHO)] of currently unknown structure † (17—20% yield) but which may derive by processes unrelated to the cross-cyclisation reaction leading to ketone (34) depicted in Scheme 2.

Scheme 2 also provides support for the observation that hydrolysis of [11-^{2}H]-(24) {and [11-^{2}H]-(23)} in $^2H_2SO_4$–CCl_4 and quenching of the reaction with ^2H_2O (0°) gives crude products showing only a very weak signal attributable to COC^1*H*Cl at τ 5.38 characteristic of ketone (34); silica gel chromatography of this product is as expected [2] accompanied by ^{2}H–^{1}H exchange (COC^{2}HCl ⟶ COC^{1}HCl) and the ketone [10-^{2}H]-(34) exhibits besides this characteristic τ 5.38 signal of unit intensity a broadened n.m.r. singlet at τ 8.4 attributable to the 10-deuteriomethylene group [in contrast to a signal centred on τ 8.60(dd) typical of ketone (34)], as well as other expected changes and generally improved resolution.‡ In this connection it is well known that both *endo*- and *exo*-protons on the adjacent 3-methylene group in the 2-norbornyl cation undergo a rapid 3,2-sigmatropic H^- shift at *ca.* 20°; [25] but enol formation by ^{1}H(^{2}H) loss and subsequent re-addition at C(5) does seem more likely as a source of ketone (34) since this ketone is absent in the product of hydrolysis of dechloroaldrin (1), and its genesis by a 4,5-H^- shift is not therefore important in the precursor ion (A). Similarly, this process can be excluded for the cation precursor of ketone (34), and in fact little evidence can be found for ketone (33) in the crude product mixture from treating the *syn*-alcohol (24) with $^2H_2SO_4$–CCl_4.

The structure of ketone (34) follows from the very close similarity of its n.m.r. and mass spectra to those of ketone (29); in addition, hydride reduction affords virtually stereospecifically alcohol (34a), τ 5.36 (d, *J* 9.75 Hz), and 5.54(q, *J* 9.75 and 4.5 Hz, *cis*-CHCl-CHOH), with the expected changes in the H-7 and -8 chemical shifts. Signals for these protons appear at τ 7.24 and 7.64 respectively in ketone (29) but in alcohol (34a) H-8 is deshielded at τ 7.48; furthermore the H-8 resonance moves slightly but significantly more rapidly to higher field than that due to H-7 in the presence of increasing proportions of Pr(fod)$_3$ shift reagent.

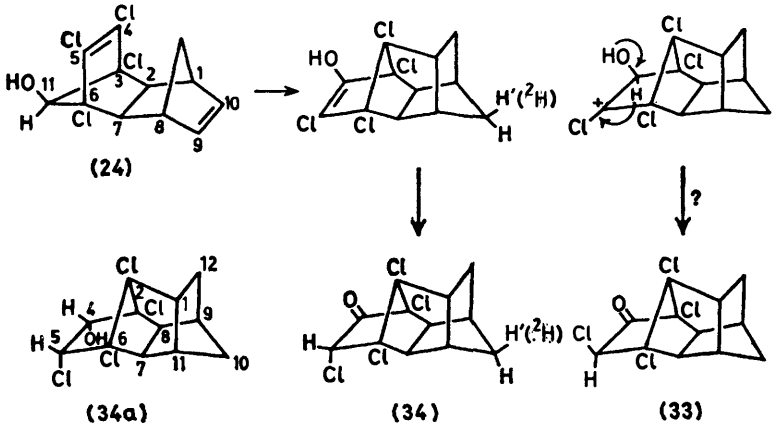
We had earlier found that bisdechloroisodrin (35)

* The numbering system of Figure 1 is used here for photoaldrin in preference to that of ref. 24.

† An *X*-ray crystallographic investigation is in progress; chemistry concerned with the formation of this product will be published later.

‡ Similar changes are seen in the products of treating mesylates (25) and (26) with $^2H_2SO_4$–CCl_4.

parallels the behaviour of its analogue (2) in giving cross-cyclised ketone (36) in protolytic hydrolysis;[26] bisdechloroaldrin (37) gives the same product, identical also with the Zn–HOAc reduction product from ketones afforded by thermolysis of its phencyclone adduct (41) with concomitant 2 H sigmatropic group transfer giving the aromatised compound (43) in analogy to well established examples.[30]

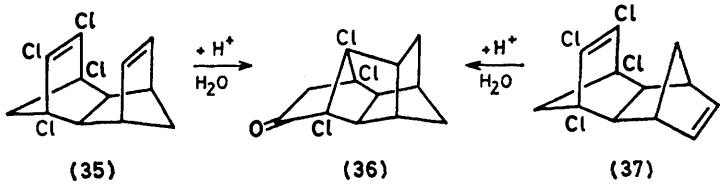


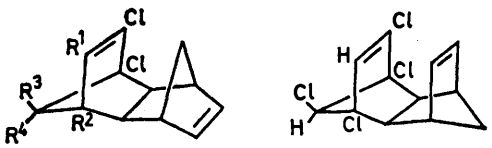
SCHEME 2

(5) and (29) [interestingly, *endo*-chloroketone (29) requires heat for this reaction, the *exo*-chloro analogue (5) being similarly reduced at *ca.* 20°].

In this connexion bisdechloroaldrin (37), whilst accessible (in modest yield) by Zn–HOAc reduction of aldrin,[27] is the principal product (70%) in 1,2,3,4-tetrachlorocyclopentadiene–norbornadiene adduction; the cycloaddition product also contains small amounts of diene dimer and adducts (38)—(40) deriving from

The n.m.r. spectrum of (43) exhibits signals at τ 5.86 and 6.0 (>C*H*Cl and C*H*ClCH_2 bridges) with a signal at τ 7.4—7.5 (CHClCH_2): irradiation of the latter causes signals at τ 5.86 and 6.0 to collapse to broad singlets (part ^4J and all ^3J removed) establishing that both *endo*-ethano-protons are coupled to the chloromethylene bridge proton. Further, mass spectrometry shows that no hydrogen is lost in the thermolysis of adduct (41).

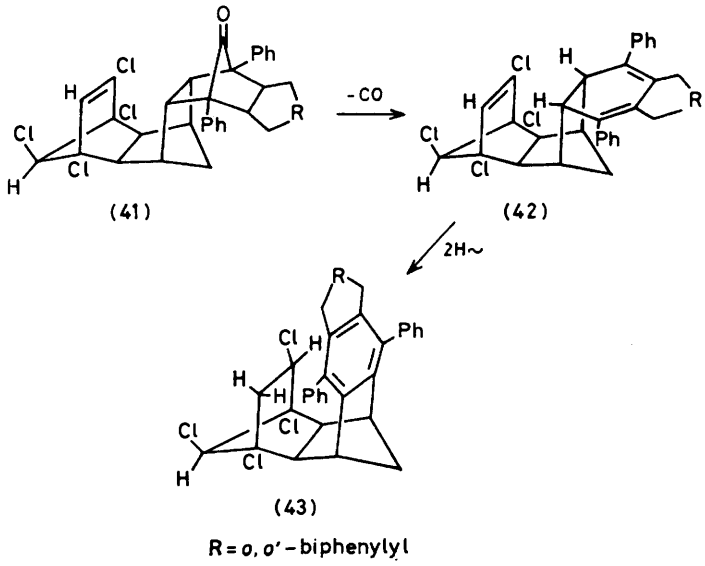




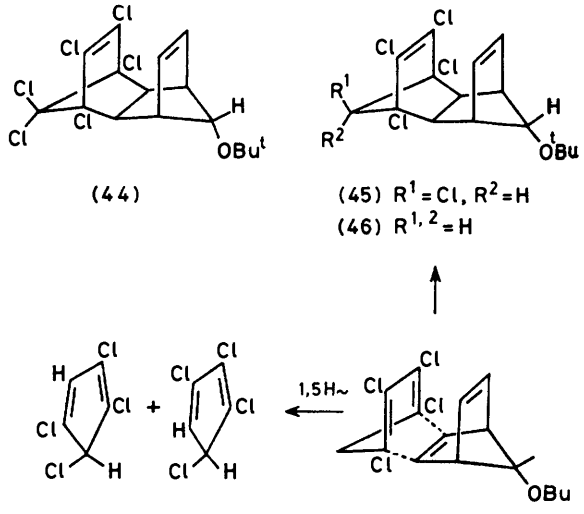
* R^3,R^4 stereochemistry assigned on the 11-H chemical shift; the *syn*-approach of 1,2,3,5-tetrachlorocyclopentadiene is supportable on theoretical grounds.[15b]

successive *thermal* rearrangements of the diene into isomeric 1,2,3,5- and 1,2,4,5-tetrachlorocyclopentadienes before addition. 'Singly' rearranged 1,2,4,5-tetrachlorocyclopentadiene adducts have been observed previously [28] in cycloadditions with 1,2,3,4-tetrachlorocyclopentadiene but consecutive *thermal* rearrangements in the diene prior to adduction, giving here compounds (39) and (40), are rare.[29] Compounds (38)—(40) are characterised mainly by mass and n.m.r. spectrometry, but proof of the stereochemistry in adduct (40) is

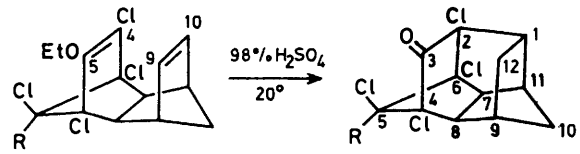
Similar consecutive *thermal* diene rearrangements occur in the higher temperature addition of 1,2,3,4-tetrachlorocyclopentadiene with 7-t-butoxynorbornadiene. Here, apart from various diene dimers, the principal product is the *endo-endo* adduct (46) (24%), identical to one of the products of $LiAlH_4$–THF reduction of compound (44).[31] We and others [31,32] have shown that norbornadien-7-yl ethers and esters give mainly *endo-endo* adducts with electron deficient dienes, and the small amounts of rearranged diene adducts



isolated here, mostly belong to the *endo-endo* series, as Cl positional isomers of adduct (46), analogous to compound (40). Not all the rearranged diene adducts have been fully characterised but their structures can quite clearly be deduced from comparison of mass and n.m.r. spectral data with the principal characterised cycloadducts (see Experimental section).

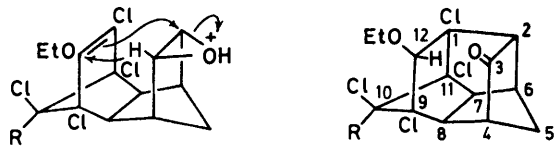


Protolytic hydrolysis of compounds (44) and (45) is discussed below, but first mention should be made of the very specific (98% H_2SO_4) hydrolysis of vinyl ether (47), and its hydride reduction product (49) giving only the products of parallel cyclisation, ketones (48) and (50) (95% isolated yield). [These same ketones are also formed by treating the vinyl ethers (47) and (49) with FSO_3H.] In $^2H_2SO_4$, the analogous *exo*-12-^{2}H-ketones are stereospecifically formed. These results can be understood in qualitative terms in that vinyl ether polarization accounts for kinetically effective *exo*-face protonation only at the sp^2 C(9); this effect is also reflected in the HOAc catalysed thermal cyclisation of the epoxides (13) and (51) with concomitant hydride shift. The role of HOAc in these reactions is to protonate the oxiran ring since the vinyl ethers themselves are stable under these conditions, and epoxide (13) is stable in non-polar solvents at 20°.[8] Simple Hückel MO



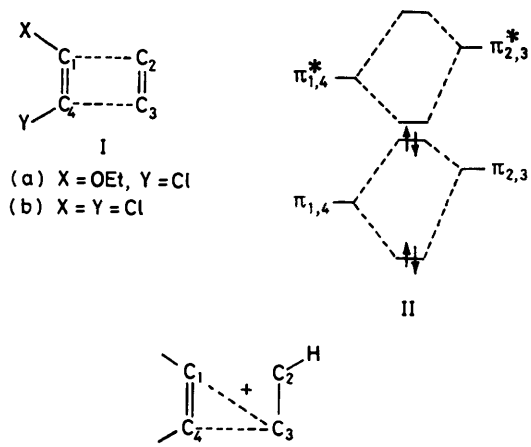
(47) R = Cl
(49) R = H
(48) R = Cl
(50) R = H

calculations correctly predict the outcome of the reaction of ethers (47) and (49) in acidic media. For this purpose it is necessary to consider the orbital interaction pattern of the disubstituted cyclobutadienoid structure in Figure 2. The vinyl substituents may be considered to alter the Coulomb integrals on their respective carbons, the site of proton attack being determined by the HOMO;



(13) R = Cl
(51) R = H
(14) R = Cl
(52) R = H

this is largely $\pi_{2,3}$ ensuring that electrophilic attack occurs here, in sharp contrast to the usual behaviour of vinyl ethers where protonation occurs β to the alkoxylated carbon. Polarization of $\pi_{2,3}$ occurs by mixing in the unsymmetrical $\pi_{1,4}$ orbital, and simple Hückel M.O. calculation indicates C-2 as the site of highest charge density (larger orbital coefficient). The resulting 'cyclopropenoid' structure (Figure 2, III) offers C(1)–C(3) (cross-bonding) and C(4)–C(3) (parallel bonding) modes;



I
(a) X = OEt, Y = Cl
(b) X = Y = Cl

II

III

FIGURE 2

simple Hückel MO calculation indicates that parallel bonding is preferred, as observed.

Rationalization of *cross*-bonding in proximate vinyl-unsubstituted diolefins can be made in terms of molecular mechanics calculations on the assumption that the product development step is rate limiting.[13] On this basis, where the difference in steric energy (ΔSE) of the neutral cross and parallel cyclised products >10 kcal mol^{-1} * the more stable compound is the exclusive

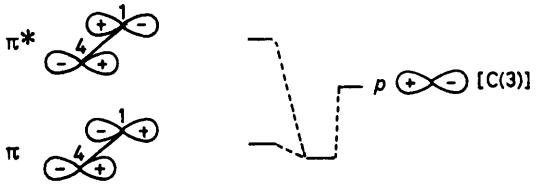


FIGURE 3

product, both types of product form if ΔSE < 10 kcal mol^{-1}. Further insight can be obtained using PMO theory [15] which, whilst taking little cognisance of steric effects, provides a complementary electronic explanation, predicting that parallel or cross cyclisation may occur critically depending on the relative energy ordering of the participating π-bonds and electrophilic reagent. The problem can be simplified by considering the sign of $\pi_{1'4}$* when mixed in with $\pi_{1,4}$ *via* interaction with the pre-formed carbocation centre C(3) (Figure 3). Following Libit and Hoffmann, and Fukui *et al.*,[15] the perturbed $\pi_{1,4}$ to second order is given by equation (1), $C'_{p,\pi}$, $C''_{\pi,\pi}$,

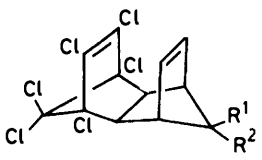
$$\pi_{1,4} = (1 + C''_{\pi,\pi})\pi_{1,4} + C'_{p,\pi^*}p + C''_{p\pi^*,\pi^*}\pi^*_{1,4} \quad (1)$$

and $C''_{\pi^*,\pi}$ being first- and second-order mixing coefficients; $C''_{\pi^*,\pi}$ is given by equation (2). The

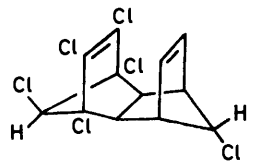
$$C''_{\pi^*,\pi} = \frac{H'_{\pi,p} \cdot H'_{\pi^*,p}}{(E_p^0 - E_{\pi^*}^0)(E_\pi^0 - E_p^0)} \quad (2)$$

numerator is >0, $(E_\pi^0 - E_{\pi^*}^0) < 0$, and hence the sign of $C''_{\pi^*,\pi}$ is determined by $(E_\pi^0 - E_p^0)$. If $E_p > E_\pi$ the mixing coefficient is >0 and the orbital coefficient at C(4) is enhanced by π + π* leading to parallel bonding; if $E_p^0 < E_\pi^0$ the orbital coefficient at C(1) will be enhanced by π − π* and cross bonding will then be favoured, [particularly if skeletal torsion can reduce the C(1)–C(3) distance]. Cross bonding is most likely to occur when $\pi_{1,4}$ is appreciably destabilised and/or the carbocation centre is stabilised. Clearly the effect of adjacent polarized groups not bonded to the π-system may effect the E_p,E_π energy ordering. Whilst we have not yet found the anticipated differentiation between parallel- and cross-cyclisation in cations derived from *anti*- and *syn*-isomeric systems (23),(25) and (24),(26) further work is planned on other appropriately substituted analogues.

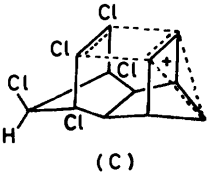
There has been considerable recent interest in the kinetic behaviour in solvolysis reactions of dinitrobenzoates of the non-halogenated tetracyclododecadienol analogous to adduct (46).[33] Our experiments with adducts (44) and (53), and the partially dechlorinated compound (45), show that none of these tetracyclic dienes form stable transannular cyclised products in H_2SO_4–Ac_2O or H_2SO_4–CCl_4 mixtures; in the latter medium diene (45) affords hexachloro-compound (54) (66%); on the other hand, heated in 1% H_2SO_4 in Ac_2O (60°–1.25 h †) compounds (44) and (53) give good yields of the stereoisomeric acetates (55) and (56). Whilst it is possible to conceive that a relatively deep



(44) R^1=H,R^2=OBu^t
(53) R^1=OBu^t,=R^2=H
(55) R^1=H,R^2=OAc
(56) R^1=OAc,R^2=H
(57) R^1=OH,R^2=H



(54)



(C)

potential delocalized cation such as (C) could account for the stereospecific formation of the hexachloro-compound (54) (the source of Cl^- being partial substrate decomposition), and the same ion could possibly account for acetate (55), such an intermediate cannot be the precursor of acetate (56); here elimination of isobutene to give alcohol (57) as the source of acetate (56) seems more likely and receives support from the isolation of alcohol (57) (>90%) when compound (53) is heated in 5% H_2SO_4 in 25% aqueous dioxan. It actually seems more likely in these conditions that a similar mechanism accounts for production of acetate (55).‡ If so, only the monodechloro-compound (45) convincingly reacts *via* delocalized cation (C), and whilst more information is required it may be that in the absence of the δ+C–Clδ— dipole associated with an *anti*-bridge methylene chlorine atom which perturbs the adjacent π-system, ion (C) becomes accessible. The non-chlorinated equivalent of cation (C) is implicated in one of the largest kinetic exaltation effects known,[34] and is therefore also unusually stable. This may well explain why compound (45) fails to yield significant amounts of cyclised products in H_2SO_4.

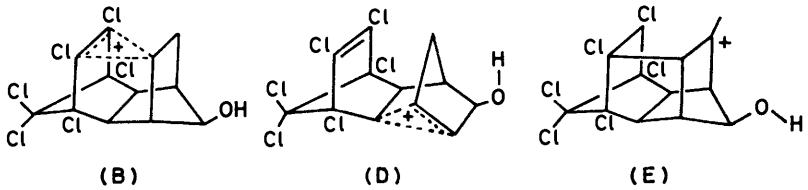
These observations are also significant in relation to the protolytic rearrangement of dieldrin (9) *via* cation (B).[6] Two pointers to mechanism and reactivity here are (i) alcohol (57) clearly does not give ion (B) [or (C)] under similar acidic conditions to those causing rearrangement in dieldrin (9) and (ii) 9,10-dihydroaldrin-

* 1 cal = 4.184 J.

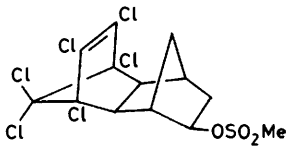
† 1 h = 60 min = 3 600 s.

‡ Unfortunately hexachloro compounds (44) and (53) are extensively decomposed in H_2SO_4.

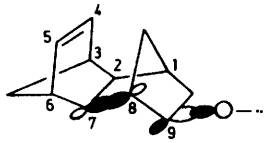
exo-9-yl methanesulphonate (58) is inefficient as a source of rearranged cations in solvolysis reactions,[5] strongly contrasting with the non-chlorinated systems where extensive rearrangement occurs.[3] For the latter compounds, *anti*-periplanar C(7)–C(8) σ participation is implicated [see structure (F)]; [33] interaction of C(7)–C(8) σ with $\pi_{4,5}$ raises its energy enabling better σ delocalization into the C(9)–O σ* orbital of the attached sulphonate group whose departure is consequently accompanied by rearrangement ultimately involving cyclisation onto $\pi_{4,5}$. In the chlorinated system (58) the π-orbital energy is reduced; attenuated C(7)–C(8) σ–π interaction with concomitantly reduced C(7)–C(8) σ–C(9)–O σ* delocalization leads to a lower reactivity and less cyclisation onto $\pi_{4,5}$. Similar considerations apply to *exo*-oxiran (9) [where *anti*-periplanar C(7)–C(8) σ–C(9)–O σ* delocalization is possible in the protonated oxiran leading to ions (D), (B), and (E)]; in *endo*-isomer (59) in which C(7)–C(8) σ delocalization is sterically unfavourable, an external nucleophile is required following protonation to cause oxiran ring opening. Consequently treatment of *endo*-oxiran (59) with BF_3–MeOH gives almost entirely unrearranged product, *trans*-diol monomethyl ether (60).



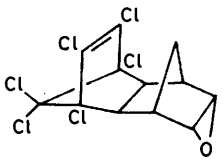
(B) (D) (E)



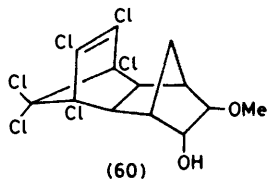
(58)



(F)



(59)



(60)

Note on Nomenclature.—Systematic naming of ketones (5), (29), and (34) and their derivatives is cumbersome and confusing in rigid formalism [see for example ketones (50) and (52)]. To facilitate location of methine protons in discussing n.m.r. data, we have used the simplest method within the convention connecting the minimum number of *continuous* rings to common bridgeheads, using the basic molecular framework numbering throughout, irrespective of functional group position. Cations shown as delocalized are not necessarily intended to imply non-classical ions, but to indicate alternative loci in bond formation or bond switching processes.

EXPERIMENTAL

N.m.r. data were obtained with Varian HA100 and JEOL PS100 spectrometers for solutions in $CDCl_3$ with tetramethylsilane as internal standard all signals having the correct relative intensities. Mass spectra refer to data from a G.E.C.–A.E.I. MS902 double focusing instrument with VG Micromass facility; halogenated ions had the correct ^{35}Cl : ^{37}Cl abundance ratios in the characteristic ion clusters. I.r. spectra were recorded on PE257 or PE197 instruments for solutions in CH_2Cl_2 or CCl_4. Chromatography refers to preparative t.l.c. on 0.8 mm silica gel GF_{254} coated plates visualised under a fluoroscope. Petroleum refers to the b.p. 60—80° fraction. Concentrated H_2SO_4 is 98% H_2SO_4–H_2O; ^2H_2SO is 99.8% isotopically pure. Simple Hückel calculations were by ICL 4-50 computer (K.B.A.)

Reduction of Bridge-carbonyl Compound (22) *to give Alcohols* (23), (24).—The carbonyl compound, prepared as previously described [19] (45 g, 96 mmol) was dried *in vacuo* at 45—55° (1—2 h), ground to a fine powder and suspended in ether (800 ml).* $LiAlH_4$ (2.0 g, 52 mmol) was added in two portions during 0.75 h to the stirred chilled (0°) solution under N_2, the solution clearing; after stirring for a further 1 h the mixture was cautiously quenched with water (2 ml), and after addition of further water (50 ml) and concentrated hydrochloric acid, the ether layer was separated, brine-washed, and dried (Na_2SO_4). The ether solution was evaporated, the residue dissolved in ethanol (100 ml) and a little insoluble matter filtered off, zinc powder (20 g) added, and the mixture stirred during 1 h, the temperature rising to 53°. Stirring was continued overnight under N_2, the mixture filtered, and the filtrate evaporated; the residual oil was dissolved in ether, the solution washed, dried, and evaporated in the usual way to give a clear oil (30 g, 98%) which solidified on scratching. Numerous small portions of the crude product were resolved by preparative t.l.c. (3 : 1 CCl_4–Et_2O) into 3,4,5,6-*tetrachlorotetracyclo*-[6.2.1.1.^{3,6}0^{2,7}]*dodeca*-4,9-*dien*-anti-11-*ol* (23), m.p. 109—110° (petroleum), $\nu_{max.}$ 3 610, 3 450, 1 140vs (non-bonded and bonded OH), and 1 585 cm^{-1} (ClC=CCl), τ 3.73 (nm,† H-9, -10) 6.09(d), and 6.94(d) (*J* 3 Hz, H-11 and OH), 7.19 (nm, H-1, -8), 7.31(s, H-2, -7), and 8.43 and 8.65 (each dnm *J ca.* 10 Hz H-12, -12), *m/e* 310 ($M^{+\cdot}$) and 275 (M – $Cl^{+\cdot}$) (both v weak), 244 ($C_7H_4Cl_4O^{+\cdot}$, RDA‡ cyclo reversion fragment, 209 (RDA – Cl), and 66 ($C_5H_6^{+\cdot}$ RDA, base peak) (Found: C, 46.35; H, 3.25. $C_{12}H_{10}Cl_4O$ requires C, 46.2; H, 3.25%). The slower running component gave as major product the syn-11-*ol isomer* of the above compound, (24), m.p. 137—138.5° (petrol) $\nu_{max.}$ 3 600, 3 560, 1 150 (intramolecularly bonded OH?), and 1 590 cm^{-1} (ClC=CCl),

* 1 l = 10^{-3} m^3.
† n = narrow
‡ RDA = retro Diels-Alder

τ 3.71 (nm, H-9, -10) 5.91(d) and 7.35(d) (*J* 11 Hz, H-11 and OH), 7.08 (nm, H-1, -8), 7.59(s, H-2, -7), and 8.52 and 8.74 (both dnm, *J* 10 Hz H-12, -12), *m/e* as for alcohol (23) (Found: C, 46.0; H, 3.4%) [Ratio (24) : (23), 2.2].

Preparative t.l.c. (3 : 1 CCl_4–Et_2O) of a small sample of the crude dibromo-alcohol mixture prior to debromination gave the *trans*-dibromo adducts of *anti*-alcohol (23) [τ 5.56(t, *exo*-9-H), 6.26 (overlapping s and t, *endo*-10-H and H-11), 6.66(d) and 7.36(d) (*J* 8 Hz H-7, -2), 7.39(s, H-1, -8), 8.20 and 7.47 (each d, *J ca.* 14 Hz H-12, -12)] and of alcohol (24) [τ 5.65(t, *exo*-9-H), 5.86(s, H-11), 6.31(t, *endo*-10-H), 6.85 and 7.56 (each d, *J* 8 Hz H-7, -2), and 8.17 and 8.43 (each dnm, *J ca.* 14 Hz, H-12, -12)].

Methylation of Alcohols (23), (24).—Small samples (*e.g.* 86 mg, 0.27 mmol) of each alcohol, treated in dioxan at 25° with sodium hydride (10 mg, 0.42 mmol) and the derived alkoxide solutions stirred overnight at 20° with several-fold excess of methyl iodide (2 ml) gave from alcohol (23), 3,4,5,6-*tetrachloro*-11-anti-*methoxytetracyclo*[6.2.1.$1^{3,6}$.$0^{2,7}$]-*dodeca*-4,9-*diene*, m.p. 89—90° (petroleum), τ 3.74 (nm, H-9, -10), 6.42(s, H-11), 6.31(s, OMe), 7.21 (nm, H-1, -8), 7.34(s, H-2, -7), and 8.46 and 8.69 (each dnm *J ca.* 10 Hz, H-12, -12), *m/e* 223 (RDA-$Cl^{+\bullet}$) and 66 ($C_5H_6^{+\bullet}$, base peak) (Found: C, 48.1; H, 3.75. $C_{13}H_{12}Cl_4O$ requires C, 47.9; H, 3.7%) and from alcohol (24) the 11-syn-*methoxy-isomer* of the above ether, m.p. 121—122.5° (petroleum), τ 3.76(nm, H-9, -10), 6.22(s, H-11), 6.37(s, OMe), 7.12 (nm, H-1, -8), 7.61(s, H-2, -7), and 8.52 and 8.77 (each dnm, *J ca.* 10 Hz, H-12, -12), *m/e* identical to that of the 11-*anti*-methoxy-compound (Found: C, 47.85; H, 3.95%). In similar preparations, heating the solutions resulted in decomposition of the sodium salt of alcohol (24), but a good yield of methyl ether was obtained from alcohol (23).

Preparation of Mesylates (25) *and* (26).—Alcohol (24) (310 mg, 1 mmol) in pyridine (5 ml) treated with methanesulphonyl chloride (137 mg, 20% excess) during 2 h, quenching with water, and filtration of the solid product gave the *mesylate* (26) (401 mg, 94%), m.p. 162—163° (CCl_4), τ 3.73(nm, H-9, -10), 5.10(s, H-11), 6.83(s, OSO_2-Me), 7.05(nm, H-1, -8), 7.53 (H-2, -7), and 8.52 and 8.72 (each dnm, *J* 10.5 Hz, H-12, -12) (Found: C, 39.8; H, 3.25. $C_{13}H_{12}Cl_4SO_3$ requires C, 40.0; H, 3.1%). In a similar experiment with alcohol (23) little evidence of reaction was visible and after warming for 1 h alcohol (50%) was recovered unchanged; standing a similar mixture of the reactants for several days at 25° however gave a good yield (>90%) of the *mesylate* (25), m.p. 129—130° (CCl_4), τ 3.70(nm, H-9, -10), 5.19(s, H-11), 6.80(s, OSO_2Me), 7.15(nm, H-1, -8), 7.30(s, H-2, -7), and 8.44 and 8.62 (each dnm, *J ca.* 10 Hz H-12, -12) (Found: C, 39.95; H, 3.1%).

Heating either of the mesylates (25) and (26) with (a) 4% LiCl in acetone at 110°–45 h, (b) 20% LiCl in dimethyl sulphoxide at 110—120°–72 h, or (c) 10% $ZnCl_2$ in dimethoxyethane at 150°–72 h effected any significant chlorine incorporation.

Protolytic Hydrolysis of Mesylates (25) *and* (26).—In a typical experiment *syn*-mesylate (26) (100 mg) dissolved in CCl_4 (5 ml) was stirred with concentrated H_2SO_4 (5 ml) for 24 h. Hydrogen chloride was evolved as the mixture was quenched in ice, and extraction (CH_2Cl_2) then washing, drying, and evaporation of the extracts gave after chromatography (3 : 1 CCl_4 : Et_2O) and crystallisation, 2,3,6-*trichloro*-5-*oxopentacyclo*[7.2.1.0.^{2,6}0^{3,8}.0^{7,11}]*dodecan*-exo-4-*yl* *methanesulphonate* (28; R = $MeSO_2$) (31 mg, 32%), m.p. 238—240° ($CHCl_3$, rather insoluble), $\nu_{max.}$ 1 779vs, 1 170, and 1 370vs cm^{-1} (strained ring CO and $MeSO_2O$), τ 5.26(s, H-4), 6.80(s, OSO_2Me), *ca.* 6.8br (m, obscured, H-11), 7.01(dm, ^2J 12.7 Hz, H-12-*endo*), 7.24(cm, H-9), 7.38—7.62(cm, overlapping H-1, -7, -8), 8.47br (m, H-10, -10), and 8.75(q, ^2J 12.7, ^3J *ca.* 6 Hz, H-12-*exo*), *m/e* 370 ($M^{+\bullet}$), 335 ($M - Cl^{+\bullet}$), 291 ($M - SO_2Me^{+\bullet}$) (Found: *m/e*, 369.962. $C_{13}H_{13}{}^{35}Cl_3SO_4$ requires *M*, 369.959) Found: *m/e*, 371, 957. $C_{13}H_{13}{}^{35}Cl_2{}^{37}ClSO_4$ requires *M*, 371.957) [*cf.* compound (27)].

In a similar experiment, mesylate (25) (300 mg) afforded after work-up, chromatography and crystallisation (CCl_4) of crude endo-4-*mesyloxy-isomer* (27) (81 mg, 28%), m.p. 136—137°, $\nu_{max.}$ 1 781vs, 1 177, and 1 370vs cm^{-1} (strained ring CO and OSO_2Me), τ 4.85(s, H-4), 6.73(s, OSO_2Me), 6.75br(m, H-11), 7.00(dm, ^2J *ca.* 13 Hz, H-12-*endo*), 7.15(dd, *J* 7 and 5 Hz) and 7.56(dq, *J ca.* 7.3 and 1.5 Hz) (H-8 and -7), 8.48(dd *J ca.* 9 Hz, H-10, -10), 8.76(qnm, *J ca.* 13 and 7 Hz, H-12-*exo*), 7.26—7.37(m, overlapping H-1, -9), *m/e* 370 ($M^{+\bullet}$), 335 ($M - Cl^{+\bullet}$), and 291 ($M - SO_2Me^{+\bullet}$) and similar to compound (28). (Found: C, 42.0; H, 3.6. $C_{13}H_{13}Cl_3SO_4$ requires C, 42.0; H, 3.5%). N.m.r. monitoring of solutions of *syn*-mesylate (26) in concentrated $^1H_2SO_4$ (and $^2H_2SO_4$) indicated that ketone (28) appeared after 0.5 h and substrate was largely converted after 25 h at 20°.

Stereomutation of Mesyloxy-ketone (28) *into Isomer* (27).—Samples of the ketones (27) and (28) (each *ca.* 20 mg) were heated in pyridine (5 ml) at 90—100° for 3 h and the product isolated by evaporation *in vacuo*; ketone (27) was recovered unchanged, but i.r. spectral comparison and co-crystallisation clearly indicated the product from ketone (28) was ketone (27).

Reaction of Mesylate (26) *with* $^2H_2SO_4$.—In similar experiments to those above, hydrolysis of mesylate (26) in concentrated $^2H_2SO_4$–CCl_4 gave the 10-*deuterio-analogue* of compound (28) with the expected changes in the n.m.r. spectrum: increased resolution at τ 6.99 and 7.22 (H-12-*endo* and H-9), the signal near 8.5 (H-10, -10) collapsing to a broad singlet, and slight changes at τ 7.35—7.62 (H-1, -7, -8), and 8.75 (H-12-*exo*).

Reduction of Compound (27).—The mesyloxy-ketone (27) (160 mg, 0.43 mmol) was stirred in dry Et_2O (*ca.* 30 ml) with $LiAlH_4$ (80 mg, 2.1 mmol) for 1 h at 25° and the product isolated as usual giving 2,3,6-*trichloro*-endo-4-*hydroxypentacyclo*[7.2.1.0.^{2,6}0^{3,8}.0^{7,11}]*dodecan*-exo-5-*yl* *methanesulphonate* (30) (80 mg, *ca.* 50%), m.p. 184—185° (CCl_4), raised to 191—192.5° by slow recrystallisation (*X*-ray sample), τ 5.01(d, *J* 2.25 Hz, H-4), 5.90(q *J* 2.25 and 3.75 Hz, H-5), 6.82(s, OSO_2Me), 6.91br (m, H-11), 7.15(nm, H-12-*endo*), 7.26(t of m, H-8), 7.69(dq, H-7), 8.58(dd, H-10, -10), 8.85(qnm, *J* 12.7, 6.7 Hz, H-12-*exo*), and 7.21—7.24 (overlapping m, H-1, -9), *m/e* 372 ($M^{+\bullet}$), 337 ($M - Cl^{+\bullet}$), 301 ($M - HCl_2^{+\bullet}$), and 276 ($M - CH_3SO_3H$) (Found: C, 42.0; H, 4.15. $C_{13}H_{15}Cl_3SO_4$ requires C, 41.8; H, 4.05%).

Boiling the monomesylate (30) in pyridine overnight failed to remove methanesulphonic acid, the substrate being largely recovered.

Reduction of Ketone (28) *with* $LiAlH_4$–THF.—Reduction of ketone (28) (35 mg, 0.1 mmol) with $LiAlH_4$ (35 mg, 0.9 mmol) in THF (*ca.* 8 ml) at 25° for 3 h followed by the usual work-up gave a product (21 mg, *ca.* 0%) exhibiting τ 5.83(d) and 6.10(d) (*J* 7.5 Hz, *cis*-CHOH·CHOH) (with no signals characteristic of $MeSO_2O$). This product adhered strongly to silica gel and was not further characterised.

Attempted Reduction of Ketone (28) *with Iodide Ion*.—When ketone (28) (65 mg) was heated with sodium iodide

(500 mg) in 5% acetic anhydride in acetic acid (5 ml) at 150—160° and 20 h, substrate was recovered unchanged. At 160—190° and 48 h slight charring occurred; the product containing traces of acetate (?) ($\nu_{max.}$ 1 760 cm^{-1}) was mainly ketone (28). Other nucleophilic displacement experiments gave only very poor yields of possible substitution products.

Protolytic Hydrolysis of Alcohols (23) *and* (24).—In a typical experiment alcohol (24) (200 mg, 64 mmol) was stirred in 20% CH_2Cl_2 in CCl_4 with concentrated H_2SO_4 (5 ml) for 17 h at 25°; chromatography (3 : 1 CCl_4–Et_2O) of the crude product (98 mg, *ca.* 50%) gave besides five minor components (each >1 mg) two main products, (a) 2,3-endo-5,6-*tetrachloropentacyclo*[7.2.1.0.^{2,6}0^{3,8}.0^{7,11}]*dodecan*-4-*one* (34) (16 mg, 9%), m.p. 89—91° (CCl_4), $\nu_{max.}$ 1 780vs cm^{-1}, τ 5.38(s, H-5), 6.80br (m, H-11), 7.04(dt, H-12-*endo*), 7.64(tm, H-8), 7.24(dm, H-7), 8.40(dd, H-10, -10′), 8.70(qnm, ^2J 12.75, ^3J 6.75 Hz, H-12-*exo*), and 7.10—7.30 (cm, H-1, -9), and closely similar to ketone (29), *m/e* 310 ($M^{+\cdot}$), 275 ($M - Cl^{+\cdot}$), and 247 ($M - CO - Cl^{+\cdot}$) and very similar to ketone (29) (Found: *m/e*, 309.949. $C_{12}H_{10}{}^{35}Cl_4O$ requires *M*, 309.948). Reduction of ketone (34) ($LiAlH_4$–Et_2O) gave mainly one product of *exo*-hydride transfer, alcohol (34a) [τ 5.37(d, *J* 9.75 Hz, H-5-*exo*) and 5.57(q, *J* 9.75 and 4.5 Hz, H-4-*exo* (*cis*-CHCl·CHOH)]. Monitoring changes in the spectrum [20 mg (34)–OH–0.5 ml $CDCl_3$] with increasing concentrations of $Pr(fod)_3$ shift reagent indicated that H-8 changed slightly more rapidly than H-7 [$Pr(fod)_3$ (mg), τ (H-7), τ (H-8): O, obscure, 7.48; 10, 7.70, 7.88; 15, 7.86, 8.12; 20, 7.92, 8.25]; the alcohol was converted to the *mesylate* (34)-OMs, m.p. 124—124.5° (CCl_4), $\nu_{max.}$ 1 380 and 1 183vs cm^{-1} (OSO_2Me), τ 4.82(d) and 5.39(d) (*J* 10.1 Hz, H-5 and -4), 6.79(s, OSO_2Me), 6.96br (m, H-11), 7.12(dt, *J* 12.7 Hz, H-12-*endo*), 7.20—7.50(cm, H-1, -7, -8, -9), 8.60(dd, *J* 10.5 Hz, H-10, -10′), and 8.84(qnm, *J* 12.7 and *ca.* 6 Hz, H-12-*exo*), *m/e* 390 ($M^{+\cdot}$), 355 ($M - Cl^{+\cdot}$), and 294 ($M - CH_3SO_3H^{+\cdot}$) (Found: C, 39.6; H, 3.6. $C_{13}H_{14}Cl_4SO_3$ requires C, 39.8; H, 3.6%). The second hydrolysis product (b) was an *aldehyde* (35 mg, 17.5%), m.p. 140°, $\nu_{max.}$ 1 720vs and 1 620ms cm^{-1} (CHO and ClC=C), τ −0.28[s, (d at 220 MHz), CHO], 5.64(s), 6.04(dt), 7.08(qnm), 7.32(td), 7.61(m), 7.79(t), 7.88(d), and 8.02br(m), *m/e* 310 ($M^{+\cdot}$), 281 ($M - CHO^{+\cdot}$), and 113 ($C_6H_6Cl^{+\cdot}$), characterised as its monodeuterio-derivative prepared as above with alcohol [11-^{2}H]-(24) [τ −0.28(s) absent, *m/e* 311, 281, and 113] (Found: C, 46.3; H, 3.25. $C_{12}{}^1H_9{}^2HCl_4O$ requires C, 46.05; H, 3.55%). Numerous experiments with and without organic solvent gave similar results as did experiments with alcohol (23).

Hydrolysis of alcohol [11-$^2H_2$]-(24) (made and purified as on p. 119 using $LiAl^2H_4$) in concentrated $^2H_2SO_4$–CCl_4–CH_2Cl_2 as above and quenching in ^2H_2O (0°) gave a product with τ 8.4br (s, ^{1}H-10, ^{2}H-10′) [rather than 8.4(dd) as in ketone (34)] and a very weak signal at τ 5.38 characteristic of ketone (34) (*exo*-^{2}H-5) [*cf.* ketones (5) and (29), τ 5.75 and 5.44 respectively for *endo*- and *exo*-H-4)]. Silica gel chromatography of this product gave ketone [10-^{2}H]-(34) and aldehyde fractions.

Similarly at higher substrate : acid ratios alcohols (23) and (24) gave dimeric, polymeric, and other compounds.

Preparation of Bisdechloroaldrin (37).—Tetrachlorocyclopentadiene [35] [sublimed *in vacuo*, m.p. 63°, τ 6.61(s), no evidence of isomers] (4.91 g, 24 mmol) was boiled in excess of norbornadiene (50 ml) for 4 h, the dienophile stripped off *in vacuo*, and the residue diluted with petroleum. Diene dimer [35] crystallised and was separated; the filtrate was concentrated and the residue chromatographed (CCl_4) to give two main fractions. Fraction (1) (4.99 g, 69%) was almost entirely *endo,exo*-3,4,5,6-tetrachlorotetracyclo-[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-diene (37) rechromatography yielding the slowly crystallising pure (thermally unstable) compound, m.p. *ca.* 50° (lit.,[27] 48—49°) [τ 3.74(m, H-9, -10), 7.20(m, H-1, -8), 7.35(m, H-2, -7), 7.39(dd, *J ca.* 7.5 Hz, H-12, -12), and 8.59(ddm, *J ca.* 10 Hz, H-11, -11), *m/e* 294 ($M^{+\cdot}$), 259 ($M - Cl^{+\cdot}$), and 228 ($M - C_6H_6{}^{+\cdot}$ RDA base peak)]. Decarbonylated adduct with tetracyclone identical to that made [36] from bisdechloroaldrin,[27] m.p. and mixed m.p. 291°. Fraction (2) (303 mg, *ca.* 4%) contained rearranged isomeric adducts (38)—(40) (and dimeric product) which were isolated after extensive chromatography) (CCl_4 and hexane) as oils: endo,exo-3,4,5-anti-11-*tetrachlorotetracyclo*[6.2.1.1^{3,6}.0^{2,7}]*dodeca*-4,9-*diene* (38), *m/e* 294 ($M^{+\cdot}$) and other fragments similar to (37), τ 3.76 (nm, H-9, -10), 5.90(nd) and 6.93(nm) (*syn*-H-11 and H-6, ^4J 1—1.5 Hz), 7.15(nm) and 7.26(nm) (H-2 and -7), 7.70(nm, (H-1, -8), and 8.31 and 8.52 (each dnm, ^2J *ca.* 9 Hz, H-12, -12); endo,exo-3,4,6-syn-11-*tetrachlorotetracyclo*[6.2.1.1^{3,6}.-0^{2,7}]*dodeca*-4,9-*diene* (39), *m/e* similar to (38), 294 ($M^{+\cdot}$) (Found: *m/e*, 295.950. $C_{12}H_{10}{}^{35}Cl_3{}^{37}Cl$ requires *M*, 295.950), τ 3.72(nm, H-9, -10), 4.24(nd) and 5.72(nd) (*J ca.* 1.5 Hz, H-5 and *anti*-H-11), 7.02br (m, H-1, -8), 7.47(nd, H-2, -7), 7.86 and 8.73 (each dnm, *J* 10.5 Hz, H-12, -12); and (40) the endo,endo-*isomer* of (39), *m/e* 294 ($M^{+\cdot}$) and similar to (38) and (39); τ 4.02 and 4.30 (each m, H-10, -9), 4.66 and 5.72 (each nd, ^4J 1—1.5 Hz, H-5 and *anti*-H-11), 6.92(s, H-2, -7), 7.02br (m, H-1, -8), 8.31 and 8.52 (each dnm, *J ca.* 9 Hz, H-12, -12) [ratio (38) : (39) : (40) variable with conditions but *e.g.* here *ca.* 3 : 2 : 1].

Characterisation of Adduct (40) *by Phencyclone Adduction and Decarbonylation.*—Adduct (40) (18 mg, 0.12 mmol) was heated with phencyclone (17 mg, 0.05 mmol) in chlorobenzene (3 ml) for 8 h under N_2, the solvent evaporated (N_2), and the crude product chromatographed (4 : 1 CCl_4–Et_2O) giving the *adduct* (41) (16 mg, 40%), m.p. 245° (vigorous decomp.), τ 1.28(d) and 2.24—3.0(cm) (ArH), 3.74(nm) and 5.66(nm) (=CH and >CHCl), 6.50 and 6.78 (each dnm, *J* 9 Hz, bridge CH_2), and 6.97(dnm, *J* 7.5 Hz) overlapping 7.07br and 7.16br (*endo*- and *exo*-ring junction and bridgehead). The crystalline adduct was heated for *ca.* 5 min at 245° (effervescence), cooled and the glassy product extracted into $CDCl_3$, τ 1.56(d) and 2.20—3.06(cm) (ArH), 5.86(nm) and 6.00(cm) (chloromethano- and chloroethano-bridges), 6.22br (m, bridgehead), 6.87br (m, ring junction), 7.43—7.50 (overlapping ms, ethano-bridge CH_2), and 7.80 and 8.21 (each dnm, bridge CH_2).

Decoupling Experiment.—Irradiation at τ 7.55 caused signals at τ 5.86—6.00 (>C*H*Cl, –CH_2C*H*Cl–) to collapse to a broad singlet; irradiation at τ 5.98 caused signals at τ 7.43—7.50 (–CH_2CHCl–) to collapse to doublet of multiplets; irradiation at τ 7.55 also caused τ 6.87(m, ring junction) to narrow. Recrystallised from CCl_4–petroleum *compound* (43) (*ca.* 10 mg) had m.p. 285—287°, *m/e* 648 ($M^{+\cdot}$) and 418 ($C_{33}H_{22}{}^{+\cdot}$, $M - C_7H_6Cl_4$, pseudo RDA cycloreversion) (Found: *m/e*, 648.091. $C_{40}H_{28}{}^{35}Cl_4$ requires *M*, 648.094. Found: *m/e*, 650.089. $C_{40}H_{28}{}^{35}Cl_3{}^{37}Cl$ requires *M*, 650.088).

Hydrolysis of Bisdechloroaldrin (37).—Adduct (37) (1.0 g, 3 mmol) was hydrolysed in concentrated H_2SO_4 [as for *e.g.* (25), (26)] giving crude product (630 mg, 63% recovery). Chromatography 3 : 1 CCl_4–Et_2O gave two main fractions (and three minor products), 2,3,6-*trichloropentacyclo*-

[7.2.1.0.^{2,6}0^{3,8}.0^{7,11}]*dodecan-5-one* (36) (211 mg, 22%), m.p. 183—184.5° (CCl_4), $\nu_{max.}$ 1 770vs cm^{-1}, τ 6.81br (m, H-11), centred at 7.19(qm, H-4, -4), 7.01(dt, *endo*-H-12), *ca.* 7.5 (obscured m), 7.6(dt, (H-8, -7), 8.39 and 8.58 (each dm, J *ca.* 11.2 Hz, H-10, 10′), 8.79(q, ^2J 12.5, ^3J *ca.* 6.0 Hz, *exo*-12-H), and 7.0—7.43(m, (H-1, -9). In $(C^2H_3)_2CO$, signals due to H-4, -4 move closer together (Δν inner signals 2 Hz compared with 9 Hz in $CDCl_3$); n.m.r. spectrum identical to that of the product of hydrolysis of bisdechloroisodrin,[26] *m/e* 276 ($M^{+\cdot}$), 248 (M − $CO^{+\cdot}$), and 241 (M − $Cl^{+\cdot}$, 100%) (Found: C, 51.65; H, 4.1. $C_{12}H_{11}Cl_3O$ requires C, 51.9; H, 4.0%). Rechromatography of the second smaller fraction gave a product (15 mg), m.p. 136—139°, *m/e* 330 ($C_{12}H_{11}Cl_5$), probably the HCl adduct of (37).

Zinc–HOAc Reduction of exo-*Chloro-ketone* (5) *and* endo-*Chloro-ketone* (29).—Ketone (5) (150 mg, 0.5 mmol) was stirred overnight with zinc dust (135 mg) in acetic acid (5 ml) at 25°; work-up by addition of water and extraction (CH_2Cl_2), after washing, drying, evaporation, and crystallisation (CCl_4), gave ketone (36) (118 mg, 88%), m.p. and mixed m.p. 183—185°. In a similar reaction with ketone (29), unchanged reactant was recovered, but heating a similar reaction mixture at reflux temperature for 2 h gave ketone (36) (94%).

Reductive Dechlorination of Vinyl Ether (47) *with* $LiAlH_4$.—Ethoxypentachloro-compound (47) (prepared as previously described [8]) (300 mg, 0.8 mmol) was stirred for 45 h with $LiAlH_4$ (100 mg, 2.6 mmol) in tetrahydrofuran (15 ml) under N_2 at the boiling point. Work-up in the usual way, then chromatography (2 : 1 petroleum–CH_2Cl_2) recovered (47) (41 mg) and an oily *monodechloro-compound* (49) (111 mg, 41%), $\nu_{max.}$ 2 860ms, 1 640vs, and 1 600m cm^{-1} (ClC=COEt), τ 3.77br and 4.1br (both m, H-9, -10), 5.61(q) and 8.64(t) (OEt), 5.66(s) (H-11), 6.98br (s, H-2, -7 and H-1, -8), and 8.39 (qm, H-12, -12), *m/e* 338 ($M^{+\cdot}$), 310 (M − $C_2H_4^{+\cdot}$), and 275 (M − Cl − $C_2H_4^{+\cdot}$) (Found: *m/e*, 337.979. $C_{14}H_{14}{}^{35}Cl_4O$ requires *M*, 337.979).

Vinyl ether (49) treated with AcOH–AcO_2H as for compound (47) [8] gave 1,9-syn-10,11-*tetrachloro*-12-*ethoxypentacyclo*[7.2.1.0.^{2,6}0^{4,8}.0^{7,11}]*dodecan*-3-*one*, m.p. 167—168° (EtOH), $\nu_{max.}$ 1 754vs cm^{-1}, τ 5.57 and 5.97 (each d, J 1.5 Hz, H-10, -12), 6.27br (m, OCH_2), 6.66br (m, H-2), 6.99 (nm, (H-4, -6), 7.08(dm, ^2J 10 Hz, H-7, -8), 8.22 (H-5, -5, ABq), and 8.78(t, CH_3), *m/e* 354 ($M^{+\cdot}$), 319 (M − $Cl^{+\cdot}$), and 291 (M − CO − $Cl^{+\cdot}$) (Found: C, 47.4; H, 4.05. $C_{14}H_{14}Cl_4O_2$ requires C, 47.2; H, 3.95%).

Hydrolysis of Vinyl Ether (49) *with* $^1H_2SO_4$ *and* $^2H_2SO_4$.—Ether (49) (190 mg, 0.56 mmol) in CCl_4 (10 ml) was stirred with H_2SO_4 (5 ml) overnight at 20°; water dilution, extraction, washing, and evaporation gave 2,4-*syn*-5,6-tetrachloropentacyclo[7.2.1.0.^{2,6}0^{4,8}.0^{7,11}]dodecan-3-one (50) [37] (87 mg, 50%), m.p. 190—191° (EtOH), $\nu_{max.}$ *ca.* 1 790vs cm^{-1}, τ 5.49(s, H-5), 6.96 and 6.98 (both d, J *ca.* 8 Hz, H-7, -8), 7.12—7.47(m) and 6.7(m) (H-1, -11, -9), 8.40 and 8.55 (both m, ^2J 14 Hz, H-12, 12), 8.22 and 8.41 (both dnm, ^2J *ca.* 11 Hz, H-10, -10′), *m/e* 310 ($M^{+\cdot}$), *m/e* 310 ($M^{+\cdot}$), 275 (M − $Cl^{+\cdot}$), and 247 (M − $COCl^{+\cdot}$) (Found: *m/e* 309.949. $C_{12}H_{10}{}^{35}Cl_4O$ requires *M*, 309.949. Found: C, 46.15; H, 3.3. $C_{12}H_{10}Cl_4O$ requires C, 46.2; H, 3.2%). A similar experiment using $^2H_2SO_4$ gave the *exo*-12-^{2}H isomer as the only significant product, m.p. 191°, n.m.r. similar but with a signal at τ 7.94br (s) replacing τ 8.40, 8.55 in (50) and sharpening of signals at τ 6.96, 6.98 (H-7, -8), *m/e* 311 ($M^{+\cdot}$), 276 (M − $Cl^{+\cdot}$), 247 (M − CO−$Cl^{+\cdot}$). Similarly, on treating vinyl ether (47) with concentrated $^2H_2SO_4$, signals at τ 7.91 and 8.51 (each dnm, *endo*- and *exo*-H-12) in the only significant product, ketone (48), collapse to τ 7.93(nm) in [*exo*-^{2}H]-(48).[8]

The same ketone (50) was obtained by treating vinyl ether (49) with neat FSO_3H.

Reductive Dechlorination of Adduct (44).—Adduct (44) [31] (434 mg, 1 mmol) was stirred with $LiAlH_4$ (100 mg, 2.6 mmol) in tetrahydrofuran (20 ml) under N_2 at the boiling point for 20 h. T.l.c. monitoring indicated product and unchanged (44); $LiAlH_4$ (50 mg) was added, stirring and heating continued for 8 h; finally the mixture was worked-up in the usual way. The crude product (388 mg) was chromatographed giving three fractions: (a) highest R_F (44) (144 mg), (b) (46) (44 mg, 12%), and (c) (45) (110 mg, 27%). Recrystallised from petroleum (c) gave pure endo,endo-3,4,5,6-syn-12-*pentachloro*-anti-11-*t-butoxytetracyclo*[6.2.1.1^{3,6}.0^{2,7}]*dodeca*-4,9-*diene* (45), m.p. 156—157°, $\nu_{max.}$ *ca.* 1 600vs cm^{-1} (ClC=CCl), τ 4.05 (' t ', H-9, -10), 5.42(s, *anti*-H-12), 6.46(nt, *syn*-H-11), 6.68(t, H-2, -7), 7.23 (sext, (H-1, -8), and 8.83(s, Bu^tO), *m/e* 400 ($M^{+\cdot}$), 364 (M − $HCl^{+\cdot}$), 308 (M − Cl − $C_4H_9^{+\cdot}$), and 236 ($C_5HCl_5^{+\cdot}$) (Found: C, 47.95; H, 4.4. $C_{16}H_{17}Cl_5O$ requires C, 47.75; H, 4.25%).

Fraction (b), recrystallised from petroleum, gave endo,-endo-3,4,5,6-*tetrachloro*-anti-11-*t-butoxytetracyclo*[6.2.1.1^{63}.-0^{2,7}]*dodeca*-4,9-*diene* (46) m.p.* 142.5—144.5°, $\nu_{max.}$ *ca.* 1 600vs cm^{-1}, τ 4.05(m, H-9, -10), 6.40br (m, *syn*-H-11), 6.54(m, H-2, -7), 7.34br (m, H-1, -8), 7.10 and 7.50 (each d, J 7 Hz, H-12, -12), and 8.83(s, Bu^tO), *m/e* 366 ($M^{+\cdot}$), 330 (M − $HCl^{+\cdot}$), 310 (M − $C_4H_8^{+\cdot}$), and 202 ($C_5H_2Cl_4^{+\cdot}$) (Found: C, 51.95, H, 5.1. $C_{16}H_{18}Cl_4O$ requires C, 52.2; H, 4.95%).

Addition of Tetrachlorocyclopentadiene to 7-*t-Butoxynorbornadiene*.—Tetrachlorocyclopentadiene (504 mg, 2.5 mmol) was heated with 7-t-butoxynorbornadiene (410 mg, 2.5 mmol) and CCl_4 (1 ml) in a sealed tube for 3 days at 100°, and the crude product chromatographed (1 : 1 petroleum–CH_2Cl_2) yielding two fractions. Further chromatography (petroleum) of each fraction gave (i) tetrachlorocyclopentadiene dimer (109 mg, 24%); and (ii) a mixture of the isomeric adducts of 2,3,4,5-tetrachlorocyclopenta-1,3-diene with isomeric tetrachlorocyclopentadienes (137 mg, 30.5%) [the mixture characterised by τ 5.29(d) and 6.20(d) (^3J < 2 Hz, CHCl and bridgehead H), 6.84 and 7.30 (each d, ^2J 9 Hz, CH_2) and τ 5.10(d) and 6.06(d) (^3J *ca.* 2.5 Hz, as above), 6.68(d), and 7.24(d) ^2J 9 Hz, as above)]; (iii) compound (46) (107 mg, 24%); (iv) *endo*,-*endo*-3,4,6-*syn*-12-tetrachloro-*anti*-11-t-butoxytetracyclo-[6.2.11.^{3,6}.0^{2,7}]dodeca-4,9-diene (27 mg, 6%), τ 4.04 and 4.36 (both m, H-9, -10), 4.64 and 5.57 (each d, J < 2 Hz, H-5, -12), 6.53(m, H-11), 6.71(m, H-1, -8), 7.22(m, H-2, -7), and 8.83 (Bu^tO), *m/e* 366 ($M^{+\cdot}$, v, weak), 330 (M − $HCl^{+\cdot}$), and 202 ($C_5H_2Cl_4^{+\cdot}$); (v) *endo,endo*-3,4,5-*syn*-12-tetrachloro-*anti*-11-t-butoxytetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-diene (17 mg, 3.8%), τ 4.09(m, H-9, -10), 5.63(d, H-12), 6.52(m, H-11), 6.88(m, H-1, -8), 6.95(m, H-6), 7.27 and 7.37 (each m, H-2, -7), and 8.83(s, Bu^tO), *m/e* 366 ($M^{+\cdot}$) and similar to (iv); (vi) a stereoisomer of (46) (44 mg, 9%).

Hydrolysis of Compound (45).—Pentachloro-compound (45) (50 mg) was stirred overnight in CCl_4 (5 ml) with H_2SO_4 (5 ml), the product was extracted directly into CH_2Cl_2, and the extracts bulked with those from the water-diluted acid residue; the washed and dried extracts were evapo-

* *Not* 112° as stated in ref. 1.

rated; the crude product (33 mg) was chromatographed (1 : 1 petroleum–CH_2Cl_2) giving 3,4,5,6-syn-11-anti-12-*hexachlorotetracyclo*[6.2.1.$1^{3,6}$.$0^{2,7}$]*dodeca*-4,9-*diene* (54) (30 mg, 66%), m.p. 125—126°, $\nu_{max.}$ 1 605vs cm^{-1} (ClC=CCl), τ 3.91(t, H-9, -10), 5.43(s, H-12), 6.07(nm, H-11), 6.50(t, H-2, -7), and 6.96(m, H-1, 8), *m/e* 362 ($M^{+\cdot}$), 327 ($M - Cl^{+\cdot}$), 291 ($M - HCl_2^{+\cdot}$), 100 ($C_5H_5Cl^{+\cdot}$ RDA), and 65 ($C_5H_5^{+\cdot}$ RDA – Cl) (Found: *m/e*, 363.873. $C_{12}H_8{}^{35}Cl_5{}^{37}Cl$ requires *M*, 363.873).

Acetolysis of Compounds (44) *and* (53).—Adduct (44) (230 mg) dissolved in 1% H_2SO_4 in Ac_2O (25 ml) was heated for 1.25 h at 60°, water was added, and the organic product was extracted with petrol; washing, drying, and evaporation gave a single product (t.l.c.) endo,endo-anti-11-*acetoxy*-3,4,5,6,12,12-*hexachlorotetracyclo*[6.2.1.$1^{3,6}$.$0^{2,7}$]-*dodeca*-4,9-*diene* (55) (150 mg, 67%), m.p. 172.5—173.5° (MeOH), τ 4.07(t, H-9, -10), 5.3(t, *syn*-H-11), 6.60(t, H-2, -7), 7.01 (sext, H-1, -8), and 7.99(s, CH_3), *m/e* 420 ($M^{+\cdot}$), 385 ($M - Cl^{+\cdot}$), 360 ($M - HOAc^{+\cdot}$), 325 ($M - Cl - HOAc^{+\cdot}$), and 270 ($C_5Cl_6^{+\cdot}$ RDA) (Found: *m/e*, 421.879. $C_{14}H_{10}{}^{35}Cl_5{}^{37}ClO_2$ requires *M*, 421.878). A similar experiment with adduct (53) gave only the syn-11-*acetoxy-isomer* (56) of acetate (55) (72%), m.p. 211—212° (petroleum), τ 4.01(nm, H-9, -10), 5.34br (s, *anti*-H-11), 6.62(t, H-2, -7), 6.72 (sext, H-1, -8), 8.00 s, CH_3), *m/e* very similar to (55), 420 ($M^{+\cdot}$), and see below.

Hydrolysis of Adduct (53).—Adduct (53) (51 mg) was heated at 85° in 25% aqueous dioxan (5 ml) containing concentrated H_2SO_4 (0.25 ml) for 5.5 h and the product isolated by vacuum evaporation, water dilution, and extraction (CH_2Cl_2). Chromatography of the evaporated extracts gave endo,endo-3,4,5,6,12,12-*hexachlorotetracyclo*[6.2.1.$1^{3,6}$.$0^{2,7}$]*dodeca*-4,9-*dien*-syn-11-*ol* (57) (42 mg, 96%), m.p. 182—183.5° (petroleum–CH_2Cl_2), τ 3.93(nm, H-9, -10), 6.11br(s, *anti*-H-12), 6.72(t, H-2, -7), 6.94(nm, H-1, -8), and 7.79[m, OH shifted to lowerfield by Eu(fod)$_3$], *m/e* 378 ($M^{+\cdot}$), 343 ($M - Cl^{+\cdot}$), 367 ($M - HCl_2^{+\cdot}$), and 270 ($C_5Cl_6^{+\cdot}$ RDA) (Found: C, 37.8; H, 2.0. $C_{12}H_8Cl_6O$ requires C, 37.85; H, 2.1%). Treated with Ac_2O–H^+ the alcohol (57) gave *syn*-acetoxy-compound (56) (m.p. and mixed m.p.).

Synthesis [27] *and Methanolysis of Aldrin* endo-9,10-*Epoxide* (58).—Aldrin was treated with I_2–AgOAc and the resulting *endo*-10-acetoxy-9,10-dihydro-*exo*-9-iodoaldrin, m.p. 196—197° (lit.,[27] 197—197.5°), converted into *endo*-epoxide (58), m.p. 138—140° (lit., 138—140°) by treatment with aqueous KOH in dioxan, τ 6.29(nm, H-9, -11), 7.10(s, H-2, -7), 7.43(nm, H-1, -8), and 8.27(nm, H-13, -13) [*cf.* dieldrin, τ 6.86(s), 7.28(s), 7.30(m), and 8.86(m)], *m/e* 377 ($M - H^{+\cdot}$), 343 ($M - Cl^{+\cdot}$), and 307 ($M - HCl_2^{+\cdot}$) (Found: C, 38.0; H, 2.15. Calc. for $C_{12}H_8Cl_6O$: C, 37.85; H, 2.1%). In an alternative approach, treatment of aldrin with *N*-bromosuccinimide in hot HOAc gave the analogous bromoacetate which hydrolysed as above gave a poorer yield of oxide (58). *endo*-Epoxide (58) (200 mg) was dissolved in MeOH–BF_3 complex (5 ml) and the mixture stood at 55—60° for 48 h. Evaporation and extraction (CH_2Cl_2) gave 9,10-dihydro-*endo*-9-hydroxy-*exo*-10-methoxyaldrin (59) (*ca.* 80%) twice recrystallised (CH_2Cl_2–petroleum), m.p. 147—148°, τ 6.1(dm, H-9), 6.64(s, OMe), 6.44(d) and 7.40(d) (*J* 8 Hz, H-2, -7), 7.10(m, H-10), 7.52(m, H-1, -8), 7.86br (s, OH), and 8.60(nq, H-12, -12), *m/e* 410 ($M^{+\cdot}$), 380 ($M - CH_2O^{+\cdot}$), 375 ($M - Cl^{+\cdot}$), and 310 ($M - CH_2O - Cl_2^{+\cdot}$, 100%) (Found: C, 37.6; H, 3.1. $C_{13}H_{12}Cl_6O_2$ requires C, 37.8; H, 2.9%). In similar experiments under a variety of conditions only diol monomethyl ether (59) and/or *endo*-epoxide (58) were found as major products.

Heating *endo*-oxide (58) at 190—200° for *ca.* 16 h failed to isomerise the compound into dieldrin (9).

X-*Ray Analysis of* (30).—*Crystal data.* $C_{13}H_{15}Cl_3O_4S$, M = 373.7, orthorhombic, a = 9.377(1), b = 10.923(2), c = 29.614(5) Å, U = 3 033 Å^3, Z = 8, D_c = 1.637 g cm^{-3}, $F(000)$ = 1 536, space group *Pbca*, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 7 cm^{-1}.

Measurements. After photographic examination the final unit cell dimensions and the intensities (θ—2θ scans) of all independent reflections with $2 \leqslant \theta(\text{Mo-}K_\alpha) \leqslant 30°$ were measured on an Enraf–Nonius CAD4F diffractometer using the methods of ref. 38. The intensities were corrected for *Lp* effects but not for absorption. Crystal decay correction was unnecessary. The analysis continued with 2 435 reflections for which $I > 3\sigma(I)$.

TABLE 2

Fractional co-ordinates (× 10^4) for (30)

Atom	*x*	*y*	*z*
Cl(2)	−4 840(2)	−1 228(1)	−1 602(1)
Cl(3)	−1 951(2)	684(2)	−1 672(1)
Cl(6)	−7 684(2)	407(2)	−1 171(1)
S	−1 631(2)	1 107(3)	−318(1)
O(1)	−2 638(5)	1 605(4)	−705(2)
O(2)	−5 359(5)	−256(5)	−520(2)
X(1)	−129(7)	1 907(10)	−404(3)
X(2)	−2 173(8)	926(21)	18(4)
X(3)	−1 162(17)	−179(7)	−459(6)
C(1)	−5 629(6)	963(5)	−2 029(2)
C(2)	−5 011(5)	390(4)	−1 590(2)
C(3)	−3 647(5)	1 062(4)	−1 434(2)
C(4)	−3 561(6)	770(5)	−929(2)
C(5)	−5 104(6)	813(5)	−761(2)
C(6)	−5 899(5)	937(4)	−1 204(2)
C(7)	−5 780(5)	2 243(4)	−1 396(2)
C(8)	−4 146(5)	2 360(4)	−1 532(2)
C(9)	−4 160(6)	2 670(5)	−2 046(2)
C(10)	−5 641(7)	3 239(6)	−2 092(2)
C(11)	−6 409(6)	2 156(5)	−1 864(2)
C(12)	−4 396(7)	1 467(5)	−2 309(2)

Structure analysis. The structure was solved using the SHELX-76 direct methods program [39] and refined by difference syntheses and full-matrix least-squares techniques [$w^{-1} = \sigma^2 + (0.02|F|)^2$ where σ is derived from counting statistics]. In the final calculations anisotropic temperature factors were used for all non-hydrogen atoms. Twelve hydrogen atoms were located in difference syntheses and the parameters of these atoms were refined, except for hydrogen bonded to O(2) which was constrained to a stereochemically acceptable position. The mesylate methyl hydrogen atoms were not located and the vibrational parameters of the terminal O and C atoms of this group strongly suggest disorder. Several models for this disorder were considered but none proved satisfactory. The terminal C and O atoms could not be distinguished from one another and the S–X (X = terminal C or O) bond lengths are anomalous (Table 1). The final difference synthesis contains regions of 1.6 eÅ^{-3} close to the sulphur atom and the converged values of R 0.076 and R_w 0.11 reflect this. The remaining atoms do not appear to be involved in the disorder of the mesylate group: their vibrational parameters are normal and they lie in regions where the final difference synthesis is featureless ($|\Delta\rho| < 0.4$ eÅ^{-3}). Their positional parameters (Table 2) are accordingly more accurately

determined.* Scattering factors and anomalous dispersion corrections were taken from ref. 40.

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