Sequential Wagner–Meerwein Rearrangements of Polychlorinated Complex Cations derived from Monodechloroisodrin and Monodechloraldrin, and the ^{1}H Nuclear Magnetic Resonance Spectra of Polychloropolycyclic Ketones and Dechloroaldrin Derivatives [1] †

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Monodechloroaldrin and monodechloroisodrin (obtained by selective removal of one of the bridge methylene chlorines from the appropriate hexachlorotetracyclododecadiene) are protonated in acids to give cations which are intercepted by *e.g.* acetic acid to give the anticipated acetates. In concentrated sulphuric acid on the other hand *both* dienes are hydrolysed with concomitant transannular ring closure to give the *same* novel tetrachloropentacyclic ketone (IX) as the initial product. Its unique formation from a common intermediate cation derived by successive Wagner–Meerwein [1.2]shifts in the initial ions formed from the two stereoisomeric dienes is demonstrated. This ketone is readily isomerised in contact with silica gel or mild bases to give a closely related ketone whose structure is established by its unusual ^{1}H n.m.r. spectrum, the interpretation of which is facilitated by deuterium labelling experiments and LAOCOON 3 computer simulation. The ^{1}H n.m.r. spectra of intermediates used for synthesis of the deuterium labelled ketones are discussed with special reference to proximity deshielding effects. Mass spectral data for most of the compounds discussed are listed.

A NUMBER of detailed studies have described the fate of secondary carbonium ions variously derived from the *endo–endo* and *endo–exo* stereoisomeric tetracyclododecenes (or dienes) characteristic of the skeletal features of the polychlorinated 'cyclodiene' pesticides isodrin (I), endrin (II), aldrin (III), and dieldrin (IV). Notable examples reveal complex skeletal interconversions by Wagner–Meerwein sigmatropic rearrangements *via* 2π three-centre delocalised cations readily formed in these purely hydrocarbon systems.[2] By comparison, the hexahalogenated ions derived from *e.g.* aldrin and isodrin show little propensity for parallel complex behaviour.[3] Whilst slow but very limited conversion of aldrin into isodrin-type structures does indeed occur *via* complex cations (for example in the solvolysis of sulphonates of aldrin alcohols [4]) it is only the members of the isodrin series of compounds which have been observed to rearrange at all readily, typically in reactions initiated by liganding of the π bond or epoxy-function to electrophilic reagents, with subsequent group shifts leading to structures such as (V) and (VI).[5,6] It can be argued that this marked difference in the tendency for rearrangement in reactions of the two stereoisomeric polyhalogenated series of compounds owes its origin to the overriding effect of the proximity of the participating π bond at the incipient electrophilic site in the isodrin series, general chlorine inductive destabilisation of cations derived from aldrin types apparently precluding the σ participation vital to rearrangement, with the result that rapid irreversible discharge of the cationic species gives largely unrearranged products.

However we have now found, by way of contrast, that monodechloroisodrin (VII) and monodechloroaldrin (VIII) [6] are hydrolytically rearranged in concentrated acids to give in each case a moderate yield of the same ketone (A) or (B) (critically dependent on the conditions of work-up). For example stirring either of the dienes (VII) or (VIII) with sulphuric acid at 20—25°, and direct extraction of the product into an inert solvent, followed by recrystallisation of the crude hydrolysate gives, besides unchanged diene, the same ketone (A) (35—75%) and several minor related products (none $>0{\cdot}3\%$) which appear to be common to the two reactions but whose detailed structures remain to be investigated.‡ Surprisingly, when purified by chromatography on silica gel (A) is quantitatively converted into a new isomeric ketone (B).

Their high frequency i.r. carbonyl absorbtion (1785vs cm^{-1}) and lack of typical dichloroethylene absorbtion (near 1600 cm^{-1}) suggests strained ring polycyclic saturated ketones for (A) and (B) whilst their mass spectra very closely correspond and also show several

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† After an observation by C. H. M. Adams, Ph.D. Thesis, University of Bristol, 1967.

‡ None of these minor products has the characteristic ^{1}H n.m.r. high field quartet near τ 8·76 seen in the major product and they could be related to or derived from ketones such as (XVIII) or hydrocarbon (XX).

[1] C. H. M. Adams, K. Mackenzie, and D. J. Cawley, *Tetrahedron Letters*, 1972, 1311.

[2] L. de Vries and S. Winstein, *J. Amer. Chem. Soc.*, 1960, **82**, 5363.

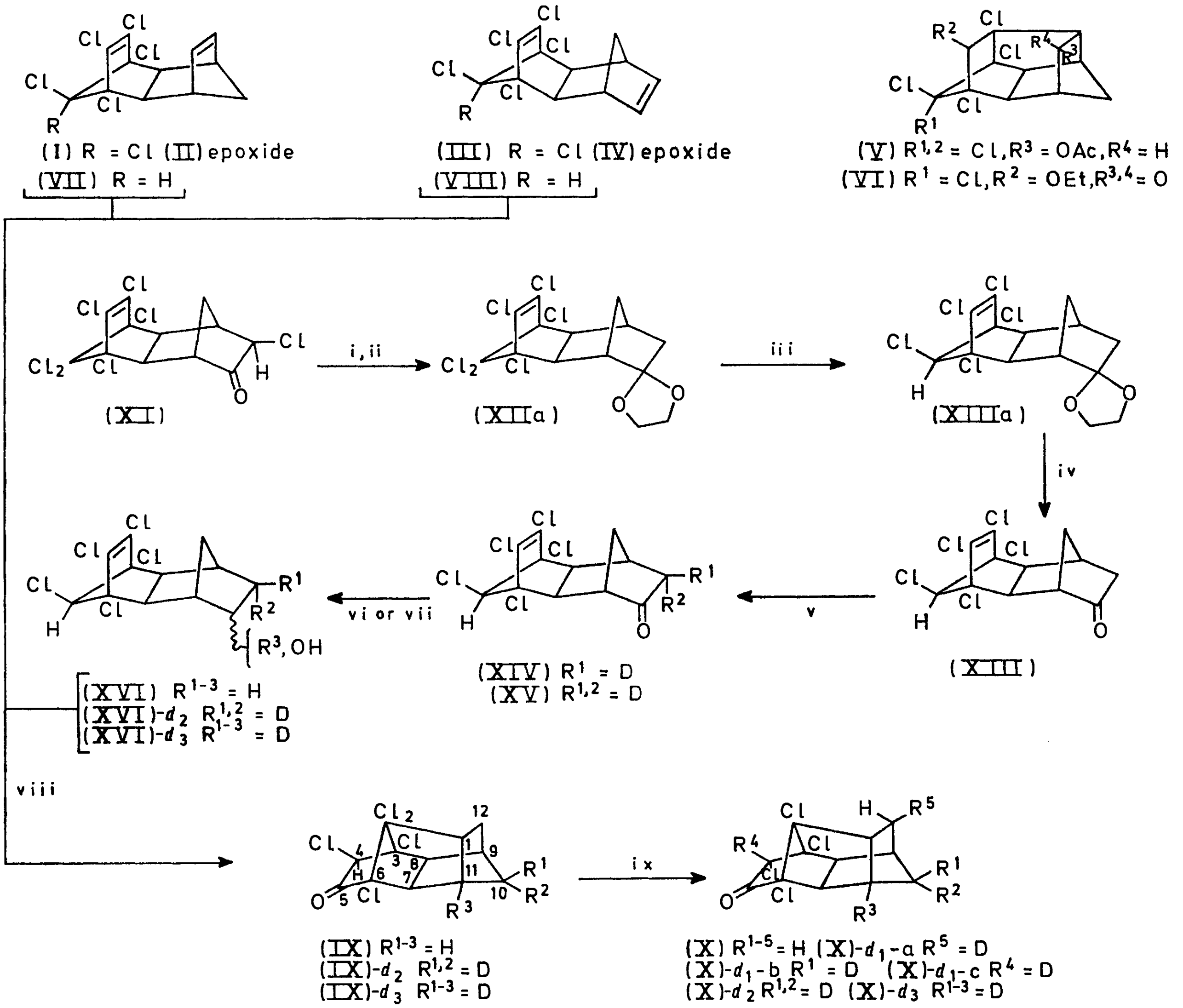
[3] S. B. Soloway, A. M. Damiana, J. W. Sims, H. Bluestone, and R. E. Lidov, *J. Amer. Chem. Soc.*, 1960, **82**, 5377.

[4] C. W. Bird, R. C. Cookson, and E. Crundwell, *J. Chem. Soc.*, 1961, 4809.

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

[6] C. H. M. Adams and K. Mackenzie, *J. Chem. Soc.*, 1969, 480.

groups of ions in common with the otherwise different mass spectra of ketones such as (XVIII) and (XIX). Thus, whilst the i.r. and especially the ^{1}H n.m.r. spectra of these novel ketones are quite unlike those of the known ketone (XVIII) [or (XIX)] they are clearly isomeric with the former.



SCHEME 1 Reagents: i, Zn–AcOH; ii, $(CH_2OH)_2$; iii, KOBu^t–DMSO–60°; iv, aq.HBr–AcOH; v, KOBu^t–MeOD; vi, $LiAlH_4$; vii, $LiAlD_4$; viii, 98% H_2SO_4–H_2O or D_2SO_4–D_2O; ix, silica gel or 0·5% KOMe–MeOH(D)

The n.m.r. spectra of the two ketones, in the following shown to be (IX) and (X), are in fact complex and unusual for chlorinated pentacyclic saturated compounds; the multiplet assignments (Table 1) rest on the evidence of decoupling and deuterium labelling experiments, and on this basis the two ketones appear structurally very similar. Significantly both show a surprisingly low field multiplet for *endo*-12-H and a correspondingly high field quartet for the geminal *exo*-12 proton, which is characteristic of all the derived protio-compounds. Additionally, the different 4-H chloromethylene singlets at τ 5·75 and 5·44 and the chemical shift difference for the 8-H resonance in the two isomers ($\Delta\tau = 0{\cdot}43$) are notable. Carbonium ion pathways which could be considered for the protolysis of dienes (VII) and (VIII) (Scheme 2[2]) offer a number of possible structures for the two novel ketones. Broadly considered however the ^{1}H n.m.r. spectral features serve immediately to rule out one candidate for ketone (A), namely the unsymmetrical structure (XXI) which would be expected to show a broad undifferentiated methylene envelope in the high field region due to the ethano-bridge protons. The large chemical shift difference for the *endo*- and *exo*-C-12 methylene protons can however be accommodated in terms of the now well known group proximity effect on the chemical shifts of methylene protons[7] in other possible structures such as (IX) or (XVII) for which models indicate that a bridgehead chlorine atom [on C-3

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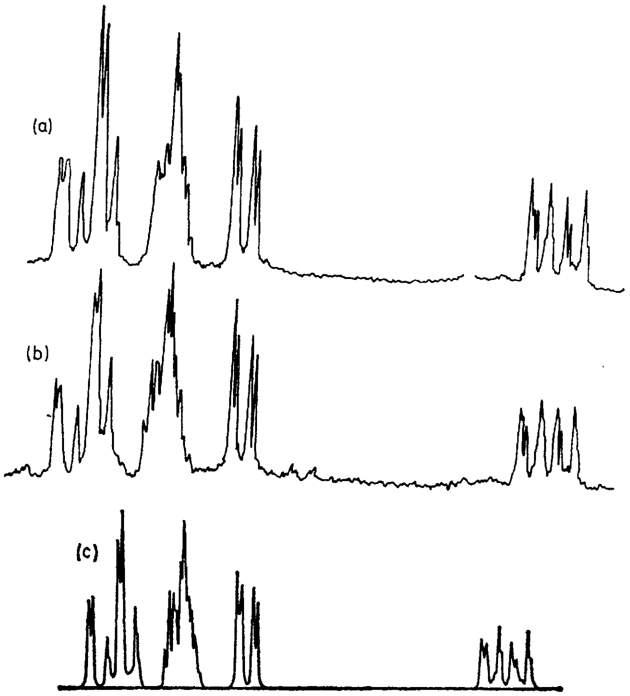
[7] S. Winstein, P. Carter, F. A. L. Anet, and A. J. R. Bourn, *J. Amer. Chem. Soc.*, 1965, **87**, 5247.

in *e.g.* (IX)] and *endo*-12-H are in contact, if not actually under compression (depending on molecular flexibility). Simple models show that the chlorine–hydrogen nuclear separation is *less* than the sum of the Van der Waals radii, but deformation of the molecule may allow relaxation near to conventional contact distance. This effect rationalises the strong deshielding observed for *endo*-12-H, with the corresponding upfield shift for the *exo*-methylene proton (and a high frequency i.r. absoptions at 3030 cm^{-1} may also be due to this effect [2]). On the grounds that heavily chlorinated norbornene rings would not be expected to rearrange easily, structure (XVII) might then seem likely for the ketone (A).* However this structure and its chloromethylene isomer can be excluded from further discussion by the following: in addition to its formation from ketone (A) by contact with silica gel, ketone (B) crystallises from solutions of (A) in weakly basic methanol, whilst in methan[^{2}H]ol rearrangement is accompanied by specific incorporation of only *one* deuterium atom, the low field n.m.r. singlet due to Cl–C–H disappearing in the product. Ketones (A) and (B) are thus apparently α-chloromethylene epimers; this is confirmed by reduction of ketone (B) to give a mixture of epimeric α-chloromethylene alcohols with typical *cis*- and *trans*-CHCl·CHOH n.m.r. parameters, clearly demonstrated by running the spectra at different field strengths, as well as by reduction with lithium aluminium deuteride, when only the lower field chloromethylene singlets appear at the correct calculated positions. Obviously these observations are quite inconsistent with structures like (XVII) for the ketones, and further discussion is therefore principally in terms of the more stable ketone (B) and its deuterio-analogues having structure (X) † which uniquely accommodates all our data for the two ketones (A) and (B).

^{1}H *N.m.r. Spectra of Ketones* (IX) *and* (X) *and their Deuteriated Analogues.*—Special interest attaches to the ^{1}H n.m.r. spectra of the novel ketones (IX) and (X) since few (if any) of the spectra of related structures have been analysed in detail. For ketone (X), attention initially centres on the high field single proton quartet at τ 8·76. This signal seems to arise from two couplings of magnitude *ca.* 6 and *ca.* 13 Hz, and double resonance experiments show couplings to the signals near τ 7·00 and 7·30, whose appearance changes significantly on irradiation of the high field quartet. Correspondingly, irradiation of the signal near τ 7·00 removes the larger coupling from the quartet, and on this basis and examination of models the signals near τ 7·00 and 8·76 are assigned to the *endo*- and *exo*-geminal methylene protons on C-12 respectively. This correlation is readily confirmed by hydrolysis of the dienes (VII) and (VIII) in deuteriosulphuric acid (see Scheme 2). After purification–rearrangement on silica gel, a fair yield of in each case a different isotopic isomer of ketone (X) is obtained [designated (X)-d_1-a and (X)-d_1-b] uncontaminated by other significant deuterium incorporation products. The two labelled ketones have virtually identical mass spectra which, besides showing weak molecular ions at *m*/*e* 311 with the correct halogen isotope abundance patterns, show fragment ions at *m*/*e* 278 ($C_{12}H_9D^{35}Cl_2$-^{37}ClO) 95 and 100% respectively, and at *m*/*e* 114 (C_6H_5-$D^{35}Cl$) 22 and 35% with *m*/*e* 116 ($C_6H_5D^{37}Cl$) 12 and 17% respectively. [The principal ions in the mass spectra of the ketones (IX) and (X) and their deuteriated analogues are summarised in Supplementary Publication SUP No. 20669 (3 pp.).‡ A full discussion of these spectra is deferred to a separate account.]



^{1}H N.m.r. spectrum of ketone (X)-d_3 (100 MzH; 500 Hz sweep width): (a), normal spectrum; (b) deuterium decoupled by double irradiation; and (c), simulated spectrum (see Table 1 for τ values) (sharp singlet at τ 5·43 neglected)

The ^{1}H n.m.r. spectra of the isotope positional isomers differ markedly. The high field single proton quartet is removed in (X)-d_1-a together with the multiplet near τ 7·0 which collapses and is obscured under signals near τ 7·07; the latter signal is changed in appearance,

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* A similar diametrical ring closure product has been tentatively identified in the minor products of reaction of isodrin with bromine.[3]

† The ketone is theoretically related to Winstein's alcohol 'VI-OH' (ref. 2, pp. 5366 *et seq.*), and as a referee has suggested we might have established its structure by the simpler expedient of reduction to this alcohol. However, the structure of the alcohol was inferred from i.r. data and its chemical relationship to the parent olefin; and clearly such chemistry would neither have yielded the complementary fundamental evidence which we have adduced for the structures of our compounds, nor necessarily have provided a basis, implicit in the present study, for structural assignments using relatively small samples of related complex compounds (*cf.* R. L. Hansen and S. Winstein, *Tetrahedron Letters*, 1960, **25**, 6; D. Kivelson, S. Winstein, P. Bruck, and R. L. Hansen, *J. Amer. Chem. Soc.*, 1961, **83**, 2938).

‡ For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue 20 (items less than 10 pp. are supplied as full size copies).

whilst the signals at τ 7·30—7·35 are less differentiated. For isomer (X)-d_1-b on the other hand the high field quartet is retained but the methylene bridge AB doublets centred at τ 8·46 and 8·52 are replaced by a broad singlet, whilst all remaining signals are sharpened, except for the signal near τ 7·60 which remains virtually unchanged. All these effects are consistent with structure (X) for ketone (B) and its formation as shown in Scheme 2 but further confirmation is obtained by double resonance experiments with monodeuterio-ketone (X)-d_1-a, summarised in Table 3, which help to confirm assignments *e.g.* of 1-, 7-, 8-, and 11-H provisionally made on the basis of signal complexity, coupling constants, and τ values.

TABLE 1

^{1}H N.m.r. chemical shifts of protons for pentacyclododecanones (IX) and (X) and their deuterium labelled analogues from first-order analysis and computed simulation

H	(IX)	(IX)-d_3	(X)	(X)-d_1-a	(X)-d_1-b	(X)-d_1-c	(X)-d_2	(X)-d_3	Simulated * (X)-d_3
4	5·75 (s)	5·76 (s)	5·44 (s)	5·44 (s)	5·45 (s)		5·43 (s)	5·43 (s)	
11	6·82 (bm)		6·80 (bm)	6·80 (bm)	6·80 (bm)	6·80 (bm)	6·80 (bm)		
12-*endo*	7·00 (dt)	6·97 (dd)	7·00 (dt)	7·00 (bs)	7·00 (dt)	7·00 (dt)	7·00 (dm)	7·01 (dd)	6·991
9	7·27 (m)	7·24 (m)	7·35 (m)	7·34 (bs)	7·37 (m)	7·35 (m)	7·34 (m)	7·34 (m)	7·340
1	7·40 (m)	7·40 (m)	7·30 (m)	7·30 (bs)	7·31 (m)	7·30 (m)	7·30 (m)	7·30 (m)	7·302
8	7·50 (m)	7·50 (m)	7·07 (t)	7·07 (t)	7·06 (m)	7·07 (t)	7·07 (t)	7·07 (dd)	7·067
7	7·60 (m)	7·59 (dd)	7·60 (dq)	7·60 (dt)	7·60 (dq)	7·60 (dq)	7·60 (dq)	7·61 (dd)	7·601
10	8·46 (dm)		8·42 (dm)	8·41 (dm)	8·42 (bs)	8·42 (dm)			
10′	8·58 (dm)		8·58 (dm)	8·58 (dm)		8·58 (dm)			
12-*exo*	8·76 (q)	8·75 (q)	8·76 (q)		8·75 (q)	8·76 (q)	8·76 (q)	8·75 (q)	8·752

* Maximum probable error 0·0005 p.p.m.

TABLE 2

Coupling constants (J/Hz) computed for ketone (X)-d_3 *

	8-H	1-H	*endo*-12-H	*exo*-12-H	7-H
7-H	7·11	1·77	0·21	−0·19	
9-H	5·39	2·08	1·85	1·15	0·15
exo-12-H	0·97		−12·74		
1-H	−0·20		0·10	6·59	
8-H			0·03		

* Maximum probable error 0·08 Hz.

TABLE 3

Double irradiation experiments with ketone (X)-d_1-a

Signal irradiated	Effect
7·30—7·40	6·80br (m) n and 7·07 coll; 7·60 (dt) becomes dd; 8·42 (dm) and 8·58 (dm) res.
7·60 (dt)	6·80br (m) and 7·30br (s) both res. to cd; 7·07 (t) and 8·41, 8·58 (dm) res.
6·80 (cm)	7·07 (t) n; 7·30—7·40 coll. to nm; 7·60 (dt) becomes dnm; 8·41, 8·58 (dm) res.
7·07 (t)	6·80br (m) becomes dm; 7·60 (dt) coll. to nm; 8·41 (dm) slightly res.

br = Broad; c = complex; coll. = collapses; d = doublet; m = multiplet; n = narrow; res. = resolved; s = singlet; t = triplet.

Some of the coupling constants deduced from first-order network construction with the n.m.r. spectra of the ketones (IX) and (X) seem slightly anomalous on the basis of roughly estimated dihedral angles between the relevant protons, and in order to confirm the data, place the structures (IX) and (X) for the ketones and their mode of formation on a firmer footing and derive additional spectroscopic information, incorporation of more deuterium into the ketones is achieved by synthesis of dechloroaldrin alcohol (XVI) and its di- and tri-deuterio-analogues as outlined in Scheme 1. Deuteriated dechloroaldrin alcohols (XVI) are then used as a source of labelled rearranged cations, and the structures of the labelled ketones which form the ultimate products of protolytic hydrolysis serve to further confirm the rearrangement pathways of Scheme 2, and when taken together with computer simulation of the deuterium decoupled ^{1}H n.m.r. spectrum (c) of ketone (X)-d_3 afford the data in Tables 1 and 2. Line shape and broadening effects in the spectrum (a) of ketone (X)-d_3 preclude its simulation, but the correspondence of spectra (b) and (c) is sufficiently close for reasonable confidence in the suggested parameters; the simulation experiments for example clearly confirm the negative value of $^2J_{exo/endo\text{-}12\text{-}H}$ and reproduce otherwise difficult to explain second-order effects observable in the high field *exo*-12H signal. The relevant spectra are illustrated in the Figure.

Finally a distinction must be made between ketone (IX) and another, possible isomer, *e.g.* ketone (IXi). These alternative structures for the initially isolated ketone can be distinguished by the fact that the 8-H in the initial product occurs at markedly higher field than in the *endo*-chloro-epimer produced by base-catalysed rearrangement ($\Delta\tau$ *ca.* 0·4). Models indicate that severe 3-Cl–*endo*-12-H compression in these systems can be relieved by skeletal twisting which results in deflection of *endo*-4-Cl in ketone (X) towards 8-H. These motions have the opposite effect in a structure such as (Xi), *endo*-5-Cl here being deflected away from 7-H. On this basis the chemical shifts for 7- and 8-H would not be expected to change quite so much in the epimers (IXi) and (Xi), and any net effect ought to appear in that of 7-H. Bearing in mind the deshielding effect of proximate chlorine the observed downfield shift in the signal for 8-H in the more stable epimeric *endo*-chloro-ketone and the relative position of this signal overlying that due to the environmentally similar *endo*-12-H proton can best be accommodated by the structures (IX) and (X) for the two ketones. The marked downfield shift of the signal due to 4-H in ketone (X) is additionally rationalised in terms of its proximity to the 'bridge methylene' chlorine at C-2.*

Synthesis of Intermediates for Scheme 1 *and their* ^{1}H *N.m.r. Spectra*.—Some points of interest arise in connexion with Scheme 1. *exo*-α-Chloro-ketone (XI) is formed by treatment of aldrin with nitrosyl chloride, followed by hydrolysis with hydrobromic acid. Addition of nitrosyl chloride is known to occur stereospecifically *cis–exo* with norbornenes.[8] The stereochemistry at the latter position additionally follows from the n.m.r. parameters for the ethylene acetal (XIa) which is conveniently formed merely by boiling ketone (XI) with ethylene glycol; the n.m.r. spectrum of the ketal shows the *endo*-chloromethylene proton coupled to the methylene bridge proton *syn* to the chloroethylene group (^{4}J 3 Hz a somewhat large four-bond 'W mode' coupling, but confirmed by double resonance; ^{4}J is usually not greater than 2 Hz in norbornenes [9]). Dechlorination of chloro-ketone (XI) is affected with zinc, and boiling the ketonic product (XII) with ethylene glycol gives acetal (XIIa). Stereoselective dechlorination of acetal (XIIa) with potassium t-butoxide in dimethyl sulphoxide [as for *e.g.* dieldrin (IV) [6]] gives dechloroacetal (XIIIa) which is hydrolysed under relatively mild conditions into dechloroketoaldrin (XIII).

Whilst bornane-2-ones have been shown to exchange the *exo*-α-proton stereoselectively in basic deuteriated media,[10] n.m.r. and i.r. spectral comparisons leave no doubt that both α-protons in ketone (XIII) are readily exchanged for deuterium, even under very mildly basic conditions (0·35% KOBu^{t} in MeOD) giving an excellent yield of isotopically pure dideuterio-ketone (XV). Monodeuterio-ketone (XIV) appears to be absent. Presumably enolate anions are stabilised in these heavily chlorinated systems, enhancing deprotonation efficiency to the extent that even the *endo*-proton is rapidly abstracted by base. Alternatively it might be that keto–enolate equilibrium is accelerated to a degree where the small propensity for *endo*-deuteriation is mitigated. The same electronic effect can be discerned in the ease of dechlorination of α-chloro-ketone (XI) with zinc.

The n.m.r. spectra of the intermediates in Scheme 1 are also of some topical interest for although the general features of the spectra of structurally related types have been analysed in some detail recently [11] most of the compounds which have been discussed elsewhere belong to the hexachloro-series. The presence or otherwise of two geminal bridge methylene chlorines allows shielding–deshielding phenomena to be observed rather well, and such effects, together with similar effects due to the presence of proximate oxygen, are well illustrated in the spectra of structures shown in Scheme 1. Variations in the position of ring junction and bridgehead n.m.r. signals within this series of compounds emphasises the fact that there is no simple relationship between ring junction stereochemistry (*i.e.* whether molecules belong to the *exo–endo* or *endo–endo* tetracyclododecane classes) and the relative positions of these signals, as might be deduced incorrectly from the necessarily somewhat limited data which have been discussed previously.[11a,c]

In contrast to the n.m.r. spectrum of aldrin [11a,c] owing to a lack of symmetry, the ethylene acetal (XIa) shows a series of nicely separated signals for each of the different types of proton. The ring junction pair 2- and 7-H give rise to cleanly separated doublets at τ 6·67 and 7·16 (^{3}J 8 Hz) which appear at lower field than the unresolved bridgehead multiplets at τ 7·47 and 7·62, in contrast to aldrin where these sets of signals appear in the reverse order. The methylene bridge geminal protons show a chemical shift difference of *ca.* τ 0·4, approximately twice that for the corresponding protons in aldrin and due largely to the exceptionally strong deshielding (by τ —0·6) experienced by the bridge proton proximate to the *exo*-10-Cl and the oxygen atom of the dioxolan ring. This effect once again reverses the expected relative chemical shifts of the two bridge protons, the proton *syn* to the olefin bridge resonating at nearly the same frequency as in aldrin, but now at higher field relative to its geminal neighbour. The magnitude of this deshielding points to a shift contribution of $\tau \nless 0{\cdot}2$ attributable to the effect of the oxygen atom, and on this basis the ring junction protons 2- and 7-H can be assigned with the latter at lower field. Removal of the electronegative chlorine atom from acetal (XIa) and its replacement with a proton effects the expected changes in the n.m.r. spectrum. The ring junction doublets remain much the same in position (the coupling actually decreases very slightly) but the bridgehead 1-H now appears as a broadened doublet at τ 7·60 (J 4·5 Hz) due to coupling with *exo*-10-H; the latter appears as a doublet of doublets centred on τ 8·06 (geminal coupling, ^{3}J 14 Hz, as well as coupling to 1-H). The signal due to *endo*-10-H is obscured under the methylene bridge signals precluding simple analysis but 1-H-*endo*-10-H coupling would appear to be small in common with other systems.[12] 8-H On the other hand remains as a rather broad singlet as would be expected.

For acetal (XIIIa) the bridge dechlorinated analogue of compound (XIIa) there is a marked upfield shift of the ring junction doublets by τ 0·3—0·4 towards the bridgehead signals; deshielding by proximate chlorine

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* Further, in the mixture of *cis*- and *trans*-alcohols formed by hydride reduction of ketone (X), 7-H is deshielded ($\tau \nless 0{\cdot}3$) in the major *endo*-alcohol component, compared to the position of this signal in the *exo*-alcohol, in accord with expectation.

[8] J. Meinwald, Y. C. Meinwald, and T. N. Baker, *J. Amer. Chem. Soc.*, 1963, **85**, 2513; 1964, **86**, 4074.

[9] (*a*) J. Meinwald and J. Lewis, *J. Amer. Chem. Soc.*, 1961, **83**, 2769; see also however J. Meinwald and Y. C. Meinwald, *ibid.*, 1963, **85**, 2514; (*b*) *cf.* P. Laszlo and P. von R. Schleyer, *ibid.*, 1964, **86**, 1171.

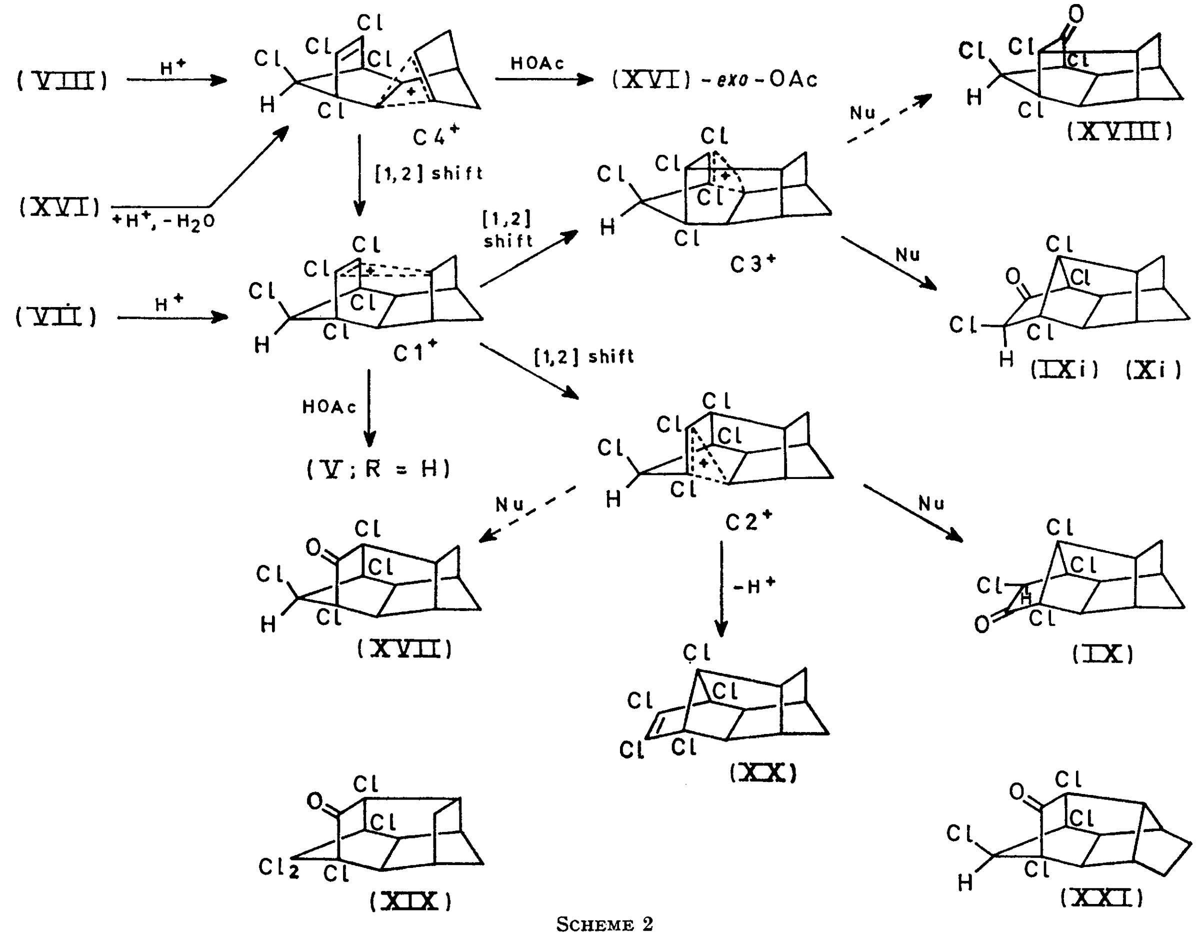
[10] A. F. Thomas and B. Willhalm, *Tetrahedron Letters*, 1965, 1309.

[11] (*a*) A. P. Marchand and J. P. Rose, *J. Amer. Chem. Soc.*, 1968, **90**, 3724; (*b*) J. D. McKinney, L. H. Keith, A. Alford, and C. E. Fletcher, *Canad. J. Chem.*, 1971, **49**, 1993; (*c*) L. H. Keith, A. L. Alford, and J. D. McKinney, *Tetrahedron Letters*, 1970, 2489.

[12] J. C. Davis and T. V. van Auken, *J. Amer. Chem. Soc.*, 1965, **87**, 3900; (*b*) M. C. Thorpe and W. C. Coburn, *J. Org. Chem.*, 1969, **34**, 2576; (*c*) W. P. Lay and K. Mackenzie, *Tetrahedron Letters*, 1970, 3241; *cf.* ref. 9*b*.

has already been referred to above,[13] and the observed upfield shift here is in line with the expectation that it is *anti*-12-Cl (relative to the double bond) which is removed by strong base, and in accord with this the sharp chloromethylene singlet appears at τ 5·71, a value similar to that for the aldrin analogue.[6] The spectra of the acetals (XIIa) and (XIIIa) are otherwise very similar.

The n.m.r. spectrum of ketoaldrin (XII) derived by dechlorination of chloro-ketone (XI) is virtually the same as that reported for this ketone prepared by another method [11b] during the course of this work; this ketone and the novel bridge dechloro-ketone (XIII) have similar spectra but differ from their acetal precursors quite markedly in that the bridgehead multiplets are now deshielded, and move downfield by τ *ca.* 0·5 into the region of the ring junction multiplets. For ketoaldrin the latter appear at τ 7·06 and 7·12 whilst the bridgehead protons resonate at τ 7·2. In the bridge dechloro-analogue (XIII) however the relative positions of these signals is reversed because proximity deshielding by bridge methylene chlorine no longer operates and the signals due to 2- and 7-H therefore move upfield to τ 7·26 and 7·33. In addition changes in geometry consequent on introduction of the carbonyl group allow comparable couplings between both *exo*- and *endo*-10-H and 1-H giving rise to a set of four doublets in this region ($^2J_{gem}$ 16, ^3J 4·0, 4·5 Hz). In confirmation, these sets of doublets disappear in deuterio-ketone (XV).



Scheme 2

In preliminary experiments, reduction of ketone (XIII) and protolytic hydrolysis of the resulting mixture of alcohols gave ketone (IX), and reduction of dideuterioketone (XV) with appropriate reagents similarly gives *endo–exo* epimeric mixtures of alcohols which are used directly in protolysis experiments. For example, stirring carbon tetrachloride solutions of the variously deuteriated alcohols (XVI) with sulphuric (or deuteriosulphuric) acid and direct extraction of the ketonic products gives the deuterio-ketones (IX)-d_2 and (IX)-d_3 as expected from the derived cations in accord with Scheme 2; these ketones are readily epimerised by silica gel into the more stable ketones (X)-d_2 and (X)-d_3. The n.m.r. multiplets for these deuteriated ketones and for (X)-d_1-c, the product of epimerisation–exchange of ketone (IX) in methan[^{2}H]ol are summarised in Table 1, alongside the data for ketones (IX) and (X).

The appearance of a range of common products in comparable amounts in each case from the protolytic hydrolysis of dienes (VII) and (VIII) points to a common source, probably ion C2$^+$ in Scheme 2. Its appearance

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[13] P. M. Subramanian, M. J. Emerson, and N. A. LeBel, *J. Org. Chem.*, 1965, **30**, 2624; *cf.* also refs. 9*a* and 12*b* for discussion of this point.

is implicated by the isolation of ketone (IX) as the most important product rather than ketone (IXi) which could arise from intermediate C3$^+$. Without a knowledge of the relative reactivity of compounds related to the various ions it is not of course possible to comment with certainty on the kinetic–thermodynamic relationships involved. However in a more nucleophilic medium (HOAc–H_2SO_4) ions C1$^+$ and C4$^+$ are almost entirely removed as acetates (V; $R^1 = H$) and (XVI)-*exo*-OAc with *ca.* only 1% of rearranged carbonyl product [$\nu_{max.}$ 1785vs cm^{-1} probably ketone (X)] appearing, suggesting kinetic control. In 98% sulphuric acid on the other hand equilibrium is probably achieved among the various cations and attention then focuses on their relative thermodynamic stabilities. In the absence of the second β-chlorine atom which would characterise the hypothetical aldrin–isodrin derived ion,* intermediate C2$^+$ is intrinsically a more stable species, although there is little to choose between ions C2$^+$ and C3$^+$ on these grounds. Critically perhaps, formation of ion C2$^+$ is accompanied by reduction of Cl–Cl nonbonded interactions present in ions C1$^+$ and C3$^+$ without drastic increase in compression effects between the ring junction and bridge methylene hydrogens; such a compression effect would surely become important in the isodrin analogue of ion C1$^+$ as it underwent the necessary twisting motion to convert it into an ion like C2$^+$ and this may explain at least in part why so few reactions of isodrin with electrophiles give products derived from ions of this type whereas there seems no prohibitive barrier to similar processes in the hydrocarbon systems.[2] As to why ion C4$^+$ so readily converts into ion C1$^+$ is more obscure, save again that the molecular motions may be facilitated compared with *e.g.* the aldrin case, quite apart from the more obvious electronic factors involved.

EXPERIMENTAL

I.r. measurements were made with a Perkin-Elmer 257 instrument for solutions in carbon tetrachloride unless otherwise stated. ^{1}H N.m.r. data, except where indicated, refer to a Varian HA 100 instrument for solutions in deuteriochloroform with tetramethylsilane as internal standard. Computer simulation of the spectrum of ketone (X)-d_3 was accomplished with an ICL 470 computer.† Mass spectra and accurate mass data were obtained with an A.E.I.–G.E.C. MS 902 mass spectrometer using a probe temperature of *ca.* 200° and a beam energy of 70 eV on line to a Linc-8 computer with digital print-out. All ions mentioned had the approximately correct halogen isotope abundance ratios. Preparative t.l.c. was carried out on silica gel ' G ' plates coated to a thickness of 1·0 mm and developed in 1 : 1 dichloromethane–light petroleum. Light petroleum refers to the fraction b.p. 60—80°. M.p.s are not corrected.

Monodechloroisodrin (VII).—The pentachlorotetracyclododecadiene (VII) was prepared essentially by the published method [6] giving from isodrin (18·24 g, 50 mmol) *endo-endo*-3,4,5,6, *syn*-12-pentachlorotetracyclo$[6.2.1.1^{3,6}.0^{2,7}]$dodeca-4,9-diene (VII) (6·5 g, 39%), m.p. and mixed m.p. 130—132°, i.r. and n.m.r. spectra identical with those reported. Compound (VII) was also made by the method of Bienick *et al.*[14]

Monodechloroaldrin (VIII).—Aldrin was similarly reduced by the alternative method of Adams and Mackenzie [6] (*e.g.* for the reductive dechlorination of dieldrin), *viz.* aldrin (3·65 g, 10 mmol) dissolved in dimethyl sulphoxide (50 ml) was treated cautiously while cooled in ice–water with potassium t-butoxide (5·6 g, 50 mmol) after which the mixture was stirred at 60° for 48 h. A markedly cleaner product was obtained by direct extraction of the product with ether than by water quenching and conventional extraction procedures, t.l.c. indicating only traces of unchanged aldrin. The crude product recrystallised from aqueous ethanol gave pure *endo-exo*-3,4,5,6,*syn*-12-pentachlorotetracyclo$[6.2.1.1^{3,6}.0^{2,7}]$dodeca-4,9-diene (VIII) (2·1 g, 64%), m.p. 91—94°, i.r. and n.m.r. spectrum identical with those reported.[6]

Hydrolysis of Monodechloroisodrin (VII) *with Sulphuric Acid.*—Monodechloroisodrin (VII) (330 mg, 1 mmol) was added to concentrated sulphuric acid (10 ml) and the mixture was stirred at 25° for 8 h, then poured onto ice, and the product was extracted with ether. The extracts were washed, dried, and evaporated in the usual way to give after several recrystallisations from chloroform–light petroleum 2,3,exo-4,6-*tetrachloropentacyclo*$[7.2.1.0^{2,6}.0^{3,8}.0^{7,11}]$*dodecan-5-one* (IX) (230 mg, 74%), m.p. 150—152°, $\nu_{max.}$ ($CHCl_3$) 1785vs cm^{-1} (α,α′-coplanar dichlorocarbonyl in a strained ring; no absorption characteristic of ClC=CCl near 1600 cm^{-1}), τ 5·75 (1H, s, 4-H), 6·82br (1H, m, 11-H), 7·00 (1H, dt, *endo*-12-H), 7·27 (1H, m, 9-H), 7·40 (1H, m, 1-H), 7·50 (1H, m, 8-H), 7·60 (1H, m, 7-H), 8·46 (1H, m, 10-H), 8·58 (1H, m, 10′-H), and 8·76 (1H, q, *exo*-12-H) with coupling constants similar to those for ketone (X) (Table 2), *m/e* 310 ($C_{12}H_{10}{}^{35}Cl_4O$).

The Hydrolysis of Monodechloroaldrin (VII) *with Sulphuric Acid.*—In a similar experiment to that above monodechloroaldrin (VIII) (300 mg, 0·99 mmol) dissolved in carbon tetrachloride (1 ml) was stirred with concentrated sulphuric acid (5 ml) for *ca.* 20 h at 25° and the product was isolated by direct extraction with further carbon tetrachloride or dichloromethane, to give, after recrystallisation from carbon tetrachloride, ketone (IX) (200 mg, 70·5%), m.p. 138—150° raised to 150° by further recrystallisation, i.r. and n.m.r. spectra identical with those from the previous experiment.

Alternative Method of Purification of Hydrolysis Products and the Isomerisation of Ketone (IX) *into Ketone* (X).—Monodechloroisodrin (1·0 g, 3 mmol) was stirred with concentrated sulphuric acid (15 ml) for 12 h at 25°, the mixture was quenched in ice, and the organic products were extracted with ether. The neutralised and dried extracts were evaporated and a portion of the crude product (65 mg) was purified by preparative t.l.c. to give, besides four minor components and a little unchanged pentachlorodiene (VII), 2,3,endo-4,6-*tetrachloropentacyclo*$[7.2.1.0^{2,6}.0^{3,8}.0^{7,11}]$*dodecan-5-one* (X) (32 mg); m.p. 165—167°. This compound was shown to be homogeneous and pure by g.l.c., $\nu_{max.}$ ($CHCl_3$) 1785vs cm^{-1} (α,α′-dihalogenocarbonyl), τ 5·44

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* Isodrin survives treatment with concentrated sulphuric acid.

† We thank Mr. J. Scott for an experimental non-iterative multispin computer programme. Data in Tables 1 and 2 were obtained with the LAOCOON 3 programme listed in K. B. Wiberg, ' Computer Programmes for Chemists ', Benjamin, New York, 1965.

[14] D. Bienick, P. N. Moza, W. Klein, and F. Korte, *Tetrahedron Letters*, 1970, 4055.

(1H, s, 4-H), 6·8br (1H, m, 11-H), 7·0 (1H, dt, *endo*-12-H), 7·07 (1H, t, 8-H), 7·30 and 7·35 (each 1H, overlapping m, 1- and 9-H respectively), 7·60 (1H, dq $\longrightarrow$ dt, 7-H), 8·42 (1H, d, 10-H), 8·58 (1H, d, 10′-H), and 8·76 (1H, q, *exo*-12-H) (Found: *m*/*e*, 311·945. $C_{12}H_{10}{}^{35}Cl_3{}^{37}ClO^{+\cdot}$ requires *M*, 311·945).

In a separate experiment, a specimen of ketone (IX) prepared as above (69 mg) was chromatographed on silica gel (5 g.) in dichloromethane–light petroleum to give ketone (X) (65 mg); m.p. and mixed m.p., i.r., and n.m.r. spectra identical with those already found.

Comparative Hydrolysis and Chromatography of Dechloroisodrin (VII) *and Dechloroaldrin* (VIII).—Dechloroisodrin (30 mg) and dechloroaldrin (30 mg) were separately hydrolysed in sulphuric acid (5 ml) and the products isolated as before to give crude ketone (17·3 and 19·2 mg respectively); the two products were chromatographed side by side on a preparative t.l.c. plate. Development of a central strip of the plate showed that the bands from the two mixtures had identical R_F values [except for unchanged dienes (VII) and (VIII)]. Repetitive t.l.c. of the minor components of hydrolysis isolated from recrystallisation liquors gave four compounds (none $>$0·3%); all of these products showed *m*/*e* 310 (or 275, $M - Cl^{+\cdot}$) and one of them also showed *m*/*e* 328 ($C_{12}H_{11}Cl_4O_2{}^{+\cdot}$ or $C_{12}H_9Cl_5{}^{+\cdot}$) possibly the hydrate of an isomer of ketone (X), or else the chlorohydrocarbon (XX). None of these minor products showed τ 8·76 characteristic of ketones (IX) or (X) however and only one of the products showed high frequency carbonyl absorption; the others had $\nu_{\max.}$ 1700—1705 cm^{-1}.

Hydrolysis of Dechloroisodrin (VIII) *with Deuteriosulphuric Acid.*—Dechloroisodrin (300 mg, 0·9 mmol) was stirred under anhydrous conditions with deuteriosulphuric acid (3 ml; 98% D_2SO_4 in 99·5% isotopically pure D_2O) for 12 h and the product was quenched in frozen D_2O (5 g); the organic product (260 mg) was isolated in the usual way and chromatographed by the dry column technique on silica gel in 2 : 1 light petroleum–dichloromethane to give a little unchanged diene (VII) and 2,3,endo-4,6-*tetrachloro*-exo-12-*deuteriopentacyclo*[7.2.1.0^{2,6}.0^{3,8}.0^{7,11}]*dodecan-5-one* (X)-d_1-a (100 mg, 35%), m.p. 166—168°, $\nu_{\max.}$ ($CHCl_3$) 1785vs cm^{-1}, *m*/*e* 311 ($C_{12}H_9D^{35}Cl_4O^{+\cdot}$), n.m.r. spectrum as that of (X) except that the quartet at τ 8·76 is absent.

Hydrolysis of Dechloroaldrin (VIII) *with Deuteriosulphuric Acid.*—Dechloroaldrin (200 mg, 0·6 mmol) was similarly treated with deuteriosulphuric acid (5 ml, as above) for 12 h and the product was isolated as before to give 2,3,endo-4,6-*tetrachloro*-syn-10-*deuteriopentacyclo*[7.2.1.0^{2,6}.0^{3,8}.0^{7,11}]-*dodecan-5-one* (X)-d_1-b (60 mg, 32%), m.p. 165—167°, $\nu_{\max.}$ ($CHCl_3$) 1785vs cm^{-1}, *m*/*e* 311 ($C_{12}H_9D^{35}Cl_4O^{+\cdot}$), n.m.r. spectrum as that of (X) except that resonance for 10′-H is absent.

Reaction of Monodechloroaldrin (VIII) *with Acetic–Sulphuric Acid.*—Monodechloroaldrin (330 mg, 1 mmol) was dissolved in warm acetic acid containing sulphuric acid (20% v/v, 10 ml) and the mixture was heated at 75—80° for 6 h. The mixture was quenched in water, the product isolated by ether extraction, and the neutralised extracts were washed, dried, and evaporated to give an oil which on recrystallisation from carbon tetrachloride–light petroleum afforded exo-endo-3,4,5,6,syn-12-*pentachlorotetracyclo*-[6.2.1.1^{3,6}.0^{2,7}]*dodec-4-en*-exo-9-*yl acetate* (XVI)–OAc (250 mg, 64%), m.p. 159—160°, $\nu_{\max.}$ 1740vs, 1235vs, and 1600ms cm^{-1} (OAc; ClC=CCl), τ 4·26 (1H, d of d, *endo*-9-H,$^3J_{cis}$ 6·5, $^3J_{trans}$ 3 Hz), 5·75 (1H, s, 12-H), 7·48 (2H, m, 1- and 8-H), 7·62 (2H, 2- and 7-H), 7·99 (3H, s, OAc), 8·37 (2H, cm, *exo*- and *endo*-10-H), and 8·62br (2H, s, 11- and 11′-H) identical to the acetate obtained by oxymercuriation of dechloroaldrin (VIII), *m*/*e* 388 ($C_{14}H_{13}{}^{35}Cl_5O_2{}^{+\cdot}$), 353 ($M - Cl^{+\cdot}$), 328 ($M - CH_3CO_2H^{+\cdot}$), 293 ($M - Cl - CH_3CO_2H^{+\cdot}$), 266 ($M - Cl - C_2H_4CO_2CH_3{}^{+\cdot}$, 100%), 258 ($M - HCl_2 - CH_3CO_2H^{+\cdot}$), and 232 ($M - Cl_2 - C_2H_3$-$OCOCH_3{}^{+\cdot}$).

The residues from recrystallisation, examined by i.r. and purified by t.l.c. showed a carbonyl component (*ca.* 1%), $\nu_{\max.}$ 1785vs cm^{-1}, *m*/*e* 310 ($C_{12}H_{10}{}^{35}Cl_4O^{+\cdot}$, 4·8%), 275 ($C_{12}H_{10}{}^{35}Cl_3O^{+\cdot}$, 100%), 247 ($M - COCl^{+\cdot}$, 38·7%), and 113 (38·7%) [*cf.* ketone (X)].

Reaction of Monodechloroisodrin (VII) *with Acetic–Sulphuric Acid.*—In a similar experiment to the above dechloroisodrin (VII) gave 1,9,syn-10,11,exo-12-*pentachloropentacyclo*[7.2.1.0^{2,6}.0^{4,8}.0^{7,11}]*dodecan*-exo-3-*yl acetate* (V; R^1 = H), m.p. 210—212°, no $\nu_{\max.}$ at 1600 cm^{-1}, τ 7·98 (3H, s, OAc) 5·6 (1H, d, 10-H), 4·63 (1H, d, *endo*-12-H), and 4·28 (1H, ct, *endo*-3-H), *m*/*e* 388 ($M^{+\cdot}$) (Found: C, 42·9; H, 3·3. $C_{14}H_{13}Cl_5O$ requires C, 43·05; H, 3·3%).

The Addition of Nitrosyl Chloride to Aldrin and Hydrolysis of the Adduct to Chloroketoaldrin (XI).—Commercial aldrin (22 g, 60 mmol) was dissolved in hot acetic acid (250 ml) and the solution filtered free of a little tarry matter. The filtrate was rapidly chilled to 10° and precooled isoamyl nitrite (20 ml, *ca.* 160 mmol) was added; the solution was briefly and rapidly agitated whilst concentrated hydrochloric acid (20 ml) was introduced. The resulting brown solution was left at 10—15° for 18—20 h, the colouration fading to deep green. Aqueous hydrobromic acid (48% w/v; 100 ml) was then added portionwise with stirring to the heated mixture during a period of 5 h, heating and stirring was continued a further 1 h, and the mixture was allowed to cool overnight. The crystalline product which separated was filtered off, washed with aqueous ethanol (50%), and dried to give endo-exo-3,4,5,6,exo-10,12,12-*heptachlorotetracyclo*[6.2.1.1^{3,6}.0^{2,7}]*dodec*-4-*en*-9-*one* (XI) (21·5 g, 86%), m.p. 193—195°. When recrystallised from ethanol the heptachloro-ketone had m.p. 196—198°, $\nu_{\max.}$ 1760vs and 1600ms cm^{-1} (α,α'-halogenocarbonyl; ClC=CCl) (Found: C, 34·9; H, 1·5. $C_{12}H_7Cl_7O$ requires C, 34·7; H, 1·7%), 2,4-*dinitrophenylhydrazone*, m.p. 241—242° (Found: C, 36·7; H, 1·7. $C_{18}H_{11}Cl_7N_4O_4$ requires C, 36·3; H, 1·9%).

Chloroketoaldrin Ethylene Acetal (XIa).—Chloroketoaldrin (5 g, 12 mmol) was heated in ethylene glycol (100 ml) just below the b.p. for 15 h; on cooling the solution deposited crystals. These were filtered off and, recrystallised from ethanol gave endo-exo-3,4,5,6,exo-10,12,12-*heptachloro*-9,9-*ethylenedioxytetracyclo*[6.2.1.1^{3,6}.0^{2,7}]*dodec-4-ene* (XIa) (4 g, 72%), m.p. 177—178°, $\nu_{\max.}$ 1600vs and 1050vs cm^{-1} (ClC=CCl; O–C–O), τ 6·01 (4H, m, OCH_2CH_2O), 6·40 (1H, d, *J* 3 Hz, *endo*-10-H), 6·67 (1H, d, *J* 8 Hz, 7-H), 7·16 (1H, d, *J* 8 Hz, 2-H), 7·47 (1H m, 1-H), 7·62 (1H, m, 8-H), 8·07 (1H, d), and 8·46 (1H, d, of quint, ^2J 13 Hz, CH_2ABq, the higher field signal coupled to *endo*-10-H ^4J 3 Hz, *syn* to ClC=CCl; irradiation at τ 6·4 caused the d of quint to collapse to a d of t whilst irradiation at τ 8·46 caused the d at τ 6·4 to collapse to an s), *m*/*e* 456 ($C_{14}H_{11}$-$Cl_7O_2{}^{+\cdot}$) (Found: C, 36·6; H, 2·5; Cl, 54·75. $C_{14}H_{11}Cl_7O_2$ requires C, 36·6; H, 2·4; Cl, 54·0%).

Dechlorination of Chloroketoaldrin (XI) *and Formation of Ethylene Acetal* (XIIa).—The chloro-ketone (XI) (4 g, 9·6 mmol) was stirred with zinc dust (3 g, 46 mg-atom) in acetic acid (60 ml) overnight, and the filtrate from the resulting clear mixture was evaporated *in vacuo*. The residual oil solidified and the product, recrystallised from methanol, gave *endo-exo*-3,4,5,6,12,12-hexachlorotetracyclo-$[6.2.1.1^{3,6}.0^{2,7}]$dodec-4-en-9-one (XII) (2·5 g, 68%), m.p. 138° (from light petroleum), $\nu_{max.}$ 1762vs, 1600ms, 1413m, 1040vs, and 1060vs (9-CO; ClC=CCl; $COCH_2$ and C–O) cm^{-1}, τ 7·06 (1H, d, ^3J 8 Hz, 7-H), 7·12 (1H, obscured d, ^3J 8 Hz, 2-H), 7·20 (2H, m, 1- and 8-H), 7·65 and 7·82 (1H, each d, ^3J 4·5, ^2J 16 Hz, *exo*-10-H), 8·12 [1H, d, ^2J 16 Hz, *endo*-10-H, overlapping with 8·14 (1H, d)], and 8·54 (1H, d, ABq), *m/e* 378 ($C_{12}H_8Cl_6O^{+\cdot}$) (Found: C, 38·4; H, 2·1. Calc. for $C_{12}H_8Cl_6O$: C, 37·9; H, 2·1%).[11b]

The ketone (XII) from the previous experiment (4·1 g, 10·7 mmol) was heated in ethylene glycol (75 ml) for *ca.* 24 h, and the solid which deposited on slow cooling of the mixture was separated (4 g, 87·5%) and recrystallised from petroleum gave endo–exo-3,4,5,6,12,12-*hexachloro*-9,9-*ethylenedioxytetracyclo*$[6.2.1.1^{3,6}.0^{2,7}]$*dodec-4-ene* (XIIa), m.p. 118—120°, $\nu_{max.}$ 1600vs, 1440ms, 1090vs, and 1182vs (ClC=CCl; CH_2; and C–O–C) cm^{-1}, τ 6·13 [4H, cm ⟶ A_2B_2, $(OCH_2)_2$] 6·78 (1H, d, J 7·5 Hz, 7-H), 7·25 (1H, d, J 7·5 Hz, 2-H) [*cf.* heptachloro-acetal (XIa)], 7·60 (1H, d, ^3J 4·5 Hz, 1-H), 7·76 (1H, s, 8-H), 8·06 (1H, dd, ^3J 4·5, ^2J 14 Hz, *exo*-10-H coupled to 1-H), 8·49 (1H, d, ^2J 14 Hz, *endo*-10-H), and 8·55 (2H, ABq, ^2J 12 Hz, CH_2 bridge) (Found: C, 39·7; H, 2·85. $C_{14}H_{12}Cl_6O_2$ requires C, 39·6; H, 2·8%).

Reductive Dechlorination of Ketoaldrin Ethylene Acetal (XIIa).—The ethylene acetal (XIIa) (2·29 g, 5 mmol) was dissolved in dimethyl sulphoxide (25 ml) and powdered potassium t-butoxide (2·8 g, 25 mmol) was cautiously added portionwise with external cooling; the resulting deeply coloured mixture was warmed at *ca.* 65° on a water-bath for 48 h, and the product extracted directly from the cooled solution with ether. Washing, drying, and evaporation of the extracts in the usual way followed by recrystallisation of the pale yellow solid product from methanol gave endo-exo-3,4,5,6,syn-12-*pentachloro*-9,9-*ethylenedioxytetracyclo*-$[6.2.1.1^{3,6}.0^{2,7}]$*dodec-4-ene* (XIIIa) (1·1 g, 52%), m.p. 158—159°, $\nu_{max.}$ 1593vs and 1085vs (ClC=CCl; and C–O–C) cm^{-1}, τ 5·71 (1H, s, *anti*-12-H), 6·11 [4H, A_2B_2, $(OCH_2)_2$], 7·00 (1H, d, J 8 Hz, 7-H), 7·46 (1H, d, J 8 Hz, 2-H), 7·53 (1H, d, J 5 Hz, 1-H), 7·68 (1H, s, 8-H), 8·05 (1H, dd, ^2J 14, ^3J 5 Hz, *exo*-10-H), 8·54 (1H, d, ^2J 14 Hz, *endo*-10-H), and *ca.* 8·62 (2H, dd, ABq, ^2J 11 Hz) (Found: C, 43·0; H, 3·35. $C_{12}H_{13}Cl_5O_2$ requires C, 43·05; H, 3·35%).

anti-12-*Dechloroketoaldrin* (XIII).—Pentachloroketone acetal (XIIIa) (1·64 g, 4 mmol) was dissolved in warm acetic acid (15 ml) and hydrobromic acid (15 ml, 48% w/v) was added. The solution was warmed at 60—70° for 45 min during which time solid gradually separated; water was added and the product was filtered off, dried, and recrystallised from aqueous methanol to give endo-exo-3,4,5,6,syn-12-*pentachlorotetracyclo*$[6.2.1.1^{3,6}.0^{2,7}]$*dodec-4-en-9-one* (XIII) (1·4 g, *ca.* 100%), m.p. 128—129°, $\nu_{max.}$ 1760vs, 1600ms, and 1416ms (9-CO; ClC=CCl; $COCH_2$) cm^{-1}, τ 7·27 (1H, d, ^3J 8 Hz, 7-H), 7·33 (1H, d, ^3J 8 Hz, 2-H), 7·10 (1H, d, J 4 Hz, 1-H), 7·16 (1H, s, 8-H), 7·72 (1H, dd, ^2J 16, ^3J 4·5 Hz, *exo*-10-H), 8·15 (1H, dd, ^2J 16, ^3J 4 Hz, *endo*-10-H), 8·16 and 8·50 (2H, each d, ABq, ^2J 12·5 Hz), and 5·66 (1H, s, *anti*-12-H) (Found: C, 41·6; H, 2·45. $C_{12}H_9Cl_5O$ requires C, 41·6; H, 2·6%), *m/e* 344 ($C_{12}H_9Cl_5O^{+\cdot}$).

Reduction of Dechloroketoaldrin (XIII) *and Hydrolysis of Dechloroaldrin Alcohols to give Tetrachloropentacyclododecan-one* (XI).—Ketone (XIII) (600 mg, 1·7 mmol) was dissolved in ether (CaH_2 dried; 25 ml) and lithium aluminium hydride (33 mg, 0·86 mmol) was added; the mixture was stirred at 25° for 20 h, and then worked-up in the usual way to give an epimeric mixture of alcohols (*ca.* 600 mg, *ca.* 100%) as a viscous oil, $\nu_{max.}$ 3630ms and 1600vs (non-bonded OH; ClC=CCl) cm^{-1}, no absorption at 1760 or 1415 cm^{-1} characteristic of C-5-CO and CH_2CO, t.l.c. indicated the two expected components. The mixture of alcohols was dissolved in carbon tetrachloride (1 ml), sulphuric acid (5 ml) was added, and the mixture was vigorously stirred at 20° for 20 h. The product was isolated from the ice-quenched mixture by extraction with carbon tetrachloride or dichloromethane, and the washed extracts were dried and evaporated. The crude product was recrystallised from carbon tetrachloride (charcoal) to give 2,3,*exo*-4,6-tetrachloropentacyclo$[7.2.1.0^{2,6}.0^{3,8}.0^{7,11}]$dodecan-5-one (IX) (230 mg, 43%), m.p. 138—146° raised to 150° by successive recrystallisation, i.r. and n.m.r. spectra identical with those of ketone obtained by similar hydrolysis of dechloroaldrin or dechloroisodrin. This material similarly isomerised into ketone (X) over silica gel.

H–D *Exchange in the Rearrangement of* exo-4-*Chloroketone* (IX) *into the* endo-4-*Chloro-epimer* (X)-d_1-c.—The ketone (IX) (100 mg) was warmed in methan[^{2}H]ol (3 ml, 99·5% isotopically pure) until dissolved and potassium t-butoxide (*ca.* 10 mg) was added; the solution was allowed to stand at 20° for 3·5 h. The crystalline product which appeared within 0·5 h was removed, cautiously washed with methan[^{2}H]ol three times, and dried *in vacuo* to give 2,3,-endo-4,6-*tetrachloro*-exo-4-*deuteriopentacyclo*$[7.2.1.0^{2,6}.0^{3,8}.0^{7,11}]$*dodecan-5-one* (X)-$d_1$-c (*ca.* 50 mg), m.p. 164°, n.m.r. spectrum identical to that of ketone (X) save for the extremely weak, virtually absent, sharp singlet at τ 5·4 (*exo*-4-H), τ 5·8 characteristic of ketone (IX) absent, *m/e* 311 ($C_{12}H_9DCl_4O^{+\cdot}$).

H–D *Exchange with Dechloroketoaldrin* (XIII).—The ketone (XIII) (600 mg, 1·7 mmol) was dissolved in methan-[^{2}H]ol (15 ml) and potassium t-butoxide (50 mg) was added. The solution was left at 20—25° overnight, then neutralised with solid CO_2, excess of methan[^{2}H]ol was distilled off, and the residual product was taken up in carbon tetrachloride. The solution was rapidly filtered and evaporated *in vacuo* to give endo-exo-3,4,5,6,syn-12-*pentachloro*-10,10-*dideuterio-tetracyclo*$[6.2.1.1^{3,6}.0^{2,5}]$*dodec-4-en-9-one* (XV) (600 mg, 100%), m.p. 125—126°, $\nu_{max.}$ 2230w, 1760vs, and 1598vs (C–D str; C-9-CO; ClC=CCl) cm^{-1} (no absorption characteristic of CH_2CO near 1415 cm^{-1}), τ 5·71 (s, *anti*-12-H), 7·18 (2H, m, 1- and 8-H), 7·30 (1H, d, ^3J 8 Hz, 2-H), and 7·36 (1H, d, ^3J 8 Hz, 7-H), and 8·21 and 8·55 (2H, each d, ABq, ^2J 12·5 Hz), signals due to *endo* and *exo*-10-H in ketone (XIII) completely absent, *m/e* 346 ($C_{12}H_7D_2Cl_5O^{+\cdot}$).

2,3,endo-4,6-*Tetrachloro*-10,10-*dideuteriopentacyclo*$[7.2.1.0^{2,6}.0^{3,8}.0^{7,11}]$*dodecan-5-one* (X)-$d_2$.—Dideuterio-ketone (XV) (348 mg, 1 mmol) was dissolved in ether (15 ml, as above) and lithium aluminium hydride (15 mg, 0·4 mmol) was added. The mixture was left for 1 h at 25°, then after a brief period of warming was quenched, and the product was isolated in the usual way. The resulting crude epimeric mixture of alcohols was dissolved in carbon tetrachloride (1 ml), sulphuric acid (5 ml) was added, and the mixture was vigorously stirred for 24 h. The ketonic product was isolated as before and purified by chromatography on silica gel using the dry column technique, giving *compound* (X)-d_2 (140 mg, 45%), m.p. 165—166°, $\nu_{max.}$

($CHCl_3$) 2240w, 2135w, and 1783vs (C–D str; 5-CO α,α′-dihalogenated) cm^{-1}, τ 5·43 (1H, s, 4-H), 6·80 (1H, m, 11-H), 7·00 (1H, dm, *endo*-12-H), 7·07 (1H, t, 8-H), 7·30 (1H, m, 1-H), 7·34 (1H, m, 9-H), 7·60 (1H, dq, 7-H), and 8·76 (1H, q, *exo*-12-H), assignments as for (X)-d_3 except for τ 6·80 absent in latter, *m/e* 312 ($C_{12}H_8D_2{}^{35}Cl_4O^{+\cdot}$).

2,3,exo-4,6-*Tetrachloro*-10,10,11-*trideuteriopentacyclo*[7.2.1.-$0^{2,6}.0^{3,8}.0^{7,11}$]*dodecan-5-one* (IX)-d_3 *and its* endo-4-*Chloro-epimer* (X)-d_3.—Dideuterio-ketone (XV) (348 mg, 1 mmol) was dissolved in dry ether (10—15 ml, as above), lithium aluminium deuteride (15 mg, 0·35 mmol) was added, and the mixture was left for 1 h at 25° in a dry-box under nitrogen. The reaction was terminated and the product isolated in the usual way. The epimeric mixture of alcohols was dried *in vacuo* and had $\nu_{max.}$ 3620ms, 3420m, 2130 and 2230w, 1598vs, and 1280vs (nonbonded and bonded OH; C–D str; ClC=CCl; OH def. and C–O str) cm^{-1}. Without further purification the product was dissolved in carbon tetrachloride (0·5 ml), deuteriosulphuric acid (5 ml, as above) was added, and the mixture, which formed an emulsion, was vigorously stirred for 20 h at 25° with rigorous exclusion of moisture. The product was directly extracted from the mixture with portions of carbon tetrachloride and the extracts were washed with deuterium oxide (2 ml), dried, and evaporated to small bulk whereupon crystals separated to give *compound* (IX)-d_3 (*ca.* 60 mg, 19·2%), m.p. 138—145 raised to 150—152° by successive recrystallisation from chloroform–light petroleum, $\nu_{max.}$ ($CHCl_3$) 2235w, 2120w, and 1785vs (C–D str; 5-CO) cm^{-1}, n.m.r. spectrum as anticipated, *m/e* 313 ($C_{12}H_7D_3{}^{35}Cl_4O^{+\cdot}$).

T.l.c. showed that the liquors from the above preparation contained mainly (X)-d_3 and traces of three other components. The combined crystals and liquors was chromatographed in 1 : 1 dichloromethane–light petroleum on a dry silica gel column, and after foreruns and fractions containing low m.p. product (10 mg) several fractions gave *compound* (X)-d_3 (75 mg, 24%), m.p. 164—165°, $\nu_{max.}$ 2240w, 2120—2140w, and 1783vs [as for *exo*-chloro-isomer (IX)-d_3 above] cm^{-1}, τ 7·00 (1H, dd, *endo*-12-H) (this pair of doublets much sharper than in the dideuterio- and protio-analogues suggesting ^4J coupling to 11-H), elsewhere as anticipated, *m/e* 313 ($M^{+\cdot}$) closely similar to the mass spectrum of isomer (IX)-d_3 above.

Hydride Reduction of Tetrachloropentacyclododecanone (X).—The ketone (X) (150 mg, 0·5 mmol) dissolved in dry ether (5 ml) was treated with lithium aluminium hydride (20 mg, *ca.* 0·5 mmol) for 1 h at 25° and the product was isolated in the usual way, dried, and dissolved in carbon tetrachloride; the solution showed $\nu_{max.}$ 3590s, 3380s, 1120—1130vs, 1290, and 1310ms [nonbonded and bonded OH; OH and CO frequencies with no absorption at 1785 cm^{-1} characteristic of ketone (X)] cm^{-1}, τ 5·34 (1H, d) and 5·61 (1H, d, ^3J 9—10 Hz, *cis*-CHCl·CHOH 75%), 5·53 (d) and 5·95 (d, ratio 1 : 1, ^3J 3 Hz, *trans*-CHCl·CHOH 25%) (couplings confirmed at 60 MHz), 7·04 (m), 7·16 (m), 7·38 (6H, 1-, 7-, 8-, 9-, 11-, and *endo*-12-H), 8·51 (1H, d, ABq), and 8·69 (1H, d, ABq), and 8·87 (1H, q, *exo*-12-H), signals shifted to higher field in the absence of the carbonyl group.

In a similar experiment with ketone (X) using lithium aluminium deuteride the mixed alcohol product showed $\nu_{max.}$ 3590ms, 2190vw, and 1260vs (nonbonded OH; C–D str; OH or CO freq.) cm^{-1}, τ 5·34(s) and 5·53(s) (ratio 4 : 1 *cis*- and *trans*-CHCl·CDOH) with other significant signals identical to those in the mixture of protio-analogues, spectra superimposable, also τ 6·98 (cm, 11-H), 7·11 (dt, 12-H), *ca.* 7·34 (cm, 9-H), 7·23—7·43 (cm, 1-, 7-, and 8-H), 7·59 (s, OH) 7·76 (dq, 7-H in *trans*-isomer), *ca.* 8·63 (CH_2 ABq), and 8·86 (q, *exo*-12-H). Dry column chromatography on silica gel failed adequately to separate the two isomers, m.p. 110°, *m/e* 313 ($C_{12}H_{11}DCl_4O^{+\cdot}$).

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