The Remarkable Transformation of Fused-ring Norbornene Bridge-methylene Alcohols into a Product identified by *X*-Ray Diffraction as containing the Novel Tetracyclo[5.3.1.$0^{2,6}$.$0^{5,9}$]undecene System

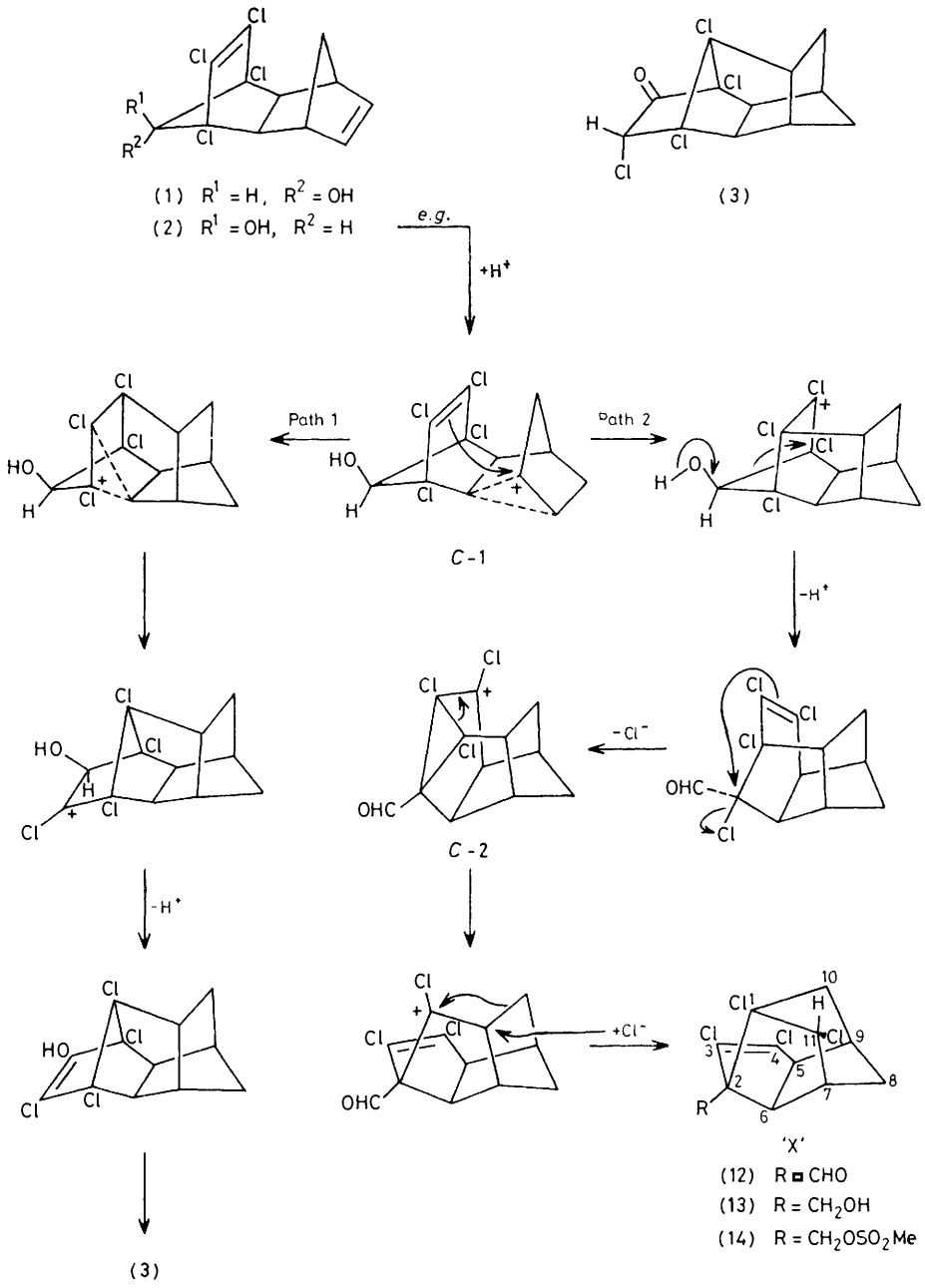
By **Kevin A. Mead, Kenneth Mackenzie,* and Peter Woodward,** School of Chemistry, The University, Bristol BS8 1TS

Treatment of *anti-* and *syn*-epimers (1) and (2) of *exo-endo*-3,4,5,6-tetrachlorotetracyclo[6.2.1.$1^{3,6}$.$0^{2,7}$]dodeca-4,9-dien-11-ol with H_2SO_4–CCl_4 gives besides the previously recognised tetrachloropentacyclododecanone (3) small but significant amounts of 1,3,4,11-tetrachloro-2-formyltetracyclo[5.3.1.$0^{2,6}$0.^{5,9}]undec-3-ene (12), an apparently novel ring system derived by a new rearrangement sequence. The structure of tetrachlorotetracycloundecene (12) follows from the *X*-ray crystal structure of the methanesulphonate (14) of its simple 2-hydroxymethyl reduction product. ^1H and ^{13}C n.m.r. characteristics of (12), its various deuteriated analogues, and their synthesis are discussed.

THE effect of substituents on the rearrangement and cyclisation modes of bridged polycyclic π-proximate cations has been the subject of both theoretical [1] and experimental investigation. We have previously reported the results of using *e.g.* bridge-methylene alcohols (1) and (2) as substrates in acid-catalysed reactions. Treatment of either *anti-* or *syn*-tetrachlorotetracyclododecadienol (1) or (2) with H_2SO_4–CCl_4 gives (in somewhat variable yield) two well defined products; one of these has been shown to be tetrachloropentacyclododecanone (3), the product of a reaction sequence involving cross-cyclisation in the relevant face-proximate π-C_{2p} cation as illustrated in Scheme 1 (path 1).[2] The second product is a compound ' X ', $C_{12}H_{10}Cl_4O$, isomeric with ketone (3), shown below to be compound (12), m.p. 139—140 °C, *m/e* 310 ($M^{+\cdot}$), 282 (M − $CHO^{+\cdot}$), and 113 ($C_6H_6Cl^{+\cdot}$) whose identity as an unsaturated aldehyde is confirmed by i.r. and n.m.r. data, $\nu_{max.}$ 2 870—2 875s and 2 720—2 730w (CHO), 1 718vs (C=O st.), and 1 620ms cm^{-1} (ClC=CCl), τ_H −0.25 (d, J *ca.* 0.6 Hz, CHO) (A), δ_C 198.3 (CHO), 129.9, and 122.5 p.p.m. (quaternary, = CCl). The offset-decoupled ^{13}C spectrum of aldehyde (12), besides displaying signals confirming these assignments, also clearly indicates chloromethylene (76.14 p.p.m., >CHCl), saturated methine (56.8, 54.5, 44.8, and 36.9 p.p.m., >CH), methylene (41.9 and 43.1 p.p.m., $>CH_2$), and saturated quaternary (71.0 and 70.9 p.p.m., >CCl, >CCHO) carbon atoms. In the ^1H resonance spectrum other counterpart signals † appear at τ 5.66 (s, CHCl) (B), 6.05 (tnd) (C), 7.08 (dd) (D), 7.32 (tnm) (E), and 7.62 (cm) (four >CH) (F), and partially resolved overlapping signals due to two $>CH_2$ groups at 7.68 (t), 7.75 (t) (G), 7.91 (nq), 7.98 (nm) (H), and 8.0 (cm) (I).

Precedent exists [3] for the extrusion of hydroxylated bridge-methylene as a formyl group in the acid-catalysed rearrangement of dieldrin (4), and a similar ring-scission must account for the formyl group in aldehyde (12) since protolysis of [11-^2H]-(1) and/or [11-^2H]-(2) gives product [12-^2H]-' X ' with no significant ^1H n.m.r. signal near τ −0.25 (^2HCO). However, whilst rearrangement of dieldrin *via* a half-cage cation intermediate *C*-3 is initiated by electrophilic attack at the oxiran ring, followed by 1,2 (Wagner–Meerwein) rearrangement, parallel cyclisation, and hydride transfer, the protolytic rearrangement of (1) and (2) *is* initiated by protonation of the remote unsubstituted 9,10-olefinic group, implicating intermediate *C*-1 in the first step, in common with the transformation into ketone (3). This is most clearly seen if the reactions are carried out in $^2H_2SO_4$–CCl_4. The mass spectrum and ^1H and ^{13}C resonance spectra of the monodeuteriated aldehyde product [^2H]-(12) $C_{12}{}^1H_9{}^2H$ Cl_4O [*m/e* 311 ($M^{+\cdot}$), 282 (M − $CHO^{+\cdot}$), and 114 ($C_6{}^1H_5{}^2HCl$)] clearly indicate deuteriation of one of the $>CH_2$ groups; the ^1H signal near τ 8.0 is simplified and reduced in intensity (the remaining signals, surprisingly, appearing little affected by this substitution). In the ^{13}C range all signals for the monodeuterioaldehyde virtually coincide with those in the decaprotio-compound except for the $>CH_2$ signal at δ 41.9 p.p.m.; this appears as an isotope-shifted $>C{}^1H{}^2H$ triplet (40.6, 41.5, and 42.4 p.p.m. due to C–^2H coupling) with residual $>C{}^1H_2$ resolved at δ 41.9 p.p.m. Further information about the genesis and structure of aldehyde (12) is obtained by $^1H_2SO_4$ or $^2H_2SO_4$ treatment of the readily accessible di- and more difficulty accessible tetra-deuterioalcohols (10) and (11) (Scheme 2) as alternative sources of cation intermediate *C*-1 implicated in the rearrangement. Protolysis of dideuterioalcohol mixture (10) gives aldehyde [$^2H_2$]-(12), $C_{12}{}^1H_8{}^2H_2Cl_4O$ [*m/e* 312 ($M^{+\cdot}$), 282 (M − $^2HCO^{+\cdot}$), and 114 ($C_6{}^1H_4{}^2HCl$)]; at 100 MHz, ^1H resonance signals (A)—(I) characteristic of the decaprotioaldehyde are absent or significantly modified as follows: (A), absent; (C), collapses from tnm to dnm; (E), very weak. Other signals are little affected or show only slightly modified resolution. A similar reaction with tetradeuterioalcohol (11) gives aldehyde [$^2H_4$]-(12), $C_{12}{}^1H_6{}^2H_4Cl_4O$ [*m/e* 313 (314), 284 (283), 116 (115) ≮ 60%. $^2H_4$ compound], τ_H (220 MHz) −0.25 (d, J *ca.* 0.6 Hz, residual CHO) (A), 5.67 (sharp s, CHCl) (B), 6.05 (dnm, J 6.8, 1.07 Hz) (C), 7.09 (qnd, J 6.8, 3.5, 0.6 Hz) (D), (E)

† Unless otherwise stated all signals are of the correct relative intensity; chemical shift (τ) and apparent multiplicities refer to 220 MHz spectra; d = doublet, m = multiplet, n = narrow, q = quartet, c = complex.



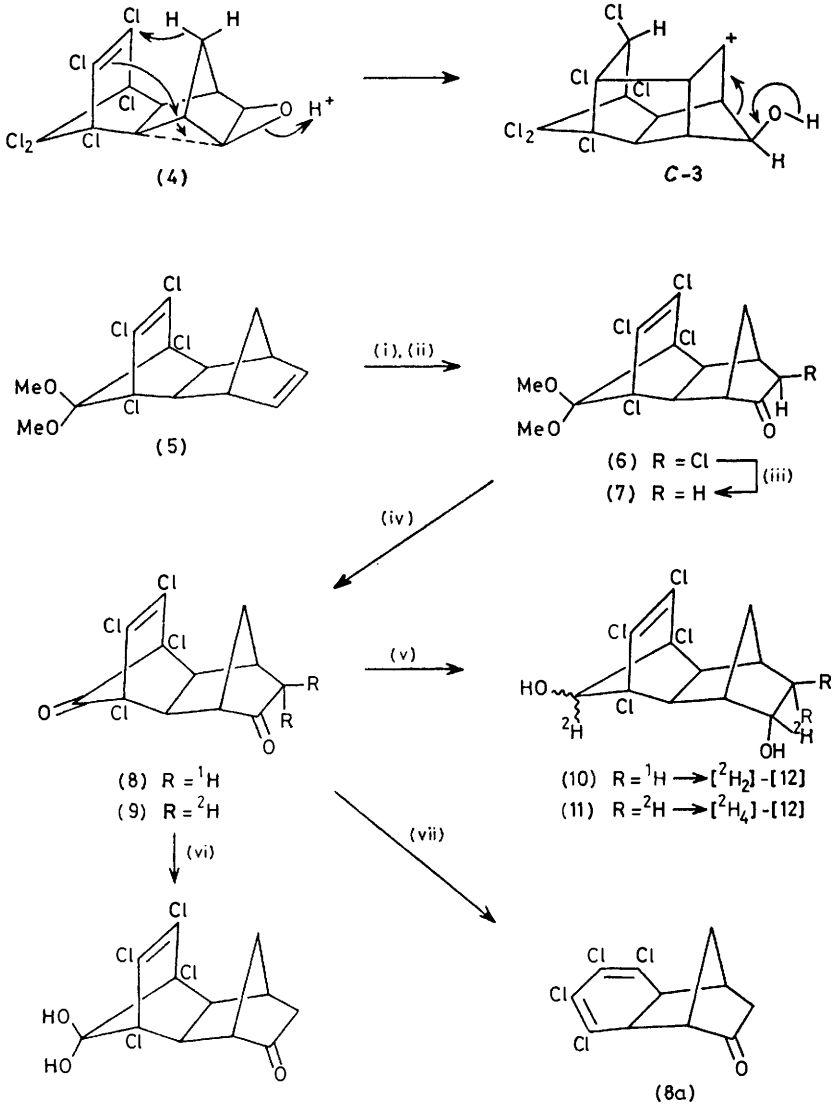
SCHEME 1

absent, 7.61 (cm) (F) (reduced complexity). One $\rangle CH_2$ group signal is cleanly resolved into two pairs of quartets at τ_H 7.68, 7.75 (^2J 13.7, other J 3.5, 2.1 Hz) (G) and 7.91, 7.98 (^2J 13.7, other J 2.1, 1.07 Hz) (H). The other $\rangle CH_2$ group signal (I) reduces to a broadened singlet of drastically reduced intensity (residual $\rangle C^1H_2$).

Attempted rationalisation of these data with possible structures for (12) deriving from familiar rearrangement processes [2,4] for cations related to *C*-1 proves elusively difficult.* However it does seem clear that the mono- and bis-deuteriated carbons in the non-chlorinated ring in substrate alcohol (11) become methine and methylene carbons in the aldehyde product (12). It follows that the initial sequences in the acid-catalysed reaction *are* protonation with concomitant Wagner–Meerwein rearrangement, as in the genesis of ketone (3), with cyclisation and then further rearrangement–ring scission.

One other important structural observation is that $LiAlH_4$–Et_2O converts aldehyde [12-^{2}H]-(12) into a primary alcohol (13) [τ_H 5.35 (d), and 8.30 (d, J *ca.* 8 Hz, C^1H^2HOH)] in which signal (C) shows the largest upfield

* For example, almost all reasonably derived structures employing mechanistic precedent suggest the $\rangle CHCl$ group might result from hydride transfer, and in the product the ^{1}H signal (B) would be expected to show at least small couplings at high resolution.



SCHEME 2 *Reagents*: (i) $^tC_5H_{11}ONO$–HCl–HOAc; (ii) aq.HBr–HOAc; (iii) Zn–HOAc–Et_2O; (iv) $^1H_2SO_4$ *or* MeO^2H–Bu^tO^- (0.3%) then $^2H_2SO_4$; (v) $LiAl^2H_4$–Et_2O; (vi) H_2O–H^+; (vii) heat, –CO

shift (+0.3 p.p.m.) whilst retaining its general appearance; in the presence of $Pr(fod)_3$ (8.1 : 1 mol. ratio) this signal is also the most strongly affected in (13) ($\Delta\tau$ +2.4) followed by (D), (E), and (B) ($\Delta\tau$ +0.7, +0.6, +0.4).

Aldehyde (12) fails to produce satisfactory crystals for an *X*-ray diffraction study but fortunately the methanesulphonate (14) of its reduction product (13) forms excellent monoclinic needles; the results of an *X*-ray crystallographic structural determination are summarised in Tables 1—3 and the structure of the methanesulphonate ester (14) is illustrated in Figures 1 and 2.

The carbon skeleton of the molecule comprises a system of three fused five-membered rings which all have the tetrahedral atom C(6) in common. All three rings are of non-planar ' envelope ' conformation, but in the case of ring C(2)—C(6) the presence of a double bond between atoms C(3) and C(4), each of which carries a substituent chlorine atom, causes the fragment C(2), C(3), Cl(3), C(4), Cl(4), and C(5) to be planar. All the remaining C atoms in the molecule are tetrahedral. The bond C(2)–C(6) is common to this ring and to the ring C(2), C(6), C(7), C(11), C(1). In this latter ring, atoms C(1) and C(11) each carry chlorine atom substituents which make a torsion angle Cl(11)–C(11)–C(1)–Cl(1) of 49.0° (see Table 3). Atoms C(2), C(6), C(7), and C(11) are, however, coplanar (torsion angle —0.3°). In this ring the bond C(6)–C(7) is common to the adjoining ring C(6)—C(9), C(5), where it is found that atoms C(5)—C(8) are substantially coplanar (torsion angle —4.0°). The bond C(5)–C(6) is, of course, common to the first ring C(2)—C(6).

The orientation of the CH_2OSO_2Me chain is presumably determined mainly by the weak intra- and intermolecular forces of the molecular array in the crystal. Interestingly the methylene protons of the CH_2OSO_2Me group appear as a well separated pair of doublets at

τ 4.68 (d) and 5.5 (d, *J* 11 Hz) in the ^{1}H resonance spectrum of the methanesulphonate, and whilst this is possibly due to their diastereoisotopic nature it could also be due to restricted rotation of the group on account of the proximate chlorine atoms Cl(1), Cl(3), and Cl(11). The

TABLE 1

Atomic positional (fractional co-ordinates) parameters with estimated standard deviations in parentheses for $C_{13}H_{14}Cl_4O_3S$

Atom	*x*	*y*	*z*
Cl(1)	0.420 90(9)	0.757 63(4)	0.413 16(5)
Cl(3)	0.584 23(11)	0.961 82(4)	0.370 54(7)
Cl(4)	1.007 69(11)	0.946 60(5)	0.340 10(7)
Cl(11)	0.327 40(8)	0.661 08(4)	0.165 73(6)
S	0.250 07(7)	0.956 91(3)	0.032 82(5)
O(1)	0.410 5(3)	0.904 93(13)	0.089 56(14)
O(2)	0.089 9(3)	0.919 35(11)	0.050 6(2)
O(3)	0.282 4(3)	0.969 48(11)	−0.080 73(15)
C(1)	0.574 1(4)	0.752 02(14)	0.313 6(2)
C(2)	0.566 7(3)	0.825 06(14)	0.233 2(2)
C(3)	0.673 4(4)	0.893 49(15)	0.289 4(3)
C(4)	0.841 1(4)	0.887 8(2)	0.277 8(3)
C(5)	0.872 7(4)	0.813 0(2)	0.216 5(3)
C(6)	0.688 4(4)	0.791 94(14)	0.150 7(2)
C(7)	0.675 7(4)	0.699 77(15)	0.152 2(2)
C(8)	0.859 7(4)	0.674 2(2)	0.211 5(3)
C(9)	0.902 4(4)	0.741 6(2)	0.297 4(3)
C(10)	0.763 4(4)	0.743 38(15)	0.379 3(2)
C(11)	0.548 2(4)	0.680 02(14)	0.235 5(3)
C(12)	0.383 3(4)	0.850 32(15)	0.180 0(3)
C(13)	0.279 1(4)	1.044 43(15)	0.109 8(3)
H(5)	0.982(7)	0.824(3)	0.175(4)
H(6)	0.662(4)	0.815(2)	0.066(3)
H(7)	0.635(4)	0.663(2)	0.082(3)
H(8A)	0.928(5)	0.669(3)	0.148(4)
H(8B)	0.854(5)	0.623(2)	0.244(3)
H(9)	1.009(5)	0.743(2)	0.332(3)
H(10A)	0.781(5)	0.786(2)	0.428(3)
H(10B)	0.762(5)	0.700(2)	0.420(3)
H(11)	0.571(5)	0.628(3)	0.277(3)
H(12A)	0.338(4)	0.883(2)	0.232(3)
H(12B)	0.321(6)	0.809(3)	0.144(4)
H(13A)	0.271(6)	1.032(3)	0.191(4)
H(13B)	0.390(6)	1.068(3)	0.110(4)
H(13C)	0.179(4)	1.077(2)	0.077(3)

^{1}H signals (B)–(I) in the aldehyde (12) become recognisable as those due to H(11), H(6) [deshielded compared to allylic H(5) by the electronegative environment], H(5) (allylic), H(7), H(9) (multiple couplings), H(10) (*syn* to ClC=CCl), H(10) (*anti* to ClC=CCl), and H(8,8′) (CH_2 AB system with further couplings) respectively. These results unequivocally indicate aldehyde (12) to be 1,3,4,11-tetrachloro-2-formyltetracyclo[5.3.1.0^{2,6}.0^{5,9}]-undec-3-ene which to the best of our knowledge has no analogues.*

Details of the mechanism of formation of the aldehyde (12) from alcohols (1) and (2) remain to be worked out but one possible reaction scheme consistent with the data above is illustrated in Scheme 1 (path 2); this implies that parallel cyclisation in cation *C*-1 competes significantly in this system with cross-cyclisation ultimately leading to ketone (3) *via* path 1, and that energetic advantage not unnaturally † derives from formation of stereoelectronically favourable cyclopropylmethyl cation *C*-2. Diversity in cyclisation pathways has been observed in other face-proximate π-C_{2p} cation ring closures [6] but is rare in halogenated systems of the type

* The compound could be considered to be an *endo*-methanotetrahydrotriquinacene; [5] with the functionality present an interesting speculation concerns its possible conversion into triquinacene derivatives.

TABLE 2

Bond lengths (Å) and inter-bond angles (°) with estimated standard deviations in parentheses for $C_{13}H_{14}Cl_4O_3S$

(i) Distances

Cl(1)–C(1)	1.796(3)	Cl(3)–C(3)	1.719(3)
Cl(4)–C(4)	1.704(3)	Cl(11)–C(11)	1.802(3)
S–O(1)	1.533(2)	S–O(2)	1.432(2)
S–O(3)	1.426(2)	S–C(13)	1.744(3)
O(1)–C(12)	1.461(3)	C(1)–C(2)	1.563(3)
C(1)–C(10)	1.551(3)	C(1)–C(11)	1.532(3)
C(2)–C(6)	1.551(4)	C(3)–C(2)	1.519(3)
C(3)–C(4)	1.321(4)	C(4)–C(5)	1.504(4)
C(5)–C(9)	1.545(4)	C(6)–C(5)	1.553(3)
C(6)–C(7)	1.571(3)	C(7)–C(8)	1.544(4)
C(9)–C(8)	1.537(4)	C(10)–C(9)	1.552(4)
C(11)–C(7)	1.533(4)	C(12)–C(2)	1.518(3)
C(5)–H(5)	1.05(6)	C(6)–H(6)	1.08(3)
C(7)–H(7)	1.05(3)	C(8)–H(8A)	0.98(4)
C(8)–H(8B)	0.95(4)	C(9)–H(9)	0.87(3)
C(10)–H(10A)	0.93(4)	C(10)–H(10B)	0.88(4)
C(11)–H(11)	1.02(4)	C(12)–H(12A)	0.94(3)
C(12)–H(12B)	0.92(4)	C(13)–H(13A)	1.00(4)
C(13)–H(13B)	0.94(5)	C(13)–H(13C)	0.98(3)

(ii) Angles

O(1)–S–O(2)	108.7(1)	O(1)–S–O(3)	104.5(1)
O(2)–S–O(3)	119.0(1)	O(1)–S–C(13)	102.9(1)
O(2)–S–C(13)	110.3(1)	O(3)–S–C(13)	110.0(1)
S–O(1)–C(12)	118.6(2)	Cl(1)–C(1)–C(2)	113.3(2)
Cl(1)–C(1)–C(10)	109.5(2)	C(2)–C(1)–C(10)	109.1(2)
Cl(1)–C(1)–C(11)	113.9(2)	C(2)–C(1)–C(11)	106.0(2)
C(10)–C(1)–C(11)	104.8(2)	C(1)–C(2)–C(3)	111.9(2)
C(1)–C(2)–C(6)	97.4(2)	C(3)–C(2)–C(6)	102.6(2)
C(1)–C(2)–C(12)	115.1(2)	C(3)–C(2)–C(12)	111.8(2)
C(6)–C(2)–C(12)	116.7(2)	Cl(3)–C(3)–C(2)	122.0(2)
Cl(3)–C(3)–C(4)	126.0(2)	C(2)–C(3)–C(4)	111.6(2)
Cl(4)–C(4)–C(3)	126.4(2)	Cl(4)–C(4)–C(5)	122.7(2)
C(3)–C(4)–C(5)	110.2(2)	C(4)–C(5)–C(6)	103.7(2)
C(4)–C(5)–C(9)	112.5(2)	C(6)–C(5)–C(9)	99.7(2)
C(2)–C(6)–C(5)	100.9(2)	C(2)–C(6)–C(7)	108.0(2)
C(5)–C(6)–C(7)	106.2(2)	C(6)–C(7)–C(8)	103.4(2)
C(6)–C(7)–C(11)	105.8(2)	C(8)–C(7)–C(11)	106.0(2)
C(7)–C(8)–C(9)	100.5(2)	C(5)–C(9)–C(8)	100.1(2)
C(5)–C(9)–C(10)	108.9(2)	C(8)–C(9)–C(10)	109.5(2)
C(1)–C(10)–C(9)	111.7(2)	Cl(11)–C(11)–C(1)	116.6(2)
Cl(11)–C(11)–C(7)	113.1(2)	C(1)–C(11)–C(7)	100.4(2)
O(1)–C(12)–C(2)	105.0(2)		

TABLE 3

Selected torsion angles (°) for compound (14)

Cl(1)–C(1)–C(2)–C(12)	−47
Cl(1)–C(1)–C(11)–Cl(11)	49
Cl(1)–C(1)–C(10)–C(9)	−178
Cl(3)–C(3)–C(4)–Cl(4)	0
Cl(3)–C(3)–C(2)–C(1)	−88
Cl(4)–C(4)–C(5)–H(5)	−36
H(11)–C(11)–C(7)–H(7)	76
H(7)–C(7)–C(8)–H(8B)	−66
H(8B)–C(8)–C(9)–H(9)	72
H(9)–C(9)–C(10)–H(10B)	−69
H(10B)–C(10)–C(1)–C(11)	−64
H(5)–C(5)–C(6)–H(6)	−28
H(6)–C(6)–C(7)–H(7)	−6

† The striking effectiveness of the cyclopropylmethyl π-system in providing a demonstrably accessible stable refuge in otherwise mechanistically demanding polycyclic cation rearrangements has recently been revealed. L.R. Schmitz and T.S. Sorensen, *Tetrahedron Lett.*, 1981, **22**, 1191.

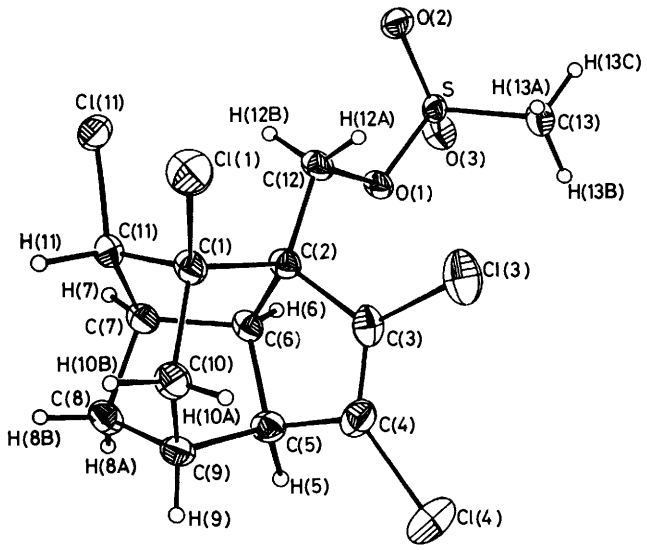


FIGURE 1 Molecular structure of $C_{13}H_{14}Cl_4O_3S$ with the crystallographic numbering system. The numbering of the carbon skeleton of the molecule follows the normal conventions of organic nomenclature

discussed here. Usually, only one of the two cyclisation modes, *either* cross *or* parallel, is observed;[2] in the experiments described here aldehyde (12) is the major isolated product, the actual product ratio being somewhat variable, but often (12) : (3) is *ca.* 2 : 1. However, the ratio of isolated products may not be a reliable guide to the actual relative importance of the alternative cyclisation pathways since the reaction is accompanied by considerable degradation, and some tarry and highly coloured by-products of unknown nature are also produced.

using a Unicam SP8-200 spectrometer. T.l.c. refers to preparative chromatography on 0.8 mm silica gel GF_{254} coated plates. H_2SO_4 is 98% w/v H_2SO_4–H_2O. $^2H_2SO_4$ and $LiAl^2H_4$ refer to materials of 99.8% isotopic purity. M.p.s are not corrected.

Crystal-Structure Determination.—Crystals of the compound (14) grow as needles elongated along *a*. Diffracted intensities were collected at 220 K from a prism (cut from a large needle) of dimensions 0.4 × 0.2 × 0.2 mm on a Nicolet *P3m* four-circle diffractometer. Of the total of 5 177 reflections measured for 2θ to 60°, 3 396 which satisfied the criterion $I \geqslant 6.0\sigma(I)$ were corrected for Lorentz, polarisation, and absorption effects and were used in the solution and refinement of the structure. Remeasurement of two check reflections every 50 reflections showed no significant crystal decay.

Crystal Data.—$C_{13}H_{14}Cl_4O_3S$, M = 392.1, monoclinic, a = 7.693(5), b = 17.007(4), c = 11.894(4) Å, β = 98.78(4)°, D_m (aqueous flotation) = 1.64 g cm^{-3}, Z = 4, D_c = 1.69 g cm^{-3}, U = 1 538(1)Å^3, $F(000)$ = 800, space group $P2_1/n$ (non-standard setting of $P2_1/c$, No. 14), Mo-K_α X-radiation (graphite monochromator), $\bar{\lambda}$ = 0.710 69 Å, μ(Mo-K_α) = 9.1 cm^{-1}.

Structure Solution and Refinement.—The chlorine atoms were located by vector methods, and all other atoms (including hydrogen) by electron-density difference syntheses. The structure was refined by blocked-cascade least-squares, with isotropic thermal parameters for the hydrogen atoms and anisotropic thermal parameters for all other atoms. A weighting scheme of the form $w = [\sigma^2(F) + 0.0014\ (F)^2]^{-1}$ [where $\sigma(F)$ is the estimated error in $F_{obs.}$ based on counting statistics only] gave a satisfactory analysis of variance. Convergence was reached at R 0.042 (R' 0.049), and the final electron-density difference synthesis showed no peaks >0.8 or <−0.5 eÅ^{-3}, the largest being in the neighbourhood of the chlorine atoms. Atomic scattering factors were from ref. 7 for hydrogen and from ref. 8 for

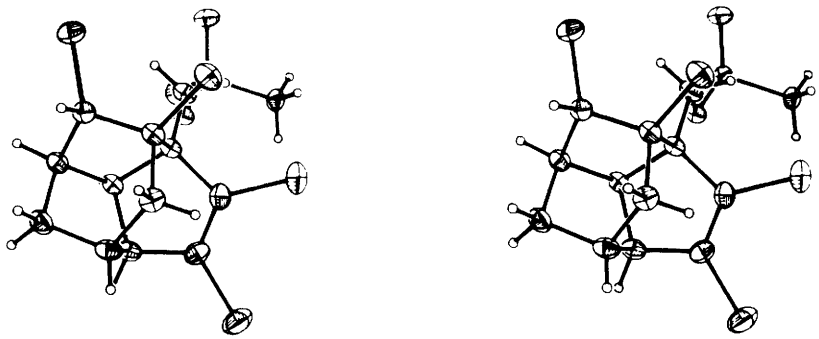


FIGURE 2 Stereoscopic view of the molecular structure of $C_{13}H_{14}Cl_4O_3S$

EXPERIMENTAL

N.m.r. data refer to solutions in $CDCl_3$ with $SiMe_4$ as internal standard; ^1H spectra were obtained with JEOL PS100 or FX200 spectrometers, all signals having the correct relative intensity unless otherwise indicated. ^{13}C Data were acquired using a JEOL FX90Q machine. Mass spectra were obtained using an AEI-GEC MS902 double-focusing instrument with VG Micromass facility; halogenated ions have the correct $^{35}Cl/^{37}Cl$ abundance ratio. I.r. spectra (in CH_2Cl_2 or CCl_4 solution) were obtained with PE257 or PE197 instruments. U.v. spectra were obtained all other atoms with corrections for anomalous dispersion. All computations were performed in the laboratory on an Eclipse (Data General) minicomputer with the SHELXTL system of programs.[9] Observed and calculated structure factors, all thermal parameters, a complete table of torsion angles, and all inter-bond angles involving the hydrogen atoms are listed in Supplementary Publication No. SUP 23263 (26 pp.).*

1,3,4,11-*Tetrachloro*-2-*formyltetracyclo*[5.3.10.^{2,6}.0^{5,9}]*un*-

* For details see Notice to Authors No. 7, *J. Chem. Soc., Perkin Trans. 2*, 1981, Index Issue.

dec-3-*ene* (12).—This was isolated and purified (t.l.c.), m.p. 140 °C (CCl_4), as previously described.[2] The aldehyde (12) (60 mg, 0.2 mmol) and $LiAlH_4$ (10 mg, *ca.* 0.25 mmol) were stirred in ether solution (8 ml) under nitrogen for 2.5 h at 20 °C and the ether layer separated from the water-quenched reaction mixture, washed, dried, and evaporated giving substantially pure alcohol (13), which without further purification was dissolved in pyridine (*ca.* 2 ml) and treated with $MeSO_2Cl$ (75 mg, *ca.* 100% excess). The solution, after standing at 20 °C for 18 h, was poured into water, and the precipitated solid extracted into ether, the extracts washed (aqueous HCl, brine), dried, and evaporated, and the residue (75 mg) recrystallised from dichloromethane–hexane giving the *methanesulphonate* (14), m.p. 147—148 °C (58 mg, 76% overall) raised to 148—149 °C by slow evaporation of an ethyl acetate solution under a petroleum atmosphere (*X*-ray sample). (Found: C, 39.8; H, 3.55. $C_{13}H_{12}Cl_4O_3S$ requires C, 39.8; H, 3.6%), *m/e* 390($M^{+\bullet}$), 354 ($M - Cl^{+\bullet}$), 311 ($M - SO_2Me^{+\bullet}$), 281 ($M - CH_2OSO_2Me^{+\bullet}$), 275 ($M - HCl - SO_2Me^{+\bullet}$), and 113 ($C_6H_6Cl^{+\bullet}$); τ (100 MHz) 4.68 (d), 5.50 (d, *J* 11 Hz, CH_2OSO_2Me at a chiral centre), 5.74 [s, H(11)], 6.46 [t, H(6)], 6.98 (s, Me), 7.1 [cm overlapping H(5,7)], 7.6 [bs, H(9)], and 7.7—8.0 [overlapping H(10,10′) and H(8,8′)].

11-*Deuteriotetrachlorotetracyclododecadienols* [11-^{2}H]-(1) *and* -(2).—A mixture of the alcohols made as previously described [2] for (1) and (2) but using $LiAl^2H_4$ for carbonyl-bridge reduction separated on t.l.c. (3 : 1 CCl_4–Et_2O) into minor product (higher R_F) *anti*-epimer [11-^{2}H]-(1), m.p. 108 °C (petroleum), $\nu_{max.}$ 3 580 (sharp vs, non-bonded OH) and 1 590 (s, ClC=CCl) cm^{-1}, τ (100 MHz) 3.67 [nm, H(9,10)], 6.98 (s, OH), 7.14 [nm, H(1,8)], 7.26 [s, H(2,7)], and 8.42, 8.65 [each dnm, *J* 10.5 Hz, H(12,12′)], and major product *syn*-isomer [11-^{2}H]-(2), m.p. 138—139.5 °C (petroleum), $\nu_{max.}$ 3 570 (br, s, bonded OH) and 1 590 (s, ClC=CCl) cm^{-1}, τ (100 MHz) 3.68 [nm, H(9,10)], 7.05 [nm, H(1,8)], 7.32 (s, OH), 7.56 [s, H(2,7)], and 8.51, 8.72 [each dnm, *J* 10.5 Hz, H(12,12′)], in each isomer the signal characteristic [2] of H(11) in alcohols (1) and (2) conspicuously absent (*syn*/*anti* ratio *ca.* 2).

Isomerization of Alcohols [11-^{2}H]-(1) *and* [11-^{2}H]-(2) *in* $^1H_2SO_4$.—Each alcohol was treated with $^1H_2SO_4$–CCl_4 as previously briefly described, separation of the major fraction of the mixed product giving aldehyde [12-^{2}H]-(12) (*ca.* 17%), m.p. 138—139 °C (CCl_4), $\nu_{max.}$ 2 870—2 875 (m, ^{2}HCO), 2 120—2 140 (w, ^{2}H–C st.), 1 710 (vs, ^{2}HC=O st.), and 1 620 (vs, ClC=CCl) cm^{-1}, τ (100 MHz) 5.66 [s, H(11)], 6.04 [tnm, H(6)], 7.08 [dd, H(5)], 7.32 [tnd, H(7)], 7.61 [cm, H(9)], 7.75(t), 7.9(d), and *ca.* 8.0 [cm, overlapping H(10,10′) and H(8,8′)]; τ −0.25 absent. The combined aldehyde fraction from several runs (47 mg, 0.15 mmol) was stirred with $LiAlH_4$ (8 mg, 0.21 mmol) in ether (5 ml) under nitrogen for 2 h and the product isolated in the usual way giving crystalline monodeuterioalcohol [12-^{2}H]-(13) (48 mg, 100%), τ (100 MHz) 5.35, (d), 8.3, (d, *J* 8 Hz, $^1H^2HCOH$), 5.62 [s, H(11)], 6.36 [tnm, H(6)], 7.09, (q) overlapping 7.18 [nm, H(5), H(7)], 7.58 [cm, H(9)], and 7.7—8.1 [overlapping m, H(10,10′) and H(8,8′)].

TABLE 4

220 MHz ^{1}H N.m.r. data for aldehyde (12) and its deuteriated analogues (τ; $CDCl_3$) with first-order *J* for [$^2H_4$]-(12)

Proton	(12)	[8-^{2}H]-(12)	[7,8,8,12-$^2H_4$]-(12)	*J*/Hz
CHO [H(12)]	−0.25 (d)	−0.25 (d)	residual, v. weak	*ca.* 0.6
H(11)	5.66 (s)	5.66 (s)	5.67 (s)	
H(6)	6.05 (tnm)	6.04 (tnm)	6.05 (dnd)	6.8, 1.07
H(5)	7.08 (dd)	7.08 (dd)	7.09 (qnd)	6.8, 3.5, 0.6
H(7)	7.32 (tnd)	7.32 (tnd)	residual, v. weak	6.7, 6.7, 1.4
H(9)	7.62 (cm)	7.61 (cm)	7.61 (cm) (narrowed)	
H(10-*syn*)	7.68 (t)	7.68 (t)	7.68 (q)	13.7, 2.1, 3.5
H(10-*syn*)	7.75 (t)	7.75 (t)	7.75 (q)	
H(10-*anti*)	7.91 (nq)	7.90 (nq)	7.91 (q)	13.7, 2.1, 1.07
H(10-*anti*)	7.98 (nm)	7.98 (nq)	7.98 (q)	
H(8,8′)	~8.0 (cm)	8.05 (bs)	8.07 (weak bs)	

Isomerization of Alcohols (1) *and* (2) *in* $^2H_2SO_4$.—In a similar experiment to that above, *syn*-alcohol (2) (300 mg, 0.9 mmol) was stirred in $^2H_2SO_4$ (5 ml) at 20 °C for 4 h and the product isolated by ice-quenching and chloroform extraction. The washed and dried products of two runs, combined and chromatographed (t.l.c., 3 : 1 CCl_4–Et_2O), gave the required aldehyde [8-^{2}H]-(12) (59 mg, *ca.* 10%), *m/e* 311 ($C_{12}{}^1H_9{}^2HCl_4O^{+\bullet}$), 282 ($M - {}^1HCO^{+\bullet}$), 114 ($C_6{}^1H_5{}^2HCl^{+\bullet}$), 78 ($C_6{}^1H_4{}^2H^{+\bullet}$), ^{1}H n.m.r. in Table 4, δ_C 198.3 (CHO), 129.97 and 122.7 [quat., C(3),C(4)], 76.2 [C(11)], 71.0 [quat., C(1)], 56.8, 54.45, 44.77, 36.9 [methine CH, C(5), C(6), C(7), C(9)], 43.21 [C(10)], 42.4, 41.5, 40.6 [$>C^1H^2H$(C-8), residual C^1H_2, δ 41.9, weak s], 70.9 p.p.m. [quat., C(2) resolved in offset ^{1}H-decoupled spectrum].

In a similar experiment using *syn*-alcohol [11-^{2}H]-(2)–$^2H_2SO_4$ the aldehyde fraction (m.p. 139—140 °C) had *m/e* 312 ($C_{12}{}^1H_8{}^2H_2Cl_4O^{+\bullet}$), 282 ($M - {}^2HCO^{+\bullet}$), 114 ($C_6{}^1H_5{}^2HCl^{+\bullet}$), and 78 ($C_6{}^1H_4{}^2H$), and a similar ^{1}H n.m.r. spectrum to the above product [8-^{2}H]-(12) with τ −0.25 absent.

Synthesis of (i) *Di- and* (ii) *Tetra-deuterioaldehydes* [7,12-$^2H_2$]-(12) *and* [7,8,8′,12-$^2H_4$]-(12).—endo, exo-1-exo-5,8,9,10-*Pentachloro*-11,11-*dimethoxytetracyclo*[6.2.1.1^{3,6}.0^{2,7}]*dodec*-9-*en*-4-*one* (6) was made (81% yield) from *exo,endo*-norbornadiene–tetrachlorodimethoxycyclopentadiene adduct (5) [7] [by hydrolysis of the NOCl adduct as described in detail [8] for the hexachloro-analogue of (5)], m.p. 170 °C (HOAc), $\nu_{max.}$ 1 770 (vs, CHClCO), 1 602 (ms, ClC=CCl), and 2 850 (ms, OMe) cm^{-1}, τ (100 MHz) 6.30 [d, *J ca.* 3 Hz, *endo*-H(5)], 6.42 (s) and 6.47 (s) (2MeO), 7.16 [m, H(3,6)], 7.30 [m, H(2,7)], 8.00 [dm, ^2J 14 Hz, H(12) *syn* to *exo*-Cl(5)], and 8.21 [dm, ^2J 14 Hz, H(12) *anti*] (Found: C, 41.8; H, 3.6. $C_{14}H_{13}Cl_5O_3$ requires C, 41.4; H, 3.2%). The 2,4-*dinitrophenylhydrazone* had m.p. 227—228 °C (Found: C, 40.8; H, 2.6. $C_{20}H_{17}Cl_5N_4O_6$ requires C, 41.0; H, 2.9%). Similarly prepared from adduct (5) using isopentyl nitrite–aqueous HBr–HOAc the exo-5-*bromotetrachloro-analogue* of the pentachloro-keto-acetal (6), m.p. 203 °C (Found: C, 37.2; H, 2.7. $C_{14}H_{13}BrCl_4O_3$ requires C, 37.3; H, 2.9%). The pentachloro-ketone (6) was readily dechlorinated using Zn–HOAc–Et_2O at *ca.* 60 °C (but not at 20 °C, *cf.* ref. 7) giving endo, exo-1,8,9,10-*tetra*-

chloro-11,11-*dimethoxytetracyclo*[6.2.1.1^{3,6}.0^{2,7}]*dodec*-9-*en*-4-*one* (7) [60% overall from (5)], m.p. 75—76 °C (from a *small* volume of petroleum), $\nu_{max.}$ 1 762 (vs, CH_2CO), 1 602 (m, ClC=CCl), 2 850 (ms, OMe), 1 412 (w-m, CH_2 scissoring) cm^{-1}, τ (100 MHz) 6.40 (s), 6.45 (s, 2MeO), 7.2—7.4 [m, 4H] and 7.84 [nm, 2H] [H(2,3,5,5,6,7)], 8.15 (m), and 8.59 [m, ^2J *ca.* 13 Hz, H(12,12)] (Found: C, 45.5; H, 3.95. $C_{14}H_{14}Cl_4O_3$ requires C, 45.2; H, 3.8%).

Keto-acetal (7) (1.0 g, 2.7 mmol) was stirred in H_2SO_4 (10 ml) for 4 h at 20 °C, the product poured onto crushed ice (precooled to −30 °C), and the solid filtered off, thoroughly washed (H_2O), and dried *in vacuo* (18 h at 20 °C then 2 h, 45 °C) giving a product (770 mg, 83%), m.p. 114—116 °C (vigorous decomp.), $\nu_{max.}$ 1 760 [vs, C(4)=O], 1 830 [vw, trace C(11)=O], 1 595 (s, ClC=CCl), 3 550 (vs, OH) cm^{-1}, sparingly soluble in $CDCl_3$, mainly the C(11) *gem*-diol hydrate of diketone (8); the diketone (8) was obtained in a similar experiment by direct extraction into CH_2Cl_2 (4 × 35 ml), the extracts being stirred with precipitated $CaCO_3$, allowed to settle overnight, and finally decanted and evaporated to give 4,11-diketone (8), m.p. 128—130 °C (vigorous decomp.) (820 mg, 89%), $\nu_{max.}$ 1 830 (sh), 1 843 [vs, C(11)=O], 1 762 [vs, C(4)=O], 1 578 (ms, ClC=CCl) cm^{-1}, τ (100 MHz), see below for (9), *i.e.* [5,5-$^2H_2$]-(8).

Diketone (8) was characterised as a norborn-2-en-7-one type by heating a small sample (*ca.* 50 mg) in toluene (3 ml) for 18 h, evaporation *in vacuo*, t.l.c., and recrystallisation of the residue (aqueous HOAc) giving *exo*-3,4,5,6-tetrachlorotricyclo[6.2.1.0^{2,7}]undeca-3,5-dien-9-one (8a) (*ca.* 30 mg), m.p. 119.5—120.5 °C. $\nu_{max.}$ 1 745 (vs, CO) and 1 612 (vs, ClC=CCl) cm^{-1}, identical to a sample (m.p. and mixed m.p.) made from α-chloroketone (6) as follows. Acetal (6) (10 g) was added to H_2SO_4 (30 ml) and the solution was left at 20 °C for 3 h and then kept at 0 °C overnight, a solid separating; pouring onto crushed ice, filtration, and drying of the precipitate gave a bridge-carbonyl product (8 g) which was heated in HOAc (40 ml) at the b.p. for 1.5 h. The solution was slightly diluted with water, and cooling precipitated exo-3,4,5,6-exo-10-*pentachlorotricyclo*[6.2.1.0^{2,7}] *undeca*-3,5-*dien*-9-*one* (7 g, 86%), m.p. 165—166 °C, $\nu_{max.}$ 1 765 (vs, CO) and 1 620 (ms, ClC=CCl) cm^{-1}, τ 6.11 [d, J 3 Hz, *endo*-H(10)], 6.73 [dd, ^2J 12, ^4J 1 Hz, H(7)], 6.90 [dd, ^2J 12, ^4J 1 Hz, H(2)] overlapping 6.82 [m, H(1,8)], and 7.66, 7.9 [each d sextet, ^2J 12 Hz, H(11) *syn* and *anti* to *exo*-Cl(10)]; *m/e* 330 ($M^{+\bullet}$), 295 (M − $Cl^{+\bullet}$), and 214 ($C_6H_2Cl_4^{+\bullet}$) (Found: C, 39.95; H, 2.2. $C_{11}H_7Cl_5O$ requires C, 39.75; H, 2.1%). The 2,4-*dinitrophenylhydrazone*, m.p. 211 °C (decomp.) (Found: C, 40.0; H, 2.3. $C_{17}H_{11}Cl_5N_4O_4$ requires C, 39.8; H, 1.95%). The *ethylene acetal*, m.p. 160—161 °C (Found: C, 41.5; H, 2.8. $C_{13}H_{11}Cl_5O_2$ requires C, 41.5; H, 2.9%). The pentachlorotricycloundecadienone above (12 g) was boiled in HOAc (180 ml) with zinc dust (9 g), the solution cooled and filtered, the filtrate heated and diluted with water to incipient cloudiness, whereupon crystals of exo-3,4,5,6-*tetrachlorotricyclo*[6.2.1.0^{2,7}]*undeca*-3,5-*dien*-9-*one* (8a) separated (9.6 g, 89%), m.p. 119.5—120.5 °C (aqueous HOAc), $\lambda_{max.}$ (EtOH) 270sh (ε 2 659), 281 (4 122), 292 (5 592), 305 (5 266), and 319 nm (3 351), *m/e* 296 ($M^{+\bullet}$), 261 (M − $Cl^{+\bullet}$), 214 ($C_6H_2Cl_4^{+\bullet}$), and 82 ($C_5H_6O^{+\bullet}$), τ 6.8—7.0 [m, H(1,2,7,8)], 7.8 [cm, H(10,10)], and 7.93 (dnm) and 8.22 (dnm) [^2J 11 Hz, H(11,11)] (Found: C, 44.7; H, 2.7. $C_{11}H_8Cl_4O$ requires C, 44.3; H, 2.7%).

(i) The diketone (8) was used directly for reduction and isomerisation to dideuterioaldehyde [7,12-$^2H_2$]-(12) as follows. Diketone (8) (700 mg, 2.05 mmol) was stirred under nitrogen with $LiAl^2H_4$ (124 mg, 2.95 mmol) in dry ether (50 ml) at 20 °C for 1 h. Work-up in the usual manner (aqueous HCl, washing, and drying) indicated reduction at C(11)=O but C(4)=O partially survived, and the product was recycled with fresh $LiAl^2H_4$ as above giving after work-up a mixture of solids, mainly *endo*-4-*syn*- and *endo*-4-*anti*-11-diols (10) (765 mg). Samples of the mixed diols (200 mg) were stirred in CCl_4 (20 ml), CH_2Cl_2 (5 ml), and H_2SO_4 (5 ml) for *ca.* 17 h and the products isolated by ice-quenching and extraction ($CHCl_3$). The combined yields of three runs were chromatographed (as above) giving dideuterioaldehyde [7,12-$^2H_2$]-(12) as one of two fractions (54 mg, 9.5%), m.p. 140—141.5 °C, $\nu_{max.}$ 2 870 (^{2}HCO), 2 100—2 150 (bw, ^{2}H–C st.), 1 710 (vs, ^{2}HCO), and 1 620 (vs, ClC=CCl) cm^{-1}, *m/e* 312 ($C_{12}{}^1H_8{}^2H_2Cl_4O^{+\bullet}$), 282 ($M$ − $^2HCO^{+\bullet}$), 114 ($C_6{}^1H_5{}^2HCl^{+\bullet}$), and 78 ($C_6{}^1H_4{}^2H^{+\bullet}$, 114-^{1}HCl), τ (100 MHz) 5.68 [s, H(11)], 6.06 [dnm, J *ca.* 6.7 Hz, H(6)], 7.08 [dd, H(5)], 7.3 [d, very weak, residual H(7)], 7.58 [cm, H(9)], *ca.* 7.75 (t), 7.88 [d, H(10) *syn*], and 7.99 [cm, H(10) *anti*, overlapping H(8,8′)].

(ii) Keto-acetal (7) (750 mg, *ca.* mmol) was dissolved in MeO^2H (10 ml), $KOBu^t$ (30 mg) added, and the mixture left at 20 °C for *ca.* 18 h. Small chips of solid CO_2 (wiped free of frost) were added and the solution evaporated *in vacuo*. The residue was dissolved in CCl_4 (5 ml) and re-evaporated to azeotrope out residual MeO^1H–MeO^2H; i.r. monitoring indicated complete loss of the characteristic $-C^1H_2CO-$ scissoring frequency near 1 412 cm^{-1}. The product, dissolved in CCl_4 (8 ml) was stirred with $^2H_2SO_4$ (6 ml) overnight and the dideuterioketone (9) (624 mg, 95%) isolated by direct extraction (CH_2Cl_2) as above, $\nu_{max.}$ 1 830 (sh), 1 843 [vs, C(11)=O], 1 762 [vs, C(4)=O], and 1 578 (ms, ClC=CCl) cm^{-1}, no absorption at 1 400—1 460 cm^{-1}, τ (100 MHz) 7.00 [nm, H(3,6)], 7.27 (d) overlapping 7.36 [d, J *ca.* 9 Hz, H(2,7)], and 8.04, 8.44 [both dm, ^2J *ca.* 13 Hz, H(12,12)].

The dideuterioketone (9) (278 mg, 0.85 mmol) was treated with $LiAl^2H_4$ (200 mg, 4.76 mmol) under N_2 in dry ether (50 ml) for 1.5 h with stirring and the product isolated in the usual manner after quenching with a little ^2H_2O. The crude tetradeuterioalcohol mixture (169 mg) treated in duplicate runs using $^1H_2SO_4$ (2.5 ml) in CH_2Cl_2 (15 ml) and the products combined and chromatographed (t.l.c.) as before gave as the main fraction [7,8,8,12-$^2H_4$]-(12) (15 mg, 6%), m.p. 141—142 °C (CCl_4), $\nu_{max.}$ 2 870 (ms, ^{2}HCO), 2 100—2 150 (w, ^{2}H–C st.), 1 710 (vs, ^{2}HCO), and 1 620 (vs, ClC=CCl) cm^{-1}; *m/e* 314 ($C_{12}{}^1H_6{}^2H_4Cl_4O^{+\bullet}$, 61%), 313 ($C_{12}{}^1H_7{}^2H_3Cl_4O^{+\bullet}$, 32%), 284 ($M^{+\bullet}$ − ^2HCO), 116 ($C_6{}^1H_3{}^2H_3Cl^{+\bullet}$), and 80 ($C_6{}^1H_2{}^2H_3{}^{+\bullet}$) and similar fragments from $M^{+\bullet}$ 313, ^{1}H n.m.r. in Table 4.

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