Halogeno-1,4-dioxans and their Derivatives. Part VI.[1] 4,4′,5,5′-Tetrachlorobi-1,3-dioxolan-2-yl

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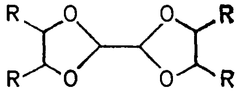
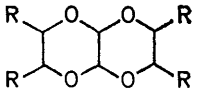
From the product of interaction of *trans*-2,3-dichloro-1,4-dioxan and concentrated sulphuric acid a compound has been isolated which is homogeneous on t.l.c. Mass, n.m.r., i.r., and Raman spectroscopy show that this is 4,4′,5,5′-tetrachlorobi-1,3-dioxolan-2-yl with the two chlorine atoms in each ring *trans*, but no decision is possible as to whether it is the racemate or the *meso*-compound. A possible mechanism of formation is indicated.

INTERACTION of *trans*-2,3-dichloro-1,4-dioxan and concentrated sulphuric acid at room temperature gives [2] a product $C_6H_6Cl_4O_4$. Repeated crystallisation yields a compound A, m.p. 137—139°, which is chromatographically homogeneous and which, in view of its reactions,[2] is either 4,4′,5,5′-tetrachlorobi-1,3-dioxolan-2-yl (Ia) or 2,3,6,7-tetrachlorohexahydro-*p*-dioxino-*p* dioxin (IIa).



(I) a: R = Cl
b: R = H



(II) a: R = Cl
b: R = H

Low resolution mass spectrometry rules out the latter structure, and indicates that the former structure is correct. Most of the major ions and the significant minor ions are shown in Schemes 1—3 (the remaining ions in the spectrum are listed in the Experimental Section). Ion formulae have been assigned on the basis of the presence of the requisite chlorine isotope peaks. Transitions supported by the presence of metastable ion peaks are indicated by *m** (experimental) values; there is more than one of these for each transition where chlorine-containing fragments are involved and the relative abundances of the metastable ions correspond with the relative abundances of the ions containing the chlorine isotopes in each case.

The fragmentation pathways are thought to be as indicated. The structures of the ions derived (Scheme 3) from the base peak ion $C_3H_3Cl_2O_2^+$ (III) are readily deduced by comparison with the known fragmentations [3] of cyclic acetals.

That the base peak ion has half the molecular weight of compound A is by itself insufficient to distinguish between structures (Ia) and (IIa). It has been shown [4] that for both bi-1,3-dioxolan-2-yl (Ib) and hexahydro-*p*-dioxino-*p*-dioxin (IIb) the base peak ion $C_3H_5O_2^+$ (IV), *m/e* 73, is the same; that from structure (IIb) is thought to arise in the manner indicated.

However, the further evidence in the mass spectrum of compound A for the bidioxolanyl structure can be summarised as follows: the relative abundances of the M^+ and $(M - 1)^+$ ions are much less (<0·3%) than that of the base peak ion; there are no metastable ions corresponding with the transition to *m/e* 141 of any ion above this; and there is an ion $C_3H_3O_2^+$ (V), *m/e* 71, nearly as abundant as the base peak ion.

In the case of the bidioxolanyl (Ib) and the *p*-dioxino-*p*-dioxin (IIb), the M^+ and $(M - 1)^+$ ions are virtually non-existent from the former but are of significant relative abundance from the latter.

If the *p*-dioxino-*p*-dioxin structure obtained for compound A, the occurrence of $C_3H_3Cl_2O_2^+$ as the base peak ion would require the breaking of three bonds with rearrangement, and it would be expected that this process would be detectable by the presence of appropriate metastable ion(s) (unfortunately, metastable ions are not mentioned in ref. 4). Now there is a series of fragmentations beginning with the ion

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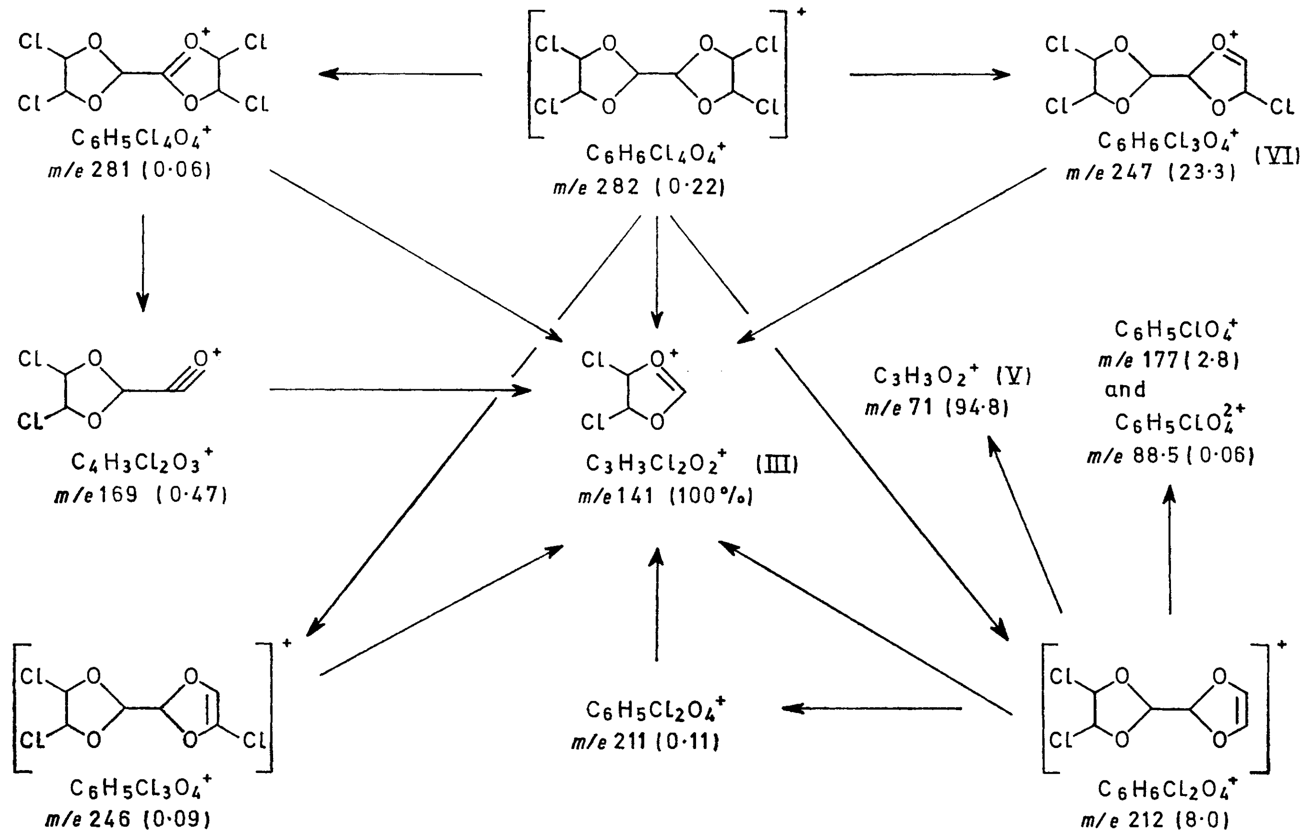
[1] Part V, R. E. Ardrey and L. A. Cort, *J. Chem. Soc.* (*C*), 1970, 2457.

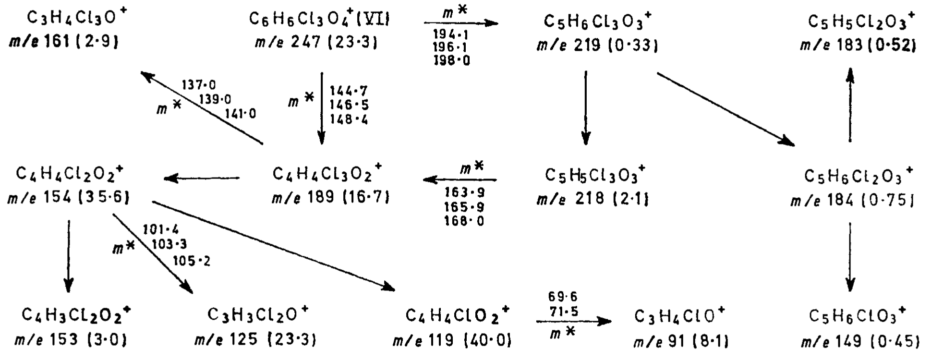
[2] L. A. Cort, *J. Chem. Soc.*, 1960, 3167.

[3] H. Budzikiewicz, C. Djerassi, and D. H. Williams, 'Mass Spectrometry of Organic Compounds,' Holden-Day, San Francisco, 1967, p. 258.

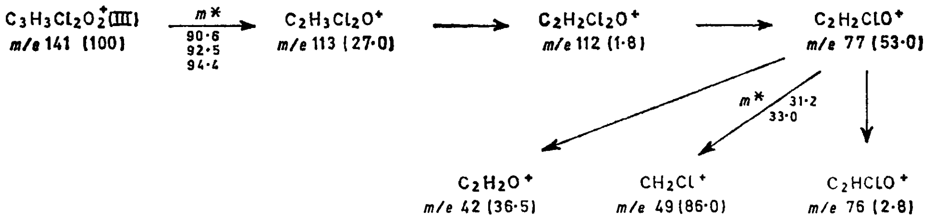
[4] B. Fuchs, *Tetrahedron Letters*, 1970, 1747.



SCHEME 1 Formation of the base peak ion from 4,4′,5,5′-tetrachlorobi-1,3-dioxolan-2-yl

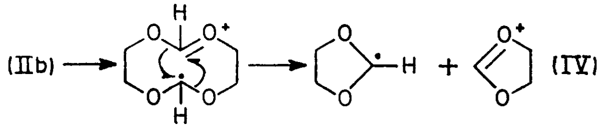


SCHEME 2 Fragmentations involving the ion $C_6H_6Cl_3O_4^+$ from 4,4′,5,5′-tetrachlorobi-1,3-dioxolan-2-y



SCHEME 3 Fragmentation of the base peak ion from 4,4′,5,5 -tetrachlorobi-1,3-dioxolan-2-yl

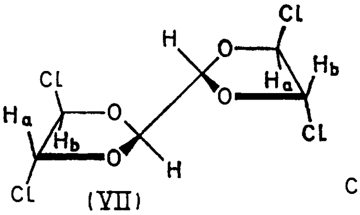
$C_6H_6Cl_3O_4^{\cdot+}$ (VI), *m/e* 247 (Scheme 2), and it is clear that the ion $C_4H_4Cl_3O_2^+$, *m/e* 189, must arise by rearrangement from either possible structure for compound A (without further study it is unprofitable to speculate on the structure of this ion). The metastable ion (*m/e* 144·7) is observed for the transition *m/e* 247 ⟶ 189, and other metastable ions are also observed in other cases (Schemes 2 and 3) where rearrangement similarly occurs. It seems reasonable to conclude that the base peak ion from compound A arises by a process other than rearrangement, since no suitable metastable ions can be detected.



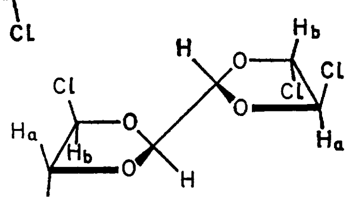
The ion $C_3H_3O_2^+$ (V), *m/e* 71 (Scheme 1), could arise from $C_6H_6Cl_2O_4^+$, *m/e* 212, or even from the base peak ion, and no rearrangement need be postulated. Again, if the ion (V) arises from (IIa) the rearrangement process should be detectable, and there are no suitable metastable ions in the spectrum.

For the bidioxolanyl structure (Ia) there are ten stereoisomeric possibilities, and seven of these can be ruled out on the basis of n.m.r. spectra. For solutions in carbon tetrachloride, deuteriochloroform, benzene, and pyridine the 60 MHz n.m.r. spectra consist of three equal-intensity singlets ($W_{\frac{1}{2}} < 1{\cdot}0$ Hz). For the benzene solution the signals have virtually the same chemical shift; spectra of solutions in mixed solvents show the progressive coalescence of these signals.

There are then three types only of magnetically non-equivalent protons, and the possible stereoisomers are those where the chlorine atoms are *trans* in each ring: the *meso*-form (VII) and a racemic pair of which (VIII) is one. These would give identical n.m.r. spectra. A surprising feature is that large coupling would be expected between H-4 and H-5 on the basis of the dihedral angle, and if coupling exists it must be 1·0 Hz or less; the reason for this must lie in the fact that the two carbon atoms involved carry four electronegative substituents, a situation for which the Karplus equation is known not to be reliable.



(VII)



(VIII)

On the grounds that in both structures (VII) and (VIII), H_a is nearer on average to all chlorine and all oxygen atoms in the molecule than is H_b, of the pair of signals in the spectra of carbon tetrachloride and deuteriochloroform solutions from H-4 and H-5, the signal further downfield is assigned to H_a.

The conformations represented by (VII) and (VIII) are for molecules which are centrosymmetric and non-centrosymmetric, respectively. Accordingly i.r. absorption and Raman spectra for the solid have been examined, for it would be expected that in the crystal the molecules, being bound to each other only by the weak van der Waals' forces, would adopt these conformations.

The results appear in the Table. For the C–H stretch region (3050—2900 cm^{-1}) bands occur in two distinct groups, but within each group there is incomplete resolution. The C–H system(s) vibrating at the lower frequencies may well be centrosymmetric, but the coincidences in the frequencies of the bands in the higher frequency group suggest non-centrosymmetricity for the second C–H system(s). Below 900 cm^{-1} C–Cl stretch, ring-Cl bend, and ring deformation frequencies would be expected. Rather less than half the bands here show convincing coincidences. In the region 1300—900 cm^{-1} would be expected ring-H bend and ring stretching frequencies. There are almost no coincidences.

Absorption frequencies (cm^{-1}) in the i.r. and Raman spectra of 4,4′,5,5′-tetrachlorobi-1,3-dioxolan-2-yl

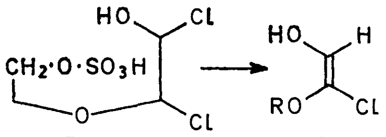
I.r. ^{a} (Nujol)	Raman ^{b} (crystal)	I.r.	Raman
3043 ^{c}	{ 3045 ^{c}	992	
	3041 ^{c}	e { 962	971
3038 ^{c}	3038 ^{c}	951	
3032 ^{c}	3032 ^{c}	833s	
2959 ^{d}	2955 ^{d}	787s	790s
2949 ^{d}	2951 ^{d}	775sh	
	1432vvw	747vw	751s
	1352	732s	
1323		680vs,br	680vw
1299vw	1299	670sh	672w
1291		482vw	490m
1272		448m	
1257	1265	406m	400m
1213	1220		378s
1206		318w	325vw
1125br	1177w	Region	288s
	1095w	not	238w
e { 1048	1037w	investigated	215vw
1039			108m
1014w	1020		

^{a} Perkin-Elmer 457; polystyrene and indene calibration. ^{b} SPEX 1401, argon laser. ^{c} Intensity profiles similar. ^{d} Intensity profiles dissimilar. ^{e} Barely resolved.

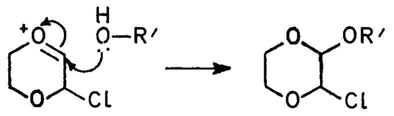
There is thus no overwhelming case for either centrosymmetry or non-centrosymmetry. On balance, the environment for C–H stretch seems to be non-centrosymmetric. Of course, within a crystal the racemate of (VIII) could be arranged so that there was a centre of (crystal) symmetry between pairs of molecules, and/or the conformation in the solid state may not be as pictured.

On the evidence adduced, compound A is 4,4′,5,5′-tetrachlorobi-1,3-dioxolan-2-yl (Ia). The two chlorine atoms in each ring are *trans*, but a decision cannot be made between the *meso*-form and the racemate. A mixture of the two is possible since the experimental conditions used for t.l.c. may not be such as would bring about a separation.

Regarding the reaction course leading to compound A, after protonation of *trans*-2,3-dichloro-1,4-dioxan there is presumably ring opening as in the normal cleavage of ethers, leading to the alcohol (IX). Repetition of the reaction at this or at a later stage would lead to racemic 1,2-dichloroethylene glycol. The derived diacetal could have configurations where the two chlorine atoms in each ring were *trans* only.



(IX) (X)



(XI) (XII)

The glyoxal portion of the diacetal could arise in two ways. An E_2 reaction is possible with compound (IX), whereby hydrogen chloride could be lost to give the enol (X). The subsequent steps leading to the diacetal can then be clearly envisaged. Alternatively, abstraction of chloride ion from the dioxan is possible, leading to the ion (XI), which would be subject to attack by alcohols to give, after loss of a proton, the acetal (XII). Ring opening and continuation of the reactions could obviously lead to the bidioxolanyl (Ia). Equally, these overall reactions could lead in theory to the fused-ring compound (IIa).

EXPERIMENTAL

The product[2] from *trans*-2,3-dichloro-1,4-dioxan and concentrated sulphuric acid after repeated crystallisation from carbon tetrachloride and then from acetone afforded compound A, m.p. 137—139°, homogeneous by t.l.c. [silica gel or alumina with carbon tetrachloride (R_F 0·49 and 0·56, respectively); detection with silver nitrate].

The mass spectrum (A.E.I. MS 12 at 70 eV; direct insertion at 130°) showed the ions given in Figures 1—3 and also the following (% relative abundances in brackets): *m/e* 142 (6·3) $C_3H_4Cl_2O_2^+$, 135 (5·3) $C_4H_4ClO_3^+$, 131 (4·6) $C_2H_5Cl_2O_2^+$, 107 (16·1) $C_3H_4ClO_2^+$, 96 (6·1) $C_2H_2Cl_2^+$, 83 (3·1) ($CHCl_2^+$, 61 (11·0) $C_2H_2Cl^+$, 48 (7·6) $CHCl^+$, and 36 (98·5) HCl^+; metastable ions *m** (after optimum tuning) 106·7, 108·5, and 110·3 with the correct relative abundances for a fragment containing Cl_2, 75·2, 73·5, 52—53, 46·3, 26·1, 25·0, and 11·8; under these conditions the relative abundance of *m/e* 142 increased to 25·7%.

The n.m.r. spectra (60 MHz) showed signals at τ (CCl_4) 3·68, 3·75, and 4·38; ($CDCl_3$) 3·62, 3·69, and 4·30; (C_5H_5N) 2·89, 2·99, and 3·93 [for a saturated solution (33°)]; (C_6H_6) 4·38, 4·40, and 4·42 [for a saturated solution (33°)].

We thank Dr. S. G. Frankiss and Mr. W. Kynaston, N.P.L., Teddington, Middlesex, for the Raman spectrum.

Note added in proof: Two recent publications also deal with the problem of stereochemistry. In the first (B. Fuchs and S. Hauptmann, *Chem. Comm.*, 1971, 705) chemical reactions confirm the structure but no stereochemistry is given, and in the second [H. H. Huang, *J. Chem. Soc.* (*B*), 1971, 1024] physical measurements, which are largely complementary to those of the present work, lead to the same conclusions regarding structure and stereochemistry.

[1/1002 *Received, June* 18*th*, 1971]