THE REACTION OF TETRACHLOROCYCLOPENTADIENONE ACETALS

WITH ALKOXIDE IONS: AN ANOMALY.

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The reactive diene 1,2,3,4-tetrachlorocyclopentadienone dimethyl acetal (I) (v_{max} 1584, 1615 cm^{-1}) formed by reaction of hexachlorocyclopentadiene with methoxide ion[1] has been success-fully exploited in numerous Diels-Alder reactions[2] and as a trap for highly reactive transient dienophiles.[3] Tetrachlorodimethoxydiene (I) reacts further with alkoxide ions and is claimed to give e.g. the unstable trimethoxy compound[4] (II) (v_{max} 1611, 1654 cm^{-1}) which is of potential interest in similar cycloadditions. We have accumulated evidence however that the triethers obtained by reaction of tetrachlorodiene acetal (I) and its analogues with alkoxide ion actually have structures such as e.g. (III).
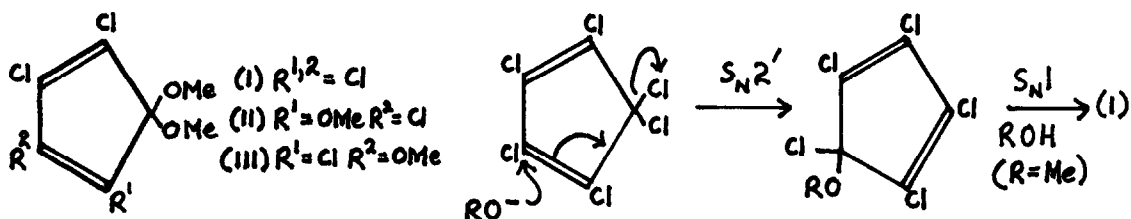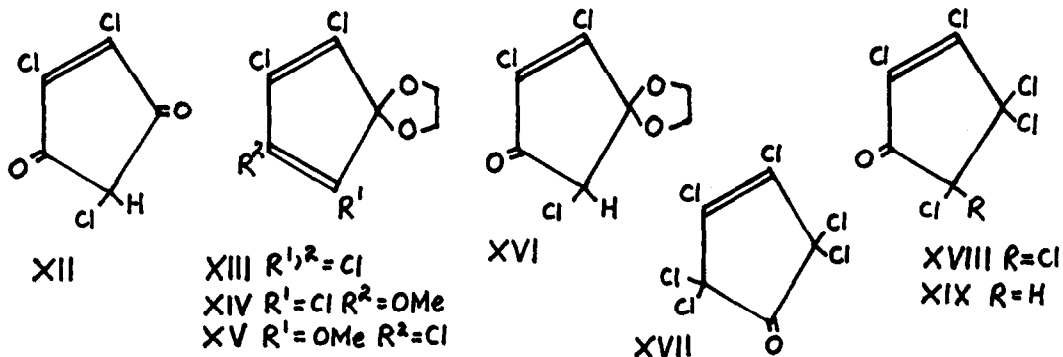

Formation of (I) involves initial S_N2' nucleophilic displacement of chlorine in the hexa-chlorodiene;[4] supporting the kinetic evidence[4] hexachlorocyclopentene dimethyl acetal (IV) does not react with methoxide ion and direct attack at an allylic gemdichloromethylene group is dis-favoured, possibly by steric hindrance. Because of an accessible S_N2' pathway the isomeric cyclopentenone acetal (V) does however react to give bis-acetal (VI). It is proposed[4] that tetrachlorodiene (I) undergoes addition-elimination with alkoxide ion to give preferentially (II) because of the intermediacy of an allylic ion (VII) more stabilised than the sterically expected ion (VIII). However difluorotetrachlorodiene (IX) reacts with methoxide ion to give vinyl ether (X), via an intermediate similar to carbanion (VIII).
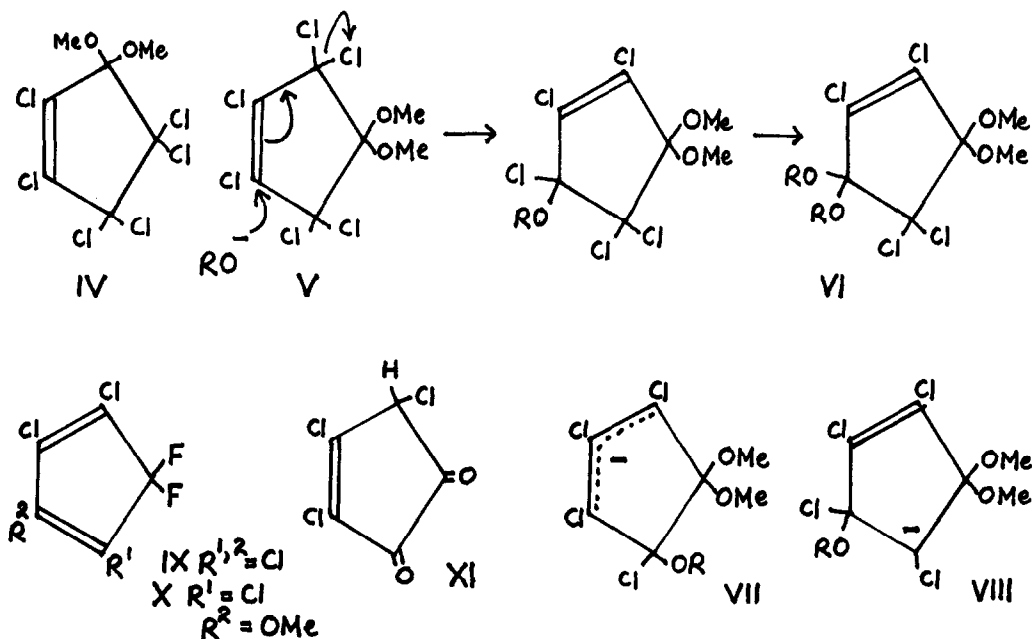
The only chemical evidence adduced for structure (II) for the trimethoxytrichlorodiene is

the hydrolysis of a methanol adduct to give diketone (XI); but since one might not expect such

a large difference between the effect of fluorine and methoxyl groups in ions like (VIII) some

doubt attaches to the claimed difference in behaviour, and therefore also to the structure of

acetal (II). Further Roedig[5] has isolated a cyclopentene-1,3-dione (XII) which has identical

physical properties to diketone '(XI)' reported by McBee.[4] These conflicting observations

prompted us to reinvestigate the structures of vinylic ethers derived from acetal (I).

Ethylene acetal (XIII)[6] yields a crystalline monomethoxy derivative* m.p. 70° $\left[\nu_{max} \ 1616, \right.$

1661 vs cm^{-1} τ 5.79(s 4H) 5.94(s 3H)] when treated with KOH/MeOH. Magnetic equivalence in the

dioxalane protons immediately suggests a β-vinylic ether structure (XIV) rather than the α-

isomer (XV) for this compound. The vinylic ether is slowly hydrolysed in wet environments at

25°; rapid selective hydrolysis effected by aqs. hydrobromic/acetic acid gives a ketone m.p.

117-118° $\left[\nu_{max} \right.$ 1756 vs; 1601 vs cm^{-1} α-chloro CO/C_5 ring and ClC=CCl τ 5.82(m 4H, 5.54(s 1H)]

whose ultraviolet absorption λ_{max} 243nm (log ε 3.99) confirms structure (XVI) when compared to

ketones (XVII)-(XIX), of which only the latter two show high intensity ultraviolet absorption

at 249-259nm (log ε 4.0). Cyclopentenone (XVII), like octachlorocyclopentene, absorbs intensely

only at shorter wavelengths (log ε 4.0 at 232nm, 1.19 at 318nm).[7]

XII

XIII $R^{1}, ^{2} = Cl$
XIV $R^{1} = Cl$ $R^{2} = OMe$
XV $R^{1} = OMe$ $R^{2} = Cl$

XVI

XVII

XVIII $R = Cl$
XIX $R = H$

Hydrolysis of acetal (XVI) in conc. sulphuric acid moreover yields a diketone (XII) m.p. 67–68° $[\nu_{max}$ 1573vs; 1722, 1748, 1779 all vs cm^{-1} ClC=CCl and 1,3-di-CO τ 5.35 ClCH)] identical in physical properties to that described by Roedig.[5]

Attempted acid hydrolysis of the trimethoxytrichlorodiene (III)[**] yields dimeric and other products[:] but adduction with maleic anhydride gives a <u>vinylic</u> <u>ether</u> $[\nu_{max}$ 1640 with τ 5.89(s 3H) ClC=COMe; τ 6.39(s), 6.40(s) 3H each C(OMe)$_2$]; this on hydrolytic ring opening, esterification and selective vinyl ether hydrolysis yields a ketone (XX) m.p. 214–216° $[\nu_{max}$ 1750vs, 1810vs cm^{-1} CO$_2$Me and α,α'-dichloro CO] τ 5.2(d 1H J 3Hz, <u>exo</u>-6-H) 6.2, 6.3(each s, 3H, 9H) 6.3(dd 1H, J 12Hz and 3Hz H-2) 6.73(d 1H J 12Hz, H-3) for which the presence of the chloromethylene n.m.r. <u>doublet</u> exhibiting long range coupling to <u>one</u> proton (^{4}J 3Hz)[10] precludes it being a Wagner-Meerwein rearrangement product derived from an adduct of diene structure (II) and accords only with revised structure (III) for the triether.

All adducts which we[11] have made with the diene (III) e.g. (XXI) consistently exhibit characteristic vinylic ether methoxyl [1]H n.m.r. resonance (τ < 6.0)[9] and typical ClC=COMe absorption near 1645 cm^{-1}. Unlike ketone (XX) however, the hydrolysis product (XXIII) of the isodrin adduct of diene (III) $|\nu_{max}$ 1744vs; 1600m, 1645m cm^{-1} τ 4.6(s 1H, CHCl)] shows only a very small chloromethylene long range coupling, the stereochemistry here presumably precluding formation of the <u>endo</u> chloroketone. Interestingly the methylene bridge protons in ketone (XXIII) have very different chemical shifts τ 7.43 (<u>syn</u>-H) and τ 8.57 (<u>anti</u>-H). For comparison these signals appear at τ 7.92 and 8.79 in the precursor adduct (XXII) and at τ 8.22 and 8.80 in the adduct of isodrin with diene (I) (XXIV) also clearly consistent with the introduction of the vinylic methoxyl group in the former adduct.
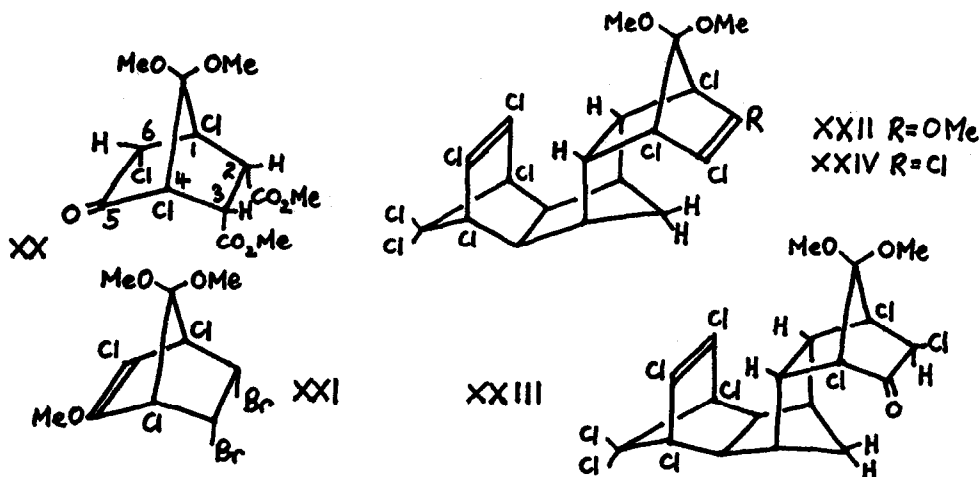
!Particularly stable carbonium ions are formed which may be the precursors of the dimeric and other products. At 77°K in FSO_3H e.s.r. evidence suggestive of the expected substituted cyclopentadienyl triplet cation[8] is observed; the deep blue matrix is stable for some time at low temperatures.

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