4,4′,5,5′-Tetrachlorobidioxolan-2-yl and Bidioxol-2-yl

By B. FUCHS* and S. HAUPTMANN

(*Department of Chemistry, Tel-Aviv University, Ramat-Aviv, Tel-Aviv, Israel*)

Summary The product of the reaction between *trans*-2,3-dichlorodioxan and sulphuric acid is shown to be 4,4′,5,5′-tetrachlorobidioxolan-2-yl from which bidioxol-2-yl is prepared.

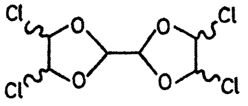
It has been reported[2] that the reaction of *trans*-2,3-dichlorodioxan with hot sulphuric acid afforded a product A, m.p. 143—144 °C, with empirical formula $C_6H_6Cl_4O_4$. Attempts at structural elucidation failed owing to its apparent inertness towards a variety of reagents, although the structures (I) and (II) have been postulated. We now report the means by which we assigned structure (I) to compound A and the preparation of some related compounds.

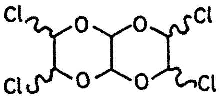
N.m.r. and mass spectrometry, although of diagnostic value for 1,4,5,8-tetraoxadecalin and bidioxolan-2-yl derivatives,[3] were not entirely unequivocal in establishing the structure of A. In its mass spectrum [*m/e* 247(10), 154(20), 141(60), 119(25), 77(55), and 71(100)] the molecular ion is absent and the $M/2^+$ ion (141) occurs with high relative abundance as required by (I).[3] On the other hand, A has a deceptively simple n.m.r. spectrum of three sharp singlets of relative intensities 1 : 1 : 1 at τ 4·33, 3·70, and 3·63. Therefore we sought further chemical evidence for the structure.

Compound A was treated with sodium–t-butyl alcohol in tetrahydrofuran and with magnesium–iodine in ether. In both cases, dechlorination took place giving (in yields of 40 and 80%, respectively) bidioxol-2-yl (III), m.p. 79—80°, τ 4·24 (2H, s) and 3·68 (4H, s), *m/e* 142(17) and 71(100),† which on catalytic hydrogenation with Pd–C, gave bidioxolan-2-yl (IV) (identical with authentic material by m.p., g.l.c., and spectra).[3,4]

Addition of chlorine to (III) in CCl_4 afforded quantitatively another 4,4′,5,5′-tetrachlorobidioxolan-2-yl B, m.p. 124—125°C, τ 4·5 (2H, s) and 3·88 (4H, s), *m/e* 247(10), 154(12), 141(100), 113(22), 107(22), 77(50), and 71(70). Dechlorination of B as before gave back (III). Thus both A and B have the same general structure (I).

Five stereoisomers of (I) are possible: two *trans-trans* isomers [*meso* and (±)] and three *cis-cis* isomers (*endo-exo*, *exo-exo*, and *endo-endo*). We assign the *cis,exo-cis,exo* relationship to B on the basis of its n.m.r. spectrum (two equivalent pairs of enantiotopic-α-chloro hydrogens and two equivalent central hydrogens) and its mode of formation. In the latter, a neighbouring-group effect may occur, where the intermediate chloronium ion is stabilized by the juxtaposed acetal oxygen atoms, causing stereospecific *cis*-attack in the second step of chlorine addition. Concerning the stereochemistry of A, we are unable to designate it since any assignment would need the coincidental similarity of chemical shifts of diastereotopic protons and/or no interaction between them. The initial formation of A is likely to proceed *via* an intermediate carbonium ion species formed in the acid-catalysed degradation of 2,3-dichlorodioxan.


(I)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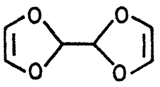
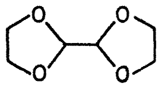
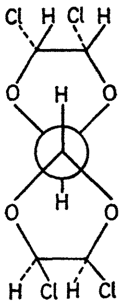

(III)


(IV)


B


(V)

The dehalogenation of A and B to (III) by Na–Bu^tOH–tetrahydrofuran apparently involves a dehydrochlorination step followed by reductive dechlorination, since attempts with sodium–tetrahydrofuran alone failed. On the other hand, the reaction with Mg–I_2 in ether apparently involves chloride replacement and deiodination of the intermediate di-iodide.[5]

The relatively high abundance of the molecular ion in the mass spectrum of bidioxol-2-yl (III) as compared to the bidioxolan-2-yl derivative,[3] could be interpreted in terms of the relative destabilization of the oxonium ion (V), although the extent of delocalization of the oxygen lone pairs in such cations is unknown as yet. This problem and the addition and cycloaddition reactions of (III) are now being studied.

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† N.m.r. spectra were recorded at 100 MHz on a Varian H-100 and at 60 MHz on a Jeol C-60HL instrument. Mass spectra were measured at 70 eV on a Perkin-Elmer–Hitachi RMU-6 mass spectrometer at Bar Ilan University, Ramat Gan, courtesy of Dr. B. Sklarcz. The main fragments are given, and, for the chloro-derivatives, only the ions with ^{35}Cl are given and not the whole isotopic clusters. The new compounds gave satisfactory elemental analyses.

[1] For previous paper in this series, see Y. Auerbach, M. Sprecher, and B. Fuchs, *Tetrahedron Letters*, 1970, 5207.

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

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

[4] J. Boeseken, F. Tellegen, and P. Cohen-Henriquez, *Rec. Trav. chim.*, 1935, **54**, 733.

[5] (a) R. K. Summerbell and R. R. Umhoefer, *J. Amer. Chem. Soc.*, 1939, **61**, 3016; (b) Cort[2] mentioned that A reacted with sodium iodide in acetone but no product was isolated. This behaviour is in accord with that of other vinyl ethers formed in such dechlorination processes (*cf.* R. K. Summerbell and D. K. A. Hyde, *J. Org. Chem.*, 1960, **25**, 1809).