Stereochemistry of the Adduct from Addition of Dichloromethylene to 3-Deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-*erythro*-hex-3-enofuranose

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WE have recently reported[1] on the addition of dichloromethylene to some unsaturated sugars. In particular, the addition of dichloromethylene to 3-deoxy-1,2 : 5,6-di-*O*-isopropylidene-α-D-*erythro*-hex-3-enofuranose (I) appeared to be essentially stereospecific, and the adduct was tentatively assigned the structure 3-deoxy-3,4-*C*-(dichloromethylene)-1,2 : 5,6-di-*O*-isopropylidene-α-D-galactofuranose (II) on the reasonable argument that the carbene would preferentially approach the trioxabicyclo[3,3,0]octane ring system from the *exo*-direction. We now present *X*-ray crystallographic evidence which unequivocally established structure (II) for the adduct.

The stereochemistry of the molecule is clearly indicated in the Figure which shows the arrangement of the atoms as viewed along the *c* axis of the unit cell.

Crystals of the adduct, grown from ethanol, are orthorhombic, space group $P2_12_12_1$, with four molecules in a unit cell of dimensions $a = 17{\cdot}50$, $b = 15{\cdot}72$, $c = 5{\cdot}44$ Å. Three-dimensional intensity data were recorded on equi-inclination Weissenberg photographs using Co-K_α radiation and estimated visually. A total of 778 independent structure amplitudes were derived. The structure was solved by Fourier methods and positional and thermal parameters refined by full-matrix least-squares. At the present stage of refinement the discrepancy R is 19%. Hydrogen atoms were not considered in the analysis and so far the thermal vibrations of the atoms have been assumed to be isotropic.

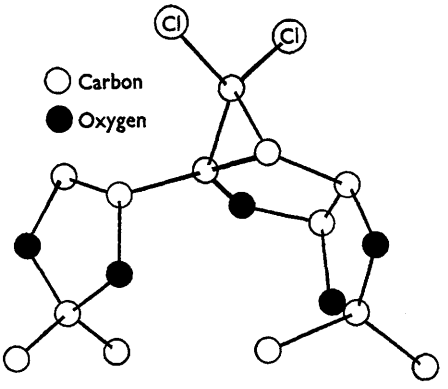
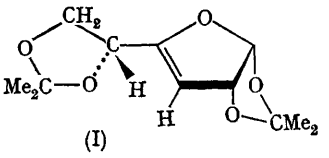


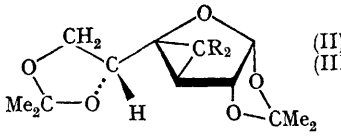
FIGURE. *Drawing of compound* (II) *as viewed along the* c *axis.*

Molecular dimensions are generally satisfactory. Average values for bond lengths are 1·51 Å for C–C, 1·41 Å for C–O, and 1·76 Å for C–Cl in reasonable agreement with the accepted values[2] of 1·54, 1·43, and 1·77 Å, respectively.

Reductive dechlorination of compound (II) gives 3-deoxy-1,2 : 5,6-di-*O*-isopropylidene-3,4-*C*-methylene-α-D-galactofuranose (III),[1] which should serve as an important reference compound in establishing the stereochemistry of other carbene adducts of the unsaturated sugar (I).



(I)



(II) R=Cl
(III) R=H

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[1] J. S. Brimacombe, M. E. Evans, E. J. Forbes, A. B. Foster, and J. M. Webber, *Carbohydrate Res.*, 1967, **4**, 239.
[2] "Table of Interatomic Distances and Configurations in Molecules and Ions," *Chem. Soc. Special Publ.*, 1965, No. 18.