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A NEW REACTION OF 1,2-O-ISOPROPYLIDENE-α-D-GLYCOFURANOSES : REARRANGEMENT INTO 1,2':2,1' DIANHYDRIDES

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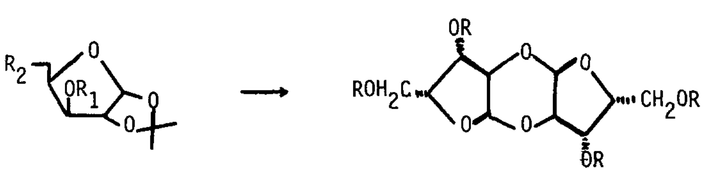
Summary : *Treatment of various 1,2-O-isopropylidene-α-D-glycofuranoses with boron trifluoride etherate in dry benzene at room temperature affords 1,2-cis glycofuranose 1',2'-cis glycofuranos 1,2':2,1' dianhydrides in excellent yield.*

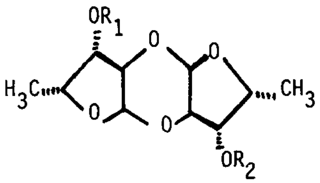
D-fructose and its (2→1) linked polymers are well known to form bimolecular dianhydrides containing a central dioxane ring when acted upon by aqueous acids[1]. Although diketose dianhydrides are typical cases, other sugar dianhydrides have been reported[2]. Low yield is a common feature of these reactions, ranking thus dianhydrides among side products. *We want to report in this letter a rearrangement of 1,2-O-isopropylidene-α-D-glycofuranoses producing a new class of dianhydrides in preparative yield.*

In a typical experiment, treatment of 3,5-di-O-benzyl-1,2-O-isopropylidene-α-D-xylofuranose[3] **1** (3g), $\{\alpha\}_D^{20}$ -43° ($CHCl_3$) with boron trifluoride etherate (3ml) in dry benzene at room temperature (4h) afforded the 1,2':2,1' dianhydride[5] **3** as the sole product (87%), $\{\alpha\}_D^{20}$ -17° ($CHCl_3$), n.m.r. (CCl_4): δ 4.99 (1H,d,$J_{1,2}$4.5Hz,H-1). **3** was converted into crystalline **4** by catalytic hydrogenolysis (Pd/C, ethanol), m.p. 162-163°, $\{\alpha\}_D^{20}$+ 21° (H_2O). The acetate **5** was easily obtained (acetic anhydride-pyridine), $\{\alpha\}_D^{20}$ +37° ($CHCl_3$). Mass spectrometric data (chemical ionisation, NH_3) (m/e 450,m+18) of the acetate **5**, together with a radiocristallographic analysis[6] of the alcohol **4**, call for the proposed symetrical dimeric structures.



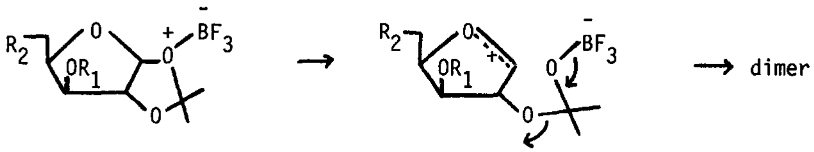
1 R_1= Bn , R_2 = OBn
2 R_1 = Bn ,R_2 = H

3 R = Bn
4 R = H
5 R = Ac



6 R_1 = R_2 = Bn
7 R_1 = R_2 = H
8 R_1 = Ac , R_2 = Bz

Similarly, 3-O-benzyl-5-deoxy-1,2-O-isopropylidene-α-D-xylofuranose[7] 2,$\{\alpha\}_D^{20}$-56° ($CHCl_3$), was converted into dianhydride 6 (88%),$\{\alpha\}_D^{20}$-18° ($CHCl_3$), n.m.r. (CCl_4):δ 4.95(1H,d,$J_{1,2}$4Hz, H-1). Selective acetylation of 7 (acetic anhydride-pyridine),followed by benzoylation (benzoyl chloride-pyridine) provided the unsymetrical derivative 8,$\{\alpha\}_D^{20}$+ 30° ($CHCl_3$). N.m.r. analysis of 8 showed the expected differentiation of the proton signals of both rings. A variety of 1,2':2,1' glycofuranose dianhydrides (xylo and ribo configuration),with different protecting groups, have been obtained in the same way. The formation of these derivatives can be rationalized as shown in the following scheme :



Rearrangement into 1,2 epoxide has not been observed. Dreiding stereomodels show that only one such structure is sterically possible,namely α-D-xylofuranose α-D-xylofuranose 1,2':2,1' dianhydride. To our knowledge,(2,4,8,10)tetraoxatricyclo $(7,3,0,0^{3,7})$dodecane system has not previously been reported.

REFERENCES AND FOOTNOTES

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4. P.A. Levene and A.L. Raymond, J.Biol.Chem., 102, 317 (1933).
5. Satisfactory elemental analyses and i.r.and n.m.r. data have been obtained for all products.
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