Preliminary communication

A novel synthesis of sugar acetals

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Sugar acetals may be prepared from acetylated sugar dithioacetals by the action of mercuric chloride in alcoholic solution¹, or by the action of bromine followed by alcoholic silver carbonate². These methods are multi-stage and give low yields of the acetal. The Claisen³ method of acetal formation has apparently not been used in the carbohydrate field, and we now report on the application of this method to protected, aldehydo sugars.

The method employed involves storage of a mixture containing the aldehydo sugar, triethyl orthoformate, absolute ethanol, and ammonium nitrate at room temperature until a product having a higher chromatographic mobility than the starting sugar is formed; a reaction time of 4—6 days is usually required.

The reaction was applied to the following sugars: 3-O-benzyl-1,2-O-cyclohexyliden α-D-xylo-pentodialdo-1,4-furanose⁴, 2,3:4,5-di-O-isopropylidene-aldehydo-L-arabinose, 2,3,4,5-tetra-O-acetyl-aldehydo-L-arabinose, 2,3,4,5,6-penta-O-acetyl-aldehydo-D-glucose, and 2,3,4,5,6-penta-O-acetyl-aldehydo-D-glactose. The reaction mixtures were subjected to preparative fractionation on alumina to give the following products.

3-O-Benzyl-1,2-O-cyclohexylidene- α -D-xylo-pentodialdo-1,4-furanose diethyl aceta (63%), colourless syrup, [α] $_{\rm D}^{20}$ -38° (c 2, chloroform) (Found: C, 67.10; H,8.52. $C_{22}H_{32}O_6$ calc.: C, 67.34; H, 8.16%).

1,2:3,4-Di-O-isopropylidene-aldehydo-L-arabinose diethyl acetal (83%), colourless syrup, $[\alpha]_D^{20}$ -6° (c 5, chloroform) (Found: C, 59.57; H, 9.41. $C_{13}H_{28}O_6$ calc.: C, 59.22; H, 9.22%).

Tetra-O-acetyl-aldehydo-L-arabinose diethyl acetal (51%), m.p. 60°, $[\alpha]_D^{20}$ -18° (c 10, chloroform) (Found: C, 51.51; H, 7.42. $C_{17}H_{28}O_{10}$ calc.: C, 52.03; H, 7.80%).

Penta-O-acetyl-aldehydo-D-glucose diethyl acetal (40%), colourless syrup, [α] $_{\rm D}^{22}$ +9° (c 5, chloroform) (Found: C, 51.32; H, 6.71. $\rm C_{20}H_{32}O_{12}$ calc.: C, 51.72; H, 6.90 Penta-O-acetyl-aldehydo-D-galactose diethyl acetal (58%), m.p. 81°, [α] $_{\rm D}^{20}$ +16° (c 6, chloroform); lit. 5 m.p. 79°, [α] $_{\rm D}^{20}$ + 17.5°.

REFERENCES

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ANNOUNCEMENT

The Carbohydrate Group (a Chemical Society Subject Group) is holding a meeting at Birkbeck College (University of London) on Tuesday 21st, September, 1971. The programme will include a lecture "Synthesis of Sugar Phosphonates" by Professor H. Paulsen (University of Hamburg), and six general papers.

Further details are available from Dr. N. A. Hughes, Department of Organic Chemistry, The University, Newcastle upon Tyne, NE1 7RU, Great Britain.

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