Preliminary communication

A new synthesis of 2-hydroxyglycals

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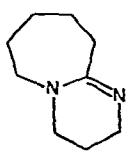
1,5-Diazabicyclo[5.4.0.]undec-5-ene (DBU, **1**) is an interesting reagent because it combines the properties of strong basicity with that of weak nucleophilicity. Therefore, it is an excellent reagent for performing elimination reactions. Its use in the preparation of alkenes has been demonstrated by Oedinger and Möller[1]. In this case, bromoalkanes were dehydrohalogenated with **1** at 80–90°, and the alkenes were obtained in yields of 80–90%. Hanessian and coworkers[2,3] have demonstrated the use of **1** and a related compound, 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) for the elimination of methanesulfonic acid from C-2 and C-3 of glycosides. We have recently become interested in the use of **1** as a reagent for the preparation of unsaturated carbohydrates. The preparation of 2-hydroxyglycals in high yields is the subject of this communication.



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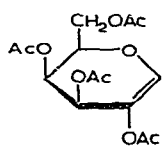

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2-Hydroxyglycals are usually prepared by reaction of polyacylglycosyl halides with diethylamine in benzene[4]; yields are generally quite low. For example, 2,3,4,6-tetra-*O*-acetyl-2-hydroxy-D-galactal (2,3,4,6-tetra-*O*-acetyl-1-deoxy-D-*lyxo*-hex-1-enopyranose, **2**) was prepared in 10% yield from 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide by this method[5]. Several variations of the procedure applied to a variety of polyacylglycosyl halides had limited success[6]. In one of these variations, **2** was obtained in a 32% yield by treatment of 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide with sodium iodide in acetone prior to reaction with diethylamine[7]. In one interesting case, the preparation of 2,3,4,6-tetra-*O*-acetyl-2-hydroxy-D-glucal (2,3,4,6-tetra-*O*-acetyl-1-deoxy-D-*arabino*-hex-1-enopyranose) in 90% yield using 1,4-diazabicyclo[2.2.2]octane was reported[8]. What follows is a typical, simple preparation of a 2-hydroxyglycal derivative using DBU (**1**).

A solution of 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (4.1 g, 10 mmoles) in *N,N'*-dimethylformamide (3 ml) was chilled in an ice-bath and DBU (**1**, 1.67 g,

11 mmoles) was added dropwise. After being kept for 3 h at room temperature, the reaction mixture was diluted with ice–water (15 ml) and stirred. A crystalline solid formed after a few minutes. It was removed by filtration and washed with cold water to give 2 (2.8 g, 85%), m.p. 108–110°. Recrystallization from ethanol raised the m.p. to 112–113.5°; $[\alpha]_D^{24}$ +4.7° (*c* 1, ethanol); lit.[3]: m.p. 110–111°; $[\alpha]_D^{21}$ +4.7° (*c* 1.3, ethanol).

In a similar manner, 2,3,4,6-tetra-*O*-acetyl-2-hydroxy-D-glucal and 2,3,6,2′,3′,4′,6′-hepta-*O*-acetyl-2-hydroxylactal have been prepared in 85% and 76% yields, respectively.

Further experiments are in progress in order to demonstrate the general utility of 1 in the synthesis of 2-hydroxyglycals and to study its effectiveness as a reagent for the preparation of a variety of unsaturated carbohydrates and nucleosides.

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