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Note

Synthesis of hexa-*O*-acetyl-β-rutinosyl chloride using the dichloromethyl methyl ether–boron trifluoride etherate reagent*

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The boron trifluoride etherate-catalyzed reaction of 1,2-*trans*-glycopyranose acetates with dichloromethyl methyl ether at 20° gives the corresponding 1,2-*trans*-glycopyranosyl chlorides in high yield[1] The procedure has been successfully applied[2] for methyl glycopyranuronate 1,2-*trans*-acetates, and the reaction was found to be stereospecific

We now report a novel extension of this method to octa-*O*-acetyl-β-cellobiose and hepta-*O*-acetyl-β-rutinose, from which hepta-*O*-acetyl-β-cellobiosyl chloride (**1**), synthesized recently by a different method[3], and hitherto unknown hexa-*O*-acetyl-β-rutinosyl chloride (**2**), respectively, were obtained in good yield The anomeric configuration of the products was proved by p m r spectroscopy

The mechanism of the reaction was explained[1,2] as proceeding *via* an acyloxonium ion intermediate, and this view is supported by our present investigation Thus, 1,3,4,6-tetra-*O*-acetyl-2-*O*-trichloroacetyl-β-D-glucopyranose (**3**) and 1,3,4,6-tetra-*O*-acetyl-2-chloro-2-deoxy-β-D-glucopyranose (**4**) do not react with the dichloromethyl methyl ether–boron trifluoride etherate reagent The failure to form the glycosyl chloride can be explained by the fact that the C-2 substituent of **3** and **4** is unable to participate with the neighbouring C-1 acetoxyl group, so that an acyloxonium intermediate cannot form By contrast, the zinc chloride[4]- or stannic tetrachloride[5]-catalyzed reaction of compound **4** with dichloromethyl methyl ether gave the known α-glycosyl chloride (**5**)

EXPERIMENTAL

The purity of the products was checked by t l c on Silica gel G (Merck) with 2 1 toluene–ether for monosaccharide derivatives, and 9 1 benzene–acetone for disaccharide derivatives Detection was effected by charring with 5% sulphuric acid in ethanol P m r spectra were recorded for solutions in chloroform-*d* or hexa-

*Synthesis of 1,2-*trans*-Glycopyranosyl Chlorides Part II For Part I, see Ref 1

methylphosphoric triamide with Me_4Si as internal standard, using a Jeol MH-100 (100 MHz) instrument

Hepta-O-acetyl-β-cellobiosyl chloride (**1**) — A solution of octa-*O*-acetyl-β-cellobiose (1 g) in chloroform (3 ml) was treated with dichloromethyl methyl ether (2 ml) and boron trifluoride etherate (0 1 ml) at 20° for 3 h, and then concentrated to dryness *in vacuo* (bath temperature, 20°) A solution of the residue in chloroform was washed with ice-cold water, dried ($MgSO_4$), and concentrated to 5 ml After the addition of ether, the crude product crystallized, and it was recrystallized from chloroform–ether to give **1** (0 71 g, 74%), m p 160°, $[\alpha]_D$ −7 5° (*c* 1 06, chloroform), and −11 3° [*c* 1 05, $P(NMe_2)_3$], lit [3] m p 172–173°, $[\alpha]_D^{22}$ −12 2° [$P(NMe_2)_3$] P m r data [$P(NMe_2)_3$] δ 6 05 (d, 1 H, $J_{1\,2}$ 8 Hz, H-1), lit [3] τ 3 92 ($J_{1\,2}$ 8–9 Hz), the H-1 signal of the α-anomer at δ 6 30 [d, $J_{1\,2}$ 3 9 Hz, $P(NMe_2)_3$] could not be observed in the spectrum of **1**

Anal Calc for $C_{26}H_{35}ClO_{17}$ Cl, 5 41 Found Cl, 5 56

Hexa-O-acetyl-β-rutinosyl chloride (**2**) — Hepta-*O*-acetyl-β-rutinose (1 g) was cleaved (2 h, 20°), by the method described for **1**, to obtain **2** (0 73 g, 76%), m p 152–153°, $[\alpha]_D$ −30 4° (*c* 1 02, chloroform) P m r data [$P(NMe_2)_3$] δ 6 10 (d, 1H, $J_{1\,2}$ 8 Hz, H-1), the H-1 signal of the α-anomer at δ 6 30 (d, $J_{1\,2}$ 3 6 Hz) could not be observed in the spectrum of **2**

Anal Calc for $C_{24}H_{33}ClO_{15}$ Cl, 5 94 Found Cl, 6 00

Treatment of **3** *and* **4** *with the dichloromethyl methyl ether–boron trifluoride etherate reagent* — Compounds **3** and **4** (0 5–0 5 g) were separately dissolved in chloroform (1–2 ml), treated with dichloromethyl methyl ether (1 ml) and boron trifluoride etherate (0 05 ml), and worked-up as described above for **1**

From the reaction mixture of **3**, 0 38 g (76%) of unreacted **3** was recovered after 4 h, m p 163–164°, $[\alpha]_D$ +16 8° (*c* 0 54 chloroform), lit [6] m p 165–166°, $[\alpha]_D$ +17 9° (chloroform)

From the reaction mixture of **4**, 82% of the unchanged starting-material could be recovered after 24 h, m p 114–115° $[\alpha]_D$ +56 2° (*c* 0 45, chloroform) lit [7] m p 114–115°, $[\alpha]_D$ +57 2° (chloroform)

3,4,6-Tri-O-acetyl-2-chloro-2-deoxy-α-D-glucopyranosyl chloride (**5**) — A solution of **4** (1 g) in chloroform (3 ml) was treated with dichloromethyl methyl ether (2 ml) and stannic tetrachloride (0 1 ml) at 20° for 1 h, or zinc chloride (0 1 g) at 50° for 4 h After working-up the reaction mixtures in the usual manner, compound **5** was obtained in 70–75% yield, m p 96–97° (from ether–light petroleum), $[\alpha]_D$ +230° (*c* 0 49, chloroform), lit [8] m p 96–97° and 99–101°, $[\alpha]_D$ +218° and +227 6° (chloroform)

Anal Calc for $C_{12}H_{16}Cl_2O_7$ Cl, 20 66 Found Cl, 20 53

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