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Preliminary Communication

Sulfurylchloride/Trifluoromethanesulfonic Acid. A Novel Promoter System for Glycoside Synthesis using Thioglycosides as Glycosyl Donors

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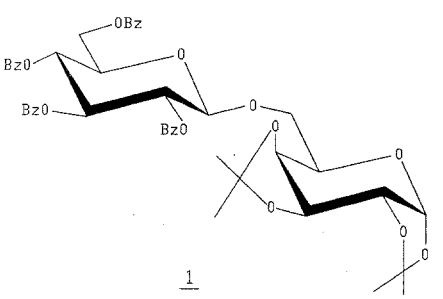
The use of thioglycosides as glycosyl donors in oligosaccharide synthesis has been reviewed [1]. This communication reports a novel method of activation of 1-thioglycosides using sulfuryl chloride in the presence of trifluoromethanesulfonic acid. The reaction of sulfuryl chloride with sulfides in the presence of a strong acid is known to produce a chlorosulfonium salt [2], and it was reasoned that this reaction could be useful in glycoside synthesis using thioglycosides of glycosyl donors. Preliminary results have indicated this to be the case.



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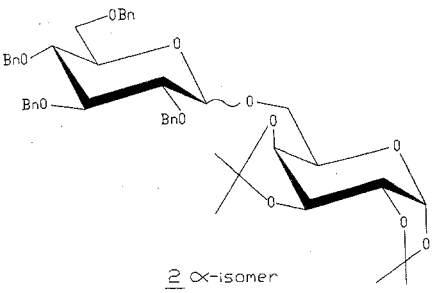

2 α-isomer
3 β-isomer

A 1 M solution of SO_2Cl_2-trifluoroacetic acid in toluene/diethyl ether (9/1 by vol, 1.5 mmol) was added to a solution of 1,2;3,4-di-*O*-isopropylidene-α-D-galactopyranose [3] (1.0 mmol) and either ethyl 2,3,4,6-tetra-*O*-benzoylthio-β-D-glucopyranoside [4] (1.2 mmol) or ethyl 2,3,4,6-tetra-*O*-benzylthio-β-D-glucopyranoside [4] (1.2 mmol) in dichloromethane (5 ml) in the presence of powdered 4Å molecular sieves (2 g) at -78°C.

The temperature was slowly increased (10-20 min) to 0°C, then saturated aqueous $NaHCO_3$ (4 ml) and ethyl acetate (20 ml) were added to the stirred mixture. After 10 min the mixture was filtered, and concentration and silica gel column chromatography of the residues afforded disaccharide derivatives. From the two experiments 6-*O*-(tetra-*O*-benzoyl-β-D-glucopyranosyl)-1,2;3,4-di-*O*-isopropylidene-α-D-galactopyranose [5] **1** or 6-*O*-(tetra-*O*-benzyl-α-D-glucopyranosyl)-1,2;3,4-di-*O*-isopropylidene-α-D-galactopyranose [6] **2** (together with its β-isomer [7] **3**) were isolated. The yield was 82% of **1**, 19% of **2** and 53% of **3**.

These preliminary experiments show that SO_2Cl_2-trifluoroacetic acid is a promising promoter system that gives good yields of the isolated oligosaccharide derivatives. The effectiveness and general usefulness of SO_2Cl_2-trifluoroacetic acid and other variations of this system for oligosaccharide synthesis are under investigation in this laboratory.

References

1 Fügedi P, Garegg PJ, Lönn H, Norberg T (1987) Glycoconjugate J 4:97-108.
2 Meerwein H, Zenner KF, Gipp R (1965) Liebigs Ann Chem 688:67-77.
3 Ballou CE, Fischer HOL (1954) J Am Chem Soc 76:3188-93.
4 Weygand F, Ziemann H (1962) Liebigs Ann Chem 657:98.
5 Garegg PJ, Norberg T (1979) Acta Chem Scand Ser B 33:116-18.
6 Lemieux RU, Hendriks KB, Stick KB, James KJ (1975) J Amer Chem Soc 97:4056-62.
7 Garegg PJ, Ortega C, Samuelsson B (1981) Acta Chem Scand Ser B 35:631-33.