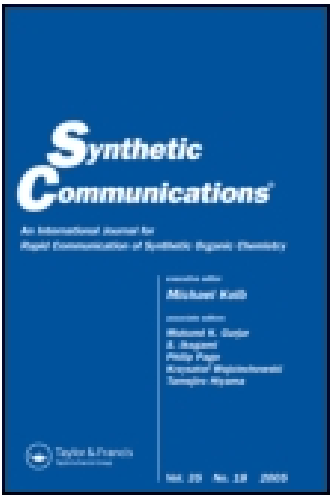

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YTTERBIUM(III) TRIS[BIS(PERFLUOROBUTYLSULFONYL)AMIDE] AS A LEWIS ACID FOR GLYCOSIDATIONS

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ABSTRACT

The reaction of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl acetate with alcohols in the presence of 5 mol% ytterbium(III) tris[bis(perfluorobutylsulfonyl)amide] as an activator afforded the corresponding glucopyranosides in good yields. This ytterbium complex also activated the benzylated glucosyl donors having trichloroacetoimidate, fluoride, and methoxyacetate as the leaving groups.

Glycosidation is a significant method for synthesizing glycosides and oligosaccharides related to natural products and their analogs for the investigation of their biological functions.[1] Most of the known glycosidation methods are based on the activation of a leaving group of a glycosyl donor.[2] Lewis acids are widely used as an activator of a leaving group, and in synthetic carbohydrate chemistry, it is very important to develop a new Lewis acid for glycosidation methods.

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Trifluoromethanesulfonic acid (TfOH) shows strong Brønstead acidity due to the effect of the powerful electron-withdrawing trifluoromethanesulfonyl (Tf) group, and their metal complexes [$M(OTf)_n$)], whose bonds between metals and OTf are very weak, indicate high Lewis acidity. They are used as efficient Lewis acids for organic reactions in many research studies.[3] More interest has been concentrated on the stronger Lewis acids provided by the perfluoroalkylsulfonyl (Rf) groups having long alkyl chains and/or by amine replaced by two Rf groups. The metal complexes, $M(ORf)_n$ and $M[N(ORf)_2]_n$, have been employed as versatile catalysts in organic reactions such as the Diels-Alder reaction, Friedel-Craft acylation, and esterification.[4–7] Mikami *et al.* have reported that ytterbium(III) tris[bis(perfluorobutylsulfonyl)amide] {$Yb[N(O_2SC_4F_9)_2]_3$} (YTA) catalyzed these reactions more efficiently than $Yb(OTf)_3$.[8,9]

The recent studies by us and other groups showed that 1-*O*-acyl sugars as glycosyl donors are useful because they are stable and easy to prepare.[10–13] However, some of them are difficult to activate, and it was reported that 2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl acetate (**1**) was not easily activated by lanthanide trifluoromethanesulfonates.[14] As part of our continuous study of glycosidation, we utilized YTA as the Lewis acid for the glycosidation of **1** and other glycosyl donors.

First of all, based on the property of the strong affinity of YTA for carbonyl groups, we investigated the reaction between **1** and *n*-octanol in CH_2Cl_2. The effect of amounts of YTA was examined. This glycosidation proceeded in the presence of a catalytic amount of YTA. The reaction conditions using only 5 mol% YTA afforded the corresponding glucoside in 71% yield with the stereoselectivity of an α/β ratio of 33/67. However, the reaction condition using less than 5 mol% YTA reduced the yields of the glucoside.

Secondly, the effect of solvents was examined using CH_2Cl_2, CH_3CN, PhH, hexafluorobenzene, and Et_2O. Although the reaction using CH_2Cl_2 gave the glucoside in good yield, the other solvents, except for CH_2Cl_2 were not suitable for this glycosidation. YTA was relatively soluble in CH_2Cl_2 but was almost insoluble in the other solvents. The solubilities of YTA were apparently important for the process of this glycosidation.

Thirdly, the effect of drying agents was examined using molecular sieves (MS) 4A, $CaSO_4$, Na_2SO_4, and $MgSO_4$. The reaction using MS 4A gave no glucoside at all because the basic component of MS 4A could reduce the acidity of YTA. The corresponding glucoside was obtained in 81% yield with an α/β ratio of 72/28 by the reaction using $CaSO_4$. Interestingly, the addition of $CaSO_4$ changed the stereoselectivity of this

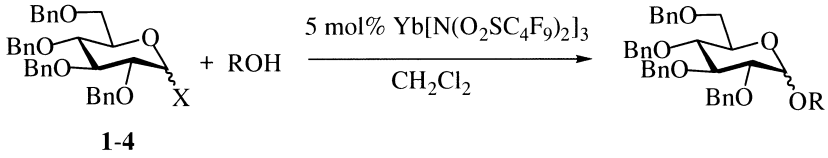

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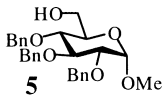
Table 1. Glycosidation Using 5 mol% $Yb[N(O_2SC_4F_9)_2]_3$

Entry[a]	X	ROH	Drying Agent	Yield/%	α/β
1[b]	OAc	*n*-Octanol	none	12	29/71
2[c]	OAc	*n*-Octanol	none	58	27/73
3	OAc	*n*-Octanol	none	74	31/69
4	OAc	*n*-Octanol	MS 4A	no reaction	—
5	OAc	*n*-Octanol	$CaSO_4$	81	72/28
6	OAc	*n*-Octanol	Na_2SO_4	22	18/82
7	OAc	*n*-Octanol	$MgSO_4$	79	32/68
8	OAc	**5**	none	68	49/51
9	$OC(O)CH_2OCH_3$	**5**	none	69	54/46
10	F	*n*-Octanol	none	64	68/32
11	F	**5**	none	69	63/37
12	$OC(NH)CCl_3$	*n*-Octanol	none	69	31/69
13	$OC(NH)CCl_3$	**5**	none	50	44/56

[a]Molar ratio Donor: ROH=1:1.
[b]3 mol% $Yb[N(O_2SC_4F_9)_2]_3$ was used.
[c]4 mol% $Yb[N(O_2SC_4F_9)_2]_3$ was used.



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glycosidation compared with the additions of other metal sulfates or none. In this glycosidation system, it seemed that the complex between ca^{2+} and the glycosyl intermediate played an important role in the appearance of the α-stereoselectivity.

Finally, we used YTA in the glycosidations using several glycosyl donors. As the glycosyl donors, 2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl methoxyacetate (**2**), 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl trichloroacetoimidate (**3**), and 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl fluoride (**4**) were used. The reactions of these glycosyl donors with *n*-octanol or methyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (**5**) afforded the corresponding glucosides in satisfactory yields. The reaction using **2** and **4** gave the α-glucosides predominantly,[15,16] and on the other hand, the β-glucosides were obtained by the reactions using **1** and **3**. We found that the stereoselectivities of glucosides were also interestingly changed by the species of the leaving groups of the glycosyl donors.

As mentioned above, we found that YTA is useful as an activator of the benzylated glycosyl donors having acetate, methoxyacetate, fluoride, and trichloroacetoimidate as the leaving groups and that, in some cases, the stereoselectivities of the glycosidation were influenced by the species of the leaving group of the glycosyl donor and the effect of the metal ion of the drying agent.

EXPERIMENTAL

^{1}H NMR and ^{13}C NMR spectra were recorded on JEOL EX-400 spectrometers with tetramethylsilane as the internal standard in $CDCl_3$.

General Procedure

To a solution of glycosyl acetate (0.2 mmol) and alcohol (0.2 mmol) in CH_2Cl_2 (4 mL) was added YTA (0.01 mmol). The resulting mixture was stirred overnight. The reaction was then quenched with sat. $NaHCO_3$ solution (5 mL). The mixture was extracted with $CHCl_3$, and the organic layer was washed with water and sat. NaCl solution. After the organic layer was dried over Na_2SO_4, the solvent was evaporated under reduced pressure. The crude product was purified by a preparative silica gel TLC to give the corresponding glucoside.

n-Octyl 2,3,4,6-tetra-*O*-benzyl-α and β-D-glucopyranoside

^{13}C NMR $\delta = 103.54$ (C-1β), 96.78 (C-1α); ^{1}H NMR $\delta = 4.75$ (d, H-1α, $J = 3.2$ Hz), 4.39 (d, H-1β, $J = 8.0$ Hz).

Methyl 6-*O*-(2,3,4,6-tri-*O*-benzyl-D-glucopyranosyl)-2,3,4,-tri-*O*-benzyl-α and β-D-glucopyranoside

^{13}C NMR $\delta = 103.70$ (C-1$'\beta$), 97.94 (C-1β), 97.85 (C-1α), 97.15 (C-1$'\alpha$); ^{1}H NMR $\delta = 3.35$ (s, OMeα), 3.33 (s, OMeβ).

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