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Note

Glycosyl trichloroacetylcarbamate: a new glycosyl donor for O-glycosylation

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Abstract—Glycosyl trichloroacetylcarbamates, readily obtained by reacting 1-hydroxy sugars with trichloroacetylisocyanate, have been found as excellent glycosyl donors, and the corresponding *O*-glycosides are formed in good to excellent yields with a fairly good degree of selectivity.

Keywords: O-glycosylation; Trichloroacetylisocyanate; Trimethylsilyltriflate; Trichloroacetylcarbamate

The importance of glycobiology and subsequently the chemistry of glycoconjugates has gained[1] enormous attention over the past few years owing to the understanding of the roles of carbohydrates in biological events. These glycoconjugates which mainly exist as glycolipids or glycoproteins play unique roles in events such as cell adhesion, cell growth, inflammation, immune response, among others.[2] Glycoconjugates procured from biological sources are often micro-heterogeneous. Therefore, clearly, there is a need to develop stereoselective methods for *O*-glycoside bond formation since in a majority of glycolipids and glycoproteins the carbohydrate moieties are linked to lipids and many proteins through *O*-glycosidic linkages. After the classical Koenigs–Knorr method[3] of *O*-glycoside bond formation, a plethora of newer methodologies have been introduced[4] in the literature addressing various aspects such as stereoselective formation and reactions of glycosyl donors, effect of temperature and solvent during *O*-glycoside bond formation, compatibility of functional groups, etc. The effectiveness of the glycosylation depends upon the nature of the leaving group at the anomeric centre and its activation with a Lewis acid or another activator. Some of the most useful leaving groups include trichloroacetimidate,[5] a thioglycoside,[6] a pentenyl-*O*-glycoside[7] and fluoride.[8] However, since not a single method is universally applicable to address the issues of glycoside bond formation with desired suitability, newer functionalities need to be introduced at the anomeric carbon atom. One such functionality that has received scant attention is a carbamate moiety,[9] prepared by reacting 1-hydroxy sugars with an appropriate isocyanate. Likewise, even carbonates[4a,10] which are structurally analogous to carbamates have even less frequently been employed in glycosylation reactions. In this regard, one of the very interesting reports by Hinklin and Kiessling[9a] dealing with the formation of glycosyl sulfonylcarbamates followed by N-alkylation to permit tunable reactivity has appeared recently. This led us to explore if new glycosyl carbamates could be prepared and assessed for *O*-glycoside bond formation, with possibly improved selectivity. To this effect, we have found that *O*-trichloroacetylcarbamte **5**, formed upon reaction of 1-hydroxy sugar **1** with trichloroacetyl isocyanate, acts as an excellent glycosyl donor permitting *O*-glycoside bond formation. It was expected that trichloroacetyl isocyanate could react more readily with 1-hydroxy sugars owing to more powerful electron withdrawing nature of the trichloroacetyl group compared to the *p*-toluenesulfonyl group. For the same reason,

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the corresponding carbamate would act as a better leaving group, perhaps not requiring added functionalisation, to permit glycosylation.

Thus, glycosyl trichloroacetylcarbamates were readily obtained by the treatment of C-1 unprotected pyranose with trichloroacetylisocyanate (1 equiv) in dichloromethane at 0 °C using a base such as Et_3N, DBU, DABCO and NaH (Table 1). Among the various bases used, DBU was found to be the best both in terms of yield and anomeric selectivity, although with each of these bases, formation of the α-anomer was always higher. Thus, glucose-, galactose- and mannose-based 1-hydroxy sugars **1**–**4** formed trichloroacetylcarbamates **5**–**8** (Scheme 1) in excellent yields (85–95%) (Table 1). The glycosyl carbamates were quickly filtered over a small silica gel column to remove any base impurity and used directly for the glycosylation reactions, since usual purification by column chromatography caused some decomposition.

Initial glycosylation reactions with tetra-*O*-benzyl glucose derived donor **5** were carried out with 2-propanol as an acceptor using different solvents (CH_2Cl_2, CH_3CN and Et_2O) and promoters ($BF_3{\cdot}Et_2O$, TMSOTf) as shown in Table 2. Thus, using acetonitrile as a solvent and $BF_3{\cdot}Et_2O$ as the promoter, at room temperature, the glycosylation was in favour of β-selectivity[11] (1:2); however, the reaction was somewhat slow (12 h) and the yield was moderate (50%). Surprisingly, no reaction occurred while using $BF_3{\cdot}Et_2O$ or TMSOTf as promoters in Et_2O. On the other hand, the use of TMSOTf in CH_2Cl_2 at 0 °C led to the reversal of the selectivity (α:β = 2:1) and with higher yield (89%). From the above results, it is clear that the use of CH_2Cl_2 as a solvent and TMSOTf as the promoter is the ideal combination.

Table 1. Formation of the glycosyl donors with different bases

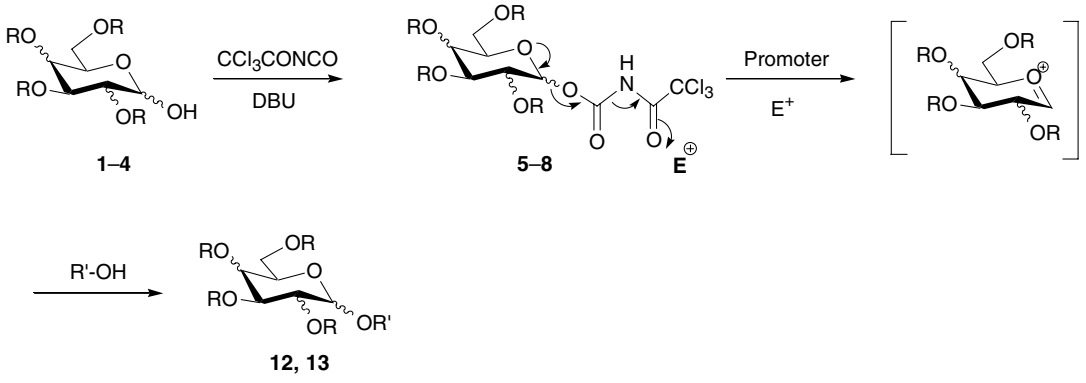
Entry	Sugar	Base (equiv)	Time (min)	Donor, yield (%) (α:β)
a	**1**	Et_3N (1.1)	30	**5**, 79 (4:1)
b	**1**	DBU (0.1)	15	**5**, 91 (12:1)
c	**1**	NaH (1.5)	5	**5**, 88 (1:1)
d	**1**	DABCO (2.0)	30	**5**, 83 (5:1)
e	**2**	DBU (0.1)	30	**6**, 86 (8:1)
f	**3**	DBU (0.1)	10	**7**, 95 (12:1)
g	**4**	DBU (0.1)	45	**8**, 86 (3:1)

In order to compare this procedure with that of Hinklin and Kiessling,[9a] we attempted allylation of donor **5** with allyl bromide and diisopropyl ethyl amine. It was observed that the allylation proceeded extremely slowly (72 h) at room temperature and in moderate yield (60%). Further, the glycosylation using this N-allylated donor with 2-propanol was also slow, requiring 48 h for the reaction to complete, although the yield was somewhat better (94%) but there was no special preference for selectivity compared to the results obtained without N-allylation. Hence, we proceeded without N-alkylation for the rest of our studies.

The general scope of the glycosylation was studied by reacting glycosyl carbamate **5** with a variety of acceptors including primary, secondary, tertiary, allylic, benzylic and phenolic functionalities, all of which formed the corresponding *O*-glycosides in good yields (Table 2). Although *tert*-butanol did react at room temperature in 72% yield, no selectivity was observed (Table 2, entry l). Interestingly, reaction with β-naphthol, under the same conditions, rearranged β-*C*-glycoside was obtained in 87% yield, an observation that is similar to the one reported by Mahling and Schmidt[12] (Table 2, entry m).

Further, several disaccharides were also readily obtained by coupling appropriate donors (**5**–**8**) and acceptors (**9**–**11**) under similar reaction conditions as above. Our results are summarised in Table 3.

The diastereoselectivity of the glycosylation reaction was found to be dependent on reaction temperature (Table 3, entries a–d). Thus, at lower temperatures more β glycosides were formed (cf. comparison of entries b and c, and l and n, Table 3) for glucose and mannose based reactions. Further, the more reactive 6-hydroxy acceptor **9** reacts with **5** even at −80 °C to yield the corresponding disaccharide (Table 3, entry d) in 73% yield with 1:4 (α:β) selectivity implying high reactivity of the



Scheme 1.

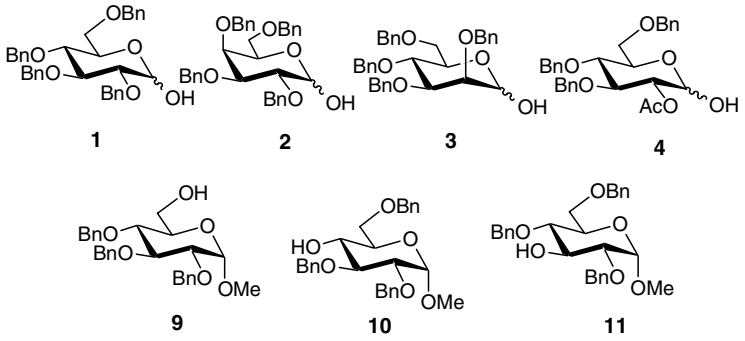


Table 2. Glycosylation of **5** with different acceptors under varying conditions

Entry	Acceptor	Solvent	Promoter	Temperature (°C), time (h)	**12**, Yield (%) (α:β)
a	*i*-PrOH	CH_2Cl_2	TMSOTf	0 (0.2)	89 (2:1)[13]
b	*i*-PrOH	CH_2Cl_2	$BF_3{\cdot}OEt_2$	25 (3)	74 (1:1)
c	*i*-PrOH	CH_3CN	$BF_3{\cdot}OEt_2$	25 (12)	50 (1:2)
d	*i*-PrOH	CH_3CN	TMSOTf	No rxn	No rxn
e	*i*-PrOH	$(Et)_2O$	TMSOTf	No rxn	No rxn
f	*i*-PrOH	$(Et)_2O$	$BF_3{\cdot}OEt_2$	No rxn	No rxn
g	Allyl alcohol	CH_2Cl_2	TMSOTf	0 (0.1)	98 (1:4)[14]
h	BnOH	CH_2Cl_2	TMSOTf	0 (0.1)	95 (1:4)[15]
i	Phenol	CH_2Cl_2	TMSOTf	0 (0.2)	93 (10:1)[13]
j	EtOH	CH_2Cl_2	TMSOTf	0 (0.2)	50 (1:1)[16]
k	$BnO(CH_2)_2OH$	CH_2Cl_2	TMSOTf	0 (0.2)	50 (1:3)[17]
l	*t*-BuOH	CH_2Cl_2	TMSOTf	0 (0.2)	50 (1:1)[13]
m	β-Naphthol	CH_2Cl_2	TMSOTf	0 (0.2)	50 (0:1)[12]

Table 3. Formation of disaccharides using TMSOTf as a promoter and CH_2Cl_2 as a solvent

Entry	Donor	Acceptor	Temperature (°C), time (min)	**13**, Yield (%) (α:β)
a	**5**	**9**	25 (5)	60 (9:1)[13]
b	**5**	**9**	0 (5)	94 (9:1)
c	**5**	**9**	−40 (10)	78 (1:4)
d	**5**	**9**	−80 (10)	73 (1:4)
e	**5**	**10**	0 (10)	67 (1:1)[18]
f	**5**	**10**	−80 (10)	65 (1:1)
g	**5**	**11**	−80 (10)	75 (1:1)[19]
h	**6**	**9**	0 (5)	92 (1:5)[20]
i	**6**	**9**	−40 (5)	85 (1:5)
j	**6**	**10**	0 (5)	76 (1:2)[21]
k	**6**	**11**	0 (5)	70 (1:1)[22]
l	**7**	**9**	0 (5)	94 (8:1)[23]
m	**7**	**9**	−40 (30)	82 (1.5:1)
n	**7**	**9**	−85 (90)	65 (1:2)
o	**7**	**10**	0 (5)	88 (1:0)[24]
p	**7**	**11**	0 (5)	76 (1:0)[19]
q	**7**	**11**	−40 (10)	56 (5:1)
r	**8**	**9**	0 (30)	74 (0:1)[25]
s	**8**	**10**	0 (40)	57 (0:1)[26]
t	**8**	**11**	0 (10)	68 (0:1)

glycosyl carbamates. Hindered acceptors (**10** and **11**) also reacted readily and produced the disaccharides; however, no selectivity was observed (Table 3, entries e–g and k). Further, as expected, mannose-derived donor **7** upon reaction with different acceptors exclusively yielded the thermodynamically stable α-glycosides (entries o and p) or as the major product (entry l). Further, with acceptor **9** generally higher α-selectivity was observed at 0 °C, or at room temperature (entries a, b, l and m) and higher β-selectivity at lower temperatures (entries c, d, h–j and n).

We have also examined the effect of neighbouring group participation in the glycosylation reaction using the donor **8** (acetyl participating group at C-2) with different acceptors (**9**–**11**). Thus, the disaccharides (Table 3, entries r–t) were obtained in moderate to good yields and with complete β-selectivity.

In conclusion, the glycosylation strategy described here, offers the possibility to obtain both α and β glycosides. Further, crude carbamate donors are good enough for the glycosylation reactions with the use of catalytic amount of TMSOTf as a promoter. Also, the present carbamate donors do not need further functionalisation for effective glycosylations. In this regard, the selectivity is comparable to the work described by Hinklin and Kiessling[9a] and thus the present method is an alternative to their work. We expect that the present glycosylation method would be useful in organic synthesis.

1. Experimental

1.1. General methods

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a JEOL JNM-LA 400 FT NMR spectrometer in a solution of $CDCl_3$ as a solvent using Me_4Si as the internal standard. Infrared spectra were recorded on a Bruker Vector 22 FT-IR spectrometer. Elemental analyses were determined using a Thermoquest CE-instruments EA-1110 automatic elemental analyser. Mass spectra were recorded on a Microscopic II Triple Quadrupole mass spectrometer using electro spray technique. Rotation values were recorded on Autopol II automatic polarimeter at the wavelength of sodium D-line (589 nm). Thin-layer chromatography (TLC) was performed on precoated plates (E. Merck, Germany). Solvents and liquid reagents were purified and dried according to the recommended procedures.

1.2. General procedure for preparation of glycosyl trichloroacetylcarbamate donors

To a stirred solution of the 1-OH sugar (1 mmol) (**1**–**4**) in dry CH_2Cl_2 was cooled to 0 °C followed by base [Et_3N (1.1 equiv) or NaH (1.5 equiv) or DABCO (2.0 equiv) or DBU (0.1 equiv)], and trichloroacetylisocyanate (1.1 mmol) was added dropwise. The mixture was stirred under nitrogen atmosphere 5–45 min (monitored by TLC), followed by evaporation of the solvent under reduced pressure and filtration through a short pack of column (SiO_2, 100–200 mesh) gave the desired donors (**5**–**8**).

1.2.1. 2,3,4,6-Tetra-*O*-benzyl-α,β-D-glucopyranosyl *N*-trichloroacetylcarbamate (5). Colourless oil, $[\alpha]_D^{30}$ +31.0 (*c* 1.0, $CHCl_3$); FTIR: ν_{max} (neat film) 1809, 1745, 1495, 1361 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (br s, α isomer) and 8.31 (br s, β isomer, 1H), 7.33–7.13 (m, 20H), 6.36 (d, *J* 3.4 Hz, α isomer) and 5.63 (d, *J* 7.8 Hz, β isomer, 1H, H-1), 4.95 (d, *J* 11.0 Hz, 1H), 4.88–4.79 (m, 2H), 4.73 (d, *J* 11.7 Hz, 1H), 4.67 (d, *J* 11.4 Hz, 1H), 4.59 (2d, *J* 11.9 Hz, 1H), 4.52–4.43 (m, 2H), 3.97 (t, *J* 9.3 Hz, 1H), 3.92 (br d, *J* 10.0 Hz, 1H), 3.79–3.71 (m, 3H), 3.65 (dd, *J* 10.8, 1.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.4, 156.9, 148.5, 147.9, 138.3, 137.9, 137.7, 137.5, 137.0, 128.5–127.6 (m), 96.0, 93.7, 91.5, 84.6, 81.2, 80.0, 78.3, 76.5, 75.4, 74.8, 73.5, 73.4, 73.3, 67.7; ESIMS: *m*/*z* 750 [M+Na]$^+$.

1.2.2. 2,3,4,6-Tetra-*O*-benzyl-α,β-D-galactopyranosyl *N*-trichloroacetylcarbamate (6). Colourless oil, $[\alpha]_D^{30}$ +41 (*c* 1.0, $CHCl_3$); FTIR: ν_{max} (neat film) 1811, 1751, 1492, 1265 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (br s, α isomer) and 8.19 (br s, β isomer, 1H), 7.41–7.24 (m, 20H), 6.42 (d, *J* 3.6 Hz, α isomer) and 5.59 (d, *J* 8.1 Hz, β isomer, 1H, H-1), 4.95 (d, *J* 11.2 Hz) and 4.88 (d, *J* 11.7 Hz, 1H), 4.81 (d, *J* 11.7 Hz, 1H), 4.74 (d, *J* 11.6 Hz, 1H), 4.73 (br s, 2H), 4.61 (d, *J* 11.4 Hz) and 4.56 (d, *J* 11.2 Hz, 1H), 4.46 (d, *J* 11.9 Hz, 1H), 4.39 (2d, *J* 11.7 Hz, 1H), 4.22 (dd, *J* 10.3, 3.7 Hz, 1H), 4.13 (br t, *J* 6.4 Hz, 1H), 4.05 (br s, 1H), 3.97 (br dd, *J* 10.2, 2.5 Hz, 1H), 3.54 (br d, *J* 6.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.3, 148.9, 138.3–137.6 (m), 128.4–127.4 (m), 95.0, 91.7, 78.4, 75.0, 74.9, 74.2, 73.7, 73.5, 73.0, 72.6, 68.2; ESIMS: *m*/*z* 750 [M+Na]$^+$.

1.2.3. 2,3,4,6-Tetra-*O*-benzyl-α,β-D-mannopyranosyl *N*-trichloroacetylcarbamate (7). Colourless oil, $[\alpha]_D^{30}$ +26 (*c* 1.5, $CHCl_3$); FTIR: ν_{max} (neat film) 1807, 1727, 1493, 1266 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.98 (br s, β isomer) and 8.48 (br s, α isomer, 1H), 7.39–7.15 (m, 20H), 6.26 (br s, α isomer) and 5.67 (br s, β isomer, 1H, H-1), 4.92 and 4.87 (2d, *J* 10.7 Hz, 1H), 4.75 (br s, 2H), 4.66–4.48 (m, 5H), 4.09 (t, *J* 9.5 Hz, 1H), 3.91 (dd, *J* 9.5, 2.9 Hz, 1H), 3.87 (m, 1H), 3.84 (t, *J* 4.1 Hz, 1H), 3.77 (dd, *J* 11.2, 4.4 Hz, 1H), 3.70 (br d, *J* 11.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.4, 148.1, 137.9–137.4 (m), 128.4–127.6 (m), 95.0, 91.5, 78.6, 75.2, 74.8, 73.8, 73.4, 73.1, 72.7, 72.2, 68.5; ESIMS: *m*/*z* 750 [M+Na]$^+$.

1.2.4. 2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α,β-D-glucopyranosyl *N*-trichloroacetylcarbamate (8). Colourless oil, $[\alpha]_D^{30}$ +46.6 (*c* 1.1, $CHCl_3$); FTIR: ν_{max} (neat film) 1819, 1760, 1267, 1228 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.99 (br s, β isomer) and 8.48 (br s, α isomer, 1H), 7.34–7.13 (m, 15H), 6.37 (d, *J* 3.7 Hz, α isomer) and 5.66 (d, *J* 8.3 Hz, β isomer, 1H, H-1), 5.10 (m, 1H), 4.86–4.74 (4d, *J* 11.2 Hz, 2H), 4.69–4.46 (6d, *J* 11.4 Hz, 3H), 4.04 (t, *J* 9.3 Hz, 1H), 3.98 (br d, *J* 10.4 Hz, 1H), 3.89–3.71 (m, 3H), 3.68 (dd, *J* 11.0, 1.7 Hz) and 3.61 (dt, *J* 9.8, 2.2 Hz, 1H), 1.98 and 1.95 (2s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.9, 169.8, 157.8, 157.3, 148.5, 147.7, 137.5–138.1 (m), 128.4–127.5 (m), 94.2, 93.6, 91.5, 91.1, 82.4, 79.3, 76.8, 76.7, 75.6, 75.4, 74.9, 73.8, 73.5, 71.7, 71.5, 67.7, 67.6, 20.7, 20.6; ESIMS: *m*/*z* 702 [M+Na]$^+$.

1.3. General procedure for the glycosylation reactions

A solution of a carbamate (**5**–**8**) (1 mmol) and an acceptor (1.5 mmol) was stirred in dry CH_2Cl_2 in the presence of freshly activated molecular sieves under nitrogen atmosphere at 0 °C. To this suspension was added dropwise a solution of TMSOTf (0.1 mmol) in the same solvent. The progress of the reaction was monitored by TLC. The reaction was then neutralised by the addition of solid $NaHCO_3$, followed by filtration and evaporation of the solvent under reduced pressure to give the crude product that was purified by column chromatography on silica gel.

1.3.1. Methyl (2-*O*-acetyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-(1→3)-2,4,6-tri-*O*-benzyl-α-D-glucopyranoside (13t) (corresponding to entry t, Table 3). Colourless oil, $[\alpha]_D^{30}$ +51.4 (*c* 0.35, $CHCl_3$), ^1H NMR (400 MHz, $CDCl_3$): δ 7.38–7.10 (m, 30H), 5.10–5.02 (m, 3H), 4.84 (d, *J* 11.5 Hz, 1H), 4.77 (d, *J* 10.8 Hz, 1H), 4.70 (d, *J* 11.5 Hz, 1H), 4.69 (d, *J* 11.2 Hz, 1H), 4.57–4.39 (m, 7H), 4.32 (t, *J* 9.3 Hz 1H), 3.82 (t, *J* 9.4 Hz, 1H), 3.73–3.52 (m, 8H), 3.50 (dd, *J* 9.5, 3.4 Hz, 1H), 3.42 (br d, *J* 8.0 Hz, 1H), 3.31 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.5, 136.2, 138.5, 138.3, 138.2, 137.8, 137.7, 128.4–127.3 (m), 100.3, 97.4, 83.2, 81.1, 78.3, 77.9, 75.6, 75.1, 75.0, 74.9, 74.8, 73.9, 73.5, 73.4, 73.3, 69.6, 68.6, 68.5, 55.0, 21.1; ESIMS: *m*/*z* 961 $[M+Na]^+$. Anal. Calcd for $C_{57}H_{62}O_{12}$: C, 72.90; H, 6.65. Found: C, 72.85; H, 6.62.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.2005.07.024.

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