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Phenyl 2-azido-2-deoxy-1-selenogalactosides: a single type of glycosyl donor for the highly stereoselective synthesis of α- and β-2-azido-2-deoxy-D-galactopyranosides

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ABSTRACT

Efficient glycosylation with phenyl 2-azido-2-deoxy-1-seleno-α-D-galactosides of glycosyl acceptors with different reactivities has been developed. The reaction provided glycosides of 2-azido-2-deoxy-D-galactose in good to high yields. The stereochemical outcome of the glycosylation of reactive acceptors (3-trifluoroacetamidopropanol and methyl 2,3-*O*-isopropylidene-α-L-rhamnopyranoside) can be broadly varied from complete β- to high α-selectivity by changing the reaction solvent, promoter and protecting groups in the donor, while the glycosylation of less reactive allyl 2,2′,3,3′,6,6′-hexa-*O*-benzoyl-β-lactoside afforded the corresponding α-glycosides exclusively.

Introduction

N-Acetyl-D-galactosamine (GalNAc) is widely distributed in living systems being a principal constituent of glycoproteins, glycolipids, proteoglycans,[1] and polysaccharides of bacterial[2] and fungal[3] origin. In these glycoconjugates, GalNAc can be bound to other monosaccharides (or to amino acids) by both α- and β-glycoside bonds. D-Galactosamine is commercially available but rather expensive; for this reason, derivatives of 2-azido-2-deoxygalactose are usually used in the synthesis of GalNAc-containing oligosaccharides or *O*-glycosylated amino acids. Most often, 2-azido-2-deoxygalactosyl donors are synthesized by azidonitration of D-galactal according to the Lemieux procedure[4] and subsequent transformation of the formed 2-azido-2-deoxygalactosyl nitrates over several synthetic steps into the corresponding 2-azido-2-deoxygalactosyl halides, imidates, and other types of glycosyl donors. Recently we reported an improved method for the homogeneous azidophenylselenylation of D-galactal derivatives leading in one step to phenyl 2-azido-2-deoxyselenogalactosides[5] that can be directly used as 2-azido-2-deoxygalactosyl donors. Thus, some phenyl 2-azido-2-deoxyselenogalactosides were employed for the α-glycosylation of L-serine and L-threonine derivatives[6,7] and simple aliphatic alcohols.[6,8,9] Also, few examples are known for the indirect application of 2-azido-2-deoxyselenogalactosides, that is, involving their prior transformation to more conventional 2-azido-2-deoxygalactosyl fluoride[10] or imidates,[9,11] in oligosaccharide synthesis. However, to the best of our knowledge, neither the direct application of 2-azido-2-deoxyselenogalactosides to the synthesis of GalN-containing oligosaccharides, nor the systematic study of factors affecting the efficiency and stereoselectivity of glycosylation by these donors has been reported thus far. Meanwhile, it would be very attractive to use a single type of glycosyl donors, which, in addition, can be efficiently obtained in one step from available D-galactal, for both stereoselective α- and β-glycosylation depending on the reaction conditions and/or protecting group pattern in the donor. In this communication, we report the results of our search for optimal conditions allowing the stereoselective synthesis of α- and β-glycosides of 2-azido-2-deoxygalactose with different glycosyl acceptors from phenyl 2-azido-2-deoxy-1-selenogalactosides.

Results and discussion

Glycosylation with fully acetylated and benzoylated selenoglycosides **1**[5] and **2** (obtained by conventional deacetylation of **1** followed by benzoylation), and 4,6-*O*-benzylidene-protected donor **3**[9] was examined. In the first step, 3-trifluoroacetamidopropanol **4**, a reactive primary alkanol often used for the introduction of a 3-aminopropyl spacer group in oligosaccharides of different types,[12]

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was chosen as a glycosyl acceptor (Scheme 1). Generally, most of the glycosyl donors and promoter systems were tested in three solvents: 'neutral' dichloromethane to reveal the intrinsic stereoselectivity of a certain donor—acceptor—promoter combination, diethyl ether which favors α-selectivity,[13] and acetonitrile which facilitates the formation of β-glycosides.[14] The results are presented in Table 1. Modulation of the glycosylation stereoselectivity by performing the reactions in the presence of various nucleophilic[15a,b] or complexing[15c] additives was not studied in this work.

(NIS–TfOH)-promoted glycosylation of **4** with acetylated donor **1** afforded an anomeric mixture of glycosides **5** and **6** in high yield with a slight predominance of the β-anomer (entry 1). The same reaction in diethyl ether demonstrated no increase in α-selectivity but pronounced temperature dependence (entries 2–5). Lowering the temperature resulted in better β-selectivity, which achieved a rather high value of 1:10 at −78 °C (entry 5). The observed temperature effect is in agreement with the published data.[16] The reaction in acetonitrile displayed the highest β-selectivity providing β-linked glycoside **6** exclusively (entry 6).

(NIS–TfOH)-promoted glycosylation with perbenzoylated donor **2** produced a mixture of glycosides **7** and **8** with a somewhat higher proportion of the α-product as compared to the acetylated counterpart **1** (cf. entries 1 and 7; 4 and 8) that may be explained by more effective remote anchimeric participation[17] of the benzoyl groups in comparison to the acetyl ones.[18] Otherwise, the stereochemical results obtained with glycosyl donor **2**, including the solvent effects (entries 8, 9), were similar to those with **1**. Application of the promoter system PhSeCl–AgOTf[19] allowed for further enhancement of α-selectivity (entries 10, 11). Thus, (PhSeCl–AgOTf)-promoted glycosylation in diethyl ether (entry 11) may certainly be regarded as a preparative route to α-glycoside **7** and similar alkyl α-glycosides.

4,6-*O*-Benzylidene-protected donor **3** was also examined. It is known[20] that the replacement of acyl groups at O-4 and O-6 by a benzylidene acetal enhances the reactivity of the glycosyl donor. However, it turned out that the increase in the donor reactivity did not affect glycosylation stereoselectivity. Thus, (NIS–TfOH)-promoted glycosylation with **3** in diethyl ether demonstrated almost the same stereochemical result as that observed for benzoylated counterpart **2** (cf. entries 7 and 12). Application of less reactive methyl triflate as the promoter, which might provide a higher proportion of 1,2-*cis*-product,[21] for glycosylation with **3** did not show any noticeable changes in stereoselectivity (entry 13).

Thus, glycosylation of the reactive primary alcohol with phenyl 2-azido-2-deoxyselenogalactosides features intrinsic β-selectivity and becomes β-stereospecific in acetonitrile. Nevertheless, reaction conditions providing good α-selectivity have been also found (PhSeCl–AgOTf, Et_2O) making these donors applicable for the practical stereoselective synthesis of both α- and β-2-azido-2-deoxygalactosides from reactive primary alcohols.

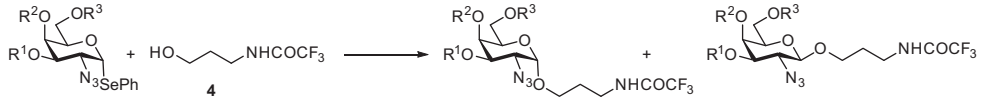
Then, glycosylation of methyl 2,3-*O*-isopropylidene-α-L-rhamnopyranoside **11** was studied (Scheme 2). This acceptor is often used in model glycosylations as a reactive secondary sugar alcohol.[13] (NIS–TfOH)-promoted coupling of donor **1** and rhamnoside **11** in dichloromethane was slightly β-stereoselective and produced a mixture of disaccharide **12** and **13** in a ratio of 1:1.7 (Table 2, entry 1). The observed stereoselectivity was very close to that in the glycosylation of acceptor **4** under the same conditions (cf. Table 1, entry 1). β-Selectivity for the glycosylation of **11** could be considerably improved by lowering the reactant concentration[22] (entry 2), however, the overall efficiency of the reaction decreased. The same rather high β-selectivity was observed for the glycosylation of **11** in acetonitrile (entry 5). Conversely, the use of diethyl ether as the reaction solvent resulted in predominant formation of α-product **12** (entry 4). [NIS–$Bi(OTf)_3$]-promoted glycosylation of **11** with **1** in dichloromethane produced somewhat more α-disaccharide **12** than the same (NIS–TfOH)-promoted reaction (cf. entries 1 and 6). As expected, [NIS–$Bi(OTf)_3$]-promoted coupling of **1** and **11** in acetonitrile provided good β-selectivity, however, at the expense of the total glycosylation efficiency (entry 7). The use of an inverse order of reagent mixing consisting of adding the donor to a solution of the acceptor and promoter allowed a two-fold increase in α-selectivity (entries 3, 8) compared to the conventional procedure, that is, addition of the promoter to a mixture of the donor and acceptor, but slightly decreased the total yield of glycosylation products.

As had occurred in the case of glycosylation of acceptor **4**, application of benzoylated donor **2** provided a higher proportion of the α-disaccharide (entry 9). Further increase in α-selectivity was

Table 1
Glycosylation of 3-trifluoroacetamidopropanol **4** by donors **1**–**3**

Entry	Donor	Promoter	Solvent	Temperature (°C)	Product (s)	Ratio[a] α:β (total yield %)[b]
1	**1**	NIS, TfOH	CH_2Cl_2	−35	**5**, **6**	1:2 (88)
2	**1**	NIS, TfOH	Et_2O	20	**5**, **6**	1:1 (95)
3	**1**	NIS, TfOH	Et_2O	0	**5**, **6**	1:1 (95)
4	**1**	NIS, TfOH	Et_2O	−35	**5**, **6**	1:3 (95)
5	**1**	NIS, TfOH	Et_2O	−78	**5**, **6**	1:10 (95)
6	**1**	NIS, TfOH	MeCN	−35	**6**	Only β (88)
7	**2**	NIS, TfOH	CH_2Cl_2	−35	**7**, **8**	1:1 (92)
8	**2**	NIS, TfOH	Et_2O	−35	**7**, **8**	1:1.3 (78)
9	**2**	NIS, TfOH	MeCN	−35	**8**	Only β (75)
10	**2**	PhSeCl, AgOTf,	CH_2Cl_2	0	**7**, **8**	2.4:1 (95)
11	**2**	PhSeCl, AgOTf	Et_2O	0	**7**, **8**	3.3:1 (95)
12	**3**	NIS, TfOH	Et_2O	−35	**9**, **10**	1:1.5 (95)
13	**3**	MeOTf	CH_2Cl_2	20	**9**, **10**	1:1.6 (91)

[a] Anomeric ratios were calculated from the ^1H NMR spectra of isolated mixtures of α- and β-anomers by integration of their characteristic signals (see Supplementary Data).
[b] Isolated yields.

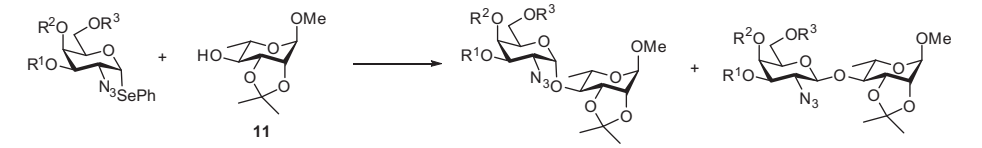


1 $R^1 = R^2 = R^3$ = Ac
2 $R^1 = R^2 = R^3$ = Bz
3 R^1 = Ac, $R^2 + R^3$ = PhCH<

5 $R^1 = R^2 = R^3$ = Ac
7 $R^1 = R^2 = R^3$ = Bz
9 R^1 = Ac, $R^2 + R^3$ = PhCH<

6 $R^1 = R^2 = R^3$ = Ac
8 $R^1 = R^2 = R^3$ = Bz
10 R^1 = Ac, $R^2 + R^3$ = PhCH<

Scheme 1.



Scheme 2.

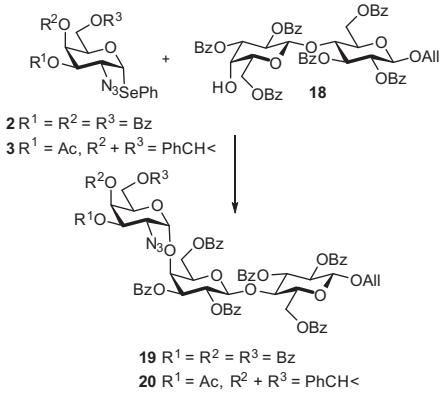
Table 2
Glycosylation of methyl 2,3-*O*-isopropylidene-α-L-rhamnopyranoside **11** by donors **1–3**

Entry	Donor	Promoter	Solvent	Temperature (°C)	Products	Ratio[c] α:β (total yield %)[d]
1	**1**	NIS, TfOH	CH_2Cl_2	−35	**12**, **13**	1:1.7 (80)
2	**1**	NIS, TfOH[a]	CH_2Cl_2	−35	**12**, **13**	1:6 (63)
3	**1**	NIS, TfOH[b]	CH_2Cl_2	−35	**12**, **13**	2:1 (50)
4	**1**	NIS, TfOH	Et_2O	−35	**12**, **13**	3.5:1 (87)
5	**1**	NIS, TfOH	CH_3CN	−35	**12**, **13**	1:6 (70)
6	**1**	NIS, Bi$(OTf)_3$	CH_2Cl_2	−10	**12**, **13**	1.2:1 (75)
7	**1**	NIS, Bi$(OTf)_3$	CH_3CN	−10	**12**, **13**	1:8 (53)
8	**1**	NIS, Bi$(OTf)_3$[b]	CH_2Cl_2	−10	**12**, **13**	2.7:1 (61)
9	**2**	NIS, TfOH	CH_2Cl_2	−35	**14**, **15**	2.5:1 (80)
10	**2**	NIS, TfOH	Et_2O	−35	**14**, **15**	3.6:1 (88)
11	**2**	NIS, TfOH	CH_3CN	−35	**14**, **15**	1:3.8 (80)
12	**2**	NIS, Bi$(OTf)_3$[b]	CH_2Cl_2	−10	**14**, **15**	7:1 (63)
13	**2**	PhSeCl, AgOTf	CH_2Cl_2	0	**14**, **15**	3:1 (72)
14	**2**	PhSeCl, AgOTf	Et_2O	0	**14**, **15**	4.7:1 (99)
15	**3**	NIS, TfOH	Et_2O	−35	**16**, **17**	2.2:1 (72)
16	**3**	MeOTf	CH_2Cl_2	20	**16**, **17**	3:1 (79)

[a] 5-Fold dilution.
[b] Inverse order of reagent mixing.
[c] Anomeric ratios were calculated from the ^1H NMR spectra of isolated mixtures of α- and β-anomers by integration of their characteristic signals (see Supplementary Data).
[d] Isolated yields.

achieved when the reaction was carried out in diethyl ether (entry 10), whereas the use of acetonitrile as the reaction solvent switched the stereoselectivity (entry 11). The highest α-stereoselectivity in dichloromethane was observed when the inverse procedure was applied to the [NIS–Bi$(OTf)_3$]-promoted reaction of compounds **2** and **11** (entry 12), but again the total yield of the glycosylation products **13** and **14** decreased. The (PhSeCl–AgOTf)-promoted coupling of **2** to **11** in dichloromethane demonstrated good intrinsic α-stereoselectivity (entry 13); the best result in terms of both efficiency and α-stereoselectivity was achieved when this glycosylation was performed in diethyl ether (entry 14).

Donor **3** in the (NIS–TfOH)-promoted glycosylation of **11** in diethyl ether demonstrated somewhat lower α-selectivity than acylated donors **1** and **2** under the same conditions (cf. entries 15 and 4, 10). The use of methyl triflate as the promoter only slightly enhanced the α-stereoselectivity of glycosylation (entry 16).



Scheme 3.

Table 3
Glycosylation of allyl 2,2′,3,3′,6,6′-hexa-*O*-benzoyl-β-lactoside **18** by donors **2** and **3**

Entry	Donor	Promoter	Solvent	Temperature (°C)	Product	Isolated yield (%)
1	**2**	NIS, TfOH	Et_2O–CH_2Cl_2 (2:1)	−35	**19**	74
2	**3**	NIS, TfOH	Et_2O	−35	**20**	80
3	**3**	MeOTf	Et_2O–CH_2Cl_2 (2:1)	20	**20**	64

In comparison to the glycosylation of primary acceptor **4**, glycosylation of the less reactive secondary acceptor **11** generally tends to form a higher proportion of 2-azido-2-deoxy-α-galactosides (for example, cf. entries 4, 7, 8 in Table 1 and entries 4, 9, 10 in Table 2). This is in agreement with the existing concept of increasing 1,2-*cis*-stereoselectivity upon decreasing acceptor reactivity.[13a,21] However, good β-selectivity is also achievable under certain conditions, for example, when the glycosylation is carried out in acetonitrile or at a lower concentration (entries 2, 5, 11).

Finally, we studied the 4′-*O*-glycosylation of hexabenzoylated allyl lactoside **18**[23] as a representative of less reactive acceptor (Scheme 3). The axial hydroxyl group at C-4 in the galactose residue is considered to be low reactive in itself; additionally, its reactivity is reduced by the presence of neighboring benzoyl protecting groups.[13a,21] It turned out that glycosylation in diethyl ether or in an ether–dichloromethane mixture (for better solubility of **18**) exclusively provided α-products **19** or **20** irrespective of the donor structure and the promoter system (Table 3). An attempt to accomplish (NIS–TfOH)-promoted β-stereoselective glycosylation of **18** with **2** by performing it in acetonitrile failed; no formation of the expected glycosides was detected.

Conclusions

In conclusion, we have demonstrated that phenyl 2-azido-2-deoxy-1-seleno-α-D-galactopyranosides can be successfully applied to the direct efficient glycosylation of glycosyl acceptors of different reactivity. Glycosylation stereoselectivity can be varied from complete β-selectivity to high α-selectivity by changing the reaction solvent, promoter and protecting group pattern in the glycosyl donor. Glycosylation of the reactive acceptors in acetonitrile generally provides high β-stereoselectivity, while α-glycoside formation prevails in diethyl ether, especially when the reactions are promoted with PhSeCl–AgOTf. The acceptor of low reactivity, allyl 2,2′,3,3′,6,6′-hexa-*O*-benzoyl-β-lactoside affords the corresponding α-glycosides exclusively. The application of this glycosylation reaction to the synthesis of biologically relevant oligosaccharides is now in progress in this laboratory and will be published in due course.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2016.01.013.

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