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Conversion of glycals into vicinal-1,2-diazides and 1,2-(or 2,1)-azidoacetates using hypervalent iodine reagents and Me_3SiN_3. Application in the synthesis of *N*-glycopeptides, pseudo-trisaccharides and an iminosugar†

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Glycals were found to react with a reagent system comprising of phenyliodine bis(trifluoroacetate) (PIFA) and Me_3SiN_3 in the presence of TMSOTf as a catalyst to form the corresponding vicinal 1,2-diazides. On the other hand, they reacted with another reagent system phenyliodine diacetate (PIDA) and Me_3SiN_3, also in the presence of TMSOTf as a catalyst, to lead to the corresponding vicinal 1,2-azidoacetates. These azido derivatives were converted into a number of 2-azido-*N*-glycopeptides, pseudotrisaccharides, and a piperidine triol derivative, an iminosugar.

Introduction

The growing importance of aminosugars,[1] *N*-glycopeptides[2] and sugar derived triazoles[3] (obtained *via* click-chemistry) in biological systems is apparent from the recent literature. Synthesis of such compounds has led to the development of a number of synthetic methodologies involving functionalization of monosaccharides, in particular glycals. In this regard, methodologies that allow attachment of an azido moiety[4] at the anomeric center are frequently used in the synthesis of *N*-glycopeptides, although there are some other ways[2e,5] of introducing a 'nitrogen' unit. The azide group also allows click-chemistry, to link with another sugar unit leading to pseudo di-, tri- or oligosaccharides, to be carried out.[3] Apart from this, introduction of an amino functionality (or an azido group) at the C-2 position of a sugar moiety, with an appropriate functional group at the anomeric carbon for effecting glycosylation, is one of the most important reactions known in carbohydrate chemistry.[1a,6] This allows access to amino sugars with the amino group at the C-2 position, a structural feature that is prevalent in a number of oligosaccharides including aminoglycoside antibiotics. Toward this endeavor, conversion of glycals into sugar derived 2-azido-1-nitrates using a combination of ceric ammonium nitrate and NaN_3 (and its improvements) in CH_3CN, a protocol developed by Lemieux *et al.*,[6a] is universally followed.

At the same time, there exist many oligosaccharides that contain *N*-glycopeptide units in which the sugar moiety carries a C-2 amino functionality, and the glycopeptide part has an Asn-linkage at the anomeric carbon.[2b,7] Interest in the synthesis of such molecules stems from the fact that protein *N*-glycosylation occurs during post-translational modifications in biological systems. This has led to newer approaches towards functionalization of glycals (or any other sugar derivative such as glycosamines) to introduce 1,2-diamino (or equivalent) functionalities that are useful in the synthesis of *N*-glycopeptides.[8] Thus, improved or alternate approaches toward the introduction of a nitrogen based functional group at C-1 and/or C-2 of a sugar moiety are important. In view of our continued interest[2f,4a–c,8a,9] in functionalizing glycals *en route* to the synthesis of iminosugars, aminosugars and glycopeptides, we herein report an easy access to 1,2-diazido sugars from glycals upon treatment with phenyliodine bis(trifluoroacetate) (PIFA) and Me_3SiN_3 reagent system. Also, we have developed conditions that allow conversion of glycals into 1-azido-2-acetoxy sugars or 2-azido-1-acetoxy sugars upon reaction with phenyliodine diacetate (PIDA) and Me_3SiN_3. Further, we have demonstrated the utility of these azido compounds in the synthesis of 2-amino-*N*-glycopeptides, pseudotrisaccharides, and an iminosugar.

Results and discussion

Hypervalent iodine reagents have gained enormous importance in recent years due to their low toxicity, ease of handling and ready availability.[10] The use of hypervalent iodine reagents, most notably PIDA, in conjunction with a halide ion source has been reported on a few occasions in functionalizing olefins,

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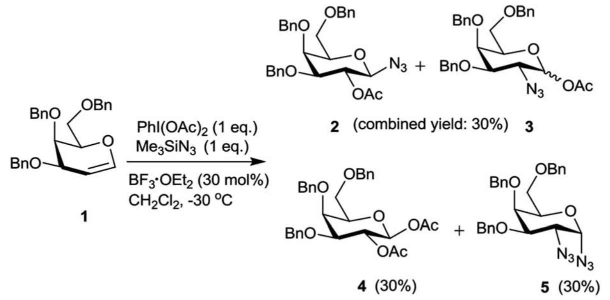
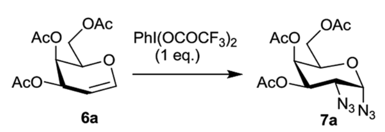


Scheme 1 Exploratory reaction of galactal derivative **1** with PIDA–Me_3SiN_3.

including glycals, to form vicinal halo alkoxides in an intermolecular fashion.[11] Introduction of a nitrogen based functional group at C-2 of a glucal derivative has also been realized in an intramolecular fashion from glucal 3-carbamate upon its reaction with PIDA along with $Rh_2(OAc)_4$.[6c] However, one of the most interesting reactions to stereoselectively convert glycals into sugar derived *trans*-1,2-diacetates involves their reaction with PIDA in presence of $BF_3 \cdot Et_2O$ as a catalyst as reported by Gin *et al.*[12] Further, the *in situ* formed *trans*-1,2-diacetates lead to *O*-glycosylation when treated with an alcohol (ROH) and TfOH (as a catalyst) in the same pot. The proposed mechanism suggests that PIDA acts as an electrophile making a π-complex with a glycal, followed by the attack of acetate ion at the anomeric carbon as well as at C-2 leading to the observed *trans*-1,2-diacetates. In view of this, and in view of the importance of amino sugars and *N*-glycopeptides (*vide supra*) we surmised that reaction of glycals with PIDA combined with Me_3SiN_3 may lead to 1,2-diazido sugars. Our initial experiments involving reaction of 3,4,6-tri-*O*-benzyl galactal **1** (Scheme 1) with both one equivalent of PIDA and Me_3SiN_3 in the presence of $BF_3 \cdot Et_2O$ or TMSOTf (30 mol%) as a catalyst led to a mixture of four products. These were 1-azido-2-acetoxy sugar **2**, 2-azido-1-acetoxy sugar **3**; 1,2-diacetoxy sugar **4** and 1,2-diazido sugar **5**. Increasing the amount of Me_3SiN_3 did not lead to increased formation of 1,2-diazides and there was always an incorporation of the acetate moiety onto galactal **1** due to competition between the azide and the acetate ions. Although, conversion of olefins into vicinal diazides is known with few reagents[13a] such as $Mn(OAc)_3$–NaN_3,[13b] azido iodine(III) reagent,[13c] $NaIO_4/NaN_3$ [13d] and Zhdankin reagent (a hypervalent iodine reagent) along with a copper catalyst,[13e] formation of sugar derived 1,2-diazides from glycals has been reported rarely.[13b,14] Thus, for example, 2,4,6-tri-*O*-acetyl galactal has been reported to react with Me_3SiN_3–PIDA–PhSeSePh[14a] to give *cis*-1,2-diazido galactal albeit in low yield and as a side product. On the other hand, more recently Xu *et al.*[14b] demonstrated that the *in situ* prepared Zhdankin reagent in presence of an iron catalyst converts a broad range of olefins, including one example of a glucal derivative, to the corresponding 1,2-diazides. In order to find an alternate route to convert glycals into sugar derived 1,2-diazides, we explored their reactivity with PIFA–Me_3SiN_3 reagent system[15] in presence of an acid catalyst. Such a reagent system has been used to introduce an azide group into aromatics and some heterocycles akin to aromatic substitution,[15a,b] for substitution of an azide moiety[15c] at benzylic positions, and more recently to perform C–H activation.[15d,e] Apart from this, an interesting intramolecular azidoarylation of alkenes using PIFA–Me_3SiN_3 combination has been reported by Antonchick *et al.*[15f] In these examples, PIFA–Me_3SiN_3 reagent system was proposed to lead to the formation of $PhI(N_3)_2$ or $PhIN_3(OCOCF_3)$ as intermediate species which act as a source of azide radical to effect the observed reactions. We expected that if $PhI(N_3)_2$ is formed as an intermediate, in presence of an acid catalyst it may convert glycals to sugar-derived 1,2-diazides in an analogous manner as sugar derived 1,2-diacetates were obtained from glycals upon reaction with PIDA as reported by Gin *et al.*[12] Towards this endeavor, initial experiments involved treatment of 3,4,6-tri-*O*-acetyl galactal **6a** with PIFA (1.0 eq.) and 2 eq. of Me_3SiN_3 in presence of $BF_3 \cdot Et_2O$ (30 mol%) at −30 °C which gave only 38% of the expected 1,2-diazide **7a** as a single isomer. Further optimizations with respect to azide source and acid catalyst (Table 1) led to the use of 3 eq. of $TMSN_3$ and 30 mol%

Table 1 Optimization of reaction conditions to form 1,2-diazides[a]



Entry	Catalyst	N_3-Source	Equiv.	Solvent	Temp (°C)	Time (h)	Yield (%)
1	None	NaN_3	2	CH_3CN	rt	24	No reaction
2	None	$TMSN_3$	2	CH_2Cl_2	0	24	No reaction
3	$BF_3 \cdot OEt_2$	$TMSN_3$	2	CH_2Cl_2	−30	0.5	38[b]
4	$BF_3 \cdot OEt_2$	$TMSN_3$	3	CH_2Cl_2	−30	0.5	44[b]
5	$BF_3 \cdot OEt_2$	Bu_4NN_3	3	CH_2Cl_2	−30	0.5	37[b]
6	TMSOTf	Bu_4NN_3	3	CH_2Cl_2	−30	0.5	33[b]
7	TMSOTf	$TMSN_3$	3	CH_2Cl_2	−30	0.5	61

[a] Reaction conditions: glycals (0.36 mmol), $TMSN_3$, $PhI(OCOCF_3)_2$ (0.36 mmol), TMSOTf (0.10 mmol), CH_2Cl_2, −30 °C, N_2 atmosphere, isolated yields after purification by silica gel column chromatography. [b] Yield based on recovered starting material.

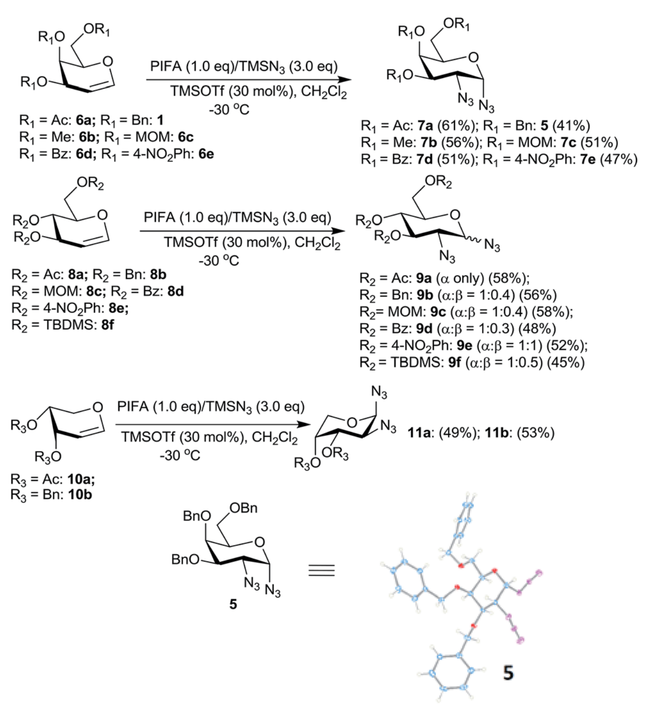
of TMSOTf at −30 °C as the best condition forming **7a** in 61% yield (entry 7, Table 1). With this optimized condition we carried out the remaining studies. Thus, a variety of differently protected glycal derivatives led to the corresponding 1,2-diazides in moderate yields (Scheme 2).

It was generally found that while the galactal derivatives led exclusively to *cis*-1,2-diazides, the glucal derivatives gave a mixture of α- and β-anomers in varied ratios with the α-anomer being major in most of the cases. The structures and the α/β ratios were established based on COSY, NOE, homonuclear decoupling and DEPT experiments.[16a] Thus, for example, in the ^{1}H NMR spectrum of compound **7a** the anomeric proton (H-1) appeared as a doublet at *δ* 5.48 with J = 4.12 Hz. The homonuclear decoupling of H-1 led the proton H-2 to appear as a doublet, from a doublet of doublet, with J = 11.00 Hz indicating that H-2 and H-3 are *trans*-diaxial. Further, in the NOE experiments no enhancement was observed for protons H-3 and H-5 when H-1 was irradiated and *vice versa* indicating that H-1 is equatorially oriented. In addition, the structure of the galactal derivative **5** was proved by single crystal X-ray analysis.[16b] Likewise, the spectral data of 1,2-diazide **9a**, derived from glucal **8a**, also showed that the azido moieties are α-oriented.[16a] Thus, in NOE experiments, irradiation of proton H-4 at *δ* 5.00 led to the enhancement of signal for H-2 at *δ* 3.61 and *vice versa* indicating that H-2 is axially oriented. On the other hand, no enhancement was observed for H-3 and H-5 protons when H-1 was irradiated at *δ* 5.44 suggesting that H-1 is equatorially oriented.

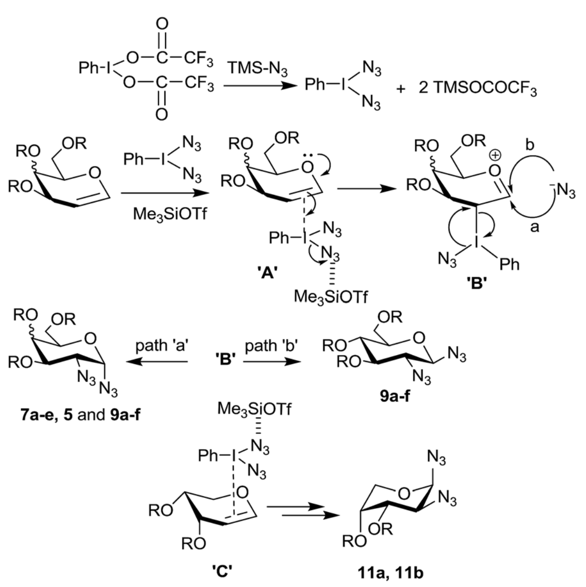
Interestingly, the arabinal derivatives **10a** and **10b** gave the corresponding 1,2-diazides **11a** and **11b** having $^{1}C_4$ conformations which was confirmed by spectral studies.[16a] In case of **11a**, irradiation of H-1 at *δ* 5.43 in the homonuclear decoupling experiment led the doublet of doublet for H-2 to appear as a doublet with J = 10.6 Hz indicating that H-2 and H-3 are diaxially oriented. Likewise, irradiation of H-4 at *δ* 5.27 caused the doublet of doublet for H-3 at *δ* 5.13 to appear as a doublet with J = 10.6 Hz. Further, in NOE experiments irradiation of H-3 did not lead to the enhancement of the signal for H-1, and also irradiation of H-2 did not show the enhancement of H-4. These data confirm that H-2 and H-3 are diaxially oriented and that **11a** possesses $^{1}C_4$ conformation. In a similar fashion, the structure of **11b** was established.

It is important to note that in the absence of an acid catalyst no reaction was found to take place between a glycal derivative and PIFA–Me_3SiN_3 reagent combination indicating that the azido radical, if formed,[15] does not add on to the electron rich glycal double bond. Therefore we presume that in the present case, the reaction does not proceed *via* radical pathway,[17a] instead it proceeds *via* ionic pathway similar to the ones proposed by Moriarty,[17b] and Kirschning.[17c] Thus, *in situ* generated $PhI(N_3)_2$ upon π-interaction (complex **A** in Scheme 3) with the double bond from the α-side (in case of a galactal and a glucal derivative) leads to intermediate **B** and transfer of the azide moiety to C-2 occurs in an S_Ni fashion from the α-side only. Following this (or simultaneously) the second azide preferentially attacks at the anomeric carbon of the galactal derivative from the α-side (path a) due to steric hindrance caused by the substituents at C-3, C-4 and C-5. In case of glucal derivatives, however, some product was also formed due to β-attack of the azide moiety *via* path b since the glucal derivatives show less steric bias from the β-side as compared to galactal derivatives.

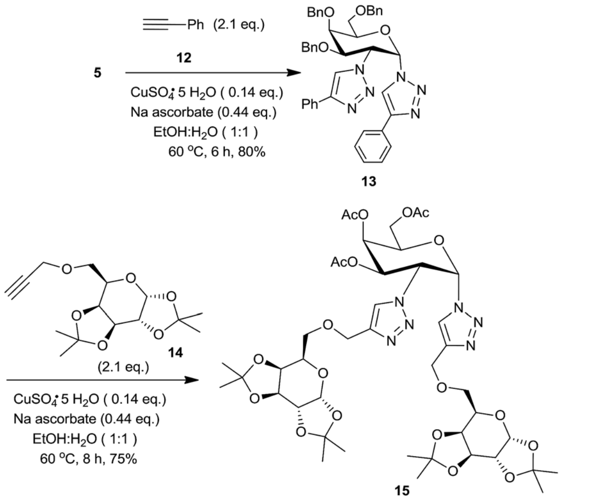
Further, in case of arabinal derivatives it appears that the double bond preferentially forms π-complex from the less hindered β-side (complex **C**), followed by azide ion attachments at C-2 and C-1 from the opposite face to the two –OR groups, in a similar manner as happens in galactal cases, eventually



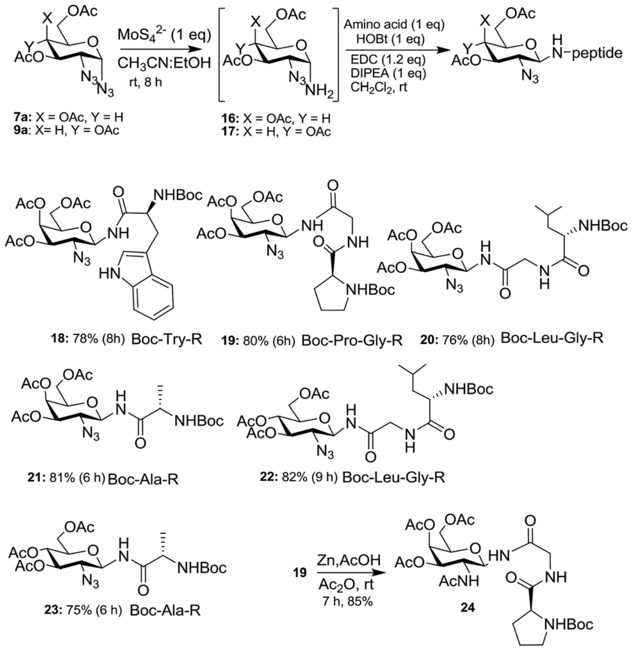
Scheme 2 Percentage yield and α/β ratio of the 1,2-diazides.



Scheme 3 Proposed mechanism for the formation of 1,2-diazides.



Scheme 4 Conversion of 1,2-diazides into bis-triazole **13** and pseudotri-saccharide **15**.



Scheme 5 Selective reduction of 1,2-diazides and synthesis of β-*N*-glycopeptides.

leading to the observed 1,2-diazides **11a** and **11b** (Scheme 3) which assume $^1C_4$ conformations. It is clear that the success of the 1,2-diazide formation is mainly due to the low nucleophilicity of the trifluoroacetate ion compared to the azide ion.

In order to demonstrate the utility of these 1,2-diazides, we have utilized the click chemistry to prepare two bis-triazoles, one from a non-sugar and the other from a sugar based alkyne. Thus, 1,2-diazide **5** was reacted with 2 eq. of phenylacetylene **12** to form the bis-triazole **13** (Scheme 4) in 80% yield using standard conditions.[3d] Likewise, a sugar derived alkyne[18] **14** led to the corresponding bis-triazole **15**, a pseudo-trisaccharide,[3] in 75% yield. The structures of these triazoles were confirmed from their spectral data.[16a]

The importance of *N*-glycopeptides is apparent from the introduction part (*vide supra*) and a number of synthetic approaches have been reported to procure them, and newer synthetic routes are still being developed. In view of this, we demonstrate the utility of 1,2-diazides **7a** and **9a** to form the corresponding 2-azido-*N*-glycopeptides **18–23** (Scheme 5). Thus, selective reduction of the anomeric azide of **7a** and **9a** was carried out with ammonium tetrathiomolybdate $[(NH_4)_2MoS_4^{2-}]$[19] to give the corresponding amino compounds **16** and **17** and, without isolating them, the crude amines were coupled with a number of amino acids and small peptides, mediated by 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC)[20a] to lead to the corresponding 2-azido-*N*-glycopeptides **18–23.** The stereochemistry of the 2-azido-*N*-glycopeptides was confirmed to be 1,2-*trans* based on COSY, HETCOR and homonuclear decoupling experiments[16a] of **18**. Thus, selective decoupling of C_1NH at δ 6.05 led the anomeric proton to appear as a doublet with coupling constant $J = 9.96$ Hz indicating that both H-1 and H-2 are axial. The facile mutarotation of free anomeric amines has been reported in many cases[4b,20b,c] and their functionalization mainly leads to the β-anomers. It is therefore not surprising that in the present case, reduction of α-azides to the corresponding free amines exclusively lead to β-glycopeptides *via* mutarotation. The azido moiety at C-2 of the azido-glycopeptide **19** was readily reduced[21] with Zn/AcOH/Ac_2O to form the 2-amino-*N*-glycopeptide **24** in 85% yield, and thus the present method forms an alternate route to 2-amino-*N*-glycopeptides.

Having explored the conversion of glycals to 1,2-diazides using PIFA–Me_3SiN_3 reagent system, we studied their reactivity with PIDA–Me_3SiN_3 under analogous conditions. As discussed above, the galactal derivative **1** (Scheme 1) upon reaction with PIDA and Me_3SiN_3 (both 1 eq.) gave a mixture of four products **2–5** and thus it was not a synthetically useful reaction. We therefore examined the reaction conditions to incorporate both, the acetate (more nucleophilic compared to trifluoroacetate ion) as well as the azide moieties onto glycals. Our aim was to procure synthetically useful 1-azido-2-acetoxy sugars and/or 2-azido-1-acetoxy sugars, and to avoid the formation of 1,2-diacetates and 1,2-diazides. After exploring various combinations of the azide source and Lewis acids (Table 2), it became clear that a combination of 3 eq. of Me_3SiN_3 and 1 eq. of PIDA along with 30 mol% of TMSOTf at −30 °C was optimum to form vicinal azidoacetates. Thus, galactal derivative **1** led to the formation of an inseparable mixture of two products, 1-azido-2-acetoxy sugar **2** and 2-azido-1-acetoxy sugar **3** in 61% combined yield (Scheme 6). The two compounds were formed in 1 : 2 ratio which was ascertained after selectively reducing the mixture of **2** and **3** with ammonium tetrathiomolybdate (*vide supra*) followed by acetylation that gave chromatographically separable **25** and unreacted **3**.[22a] Further, 2-azido-1-acetoxy sugar **3** was found to be a mixture of two anomers ($\alpha/\beta = 63/37$). The glucal derivative **8b**, on the other hand, gave a chromatographically separable mixture of **26** [16a] and **27** [22a] (α/β anomers = 60/40) in 1 : 2 ratio. Compound **26** was again reduced and acetylated to form **28** [22b]

Table 2 Optimization of reaction conditions to form vicinal-azidoacetates from galactal derivative **1**[a]

							Yield (%)		
Entry	Catalyst	N_3-Source	Equiv.	Solvent	Temp (°C)	Time (h)	(**2** + **3**)	**4**	**5**
1	$BF_3 \cdot OEt_2$	$TMSN_3$	1	CH_2Cl_2	−30	1	30%	30%	21%
2	$BF_3 \cdot OEt_2$	$TMSN_3$	2	CH_2Cl_2	−30	1	20%	20%	40%
3	$BF_3 \cdot OEt_2$	$TMSN_3$	3	CH_2Cl_2	−30	0.5	52%	—	12%
4	$BF_3 \cdot OEt_2$	Bu_4NN_3	3	CH_2Cl_2	−30	0.5	46%	—	17%
5	TMSOTf	Bu_4NN_3	3	CH_2Cl_2	−30	0.5	38%	—	30%
6	TMSOTf	$TMSN_3$	3	CH_2Cl_2	−30	0.5	61%	—	—

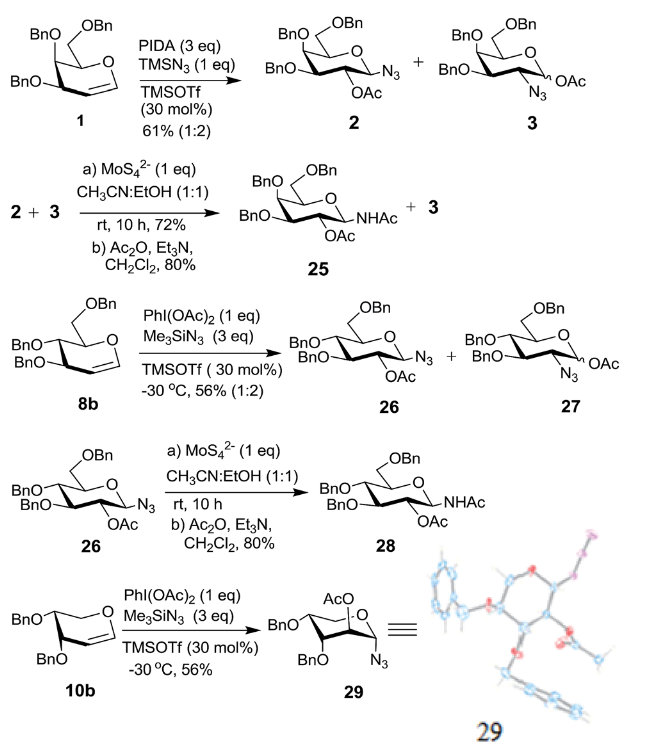
[a] Reaction conditions: glycals (0.36 mmol), $TMSN_3$ (1.10 mmol), $PhI(OAc)_2$ (0.36 mmol), TMSOTf (0.10 mmol), CH_2Cl_2, −30 °C, N_2 atmosphere, isolated yields after purification by silica gel column chromatography.

which was spectroscopically characterized. Interestingly, the arabinal derivative **10b** (ref. 23) led to a single product **29** in 56% yield whose structure was established based on spectral data and also by single crystal X-ray analysis.[16b]

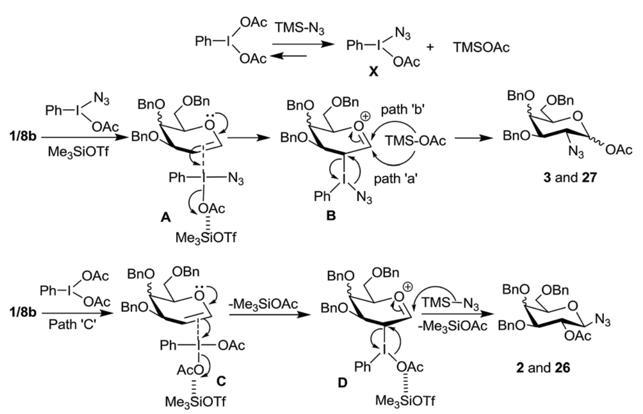
Based on these product distributions in the reactions with glycal derivatives **1** and **8b** with PIDA–Me_3SiN_3 reagent system we propose a tentative mechanism as shown in Scheme 7. Accordingly, we expect PIDA to react with excess of Me_3SiN_3 (3 eq.) resulting into species **X** and TMSOAc with the equilibrium being more favorable on the right side. Reaction of glycals **1** and **8b** with the species **X** in presence of TMSOTf should lead to a π-complex **A** which should generate another molecule of TMSOAc on the way to intermediate '**B**'. Thus, chances of TMSOAc acting as a preferred nucleophile to form products **3** and **27** appear to be high compared to $TMSN_3$. Subsequently, the intermediate **B** will undergo attack of the acetate ion either from α- or β-side (paths a and b) at the anomeric carbon accompanied by an S_Ni type reaction with the azide ion at C-2 to give compounds **3** and **27** with the loss of PhI. Likewise, formation of **2** and **26** can be rationalized by invoking intermediates **C** (a π-complex) and **D** in the reaction of glycals with PIDA. The π-complex **C** will expel a molecule of TMSOAc only upon the formation of the intermediate **D.** Thus at any given time, during this pathway, more amount of Me_3SiN_3 is available to attack at intermediate **D** which leads to the observed products **2** and **26.**

In case of arabinal derivative **10b**, a complex similar to '**C**' should form from the β-face to avoid the steric repulsions from the two –OBn groups. This should be followed by azide ion attack in an intermolecular fashion from the axial orientation at the anomeric carbon. Subsequent acetate ion attack at C-2 occurs, in an intramolecular fashion, again from the axial side leading to the observed product **29**. It is however not clear at this moment why the product **29** prefers to have $^4C_1$ conformation as against compounds **11a** and **11b** which prefer $^1C_4$ conformations.

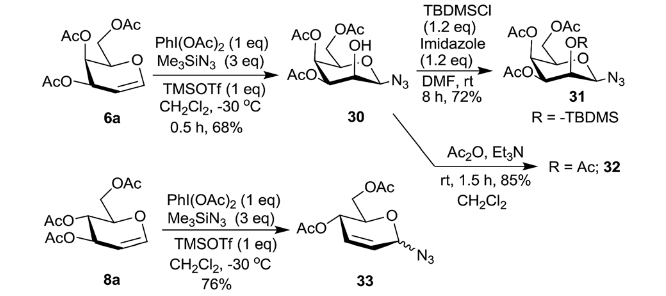
We further checked the reactivity of 2,4,6-tri-*O*-acetylated glycals **6a** and **8a** towards the PIDA–Me_3SiN_3 reagent system. The reaction was extremely sluggish in presence of 30 mol% of TMSOTf even at room temperature for prolonged reaction



Scheme 6 Reaction of glycal derivatives 1, 8b and 29 with PIDA–Me_3SiN_3.



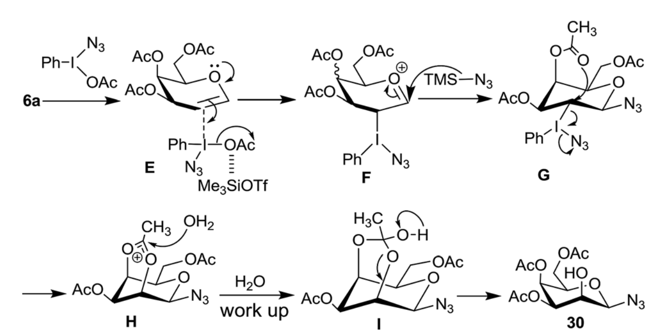
Scheme 7 Proposed mechanisms for the reaction of glycals with PIDA and Me_3SiN_3.



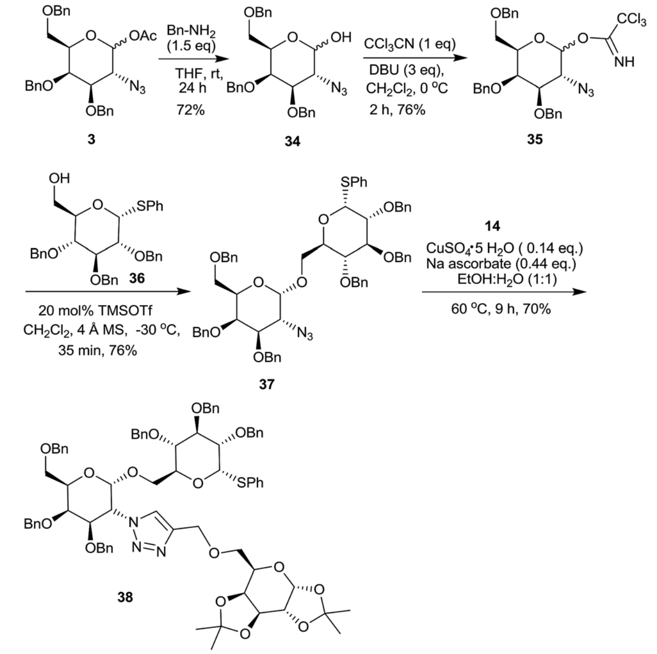
Scheme 8 Reaction of glycal derivatives **6a** and **8a** with PIDA–Me_3SiN_3.

times. Gradual increase in the amount of TMSOTf ultimately led to the use of 1 eq. of it for complete consumption of the starting material at −30 °C. However, the galactal derivative **6a**, interestingly, led to 2-hydroxy-1-azido sugar **30** as a product in 68% yield (Scheme 8) whose structure was established based on spectral data including COSY, NOE, homonuclear decoupling and DEPT experiments.[16a] Thus, in NOE experiments, irradiation of H-3 at δ 4.89, led to the enhancement of the signals for protons H-1 and H-5 at δ 4.19 and δ 3.96 respectively. Also, when H-1 at δ 4.19 was irradiated, the signals for H-3 and H-5 were enhanced suggesting that H-1 is axially oriented. In the homonuclear decoupling experiment of **30** when H-4 at δ 5.36 was irradiated, the proton H-3 appeared as a doublet with J = 3.68 Hz suggesting that H-2 is equatorially oriented. These data support the structure assigned to **30**. Compound **30** was also derivatized to **31** and **32** and their structures confirmed based on spectral analysis. On the other hand, the glucal derivative **8a** led to the Ferrier reaction to form **33**[24] in 76% yield as an anomeric mixture ($\alpha : \beta = 60 : 40$).

Mechanistically, in case of 2,4,6-tri-*O*-acetyl galactal **6a**, the intermediate **F** (Scheme 9), resulting from the π-complex **E**, should allow azide ion attack from the β-side leading to the intermediate **G**. It is possible that intermediate **G** then undergoes intramolecular participation by C_4–OAc group to form intermediate **I** which then hydrolytically decomposes to give **30**. Since the glucal derivative **8a** does not give similar reaction, instead undergoes the Ferrier reaction, intramolecular participation of C_4–OAc group in **6a** becomes crucial.



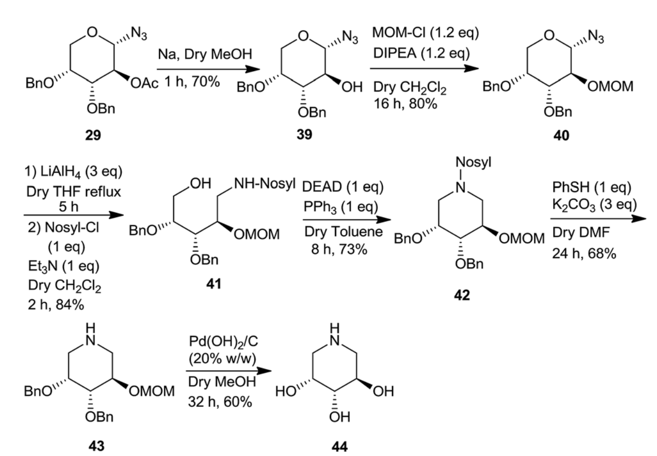
Scheme 9 Proposed mechanisms for the reaction of glycal **6** with PIDA and Me_3SiN_3.



Scheme 10 Synthesis of a pseudotrisaccharide **38**.

In view of the importance of 2-amino-*O*-glycosides, 1-acetoxy-2-azido galactose derivative **3** was hydrolyzed[25] with benzyl amine to form 2-azido-3,4,6-tri-*O*-benzyl-galactopyranose **34** (Scheme 10). The corresponding trichloroacetimidate **35**, a glyosyl donor, was readily prepared by following a literature procedure[26] and was reacted with **36**,[27] an orthogonal glycosyl acceptor having a thioglycoside linkage, followed by the click reaction with sugar derived alkyne **14** to form a pseudotrisaccharide **38**.[16a]

Further, we also show the importance of 1-azido-2-acetoxy sugar derivative **29** in the synthesis of a piperidine triol **44**, that belongs to a class of potential glycosidase inhibitors[9h,i] (Scheme 11). Thus, the acetate moiety of azidoacetate **29** was deprotected and converted to the MOM derivative **40** *via* **39** under standard reaction conditions. Subsequently, the



Scheme 11 Synthesis of a piperidine derivative **44** from the azidoacetate **29**.

anomeric azide group was reduced with $LiAlH_4$ followed by protection of the resulting amine as *N*-nosyl group to give **41** which was cyclized to the piperidine derivative **42** under the Mitsunobu conditions. Deprotections of the nosyl, benzyl and the MOM groups led to the formation of the piperidine **44**, an iminosugar as a potential glycosidase inhibitor.[28]

Conclusions

In conclusion, we have shown that the reagent system PIFA–Me_3SiN_3 in presence of TMSOTf as a catalyst conveniently converts glycals into the corresponding 1,2-diazido derivatives. These vicinal azido derivatives are converted to 2-azido-*N*-glycopeptides, which are convenient precursors of 2-amino-*N*-glycopeptides, and also into a pseudotrisaccharide **15**. Likewise, glycals are converted into a mixture of 1-azido-2-acetoxy sugars and 2-azido-1-acetoxy sugars using the reagent system PIDA–Me_3SiN_3 in the presence of TMSOTf as a catalyst. The –OAc group of 2-azido-1-acetates can be hydrolyzed and converted into a trichloroacetimidate group for effecting glycosylations. One of the azidoacetates **3** was converted into a pseudo-trisaccharide **38** after glycosylation followed by click chemistry. Further, 1-azido-2-acetoxy sugar derivative **29**, derived from the arabinal derivative **10b**, was eventually converted into a piperidine triol **44**, a potential glycosidase inhibitor. Tentative mechanisms have been proposed to account for the formation of different azido sugars.

Conflicts of interest

There are no conflicts to declare.

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