



Preparation of sugar-derived 1,2-diamines via indium-catalyzed aza-Henry-type reaction: application to the synthesis of 6-amino-1,6-dideoxynojirimycin

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ABSTRACT

The combination of (*p*-methoxyphenyl)imine, a bromonitroalkane, and zinc in the presence of catalytic indium allows straightforward access to β -nitroamine derivatives. The use of chiral sugar-derived imines furnished the corresponding β -nitroamines in high yields and stereoselectivities, from which the corresponding 1,2-diamines were easily obtained. The synthetic utility of the sugar-derived 1,2-diamines in the preparation of iminosugars was illustrated in a concise synthesis of 6-amino-1,6-dideoxynojirimycin.

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The aza-Henry (or nitro-Mannich) reaction involves nucleophilic addition of nitroalkanes to imines,¹ and results in the formation of a carbon–carbon bond with concomitant generation of a β -nitroamine, from which a wide variety of other organic compounds can be derived by functional transformations of the nitro group. Particularly interesting is the reduction of the nitro group to an amine, giving rise to the corresponding 1,2-diamines,² of great value in both synthesis and biology.³ The 1,2-diamino moiety is present in many natural products that have relevant biological properties⁴ and several synthetic diamine derivatives have also been employed as medicinal agents, in particular as antitumoral agents.⁵ Their use in organic synthesis has also increased exponentially in the past few years, especially as intermediates in the synthesis of heterocycles⁶ and in the field of catalytic asymmetric synthesis.⁷ When applied to sugar-derived imines, the aza-Henry reaction gives rise to homologated β -nitroamines, precursors of the corresponding sugar-derived 1,2-diamines. The preparation of sugar-derived vicinal diamines is an important objective in organic synthesis, given their value in asymmetric catalysis⁸ and their potential as intermediates in the preparation of iminosugars.

Iminosugars, analogues of pyranoses in which the oxygen atom of the heterocyclic ring is replaced by a nitrogen atom and the anomeric hydroxyl is absent, are almost always inhibitors of the corresponding glycosidases.⁹ As glycosidases are involved in a number

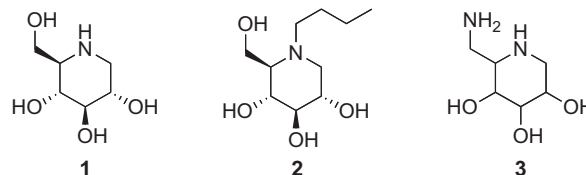


Figure 1. Biologically active iminosugars.

of metabolic pathways,¹⁰ the inhibition of glycosidases has become a powerful strategy for the treatment of several important diseases, such as diabetes, cancer, and viral infections, including AIDS.¹¹ Deoxymanno-jirimycin (DMJ) **1** (Fig. 1), for example, is a potent inhibitor of glycosidases¹² and some analogues, such as **2** are therapeutically useful drugs.¹³ Therefore, derivatives of DMJ provide an opportunity for altering and hopefully increase the specificity of inhibition of individual glycosidases.

We became interested in the synthesis of 6-amino derivatives of iminosugars **3**, not only for their biological interest but also for their potential as stereodifferentiating agents in asymmetric catalysis. For this purpose, we envisioned a synthetic strategy involving an aza-Henry reaction of sugar imines as a key step for the formation of the intermediate 1,2-diamines. Consequently, we started our investigations by developing a general, cheap, and scalable procedure to prepare the starting sugar-derived β -nitroamines.

In connection with our interest in the application of Barbier-type reactions to carbohydrate chemistry,¹⁴ we have recently described an efficient preparation of β -nitroamines by the addition

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of bromonitroalkanes to sugar imines.¹⁵ The indium promoted addition of bromonitroalkanes^{15a} constitutes a very convenient alternative to the classic aza-Henry reaction, as it is very simple from the experimental point of view and performs better in terms of yields and substrate scope. However, an important drawback of this procedure would be its high cost, derived from having to use stoichiometric amounts of indium. Having to scale up the aza-Henry reaction to obtain preparative quantities of the intermediate β -nitro-amines, the use of a catalytic amount of indium would be desirable. We decided to study the addition of bromonitroalkanes to imines using catalytic amounts of indium metal in the presence of a cheap secondary reducing agent.¹⁶

In a preliminary experiment, the addition of bromonitromethane **5a** to *N*-(cyclohexylmethylene)-4-methoxybenzenamine **4a** as the model was studied with different additives (Scheme 1, Table 1).

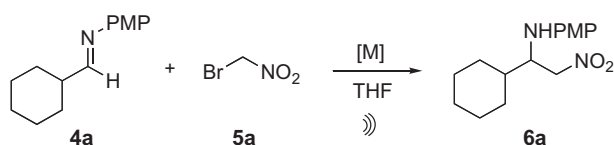
The reaction can be mediated by stoichiometric indium, giving high conversions (entry 1).^{15a} Neither aluminum nor zinc alone was effective in promoting the reaction (entries 2 and 5, respectively). Manganese activated by TMSCl also failed to produce the desired 2-nitroamine (entry 7), while tin(II) chloride afforded good yields of the addition product (entry 9).¹⁷

On the other hand, when those metals were combined with catalytic amounts of indium, the desired nitroamine **6a** was obtained in all cases. The best catalytic system consisted of a catalytic amount of indium combined with an excess of Zn dust (entries 3 and 4). The most favorable conditions to achieve the indium catalyzed Henry-type reaction are the use of a catalytic amount of indium (as low as 0.12 equiv) together with a 10 mol excess of zinc dust (entry 4). Reducing the zinc to 5 equiv resulted in a lower conversion (entry 3). The reaction failed in the absence of indium, which excludes the direct involvement of zinc as promoter. As in the case of the indium-catalyzed addition of the bromonitroalkanes to aldehydes,¹⁶ the proposed mechanism involves the regeneration of the indium reactive species due to the reducing character of zinc.

Aluminum and manganese, on the other hand, were less effective than zinc, giving low yields of nitroalcohol **6a** (entries 6 and 8, respectively). Finally, the system tin(II) chloride/catalytic indium afforded similar results than both stoichiometric indium and the system zinc/catalytic amount of indium. In this case, as tin(II) chloride alone can promote the reaction and yield the desired nitroamine **6a** albeit in slightly lower yield, the mechanism of the reaction is not clear. However, we decided to focus on the zinc/indium system, as zinc is considerably cheaper than tin(II) chloride.

With the established optimal conditions we then investigated the generality of the procedure. Thus, to a sonicated mixture of an appropriate bromonitroalkane **5a–c**¹⁸ (0.6 mmol) (Fig. 2), indium (0.055 mmol), and zinc (5.00 mmol) in THF (1 mL) the corresponding *p*-methoxyphenylimine derivative **4a–f** (0.50 mmol) was added and the mixture was sonicated for 6 h. In all cases, the desired β -nitroamines **6b–g** were isolated in good yields (Scheme 2, Table 2).

Once we found a general and economic procedure for the preparation of racemic β -nitroamines, this methodology was applied to sugar-derived imines to furnish the corresponding chiral β -nitroamines, from which the corresponding 1,2-diamines would be



Scheme 1. Indium-catalyzed addition of bromonitromethane **5a** to imine **4a**.

Table 1

Screening conditions for the indium-catalyzed addition of bromonitromethane **5a** to imine **4a**

Entry	Conditions	Conversion (%)
1	1 equiv In	80
2	5 equiv Zn	0
3	5 equiv Zn/0.12 equiv In	68
4	10 equiv Zn/0.12 equiv In	79
5	5 equiv Al	0
6	5 equiv Al/0.12 equiv In	35
7	5 equiv Mn/5 equiv TMSCl	0
8	5 equiv Mn/5 equiv TMSCl/0.25 equiv In	41
9	2 equiv SnCl ₂	72
10	2 equiv SnCl ₂ /0.12 equiv In	78

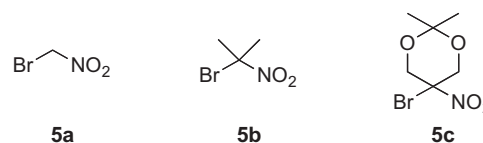
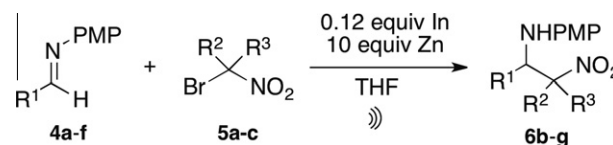


Figure 2. Bromonitroalkanes **5a–c**.



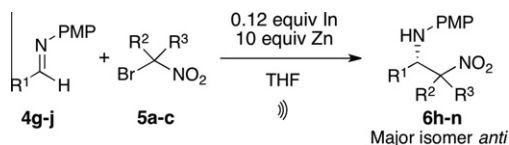
Scheme 2. Indium-catalyzed addition of bromonitroalkanes **5a–c** to imines **4a–f**.

easily available. Thus, the above conditions were tested in the reaction of sugar-derived imines **4g** and **4g** with bromonitroalkanes **5a–c**. When the reaction was carried out in the presence of a (*p*-methoxy-phenyl)imine **4g** and **4g**, indium, and zinc under the conditions described above, the corresponding nitroamines **6h–n** were obtained in all cases in good yields as isomeric mixtures from which the major *anti* isomers were isolated as pure compounds (Scheme 3, Table 3). The excellent *anti* diastereoselectivity can be explained in terms of a lowering of the C–N antibonding orbital, which would bring about increased stabilization of a Felkin–Anh antiperiplanar nucleophilic addition of the organoindium species to the imine carbonyl (Fig. 3).¹⁹ These results are in accordance with those observed in the stoichiometric indium-mediated reaction.^{15a}

Given the excellent results obtained in the preparation of sugar β -nitroamines, we aimed next at the preparation of the corresponding orthogonally protected 1,2-diamines, valuable intermediates according to our synthetic objectives. Although there are numerous protocols for the reduction of nitro compounds to amines,²⁰ the reduction of β -nitroamines is complicated by the inherent instability of this function.²¹ SmI₂ has been widely used as a mild reductant for the conversion of β -nitroamines to 1,2-diamines.²² β -Nitroamines have also been reduced with Zn in the presence of a proton source²³ and with catalytic amount of In with Zn as a stoichiometric reductant.²⁴ The reduction of the nitro group was evaluated for model nitrosugars **6h**, **6i**, and **6k**. Treatment of these nitroamines with SmI₂/H₂O in the presence of pyrrolidine^{25,15a} afforded the corresponding 1,2-diamines **7h**, **7i**, and **7k** in good yield and without any loss of the stereochemical integrity (Scheme 4, Table 4). On the other hand, when the reduction was carried out with Zn powder in the presence of diluted hydrochloric acid as the proton source, 1,2-diamines **7h**, **7i**, and **7k** were also obtained, albeit in lower yield.^{15a} It is somehow surprising that the acetonide protecting groups are stable toward the addition of

Table 2
Synthesis of 2-nitroamines **6b–g**

Entry	4	R ¹	5	R ²	R ³	6	Yield (%)
1	4a	C ₆ H ₁₁	5b	CH ₃	CH ₃	6b	78
2	4b	<i>p</i> -OMe-C ₆ H ₄	5c	2,2-Dimethyl-1,3-dioxane	—	6c	35
3	4c	C ₆ H ₅	5a	H	H	6d	59
4	4d	CH ₃ (CH ₂) ₆	5b	CH ₃	CH ₃	6e	80
5	4e	^{<i>i</i>} Pr	5a	H	H	6f	69
6	4f	^{<i>i</i>} Bu	5b	CH ₃	CH ₃	6g	68



Scheme 3. Indium catalyzed addition of bromonitroalkanes **5a–c** to chiral sugar imines **4g–j**.

Table 3
Synthesis of enantiopure 2-nitroamines **6h–l**

Entry	4	R ¹	5	6	Yield ^a (%)	<i>anti/syn</i> ^b
1	4g	BnO	5a	6h	76	4/1
2	4h	TBSO	5a	6i	79	4/1
3			5b	6j	79	5/1
4	4i	OBn	5a	6k	71	4/1
5			5c	6l	73	6/1
6	4j		5b	6m	73	5/1
7			5c	6n	75	6/1

^a Isolated yields of pure β-nitroamines after column chromatography.

^b Determined by 300 MHz ¹H NMR analysis of the corresponding crude products.

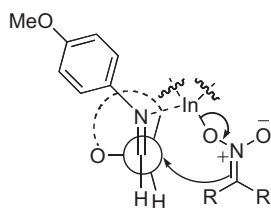
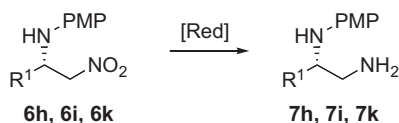


Figure 3. Felkin–Ahn model for the attack on sugar imines **4g–j**.



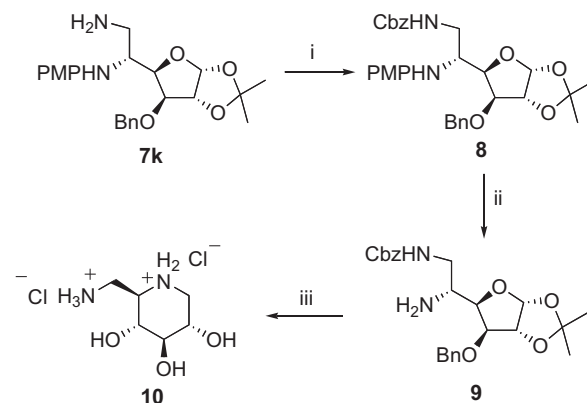
Scheme 4. Reduction of β-nitroamines **6h**, **6i**, and **6k**.

Table 4
Synthesis of 1,2-diamines **7h**, **7i**, and **7k**

Entry	6	R ¹	7	Yield (%)
1	6h	BnO	7h	87 ^a 69 ^b
2	6i	TBSO	7i	84 ^a 62 ^b
3	6k	OBn	7k	85 ^a 62 ^b

^a SmI₂/H₂O/pyrrolidine.

^b Zn/HCl/2-propanol.



Scheme 5. Reagents and conditions: (i) CbzNH₂, NaHCO₃ (sat. aq), EtOAc, rt, 2 h, 91%; (ii) CAN, CH₃CN, rt, 1 h, 79%; (iii) (a) TFA/H₂O 1:1, rt, 14 h; (b) NaHCO₃, THF, 40 °C, 24 h; (c) Pd–C, NH₄CO₂, MeOH, 50 °C, 16 h; (d) AcCl, MeOH, 16 h, 39%.

1 M aqueous HCl, which is probably due to the excess of zinc quickly consuming the protons before most of acetone decomposed.

To illustrate the synthetic utility of these sugar-derived 1,2-diamines in the field of azasugar synthesis, our strategy was first applied to the synthesis of D-glucose 6-amino derivative of 1-DNJ **10**. This iminosugar plays an important role in glycosidase studies, not only because of its weak inhibition properties, but also because it is a synthetic precursor of a wide range of glycosidase inhibitors.²⁶ However, very few syntheses of 6-amino-1-deoxynojirimycin have been reported.²⁷ We have developed a short route to azasugar **10**, synthesized from diamine **7k** in five steps (Scheme 5).

Thus, protection of the primary amino group on diaminosugar **7k** with benzyloxycarbonyl chloride under Schotten–Baumann conditions and removal of the PMP protecting group of resulting

diamine **8** on treatment with cerium ammonium nitrate, yielded orthogonally protected diamine **9**. Acidic hydrolysis of the acetamide protecting group, followed by basic treatment and catalytic hydrogenation gave the desired azasugar **10**, isolated as its dihydrochloride salt after treatment with methanolic hydrochloric acid.

In summary, we have demonstrated that zinc can be used in the addition of bromonitroalkanes to imines in the presence of a catalytic amount of indium to afford the corresponding β -nitroamines. This economic protocol can be easily scaled up to preparative amounts and performs better than the classical base-catalyzed reaction in terms of yields and substrate scope. When applied to sugar-derived imines, this methodology allows the preparation of carbohydrate β -nitroamines, from which the corresponding 1,2-diamines were easily derived. As a first practical application of the novel orthogonally protected carbohydrate 1,2-diamines, we reported here a new route to iminosugar 6-amino-1,6-dideoxynojirimycin. This approach is shorter and more efficient than the previously reported synthetic routes.

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Supplementary data

Supplementary data (experimental procedures for the preparation of nitroamines **6a–n**, diamines **7h**, **7i**, **7k** and iminosugar **10**) associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.tetlet.2013.02.041>.

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