Synthesis of Sugar-Derived 2-Nitroalkanols via Henry Reaction Promoted by Samarium Diiodide or Indium

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Abstract: We present herein an improved synthesis of nitro sugars, consisting of a Henry-type reaction of bromonitromethane and sugar aldehydes. The reaction can be promoted by either SmI_2 or indium metal, yielding in both cases high yields and good diastereoisomeric ratios. However, while the SmI_2-promoted reaction is very sensitive to steric factors and only gives satisfactory results with bromonitromethane, the indium-mediated reaction is not subjected to this limitation, giving excellent results with bromonitromethane as well as more hindered bromonitroalkanes.

Key words: carbohydrates, Henry reaction, 2-nitroalkanols, samarium, indium

Nitro sugars are valuable compounds and synthetic intermediates of growing chemical interest that have been known for more than 40 years. Thus, the first review on nitro sugar chemistry was published in 1969,[1] and the advances in this field during the 1970s and the early 1980s were reviewed in 1986.[2]

Initially, nitro sugars were mainly used for the preparation of the corresponding amino sugars, due to their biological importance. Later on, some biologically active nitro sugars were reported,[3] and it was discovered that the nitro group mimics the carboxyl group in several biological systems.[4]

In the last 20 years, nitro sugars have become powerful chemical tools on account of their utility for the construction of carbon–carbon bonds prior to the transformation of the nitro group into a variety of other functionalities.[5] As a result, a diverse range of functionalized carbohydrates and derivatives such as carbasugars, cyclitols, and heterocycles have been prepared.[6]

The base-catalyzed reaction of nitroalkanes and sugar aldehydes (the Henry reaction)[7] is one of the most common procedures for the preparation of nitro sugars, as well as for lengthening the carbon skeleton of a carbohydrate.[8] Nevertheless, the classical base-catalyzed nitroaldol reaction suffers from some important drawbacks. For example, the reversibility of the reaction means that the β-nitroalkanols are often obtained with poor stereochemical control.[9] Although several methods have been developed to avoid this problem, they are often experimentally complex, and in most cases very specific conditions are required.[10] In addition, when either the starting carbonyl compound or the resulting 2-nitroalkanols are base-sensitive, the nitroaldol conditions can give rise to undesired side reactions and thus furnish the target 2-nitroalkane-1-ols in low yields. On the other hand, it is known that the nitroaldol reaction is very sensitive to steric factors and 'becomes less and less satisfactory the more substituents there are attached to the C atoms to be linked together'.[11] Hence sterically hindered nitroalkanes are less reactive and usually fail to give the desired nitroaldol products in good yields. Thus, the nitroaldol condensation of α,α-dialkyl nitroalkanes[12] has not been widely used in organic synthesis, despite the usefulness of the resulting 1,1-alkyl-1-nitroalkan-2-ols.[13]

In order to circumvent these limitations, great efforts have been devoted to develop alternative procedures for the preparation of 2-nitroalkanols that obviate the use of bases and allow β-nitroalkanols derived from hindered nitroalkanes to be obtained in good yields. A recent contribution by Concellón et al.[14] revealed the SmI_2-promoted reaction of bromonitromethane with aldehydes;[15] an approach that allows 2-nitroalkanols to be obtained in high yield and with good stereoselectivity under very mild reaction conditions. In addition, the indium-mediated addition of bromonitromethane to aldehydes has also been recently described.[16]

As carbohydrates are highly functionalized substrates, the Henry reaction has to be accomplished on compounds that usually are acid- or base-sensitive. From this perspective, the application of novel procedures, which allow the preparation of nitro sugars in high yield and diastereoisomeric ratio, is of great interest.

As part of our interest in the search for more efficient procedures for the preparation of nitro sugars, we initially studied the addition reaction of bromonitromethane to sugar-derived aldehydes **1** promoted by samarium diiodide. Thus, treatment of a solution of bromonitromethane (**2**, 1 equiv) and the aldehyde **1** (1 equiv) in THF with a solution of SmI_2 (1 equiv) in THF (0.1 M) at room temperature gave in all cases the corresponding nitro sugars **3**[17] in high yields and good diastereoisomeric ratios (Scheme 1, Table 1).[18]

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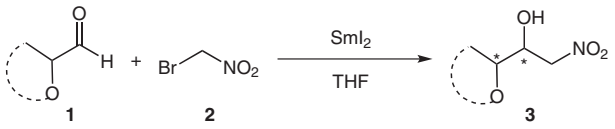


Scheme 1 SmI_2-promoted Henry-type reaction of bromonitromethane and sugar aldehydes

The stereoselectivity obtained in the addition of bromonitromethane (**2**) to aldehydes **1** can easily be explained through the Felkin–Anh model; the nitronate attack on the *si* face giving preferentially to the *anti* stereoisomers (Figure 1).

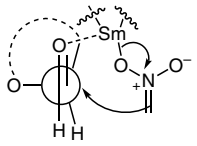


Figure 1 Felkin–Anh model

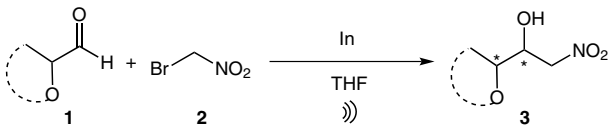
Regarding the mechanism of this transformation, it was previously stated that the reaction is promoted by traces of iodide released from the SmI_3 with is always present in the THF solutions of SmI_2.[14]

A comparison between the results obtained when the reaction was carried out using SmI_2 and the results reported in the literature for typical Henry reaction conditions reveals that the reaction is more diastereoselective and better yields were obtained when SmI_2 was utilized.

Regarding the chemoselectivity, the SmI_2-mediated Henry reaction, as with the classical Henry reaction, has been found to be very sensitive to steric factors. Thus, the reaction with more hindered bromonitroalkanes, as 2-bromonitropropane or 5-bromo-2,2-dimethyl-5-nitro-1,3-dioxane, failed to give the corresponding sugar-derived 2-nitroalkanols.

Next, the indium-mediated reaction of bromonitromethane with aldehydes **1** was assessed. Thus, sonication of mixtures of one equivalent of the corresponding aldehyde **1**, one equivalent of indium and 1.5 equivalents of bromonitromethane in THF once again afforded, in all cases, the corresponding nitro sugars **3** in high yields and good diastereoisomeric ratios (Scheme 2, Table 1).[19]

Regarding the mechanism of these indium-mediated transformations, it should be noted that, in contrast to the SmI_2-mediated reaction of bromonitromethane with aldehydes, which is promoted by the iodide released by traces of SmI_3, the synthesis of nitro alcohols **3a**–**g** using one equivalent of indium is consistent with the typical role of indium as a monoelectronic reducing agent in Barbier-type processes.[20]

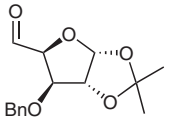
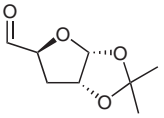
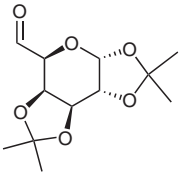
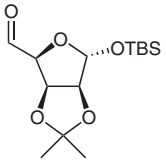
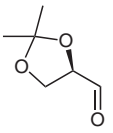
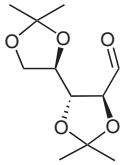
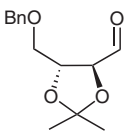


Scheme 2 Indium-promoted Henry-type reaction of bromonitromethane and sugar aldehydes

This different mechanism leads to a different result when using sterically hindered bromonitroalkanes. In this case, the reaction is not as sensitive to steric factors, and indium-mediated reaction of aldehydes **1** and 2-bromonitropropane (**4**) or 5-bromo-2,2-dimethyl-5-nitro-1,3-dioxane (**6**) afforded the corresponding nitro sugars **5**[21] and **7**,[22] respectively, in good yields and total *anti* stereoselectivity (Scheme 3, Table 2).

In conclusion, we have presented a very attractive synthetic route to obtain nitro sugars via Henry-type reaction of bromonitromethane and sugar aldehydes. This improved synthesis is more efficient than the previously described synthesis of the same compounds via classical Henry reaction conditions. The reaction can be performed with either SmI_2 or indium metal. This study reveals that

Table 1 SmI_2- or In-Promoted Synthesis of Nitro Sugars from Sugar Aldehydes

Entry	Aldehyde **1**	Nitro sugar **3**	Promoter	Yield (%)	dr (*anti*/*syn*)
1		**3a**	SmI_2 In	75 78	100: 0 90:10
2		**3b**	SmI_2 In	81 80	78:22 79:21
3		**3c**	SmI_2 In	83 82	85:15 83:17
4		**3d**	SmI_2 In	91 80	91: 9 90:10
5		**3e**	SmI_2 In	89 86	81:19 80:20
6		**3f**	SmI_2 In	86 88	61:39 78:22
7		**3g**	SmI_2 In	88 71	76:24 82:18

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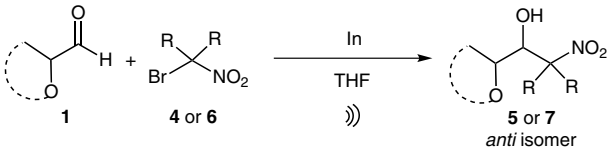
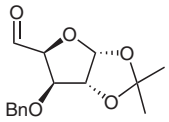
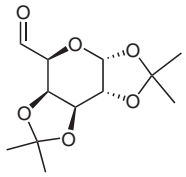
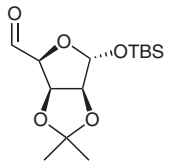
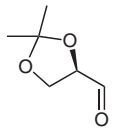
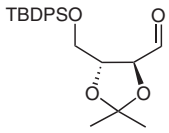
comparable yields and diastereoselectivities were obtained in both cases, and the main difference between both processes lies in the chemoselectivity: while the SmI_2-promoted reaction is very sensitive to steric factors the indium-mediated reaction is less subject to this limitation.



Scheme 3 Indium-promoted Henry-type reaction of 2-bromonitropropane or 5-bromo-2,2-dimethyl-5-nitro-1,3-dioxane and sugar aldehydes

Table 2 Indium-Promoted Synthesis of Nitro Sugars from Sugar Aldehydes

Entry	Aldehyde **1**	Bromo nitroalkane	Nitro sugar	Yield (%)
1		**4**	**5a**	70
		6	**7a**	70
2		**6**	**7b**	71
3		**4**	**5c**	68
		6	**7c**	75
4		**4**	**5d**	69
5		**4**	**5e**	71
		6	**7e**	72

Acknowledgment

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(16) Soengas, R. G.; Estévez, A. M. *Eur. J. Org. Chem.* **2010**, 5190.
(17) **Representative Analytical Data**
3-*O*-Benzyl-6-deoxy-6-nitro-1,2-*O*-isopropyliden-α-D-glucofuranose (3a)
Yellow oil; $[\alpha]_D^{20}$ –26.8 (*c* 1.0 in $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.49–7.30 (m, 5 H), 5.91 (d, *J* = 3.7 Hz, 1 H), 4.76–4.60 (m, 4 H), 4.56–4.42 (m, 2 H), 4.14–4.06 (m, 2 H), 2.58 (d, *J* = 4.9 Hz, 1 H), 1.47 (s, 3 H), 1.32 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.8 (C), 128.8 (2 × CH), 128.4 (CH), 127.9 (2 × CH), 112.1 (C), 105.1 (CH), 82.0 (CH), 80.9 (CH), 79.9 (CH), 78.5 (CH_2), 72.1 (CH_2), 66.3 (CH), 26.9 (CH_3), 26.1 (CH_3) ppm. MS (ESI^+): *m/z* (%) = 362 (15) $[M + Na]^+$, 357 (100) $[M + NH_4]^+$, 316 (1), 288 (8), 282 (1). HRMS (ESI^+): *m/z* calcd for $[C_{16}H_{21}NO_7Na]^+$ $[M + Na]^+$: 362.1216; found: 362.1210; R_f = 0.33 (hexane–EtOAc = 3:1).
7-Deoxy-1,2:3,4-di-*O*-isopropylidene-7-nitro-D-glycero-β-D-galacto-heptopyranose (3c)
Yellow oil; $[\alpha]_D^{20}$ –49.4 (*c* 0.6 in $CHCl_3$). ^1H NMR (300

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MHz, $CDCl_3$): δ = 5.49 (d, *J* =5.0 Hz, 1 H), 4.78 (app d, *J* = 11.2 Hz, 1 H), 4.65 (dd, *J* = 8.0, 2.5 Hz, 1 H), 4.51–4.47 (m, 2 H), 4.43 (dd, *J* = 8.0, 2.0 Hz, 1 H), 4.34 (dd, *J* = 4.9, 2.5 Hz, 1 H), 3.73 (dd, *J* = 8.2, 2.0 Hz, 1 H), 2.89 (d, *J* = 5.9 Hz, 1 H), 1.51 (s, 3 H), 1.46 (s, 3 H), 1.37 (s, 3 H), 1.32 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 109.6 (C), 108.9 (C), 96.2 (CH), 78.1 (CH_2), 70.6 (CH), 70.5 (CH), 70.1 (CH), 67.7 (CH), 67.4 (CH), 25.9 (2 × CH_3), 24.8 (CH_3), 24.3 (CH_3) ppm. MS (ESI$^+$): *m/z* (%) = 342 (24) $[M + Na]^+$, 337 (100) $[M + NH_4]^+$, 320 (19) $[M + H]^+$, 262 (48). HRMS (ESI$^+$): *m/z* calcd for $[C_{13}H_{22}NO_8]^+$ $[M + H]^+$: 320.1340; found: 320.1339. R_f = 0.20 (hexane–EtOAc = 3:1).

(18) **General Procedure for the Samarium Diiodide Mediated Reaction of Bromonitromethane and Aldehydes**
SmI_2 (0.8 mmol, 0.1 M) in THF (8 mL) was added to a stirred solution of bromonitromethane (0.8 mmol) and the corresponding aldehyde (0.8 mmol) in THF (5 mL). After stirring the reaction mixture at r.t. for 5 h it was quenched with aq HCl (10 mL, 0.1 M) and extracted with CH_2Cl_2 (3 × 25 mL). The combined extracts were washed with an aq sat. solution of $Na_2S_2O_3$ (20 mL), then dried over $MgSO_4$, filtered, and the solvent was evaporated in vacuo. The residue was purified by flash column chromatography with mixtures of EtOAc–hexane.

(19) **General Procedure for the Indium-Mediated Reaction of Bromonitroalkanes and Aldehydes**
To a suspension of indium powder (0.5 mmol) in THF (1 mL) was added the bromonitroalkane (0.6 mmol), and the mixture was sonicated for 20 min. The corresponding aldehyde (0.5 mmol) was added, and sonication was continued for a further 4 h. The reaction mixture was neutralized with sat. aq $NaHCO_3$, diluted with H_2O (10 mL), and extracted with Et_2O (3 × 25 mL). The combined organic layers were dried over $MgSO_4$, filtered, and the solvent was evaporated in vacuo. The residue was purified by flash column chromatography with mixtures of EtOAc–hexane.

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(21) **Representative Analytical Data**
1-*O*-*tert*-Butyldimethylsilyl-2,3-di-*O*-isopropylidene-5(*R*)-(1-methyl-1-nitroethyl)-α-D-lyxofuranose (5c)
Yellow oil; $[\alpha]_D^{23}$ –21.3 (*c* 0.4 in $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.09 (s, 1 H, 1-H), 4.84 (dd, 1 H, *J* = 3.8, 5.8 Hz), 4.53–4.63 (m, 2 H), 3.80–4.48 (m, 2 H), 2.85 (d, 1 H, *J* = 5.6 Hz, OH), 1.61 (s, 6 H, 2 × CH_3), 1.31, 1.47 (2 × s, 6 H, 2 × CH_3), 0.86 (s, 9 H, 3 × CH_3), 0.10 (s, 3 H, CH_3), 0.11 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 113.12 (C), 106.13 (CH), 91.1 (C), 84.3 (CH), 81.1 (CH), 79.3 (CH), 73.9 (CH), 69.6 (CH), 26.3 (CH_3), 25.0 (CH_3), 24.0 (CH_3), 21.0 (CH_3), 19.8 (C), 17.8 (3 × CH_3), –4.5 (CH_3), –5.5 (CH_3) ppm. ESI-MS: *m/z* (%) = 488 (10) $[M + H]^+$. HRMS: *m/z* calcd for $C_{26}H_{38}NO_6Si$ $[M + H]^+$: 488.2462; found: 488.2471. R_f = 0.30 (hexane–EtOAc = 7:1).
4-*O*-*tert*-Butyldiphenylsilyl-2,3-di-*O*-isopropylidene-1(*S*)-(1-methyl-1-nitroethyl)-D-threitol (5e)
Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.66–7.73 (m, 4 H, 4 × HAr), 7.35–7.48 (m, 6 H, 6 × HAr), 4.10–4.23 (m, 2 H), 3.83–3.90 (m, 2 H), 3.66–3.74 (m, 1 H), 1.67, 1.69 (2 × s, 6 H, 2 × CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 135.7 (C), 135.6 (C), 128.1 (CH), 128.0 (CH), 127.8 (CH), 127.7 (CH), 127.6 (CH), 110.2 (C), 91.3 (C), 81.0 (CH), 79.6 (CH), 76.3 (CH), 65.2 (CH_2), 26.7 (CH_3), 26.6 (CH_3), 23.3 (CH_3), 21.6 (CH_3), 19.3 (CH_3) ppm. ESI-MS: *m/z* (%) = 505 (100) $[M + Na]^+$: 488 (20) $[M + H]^+$. HRMS: *m/z* calcd for $C_{26}H_{38}NO_6Si$ $[M + H]^+$: 488.2462; found: 488.2484. R_f = 0.29 (hexane–EtOAc = 4:1).

(22) **Representative Analytical Data**
3-*O*-Benzyl-5(*R*)-(2,2-dimethyl-5-nitro-1,3-dioxan-5-yl)-1,2-*O*-isopropylidene-α-D-xylofuranose (7a)
Yellow oil; $[\alpha]_D^{24}$ –39.7 (*c* 1.2 in $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36–7.24 (m, 5 H, 5 × HAr), 5.91 (d, 1 H, $J_{1,2}$ = 3.7 Hz, 1-H), 4.42–4.57 (m, 5 H), 4.05–4.34 (m, 5 H), 1.34, 1.39, 1.43, 1.45 (4 × s, 12 H, 4 × CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.8 (C), 129.2 (2 × CH), 128.9 (CH), 128.3 (2 × CH), 112.6 (C), 105.6 (C), 99.5 (CH), 90.2 (C), 82.5 (CH), 81.3 (CH), 78.7 (CH_2), 72.4 (CH), 70.4 (CH), 62.8 (CH_2), 61.1 (CH_2), 26.5 (CH_3), 25.6 (CH_3), 21.5 (CH_3), 20.6 (CH_3) ppm. ESI-MS: *m/z* (%) = 440 (21) $[M + H]^+$, 462 (100) $[M + Na]^+$. HRMS: *m/z* calcd for $C_{21}H_{30}NO_9$ $[M + H]^+$: 440.1915; found: 440.1894. R_f = 0.31 (hexane–EtOAc = 3:1).
1,2:3,4-Di-*O*-isopropylidene-6(*R*)-(2,2-dimethyl-5-nitro-1,3-dioxan-5-yl)-β-D-galacto-heptopyranose (7b)
Colorless oil; $[\alpha]_D^{25}$ +33.4 (*c* 0.9 in $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.50 (d, 1 H, *J* = 5.1 Hz, H-1), 4.52–4.71 (m, 3 H), 4.03–4.37 (m, 5 H), 3.92 (dd, 1 H, *J* = 8.9, 1.9 Hz,), 3.16 (d, 1 H, *J* = 7.1 Hz, OH), 1.33, 1.35, 1.36, 1.45, 1.46, 1.59 (6 × s, 18 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 109.6 (C), 109.1 (C), 98.9 (C), 96.1 (CH), 89.9 (C), 70.8 (CH), 70.6 (CH), 70.5 (CH), 70.0 (CH), 66.6 (CH), 62.7 (CH_2), 61.1 (CH_2), 27.3 (CH_3), 25.8 (CH_3), 25.6 (CH_3), 24.3 (CH_3), 19.5 (CH_3) ppm. ESI-MS: *m/z* (%) = 420 (31) $[M + H]^+$, 442 (9) $[M + Na]^+$. HRMS: *m/z* calcd for $C_{18}H_{30}NO_{10}$ $[M + H]^+$: 420.1870; found: 420.1863. R_f = 0.31 (hexane–EtOAc = 2:1).

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