# A Practical Synthesis of Sugar-Derived Cyclic Nitrones: Powerful Synthons for the Synthesis of Iminosugars

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**Abstract:** Sugar-derived cyclic nitrones were synthesized from the corresponding aldoses through an efficient and practical procedure involving a seven-step reaction sequence in good to excellent overall yield (10–42%). This synthetic strategy, requiring only inexpensive reagents, is easy to perform and hence suitable for large-scale preparations.

**Key words:** sugar-derived cyclic nitrones, synthesis, iminosugars, nitrones

Iminosugars,[1] the 'nitrogen-in-the-ring' analogues of pyranoses and furanoses, have attracted considerable attention from synthetic organic chemists due to their remarkable biological activities.[2] A number of iminosugars, both synthetic and naturally occurring, have been shown to be selective and potent inhibitors of glycosidases, glycosyltransferases or other carbohydrate processing enzymes.[3] Furthermore, an increasing number of iminosugar family members have exhibited great potential as pharmaceuticals.[1a,2c] Although great effort has been expended and numerous synthetic procedures have been developed for the synthesis of iminosugars,[4] efficient methods for the rapid generation of iminosugars with the structural diversity necessary for in-depth structure–activity studies are still lacking. Among the existing approaches, synthetic methods based on sugar-derived cyclic nitrones have emerged as a potentially powerful strategy for the diversity-oriented synthesis of iminosugars due to the reactivity of the nitrone functionality.

Nitrones have been shown to be very diverse synthetic intermediates for the construction of structurally complex molecules[5,6] because they are capable of undergoing a variety of synthetically useful reactions, such as: 1,3-dipolar cycloadditions,[7] nucleophilic additions,[8,9] and pinacol-type coupling reactions, etc.[10] Enantiomerically pure polyfunctional cyclic nitrones, which have been widely used in the synthesis of various natural and biologically active nitrogen-containing compounds,[6,9,11,12] are especially valuable in organic synthesis. Therefore, the search for efficient and practical synthetic approaches toward cyclic nitrones is of ongoing interest.

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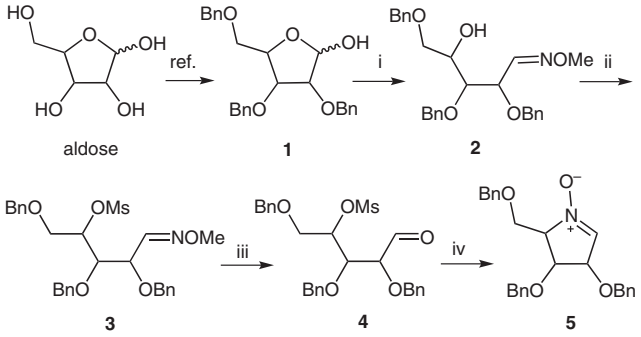
Methods for the synthesis of cyclic nitrones[13] include oxidation of hydroxylamines,[14] amines[15] and imines,[16] condensation of ketones with hydroxylamines,[17] and N-alkylation of oximes.[18] Among the existing methods, N-alkylation of oximes is the most widely used strategy for the formation of the nitrone functionality due to the relative ease with which the regio- and stereoselectivity involved in the transformation can be controlled. A number of methods have been developed for the synthesis of sugar-derived cyclic nitrones[18,19] from the readily available sugar hemi-acetals. In these approaches the key steps include addition of O-silylated hydroxylamine or $H_2NOTHP$ to the hemi-acetal to form the O-protected oxime, followed by mesylation of the exposed OH, and then intramolecular N-alkylation of the oxime. The drawbacks associated with these procedures are that large amounts of side-products are commonly formed from the reaction and tedious work-up procedures are required; hence, these procedures are not suitable for large-scale preparations. In our earlier work we have tried to improve the synthetic procedure[12b] by using the Wittig reaction to open the cyclic sugar hemi-acetal ring; this was relatively easy to work-up but was still not suitable for large-scale preparations due to critical reaction conditions. Goti's one-pot procedure[18d] using $NH_2OH$ instead of $NH_2$–$OSiR_3$ provided a shortened synthetic route, but its overall yield was poor. Herein, we report an improved procedure for the synthesis of cyclic nitrones from sugar hemi-acetals that is based on our previous method. The key improvement was the use of $NH_2OMe$ instead of the Wittig reagent to open the hemi-acetal ring.

The synthesis of five-membered cyclic nitrones was first investigated (Scheme 1). Sugar hemi-acetals 2,3,5-tri-*O*-benzylfuranoses **1** were prepared through the reported method from the corresponding aldoses in three steps.[20a] Compound **1** was treated with *O*-methylhydroxylamine hydrochloride in the presence of pyridine to form *O*-methyl oxime ether **2**. The exposed hydroxy group was then mesylated to produce the oxime ether **3**. Hydrolysis of **3** by using an aqueous solution of formaldehyde (37%) in THF, catalyzed by TsOH, afforded aldehyde **4**. Treatment of **4** with hydroxylamine hydrochloride resulted in the formation of the desired nitrone **5** (Scheme 1, Table 1). It is remarkable that this seven-step synthesis was virtually all conducted as a one-pot synthesis where only basic work-

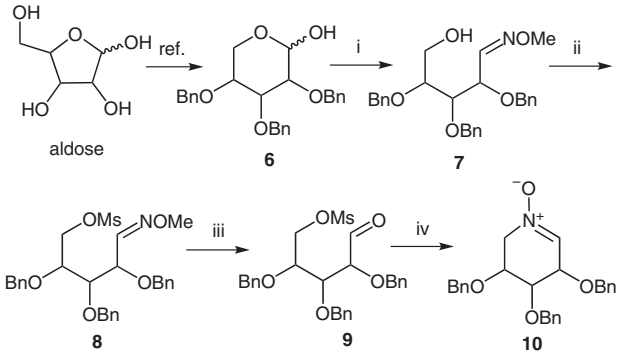
up was required between each step of the reaction sequence, i.e. the crude intermediates **1**, **2**, **3**, and **4** were used directly in the next step of reaction without further purification. Only the final products, nitrones **5**, were subjected to further purification by column chromatography (**5a** and **5b**) or recrystallization (**5c** and **5d**). The synthesis was carried out on a multi-gram scale, producing up to 100 g of nitrones in good to excellent overall yields (23–35% in seven steps based on the aldoses, or 36–40% in four steps based on the sugar hemi-acetals **1**; Table 1).[21]




**1a** 2,3,5-tri-O-benzyl-D-arabinofuranose
**1b** 2,3,5-tri-O-benzyl-L-arabinofuranose
**1c** 2,3,5-tri-O-benzyl-D-ribofuranose
**1d** 2,3,5-tri-O-benzyl-D-xylofuranose

**Scheme 1** *Reagents and conditions*: (i) pyridine, $NH_2OMe{\cdot}HCl$; (ii) $Et_3N$, MsCl $CH_2Cl_2$; (iii) *p*-TsOH, aq HCHO (37%), THF; (iv) $NH_2OH{\cdot}HCl$, $NaHCO_3$, $H_2O$, MeOH, r.t. to 60 °C.

The procedure was then successfully extended to the synthesis of six-membered cyclic nitrones (Scheme 2). Sugar hemi-acetals 2,3,4-tri-*O*-benzyl-pyranose **6** were prepared through the reported method from the corresponding aldoses in three steps.[20b] Cyclic nitrones **10** were prepared following the procedure described above in good to excellent overall yields (10–42% in seven steps based on the aldoses, or 14–54% in four steps based on the sugar hemi-acetals **6**; Table 1). The synthesis of **10** was found to be as robust as the synthesis of **5** in that it was performed on multi-gram scale and that all the crude intermediates **6**, **7**, **8**, and **9** were used directly in the subsequent reaction without further purification. While the overall yields were generally good to excellent, there was one exception in the case of the synthesis of **10c**, where the overall yield was only 10% over the seven steps, based on D-ribose (Table 1, entry 7).




**6a** 2,3,4-tri-O-benzyl-D-arabinopyranose
**6b** 2,3,4-tri-O-benzyl-L-arabinopyranose
**6c** 2,3,4-tri-O-benzyl-D-ribopyranose
**6d** 2,3,4-tri-O-benzyl-D-xylopyranose

**Scheme 2** *Reagents and conditions*: (i) for **7a**, **7b**, and **7c**: $H_2NOMe{\cdot}HCl$, pyridine, $CH_2Cl_2$, r.t.; for **7d**: $H_2NOMe{\cdot}HCl$, $NaCO_3$, EtOH–$H_2O$, reflux; (ii) MsCl, $Et_3N$, $CH_2Cl_2$, 0 °C; (iii) TsOH, aq HCHO (37%), THF, r.t.; (iv) $NH_2OH{\cdot}HCl$, $NaHCO_3$, EtOH–$H_2O$ (4:1), r.t., 24 h, then 40 °C.

The relatively poor overall yield of **10c** resulted from the poor yield of the final cyclization step; in this case the intermediate oxime **11c** (Figure 1) could also be isolated. Attempts to improve the yield of **10c** by optimizing the reagents and reaction conditions, unfortunately failed. It is worth mentioning that hemi-acetal **6d**, which was derived from D-xylose, reacted poorly with $MeONH_2{\cdot}HCl$ in the presence of pyridine in $CH_2Cl_2$ at room temperature. However, when the reaction was conducted at reflux in EtOH–$H_2O$, in the presence of $Na_2CO_3$, the desired oxime ether **7d** was obtained in 92% yields.

**Table 1** Synthesis of Sugar-Derived Cyclic Nitrones

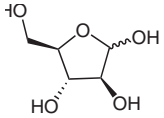
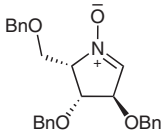
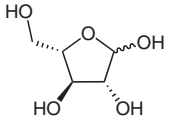
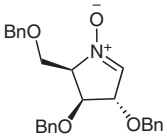
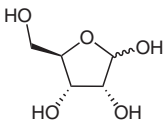
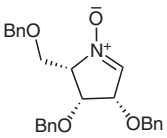
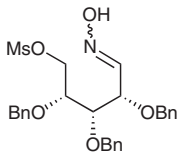
| Entry | Starting material | | Cyclic nitrone[a] | | Yield (%)[b] |
|---|---|---|---|---|---|
| 1 | D-arabinose |  | **5a** |  | 23 (38)[c] |
| 2 | L-arabinose |  | **5b** |  | 32 (38)[c] |
| 3 | D-ribose |  | **5c** |  | 30 (36)[c] |

**Table 1** Synthesis of Sugar-Derived Cyclic Nitrones (continued)

| Entry | Starting material | Cyclic nitrone[a] | Yield (%)[b] |
|---|---|---|---|
| 4 | D-xylose | **5d** | 35 (40)[c] |
| 5 | D-arabinose | **10a** | 42 (52)[c] |
| 6 | L-arabinose | **10b** | 35 (43)[c] |
| 7 | D-ribose | **10c** | 10 (14)[c] |
| 8 | D-xylose | **10d** | 34 (54)[c] |

[a] Compounds **10a**, **10b**, and **10c** are novel compounds.
[b] Method A: Isolated overall yields in seven steps based on the corresponding aldoses.
[c] Method B: Overall four-step yield based on the corresponding sugar hemi-acetals **1** or **6** are shown in brackets.




**11c**

**Figure 1** Structure of compound **11c**

In summary, a practical and efficient method has been developed for the synthesis of sugar-derived cyclic nitrones, starting from the aldose, through a seven-step reaction sequence. The merits of this new procedure are that it is: (a) general and robust for the synthesis of both five- and six-membered cyclic nitrones; (b) easy work-up after each reaction step, and (c) amenable to large-scale preparation.

**Supporting Information** for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

## Acknowledgment

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(21) **General methods for the synthesis of 5 and 10:**
**Method A**: Compounds **1** and **6** were prepared from the corresponding aldoses (90 g 0.6 mol) in three steps according to the literature[20] and were used directly in the next step without further purification. $NH_2OMe{\cdot}HCl$ (55.12 g, 0.66 mol, 1.1 equiv) and $Et_3N$ (91.9 mL, 0.66 mol, 1.1 equiv) were added to a solution of crude compound **1** or **6** (crude product prepared from 0.6 mol aldose) in anhydrous $CH_2Cl_2$ (300 mL). The reaction reached completion after vigorous stirring for about 12 h. The reaction mixture was then concentrated in vacuo and the resulting mixture was dissolved in EtOAc–$H_2O$. The organic phase was separated and the aqueous phase was extracted with EtOAc (3 × 150 mL). The combined organic phases were dried with anhydrous $Na_2SO_4$ and filtered, the filtrate was concentrated in vacuo to give the crude product **2** or **7**, which was used directly in the next step of reaction without further purification. To an ice-cooled solution of **2** or **7** in $Et_3N$ (91.9 mL, 0.66 mol, 1.1 equiv) and $CH_2Cl_2$ (300 mL), was added methanesulfonyl chloride (51.08 mL, 0.66 mol, 1.1 equiv) slowly, and the mixture was allowed to warm gradually to r.t. After 1 h, the reaction mixture was quenched by addition of $H_2O$ (200 mL). The organic phase was separated and the aqueous phase was extracted with EtOAc (3 × 150 mL). The combined organic phases were dried over anhydrous $MgSO_4$. After filtration, the solvent was removed in vacuo to give crude product **3** or **8** as a yellow oil, which was used directly in the next step without further purification. To a well-stirred solution of **3** or **8** in THF (400 mL), *p*-TsOH (114 g, 0.6 mol) and aq HCHO (37%, 150 mL) were added subsequently. After stirring for 36 h, the reaction was neutralized with sat. aq $NaHCO_3$. EtOAc (600 mL) was added to the reaction mixture, the organic phase was separated and the aqueous phase was extracted with EtOAc (3 × 150 mL). The combined organic phases were dried with anhydrous $Na_2SO_4$. After filtration, the filtrate was concentrated in vacuo, the resulting crude product **4** or **9** was used directly in the next step of reaction without further purification. A solution of $NH_2OH{\cdot}HCl$ (93.15 g, 1.35 mol) and $NaHCO_3$ (113.4 g, 1.35 mol) in $H_2O$ (150 mL) was added to the solution of crude **4** or **9** in EtOH (600 mL) dropwise. The reaction mixture was stirred at r.t. for 12 h and then stirred at about 60 °C until TLC showed the reaction to have reached completion. The solvents were removed in vacuo and the residue was dissolved in EtOAc

(300 mL) and $H_2O$ (200 mL). The organic phase was separated and the aqueous phase was extracted with EtOAc (3 × 150 mL). The combined organic phases were dried with anhydrous $Na_2SO_4$. After filtration and concentration in vacuo, the resulting crude product was either recrystallized or purified by flash column chromatography (petroleum ether–EtOAc, 2:1→1:2). **Method B**: The same procedure as method A was used with purified compounds **1** and **6** as starting material. Compound **5a**: 129.0 g (23% from 200 g D-arabinose); 79.4 g from 210.3 g **1a** (38%). Yellow oil; $[\alpha]_D^{20}$ –78 (*c* 1.08, $CH_2Cl_2$) {Lit[18d] $[\alpha]_D^{23}$ –75.9 (*c* 0.54, $CH_2Cl_2$)}. IR (thin film): 3030 (w), 2866 (m), 1582 (s), 1496 (w), 1454 (s), 1363 (m), 1095 (s), 737 (s), 697 (s) $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ = 7.27–7.14 (m, 15 H, Ph), 6.73 (s, 1 H, H-2), 4.67 (t, *J* = 2.1 Hz, 1 H, H-3), 4.58–4.38 (m, 6 H, PhC*H*$_2$), 4.28 (dd, *J* = 7.6, 4.5 Hz, 1 H, H-4), 4.08–4.03 (m, 1 H, H-5), 3.90 (dd, *J* = 10.1, 4.3 Hz, 1 H, H-6), 3.73 (dd, *J* = 10.1, 1.6 Hz, 1 H, H-6). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 138.0, 137.4, 137.3, 133.4 (C-2), 128.7, 128.6, 128.4, 128.2, 128.1, 128.0, 127.9, 127.6 (Ph), 83.2 (C-3), 80.6 (C-4), 74.2 (C-5), 73.6, 73.2, 72.5, 64.5 (C-6). Compound **10a**: 88.2 g (42% from 75 g D-arabinose); 94 g from 181.6 g **6a** (52%). Light-yellow oil; $[\alpha]_D^{20}$ –44 (*c* 1.17, $CHCl_3$). IR (thin film): 2960 (s), 2925 (s), 2855 (s), 1597 (w), 1454 (m), 1260 (s), 1023 (s), 800 (s), 739 (m), 698 (m) $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ = 7.33–7.25 (m, 15 H, Ph), 7.01 (d, *J* = 2.9 Hz, 1 H, H-2), 4.94–4.58 (m, 6 H, $PhCH_2$), 4.31 (d, *J* = 3.6 Hz, 1 H, H-3), 4.06–3.82 (m, 4 H, H-6, H-4, H-5). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 137.6, 137.3, 128.6, 133.4 (C-2), 128.6, 128.5, 128.2, 128.1, 128.0, 127.9, 127.8 (Ph), 74.6, 73.5, 72.9, 72.8, 72.1, 71.4 (C-3, C-4, C-5), 60.0 (C-6). TOF-HRMS (ESI+): *m*/*z* $[M + H]^+$ calcd for $C_{26}H_{28}NO_4$: 418.2013; found: 418.2001.