piophenone in 150 mL of ether was added dropwise with efficient stirring. Shortly after the addition was completed, 200 mL of 5% HCl was added to the still cold solution. The layers were separated, and the aqueous portion was extracted with ether (3 × 50 mL). The combined ether phase was washed with water, bicarbonate, and brine and then dried and evaporated to give 56.9 g (quantitative yield) of crude 1,1-diphenyl-1-propanol. This material was taken up in 400 mL of glacial acetic acid containing 7 mL of concentrated HCl, and the mixture was refluxed for 0.5 h. The green solution was cooled, diluted with 400 mL of water, and extracted with CH_2Cl_2 (3 × 80 mL). The combined organic phase was washed with water, bicarbonate, and brine and then dried (K_2CO_3) and evaporated to give 50.9 g of crude discolored product. Vacuum distillation gave 44.4 g (89%) of pure **2** as a colorless liquid, bp 108 °C (1 Torr), which solidified to a low-melting crystalline mass on standing: NMR (60 MHz) δ 1.75 (d, 3 H, J = 7 Hz), 6.1 (q, 1 H, J = 7 Hz), and 7.0–7.4 (m, 10 H).

Tetraphenylbutadiene (1, R = R′ = H): The Stoichiometric Ratio Reaction. This general procedure was used for all the materials listed in Table I, with the modifications shown in the footnotes. An ice-bath-cooled solution of **2** (1.20 g, 6.19 mmol) in 35 mL of THF was treated with 4.1 mL of 1.6 M *n*-butyllithium in hexane (6.5 mmol) to give a blood red solution. After a few minutes, this was mixed with a solution of 1.13 g (6.22 mmol) of benzophenone in 40 mL of THF. The red color typically changed to yellow-green when about half of the ketone had been added. Dilute HCl was added, at times that ranged from 15 min to 24 h after addition of the ketone with no effect on the yield. The mixture was separated, and the aqueous phase extracted with ether. The combined organic phase was washed with brine and then dried and evaporated to give a viscous oil. Chromatography (silica gel, graded elution, hexanes to CH_2Cl_2) at this stage was used to isolate the alcohol **5**, although this step is not necessary for TPB isolation. The product was taken up in 100 mL of HOAc containing 2 mL of concentrated HCl and refluxed for 1 h to effect dehydration. The crude product in CH_2Cl_2 solvent was washed with KOH solution to remove the acid, dried, and evaporated to give a discolored oil. Column chromatography (silica gel, 10% CH_2Cl_2 in hexanes) gave 0.555 g (25%) of 1,1,4,4-tetraphenyl-1,3-butadiene, identical (NMR, melting point) with authentic commercial material.

Tetraphenylbutadiene: The 2-fold Excess *n*-BuLi Reaction. The procedure was essentially identical with that described above, except that 7.4 mL of *n*-butyllithium (11.9 mmol) was used to prepare **3** from 1.099 g (5.70 mmol) of **2**, and 5.5 mmol of benzophenone was added. The solution remained red after addition of the benzophenone. The solution was divided at this point, with ca. half being quenched by water and the remainder by D_2O. The alcohol mixtures (**5** + **7**) and (**5d** + **7d**), respectively, were isolated by silica gel chromatography and exhibited the NMR characteristics described in the text. The yields of TPB isolated from two analogous experiments with dehydration of the crude alcohols were 60 and 65%.

Bis(*n*-propyl)-TPB (9). A solution of 14.4 g (0.074 mol) of **2** in 300 mL of THF was cooled in an ice bath and treated with 100 mL of 1.6 M *n*-butyllithium in hexane (0.16 mol), added dropwise over a 20-min period. To the resulting deep red solution was added, over a 2-h period, a solution of 19.4 g (0.073 mol) of 4,4′-di-*n*-propylbenzophenone[19] in THF. The still red solution was quenched shortly after addition by treatment with dilute HCl, which gave a golden orange coloration. The organic layer was separated and combined with 2 × 50-mL ether extractions. It was washed with water and brine and then dried and evaporated to give a dark orange oil, which was subjected to dehydration conditions by refluxing in 300 mL of HOAc containing 4 mL of concentrated HCl. This mixture was treated in the usual way to give 38.5 g of crude product as a brown oil. Recrystallization from ethanol (four times, after decanting from small amounts of less soluble brown oils) gave 15.6 g (48%) of **9**: mp 100–101 °C; NMR δ 0.90 and 0.97 (2 t, 3 H each, J = 7 Hz), 1.5–1.8 (m, 4 H), 2.51 and 2.62 (2 t, 2 H each, J = 7 Hz), 6.77 (AB q, 2 H, vinylic), and 7.0–7.4 (m, 18 H); MS 444 (6.8), 443 (37.1), 442 (M^+, 100), 279 (7.5), 251 (14.1), 191 (7.7), 167 (9).

(19) Muraoka, M.; Itoh, T.; Mizuma, T.; Toyoshima, S. *Chem. Pharm. Bull.* **1960**, *8*, 860.

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A Route to Functionalized Branched-Chain Amino Sugars via Nitrous Acid Promoted Spiroaziridine Formation

Ricardo José Alves,† Sergio Castillon,† Aimée Dessinges,† Pal Herczegh,† J. Cristobal Lopez,† Gabor Lukacs,*† Alain Olesker,† and Ton That Thang‡

Institut de Chimie des Substances Naturelles du CNRS, 91198 Gif-sur-Yvette Cedex, France, Equipe de Recherche ERA 948 CNRS, USTL, 34060 Montpellier, France

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The natural occurrence of branched-chain amino and nitro sugars has stimulated extensive research for their synthesis.[1] Methodology for the preparation of isomeric 3-amino-3-deoxy-3-*C*-methyl carbohydrates is well documented.[1] Synthetic schemes involve hydrogenolytic opening of aziridine intermediates generated from cyanhydrines or spirooxiranes. As a continuation of our interest in this area,[2,3] we present in this paper a general method allowing access to functionalized branched-chain amino sugars. Our approach is outlined in Scheme I, its key steps are nitrous acid promoted aziridine formation followed by nucleophilic ring opening of the aziridines.

When methyl 4,6-*O*-benzylidene-3-deoxy-α-D- (**1**) and -β-D-*threo*hexopyranosid-2-ulose (**2**) were separately treated with trimethylsilyl cyanide in a methanolic solution saturated with ammonia, ketone **1** gave stereospecifically an α-amino nitrile with an equatorial amine **3**, while **2** afforded a 2.5:1 mixture of **4a** and **4b**, the former α-amino nitrile having an axial amine being the major compound of the reaction.

Stereochemical proof of the Strecker reaction products was obtained by carbon-13 NMR spectroscopy as described.[2] Chemical shift of the C-4 signal of the α-amino nitriles was diagnostic for the stereochemistry of the C-2 quaternary carbon center of these molecules. In the spectrum of the axial amine **4a** C-4 is shielded by about 2.5 ppm relative to this signal in the spectrum of equatorial amines **3** and **4b**. The same tendency was observed in the carbon-13 NMR spectrum of the corresponding cyanohydrines from which both isomers were available from another study. The axial carbon–oxygen bond at C-2 has greater shielding effect on the C-4 resonance than an axially disposed carbon–carbon linkage.

Direct transformation by metal hydrides [DIBAH, $LiAl(OEt)_3H$, $LiAl(OEt)_2H_2$] of the *N*-acetyl and *N*-tosyl derivatives of the α-amino nitriles into the corresponding protected α-amino aldehydes failed. Therefore the nitrile function of the *N*-tosyl derivatives **5** and **6** were first reduced by lithium aluminium hydride to the corresponding primary amines **7** and **8**, respectively, and the latter deaminated by sodium nitrite in aqueous acetic acid. These reactions furnished respectively *N*-tosyl spiroaziridines **9** and **10** in excellent yield (84–89%). Nucleophilic ring opening of the *N*-tosylaziridines with sodium acetate in *N*,*N*′-dimethylformamide proceeded regiospe-

† Institut de Chimie des Substances Naturelles du CNRS.
‡ Equipe de Recherche, ERA 948.

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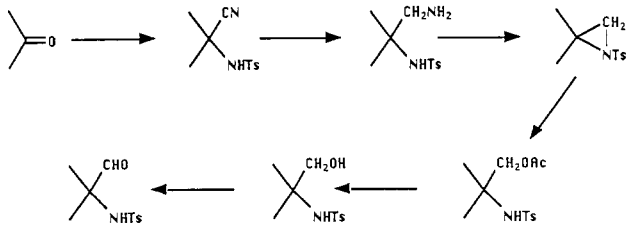
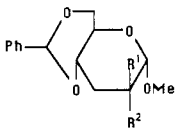
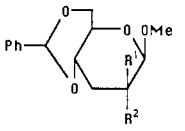
Scheme I



cifically, giving the *C*-acetoxymethyl compounds **11** and **12**, which in the presence of base afforded respectively the *C*-hydroxymethyl compounds **13** and **14**. Pyridinium chlorochromate oxidation of **13** and **14** gave respectively the desired *C*-formyl sugars **15** and **16** ready for the synthesis of any functionalized branched-chain amino sugar.





1 $R^1, R^2 = O$

2 $R^1, R^2 = O$

3 $R^1 = CN$; $R^2 = NH_2$

4a $R^1 = NH_2$; $R^2 = CN$

4b $R^1 = CN$; $R^2 = NH_2$

5 $R^1 = CN$; $R^2 = NHTs$

6 $R^1 = NHTs$; $R^2 = CN$

7 $R^1 = CH_2NH_2$; $R^2 = NHTs$

8 $R^1 = NHTs$; $R^2 = CH_2NH_2$

11 $R^1 = CH_2OAc$; $R^2 = NHTs$

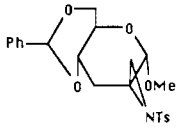
12 $R^1 = NHTs$; $R^2 = CH_2OAc$

13 $R^1 = CH_2OH$; $R^2 = NHTs$

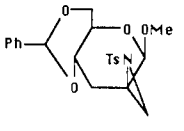
14 $R^1 = NHTs$; $R^2 = CH_2OH$

15 $R^1 = CHO$; $R^2 = NHTs$

16 $R^1 = NHTs$; $R^2 = CHO$



9



10

Experimental Section

General Procedures. The melting points were determined with a Büchi apparatus and are uncorrected. A Perkin-Elmer Model 141 MC polarimeter and 1-dm tubes were used for measurement of specific rotations. ^1H NMR spectra were recorded in chloroform-*d* solution at 400 MHz. The ^{13}C NMR spectra were measured in chloroform-*d* solution at 50.31 MHz with a Bruker WP-200 spectrometer. Chemical shifts are given in parts per million, and tetramethylsilane was the internal standard (δ 0.000). Carbon-13 chemical shifts for aromatic carbons are not given. Microanalysis were performed by the Service Central de Microanalyse du CNRS. Silica gel 60 PF_{254} (Merck) activated at 120 °C was the support for TLC and for column chromatography. The term "standard workup" means that the organic layer was washed with water, dried over Na_2SO_4, and filtered, and the solvent was removed at reduced pressure.

Methyl 2-Amino-4,6-*O*-benzylidene-2-*C*-cyano-2,3-dideoxy-α-D-*ribo*-hexopyranoside (3). To a solution of **1** (1.58 g, 6 mmol) in saturated methanolic ammonia solution (100 mL) was added trimethylsilyl cyanide (1.7 mL, 10.5 mmol) at 0 °C. The mixture was kept for 3 days at 50 °C. After evaporating the solvent, chromatography of the residue gave pure syrupy **3** (1.17 g, 68%): $[\alpha]^{22}_D$ +35° (*c* 1.7, chloroform); mass spectrum, *m/z* 290 ($M^{\bullet+}$); ^1H NMR δ 7.52 and 7.38 (m, 5 H, Ph), 5.62 (s, 1 H, H-7), 4.72 (s, 1 H, H-1), 4.30 (dd, 1 H, $J_{6a,6e}$ = 10 Hz, $J_{5,6e}$ = 5 Hz, H-6e), 3.92 (td, 1 H, $J_{3a,4} = J_{4,5}$ = 10 Hz, $J_{3e,4}$ = 5 Hz, H-4), 3.85 (t, 1 H, $J_{5,6a} = J_{6a,6e}$ = 10 Hz, H-6a), 3.78 (td, 1 H, $J_{4,5} = J_{5,6a}$ = 10 Hz, $J_{5,6e}$ = 5 Hz, H-5), 3.50 (s, 3 H, OMe), 2.40 (dd, $J_{3e,4}$ = 5 Hz, $J_{3a,3e}$ = 10 Hz, H-3e), 2.08 (t, $J_{3a,4} = J_{3a,3e}$ = 10 Hz, H-3a), 1.83 (br s, 2 H, NH_2); ^{13}C NMR δ 120.7 (CN), 102.2 (C-7), 100.1 (C-1), 75.5 (C-4), 69.2 (C-6), 64.5 (C-5), 55.8 (OMe), 54.6 (C-2), 37.9 (C-3). Anal. Calcd for $C_{15}H_{18}N_2O_4$: C, 62.07; H, 6.20; N, 9.65. Found: C, 62.00; H, 6.31; N, 9.89.

Methyl 4,6-*O*-Benzylidene-2-*C*-cyano-2,3-dideoxy-2-[(*p*-tolylsulfonyl)amino]-α-D-*ribo*-hexopyranoside (5). To a solution of **3** (1.17 g, 4 mmol) in dry pyridine (30 mL) was added at room temperature *p*-toluenesulfonyl chloride (2.5 g, 13.1 mmol), and the mixture was kept overnight. Standard workup was followed by chromatography (hexane–ethyl acetate, 6:4) to give pure **5** (1.75 g, 66%): mp 160 °C; $[\alpha]^{22}_D$ 40° (*c* 1.3, chloroform); mass spectrum, *m/z* 444 ($M^{\bullet+}$). Anal. Calcd for $C_{22}H_{24}N_2SO_6$: C, 59.46; H, 5.40; N, 6.30; S, 7.20. Found: C, 59.44; H, 5.50; N, 6.32; S, 7.30.

Methyl 2-*C*-(Aminomethyl)-4,6-*O*-benzylidene-2,3-dideoxy-2-[(*p*-tolylsulfonyl)amino]-α-D-*ribo*-hexopyranoside (7). To a solution of **5** (4.1 g, 9.2 mmol) in dioxane (300 mL) was added lithium aluminium hydride (2 g), and the mixture was stirred at room temperature for 1 h. Excess of reagent was decomposed with ethyl acetate and standard workup, followed by chromatography (chloroform–methanol, 9:1) gave pure **7** (2.4 g, 58%): mp 150 °C; $[\alpha]^{22}_D$ 51° (*c* 0.86, chloroform); mass spectrum, *m/z* 448 ($M^{\bullet+}$); ^1H NMR δ 7.90–7.10 (m, 9. H, 2 Ph), 5.50 (s, 1 H, C-7), 4.70 (s, 1 H, H-1), 3.80–3.05 (m, 4 H, H-4, H-5, H-6a, H-6e), 3.48 (s, 3 H, OMe), 3.05 (s, 2 H, CH_2NH_2), 2.95–2.70 (m, 2 H, H-3a, H-3e), 2.40 (s, 3 H, Ar Me). Anal. Calcd for $C_{22}H_{28}N_2SO_6$: C, 58.93; H, 6.25; N, 6.25; S, 7.14. Found: C, 59.00; H, 6.30; N, 6.17; S, 7.20.

Spiro[methyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-*ribo*-hexopyranoside-2,2′-*N*-(*p*-tolylsulfonyl)aziridine] (9). To a solution of **7** (465 mg, 1.12 mmol) in 90% acetic acid (20 mL) was added drop by drop a solution of sodium nitrite (500 mg, 7.2 mmol) in water (3 mL). After being stirred for 1 h, the mixture was poured into a saturated solution of sodium hydrocarbonate. Standard workup and recrystallization of the residue from ethyl ether gave **9** (428 mg, 89%): mp 178 °C; $[\alpha]^{22}_D$ 89° (*c* 0.7, chloroform); mass spectrum, *m/z* 431 ($M^{\bullet+}$); ^1H NMR δ 7.90–7.10 (m, 9 H, 2 Ph), 5.51 (s, 1 H, H-7), 4.35 (s, 1 H, H-1), 3.87 (td, 1 H, $J_{3a,4} = J_{4,5}$ = 10 Hz, $J_{3e,4}$ = 5 Hz, H-4), 3.77–3.67 (m, 3o H, H-5, H-6a, H-6e), 3.38 (s, 3 H, OMe), 2.62 and 2.49 (2 s, 2 H, CH_2NTs), 2.42 (s, 3 H, Ar Me), 2.17 (dd, 1 H, $J_{3a,3e}$ = 10 Hz, $J_{3e,4}$ = 5 Hz, H-3e), 1.77 (t, 1 H, $J_{3a,3e} = J_{3a,4}$ = 10 Hz, H-3a); ^{13}C NMR δ 101.9 (C-7), 101.1 (C-1), 77.5 (C-4), 69.4 (C-6), 64.6 (C-5), 55.3 (OMe), 49.6 (C-2), 37.7 (C-3), 30.7 (C-8), 21.7 (Ar Me). Anal. Calcd for $C_{22}H_{25}NSO_6$: C, 61.25; H, 5.80; N, 3.25; S, 7.42. Found: C, 61.18; H, 5.88; N, 3.31; S, 7.42.

Methyl 2-*C*-(Acetoxymethyl)-4,6-*O*-benzylidene-2,3-dideoxy-2-[(*p*-tolylsulfonyl)amino]-α-D-*ribo*-hexopyranoside (11). To a solution of **9** (100 mg, 0.23 mmol) in *N,N′*-dimethylformamide (3 mL) was added sodium acetate (200 mg, 2.43 mmol), and the mixture was heated to 130 °C for 6 h. After dilution with water and the usual workup, the residue was chromatographed (hexane–ethyl acetate, 3:2) to give **11** (91 mg, 80%): mp 162 °C; $[\alpha]^{22}_D$ 45° (*c* 4.9, chloroform); mass spectrum, *m/z* 491 ($M^{\bullet+}$); ^1H NMR δ 7.90–7.10 (m, 9 H, 2 Ph), 5.50 (s, 1 H, H-7), 5.08 (s, 1 H, NH), 4.62 (s, 1 H, H-1), 4.47 and 4.38 (2 d, 2 H, $J_{8,8'}$ = 11 Hz, CH_2OAc), 4.15 (dd, 1 H, $J_{6a,6e}$ = 10 Hz, $J_{5,6e}$ = 5 Hz, H-6e), 3.78 (td, 1 H, $J_{3a,4} = J_{4,5}$ = 10 Hz, $J_{3e,4}$ = 5 Hz, H-4), 3.70 (t, 1 H, $J_{6a,6e} = J_{5,6a}$ = 10 Hz, H-6a), 3.57 (td, 1 H, $J_{4,5} = J_{5,6a}$ = 10 Hz, $J_{5,6e}$ = 5 Hz, H-5), 3.45 (s, 3 H, OMe), 2.43 (s, 3 H, Ar Me), 2.40 (dd, 1 H, $J_{3a,3e}$ = 10 Hz, $J_{3e,4}$ = 5 Hz, H-3e), 1.92 (t, 1 H, $J_{3a,3e} = J_{3a,4}$ = 10 Hz, H-3a), 1.77 (s, 3 H, OAc); ^{13}C NMR δ 102.2 (C-7), 98.5 (C-1), 74.4 (C-4), 69.3 (C-6), 64.4 (C-5), 62.8 (CH_2OAc), 60.6 (C-2), 55.7 (OMe), 33.9 (C-3), 21.5 (OAc), 20.4 (Ar Me). Anal. Calcd for $C_{24}H_{29}NSO_8$: C, 60.28; H, 5.90; N, 2.85; S, 6.51. Found: C, 60.31; H, 5.94; N, 2.91; S, 6.47.

Methyl 4,6-*O*-Benzylidene-2,3-dideoxy-2-*C*-(hydroxymethyl)-2-[(*p*-tolylsulfonyl)amino]-α-D-*ribo*-hexopyranoside

(1) Yoshimura, J. *Adv. Carbohydr. Chem. Biochem.* **1984**, *42*, 69.
(2) Thang, T. T.; Winternitz, F.; Olesker, A.; Lagrange, A.; Lukacs, G. *J. Chem. Soc., Chem. Commun.* **1979**, 153.
(3) Thang, T. T.; Laborde, M.; Olesker, A.; Lukacs, G. *J. Chem. Soc., Chem. Commun.*, in press.

(13). To a solution of 11 (100 mg, 0.2 mmol) in dry methanol (20 mL) was added a catalytic amount of sodium methoxide, and the mixture was stirred at room temperature for 2 h. Standard workup gave syrupy 13 (80 mg, 91%): $[\alpha]^{22}_D$ 48° (c 0.32, chloroform); mass spectrum, m/z 449 ($M^{\bullet+}$); ^{1}H NMR δ 7.75–7.23 (m, 9 H, 2 Ph), 5.42 (s, 1 H, H-7), 5.2 (s, 1 H, NH), 4.3 (s, 1 H, H-1), 3.3 (s, 3 H, OMe), 2.41 (s, 3 H, Ar Me), 2.05 (dd, 1 H, $J_{3a,3e}$ = 10 Hz, $J_{3e,4}$ = 5 Hz, H-3e), 1.56 (t, H, $J_{3a,3e} = J_{3a,4}$ = 10 Hz, H-3a). Anal. Calcd for $C_{22}H_{27}NSO_7$: C, 58.80; H, 6.01; N, 3.11; S, 7.13. Found: C, 58.87; H, 5.99; N, 3.09; S, 7.18.

Methyl 4,6-*O*-Benzylidene-2,3-dideoxy-2-*C*-formyl-2-[(*p*-tolylsulfonyl)amino]-α-D-*ribo*-hexopyranoside (15). Molecular sieves (0.5 g, 4 Å) were stirred in dry dichloromethane (4 mL) for 10 min. Then pyridinium chlorochromate (190 mg, 0.87 mmol) was added, and the mixture was stirred for another 10 min. To this mixture was added 13 (100 mg, 0.29 mmol), and stirring was maintained for 90 min. After standard workup 15 (86 mg, 86%) was isolated: mp 175–176 °C; $[\alpha]^{22}_D$ 90° (c 0.3, chloroform); mass spectrum, m/z 447 ($M^{\bullet+}$); ^{1}H NMR (C_6D_6) δ 9.55 (s, 1 H, CHO), 7.60–7.10 (m, 9 H, 2 Ph), 5.15 (s, 1 H, H-7), 4.41 (s, 1 H, H-1), 3.95 (dd, 1 H, $J_{6a,6e}$ = 10 Hz, $J_{5,6a}$ = 5 Hz, H-6e), 3.73 (m, 1 H, H-5), 3.57 (td, 1 H, $J_{3a,4} = J_{4,5}$ = 10 Hz, $J_{3e,4}$ = 5 Hz, H-4), 3.35 (t, 1 H, $J_{6a,6e} = J_{5,6a}$ = 10 Hz, H-6a), 2.78 (s, 3 H, OMe), 2.48 (dd, 1 H, $J_{3a,3e}$ = 10 Hz, $J_{3e,4}$ = 5 Hz, H-3e), 1.83 (s, 3 H, Ar Me), 1.58 (t, 1 H, $J_{3a,3e} = J_{3a,4}$ = 10 Hz, H-3a); ^{13}C NMR δ 195.2 (CHO), 102.0 (C-7), 96.2 (C-1), 73.6 (C-4), 69.0 (C-6), 65.9 (C-2), 63.9 (C-5), 55.6 (OMe), 32.1 (C-3), 21.6 (Ar Me). Anal. Calcd for $C_{22}H_{25}NSO_7$: C, 59.06; H, 5.59; N, 3.13; S, 7.16. Found: C, 59.01; H, 5.62; N, 3.19; S, 7.09.

Methyl 2-Amino-4,6-*O*-benzylidene-2-*C*-cyano-2,3-dideoxy-β-D-*arabino*-hexopyranoside (4a) and Methyl 2-Amino-4,6-*O*-benzylidene-2-*C*-cyano-2,3-dideoxy-β-D-*ribo*-hexopyranoside (4b). To a solution of 2[4] (800 mg, 3.0 mmol) in saturated methanolic ammonia solution (50 mL) in a metal vessel was added trimethylsilyl cyanide (1.68 mL, 12.6 mmol) at 0 °C. The mixture was then cooled to −78 °C and ammonia was bubled for 35 minutes. The vessel was tightly closed and was shaken at room temperature for 5 days. After the solvent was evaporated, chromatography of the residue (0.8 g, hexane–ethyl acetate, 7:3) gave first **4a** (500 mg, 57%): mp 160–162 °C; $[\alpha]^{22}_D$ −29° (c 1.24, chloroform); mass spectrum, m/z 290 ($M^{\bullet+}$); ^{1}H NMR (80 MHz) δ 7.50–7.20 (m, 5 H, Ph), 5.48 (s, 1 H, H-7), 4.60 (s, 1 H, H-1), 4.28 (dd, 1 H, $J_{6a,6e}$ = 10 Hz, $J_{5,6e}$ = 5 Hz, H-6e), 4.13–3.85 (m, 1 H, H-4), 3.80 (t, 1 H, $J_{5,6a} = J_{6,6e}$ = 10 Hz, H-6a), 3.65–3.33 (m, 1 H, H-5), 3.60 (s, 3 H, OMe), 2.44 (dd, 1 H, $J_{3e,4}$ = 5 Hz, $J_{3a,3e}$ = 12 Hz, H-3e), 2.25 (t, 1 H, $J_{3a,3e} = J_{3a,4}$ = 12 Hz, H-3a), 1.90 (br s, 2 H, NH_2); ^{13}C NMR δ 121.1 (CN), 105.4 (C-1), 102.4 (C-7), 72.3 (C-4), 71.4 (C-6), 68.7 (C-5), 57.8 (OMe), 53.6 (C-2), 39.1 (C-3), and then **4b** (200 mg, 23%): mp 138–140 °C; $[\alpha]^{22}_D$ −72° (c 1.0, chloroform); mass spectrum, m/z 290 ($M^{\bullet+}$); ^{1}H NMR (80 MHz) δ 7.60–7.25 (m, 5 H, Ph), 5.59 (s, 1 H, H-7), 4.38 (dd, 1 H, $J_{6a,6e}$ = 10 Hz, $J_{5,6e}$ = 5 Hz, H-6e), 4.25 (s, 1 H, H-1), 4.13–3.77 (m, 1 H, H-4), 3.90 (t, 1 H, $J_{6a,6e} = J_{5,6a}$ = 10 Hz, H-6a), 3.73–3.30 (m, 1 H, H-5), 3.59 (s, 3 H, OMe), 2.38 (dd, 1 H, $J_{3a,4}$ = 5 Hz, $J_{3a,3e}$ = 12 Hz, H-3a); ^{13}C NMR δ 120.9 (CN), 105.6 (C-1), 102.1 (C-7), 74.9 (C-4), 71.6 (C-6), 68.8 (C-5), 57.6 (OMe), 55.0 (C-2), 39.1 (C-3). Anal. Calcd for $C_{15}H_{18}N_2O_4$ (**4a**): C, 62.07; H, 6.20; N, 9.65. Found: C, 62.08; H, 6.10; N, 9.81. $C_{15}H_{18}N_2O_4$ (**4b**): C, 62.07; H, 6.20; N, 9.65. Found: C, 62.01; H, 6.24; N, 9.68.

Methyl 4,6-*O*-Benzylidene-2-*C*-cyano-2,3-dideoxy-2-[(*p*-tolylsulfonyl)amino]-β-D-*arabino*-hexopyranoside (6). To an ice-cooled solution of **4a** (428 mg, 1.48 mmol) in dry pyridine (15 mL) was added *p*-toluenesulfonyl chloride (564 mg, 2.96 mmol), and the mixture was kept overnight at room temperature. Standard workup afforded 6 (460 mg, 70%): mp 245–247 °C dec; $[\alpha]^{22}_D$ −27.7° (c 1.36, chloroform); mass spectrum, m/z 444 ($M^{\bullet+}$); ^{1}H NMR (80 MHz) δ 7.80–7.19 (m, . H, 2 Ph), 5.34 (br s, 2 H, H-7 and NH), 4.60 (s, 1 H, H-1), 4.25 (dd, 1 H, $J_{6a,6e}$ = 10 Hz, $J_{5,6e}$ = 5 Hz, H-6e), 3.95–3.41 (m, 3 H, H-4, H-5 and H-6a), 3.56 (s, 3 H, OMe), 3.29 (dd, 1 H, $J_{3e,3a}$ = 11 Hz, $J_{3e,4}$ = 5 Hz, H-3e), 2.41 (s, 3 H, Ar Me), 1.96 (t, 1 H, $J_{3e,3a} = J_{3a,4}$ = 11 Hz, H-3a). Anal. Calcd for $C_{22}H_{24}N_2SO_6$: C, 59.46; H, 5.40; N, 6.30; S, 7.20. Found: C, 59.52; H, 5.47; N, 6.21; S, 7.14.

Methyl 2-*C*-(Aminomethyl)-4,6-*O*-benzylidene-2,3-dideoxy-2-[(*p*-tolylsulfonyl)amino]-β-D-*arabino*-hexopyranoside (8). To a solution of 6 (294 mg, 0.66 mmol) in dry tetrahydrofuran (20 mL) was added lithium aluminium hydride (300 mg), and the mixture was stirred at room temperature for 3 h under an argon atmosphere. Excess of the reagent was decomposed with ethyl acetate and then 1% sodium hydroxide solution. Standard workup gave crude 8 (260 mg, 87%), which was used without further purification.

Spiro[methyl 4,6-*O*-benzylidene-2,3-dideoxy-β-D-*arabino*-hexopyranoside-2,2′-*N*-(*p*-tolylsulfonyl)aziridine] (10). To an ice-cooled solution of 8 (200 mg, 0.45 mL) in 90% acetic acid (10 mL) was added a solution of sodium nitrite (246 mg) in water (2 mL). The mixture was stirred for 1 h in an ice bath and then poured into a saturated solution of sodium hydrocarbonate. Standard workup and chromatography (hexane–ethyl acetate, 7:3) gave pure 10 (161 mg, 84%): mp 148–150 °C; $[\alpha]^{22}_D$ −45.8° (c 0.74, chloroform); mass spectrum, m/z 431 ($M^{\bullet+}$); ^{1}H NMR (400 MHz) δ 7.9–7.23 (m, . H, 2 Ph), 5.63 (s, 1 H, H-7), 4.53 (s, 1 H, H-1), 4.37–4.22 (m, 2 H, H-4 and H-6e), 3.90 (t, 1 H, $J_{6e,6a} = J_{5,6a}$ = 10 Hz, H-6a), 3.65 (td, 1 H, $J_{5,6a} = J_{4,5}$ = 10 Hz, $J_{5,6e}$ = 5 Hz, H-5), 3.47 (s, 3 H, OMe)8 2.95 (dd, 1 H, $J_{3e,3a}$ = 14 Hz, $J_{3e,4}$ = 5 Hz, H-3e), 2.43 and 2.29 (2 s, 2 H, CH_2NTs), 2.43 (s, 3 H, Ar Me), 2.35 (dd, 1 H, $J_{3e,3a}$ = 14 Hz, $J_{3a,4}$ = 10 Hz, H-3a); ^{13}C NMR δ 101.8 (C-7), 101.7 (C-1), 75.9 (C-4), 71.5 (C-6), 69.3 (C-5), 57.2 (OMe), 49.6 (C-2), 35.8 (C-3), 31.8 (C-8), 21.7 (Ar Me). Anal. Calcd for $C_{22}H_{25}NSO_6$: C, 61.25; H, 5.80; N, 3.25; S, 7.42. Found: C, 61.30; H, 5.84; N, 3.32; S, 7.35.

Methyl 2-*C*-(Acetoxymethyl)-4,6-*O*-benzylidene-2,3-dideoxy-2-[(*p*-tolylsulfonyl)amino]-β-D-*arabino*-hexopyranoside (12). This compound (60%) was prepared from 10 as described for 11 from 9: mp 145–147 °C; $[\alpha]^{20}_D$ −75° (c 1.0, chloroform); mass spectrum, m/z 491 ($M^{\bullet+}$); ^{1}H NMR δ 7.90–7.20 (m, 9 H, 2 Ph), 5.20 (s, 1 H, NH), 4.90 (s, 1 H, H-7), 4.40 (s, 1 H, H-1), 4.40 and 4.00 (2 d, 2 H, $J_{8,8'}$ = 11 Hz, CH_2OAc), 4.20 (dd, $J_{6a,6e}$ = 10 Hz, $J_{5,6e}$ = 5 Hz, H-6e), 3.52 (t, 1 H, $J_{6a,6e} = J_{5,6a}$ = 10 Hz, H-6a), 3.5 (s, 3 H, OMe), 3.35 (td, 1 H, $J_{5,6a} = J_{4,5}$ = 10 Hz, $J_{5,6e}$ = 5 Hz, H-5), 3.05 (td, 1 H, $J_{3a,4} = J_{4,5}$ = 10 Hz, $J_{3e,4}$ = 5 Hz, H-4), 2.70 (dd, 1 H, $J_{3a,3e}$ = 20 Hz, $J_{3e,4}$ = 5 Hz, H-3e), 2.4 (s, 3 H, Ar Me), 2.0 (s, 3 H, OAc), 1.70 (t, 1 H, $J_{3a,3e} = J_{3a,4}$ = 20 Hz, H-3a). Anal. Calcd for $C_{24}H_{29}NSO_8$: C, 60.28; H, 5.90; N, 2.85; S, 6.51. Found: C, 60.20; H, 5.93; N, 2.91; S, 6.42.

Methyl 4,6-*O*-Benzylidene-2,3-dideoxy-2-*C*-(hydroxymethyl)-2-[(*p*-tolylsulfonyl)amino]-β-D-*arabino*-hexopyranoside (14). This compound (80%) was prepared from 12 as described for 13 from 11: mp 220–223 °C; $[\alpha]^{22}_D$ −65° (c 0.95, chloroform); mass spectrum, m/z 449 ($M^{\bullet+}$); ^{1}H NMR δ 7.90–7.10 (m, . H, 2 Ph), 5.80 (s, 1 H, NH), 4.90 (s, 1 H, H-7), 4.4 (s, 1 H, H-1), 4.20 (dd, 1 H, $J_{6a,6e}$ = 10 Hz, $J_{5,6e}$ = 5 Hz, H-6e), 3.80 and 3.60 (2 d, 2 H, $J_{8,8'}$ = 11 Hz, CH_2OH)), 3.57 (s, 1 H, OH), 3.50 (t, 1 H, $J_{6a,6e} = J_{5,6a}$ = 10 Hz, H-6a), 3.50 (s, 3 H, OMe), 3.35 (dt, 1 H, $J_{4,5} = J_{5,6a}$ = 10 Hz, $J_{5,6e}$ = 5 Hz, H-5), 3.05 (dt, 1 H, $J_{3a,4} = J_{4,5}$ = 10 Hz, $J_{3e,4}$ = 5 Hz, H-4), 2.70 (dd, 1 H, $J_{3a,3e}$ = 10 Hz, $J_{3e,4}$ = 5 Hz, H-3e), 2.40 (s, 3 H, Ar Me), 1.68 (t, 1 H, $J_{3a,3e} = J_{3a,4}$ = 10 Hz). Anal. Calcd for $C_{22}H_{27}NSO_7$: C, 58.80; H, 6.01; N, 3.11; S, 7.13. Found: C, 58.92; H, 5.98; N, 3.07; S, 7.17.

Methyl 4,6-Benzylidene-2,3-dideoxy-2-*C*-formyl-2-[(*p*-tolylsulfonyl)amino]-β-D-*arabino*-hexopyranoside (16). This compound (72%) was prepared from 14 as described for 15 from 13: syrup; $[\alpha]^{22}_D$ −72° (η = 1.0, chloroform); mass spectrum, m/z 447 ($M^{\bullet+}$); ^{1}H NMR δ 9.80 (s, 1 H, CHO), 7.90–7.20 (m, 9 H, 2 Ph), 5.80 (s, 1 H, NH), 4.90 (s, 1 H, H-7), 4.50 (s, 1 H, H-1), 4.30 (dd, 1 H, $J_{6a,6e}$ = 10 Hz, $J_{5,6a}$ = 5 Hz, H-6e), 3.55 (t, 1 H, $J_{6a,6e} = J_{5,6a}$ = 10 Hz, H-6a), 3.50 (s, 3 H, OMe), 3.45 (m, 1 H, H-5), 3.45 (s, 3 H, OMe), 2.95 (dt, 1 H, $J_{3a,4} = J_{4,5}$ = 10 Hz, $J_{3e,4}$ = 5 Hz, H-4), 2.50 (dd, 1 H, $J_{3a,3e}$ = 10 Hz, $J_{3e,4}$ = 5 Hz, H-3e), 2.40 (s, 3 H, Ar Me), 2.40 (t, 1 H, $J_{3a,3e} = J_{3a,4}$ = 10 Hz, H-3a); ^{13}C NMR δ 200.9 (CHO), 103.1 (C-7), 102.0 (C-1), 73.6 (C-4), 70.9 (C-5), 68.7 (C-6), 57.3 (OMe), 30.6 (C-3), 21.7 (Ar Me). Anal. Calcd for $C_{22}H_{25}NSO_7$: C, 59.06; H, 5.59; N, 3.13; S, 7.16. Found: C, 59.11; H, 5.49; N, 3.17; S, 7.22.

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