Tetrahedron Vol 49, No 4, pp 901-910, 1993
Printed in Great Britain

0040-4020/93 $6 00+ 00
© 1993 Pergamon Press Ltd

Stereocontrolled Synthesis of Aziridine-2-Lactones from D-Ribose and D-Lyxose

Laurent Dubois and Robert H. Dodd*

Institut de Chimie des Substances Naturelles, C N R S , 91198 Gif-sur-Yvette, France

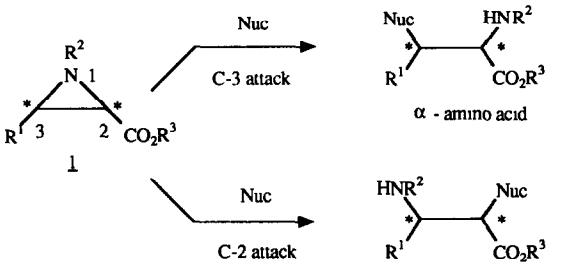
(*Received in Belgium* 29 *October* 1992)

Summary *The synthesis of (1S,4S,5R)-N-acetyl-4-methoxymethyl-3-oxa-6-azabicyclo[3 1 0]hexan-2-one* ***15a****, an optically pure, cyclic analogue of aziridine-2-carboxylates, is described starting from D-ribose Key steps include triphenylphosphine-promoted conversion of a 3-azido-2-tosyl-D-xylofuranoside (****10a****) to its corresponding 2,3-aziridine* ***12a****, selective cleavage of a 1-O-t-butyldimethylsilyl blocking group followed by TPAP oxidation of the anomeric hemiacetal group to the lactone* ***15a*** *The procedure is directly applicable to D-lyxose to give the enantiomerically pure (1R,4S,5S) isomer of* ***15a, 15b***

Résumé *Le present travail décrit la synthèse, à partir du D-ribose, du N-acétyl-méthoxyméthyl-4-oxa-3-aza-6-bicyclo[3 1 0]hexanone-2-(1S,4S,5R)* ***15a****, analogue cyclique optiquement pur, d'aziridine-2-carboxylates Les étapes-clé de cette synthèse concernent la transformation de l'azido-3-tosyl-2-D-xylofuranoside* ***10a*** *en l'aziridine-2,3 correspondante* ***12a*** *par action de la triphénylphosphine, la déprotection selective du groupement protecteur silylé suivie de l'oxydation par le TPAP de l'hémiacetal anomerique conduisant à la lactone* ***15a*** *Cette synthèse est directement applicable au D-lyxose pour conduire à l'isomère (1R,4S,5S) de* ***15a*** *enantiomériquement pur,* ***15b***

Stereochemically-defined aziridine-2-carboxylates **1** are proving to be useful intermediates for the synthesis of modified, optically active amino acids Either substituted α-amino acids (general case)[1-5] or β-amino acids[2,3] may be prepared by nucleophilic attack of the aziridine ring at C-3 or C-2, respectively (scheme 1) Ring-opening is promoted by Lewis acids and the presence of an electron-withdrawing group on the nitrogen atom (e g **1**, R^2 = acetyl). The large number of nucleophiles which have been employed for this type of reaction (alcohols[1], Wittig reagents[2], organocuprates[3], halides[6], amines[7], thiols[8], phosphites[9] and malonates[10]) makes accessible a great variety of optically pure, substituted amino acids

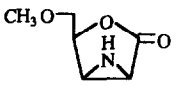
Scheme 1



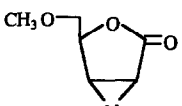
(R^2 electron-withdrawing group)

For this purpose, the stereospecific synthesis of the aziridine-2-carboxylate precursors **1** is necessary This has so far been achieved by only a limited number of methods (starting from an α-amino acid[11] , *via* a prior Sharpless epoxidation of a double bond[12a] , by addition of phthalimidonitrene to

α,β-unsaturated esters[12b]) However, the use of readily-available carbohydrates as a source of chirality for the preparation of such optically active aziridine-2-carboxylates has remained unexploited. In this connection, we wished to investigate the synthesis and reactivity of derivatives of 2,3-dideoxy-2,3-aziridinolyxono-(or ribono-)lactone **2** (or **3**) as carbohydrate-derived, stereochemically-defined cyclic analogues of aziridine-2-carboxylates **1**. The anecdotal preparation of a 5-amino-5-deoxy analogue of **2** has been reported by Kusumoto and co-workers[13] in their synthetic route to streptolidine. More recently, the N-acetyl-5-O-acetyl derivative of **2** was prepared *via* an intramolecular nitrene addition to the double bond of a 2-penten-4-olide.[14] However, neither of these procedures allows access to the D-ribonolactones of type **3**. Since we wished to synthesize both D- and L-amino acids starting from easily available D-sugars, our synthetic strategy had to be applicable to the preparation of both **2** and **3**. We report herein a practical synthesis of aziridine-2-lactones of types **2** and **3** starting from D-ribose and D-lyxose, respectively.



2



3

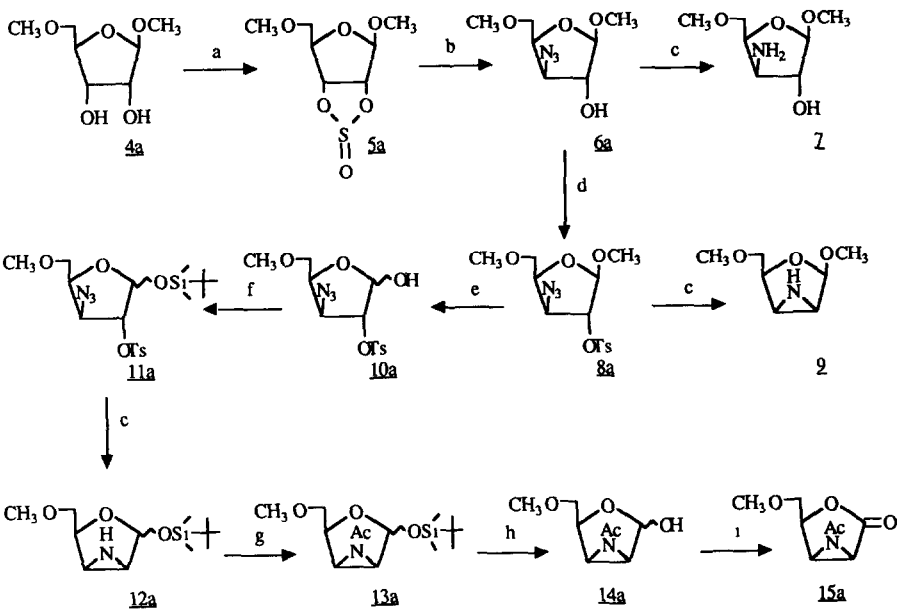
Because of the well-documented epimerization of C-2 substituents on sugar lactones,[14,15] it seemed essential to first construct the 2,3-aziridine starting from an appropriate glycoside, reserving for the final steps both deprotection and oxidation of the anomeric hydroxyl group to the lactone. Gero and co-workers[16] have shown that 2,3-aziridinolyxofuranosides may be obtained by selective displacement of the 3-O-tosyl group of the corresponding 2,3-di-O-tosyl derivative with sodium azide followed by intramolecular cyclization to the aziridine after reduction of the azide to an amine. A more efficient method of introducing an azide group at the C-3 position of a furanoside makes use of 2,3-cyclic sulfite intermediates.[17] This methodology was adopted for our synthetic sequence to **2** and **3**. Thus, as a model system, the simplest, protected furanoside available, methyl 5-O-methyl-β-D-ribofuranoside **4a**,[18] (Scheme 2) was treated with thionyl chloride and triethylamine at 0°C in tetrahydrofuran to give the stable 2,3-cyclic sulfite intermediate **5a** as a 1:1 mixture of the *exo* and *endo* isomers (due to asymmetry at the sulfur atom), as estimated by ^{1}H-NMR. Treatment of **5a** with sodium azide in N,N-dimethylformamide at reflux temperature gave exclusively the C-3 azido derivative **6a**. The *trans* arrangement of H-1 and H-2 in **6a**, indicative of substitution at C-3, was confirmed by its ^{1}H-NMR spectrum which showed a sharp singlet for the anomeric proton. This high regioselectivity of opening of cyclic sulfites by azide anion has been previously observed in other carbohydrate derivatives.[17]

It was initially hoped that a Staudinger-type reduction of the azide group of **6a** would directly yield the desired 2,3-aziridine (e.g. **9**). This was based on literature precedent in which both cyclic[19] and acyclic[19a,20] vicinal azido-alcohols have been shown to give aziridines upon treatment with tertiary phosphines. However, when compound **6a** was treated with triphenylphosphine in tetrahydrofuran, only the 3-deoxy-3-amino xylofuranoside **7** could be isolated after work-up. Presumably, the *trans* arrangement of the 2,3 substituents prevents the hydroxyl group from reacting intramolecularly with the initially formed phosphinimine at C-3[19b,20a]. This result is in contrast with non-carbohydrate systems in

which a *trans* azido-alcohol has in fact been shown to give an aziridine under the same conditions [19a]

In the pyranose series, Pinter[21] has shown that *trans* azido-alcohols can be converted to aziridines if the hydroxyl group is first tosylated and the product treated sequentially with triphenylphosphine and aqueous base With this in mind, compound **6a** was transformed into its 2-O-tosyl derivative **8a** The latter was then treated successively with triphenylphosphine and aqueous sodium hydroxide, affording aziridine **9** in 58% yield The ^{1}H-NMR data of **9** was consistent with the assigned structure, notably with regard to the characteristic high-field chemical shifts of H-2 and H-3 (centered at 2 7 ppm) This represents the first example of application of the Staudinger reaction to the preparation of aziridines in the furanoside series

Scheme 2



a) $SOCl_2$, NEt_3, THF, 0°C, b) NaN_3, DMF, 155°C, c) triphenylphosphine, THF, 2h then 2N NaOH, 80°C d) TosCl, pyridine, e) 4N HCl, dioxane, 100°C, f) $(CH_3)_3C(CH_3)_2SiOSO_2CF_3$, lutidine, CH_2Cl_2, g) Ac_2O, pyridine ,0°C, h) TBAF, THF, 0 to 25°C, i) TPAP, NMO, CH_3CN, Molecular sieves, r t

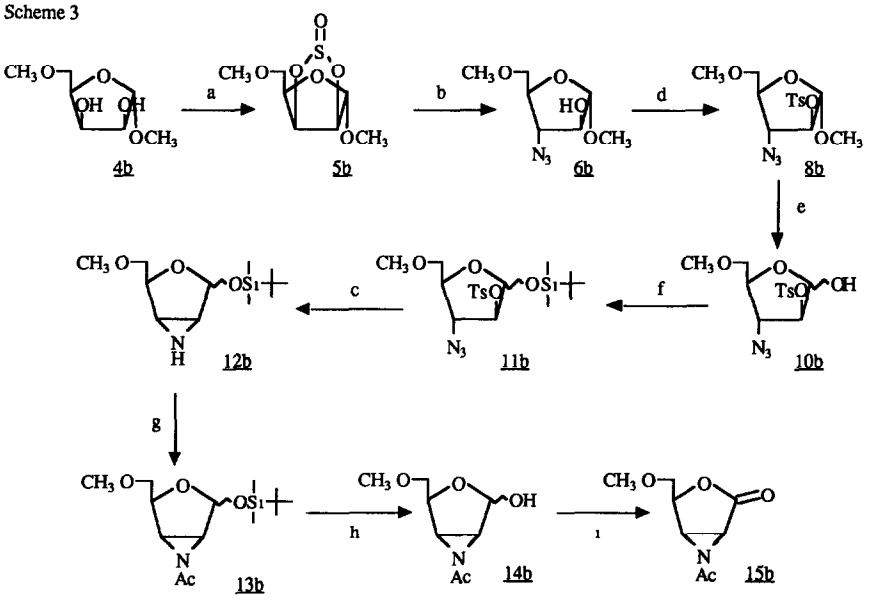
Because hydrolysis of the anomeric methoxy group of **9** to the free hydroxyl (a necessary step before oxidation to the desired lactone) could not be expected to leave the aziridine functionality intact,[22] the possibility of introducing a more labile trialkylsilyl ether linkage at the anomeric position of the aziridine precursor **8a** was investigated Thus, the xylofuranose **10a** was first prepared in 80% yield by treatment of **8a** with 4N hydrochloric acid in dioxane The ^{1}H-NMR spectrum of **10a** showed a 2 3 mixture of the α and β anomers, respectively However, loss of optical purity at this position was not critical in view of the anticipated oxidation to a lactone function The free hydroxyl group of **10a** was then protected with a t-butyldimethylsilyl group by reaction with t-butyldimethylsilyl triflate,[23] yielding **11a** Using the same conditions as those utilized for the preparation of aziridine **9** from **8a** (triphenylphosphine followed by aqueous sodium hydroxide), azide **11a** was transformed into the

aziridine silyl ether derivative **12a** in 65% yield. The structure of **12a** was corroborated by its ^{1}H-NMR spectrum which showed H-2 and H-3 as multiplets at 2 56 ppm (upfield from resonances at 4 55 and 4.35 ppm, respectively, in the precursor **11a**)

The free amine function of **12a** was then protected as its N-acetate **13a** using acetic anhydride in pyridine, and this compound underwent clean desilylation in the presence of tetra-n-butylammonium fluoride in tetrahydrofuran, affording the aziridinolyxofuranose **14a** in good yield Although fluoride anion has been shown to open aziridine rings,[24] no such reaction was observed in the case of **13a**. Finally, oxidation of the free hydroxyl group of **14a** was achieved in high yield (88%) using catalytic tetra-n-propylammonium perruthenate (TPAP) in the presence of N-methylmorpholine N-oxide,[26] giving the desired 2,3-aziridinolyxonolactone **15a**. The ^{1}H-NMR spectrum of **15a** showed a downfield shift for H-2 and H-3 (3 65 and 3.75 ppm respectively, compared to 3 38 ppm for these protons in precursor **14a**), while the ^{13}C-NMR showed the required two carbonyl carbons at 168 8 and 179.5 ppm The two non-equivalent carbonyl functions were also evident from the infrared spectrum of **15a** which showed absorptions at 1714 and 1792 cm^{-1} These spectral data were comparable to those of the 5-O-acetyl analogue of **15a** prepared by Dreiding.[14]

Application of this reaction scheme to methyl 5-O-methyl-α-D-lyxofuranoside **4b**[25] (Scheme 3) gave the aziridinoribonolactone analogue **15b** in a straightforward fashion Only minor differences were observed between the reactivities of the *lyxo* and *ribo* series of molecules A notable exception, however, was the opening of the sulfite intermediate **5b** with sodium azide which proceeded much more

Scheme 3



Conditions see Scheme 2

easily than in the case of the *ribo* derivative **5a** (1 5 h instead of 48 h reflux) This result can be attributed to the fact that the C-4 substituent in **5b** presents less steric hindrance to C-3 attack than in **5a** This geometrical difference, however, has no influence on regioselectivity of attack since for both **5a** and **5b**, only C-3 substitution by azide was observed. It can thus be concluded that this high regioselectivity of nucleophilic substitution on cyclic sulfites is governed by electronic rather than steric factors

The synthetic sequence here described now makes available optically pure cyclic aziridine-2-carboxylates **15a** and **15b** from D-ribose and D-lyxose, respectively This methodology can obviously be applied to starting materials having protecting groups other than methyl at C-5 The reactivity of aziridines **15a** and **15b** towards nucleophiles and their conversion into novel amino acid analogues are currently under investigation.

EXPERIMENTAL

General methods.
Melting points were determined on a Buchi apparatus and are uncorrected. IR spectra of samples were obtained either as KBr pellets (for solids) or as films (for oils) with a Nicolet 205 FT-IR spectrometer ^{1}H-NMR and ^{13}C-NMR spectra were determined on a Bruker WP 200 MHz instrument. Chemical shifts are given as δ values with reference to Me_4Si as internal standard Electron impact mass spectra were done on an AEI MS-50 spectrometer High-resolution mass spectra were obtained using a Kratos MS-80 spectrometer Optical rotations were determined with a Perkin-Elmer 241 polarimeter Thin-layer chromatography was performed on Merck silica gel 60 plates with fluorescent indicator The plates were visualized with UV light (254 nm) and with 3.5% solution of phosphomolybdic acid in ethanol. All column chromatography was conducted on Merck 60 silica gel (230-400 mesh) at medium pressure (200 mbar) Elemental analyses were performed at the ICSN,CNRS, Gif-sur-Yvette, France

Methyl 5-O-methyl-2,3-O-sulfinyl-β-D-ribofuranoside (5a).- To a solution of methyl 5-O-methyl-β-D-ribofuranoside (**4a** , 13.3 g, 75 mmol) in dry tetrahydrofuran (200 mL) held at 0 °C under a nitrogen atmosphere was added triethylamine (32.2 mL, 0 3 mol) followed by the dropwise addition of thionyl chloride (19 mL, 225 mmol) The solution was stirred for 3 h at 0 °C, chloroform (50 mL) was added and the mixture was washed with water (3 x 100 mL) The organic phase was dried (Na_2SO_4) and concentrated under reduced pressure at a bath temperature not exceeding 35 °C The oily residue was purified by column chromatography (ethyl acetate-heptane, 1 2), affording a mixture of the *endo* and *exo* isomers **5a** (14 g, 83%) as colorless needles, $[\alpha]_D^{20}$ - 49° (c 6 8, $CHCl_3$) ; ^{1}H-NMR ($CDCl_3$) · δ 3 40 (m, 6H, CH_2OCH_3 and OCH_3), 3 50 (m, 2H, $J_{4,5}$ 8 0 Hz, H-5), 4 40 (t, 0.5 H, H-4 *endo* (or *exo*)), 4 70 (m, 0 5 H, $J_{3,4}$ 2 0 Hz, H-4 *exo* (or *endo*)), 5 03 (m, 1H, $J_{2,3}$ 6 0 Hz, H-3), 5 30 (m, 1 5 H, H-1 and H-2 *endo* (or *exo*)), 5 44 (d, 0 5 H, H-2 *exo* (or *endo*)) Anal Calcd for $C_7H_{12}O_6S$ 1/50 C_7H_{16} C, 37 91 , H, 5 45 ; S, 14 15 Found · C, 37 97 , H, 5 50 ; S, 14 21

Methyl 5-O-methyl-2,3-O-sulfinyl-α-D-lyxofuranoside (5b). - In the same manner as above, methyl 5-O-methyl-α-D-lyxofuranoside gave the sulfite **5b** (98%), $[\alpha]_D^{20}$ + 46 7° (c 2 28, $CHCl_3$) , ^{1}H-NMR ($CDCl_3$) δ 3 38 (s, 1 5H, *endo* (or *exo*) OCH_3), 3 40 (s, 1 5H, exo (or *endo*) OCH_3), 3 42 (s, 3H, OCH_3), 3 70 (m, 2H, $J_{5a,5b}$ 6 8 Hz, $J_{4,5}$ 5 6 Hz, H-5), 4 35 (m, 1H, $J_{3,4}$ 3 0 Hz, H-4), 5 05 (m, 1H, H-3), 5 30 (m,2H, H-1 and H-2) Anal Calcd for $C_7H_{12}O_6S$ C, 37 50 , H, 5 35 , S, 14 28 Found C, 37 52 , H, 5 32, S, 14 08

Methyl 3-azido-3-deoxy-5-methyl-β-D-xylofuranoside (6a) - To a vigorously stirred solution of sulfite **5a** (21 7 g, 0 103 mol) in anhydrous N,N-dimethylformamide (400 mL) was slowly added powdered sodium azide (20 1 g, 0 309 mol) and the mixture was refluxed for 48 h The solvent was then removed under reduced pressure and the residue was partitioned between ethyl acetate (200 mL) and water (200 mL) The organic phase was separated, dried (Na_2SO_4) and concentrated under reduced pressure Column chromatography of the oily residue (ethyl acetate-heptane 1 1) gave **6a** (11 5g, 55%)

as a pale yellow syrup, $[\alpha]_D^{20}$ - 66° (c 7.6, $CHCl_3$), ^{1}H-NMR ($CDCl_3$) δ 3 40 (s, 3H, OCH_3), 3.44 (s, 3H, OCH_3), 3.50 (br s, 1H, D_2O-exchangeable, OH), 3.65 (m, 2H, $J_{4,5}$ 6 0 Hz, H-5), 4 10 (dd, 1H, $J_{3,4}$ 6.0 Hz, H-3), 4.25 (s, 1H, H-2), 4.50 (q, 1H, H-4), 4.85 (s, 1H, H-1), ^{13}C-NMR ($CDCl_3$) : δ 55.7 ($CHO\underline{C}H_3$), 59 3 ($CH_2O\underline{C}H_3$), 66.8 (C-3), 72.1 (C-5), 79.3 (C-4 (or C-2)), 79.7 (C-2 (or C-4)), 109 3 (C-1). Anal. Calcd for $C_7H_{13}N_3O_4$: C, 41 37, H, 6 40 , N, 20 68 Found . C, 41.51 , H, 6 33 , N, 20 98

Methyl 3-azido-3-deoxy-5-O-methyl-α-D-arabinofuranoside (6b).- In the same manner as above (except that reflux time was decreased to 1.5 h), sulfite **5b** gave the azide **6b** (65%), $[\alpha]_D^{20}$ + 112 7 (c 0 66, $CHCl_3$) ; IR · ν 3444 (OH), 2114 cm^{-1} (N_3) ; ^{1}H-NMR ($CDCl_3$) δ 3 35 (s, 3H, OCH_3), 3 40 (br s, 1H, OH), 3.45 (s, 3H, OCH_3), 3 60 (oct, 2H, $J_{5a,5b}$ 10.0 Hz, $J_{4,5}$ 2.4 Hz, H-5), 3.76 (d, 1H, $J_{3,4}$ 3.0 Hz, H-3), 4.08 (s, 1H, H-2), 4.15 (m, 1H, H-4), 4 85 (s, 1H, H-1) ; ^{13}C-NMR ($CDCl_3$) δ 55 1 ($CHO\underline{C}H_3$), 59.5 ($CH_2O\underline{C}H_3$), 67 1 (C-3), 72.2 (C-5), 79 4 (C-4), 81 7 (C-2), 109.6 (C-1) Anal Calcd for $C_7H_{13}N_3O_4$· C, 41.37 , H, 6 40 ; N, 20.68 Found : C, 41 47 , H, 6.37 ; N, 20.73

Methyl 3-amino-3-deoxy-5-O-methyl-β-D-xylofuranoside (7) - A solution of the azido-alcohol **6a** (235 mg, 1 15 mmol) and triphenylphosphine (331 mg, 1.26 mmol) in tetrahydrofuran (15 mL) was stirred for 3 h at room temperature. After addition of aqueous 2N NaOH (5 mL, 10 mmol) to the reaction mixture, the solution was refluxed for 30 min. The solution was cooled and ethyl acetate (50 mL) followed by saturated aqueous NaCl solution (20 mL) were added The organic phase was then extracted, dried (Na_2SO_4) and the solvents were removed *in vacuo* The residue was purified by column chromatography (ethyl acetate-methanol 9:1), yielding compound **7** (155 mg, 76%) as a pale yellow oil , ^{1}H-NMR ($CDCl_3$) : δ 2 78 (br s, 3H, exchangeable with D_2O, NH_2 and OH), 3 30 (d, 1H, $J_{3,4}$ 6.0 Hz, H-3), 3 38 (s, 3H, OCH_3), 3 41 (s, 3H, OCH_3), 3.60 (m, 2H, $J_{4,5}$ 6.0 Hz, H-5), 4 05 (s, 1H, H-2), 4.40 (q, 1H, H-4), 4 78 (s, 1H, H-1). Anal. Calcd for $C_7H_{15}NO_4$. 1/3 CH_3OH · C, 46 87 ; H, 8 70 , N, 7.46 Found: C, 46.95 ; H, 8 20 , N, 7.10

Methyl 3-azido-3-deoxy-5-O-methyl-2-O-p-toluenesulfonyl-β-D-xylofuranoside (8a).- To a vigorously stirring solution of the azido alcohol **6a** (10.4 g, 51 mmol) in pyridine (400 mL) was added p-toluenesulfonyl chloride (29 4 g, 155 mmol). The reaction mixture was stirred for 48 h at room temperature after which the solvent was removed under reduced pressure. The residue was partitioned between ethyl acetate (200 mL) and water (200 mL). The organic phase was extracted, dried (Na_2SO_4) and evaporated *in vacuo* Chromatography of the residue (heptane-ethyl acetate, 4:1) gave **8a** (16.9 g, 93%) as a pale yellow syrup, $[\alpha]_D^{20}$ - 23 6° (c 0.77, $CHCl_3$) ; ^{1}H-NMR ($CDCl_3$) . δ 2 48 (s, 3H, tosyl CH_3), 3.28 (s, 3H, OCH_3), 3.38 (s, 3H, OCH_3), 3 55 (d, 2H, $J_{4,5}$ 6 0 Hz, H-5), 4 32 (dd, 1H, $J_{2,3}$ < 1 0 Hz, $J_{3,4}$ 6.0 Hz, H-3), 4 42 (q, 1H, H-4), 4.72 (d, 1H, H-2), 4 82 (s, 1H, H-1), 7 40 (d, 2H, H_{arom}), 7 85 (d, 2H, H_{arom}) ; ^{13}C-NMR ($CDCl_3$) δ 21 7 (tosyl $\underline{C}H_3$), 55 8 ($CHO\underline{C}H_3$), 59 2 ($CH_2O\underline{C}H_3$), 64.9 (C-3), 71.5 (C-5), 79 4 (C-4), 86.1 (C-2), 106 7 (C-1), 128.1 ($\underline{C}H_{arom}$), 130.2 ($\underline{C}H_{arom}$), 133 2 (C_{arom}), 145 7 (C_{arom}) Mass spectrum m/z 329 (M^+ - N_2). Anal Calcd for $C_{14}H_{19}N_3O_6S$. 1/20 C_7H_{16} C, 47 56 ; H, 5 46 ; S, 8 84 Found · C, 47 86 , H, 5 12 , S, 9 23

Methyl 3-azido-3-deoxy-5-O-methyl-2-O-p-toluenesulfonyl-α-D-arabinofuranoside (8b).- In the same manner as above (except that column chromatography was performed using dichloromethane-methanol (99 1)), azido alcohol **6b** gave the tosylate **8b** (98%), $[\alpha]_D^{20}$ + 68 6° (c 0.88, $CHCl_3$) ; IR ν 2112 (N_3), 1375 cm^{-1} (SO_2) , ^{1}H-NMR ($CDCl_3$) δ 2 50 (s, 3H, tosyl CH_3), 3 35 (s, 3H, OCH_3), 3 37 (s, 3H, OCH_3), 3.58 (d, 2H, $J_{4,5}$ 4 3 Hz, H-5), 3 90 (m, 2H, $J_{2,3}$ 2.5 Hz, H-3 and H-4), 4 65 (d, 1H, H-2), 4 90 (s, 1H, H-1), 7 40 (d, 2H, H_{arom}), 7 85 (d, 2H, H_{arom}) , ^{13}C-NMR ($CDCl_3$) δ 21 7 (tosyl $\underline{C}H_3$), 55 1 ($CHO\underline{C}H_3$), 59 6 ($CH_2O\underline{C}H_3$), 65 7 (C-3), 71 2 (C-5), 80 0 (C-4), 87.6 (C-2), 106 1 (C-1), 128 2 (CH_{arom}), 130 1 (CH_{arom}), 132 6 (C_{arom}), 145 7 (C_{arom}). Anal Calcd for $C_{14}H_{19}N_3O_6S$ 1/2 CH_3OH . C, 46 64 H, 5 63 , N, 11 26. Found C, 46 72 , H, 5 29 , N, 10 93

Methyl 2,3-dideoxy-2,3-aziridino-5-O-methyl-β-D-lyxofuranoside (9).- Following the procedure used for the preparation of **7**, azido-tosylate **8a** gave aziridine **9** (60%), $[\alpha]_D^{20}$ -62° (c 1 0, $CHCl_3$) ; ^{1}H-NMR ($CDCl_3$) δ 1 70 (br s, 1H, exchangeable with D_2O, NH), 2 64 (br s, 2H, H-2 and H-3), 3 40 (s, 3H, OCH_3), 3 45 (s, 3H, OCH_3), 3 57 (dd, 2H, $J_{4,5}$ 3 0 Hz, $J_{5a,5b}$ 5 7 Hz, H-5), 4 10 (t, 1H, H-4), 5 04 (s, 1H, H-1) Anal Calcd for $C_7H_{15}NO_4$ 1/3 H_2O · C, 50 91 , H, 8 28 , N, 8 48 Found C, 50.95 , H, 7 99 , N, 8 08

3-Azido-3-deoxy-5-O-methyl-2-O-p-toluenesulfonyl-α,β-D-xylofuranose (10a).- A solution of the azido-tosylate **8a** (16.9 g, 47 3 mmol) in dioxane (300 mL) and aqueous 4N hydrochloric acid (200 mL) was refluxed for 16 h The reaction mixture was cooled to room temperature, ethyl acetate (300 mL) was added and the mixture was washed with saturated aqueous NaCl solution (200 mL) The organic

phase was dried (Na_2SO_4), the solvents were removed under reduced pressure and the residue was chromatographed (heptane-ethyl acetate, 2·1), yielding pure **10a** (14 1 g, 87%) as a syrup, $[\alpha]_D^{20}$ - 8.9 (c 6 5, $CHCl_3$) ; ^{1}H-NMR ($CDCl_3$) : δ 2.45 (s, 3H, tosyl CH_3), 3 33 (s, 1 8 H, β-OCH_3), 3 35 (s, 1.2 H, α-OCH_3), 3 51 (m, 2H, $J_{5\alpha,5b}$ 5.5 Hz, $J_{4,5}$ 3.5 Hz, H-5α and H-5β), 4 20 (br s, 1H, OH), 4.23 (dd, 1H, $J_{2,3\beta}$ 5 0 Hz, $J_{2,3\alpha}$ 4.0 Hz, H-3α and H-3β), 4.40 (m, 1H, $J_{4,5}$ 3 5 Hz, H-4α and H-4β), 4 75 (q, 0.4 H, $J_{1,2\alpha}$ 4 0 Hz, H-2α), 4 80 (dd, 0.6 H, $J_{1,2\beta}$ 1 0 Hz, $J_{2,3\beta}$ 5 0 Hz, H-2β), 5 13 (d, 0 6 H, H-1β), 5 43 (d, 0 4 H, H-1α), 7.40 (d, 2H, CH_{arom}), 7.85 (d, 2H, CH_{arom}) ; ^{13}C-NMR ($CDCl_3$) δ 21.7 (tosyl CH_3), 59.3 (CH_2OCH_3), 63 4 (C-3α (or β)), 65 2 (C-3β (or α)), 70 9 (C-5), 75 2 (C-4α (or β)), 79.1 (C-4β (or α)), 81 6 (C-2α (or β)), 87 9 (C-2β (or α)), 94 1 (C-1α (or β)), 100 9 (C-1β (or α)), 128 1 (CH_{arom}), 130 2 (CH_{arom}), 133.2 (C_{arom}), 145 7 (C_{arom}) Anal Calcd for $C_{13}H_{17}N_3O_6S$ C, 45 48 ; H, 4 95 , N, 12 24 Found C, 45.20 ; H, 4 96 ; N, 11 98

3-Azido-3-deoxy-5-O-methyl-2-O-p-toluenesulfonyl-α,β-D-arabinofuranose (10b).- In the same manner as above (except that reflux time was prolonged to 48 h and that chromatography was effected using heptane-ethyl acetate 4 1 followed by heptane-ethyl acetate 1:1), azido-tosylate **8b** gave **10b** (60%), $[\alpha]_D^{20}$ + 21 3° (c 2.4, $CHCl_3$) ; IR ν 3425 (OH), 2111 (N_3), 1371 cm^{-1} (SO_2) , ^{1}H-NMR ($CDCl_3$) δ 2 45 (s, 3H, tosyl CH_3), 3.40 (s, 2H, α-CH_2OCH_3), 3.42 (s, 1H, β-CH_2OCH_3), 3 60 (m, 3H, $J_{4,5}$ 6.0 Hz, H-5 and OH), 3 90 (m, 1H, $J_{3,4}$ 4 8 Hz, $J_{2,3}$ 2.0 Hz, H-3α and H-3β), 4 20 (m, 1H, $J_{4,5}$ 6 0 Hz, H-4α and H-4β), 4.60 (dd, 0 33 H, $J_{1,2\beta}$ 3 7 Hz, $J_{2,3}$ 2.7 Hz, H-2β), 4 65 (d, 0 66 H, H-2α), 5 20 (d, 0 33 H, H-1β), 5.40 (s, 0 66 H, H-1α), 7 40 (d, 2H, CH_{arom}), 7 85 (d, 2H, CH_{arom}) , ^{13}C-NMR ($CDCl_3$) · δ 21 8 (tosyl CH_3), 59 5 (α- (or β)-CH_2OCH_3), 61.8 (β- (or α-)CH_2OCH_3), 62 5 (C-3α (or β)), 65 7 (C-3β (or α)), 71 3 (C-5α (or β)), 72 3 (C-5β (or α)), 79 1 (C-4α (or β)), 80 4 (C-4β (or α)), 82.4 (C-2α (or β)), 87.9 (C-2β (or α)), 94.5 (C-1α (or β)), 100 2 (C-1β (or α)), 128 2 (CH_{arom}), 130 1 (CH_{arom}), 132 8 (C_{arom}), 145 8 (C_{arom}) Anal Calcd for $C_{13}H_{17}N_3O_6S$ · C, 45 48 ; H, 4 95 , S, 9.32 Found C, 45 61, H, 5 18 ; S, 9 20

tert-Butyldimethylsilyl 3-azido-3-deoxy-5-O-methyl-2-O-p-toluenesulfonyl-α,β-D-xylofuranoside (11a) - To a solution of the azido-tosylate derivative **10a** (13 g, 38 mmol) and 2,4-lutidine (6.3 mL, 88 mmol) in anhydrous dichloromethane (200 mL) held at 0° C under a nitrogen atmosphere was added tert-butyldimethylsilyl trifluoromethanesulfonate (13 mL, 68 mmol) The reaction mixture was stirred for 2 h at 0° C after which ice-cold saturated aqueous $NaHCO_3$ (100 mL) was added. The mixture was diluted with dichloromethane (3 mL), the organic phase was separated, washed with water (2 x 50 mL) and dried (Na_2SO_4) The residue obtained after evaporation of the solvents *in vacuo* was purified by column chromatography (heptane-ethyl acetate 4 1), yielding **11a** as a colorless syrup (14 9g, 86%), $[\alpha]_D^{20}$ - 8 3° (c 0 6, $CHCl_3$) ; ^{1}H-NMR ($CDCl_3$) δ 0 18 (d, 6H, α- and β-$Si(CH_3)_2$), 0 85 (d, 9H, α- and β-$C(CH_3)_3$), 2 50 (s, 3H, tosyl CH_3), 3 35 (d, 3H, α- and β-CH_2OCH_3), 3 60 (m, 2H, $J_{4,5\alpha}$ 8.4 Hz, $J_{4,5\beta}$ 5 0 Hz, H-5α and H-5β), 4 05 (m, 0 6 H, H-3α (or β)), 4 35 (m, 1.4 H, H-3β (or α) and H-4), 4 55 (m, 0 4 H, $J_{1,2\alpha}$ 5.0 Hz, H-2α), 4 63 (s, 0.6 H, H-2β), 5 20 (s, 0 6 H, H-1β), 5.34 (d, 0 4 H, H-1α), 7 40 (d, 2H, CH_{arom}), 7 85 (d, 2H, CH_{arom}) , ^{13}C-NMR ($CDCl_3$) δ - 4 1 (Si-CH_3), - 4.4 (Si-CH_3), 18 0 ($C(CH_3)_3Si$), 21 7 (tosyl CH_3), 25 6 ($C(CH_3)_3Si$), 59.3 (CH_2OCH_3), 63.0 (C-3α (orβ)), 64.8 (C-3β (or α)), 71.2 (C-5α (or β)), 71 6 (C-5β (or α)), 74 7 (C-4α (or β)), 79 5 (C-4β (or α)), 82.1 (C-2α (or β)), 87 6 (C-2β (or α)), 94 2 (C-1α (or β)), 100 9 (C-1β (or α)), 128 1 (CH_{arom}), 130.3 (CH_{arom}), 133.2 (C_{arom}), 145 7 (C_{arom}) Mass spectrum m/z 457 (M^+) Anal Calcd for $C_{19}H_{31}N_3O_6SSi$ C, 49 89 , H, 6 78 ; N, 9 19 Found · C, 49 86, H, 6 69 , N, 9 01

tert-Butyldimethylsilyl 3-azido-3-deoxy-5-O-methyl-2-O-p-toluenesulfonyl-α,β-D-arabino-furanoside (11b) - In the same manner as above (except that the reaction time was prolonged to 3 h), azido-tosylate **10b** gave **11b** (76%), ^{1}H-NMR ($CDCl_3$) δ 0 20 (m, 6H, α- and β-$Si(CH_3)_2$), 1 10 (d, 9H, α- and β-$C(CH_3)_3$), 2 60 (s, 3H, tosyl CH_3), 3 55 (d, 3H, α- and β-CH_2OCH_3), 3.65 (m, 2H, $J_{4,5}$ 5 0 Hz, H-5α and H-5β), 4 00 (dd, $J_{2,3\beta}$ 5 0 Hz, $J_{2,3\alpha}$ 2 5 Hz, $J_{3,4}$ 2 5 Hz, H-3α and H-3β), 4.25 (m, 1H, H-4α and H-4β), 4 60 (m, 0 33 H, $J_{1,2\beta}$ 3 7 Hz, H-2β), 4 77 (d, 0 66 H, H-2α), 5.45 (s, 0 66 H, H-1α), 5 50 (d, 0 33 H, H-1β), 7 50 (d, 2H, CH_{arom}), 8 00 (d, 2H, CH_{arom}) , ^{13}C-NMR ($CDCl_3$) δ - 5 6 (Si-CH_3), - 4 6 (Si-CH_3), 17 7 ($C(CH_3)_3Si$), 21 6 (tosyl CH_3), 25 6 ($C(CH_3)_3$), 59 1 (CH_2OCH_3), 64 2 (C-3α (or β)), 65 7 (C-3β (or α)), 71 3 (C-5α (or β)), 71.4 (C-5β (or α)), 78 0 (C-4α (or β)), 80.2 (C-4β (or α)), 81.7 (C-2α (or β)), 89 1 (C-2β (or α)), 94 7 (C-1α (or β)), 100 3 (C-1β (or α)), 128 0 (CH_{arom}), 129.9 (CH_{arom}), 132 8 (C_{arom}), 145 4 (C_{arom}) Anal Calcd for $C_{19}H_{31}N_3O_6SSi$ 1/2 H_2O C, 48.92 , H, 6.86 ; N, 9 01 Found · C, 48.87 , H, 6 56 , N, 8 87

tert-Butyldimethylsilyl 2,3-dideoxy-2,3-aziridino-5-O-methyl-α-D-lyxofuranoside (12a) - A solution of compound **11a** (14 5 g, 31 mmol) and triphenylphosphine (9.1 g, 34 mmol) in anhydrous tetrahydrofuran (200 mL) was refluxed for 2 h A solution of 2N NaOH (100 mL) was then added and reflux was continued for another 30 min The reaction mixture was cooled to room temperature, ethyl

acetate (100 mL) was added and the mixture was washed with water (2 x 50 mL). The organic phase was dried (Na_2SO_4), the solvents evaporated *in vacuo* and the residue was purified by column chromatography (heptane-ethyl acetate 1:1 followed by diethyl ether), yielding aziridine **12a** (6 7 g, 82%) as a pale yellow syrup, $[\alpha]_D^{20}$ - 6 7° (c 2.1, $CHCl_3$) ; ^{1}H-NMR ($CDCl_3$) δ 0 12 (d, 6H, Si(CH_3)$_2$), 0.90 (d, 9H, α- and β-C(CH_3)$_3$), 2 56 (m, 2H, H-2 and H-3), 3.40 (s, 3H, α- and β-CH_2OCH_3), 3 53 (d, 1 2 H, $J_{4,5}$ 4 0 Hz, H-5α (or β)), 3 59 (t, 0.8 H, $J_{4,5}$ 1 7 Hz, H-5β (or α)), 4 01 (t, 0 6 H, H-4α (or β)), 4 25 (t, 0.4 H, H-4β (or α)), 5 30 (s, 0 4 H, H-1α (or β)), 5 40 (s, 0.6 H, H-1β (or α)) , ^{13}C-NMR ($CDCl_3$) δ - 4 28 (SiCH$_3$), 18.0 (C(CH$_3$)$_3$Si), 25 8 (α- and β-C(CH$_3$)$_3$), 34 3, 35.7, 37 8, and 38 8 (α- and β-C-3 and C-2), 59 5 (CH_2OCH_3), 71 9 (C-5α (or β)), 72 2 (C-5β (or α)), 74 7 (C-4α (or β)), 75.2 (C-4β (or α)), 97 9 (C-1) Anal. Calcd for $C_{12}H_{25}NO_3Si$ 1/15 C_7H_{16} : C, 56 31 ; H, 9 81 ; N, 5.27 Found · C, 56.64 , H, 9 49, N, 5 16

tert-Butyldimethylsilyl 2,3-dideoxy-2,3-aziridino-5-O-methyl-α,β-D-ribofuranoside (12b).- In the same manner as above, compound **11b** gave **12b** (62%), $[\alpha]_D^{20}$ - 30 7° (c 0.48, CHCl3) , ^{1}H-NMR ($CDCl_3$) : δ 0 20 (m, 6H, Si(CH_3)$_2$), 1.00 (s, 9H, C(CH_3)$_3$), 2 70 (m, 2H, H-2 and H-3), 3.47 (s, 4H, NH and α- and β-CH_2OCH_3, partly exchangeable with D_2O), 3 55 (dd, 2H, $J_{4,5}$ 3.5 Hz, H-5α and H-5β), 4.30 (t, 1H, H-4α and H-4β), 5.40 (s, 0.6 H, H-1α (or β)), 5 71 (s, 0.4 H, H-1β (or α)) , ^{13}C-NMR ($CDCl_3$) δ - 4 55 (SiCH$_3$), - 5.16 (SiCH$_3$), 17 9 (C(CH$_3$)$_3$Si), 25 6 (α- and β-C(CH$_3$)$_3$), 36.8 and 38 7 (α- and β-C-3 and C-2), 59 2 (CH_2OCH_3), 74 3 (C-5α and C-5β), 77 8 (C-4α and C-4β), 98 0 (C-1α and C-1β) Anal. Calcd for $C_{12}H_{25}NO_3Si$ C, 55.59 , H, 9 65 , N, 5 40 Found · C, 55 72 , H, 9 42 , N, 5.13

tert-Butyldimethylsilyl N-acetyl-2,3-dideoxy-2,3-aziridino-5-O-methyl-α,β-D-lyxofuranoside (13a) - A solution of aziridine **12a** (2 6 g, 10 mmol) and acetic anhydride (15 mL) in pyridine (100 mL) was left overnight at 4° C. The reaction mixture was then concentrated *in vacuo* and the residue was partitioned between ethyl acetate (100 mL) and water (100 mL) The organic phase was separated, dried (Na_2SO_4) and the solvents removed *in vacuo* The residue was purified by column chromatography (heptane-ethyl acetate 3·1), yielding the N-acetylated aziridine **13a** (2 9 g, 98%) as a syrup, $[\alpha]_D^{20}$ - 0 4° (c 0 24, $CHCl_3$) , ^{1}H-NMR ($CDCl_3$) δ 0 15 (m, 6H, Si(CH_3)$_2$), 0 90 (d, 9H, α- and β-C(CH_3)$_3$), 2 14 (s, 1 5 H, α- (or β-)-$COCH_3$), 2 18 (s, 1.5 H, β- (or α-)-$COCH_3$), 3 30 (m, 2H, $J_{3,4}$ < 1 0 Hz, $J_{2,3}$ 3.8 Hz, H-2 and H-3), 3 42 (d, 3H, CH_2OCH_3), 3 65 (m, 2H, $J_{5a,5b}$ 7.8 Hz, $J_{4,5}$ 5 0 Hz, H-5), 4 02 (dt, 0 6 H, H-4α (or β)), 4 22 (dt, 0 4 H, H-4β (or α)), 5 36 (s, 1H, H-1) , ^{13}C-NMR ($CDCl_3$) δ - 4 3 (SiCH$_3$), 18.0 (C(CH$_3$)$_3$Si), 23.4 (CH$_3$C = O), 25 8 (α- and β-C(CH$_3$)$_3$), 43 6 (C-2 (or C-3)), 44 8 (C-3 (or C-2)), 59 5 (CH_2OCH_3), 71.7 (C-5α (or β)), 72.0 (C-5β (or α)), 74 7 (C-4α (or β)), 75 3 (C-4β (or α)), 97 0 (C-1α (or β)), 96 3 (C-1β (or α)), 170 2 (CH$_3$C = O) Anal Calcd for $C_{14}H_{27}NO_4Si$ · C, 55 81 , H, 8 97 ; N, 4 65 Found C, 55 70 ; H, 8 77 , N, 4 49

tert-Butyldimethylsilyl N-acetyl-2,3-dideoxy-2,3-aziridino-5-O-methyl-α,β-D-ribofuranoside (13b) - In the same manner as above, compound **12b** gave **13b** (95%), $[\alpha]_D^{20}$ - 65 7° (c 0 54, $CHCl_3$) , ^{1}H-NMR ($CDCl_3$) δ 0 15 (m, 6H, Si(CH_3)$_2$), 0 90 (d, 9H, α- and β-C(CH_3)$_3$), 2 10 (s, 1H, β-CH_3C = O), 2.20 (d, 2H, α-CH_3C = O), 3 15 (d, 0.7 H, $J_{2,3\alpha}$ 4 0 Hz, H-3α), 3 20 (d, 0 3 H, $J_{2,3\beta}$ 4 0 Hz, H-3β), 3 28 (dd, 1H, $J_{1,2}$ 1 5 Hz, H-2α and H-2β), 3.35 (d, 3H, α- and β-CH_2OCH_3), 3 50 (d, 2H, $J_{4,5}$ 3 5 Hz, H-5α and H-5β), 4 30 (t, 0 3 H, $J_{4,5\beta}$ 6 0 Hz, H-4β), 4 42 (dd, 0 7 H, $J_{4,5\alpha}$ 3 5 Hz, H-4α), 5 40 (s, 0 3 H, H-1β), 5.55 (d, 0 7 H, $J_{1,2\alpha}$ 1 5 Hz, H-1α) , ^{13}C-NMR ($CDCl_3$) δ - 2 1 (SiCH$_3$), - 1 2 (SiCH$_3$), 17 8 (C(CH$_3$)$_3$Si), 23 9 (α- and β-C(CH$_3$)$_3$), 25 5 (CH$_3$C = O), 40 6 (C-2 (or C-3)), 44 0 (C-3 (or C-2)), 59 1 (CH_2OCH_3), 73 3 (C-5), 74 7 (C-4α (or β)), 75 5 (C-4β (or α)), 95 5 (C-1α (or β)), 97 2 (C-1β (or α)), 180 2 (CH$_3$C = O) Anal Calcd for $C_{14}H_{27}NO_4Si$ 1/6 H_2O C, 55 26 , H, 8 99 , N, 4 60 Found C, 55 31 , H, 8 87 , N, 4 47

N-Acetyl-2,3-dideoxy-2,3-aziridino-5-O-methyl-α,β-D-lyxofuranose (14a) - To a solution of aziridine **13a** (790 mg, 3 05 mmol) in dichloromethane (100 mL) held at 0° C was added dropwise a 1 M solution of tetrabutylammonium fluoride (5 3 mL, 5 3 mmol) in tetrahydrofuran The reaction mixture was stirred for 2 h at 0° C after which the solvents were removed *in vacuo* The residue was purified by column chromatography (heptane-ethyl acetate 1 3), yielding **14a** as a white solid (396 mg, 69%), m p 82-83° C , ^{1}H-NMR ($CDCl_3$) δ 2.14 (s, 3H, CH_3C = O), 3 38 (m, 2H, H-2 and H-3), 3 42 (s, 3H, CH_2OCH_3), 3 60 (dd, 2H, $J_{4,5}$ 4 8 Hz, C-5), 4 10 (br s, 1H, OH), 4 33 (dt, 1H, $J_{3,4}$ < 1 Hz, H-4), 5 42 (s, 1H, H-1) Anal Calcd for $C_8H_{13}NO_4$ C, 51 33 , H, 6 95 , N, 7 48 Found C, 51 54 , H, 7 07 , N, 7 41

N-Acetyl-2,3-dideoxy-2,3-aziridino-5-O-methyl-α,β-D-ribofuranose (14b) - In the same manner as above, compound **13b** gave **14b** (59%), $[\alpha]_D^{20}$ - 54 6° (c 1 24, $CHCl_3$) , ^{1}H-NMR ($CDCl_3$) δ 2 10 (s, 3H, CH_3C = O), 3 26 (s, 2H, H-2 and H-3), 3 47 (s, 3H, CH_2OCH_3), 3 58 (t, 2H, $J_{4,5}$ 2 8 Hz, H-5), 4.42 (t, 1H, H-4), 4 75 (br s, 1H, OH), 5 30 (s, 1H, H-1) , ^{13}C-NMR ($CDCl_3$) δ 23 5

($\underline{C}H_3C$ = O), 40 5 (C-2 (or C-3)), 44 3 (C-3 (or C-2)), 59 3 ($O\underline{C}H_3$), 72 6 (C-5), 75 1 (C-4), 94.7 (C-1), 170 2 (C = O) Anal Calcd for $C_8H_{13}NO_4$ C, 51 33 ; H, 6 95 , N, 7.48 Found : C, 51 05 ; H, 6.85 ; N, 7 20

(1S,4S,5R)-N-Acetyl-4-methoxymethyl-3-oxa-6-azabicyclo[3.1.0]hexan-2-one (15a) - To a mixture of **14a** (66 5mg, 0.36 mmol) and freshly-activated 4 Å molecular sieve (200 mg) was added 4-methylmorpholine N-oxide (62 mg, 0 54 mmol) and tetrapropylammonium perruthenate (6.2 mg, 0.02 mmol) The reaction mixture was stirred for 3 h at room temperature and then filtered through a pad of silica gel The pad was washed with ethyl acetate (3 x 50 mL) and the combined filtrate and washings were concentrated *in vacuo* (bath temperature < 40 °C) The residue was purified by column chromatography on silica gel (heptane-ethyl acetate 1·2) yielding **15a** (58 mg, 88%) as a clear oil, $[\alpha]_D^{20}$ - 127 (c 0.5, $CHCl_3$) , IR : ν 1792 (O$\underline{C}$ = O), 1714 cm^{-1} (N$\underline{C}$ = O) , ^{1}H-NMR ($CDCl_3$) δ 2 20 (s, 3H, $C\underline{H}_3C$ = O), 3 45 (s, 3H, $OC\underline{H}_3$), 3.65 (d, 1H, $J_{2,3}$ 3 5 Hz, H-2), 3.70 (dd, 2H, $J_{4,5a}$ 2.0 Hz, $J_{4,5b}$ 5 0 Hz, H-5), 3 75 (dd, 1H, $J_{3,4}$ 2 Hz, H-3), 4 65 (sext,1 H, H-4) , ^{13}C-NMR ($CDCl_3$) . δ 23.4 ($\underline{C}H_3C$ = O) , 37 3 and 41 2 (C-2 and C-3), 59.5 ($O\underline{C}H_3$), 70 63 (C-5), 76.9 (C-4), 168 8 ($CH_3\underline{C}$ = O), 179.5 (O-$\underline{C}$ = O) Mass spectrum m/z 185.0690 (calcd for $C_8H_{11}NO_4$ · 185 0692) Anal Calcd for $C_8H_{11}NO_4$ 1/4 H_2O C, 50 65 , H, 6 06 , N, 7 30. Found C, 50 54 , H, 6 05 , N, 7 36

(1R,4S,5S)-N-Acetyl-4-methoxymethyl-3-oxa-6-azabicyclo[3.1.0]hexan-2-one (15b).- In the same manner as above, **14b** gave **15b** (83%), $[\alpha]_D^{20}$ - 89 7 (c 1.37, $CHCl_3$) ; IR ν 1787 (OC = O), 1712 cm^{-1} (NC = O) , ^{1}H-NMR ($CDCl_3$) δ 2 15 (s, 3H, $C\underline{H}_3C$ = O), 3.40 (s, 3H, $OC\underline{H}_3$), 3 50 (d, 1H, $J_{2,3}$ 2.4 Hz, H-2), 3 65 (d, 1H, H-3), 3 70 (d, 2H, $J_{4,5}$ 1 5 Hz, H-5), 4 85 (t, 1H, H-4) , ^{13}C-NMR ($CDCl_3$) δ 23 4 ($\underline{C}H_3C$ = O), 37 6 and 49 3 (C-2 and C-3), 59 8 ($O\underline{C}H_3$), 71 7 (C-5), 75 3 (C-4), 169 3 ($CH_3\underline{C}$ = O), 178 6 (O-$\underline{C}$ = O) Anal Calcd for $C_8H_{11}NO_4$ C, 51 89 , H, 5 94 , N, 7 56 Found C, 51 84 ; H, 6 03 ; N, 7 33

Acknowledgements

We thank Dr Pierre Potier for his ongoing interest in this work.

This study was financed by DRET contract n° 89/157 Laurent Dubois also thanks DRET for a fellowship

REFERENCES AND NOTES

1 Nakajima, K , Neya, M , Yamada, S , Okawa, K *Bull Chem. Soc. Jpn* **1982,** *55*, 3049-3050
2 Baldwin, J E , Adlington, R M ; Robinson, N G *J Chem. Soc , Chem. Commun.* **1987**,153-155
3 Baldwin, J E , Adlington, R. M , O'Neil,I A ; Schofield, C , Spivey, A. C , Sweeney, J B *J Chem. Soc , Chem Commun.* **1989**, 1852-1854
4 Sato, K , Kozikowski, A P. *Tetrahedron Lett* **1989**, *30*, 4073-4076
5 Shima, I , Shimazaki, N , Imai, K , Hemmi, K , Hashimoto, M *Chem Pharm. Bull.* **1990**, *38*, 564-566
6 Okawa, K , Nakajima, K , Tanaka, T , Neya, M *Bull Chem Soc Jpn.* **1982,** *55*, 174-176
7 Nakajima, K ; Tanaka, T ; Morita, K , Okawa, K *Bull Chem Soc Jpn* **1980**, *53*, 283-284
8 Parry, R J , Naidu, M V *Tetrahedron Lett* **1983,** *24*, 1133-1134
9 Vaultier, M ; Oualı, M S ; Carrié, R. *Bull Soc Chim. Fr* Part II, **1979**, 343-346
10 Bouayad, Z ; Chanet-Ray, J , Ducher, S , Vessière, R. *J Heterocyclic Chem.* **1991,** *28*, 1757-1767
11 Nakajima, K , Takai, F., Tanaka, T , Okawa, K *Bull Chem Soc Jpn.* **1978,** *51*, 1577-1578.
12 a) Legters, J ; Thijs, L., Zwanenburg, B *Rec Trav Chim. Pays Bas* **1992,** *111*, 211-214 b) Chilmonczyk, Z., Egli, M , Behringer, C , Dreiding, A.S *Helv Chim Acta*, **1989**, *72*, 1095-1106
13 Kusumoto, S , Tsuji, S , Shiba, T *Bull Chem Soc Jpn* **1974**, *47*, 2690-2695
14 Egli, M ; Dreiding, A. S *Helv Chim. Acta* **1986**, *69*, 1442-1460
15 a) Ariza, J , Font, J., Ortuno, R M *Tetrahedron* **1990**, *46*, 1931-1942 b) Barton, D H. R , Benechie, M , Khuong-Huu, F , Potier, P , Reyna-Pinedo, V *Tetrahedron Lett* **1982**, *23*, 651-654 c) Ortuno, R. M , Cardellach J Font, J *J Heterocyclic Chem* **1987**, *24*, 79-84

16. Cleophax, J., Gero, S. D.; Hildesheim, J , Sepulchre, A M., Guthrie, R D ; Smith, C W *J Chem. Soc. (C)* **1970**, 1385-1390.
17 Guiller, A.; Gagnieu, C H.; Pacheco, H *Tetrahedron Lett* **1985**, *26*, 6343-6344.
18. Holy, A., Ludzisa, A., Votruba, I ; Sediva, K ; Pischel, H *Coll Czech. Chem. Commun.* **1985**, *50*, 393-417.
19 a) Ittah, Y ; Sasson, Y.; Shahak, I., Tsaroom, S.; Blum, J *J. Org Chem.* **1978**, *43*, 4271-4273 b) Williet, A ; Müller, E. P., Peringer, P. *Helv Chim. Acta* **1983**, *66*, 2467-2480
20 a) Knouzi, N , Vaultier, M.; Carrié, R. *Bull Soc. Chim. France* **1985**, 815-819 b) Chakraborty, T K.; Gangakhedkar, K. K. *Tetrahedron Lett* **1991**, *32*, 1897-1898.
21 Pinter, I ; Kovacs, J ; Messmer, A ; Kalman, A., Toth, G , Lindberg, B K *Carbohydr. Res.* **1979**, *72*, 289-296
22 Buss, D. H.; Hough, L.; Richardson, A C *J Chem. Soc.* **1965**, 2736-2743.
23 Jeganathan, S ; Vogel, P. *J Chem. Soc., Chem. Commun.* **1989**, 993-995.
24 Alvernhe, G.; Lacombe, S.; Laurent, A. *Tetrahedron Lett* **1980**, *21*, 289-292.
25 Klemer, A ; Brandt, B.; Hofmeister, U., Rüter, E A. *Liebigs Ann. Chem.* **1983**, 1920-1929
26 Griffith, W. P., Ley, S V *Aldrichimica Acta* **1990**, *23*, 13-19 and references therein