# A Study of the Epoxidation of 6-Deoxyhex-5-enopyranosides. 1,5-Dicarbonyl Derivatives and Novel Synthetic Routes to D-*xylo*-Hexos-5-ulose and D-*lyxo*-Hexos-5-ulose

Philomena M. Enright,[†] Manuela Tosin,[†] Mark Nieuwenhuyzen,[‡] Linda Cronin,[†] and Paul V. Murphy*,[†]

*Department of Chemistry, Centre for Synthesis and Chemical Biology, Conway Institute of Biomolecular and Biomedical Research, University College Dublin, Belfield, Dublin 4, Ireland, and School of Chemistry, Queen's University, Belfast BT9 5AG, Antrim, Northern Ireland*

*paul.v.murphy@ucd.ie*

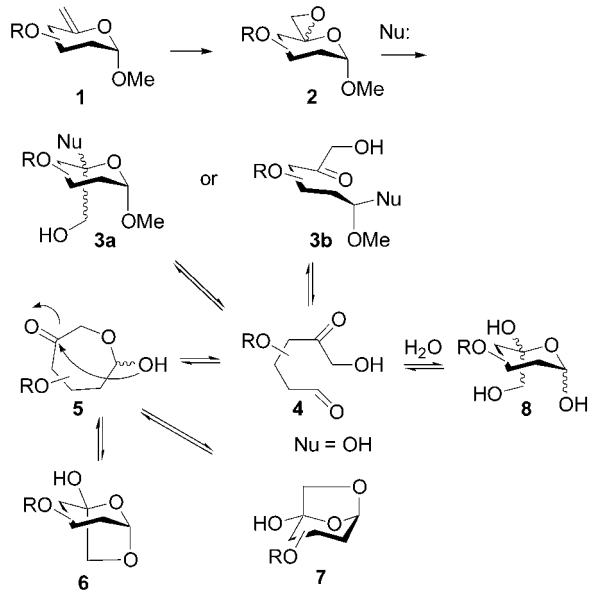
*Received December 15, 2001*

The work described deals with the isolation and characterization of epoxides from 6-deoxyhex-5-enopyranosides and preliminary exploration of their synthetic potential. Prolonged epoxidation reaction times led to their hydrolysis in situ and gave novel protected D-hexos-5-ulose derivatives (sugar 1,5-dicarbonyls). Some reactions of the hexos-5-uloses were studied, and in some cases septanoside (seven-membered-ring saccharide) derivatives were isolated. Novel routes to D-*xylo*-hexos-5-ulose and D-*lyxo*-hexos-5-ulose, of interest as intermediates in the synthesis and biosynthesis of inositols and aza sugars, are also described. The structures of the epoxides and novel hexos-5-uloses were established by NMR and X-ray crystallographic methods.

## Introduction

Much recent interest has focused on the synthetic potential of glycals as their epoxides and other derivatives can be used in the preparation of oligosaccharides, glycoconjugates, and a variety of other carbohydrate derivatives of biological and medical interest.[1] 6-Deoxyhex-5-enopyranosides **1**, which are further enol ethers with "*exo*-glycal" functionality, have proven to be useful intermediates in synthesis, as illustrated by the preparation of carbacycles by Ferrier and other rearrangement (Sinay) reactions.[2] Despite these and other successes, there is little work reported in the literature on the synthesis and reactions of their epoxides[3] or other small ring adducts. Reactions of epoxides **2** with reducing reagents or nucleophiles (Scheme 1) could provide useful intermediates for the synthesis of a range of biologically interesting carbohydrate derivatives for the synthesis of novel glycosaminoglycan derivatives,[4] novel aminoglycosides with potential as RNA binding agents,[5] or other glycomimetics.[6] We have recently shown that they can be used in the synthesis of the glycosidase inhibitor deoxymannojirimycin.[7] In this paper we provide a full account[8] concerning the isolation of the epoxides from 6-deoxyhex-5-enopyranosides, their hydrolysis to give novel protected D-hexos-5-ulose derivatives, and the synthesis of the parent hexos-5-uloses D-*xylo*-hexos-5-ulose and D-*lyxo*-hexos-5-ulose.[9] These hexos-5-uloses are of interest as they have been postulated as intermediates

**Scheme 1**




[†] University College Dublin.
[‡] Queen's University.

(1) For reviews see: (a) Danishefsky, S. J.; Bilodeau, M. T. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1380. (b) Ferrier, R. J. *Top. Curr. Chem.* **2001**, *215*, 153.

(2) (a) Ferrier, R. J.; Middleton, S. *Chem. Rev.* **1993**, *93*, 2779. (b) Dalko, P.; Sinaÿ, P. *Angew. Chem., Int. Ed.* **1999**, *38*, 773. (c) Ferrier, R. J. *Top. Curr. Chem.* **2001**, *215*, 277.

(3) As far as we are aware only one synthesis of their epoxides had been reported previously: Defaye, J. *C. R. Hebd. Seances Acad. Sci.* **1962**, *255*, 794.

(4) Lander, A. D. *Chem. Biol.* **1994**, *1*, 73.

(5) Alper, P. B.; Hendrix, M.; Sears, P.; Wong, C.-H. *J. Am. Chem. Soc.* **1998**, *120*, 1965.

(6) Wong, C.-H. *Acc. Chem. Res.* **1999**, *32*, 376.

(7) O'Brien, J.; Tosin, M.; Murphy, P. V. *Org. Lett.* **2001**, *3*, 3353.

(8) Parts of the work described herein have been communicated recently; see: Enright, P. M.; O'Boyle, K. M.; Murphy, P. V. *Org. Lett.* **2000**, *2*, 3929. See also ref 7.

(9) For previous syntheses of protected and unprotected hexos-5-uloses see: (a) Heusinger, H. *Carbohydr. Res.* **1988**, *181*, 67. (b) Kiely, D. E.; Fletcher, H. G., Jr. *J. Org. Chem.* **1969**, *34*, 1386. (c) Helferich, B.; Bigelow, N. M. *Z. Physiol. Chem.* **1931**, 200. (d) Blattner, R.; Ferrier, R. J. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1523. (e) Ferrier, R. J.; Tyler, P. C. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1528. (f) Barili, P. L.; Bergonzi, M. C.; Berti, G.; Catelani, G.; D'Andrea, F.; De Rensis, F. *J. Carbohydr. Chem.* **1999**, *18*, 1037. (g) Barili, P. L.; Berti, G.; Catelani, G.; D'Andrea, F.; De Rensis, F.; Goracci, G. *J. Carbohydr. Chem.* **1998**, *17*, 1167−1180. (h) Barili, P. L.; Berti, G.; Catelani, G.; D'Andrea, F.; DeRensis, F. *Tetrahedron* **1997**, *53*, 8665.

10.1021/jo016378c CCC: $22.00 
Published on Web 04/30/2002

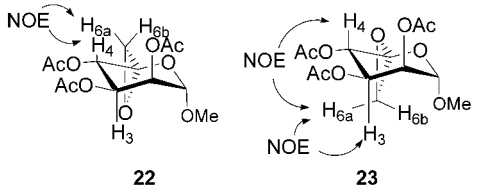



**Figure 1.** Use of NOE experiments to assign the stereochemistry of epoxides.

in the biosynthesis[10] of inositols and aza sugars and are also synthetic prescursors to both aza sugars[11] and inositols.[12]

## Results and Discussion

**Synthesis and Structure of Epoxides.** A series of epoxidation reactions of **9**−**15**[13] were investigated (Table 1), and epoxides could be isolated in high yields from acetylated and benzylated hex-5-enopyranosides (entries 4, 7, and 10) using methyl(trifluoromethyl)dioxirane, generated in situ.[14] Epoxidation with MCPBA in dichloromethane[15] in the presence of aqueous sodium bicarbonate buffer[16] also worked well (entries 6 and 9). Attempts to separate the epoxides by silica gel chromatography led to depleted yields (entries 3 and 8). However, the crude product is sufficiently pure that it can be used for further synthetic transformations (entry 14), and the epoxides are stable once isolated.[17] The $^1$H NMR spectral data for **19** were in good agreement with those reported previously by Defaye.[3] The stereochemical configuration at C-5 (*R*) of this product, previously not determined, was established by X-ray crystallography. The configuration at C-5 can also be determined using NOE experiments. The isomer **22** showed an NOE enhancement between H-6a and H-4 but not between H-6a and H-3, whereas **23** showed enhancements between H-6a and H-4 and also between H-6a and H-3 (Figure 1).

**Formation of Hexos-5-uloses from Epoxides.** Prolonged reaction times (Table 1) in the epoxidation of **9**−**15** (entries 1, 2, 5, and 11−13), the attempted separation of epoxides by chromatography, and the hydrolysis of **19**/**20** at 60 °C in acetonitrile (entry 14) led to the formation of 1,5-dicarbonyl derivatives (hexos-5-uloses). The most efficient formation of the hexos-5-uloses was observed when methyl(trifluoromethyl)dioxirane was again used. Lower yields and conversions were observed for reactions with dimethyldioxirane and other epoxidizing agents.[18] The galactose derivative **28/29** was isolated (48%) from the reaction of methyl(trifluoromethyl)dioxirane with **15**. Efforts to obtain the epoxides from the TMS-protected **10**, by careful monitoring of the reaction carried out at room temperature, were not successful and surprisingly gave the hemiketal **17** (71%); attempts to purify this material further by distillation led to its efficient conversion to **18** (75%).[19] A hemiketal related to **17** was also observed previously by Chapleur and co-workers from the dihydroxylation of methyl 2,3-di-*O*-benzyl-4-*O*-methanesulfonyl-6-deoxy-α-D-*xylo*-hex-5-enopyranoside (using $RuCl_3$/$NaIO_4$); this compound eliminated methanol during chromatography, and the product thus obtained also had a bicyclic structure, **6**.[20] In our hands the dihydroxylation of TMS-protected and acetyl-protected hex-5-enopyranosides using similar conditions did not proceed in good yields to give the hexos-5-uloses.

It was generally noted that the epoxides with their oxygen atom in an equatorial orientation (*S* configuration) were more susceptible to hydrolysis during chromatography; this is consistent with the greater reactivity of equatorial pyranosides. The formation of hexos-5-uloses in these reactions is explained by the hydrolysis of the initially formed epoxide, giving a hemiketal, **3a**, or possibly a hemiacetal, **3b**, that ultimately loses methanol (Scheme 1). The formation of **17** from **10** would suggest attack by water at C-5 is favored. However, this does not preclude the possible attack of water at C-1 in other cases to give **3b**, which would ultimately have the same consequences. The relatively facile hydrolysis of the epoxides formed in these reactions can be compared with that of similarly reactive epoxides derived from 4-deoxy-L-*threo*-hex-4-enopyranoside, which have been shown to give bisglycosides when reacted with methanol.[21]

**Structure of Hexos-5-uloses.** The hexos-5-uloses isolated could adopt the structure of one or more of the tautomers **4**−**7** or possibly that of hydrated compound **8** (Scheme 1). However, the bicyclic structure **6**, which disguises both carbonyl groups and has the pyranose ring in a $^4C_1$ conformation, is favored in all cases.[22] It is adopted exclusively by the protected 5-keto-D-glucose and 5-keto-D-mannoses (**16**, **18**, **21**, **26**, **27**, and **30**) in $CDCl_3$. There is no evidence in the NMR or IR spectra to support the presence of open chain **4** or septanos-5-ulose structures **5** in any of the equilibrium product mixtures.[23] However, there is evidence for a dynamic equilibrium between **28** and **29** which presumably occurs via a septanos-5-ulose intermediate; the $^1$H NMR of the product recorded directly after silica chromatography indicated a 60:40 mixture of **28** and **29**, and this ratio

(10) (a) Wong, Y.-H. H.; Sherman, W. R. *J. Biol. Chem.* **1981**, *256*, 7077. (b) Eisenberg, F., Jr.; Maeda, T. In *Inositols and Phosphoinositides*; Bleasdale, J. E., Eichberg, J., Hauser, G., Eds.; Humana: Totowa, NJ, 1985; p 3. (c) Hardick, D. J.; Hutchinson, D. W.; Trew, S. J.; Wellington, E. M. H. *Chem. Commun.* **1991**, 729.

(11) For the synthesis of aza sugars using 1,5-dicarbonyl sugars, see: (a) Baxter, E. W.; Reitz, A. B. *J. Org. Chem.* **1994**, *59*, 3175. (b) D'Andrea, F.; Catelani, G.; Mariani, M.; Vecchi B. *Tetrahedron Lett.* **2001**, *42*, 1139. (c) Barili, P. L.; Berti, G.; Catelani, G.; D'Andrea, F.; DeRensis, F.; Puccioni, L. *Tetrahedron* **1997**, *53*, 3407.

(12) Hexos-5-uloses have also been used in a synthesis of inositols; see: Pistara, V.; Barili, P. L.; Catelani, G., D'Andrea, F.; Fisichella, S. *Tetrahedron Lett.* **2000**, *41*, 3253.

(13) Modifications of literature methods were used for the synthesis of **9**−**15.** Full details are provided in the Supporting Information. (a) Semeria, D.; Phillipe, M.; Delaumeny, J.-M.; Sepulchre, A.-M.; Gero, S. D. *Synthesis* **1983**, 710. (b) Sakairi, N.; Kuzuhara, H. *Tetrahedron Lett.* **1982**, *23*, 50, 5327. (c) Takeo, K.; Fukatsu, T.; Yasato, T. *Carbohydr. Res.* **1982**, *107*, 71. (d) Ferrier, R. J.; Prasit, P. *Carbohydr. Res.* **1980**, *82*, 263−272. (e) Sugawara, F.; Kuzuhara, H. *Agric. Biol. Chem.* **1981**, *45*, 301. (f) Defaye, J.; Gadelle, A.; Wong, C. C. *Carbohydr. Res.* **1981**, *94*, 131. (g) Bernet, B.; Vasella, A. *Helv. Chim. Acta* **1979**, *62*, 2411. (h) Lehmann, *Carbohydr. Res.* **1966**, *2*, 1. (i) Das, S. K.; Mallet, J.-M.; Sinaÿ, P. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 493.

(14) Yang, D.; Wong, M.-K.; Yip, Y.-C. *J. Org. Chem.* **1995**, *60*, 3887.

(15) Hydrolysis of the epoxides was more pronounced if diethyl ether was used as a solvent.

(16) Anderson, W. K.; Veysoglu, T. *J. Org. Chem.* **1973**, *38*, 12, 2267.

(17) Decomposition did not occur after storage in a freezer for 3 weeks.

(18) Further details are provided in the Supporting Information.

(19) Some conversion of **17** to **18** was also observed in $CDCl_3$ by NMR.

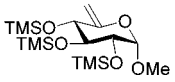
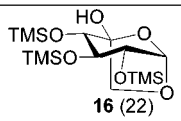
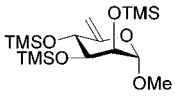
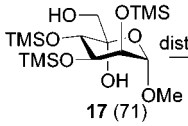
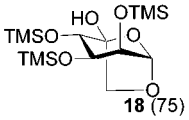
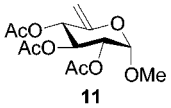
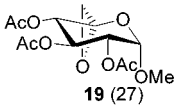
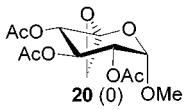
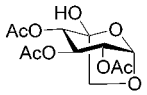
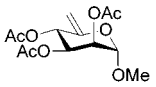
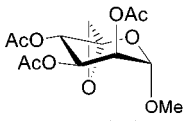
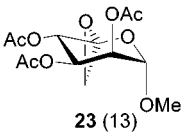
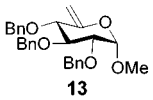
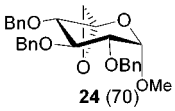
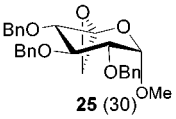
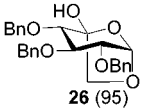
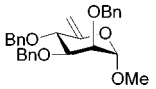
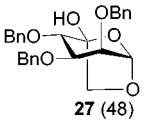
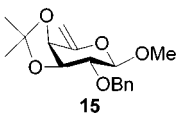
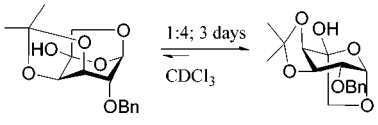
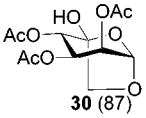
(20) Taillefumier, C., Lakhrissi, M., Chapleur, Y. *Synlett* **1999**, 697.

(21) Barili, P. L.; Berti, G.; Catelani, G.; D'Andrea, F.; De Rensis, F. *Tetrahedron* **1997**, 8665.

(22) The spectra were recorded in $CDCl_3$ and also DMSO-$d_6$ and acetone-$d_6$.

(23) The $^1$H NMR spectra were recorded in $CDCl_3$, and the IR spectra were obtained by liquid film method, by KBr method, or for a solution in $CHCl_3$.

**Table 1. Synthesis of Epoxides and Hexos-5-uloses**

| entry | **reactant** | method,[a] reaction time | **products** (% yield) | |
|---|---|---|---|---|
| 1 |  **9** | A, 15 h |  **16** (22) | |
| 2 |  **10** | C, 1.5 h |  **17** (71) |  **18** (75) |
| 3 |  **11** | A, 15 h |  **19** (27) |  **20** (0) |
| 4 | **11** | C, 2 h | **19** (49) | **20** (49) |
| 5 | **11** | D, 12 h |  **21** (12-50)[b] | |
| 6 |  **12** | B, 2 h |  **22** (61) |  **23** (13) |
| 7 | **12** | C, 1.5 h | **22** (54) | **23** (40) |
| 8 | **12** | D, 1 h | **22** (20) | **23** (10) |
| 9 |  **13** | B, 45 min |  **24** (70) |  **25** (30) |
| 10 | **13** | C, 1 h | **24** (30) | **25**(70) |
| 11 | **13** | D, 15 h |  **26** (95) | |
| 12 |  **14** | D, 15 h |  **27** (48) | |
| 13 |  **15** | D, 15 h |  **28** | **29** |
| 14 | **19/20** | E, 1.5 h |  **30** (87) | |

[a] Reagents and conditions: (A) MCPBA, $CH_2Cl_2$, 0.5 M $NaHCO_3$, chromatography; (B) MCPBA, $CH_2Cl_2$, 0.5 M $NaHCO_3$, no chromatography; (C) 1,1,1-trifluoroacetone, oxone, $NaHCO_3$, $Na_2EDTA$, $CH_3CN$, $H_2O$, no chromatography; (D) 1,1,1-trifluoroacetone, oxone, $NaHCO_3$, $Na_2EDTA$, $CH_3CN$, $H_2O$, chromatography; (E) $H_2O$, MeCN, 60 °C, chromatography. [b] Prolonged exposure to chromatography reduces the yield.

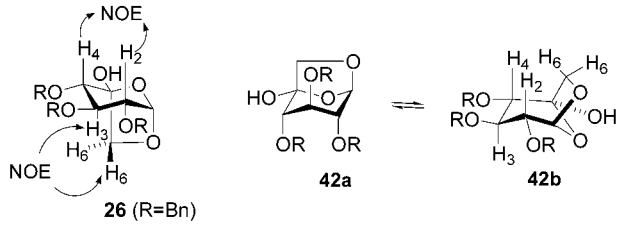
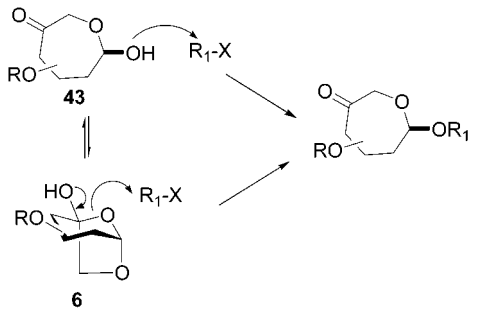
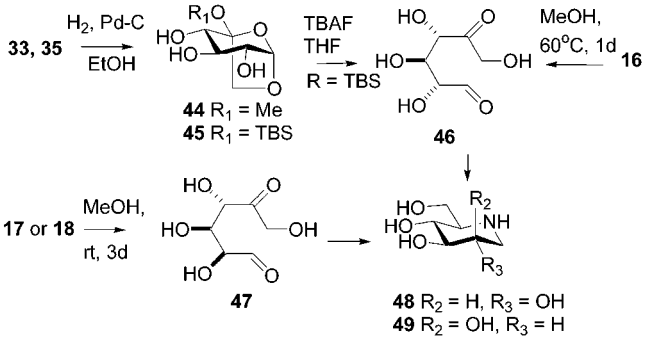



**Figure 2.** Use of NOE experiments to determine the hexos-5-ulose structure.

**Scheme 2**




**Scheme 3**




changed to 25:75 over 3 days.[24] The coupling constants in the $^1$H NMR spectra and 2D NOESY experiments were used to confirm the structures proposed for all of the products in $CDCl_3$; the rationale used is illustrated for **26** (Figure 2). Thus, the $^1$H and $^{13}$C NMR spectra of the product obtained from the reaction of **13** (Table 1, entry 11) indicated the preferred structure for the product to be either one with idose configuration **26** or one with glucose configuration **42b**, which has the pyranose ring in a twist boat conformation; the tautomer with glucose configuration **42a**, with its pyranose ring in a $^1C_4$ conformation, is excluded on the basis of the coupling constants for the ring protons in the $^1$H NMR spectrum. The 2D NOESY experiments showed cross-peaks, possible only for structure **26**, between H-3 and one of the H-6 protons; cross-peaks were not observed between H-2 and H-6 or between H-4 and H-6 as would have been expected for **42b**. A similar rationale was used in assigning all structures described herein. Crystals (needles) were obtained for **26**, and its structure was determined by X-ray crystallographic methods; the structure in the solid state was the same as that observed in solution.

**Reactions of Hexos-5-uloses.** Some reactions of the hexos-5-uloses were studied (Table 2). The reaction of **26** with excess acetic anhydride and pyridine gave the monoacetate **32** rather than a product with three acetates as would have been expected for a compound with structure **8**.[25] 2D NOESY spectra were also obtained for **31**−**35**, **37**, and **39** to confirm that tautomerization to compounds with glucose configuration did not occur during the course of the reactions (Table 2). It was interesting to observe the formation of septanoside products **36** and **38** as byproducts in two cases; the stereochemical configuration of these compounds was assigned on the basis of cross-peaks observed between H-1 and H-3 in 2D NOESY spectra. The reduction of **36** and **38** with $NaBH_4$ was also investigated to aid the stereochemical assignment; reduction of **38** gave two diastereoisomeric alcohols, whereas reduction of **36** gave a single alcohol. The coupling constants for the anomeric protons ($J_{1,2}$) of these alcohols were between 6.2 and 7.6 Hz; these values are consistent with those described for related septanosides that have a 1,2-*trans* configuration.[26] The acetylation of the galactose derivative **28/29** unexpectedly gave as the major products a compound with talose configuration **40** (20%) and the septanoside **41** (48%). The structure assigned to **40** was strongly supported by the analysis of coupling constants in the $^1$H NMR spectrum and NOESY experiments.[27] The formation of the septanosides can be rationalized (Scheme 2) by trapping of the more nucleophilic seven-membered-ring tautomer **43**, possibly present in small amounts in solution, or directly from **6**.

**Synthesis of D-*xylo*-Hexos-5-ulose and D-*lyxo*-Hexos-5-ulose.** The preparation of D-*xylo*-hexos-5-ulose (**46**) and D-*lyxo*-hexos-5-ulose (**47**) (5-keto-D-glucose and 5-keto-D-mannose) was investigated as these compounds have, respectively, been used in the synthesis of the glycosidase inhibitors[28] 1-deoxynojirimycin (**48**) and 1-deoxymannojirimycin (**49**) and they have also been postulated as intermediates in the biosynthesis of inositols. Attempts to directly remove the protecting groups from **21** and **26** were not successful, but the labile TMS groups were easily removed, using methanol, from **16** to give **46**, and from **17** or **18** to give **47** (Scheme 3). Alternatively, the benzyl protecting groups were removed from **33** and **35** by catalytic hydrogenation using Pd−C in ethanol to give the unprotected glycosides **44** and **45**, respectively. The TBS group can be removed from **45** to give **46** by treatment with TBAF in THF (Scheme 3), illustrating that this is a strategy that could be utilized for the protection of the 1,5-dicarbonyl products.[29] Selective manipulation of the hydroxyl groups of **45** (or **44**) could be possible, and the resulting products could be investigated for the synthesis of oligosaccharides containing aza sugars.

(24) The NMR spectra were obtained in $CDCl_3$.

(25) Detailed studies on equilibrium product mixtures in aqueous solutions of unprotected hexos-5-uloses have been carried out, and hydrated structures are observed under these conditions. See: (a) Kiely, D. E.; Harry-O'Kuru, R. E.; Morris, Jr., P. E.; Morton, D. W.; Riordan, J. M. *J. Carbohydr. Chem.* **1997**, *16*, 1159. (b) Riordan, J. M.; Morris, P. E., Jr.; Kiely, D. E. *J. Carbohydr. Chem.* **1993**, *12*, 865.

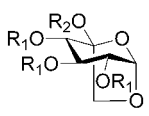
(26) Compounds with a 1,2-*trans* configuration that are known are derivatives of methyl $\beta$-D-glucoseptanoside and methyl $\alpha$-L-idoseptanoside. Derivatives of septanosides with a 1,2-*cis* configuration (methyl $\alpha$-D-glucoseptanoside and methyl $\beta$-L-idoseptanoside) have $J_{1,2}$ values of 2−3 Hz. See: (a) Stevens, J. D. *Aust. J. Chem.* **1975**, *28*, 525. (b) Ng, C. J.; Stevens, J. D., *Carbohydr. Res.* **1996**, *284*, 241. (c) Ng. C. J.; Craig, D. C.; Stevens, J. D. *Carbohydr. Res.* **1996**, *284*, 249.

(27) NOE cross-peaks were not observed between H-3 and H-6 protons as would be expected for the compound with galactose configuration.

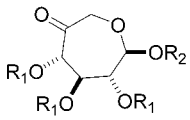
(28) (a) Hughes, A. B.; Rudge, A. J. *Nat. Prod. Rep.* **1994**, 135. (b) Fleet, G. W. J. *Glycobiology* **1992**, *2*, 199 and references therein.

(29) The use of more than 1 equiv of TBAF leads to formation of unidentified products.

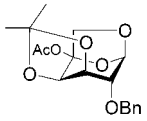
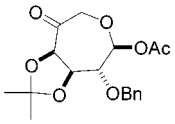
**Table 2. Reactions of Hexos-5-uloses**



**31-35, 37, 39**



**36, 38**

| entry | reactant | reagents and conditions[a] | product (yield, %) | $R_1$, $R_2$ |
|---|---|---|---|---|
| 1 | **21** | D | **31** (63) | Ac, TBS |
| 2 | **26** | A | **32** (58) | Bn, Ac |
| 3 | **26** | B | **33** (78) | Bn, Me |
| 4 | **26** | C | **34** (66)[b] | Bn, Tf |
| 5 | **26** | D | **35** (48) | Bn, TBS |
| 6 | **26** | E | **35** (38), **36** (16) | Bn, TBS |
| 7 | **26** | F | **37** (45), **38** (16) | Bn, 2-BrBz |
| 8 | **26** | G | **39** (63) | Bn, Ms |
| 9 | **28**/**29** | A |  **40** (25)  **41** (48) | |

[a] Reagents and conditions: (A) $Ac_2O$, Py, DMAP (cat.), 25 °C, 15 h; (B) NaH (2 equiv), MeI (2 equiv), DMF, 25 °C, 12 h; (C) $Tf_2O$ (2 equiv), 2,6-lutidine (4 equiv), $CH_2Cl_2$, −40 to +25 °C, 15 h; (D) TBSOTf (1.5 equiv), 2,6-lutidine (2 equiv), $CH_2Cl_2$; (E) TBSOTf (2 equiv), pyridine, −40 to +25 °C, 15 h; (F) 2-bromobenzoyl chloride (2 equiv), DMAP (cat.), pyridine, 0−25 °C, 15 h; (G) MsCl (2 equiv), DMAP, pyridine, 2.5 h. [b] Yield based on the amount of recovered starting material.

## Conclusions

In summary we have described the preparation and isolation of epoxides in high yields from hex-5-enopyranosides. Hydrolysis of these epoxides gives novel protected hexos-5-uloses with interesting bicyclic structures. Some novel reactions of the protected hexos-5-uloses were studied, and these gave, in some cases, septanoside derivatives. Application of the methodology to the synthesis of unprotected D-hexos-5-uloses, which are of interest as intermediates in the synthesis and biosynthesis of aza sugars and inositols, has been achieved, and the methodology has potential for the synthesis of other 1,5-dicarbonyl derivatives. Current work is concerned with further exploration of the synthetic potential of the hex-5-enopyranosides and their epoxides. In particular the syntheses of aza sugars and iduronic acids are being explored, and the biological activity of these compounds will be reported in due course.

## Experimental Section

**Epoxidations with Methyl(trifluoromethyl)dioxirane.**[21] 1,1,1-Trifluoroacetone (10 equiv) and $Na_2EDTA$ (50 mL of a $4.0 \times 10^{-4}$ M aq solution, 0.01 mol) were added to a cooled solution (0 °C) of the hex-5-enopyranoside (1 equiv) in MeCN. A mixture of oxone (5 equiv) and $NaHCO_3$ (7 equiv) was added in portions every 5 min for 1 h. The reaction was then stirred for the indicated time or worked up immediately and was poured into ice-cold water. The products were extracted with $CH_2Cl_2$ (3×). The combined extracts were dried ($MgSO_4$) and filtered, and the solvent was removed under diminished pressure.

**Methyl 2,3,4-Tri-*O*-acetyl-5,6-anhydro-5-hydroxy-α-D-glucopyranoside (19/20). (i)** *m*-Chloroperbenzoic acid (1.196 g, 5.3 mmol) was added over 30 min in small portions to a stirred mixture of **11** (2 g, 5.3 mmol) and 0.5 M $NaHCO_3$ (16.8 mL) in $CH_2Cl_2$ (120 mL).[16] The mixture was stirred at room temperature overnight, and the two phases were separated. The organic phase was dried ($Na_2SO_4$) and the solvent removed under diminished pressure. The residue was purified by chromatography using an EtOAc/petroleum ether gradient (1:4 to 1:1) to give recovered **11** (0.7 g) followed by **19** as a white solid (0.56 g, 27%): $[\alpha]^{20}_D$ +92.1° (*c* 0.152, $CHCl_3$); $^1$H NMR ($CDCl_3$, 270 MHz) $\delta$ 5.76 (apt t, 1H, $J$ = 9.9 Hz), 5.53 (d, 1H, $J$ = 9.9 Hz), 5.00 (m, 2H), 3.43 (s, 3H), 2.84 (d, 1H $J$ = 4.2 Hz), 2.53 (d, 1H, $J$ = 4.2 Hz), 2.10, 2.04, 2.03 (each s, each 3H); $^{13}$C NMR ($CDCl_3$) $\delta$ 170.4, 170.1, 169.7 (each s, each OAc), 98.5 (d), 79.1 (s), 71.1, 68.3, 66.8 (each d), 56.7 (q), 45.7 (t), 20.9, 20.8, 20.7 (each q); IR (KBr disk) $\nu$ 2940, 1750, 1372, 1217, 1040, 730 cm$^{-1}$; CI-HRMS *m*/*z* found 319.1029, required 319.1029 $[M + H]^+$.

(ii) 1,1,1-Trifluoroacetone (0.96 mL, 13 mmol), $Na_2EDTA$ (7.5 mL of a 0.4 mM aq solution), **11** (0.4 g), oxone (2.8 g, 6.5 mmol), and $NaHCO_3$ (0.64 g) were treated as described above, and reaction was carried out for 2 h and gave a 50:50 mixture of **19** and **20** (0.416 g, 99%) as a colorless syrup. Selected $^1$H NMR data for isomer **20**: $\delta$ ($CDCl_3$) 3.46 (s, 3H), 3.01 (d, 1H, $J$ = 4.5 Hz), 2.86 (d, 1H, $J$ = 4.5 Hz).

**Methyl 2,3,4-Tri-*O*-acetyl-5,6-anhydro-5-hydroxy-α-D-mannopyranoside (22/23).** (i) Alkene **12** (2.0 g, 6.62 mmol) was dissolved in a mixture of dichloromethane (66 mL) and 0.5 M aqueous sodium bicarbonate (20 mL); solid *m*-chloroperbenzoic acid (2.07 g, 6.62 mmol) was slowly added, and the solution was stirred at room temperature for 2 h, after which time the reaction did not proceed further (TLC analysis). The two phases were separated, and the organic phase was washed with 1 N sodium hydroxide (20 mL) and water (20 mL) and then dried ($Na_2SO_4$); the solvent was removed at room temperature under reduced pressure to yield a white clear oil (2.08 g) which NMR analysis revealed to be a mixture of **22** (61%), **23** (13%), and **12** (25%). TLC analysis indicated the epoxides had identical $R_f$ values (0.7; EtOAc/petroleum ether, 1:1). Chromatography (silica gel prepacked with EtOAc/petroleum ether/$Et_3N$, 100:10:1; eluant EtOAc/petroleum ether gradient, 1:10 to 1:0) gave recovered **12** (0.5 g, 25%) and **22** (clear oil, 0.74 g, 35%): $[\alpha]_D$ +19.0° (*c* 0.45, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 5.81 (d, 1H, $J$ = 10.5 Hz), 5.59 (dd, 1H, $J$ = 3.2, 10.5 Hz), 5.41 (dd, 1H, $J$ = 1.9 Hz), 4.78 (d, 1H, $J$ = 1.9 Hz), 3.42 (s, 3H), 2.85 (d, 1H, $J$ = 4.0 Hz), 2.57 (d, 1H, $J$ = 4.0 Hz), 2.17, 2.05, 2.01 (each s, each 3H); $^{13}$C NMR ($CDCl_3$) $\delta$ 170.4, 170.1, 169.7 (each s), 100.4 (d), 79.9 (s), 70.1, 67.4, 64.3 (each d), 56.4 (q), 46.4 (t), 21.0, 20.8, 20.7 (each q); IR ($CH_2Cl_2$ solution) $\nu$ 2937, 1751, 1489, 1433, 1373, 1246, 1221, 1162, 1118, 1071, 1020, 981, 957, 884, 844, 789, 728 cm$^{-1}$; CI-HRMS *m*/*z* found 336.1294, required 336.1294 $[M + NH_4]^+$. Anal. Calcd for $C_{13}H_{18}O_9$: C, 49.06; H, 5.70. Found: C, 48.76; H, 5.63.

(ii) Alkene **12** (0.66 g, 2.18 mmol) was dissolved in acetonitrile (20 mL) and $Na_2EDTA$ (0.4 mM, 11 mL). To this solution, vigorously stirred in an ice bath, was added 1,1,1-trifluoroacetone (2 mL, 10 equiv) through a precooled syringe, and then a mixture of oxone (6.7 g, 5 equiv) and sodium hydrogen carbonate (1.28 g, 7 equiv) was added in small portions over 60 min. After 1 h and 45 min, no more starting material was detected by TLC and the solution was worked up as described above and gave a white clear oil (0.65 g, 94%) which was a mixture of **22** (54%) and **23** (40%). The crude product was slowly eluted (EtOAc/petroleum ether gradient, 1:4 to 1:0) through a column of silica gel (prepacked with EtOAc/petroleum ether/$NEt_3$, 100:20:1) in an attempt to separate the two epoxides. However, only a 2:1 mixture of **22** and **23** was recovered (0.21 g, 30%).

NMR data for **23**: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 5.48−5.44 (overlapping signals, 2 H), 5.29 (dd, 1H, $J$ = 3.6, 2.7 Hz), 4.87 (d, 1H, $J$ = 3.6 Hz), 3.47 (s, 3H), 2.97 (d, 1H, $J$ = 4.8 Hz), 2.87 (d, 1H, $J$ = 4.8 Hz), 2.15 (s, 3H), 2.06 (s, 6H); $^{13}$C NMR ($CDCl_3$) $\delta$ 170.3, 169.9, 169.3 (each s), 99.8 (d), 80.3 (s), 69.1, 68.6, 66.3 (each d), 57.0 (q), 49.9 (t), 20.8−20.7 (3 s, each q).

**Methyl 2,3,4-Tri-*O*-benzyl-5,6-anhydro-5-hydroxy-α-D-glucopyranoside (24/25).** (i) Compound **13** (1.0 g, 2.23 mmol) was dissolved and vigorously stirred in dichloromethane (22 mL) and 0.5 M aqueous sodium bicarbonate (6.6 mL); *m*-chloroperbenzoic acid (0.7 g, 2.23 mmol) was slowly added, and after 45 min, no more starting material was detected by TLC and the two phases were separated. The organic phase was washed with 1 N sodium hydroxide (7 mL) and water (7 mL) and dried ($Na_2SO_4$); removing the solvent at room temperature under reduced pressure gave a white oily residue (1.04 g, 100%). NMR analysis of this crude product indicated it contained **24** (70%) and **25** (30%). TLC analysis revealed one spot ($R_f$ = 0.42; EtOAc/petroleum ether, 1:4). Chromatography (silica gel packed with EtOAc/petroleum ether/$NEt_3$, 10:100:1; gradient elution with EtOAc/petroleum ether, 1:10 to 1:1) gave a white solid which was a 10:1 mixture **24** and **25** (0.23 g, 24%): IR (KBr) $\nu$ 3086, 3062, 3030, 2906, 1879, 1742, 1605, 1496, 1453, 1360, 1285, 1210, 1167, 1099, 1036, 1003, 914, 740, 696 cm$^{-1}$; ES-HRMS *m*/*z* found 480.2389, required 480.2386 $[M + NH_4]^+$. Anal. Calcd for $C_{28}H_{30}O_6$: C, 72.71; H, 6.54. Found: C, 72.41; H, 6.46.

NMR data for **24**: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.39−7.24 (ms, 15H, aromatic H), 4.99, 4.85 (each d, 2H, $J$ = 10.8 Hz), 4.90, 4.61 (each d, 2H, $J$ = 11.6 Hz), 4.83, 4.69 (each d 1H, $J$ = 12.1 Hz), 4.64 (d, 1H, $J$ = 3.4 Hz), 4.29 (apt t, 1H, $J$ = 9.6 Hz), 3.89 (d, 1H, $J$ = 9.6 Hz), 3.61 (dd, 1H, $J$ = 9.6, 3.4 Hz), 3.40 (s, 3H), 2.65 (AB d, 2H, $J$ = 4.9 Hz); $^{13}$C NMR ($CDCl_3$) $\delta$ 138.8, 138.3, 137.9 (each s), 128.8, 128.3, 128.2 (each d), 99.9 (d), 80.5 (s), 80.0, 79.9, 75.8 (each d), 76.1, 75.4, 73.8 (each t), 56.6 (q), 45.7 (t).

NMR data for **25**: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.36−7.23 (m, 15H, aromatic H), 4.88−4.80 and 4.72−4.58 (each m, each 2H), 4.83 and 4.66 (AB d, 2H, $J$ = 11.6 Hz), 4.61 (d, 1H, $J$ = 3.8 Hz), 4.01 (apt t, 1H, $J$ = 9.5 Hz), 3.81 (d, 1H, $J$ = 9.4 Hz), 3.64 (dd, 1H, $J$ = 3.8 Hz), 3.42 (s, 3H), 3.15 (d, 1H, $J$ = 5.2 Hz), 2.81 (d, 1H, $J$ = 5.2 Hz); $^{13}$C NMR ($CDCl_3$) $\delta$ 138.9, 138.3, 138.2 (each s), 128.8−127.9 (15 signals, each d), 99.7 (d), 81.8 (s), 80.3, 79.5, 77.7 (each d), 76.2, 75.3, 74.0 (each t), 56.2 (q), 50.5 (t).

(ii) The alkene **13** (1.0 g, 2.23 mmol) was dissolved in acetonitrile (20 mL) and $Na_2EDTA$ (0.4 mM, 11 mL) and vigorously stirred in an ice bath; cold 1,1,1-trifluoroacetone (2 mL, 10 equiv) was poured into the solution through a precooled syringe, and then a mixture of oxone (6.83 g, 5 equiv) and sodium hydrogen carbonate (1.30 g, 7 equiv) was added in small portions over 60 min. After 1 h, no more starting material was detectable by TLC and the reaction was immediately worked up as described above and gave a white oil (1.1 g, 100%) which NMR analysis confirmed to be a mixture of **24** (30%) and **25** (70%). After column chromatography, only a 7:3 mixture of **24** and **25** was recovered (0.1 g, 10%), as well as **26** (white solid, 0.57 g, 57%).

**2,3,4-Tri-*O*-trimethylsilyl-1,6-anhydro-β-L-idopyranos-5-ulo-5-hydrate (16).** *m*-Chloroperbenzoic acid (0.129 g, 0.5 mmol) was slowly added to a stirred mixture of **9** (0.25 g, 0.5 mmol) and 0.5 M $NaHCO_3$ (1.9 mL) in $CH_2Cl_2$ over 30 min. The mixture was stirred at room temperature overnight, and then the two phases were separated. The organic phase was washed successively with 1 M NaOH and water and dried ($Na_2SO_4$), the solvent removed under diminished pressure, and the residue purified by chromatography (EtOAc/petroleum ether, 1:10, as eluant) to give the title compound (0.055 g, 22%): $[\alpha]^{20}_D$ −3.57° (*c* 0.224, $CHCl_3$); $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 5.20 (d, 1H, $J$ = 1.8 Hz), 4.14 (d, 1H, $J$ = 7.8 Hz), 3.65 (dd, 1H, $J$ = 1.8, 7.3 Hz), 3.59 (apt t, 1H, $J$ = 7.3 Hz), 3.54 (dd, $J$ = 7.3, 1.8 Hz), 3.26 (dd, 1H, $J$ = 1.8, 7.8 Hz); $^{13}$C NMR $\delta$ 103.2 (s), 101.0 (d), 77.5, 77.4 (each d), 68.6 (t), 0.5, 0.4, 0.2 (each q); IR (liquid film) $\nu$ 3396, 2957, 1642, 1391, 1252, 1094, 888, 844, 751 cm$^{-1}$; CI-HRMS m/z found 412.2007, required 412.2010 $[M + NH_4]^+$.

**Methyl 2,3,4-Tri-*O*-trimethylsilyl-α-D-manno-5-hydrato-5-ulo-1,5-pyranoside (17).** Alkene **10** (0.5 g, 1.27 mmol) was dissolved in acetonitrile (9.5 mL) and aqueous $Na_2EDTA$ (4.0 × 10$^{-4}$ M, 6.4 mL), the solution was cooled to 0 °C, and cold 1,1,1-trifluoroacetone (1.27 mL, 10 equiv) was added through a precooled syringe. To this vigorously stirred were added mixture oxone (3.81 g, 5 equiv) and sodium hydrogen carbonate (0.83 g, 7 equiv) in small portions over 60 min. After 30 min the TLC plate showed that **11** had been consumed and a unique spot ($R_f$ = 0.5; EtOAc/petroleum ether, 1:4). The reaction was quenched with ice-cold water (30 mL) at the end of the addition, and the product was extracted in dichloromethane (30 mL) and washed twice with cold water and dried ($MgSO_4$). The solvent was removed at room temperature under reduced pressure to yield a colorless oil identified as **17** (0.385 g, 71%): $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 5.83 (d, 1H, $J$ = 1.8 Hz), 4.77 (d, 1H, $J$ = 8.2 Hz), 3.94 (apt t, 1H, $J$ = 2.9 Hz), 3.83 (dd, 1H, $J$ = 2.9, 8.2 Hz), 3.81 (d, 1H, $J$ = 3.9 Hz), 3.50 (s, 3H), 3.47 (d, 1H, $J$ = 3.9 Hz), 2.00−1.60 (2 br s, 2H), 0.21, 0.17, 0.14 (each s, each 9H); $^{13}$C NMR ($CDCl_3$) $\delta$ 99.4 (s), 97.8 (d), 76.2, 69.9, 68.9 (each d), 64.5 (t), 56.8 (q), 0.3, 0.2, 0.0 (9 signals, each q).

**2,3,4-Tri-*O*-trimethylsilyl-1,6-anhydro-β-L-gulopyranos-5-ulo-5-hydrate (18).** Kugelrohr distillation of **17** (0.068 g, 0.16 mmol) at 0.1 mmHg in the bp range 100−110 °C gave the title compound (0.051 g, 0.12 mmol, 75%): $[\alpha]^{20}_D$ −0.4° (*c* 0.5, $CHCl_3$); $^1$H NMR ($CDCl_3$, 270 MHz) $\delta$ 5.04 (d, 1H, $J$ = 2.4 Hz), 3.86 (d, 1H, $J$ = 7.7 Hz), 3.70 (dd, 1H, $J$ = 1.5, 7.7 Hz), 3.58 (dd, 1H, $J$ = 4.2, 2.4 Hz), 3.49 (dd, 1H, $J$ = 7.7, 4.2 Hz), 3.08 (dd, 1H, $J$ = 7.7, 1.7 Hz), 0.01, −0.02 (each s, each 3H); $^{13}$C NMR ($CDCl_3$) $\delta$ 102.2 (d), 100.8 (s), 74.5, 72.9, 71.8 (each d), 66.4 (t), 0.5, 0.4, 0.2 (each q); IR (liquid film) $\nu$ 3424, 1957, 2902, 1735, 1251, 1122, 896, 841, 754 cm$^{-1}$; CI-HRMS *m*/*z* found 412.2006, required 412.2006 $[M + NH_4]^+$.

**2,3,4-Tri-*O*-acetyl-1,6-anhydro-β-L-idopyranos-5-ulo-5-hydrate (21).** Reaction of **11** (0.38 g, 1 mmol), 1,1,1-trifluoroacetone (1 mL, 0.01 mol), $Na_2EDTA$ (5 mL of a 4.0 × 10$^{-4}$ M aq solution), oxone (3 g, 5 mmol), and $NaHCO_3$ (0.65 g, 7 mmol) in MeCN (7.5 mL) for 15 h gave the title compound after chromatography using a short column of silica gel (0.152 g, 50%): $[\alpha]^{20}_D$ +34.8° (*c* 0.046, $CHCl_3$); $^1$H NMR ($CDCl_3$, 270 MHz) $\delta$ 5.46 (d, 1H, $J$ = 2.0 Hz), 5.40 (apt t, 1H, $J$ = 8.5 Hz), 5.14 (dd, 1H, $J$ = 2.0, 8.5 Hz), 4.91 (dd, 1H, $J$ = 2.0, 8.5 Hz), 4.60 (s), 4.16 (d, 1H, $J$ = 8.5 Hz), 3.51 (dd, 1H, $J$ = 8.5, 2.0 Hz), 2.04, 2.08, 2.12 (each s); $^{13}$C NMR $\delta$ 173.1, 170.9, 170.6 (each s), 103.1 (s), 99.0 (d), 74.7, 74.6, 74.5 (each d), 70.7 (t), 21.4, 21.3 (each q); IR (liquid film) $\nu$ 3379, 2917, 1731, 1369, 1225, 1041 cm$^{-1}$; CI-HRMS *m*/*z* found 322.1138, required 322.1140 $[M + NH_4]^+$.

**2,3,4-Tri-*O*-acetyl-1,6-anhydro-β-L-gulopyranos-5-ulo-5-hydrate (30).** A mixture of epoxides **19** and **20** (0.36 g, 1.13 mmol) was stirred in acetonitrile (15 mL) and deionized water (15 mL) at 60 °C for 90 min. The solvent was removed under reduced pressure (azeotroping with toluene). The crude product was purified by column chromatography (EtOAc/petroleum ether gradient, 1:1 to 1:0; silica gel prepacked with EtOAc/petroleum ether/$NEt_3$, 50:50:1) and gave **30** (0.30 g, 87%): $R_f$ = 0.6 (EtOAc/petroleum ether, 1:1); $[\alpha]_D$ −20.0° (*c* 0.2, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 5.45 (d, 1H, $J$ = 2.3 Hz), 5.35

(dd, 1H, $J$ = 4.8, 9.7 Hz), 5.25 (dd, 1H, $J$ = 1.5 Hz), 5.22 (dd, 1H, $J$ = 4.8, 2.3 Hz), 4.07 (d, 1H, $J$ = 8.3 Hz), 3.43 (dd, 1H, $J$ = 8.3 Hz), 2.14, 2.13, 2.01 (each s, each 3H); $^{13}$C NMR ($CDCl_3$) $\delta$ 172.7, 170.2, 169.8 (each s), 102.1 (s), 99.2 (d), 73.2, 69.5, 68.0 (each d), 66.7 (t), 21.0, 20.9, 20.7 (each q); IR ($CH_2Cl_2$ solution) $\nu$ 3588, 3053, 2987, 1754, 1423, 1373, 1265, 1230, 1056, 738, 705 cm$^{-1}$; CI-HRMS $m/z$ found 322.1136, required 322.1138 $[M + NH_4]^+$.

**2,3,4-Tri-*O*-benzyl-1,6-anhydro-*β*-L-idopyranos-5-ulose (26).** **13** (4.5 g, 0.01 mol), 1,1,1-trifluoroacetone (10 mL, 0.1 mol), $Na_2EDTA$ (50 mL of a 4.0 × 10$^{-4}$ M aq solution), oxone (30 g, 0.05 mol), and $NaHCO_3$ (6.51 g, 0.07 mol) in MeCN (70 mL) were reacted as described above for 12 h. Chromatography (EtOAc/petroleum ether gradient, 1:4 to 1:1) gave the title compound as a white solid (4.36 g, 95%): $[\alpha]^{20}_D$ +34.5° ($c$ 1.0, $CHCl_3$); mp 98−99 °C; $^1$H NMR ($CDCl_3$, 270 MHz) $\delta$ 7.22−7.34 (ms, 15H, aromatic), 5.26 (d, 1H, $J$ = 2.0 Hz), 4.61−4.94 (ms, 6H), 4.19 (d, 1H, $J$ = 8.0 Hz), 3.79 (apt t, 1H, $J$ = 8.0 Hz), 3.68 (dd, 1H, $J$ = 2.0, 8.0 Hz), 3.53 (dd, 1H, $J$ = 8.0, 2.0 Hz), 3.31 (dd, 1H, $J$ = 8.0, 2.0 Hz); $^{13}$C NMR $\delta$ 138.4, 138.2, 137.7 (each s, each aromatic C), 128.8−127.7 (18C, each d, each aromatic CH), 103.5 (s), 98.4 (d), 82.6 (d), 82.0 (d), 75.6, 74.7, 73.0 (each t), 68.5 (t); IR (solution in $CHCl_3$) $\nu$ 3356, 2323, 1453, 1344, 1208, 1067, 1003, 836, 754 cm$^{-1}$; CI-HRMS $m/z$ found 466.2290, required 466.2291 $[M + NH_4]^+$.

**2,3,4-Tri-*O*-benzyl-1,6-anhydro-L-gulopyranos-5-ulose (27).** Reaction of 1,1,1-trifluoroacetone (2 mL, 20 mmol), $Na_2EDTA$ (10 mL of a 4.0 × 10$^{-4}$ M aq solution), **14** (0.899 g, 2 mmol), oxone (6 g, 10 mmol), and $NaHCO_3$ (1.3 g, 14 mmol) in MeCN (15 mL) for 15 h gave **27** as a clear syrup (0.432 g, 48%) after chromatography (EtOAc/petroleum ether, 1:4): $[\alpha]^{20}_D$ +14.2° ($c$ 0.8, $CHCl_3$); $^1$H NMR ($CDCl_3$, 270 MHz) $\delta$ 7.32−7.27 (ms, 15H), 5.28 (d, 1H, $J$ = 2.0 Hz), 4.72 (m, 6H), 3.99 (d, 1H, $J$ = 9.0 Hz), 3.99 (dd, 1H, $J$ = 1.0, 9.0 Hz), 3.73 (dd, 1H, $J$ = 4.5, 9.0 Hz, H-3), 3.66 (dd, 1H, $J$ = 4.5, 2.0 Hz), 3.24 (dd, 1H, $J$ = 1.0, 9.0 Hz); $^{13}$C NMR ($CDCl_3$) $\delta$ 138.5, 138.0, 137.8 (each s), 128.8−127.5 (18C, each d), 102.6 (s), 99.4 (d), 81.4 (d), 78.5 (d), 75.0 (d), 75.2, 73.1, 73.0 (each t), 66.9 (t); IR (liquid film) $\nu$ 3421, 2929, 1454, 1364, 1260, 1112, 799, 697 cm$^{-1}$; CI-HRMS $m/z$ found 466.2230, required 466.2220 $[M + NH_4]^+$.

**2-*O*-Benzyl-3,4-di-*O*-isopropylidene-1,6-anhydro-*β*-L-talopyranos-5-ulose (28) and 2-*O*-Benzyl-3,4-di-*O*-isopropylidene-1,6-anhydro-α-D-galactopyranos-5-ulose (29).** Reaction of 1,1,1-trifluoroacetone (1.63 mL, 16.3 mmol), $Na_2EDTA$ (8.15 mL of a 4.0 × 10$^{-4}$ M aq solution), **15** (0.50 g, 1.63 mmol), oxone (4.9 g, 8.1 mmol), and $NaHCO_3$ (1.06 g, 11.4 mmol) in MeCN (11.4 mL) for 15 h gave an interconverting mixture of the title compounds as a clear syrup (0.27 g, 48%) after chromatography (EtOAc/petroleum ether, 1:5 to 1:1, gradient elution); CI-HRMS $m/z$ found 326.1606, required 326.1603 $[M + NH_4]^+$.

Selected NMR data for **28**: $^1$H NMR ($CDCl_3$, 270 MHz) $\delta$ 7.26−7.36 (ms, 5H), 5.38 (s, 1H), 3.36 (d, $J$ = 7.9 Hz), 1.53, 1.33 (each s, each 3H); $^{13}$C NMR ($CDCl_3$) $\delta$ 137.1 (s), 127.9−128.5 (3 d), 109.0 (s), 102.0 (s), 100.9 (d), 77.5, 76.6, 75.2 (each d), 72.2, 66.3 (each t), 26.0, 24.2, 21.9 (each q).

Selected NMR data for **29**: $^1$H NMR ($CDCl_3$, 270 MHz) $\delta$ 7.26−7.36 (ms, 5H, aromatic H), 5.42 (d, 1H, $J$ = 2.6 Hz), 4.71, 4.61 (each d, each 1H, $J$ = 12.2 Hz) 3.47 (dd, 1H, $J$ = 4.6, 2.6 Hz), 1.47, 1.40 (each s, each 3H); $^{13}$C NMR ($CDCl_3$) $\delta$ 137.4 (s), 127.9−128.5 (3 d), 111.7 (s), 101.1 (s), 100.1 (d), 78.7, 78.2, 77.5 (each d), 71.5, 69.1 (each t), 27.4, 26.2, 21.9 (each q).

**2,3,4-Tri-*O*-acetyl-5-*O*-*tert*-butyldimethylsilyl-1,6-L-anhydroidopyranos-5-ulose (31).** *tert*-Butyldimethylsilyl trifluoromethanesulfonate (0.59 mL, 2.4 mmol) was added dropwise to a solution of **21** (0.196 g, 0.65 mmol) and 2,6-lutidine (0.52 mL, 4.2 mmol) in anhydrous $CH_2Cl_2$ at −40 °C under a $N_2$ atmosphere. The reaction mixture was allowed to warm to room temperature and stirred for a further 1.5 h. Water and $CH_2Cl_2$ were then added, and the two phases were separated. The organic phase was washed with 5% $CuSO_4$ and water (2×) and dried ($Na_2SO_4$) and the solvent removed under diminished pressure. The residue was purified using column chromatography (gradient elution, EtOAc/petroleum ether, 1:10 to 1:4), affording the title compound as a clear syrup (0.17 g, 63%): $[\alpha]^{20}_D$ +12.3° ($c$ 1.46, $CHCl_3$); $^1$H NMR ($CDCl_3$, 270 MHz) $\delta$ 5.43 (d, 1H, $J$ = 1.8 Hz), 5.26 (apt t, 1H, $J$ = 8.4 Hz), 5.13 (dd, 1H, $J$ = 1.8 Hz), 4.89 (dd, 1H, $J$ = 1.8, 8.4 Hz), 4.18 (d, 1H, $J$ = 8.4 Hz), 3.39 (dd, 1H, $J$ = 1.8, 8.4 Hz), 2.06, 2.03, 1.99 (each s, each 3H), 0.82 (s, 9H), 0.16 (s, 6H); $^{13}$C NMR ($CDCl_3$) $\delta$ 170.3, 170.2, 169.7 (each s), 102.7 (s), 98.2 (d), 74.2, 73.7, 71.0 (each d), 69.7 (t), 25.4 (s), 17.7 (q), 0.43, 0.24 (each q); IR (liquid film) $\nu$ 2960, 2860, 1748, 1473, 1369, 1227, 1130, 1042, 842, 685 cm$^{-1}$; CI-HRMS $m/z$ found 436.2004, required 436.2002 $[M + NH_4]^+$.

**2,3,4-Tri-*O*-benzyl-5-*O*-acetyl-1,6-anhydro-*β*-L-idopyranos-5-ulose (32).** A catalytic quantity of DMAP (10 mg) was added to a solution of **26** (0.1 g, 0.2 mmol) in acetic anhydride (5 mL) and pyridine (5 mL). The mixture was stirred overnight. Water and EtOAc were added and the layers separated. The aq layer was further extracted with EtOAc. The combined organic extracts were washed with aq $NaHCO_3$ and water and dried ($MgSO_4$), and the solvent was removed under diminished pressure. Chromatography (EtOAc/petroleum ether gradient, 1:8 to 1:4) gave **26** as a clear syrup (0.073 g, 67%): $[\alpha]^{20}_D$ +42.3° ($c$ 1.0, $CHCl_3$); $^1$H NMR ($CDCl_3$, 270 MHz) $\delta$ 7.31−7.24 (ms, 15H), 5.35 (d, 1H, $J$ = 2.0 Hz), 4.89−4.62 (m, 6H), 4.35 (d, 1H, $J$ = 8.0 Hz), 4.31 (dd, 1H, $J$ 2.0, $J$ = 8.0 Hz), 3.83 (apt t, 1H, $J$ = 8.0 Hz), 3.80 (dd, 1H, $J$ = 8.0, 2.0 Hz), 3.63 (dd, 1H, $J$ = 8.0, 2.0 Hz), 2.00 (s, 3H); $^{13}$C NMR $\delta$ 168.0 (s), 138.3, 138.0, 137.7 (each s), 128.6−127.7 (18C, each d), 104.2 (s), 99.3, 82.5, 82.4, 80.4 (each d), 75.5, 74.9, 73.1 (each t), 68.1 (t), 21.6 (q); IR (liquid film) $\nu$ 2923, 1761, 1454, 1363, 1219, 1074, 737 cm$^{-1}$; CI-HRMS $m/z$ found 508.2346, required 508.2335 $[M + NH_4]^+$.

**2,3,4-Tri-*O*-benzyl-5-*O*-methyl-1,6-anhydro-*β*-L-idopyranos-5-ulose (33).** Iodomethane (0.16 g, 1.6 mmol) was added dropwise to a solution of **26** (0.35 g, 0.8 mmol) and sodium hydride (62 mg, 1.6 mmol) in anhydrous DMF at 0 °C under a $N_2$ atmosphere. The reaction mixture was stirred for 15 h. Water and EtOAc were added and the layers separated. The aq layer was further extracted with EtOAc. The organic extracts were combined and dried ($MgSO_4$), and the solvent was removed under diminished pressure. Chromatography (EtOAc/petroleum ether, 1:4) gave the title compound as a clear syrup (0.284 g, 79%): $[\alpha]^{20}_D$ +17.4° ($c$ 0.26, $CHCl_3$); $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.18−7.28 (ms, 15H), 5.18 (d, 1H, $J$ = 2.0 Hz), 4.83−4.56 (ms, 6H), 3.93 (d, 1H, $J$ = 8.0 Hz), 3.71 (apt t, 1H, $J$ = 8.0 Hz), 3.68 (dd, 1H, $J$ = 2.0, 8.0 Hz), 3.56 (dd, 1H, $J$ = 8.0, 2.0 Hz), 3.47 (dd, 1H, $J$ = 8.0, 2.0 Hz), 3.42 (s, 3H, OMe); $^{13}$C NMR ($CDCl_3$) $\delta$ 138.5, 137.9 (each s), 129.6−127.6 (18C, each d), 106.3 (s), 98.3, 82.7, 82.3, 81.3 (each d), 75.5, 74.4, 73.0, 63.5 (each t), 50.6 (q); IR (liquid film) $\nu$ 1651, 1453, 1365, 1260, 1098 cm$^{-1}$; CI-HRMS $m/z$ found 480.2387, required 480.2386 $[M + NH_4]^+$.

**2,3,4-Tri-*O*-benzyl-5-trifluoromethanesulfonyl-1,6-anhydro-*β*-L-idopyranos-5-ulose (34).** Trifluoromethanesulfonic anhydride (0.054 mL, 0.32 mmol) was added dropwise to a stirred solution of **26** (0.072 g, 0.16 mmol) and 2,6-lutidine (0.075 mL, 0.64 mmol) in $CH_2Cl_2$ (2 mL) at −40 °C under $N_2$. The reaction mixture was allowed to attain room temperature and stirred for a further15 h. The mixture was then diluted with $CH_2Cl_2$, washed successively with 5% $CuSO_4$ and water (2×), and dried ($Na_2SO_4$) and the solvent removed under diminished pressure. Chromatography (EtOAc/petroleum ether, 1:6, as eluant) gave recovered **26** (22 mg) followed by the title compound as a clear syrup (45 mg, 48%): $[\alpha]^{20}_D$ +15.4° ($c$ 1.0, $CHCl_3$); $^1$H NMR ($CDCl_3$, 270 MHz) $\delta$ 7.25−7.32 (ms, 15H), 5.42 (d, 1H, $J$ = 2.0 Hz), 4.87−4.56 (m, 6H), 4.37 (d, 1H, $J$ = 8.0 Hz), 4.08 (dd, 1H, $J$ = 2.0, 8.0 Hz), 3.94 (dd, 1H), 3.78 (apt t, 1H, $J$ = 8.0 Hz), 3.63 (dd, 1H, $J$ = 2.0, 8.0 Hz); $^{13}$C NMR $\delta$ 137.8, 137.3, 137.0 (each s, each aromatic C), 128.7−127.8 (18C, each d, each aromatic CH), 111.0 (s), 100.1, 82.1, 82.0, 81.5 (each d), 75.6, 75.3, 73.3 (each t), 67.5 (t); IR (liquid film) 2922, 1601, 1420, 1215, 1091, 799 cm$^{-1}$; CI-HRMS $m/z$ found 598.1728, required 598.1722 $[M + NH_4]^+$.

**2,3,4-Tri-*O*-benzyl-5-*O*-*tert*-butyldimethylsilyl-1,6-anhydro-*β*-L-idopyranos-5-ulose (35).** *tert*-Butyldimethylsilyl trifluoromethanesulfonate (0.23 mL, 1 mmol) was added dropwise to a stirred solution of **26** (0.3 g, 0.67 mmol) and 2,6-

lutidine (0.15 mL, 1.3 mmol) in $CH_2Cl_2$ (5 mL) under $N_2$ at −40 °C. The reaction mixture was allowed to warm to room temperature and stirred for a further 2 h. The solution was then diluted with $CH_2Cl_2$, washed with 5% $CuSO_4$ and water (2×), and dried ($Na_2SO_4$) and the solvent removed under diminished pressure. The title compound (0.22 g, 58%) was obtained as a clear syrup after chromatography (EtOAc/petroleum ether, 1:10); $[\alpha]^{20}_D$ +15.4° (*c* 1.0, $CHCl_3$); $^1$H NMR ($CDCl_3$, 270 MHz) $\delta$ 7.23−7.13 (ms, 15H, aromatic), 5.23 (d, 1H, $J$ = 2.0 Hz), 4.91−4.55 (m, 6H), 4.10 (d, 1H, $J$ = 8.0 Hz), 3.65 (apt t, 1H, $J$ = 8.0 Hz), 3.53 (dd, 1H, $J$ = 2.0, 8.0 Hz), 3.45 (dd, 1H, $J$ = 8.0, 2.0 Hz), 3.31 (dd, 1H, $J$ = 8.0, 2.0 Hz), 0.82 (s, 9H), 0.09 (s, 6H); $^{13}$C NMR ($CDCl_3$) $\delta$ 139.0, 138.4 (each s), 128.9−128.0 (18C, each d), 105.1 (s), 98.8, 84.9, 82.9, 82.4 (each d), 76.0, 75.3, 73.4, 73.3 (each t), 26.2 (q), 18.3 (q), 1.44, 0.43 (q); IR (liquid film) $\nu$ 2928, 1454, 1364, 1274, 1205, 1091, 859 cm$^{-1}$. CI-HRMS *m*/*z* found 580.3101, required 580.3094 $[M + NH_4]^+$.

**1-*O*-*tert*-Butyldimethylsilyl-2,3,4-tri-*O*-benzyl-*β*-D-xylo-hexoseptanosid-5-ulose (36).** *tert*-Butyldimethylsilyl trifluoromethanesulfonate (0.2 mL, 0.88 mmol) was added dropwise to a solution of **26** (0.2 g, 0.44 mmol) in pyridine (5 mL) at −40 °C under a $N_2$ atmosphere. After 3 h, water and EtOAc were added and the layers were separated. The aq layer was further extracted with EtOAc (2×), the combined organic layers were subsequently washed with 5% $CuSO_4$ (2×) and water (3×) and dried ($Na_2SO_4$), and the solvent was removed under diminished pressure. The residue was purified by chromatography using EtOAc/petroleum ether (1:10) to give **35** (97 mg, 38%) followed by the title compound as a clear syrup (40 mg, 16%): $[\alpha]^{20}_D$ +8.23° (*c* 0.158, $CHCl_3$); $^1$H NMR ($CDCl_3$, 270 MHz) $\delta$ 7.35−7.24 (ms, 15H), 4.79 (d, 1H, $J$ = 5.3 Hz), 4.77−4.44 (m, overlapping signals, 7H), 4.26 (d, 1H, $J$ = 18.0 Hz), 4.09 (d, 1H, $J$ = 18.0 Hz), 3.79 (apt t, 1H, $J$ = 7.3 Hz), 3.66 (dd, 1H, $J$ = 7.3, 5.3 Hz), 0.89 (s, 9H), 0.07 (s, 6H); $^{13}$C NMR ($CDCl_3$) $\delta$ 208.0 (s), 138.3, 137.9, 137.5 (each s), 128.5−127.7 (15C, each d), 100.3, 85.7, 83.1, 81.8 (each d), 74.7, 74.6, 72.9, 71.3 (each t), 25.7, 18.0, 1.11, 0.09 (each q); IR (liquid film) $\nu$ 2927, 1736, 1454, 1259, 1094, 837, 698 cm$^{-1}$; CI-HRMS *m*/*z* found 580.3091, required 580.3094 $[M + NH_4]^+$.

**2,3,4-Tri-*O*-benzyl-5-*O*-(2-bromobenzoyl)-1,6-anhydro-*β*-L-idopyranos-5-ulose (37) and 1-*O*-(2-Bromobenzoyl)-2,3,4-tri-*O*-benzyl-*β*-D-xylo-hexoseptanosid-5-ulose (38).** 2-Bromobenzoyl chloride (0.27 mL, 2.6 mmol) was added to a solution of **26** (0.29 g, 0.66 mmol) in pyridine (5 mL) at 0 °C under a $N_2$ atmosphere. After 12 h, water and EtOAc were added and the layers separated. The aq layer was further extracted with EtOAc (2×), the combined organic phases were subsequently washed with 5% $CuSO_4$ (2×) and water (3×) and dried ($Na_2SO_4$), and the solvent was removed under diminished pressure. Chromatography (EtOAc/petroleum ether, 1:10) gave the title compounds **37** (0.19 g, 45%) and **38** (0.1 g, 16%). Analytical data for **37**: $[\alpha]_D$ +50° (*c* 0.058, $CHCl_3$); $^1$H NMR ($CDCl_3$ $\delta$ 7.64 (ms, 19H), 5.40 (d, 1H, $J$ = 1.8 Hz), 4.75 (m, 6H), 4.51 (d ($J$ = 7.9 Hz) and dd ($J$ = 7.9, 1.8 Hz) overlapping, 2H), 3.95 (dd, 1H, $J$ = 7.9, 1.8 Hz), 3.88 (apt t, 1H, $J$ = 7.9 Hz), 3.69 (dd, 1H, $J$ = 7.9, 1.8 Hz); $^{13}$C NMR ($CDCl_3$) $\delta$ 162.8 (s), 138.3, 137.7, 137.6 (each s, each aromatic C), 134.7, 133.4, 131.9 (each d), 128.6−127.2 (20C, each d), 122.4 (s), 105.1 (s), 99.5, 82.5, 82.4, 80.4 (each d), 75.4, 74.9, 73.1 (each t), 68.19 (t); IR (liquid film) $\nu$ 2911, 1733, 1567, 1454, 1245, 1089, 740 cm$^{-1}$; CI-HRMS *m*/*z* found 648.1573, required 648.1596 $[M + NH_4]^+$.

Analytical data for **38**: $[\alpha]^{20}_D$ +17.7° (*c* 0.096, $CHCl_3$); $^1$H NMR ($CDCl_3$, 270 MHz) $\delta$ 7.25 (ms, 19H), 5.82 (d, 1H, $J$ = 5.1 Hz), 4.77 (d, 1H, $J$ = 6.5 Hz), 4.74−4.40 (ms, 6H), 4.36, 4.25 (each d, each 1H, $J$ = 17.0 Hz), 3.93 (apt t, 1H, $J$ = 6.5 Hz), 3.82 (apt t, 1H, $J$ = 6.5 Hz); $^{13}$C NMR ($CDCl_3$) $\delta$ 206.2, 163.9 (each s), 137.7, 137.2, 137.0 (each s), 134.6−127.2 (24C, each d), 122.4 (s), 97.2, 85.5, 80.0 (each d), 74.8, 74.5, 73.2 (each t), 72.9 (t, C-6); IR (KBr) $\nu$ 2300, 1742, 1590, 1497 cm$^{-1}$; ES-HRMS *m*/*z* found 648.1599, required 648.1596 $[M + NH_4]^+$.

**2,3,4-Tri-*O*-benzyl-5-*O*-methanesulfonyl-1,6-anhydro-*β*-L-idopyranos-5-ulose (39).** Compound **26** (0.25 g, 0.55 mmol) and DMAP (cat.) were dissolved in anhydrous pyridine (2.5 mL) under a $N_2$ atmosphere. The mixture was cooled to 0 °C, and methanesulfonyl chloride (0.086 mL, 1.1 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. Water and $CH_2Cl_2$ were added and the layers separated. The aq layer was further extracted with $CH_2Cl_2$ (3×). The combined organic extracts were washed with 5% $CuSO_4$ (2×) and water (3×) and dried ($Na_2SO_4$), and the solvent was removed under diminished pressure. Chromatography (EtOAc/petroleum ether, 1:4) gave the title compound as a clear syrup (0.184 g, 63%): $[\alpha]^{20}_D$ +12.8° (*c* 0.25, $CHCl_3$); $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 7.20−7.35 (ms, 15H), 5.39 (d, 1H, $J$ = 2.0 Hz), 4.60−4.94 (m, 6H), 4.31 (d, 1H, $J$ = 8.0 Hz), 4.20 (dd, 1H, $J$ = 2.0, 8.0 Hz), 3.90 (dd, 1H, $J$ = 2.0, 8.0 Hz), 3.75 (apt t, 1H, $J$ = 8.0 Hz), 3.59 (dd, 1H, $J$ = 2.0, 8.0 Hz), 3.15 (s, 3H); $^{13}$C NMR ($CDCl_3$) $\delta$ 138.5, 138.0, 138.9 (each s), 128.9−128.0 (18C, each d), 108.1 (s), 100.4, 82.9, 82.5, 82.3 (each d), 75.9, 75.3, 73.5 (each t), 68.4 (t), 42.2 (q); IR (film) $\nu$ 2952, 1454, 1371, 1191, 1069, 787 cm$^{-1}$; CI-HRMS *m*/*z* found 544.2005, required 544.2002 $[M + NH_4]^+$.

**2-*O*-Benzyl-3,4-di-*O*-isopropylidene-5-*O*-acetyl-1,6-anhydro-α-D-galactopyranos-5-ulose (40) and 1-*O*-(Acetyl)-*O*-benzyl-3,4-di-*O*-isopropylidene-α-L-arabino-hexoseptanosid-5-ulose (41).** Hexos-5-ulose **28/29** (0.22 g, 0.7 mmol) was dissolved in acetic anhydride (1 mL) and pyridine (1 mL), and the mixture was allowed to stand for 24 h. Excess reagents were removed using a rotary evaporator, and xylene (2 × 25 mL) was distilled from the residue. Chromatography (EtOAc/petroleum ether, 1:10 to 1:5, gradient elution) gave in order of elution **40** (50 mg, 20%) and **41** (0.12 g, 48%). A third fraction (70 mg, 28%) was obtained. $^1$H NMR spectral data indicated this fraction was a 1.5:1.0:0.5 mixture of 2-*O*-benzyl-3,4-di-*O*-isopropylidene-5-*O*-acetyl-1,6-anhydro-*β*-D-talopyranos-5-ulose ($\delta$ 6.12, d, $J$ = 3.5 Hz), **40**, and 1-*O*-(acetyl)-*O*-benzyl-3,4-di-*O*-isopropylidene-*β*-L-*arabino*-hexoseptanosid-5-ulose ($\delta$ 5.41, d, $J$ = 1.6 Hz).

Analytical data for **40**: $^1$H NMR ($CDCl_3$, 300 MHz); $\delta$ 7.26−7.36 (ms, 5H), 6.04 (d, 1H, $J$ = 7.8 Hz), 5.11 (d, 1H, $J$ = 8.5 Hz), 4.71 (dd, 1H, $J$ = 9.2 Hz), 4.88, 4.62 (each d, each 1H, $J$ = 11.7 Hz), 4.12, 4.27 (each d, each 1H, $J$ = 18.8 Hz), 3.63 (dd, $J$ = 9.2, 7.8 Hz), 2.02, 1.60, 1.44 (each s, each 3H); $^{13}$C NMR ($CDCl_3$) $\delta$ 206.2 (s), 169.6 (s), 137.9 (s), 128.6, 128.2, 128.1 (each d), 111.6 (s), 93.5, 80.8, 80.0, 77.8 (each d), 74.8, 68.4 (each t), 27.2, 25.2, 21.1 (each q); CI-HRMS *m*/*z* found 368.1708, required 368.1709 $[M + NH_4]^+$.

Analytical data for **41**: $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.26−7.36 (ms, 5H, aromatic H), 5.54 (d, 1H, $J$ = 1.2 Hz), 4.67 (dd, 1H, $J$ = 7.2, 1.5 Hz), 4.69, 4.61 (each d, each 1H, $J$ = 12.0 Hz), 4.40 (dd, 1H, $J$ = 1.5 Hz), 4.33 (d, 1H, $J$ = 8.2 Hz), 3.78 (dd, 1H, $J$ = 8.2, 1.5 Hz), 3.61 (s, 1H), 2.12 (s, 3H), 1.56, 1.34 (each s, each 3H); $^{13}$C NMR ($CDCl_3$) $\delta$ 168.0 (C=O), 137.4 (s), 128.8, 128.3, 128.1 (each d), 109.5, 104.6 (each s), 101.5 (d), 78.0, 77.2, 74.4 (each d), 72.5, 65.2 (each t), 26.1, 24.5, 21.9 (each q); CI-HRMS *m*/*z* found 368.1706, required 368.1709 $[M + NH_4]^+$.

**5-*O*-Methyl-1,6-anhydro-*β*-L-idopyranos-5-ulose (44).** Compound **33** (0.126 g, 0.27 mmol) and Pd−C (0.13 g) in EtOH (10 mL) were stirred in a Parr hydrogenation apparatus at 40 psi for 12 h. The reaction mixture was then filtered and the solvent removed under diminished pressure. Chromatography (EtOAc/MeOH, 3:1) gave **44** (0.041 g, 79%): $[\alpha]^{20}_D$ +13.3° (*c* 0.6, $CHCl_3$); $^1$H NMR ($D_2O$, 270 MHz) $\delta$ 5.21 (d, 1H, $J$ = 1.6 Hz), 3.88 (d, 1H, $J$ = 7.4 Hz), 3.75 (d, 1H, $J$ = 7.4 Hz), 3.56−3.42 (ms, 3H), 3.40 (s, 3H); $^{13}$C NMR ($D_2O$) $\delta$ 108.4 (s), 103.4, 77.0, 74.2 (each d), 67.2 (t), 54.0 (q); IR (liquid film) $\nu$ 2924, 2853, 2359, 1453, 1362, 1270, 1094, 697 cm$^{-1}$; CI-HRMS *m*/*z* found 210.0977, required 210.0976 $[M + NH_4]^+$.

**5-*O*-*tert*-Butyldimethylsilyl-1,6-anhydro-L-idopyranos-5-ulose (45).** Compound **35** (0.45 g, 0.8 mmol) and 10% Pd−C (0.45 g) in EtOH (20 mL) were placed in a hydrogenation apparatus overnight (50 psi). The resulting mixture was filtered and the solvent removed under diminished pressure. Chromatography of the residue (EtOAc/MeOH, 3:1) gave **45** as a white solid (0.165 g, 71%): $[\alpha]^{20}_D$ +45° (*c* 0.1, $CHCl_3$); $^1$H NMR ($CDCl_3$, 270 MHz) $\delta$ 5.31 (s, 1H), 4.04 (d, 1H, $J$ = 7.6

Hz), 3.60 (s, 3H), 3.31 (d, 1H, $J = 7.6$ Hz), 0.89 (s, 9H), 0.19, 0.18 (each s, each 3H); $^{13}$C NMR ($CDCl_3$) $\delta$ 103.7 (s), 100.7 (d), 75.9, 75.1, 74.7 (each d), 68.3 (t), 25.6 (q), 17.8 (q), −3.1, −3.2 (each q); IR (KBr disk) $\nu$ 3529, 3438, 2937, 1365, 1254, 1128, 857, 688 cm$^{-1}$; CI-HRMS *m/z* found 310.1681, required 310.1682 $[M + NH_4]^+$.

**D-*xylo*-Hexos-5-ulose (46).** (i) Tetrabutylammonium fluoride (0.5 mL, 0.5 mmol, 1 M in THF) was added to a solution of 5-*O*-*tert*-butyldimethylsilyl-1,6-anhydro-L-idopyranos-5-ulose (0.14 g, 0.5 mmol) in THF (10 mL), and the resulting yellow solution was stirred for 1 h. The solvent was then removed under diminished pressure and the residue purified by chromatograhy using a short column of silica gel (EtOAc/MeOH, 3:1, as eluant). The title compound was obtained as a clear oil (0.085 g, 100%): $[\alpha]^{20}_D$ −10.5° (*c* 0.43, $H_2O$); ES-LRMS *m/z* found 177, required 177 $[M - H]^-$. The $^1$H and $^{13}$C NMR (300 MHz, $D_2O$) data are in excellent agreement with those previously reported. The NMR data are complex due to interconverting isomers and have been assigned and discussed in detail previously.[25b]

(ii) The title compound was also prepared by heating a solution of **16** (30 mg, 0.08 mmol) in MeOH (3 mL) at reflux for 5 h. The solvent was removed under diminished pressure, and subsequent chromatography of the residue (EtOAc/MeOH, 3:1, as eluant) gave the title compound (13 mg, 85%).

**D-*lyxo*-Hexos-5-ulose (47).** Hemiketal **17** (0.280 g, 0.66 mmol) was dissolved in methanol (5 mL), and the solution was stirred at room temperature for 3 days, after which the solvent was removed under reduced pressure to yield **47** as a white solid (0.110 g, 94%): $[\alpha]_D$ −19.89° (*c* 0.19, $H_2O$); ES-LRMS *m/z* found 177 $[M - H]^-$, 355 $[2M - H]^-$. The $^1$H and $^{13}$C NMR (300 MHz, $D_2O$) data are in excellent agreement with those previously reported. The NMR data are complex due to interconverting isomers and have been assigned and discussed in detail previously.[25a]

**Acknowledgment.** We thank Professor Richard J. K. Taylor, the NMR Centre UCD, Enterprise Ireland (Grants Sc/97/547 and Sc/00/182), Limerick Co. Council (scholarship to P.M.E.), Dublin Corp. (scholarship to M.T.), and University College Dublin (Presidents award) for support, and the Health Research Board (Ireland) and Wellcome Trust for an equipment grant.

**Supporting Information Available:** Full details of the synthesis of hex-5-enopyranosides **9**−**15**, other epoxidations investigated, analytical data for alcohols obtained from reduction of **36** and **38**, $^1$H and $^{13}$C NMR and selected NOE spectra for all new compounds, and X-ray crystal structures of **19** and **26**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO016378C