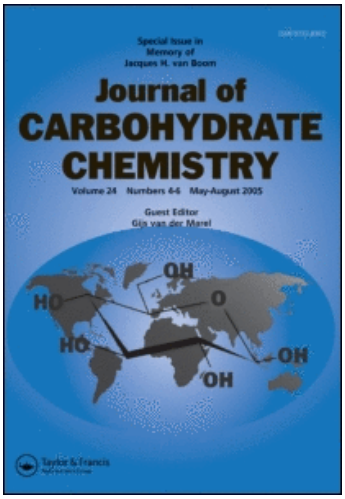

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AN IMPROVED METHOD FOR THE REGIOSELECTIVE OXIDATION OF STANNYLENE ACETALS AND DIMERIZATION OF THE α-HYDROXYKETONE PRODUCTS[1]

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ABSTRACT

Dibutylstannylene acetals, particularly those derived from terminal diols, were found to be oxidized regiospecifically to α-hydroxyketones in good to excellent yield by *N*-bromosuccinimide. One of the products, 3-deoxy-1,2-*O*-isopropylidene-α-D-*erythro*-hexofuranos-5-ulose (**8**), exists to about 20% in solution as a mixture of dimers. One of the dimers can be obtained as a solid and its structure was determined tentatively by a combination of NMR experiments and MM3 molecular mechanics calculations.

INTRODUCTION

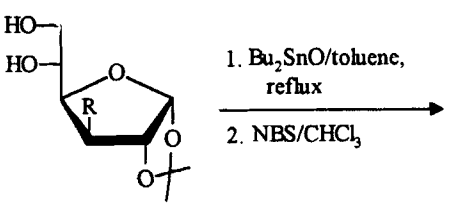
Dialkylstannylene acetals are readily prepared from diols or polyols by refluxing with dialkyltin oxide with azeotropic removal of water.[2] David showed in 1974 that dibutylstannylene acetals are oxidized by bromine at the speed of a titration.[3] The products of the reaction are α-hydroxyketones and normally only a single regioisomer is obtained.[4,5,6,7,8] The products are obtained in excellent yields for stannylene acetals derived from simple diols[3] but the yields from carbohydrate-derived diols are usually lower,[4,5,6,8] and those from terminal carbohydrate diols are often below 50%.[4] In

addition, if a base is not added to the reaction mixture the released hydrogen bromide causes the reaction to slow.[4,6] Rather unusual bases, such as tributyltin methoxide, have been found to be most effective.[4,6] Although the reaction has been considered to be a very promising method to convert diols regioselectively to α-hydroxyketones,[2,9] it has been employed in only a few syntheses.[6,10,11,12] Tributyltin ethers react similarly with bromine and it has been suggested that the yields are higher than with stannylene acetals.[7] However, more recent studies have found that for terminal diols the tributyltin ether method gives lower yields.[12]

We have been interested in understanding the causes of the regioselectivity obtained in reactions of stannylene acetals.[13] Because of the unexploited promise of this oxidation and because we were particularly interested in terminal carbohydrate-derived diols, we decided to examine oxidizing reagents other than bromine. *N*-bromosuccinimide (NBS) was found to be the best of those we studied. We report here the results of the oxidation of stannylene acetals with NBS and also consider the dimerization of the α-hydroxyketone products.

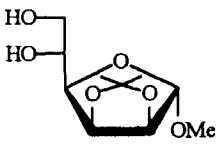
RESULTS AND DISCUSSION

Reactions. The diols used in this study were 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose (**1**), 1,2-*O*-isopropylidene-3-*O*-methyl-α-D-glucofuranose (**2**), 3-deoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranose (**3**), methyl 2,3-*O*-isopropylidene-α-D-mannofuranoside (**4**), and benzyl 4,6-*O*-benzylidene-α-D-galactopyranoside (**5**). All the diols were converted to their corresponding dibutylstannylene acetals by refluxing with one equivalent of dibutyltin oxide in toluene. The acetals were directly oxidized with NBS in chloroform at room temperature. In all cases single products were obtained. For the terminal or primary-secondary 1,2-diols, yields were excellent (compounds **1** and **2**, 90% and 95%, respectively) or good (compounds **3** and **4**, 84% and 81%, respectively). The secondary-secondary diol **5** was regioselectively oxidized to one product in 44% yield but 55% of the starting material **5** was recovered giving a yield of 97% based on consumed **5**. Conditions could not be found to get the reaction to go to completion.



1 R = OBn
2 R = OMe
3 R = H

6 R = OBn, 90%
7 R = OMe, 95%
8 R = H, 84%



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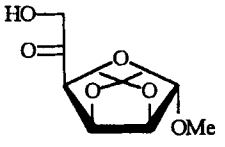

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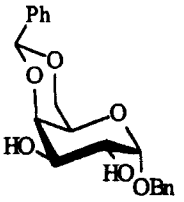

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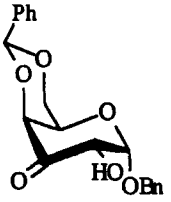

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Structures of the oxidation products were established primarily from their ^1H and ^{13}C NMR spectra, using COSY and HETCOR experiments to confirm assignments. The oxidation was highly regioselective in a consistent fashion. All of the terminal diols (**1-4**) gave α-hydroxyketones (**6-9**). Compound **5**, a 2,3-diol on a pyranose ring, gave the 2-hydroxy-3-ketone (**10**).

The products obtained are consistent with the idea that the reaction is initiated by the most nucleophilic oxygen in the stannylene acetal attacking the electrophilic oxidizing agent. Tin-119 NMR spectra of chloroform-*d* solutions of dibutylstannylene acetals of compounds **1** to **5** indicate that the acetals are present either as a single dimer (**1**, **2**, **4**,

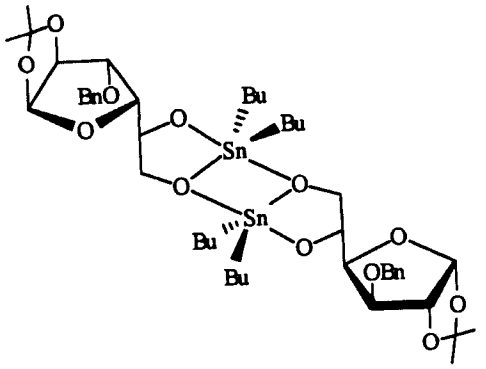

Fig. 1. The dimeric structure of dibutylstannylene acetal derived from compound **1**

5) (to the level of detection) or as a mixture in which the major dimer constitutes > 90% (**3**).[13,14] For **1** to **4**, the major dimer has O-5 dicoordinate,[14] for **5** O-3 is dicoordinate.[13,14] See Figure 1 for the structure of the dimer of **1**. Dicoordinate oxygens were found to be more nucleophilic in acylation and alkylation reactions.[13]

Dimer Formation. Oxidation of the dibutylstannylene acetal derived from diol **3** was complete almost instantaneously. TLC indicated that the reaction mixture contained one major product, the monomeric α-hydroxyketone **8**, plus a minor component with a much smaller R_F value that was later considered to be a mixture of dimeric structures based on the following information.

The major product was isolated by directly placing the reaction mixture on a flash column for purification. Despite the large difference in R_F values, the syrup that was isolated still contained the apparent impurity. The ^1H NMR spectrum indicated that the syrup was a mixture of **8** (major) and minor amounts of other complex components. Compound **8** was a monomeric α-hydroxyketone based upon a carbonyl absorption in its IR spectrum and a signal at 207 ppm due to a ketone carbon in its ^{13}C NMR spectrum.

On being kept under pentane for 12 h, the syrup deposited a colorless solid in high yield. Recrystallization from ethyl acetate and hexane afforded fine crystals (**8a**) that gave a very different ^1H NMR spectrum than that of **8** when the spectrum was recorded as soon as possible after the chloroform-*d* solution was prepared. However, the peaks assigned to **8** grew into the new spectrum with time (see Fig. 2) and after 24

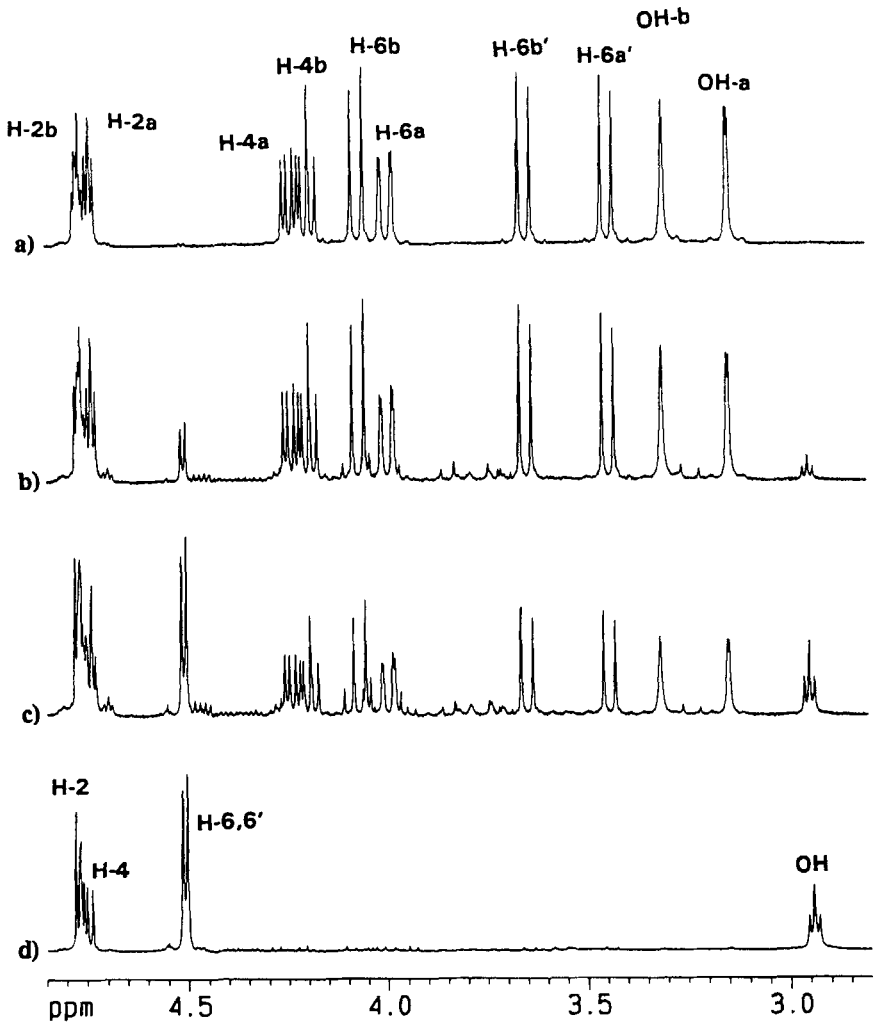

Fig. 2. Part of the 400.14 MHz ^{1}H NMR spectra of the crystalline dimer of compound **8** as a function of time: a) 5 minutes after making up the 0.1 M solution in chloroform-*d*, b) after 90 minutes, c) after 4 h, d) after 22.5 h.

h the spectrum was similar to that of the syrup obtained from the column. The presence of an equilibrium was confirmed by variable temperature measurements; in the ^{1}H and ^{13}C NMR spectra of samples that had been kept 2 h at 60 °C before recording, the signals assigned to compounds other than **8** had been reduced so that they were only just perceptible. Allowing the heated sample to sit for 24 h resulted in spectra identical to

the original spectra. The behaviour of the specific rotation of this compound provides further evidence for an equilibrium between monomer and dimer. The -30° $[\alpha]_D$ value measured in chloroform at 21 °C just after solution preparation from crystalline material gradually increased to a final value of -70°.

The NMR spectra recorded shortly after the crystalline material (**8a**) dissolved were consistent with it being a nonsymmetrical dimer of **8**. Both the ^1H and ^{13}C NMR spectra contained two sets of peaks having equal intensities. The only signal which occurred at the same chemical shift for both halves was that of C-1. A particularly noticeable difference from the spectra of the monomer occurred for the H-6 and H-6' signals; in the monomer, they were observed as either a singlet at 4.50 ppm or, if the sample was carefully dried, as a doublet due to coupling to the OH proton. In the dimer, an AX pattern and an AMX were observed for the two sets of H-6 and H-6' signals with doublets at 3.64 and 4.07 ppm coupled by -11.8 Hz and a doublet of doublets at 3.99 ppm and a doublet at 3.44 ppm coupled by -11.6 Hz. The chemical shift differences and coupling constants observed are typical of axial and equatorial protons in conformationally fixed 1,4-dioxane rings as expected in the dimer. The additional coupling of 2.1 Hz of the signal at 3.99 ppm was to an OH proton. The asymmetry in the dimer arises because the two new stereogenic hemiacetal centres must have opposite chirality if the two furanosyl groups are to be equatorial and the two new anomeric hydroxyl groups axial in the 1,4-dioxane ring; thus one new stereogenic center is *R*, the other *S*.

Assignment of which half of the dimer contains which stereogenic center can be made tentatively by means of a combination of molecular mechanics calculations and NMR experiments. In a COSY spectrum, the signals for H-3b and H-3b' at almost identical chemical shifts showed weak cross peaks with H-6b and H-6b' while the a-pairs did not show cross-peaks. In a NOSEY spectrum, the signal for H-4b showed a cross-peak with both H-6b and H-6b' but no cross-peaks to H-6 signals were observed for H-4a. Both observations allow the assignment of the pairs of H-6 signals to particular monomer units in the dimer. The NOSEY observation indicates that conformations in which H-4 is close to the H-6 hydrogens are more populated at the "b" end of the molecule.

TABLE. Conformations of Dimer **8a**

Conformer	Torsional Angles[a]				Energy[b]
	O-4a C-4a C-5a O-5a	O-4b C-4b C-5b O-5b	C-6a C-5a O-5a' H-OHa	C-6b C-5b O-5b' H-OHb	(kcal-mol^{-1})
1a	174.2	-61.6	33.0	-37.5	0.0
1b	173.7	-63.0	37.9	-153.6	0.22
1c	-172.8	-65.1	-74.0	-154.1	0.56
1d	-173.0	-63.7	-72.1	-35.2	0.17
2a	73.6	-61.6	41.5	-37.0	0.42
2b	72.3	-63.6	156.0	-39.1	0.48

a. Torsional angles (°); O-5 is in the 1,4-dioxane ring, O-5' is the OH O.

b. The energies reported are strain energies relative to the global minimum.

MM3 Molecular mechanics calculations were performed to try to evaluate the conformational properties of dimer **8a**. The program used was MM3(89),[15] modified to run on a 486 microcomputer. The parameters present in the program and an improved set of OCCO torsional parameters[16] were both tried; the results differed by < 0.2 kcal-mol^{-1}. Similarly, using the dielectric constant of chloroform (4.7) rather than the default value (1.5) had very little effect on the results. Numerical values reported are with the standard parameters and the default dielectric constant. The conformational space accessible was evaluated by first driving the two inter-ring torsional angles in 45° steps. Two rotamers were found to be > 2 kcal-mol^{-1} more stable than the rest. For each of these conformations, the effects of torsions about the two hemiacetal OHs were evaluated by driving the appropriate torsional angles in 120° steps. Of the 18 possible conformers, six were within 2 kcal-mol^{-1} of the overall minimum. These conformations were then fully minimized. The Table lists their torsional angles and strain energies with respect to the overall minimum. The conformations of the furanose rings were checked by

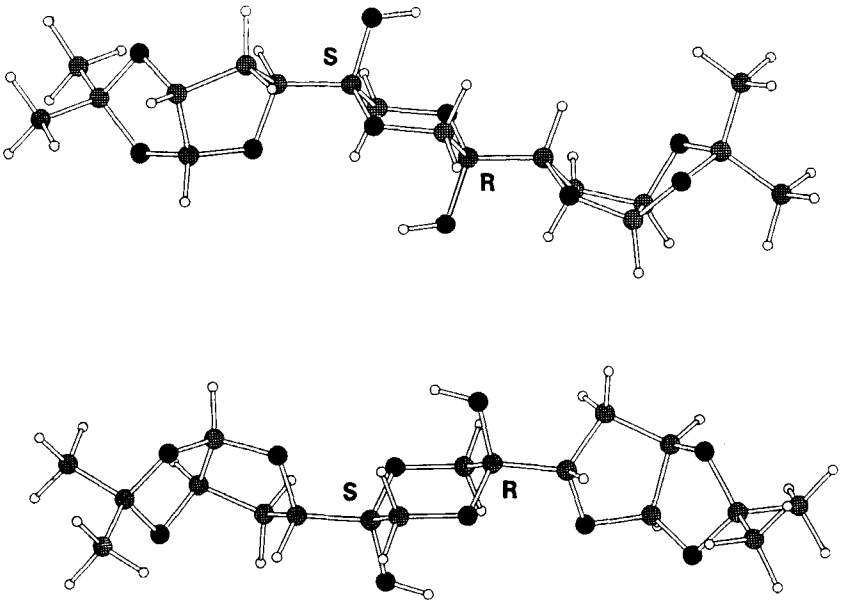

Fig. 3. Two of the minimum energy conformations of the crystalline dimer (**8a**): top, conformer 1a; bottom, conformer 2a. Oxygen atoms are represented by solid black circles, carbon atoms by checked circles, and hydrogen atoms by open circles. The positions of the new stereogenic centers are shown by the labels *S* and *R*. The "b" end of the dimer is on the left for both conformers.

arbitrarily starting with alternative geometries. Only one conformation of the furanose rings gave minimum energies for the overall conformations; a $^3T_4$ conformation which has the 1,4-dioxane ring at an equatorial position and the torsional angle at the position of the fused *O*-isopropylidene ring small (-13 to -13.6°).

The calculations indicate that only the rotamer with H-4 *gauche* to C-6 is significantly populated at the (*S*)-end of the central 1,4-dioxane ring. At the (*R*)-end of the central 1,4-dioxane ring, rotamers with H-4 *gauche* to C-6 and H-4 *anti* to C-6 are both significantly populated. A *gauche* relationship between H-4 and C-6 is necessary for H-4 to be within 3 Å of an H-6. On this basis, H-4 in the monomer unit containing the *S*-center will spend more time close to the H-6s. Hence, the NMR signals labelled b in the experimental section and elsewhere were assigned to the monomer unit having the new *S*-stereogenic center. Figure 3 shows two of the low energy conformations that have different rotameric orientations at the (*R*)-end of the 1,4-dioxane ring.

The spectra of the original syrup indicated that more than one dimer was present. In the region of the ^1H NMR spectrum where anomeric protons absorb, a single doublet and a set of two equal intensity doublets appeared in addition to signals assigned to **8** and **8a**. The single doublet could be due either to a symmetrical dimer or to the hydrated monomer. The pair of doublets must be assigned to a non-symmetrical dimer that could be another 1,4-dioxane derivative, a 1,3-dioxolane derivative or a mixed dimer with only one center as a hemiacetal. An integral of the spectrum of the syrup indicated that the monomer constituted 70 $\pm$ 5 % of the mixture; in the more dilute (0.1 M) sample obtained by allowing the dimer to equilibrate, the monomer made up 83 $\pm$ 5 % of the mixture.

There was no evidence for dimerization of any of the other α-hydroxyketones obtained here. Steric effects must play a major role in the stability of dimers relative to monomers. The absence of a substituent at C-3 in **8** allows it to dimerize to some extent.

Other α-hydroxycarbonyl compounds dimerize; both glycolaldehyde[17] and 1,3-dihydroxyacetone[18] exist as dimers having 1,3-dioxane rings in the solid. Glycolaldehyde and also glyceraldehyde equilibrate to complex mixtures containing monomer, 1,3-dioxane-ring-containing dimers, 1,3-dioxolane-ring-containing dimers and hydrated monomers in solvents containing water.[8, 17] The equilibrium mixture present for 1,3-dihydroxyacetone in water and in dimethylsulfoxide contained no dimer to the limit of observation on a 60 MHz NMR spectrometer.[18] Several carbohydrates containing α-hydroxyketones on pyranose rings have been observed to dimerize. Solutions of 2,3-*O*-isopropylidene-β-D-*threo*-hexo-2,4-diulopyranose are reported to contain 40% of a symmetric dimer which is pictured as having C_i symmetry.[8, 17] The structure shown is clearly wrong since the two halves of the dimer cannot be related by an S_2 axis if both halves are derived from D-fructose. Similarly, the C_i-symmetric structure shown for the dimer of 1,2-*O*-isopropylidene-β-D-*threo*-hexo-2,5-diulopyranose must also be incorrect.[8] Methyl β-L-*threo*-pentopyranosid-4-ulose is also reported to contain dimers of unspecified structure.[5] Dimers have also been obtained from carbohydrate-derived β-hydroxy carbonyl compounds[19] although the dimers of some β-hydroxy carbonyl carbohydrate derivatives are not present in aqueous solutions in appreciable concentrations.[20]

The unrecognized formation of dimers from carbohydrate-derived α-hydroxyketones appears to have had an impact on their synthetic utility. During the

synthesis of isopropylidenedioxytetrahydrofuran derivatives, Marco[21] tried to prepare compound **8** with two different sequences which had as their last steps removal of *t*-butyldimethylsilyl and pivaloyl groups from O-6. The last deprotection steps were reported to fail but we suspect that a complex mixture of dimer and monomer was obtained which could not be separated or identified. The same group reported the synthesis of compound **8** through bromolysis of the tributyltin ether but claimed that it was extremely unstable.[22] In our hands it is quite stable.

EXPERIMENTAL

General Procedures. Melting points were determined using a Fisher-Johns melting point apparatus and are uncorrected. TLC was performed on Silica Gel 60 (Merck, aluminum sheets). Separations or purifications were performed by "Dry-Column" Flash Chromatography (DCFC) on Silica Gel 60 PF-254 (Merck). ^1H and ^{13}C NMR spectra were recorded with Bruker AC 250F or AMX 400 spectrometer for solutions in $CDCl_3$ at 20 °C, except where specified, and chemical shifts are referenced to internal Me_4Si. Assignments of ^1H NMR spectra were made by first-order analysis using COSY experiments to confirm assignments where necessary; ^{13}C NMR spectra were assigned by HETCOR experiments. Specific rotations were determined with a Perkin-Elmer 141 polarimeter at 21 °C, and IR spectra were recorded on a Nicolet 205 FTIR spectrophotometer. Microanalyses were performed by Canadian Microanalytical Service Ltd., Vancouver, B. C. Molecular mechanics calculations were performed with the MM3(89) program modified to run on 386 and 486 microcomputers using an NDP Fortran compiler (version 4.0.2). Structures were drawn with the program ATOMS.

General methods for oxidation of dibutylstannylene acetals with *N*-bromosuccinimide. The diol (1 mmol) was refluxed with dibutyltin oxide (1 equiv) for 12 h in toluene (20 mL) in an apparatus for the continuous removal of water. The toluene was removed on a vacuum line at 20 °C and the residue was dried for 30 m under reduced pressure (0.1 torr). The residue was taken up in dry chloroform (10 mL) and *N*-bromosuccinimide (NBS, 1 equiv) was added. The stirred reaction mixture was monitored by TLC. The reaction was complete at times ranging from 2 to 30 m. The mixture was poured directly onto a column for separation using the eluent listed for each compound.

3-*O*-benzyl-1,2-*O*-Isopropylidene-α-D-*xylo*-hexofuranos-5-ulose (6). Oxidation of the dibutylstannylene acetal derived from 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose (**1**)[23] with NBS was finished within 5 m. The eluent for column separation was the mixture of hexane and ethyl acetate (from 4:1 to 2:1). Evaporation of solvent from the corresponding fractions afforded **6** (280 mg, 90%). Colorless crystals were obtained from ethyl acetate-hexane: mp 117-8 °C, lit.[24] 115-6 °C (hemihydrate); $[\alpha]_D^{21}$ -114.5° (*c* 1.00, chloroform), lit.[23] $[\alpha]_D^{20}$ -110.5° (*c* 1.13, chloroform, hemihydrate); IR (nujol) 3491 cm^{-1} (OH), 1725 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, 250.13 MHz) δ 7.18-7.34 (m, 5H, aromatic H), 6.05 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 4.82 (d, 1H, $J_{3,4}$ = 3.6 Hz, H-4), 4.60 (d, 1H, H-2), 4.57 (d, 1H, $J_{ArC\text{-}Ha,ArC\text{-}Hb}$ = -11.7 Hz, ArC-Ha), 4.52 (d, 1H, H-6), 4.48 (d, 1H, $J_{6,6'}$ = -20.4 Hz, H-6'), 4.47 (d, 1H, ArC-Hb), 4.31 (d, 1H, H-3), 2.87 (br, 1H, OH), 1.47 (s, 3H, CH_3-*endo*), 1.32 (s, 3H, CH_3-*exo*); ^{13}C NMR ($CDCl_3$, 62.90 MHz) δ 208.2 (C-5), 136.6 (C_{arom}), 128.6, 128.2, 127.7 (CH_{arom}), 112.7 (C_{acetal}), 106.0 (C-1), 84.5 (C-4), 83.4 (C-3), 81.7 (C-2), 72.6 (C_{Benzyl}), 68.3 (C-6), 26.9 ($CH_{3\ endo}$), 26.3 ($CH_{3\ exo}$).

Anal. Calcd for $C_{16}H_{20}O_6$: C, 62.33; H, 6.54. Found: C, 62.04; H, 6.37.

1,2-*O*-Isopropylidene-3-*O*-methyl-α-D-*xylo*-hexofuranos-5-ulose (7). Oxidation of the dibutylstannylene acetal derived from 1,2-*O*-isopropylidene-3-*O*-methyl-α-D-glucofuranose (**2**)[25] with NBS was finished within 5 m. Column chromatography (hexane:ethyl acetate from 4:1 to 2:1) afforded compound **7** (yield 95%) as a syrup: $[\alpha]_D^{21}$ -129.3° (*c* 1.30, chloroform), lit.[26] -92.5° (*c* 1, acetone); ^1H NMR ($CDCl_3$, 250.13 MHz) δ: 6.01 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 4.77 (d, 1H, $J_{3,4}$ = 3.7 Hz, H-4), 4.58 (d, 1H, H-2), 4.50 (d, 1H, $J_{6,6'}$ = -20.5 Hz, H-6), 4.41 (d, 1H, H-6'), 4.06 (d, 1H, H-3), 3.32 (s, 3H, OCH_3), 1.47 (s, 3H, CH_3-*endo*), 1.33 (s, 3H, CH_3-*exo*), lit.[4] chemical shifts agreed within 0.05 ppm, $J_{1,2}$ = 3.5 Hz, $J_{3,4}$ = 4 Hz; ^{13}C NMR ($CDCl_3$, 62.90 MHz) δ 208.0 (C-5), 112.6 (C_{acetal}), 105.9 (C-1), 85.7 (C-3), 84.4 (C-4), 81.0 (C-2), 68.1 (C-6), 58.3 (OCH_3), 26.9 ($CH_{3\ endo}$), 26.2 ($CH_{3\ exo}$).

3-Deoxy-1,2-*O*-isopropylidene-α-D-*erythro*-hexofuranos-5-ulose (8). Oxidation of the dibutylstannylene acetal derived from 3-deoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranose (**3**)[27] with NBS was finished in 1 m. Column separation (hexane:ethyl acetate from 4:1 to 2:1) afforded **8** (yield 84%) as a syrup: $[\alpha]_D^{21}$ 70.0° (*c* 1.30, chloroform);[28] IR ($CHCl_3$) 1724 cm^{-1} (s, C=O), 3515 cm^{-1} (m, OH); ^1H NMR ($CDCl_3$,

400.14 MHz) δ 5.91 (d, 1H, $J_{1,2}$ = 4.5 Hz, H-1), 4.77 (dd, 1H, $J_{2,3'}$ = 4.4 Hz, H-2), 4.75 (dd, 1H, $J_{3,4}$ = 5.3 Hz, $J_{3',4}$ = 11.0 Hz, H-4), 4.50 (d, 2H, $J_{6,OH}$ = 4.6 Hz, 2H-6), 2.94 (t, 1H, OH), 2.46 (dd, 1H, $J_{3,3'}$ = -13.7 Hz, H-3), 1.81 (ddd, 1H, H-3'), 1.51 (s, 3H, CH_3-*endo*), 1.36 (s, 6H, CH_3-*exo*), ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 209.1 (C-5), 112.1 (C_{acetal}), 106.1 (C-1), 80.6 (C-4), 79.6 (C-2), 65.8 (C-6), 36.4 (C-3), 26.7 ($CH_{3\ endo}$), 26.1 (2 $CH_{3\ exo}$). The syrup deposited a colorless solid on being kept under vacuum or under pentane. Recrystallization of the solid (**8a**) from ethyl acetate-hexane provided a very fine powder, a dimer of compound **8**: mp 119-22 °C; IR (Nujol) 3442 cm^{-1} (OH), no C=O absorption; ^1H NMR ($CDCl_3$, 400.14 MHz) δ[29] 5.86 (d, 1H, $J_{1a,2a}$ = 3.5 Hz, H-1a), 5.83 (d, 1H, $J_{1b,2b}$ = 3.5 Hz, H-1b), 4.77 (m, 1H, H-2b), 4.74 (m, 1H, H-2a), 4.24 (dd, 1H, $J_{3a,4a}$ = 4.4 Hz, $J_{3a',4a}$ = 11.0 Hz, H-4a), 4.19 (t, 1H, $J_{3b,4b}$ + $J_{3b',4b}$ = 15.2 Hz, H-4b), 4.07 (d, 1H, $J_{6b,6b'}$ = -11.8 Hz, H-6b), 3.99 (dd, 1H, $J_{6a,6a'}$ = -11.6 Hz, $J_{6a,OH-a}$ = 2.1 Hz, H-6a), 3.64 (d, 1H, H-6b'), 3.44 (d, 1H, H-6a'), 3.28 (s, 1H, OH-b), 3.13 (d, 1H, OH-a), 2.13-2.18 (m, 2H, H-3b and H-3b'), 1.98 (dd, 1H, $J_{3a,3a'}$ = -13.1 Hz, H-3a), 1.76 (ddd, 1H, $J_{2a,3a'}$ = 4.6 Hz, H-3a'), 1.50 (br, 6H, $CH_{3\ a+b}$-*endo*) 1.32 (br, 6H ,$CH_{3\ a+b}$-*exo*); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 112.0, 111.8 (C_{acetal} a,b), 105.7 (C-1a,b), 92.6, 92.0 (C-5a,b), 80.6 (C-2b), 80.2 (C-2a), 79.9 (C-4b), 79.7 (C-4a), 64.1 (C-6a), 62.2 (C-6b), 32.7 (C-3a), 32.3 (C-3b), 26.9, 26.8, 26.3, 26.2 (4 CH_3).

Anal. Calcd for $C_{18}H_{28}O_{10}$: C, 53.46; H, 6.98. Found: C, 53.42; H, 6.84.

Methyl 2,3-*O*-isopropylidene-α-D-*lyxo*-hexofuranosid-5-ulose (9). Oxidation of the dibutylstannylene acetal derived from methyl 2,3-*O*-isopropylidene-α-D-mannofuranoside (**4**)[30] with NBS was complete in 15 m. The eluents used for column separation were mixtures of hexane and ethyl acetate (from 19:1 to 2:1). Hydroxyketone **9** was obtained (yield, 81%) as a solid, which was recrystallized from ethyl acetate-hexane, giving colorless needles: mp 110-1 °C; $[\alpha]_D^{21}$ -20.3° (*c* 1.00, chloroform); IR (Nujol) 3500-3400 cm^{-1} (OH), 1727 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, 250.13 MHz) δ 5.04 (s, 1H, H-1), 5.03 (dd, 1H, $J_{3,4}$ = 4.1 Hz, $J_{2,3}$ = 5.8 Hz, H-3), 4.60 (d, 1H, H-4), 4.58 (d, 1H, H-2), 4.55 (dd, 1H, $J_{6,6'}$ = -20.1 Hz, $J_{6,OH}$ = 4.8 Hz, H-6), 4.45 (d, 1H, $J_{6',OH}$ = 4.0 Hz, H-6'), 3.35 (s, 3H, OCH_3), 3.03 (dd, 1H, OH), 1.43 (s, 3H, CH_3-*endo*), 1.28 (s, 3H, CH_3-*exo*); ^{13}C NMR ($CDCl_3$, 62.90 MHz) δ 206.8 (C-5), 113.2 (C_{acetal}), 107.7 (C-1), 84.1 (C-2), 83.6 (C-4), 81.0 (C-3), 67.9 (C-6), 55.1 (OCH_3), 25.8 (CH_{3endo}), 24.3 ($CH_{3\ exo}$).

Anal. Calcd for $C_{10}H_{16}O_6$: C, 51.72; H, 6.95. Found: C, 51.76; H, 6.90.

Benzyl 4,6-*O*-benzylidene-α-D-*xylo*-hexopyranosid-3-ulose (10). Oxidation of the dibutylstannylene acetal derived from benzyl 4,6-*O*-benzylidene-α-D-galactopyranoside (**5**)[13] with NBS was carried out for 20 m in chloroform. Column separation (hexane:ethyl acetate from 9:1 to 2:1) gave a white solid, compound **10**, (yield 44%) and starting material (55%). Compound **10** had mp 146-9 °C; $[\alpha]_D^{21}$ +141.0°; IR (Nujol) 3400-3260 cm^{-1} (OH), 1744 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, 250.13 MHz) δ 7.24-7.50 (m, 10H, aromatic H), 5.58 (s, 1H, acetal H), 5.40 (d, 1H, $J_{1,2}$ = 4.3 Hz, H-1), 4.97 (d, 1H, H-2), 4.72 (d, 1H, $J_{ArC\text{-}Ha,ArC\text{-}Hb}$ = -12.1 Hz, ArC-Ha), 4.63 (d, 1H, ArC-Hb), 4.54 (d, 1H, $J_{4,5}$ = 1.2 Hz, H-4), 4.32 (dd, 1H, $J_{5,6}$ = 2.30 Hz, $J_{6,6'}$ = -12.8 Hz, H-6), 4.11 (dd, 1H, $J_{5,6'}$ = 1.8 Hz, H-6'), 3.83 (m, 1H, H-5), 3.08 (br, 1H, OH); ^{13}C NMR ($CDCl_3$, 62.90 MHz) δ 200.8 (C-3), 136.9, 136.5 (C_{arom}), 129.4, 128.6, 128.4, 128.2, 127.9, 126.1 (CH_{arom}), 101.7 (C-1), 100.6 (C_{acetal}), 81.1 (C-4), 73.9 (C-2), 70.5 (C_{Benzyl}), 68.7 (C-6), 65.2 (C-5).

Anal. Calcd for $C_{20}H_{20}O_6$: C, 67.41; H, 5.66. Found: C, 67.25; H, 5.64.

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