Communications to the Editor

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REGIOSELECTIVE OXIDATION OF A β-L-ARABINOPYRANOSIDE *VIA* CYCLIC TIN INTERMEDIATE. FACILE SYNTHESIS OF 4-AMINO-4-DEOXY-L-ARABINOSE, AN AMINO-SUGAR FOUND IN LIPOPOLYSACCHARIDES OF SOME *SALMONELLA* R MUTANT STRAINS[1)]

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Stannylation of methyl β-L-arabinopyranoside with Bu_2SnO followed by brominolysis afforded methyl β-L-*threo*-pentopyranos-4-uloside regioselectively, which was characterized as the oxime. Hydrogenation of this gave methyl 4-amino-4-deoxy-β-L-arabinopyranoside which was identified by converting to the known N-acetyl-di-O-mesyl derivative.

KEYWORDS —— oxidation; brominolysis; dibutyltin oxide; 4-amino-4-deoxy-L-arabinose; amino-sugar; methyl β-L-*threo*-pentopyranos-4-uloside

Brominolysis of a stannylene derivative of a 1,2-glycol is known to give an α-ketol at the speed of a titration.[2)] On the other hand, we have recently shown that such stannylene derivatives can be formed regioselectively even in polyhydroxy compounds such as carbohydrates, thus achieving selective mono-acylation of carbohydrates without use of blocking-deblocking technique.[3)] These reports promted us to investigate the oxidation of carbohydrates *via* cyclic tin intermediate without blocking the other hydroxyl groups. This communication treats this problem for a β-L-arabinopyranoside.

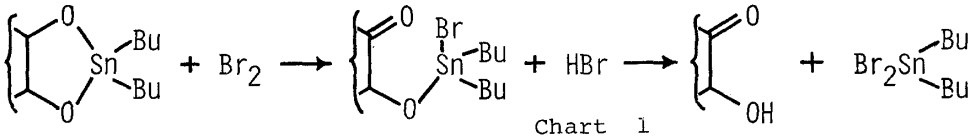


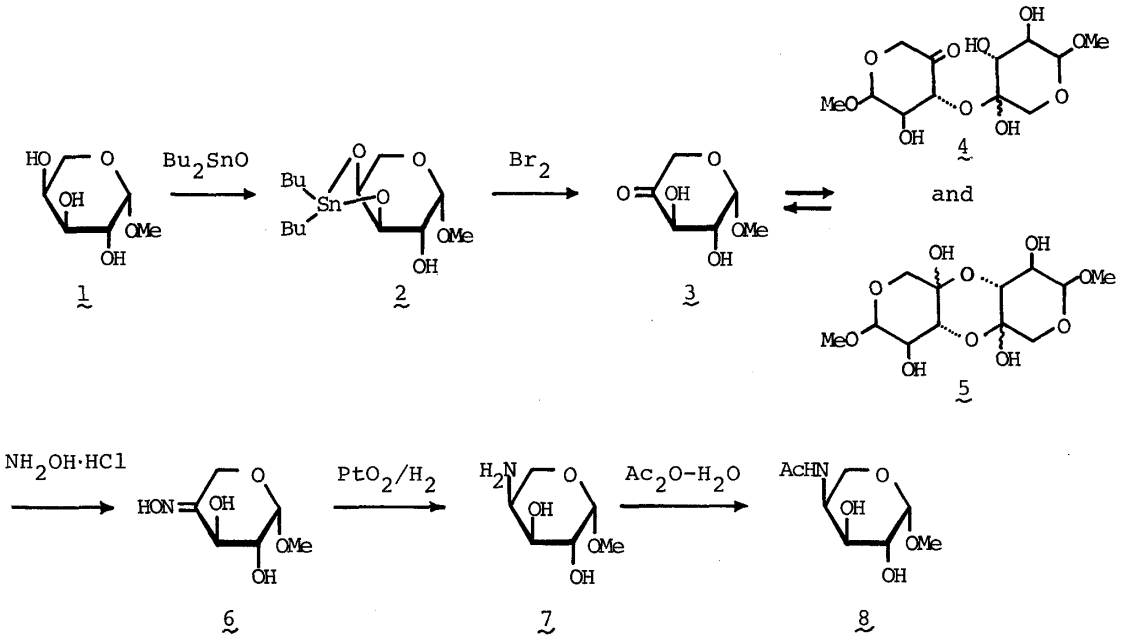
Chart 1

Stannylation of methyl β-L-arabinopyranoside (1) with an excess of Bu_2SnO (3 eq) in boiling methanol for 6 h followed by bromination in $CHCl_3$ with eq mol of Br_2 afforded a syrupy product in 60-70% yield. For the following reasons we conclude that the product is methyl β-L-*threo*-pentopyranos-4-uloside (3).

Although the product in the reaction mixture showed only one spot on TLC, after chromatography on silica gel it changed into two spots whose ^{1}H-NMR spectrum exhibited three OMe peaks (δ 3.30, 3.34, and 3.41) revealing that it is a mixture of at least three compounds. However, $NaBH_4$ reduction of this mixture gave methyl β-L-arabinopyranoside (1) and methyl α-D-xylopyranoside (identified by GC of the TMS derivative and TLC on HBO_3 impregnated plate) in a ratio of ca. 1 : 1, no other

product being found in the reaction mixture. These facts indicate that the ketonic function is at C-4. Corresponding to the ^{1}H-NMR evidence, GC of the TMS derivative showed three peaks. The GC-MS revealed that one is a monomeric (M^+ m/z 306) and the other two are dimeric forms (M^+ m/z 612)(Fig. 1). Therefore we conclude that the monomer rapidly dimerizes to 4 and/or 5, all of which behave as a monomer (3) on hydride reduction.

Treatment of the above mixture with hydroxylamine (3 h, in MeOH) gave an oxime (6),[4] mp 138-139°C, as a single product, which was also obtained in 57% yield from methyl β-L-arabinopyranoside (1) by the above described three successive treatments without isolation of the intermediates.



1 2 3 4 5 6 7 8 9

Chart 2

Catalytic hydrogenation of the oxime (6) over PtO_2 in AcOH converted it stereoselectively to methyl 4-amino-4-deoxy-β-L-arabinopyranoside (7), whose corresponding amino-sugar, 4-amino-4-deoxy-L-arabinose, is found in the lipopolysaccharides of some Salmonella R mutant strains.[5] Since the compound (7) was a syrup, it was characterized by converting to the crystalline N-acetyl-di-O-mesyl derivative (9),[6] mp 162-163°C, by N-acetylation followed by O-mesylation of the resulting N-acetate (8). The product (9) was completely identical with the sample (lit. mp 158-159°C [7]) prepared from methyl α-D-xylopyranoside by the known procedure.[7]

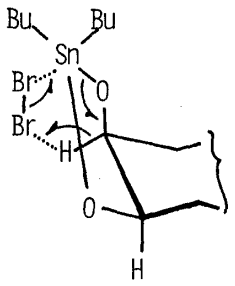


Chart 3

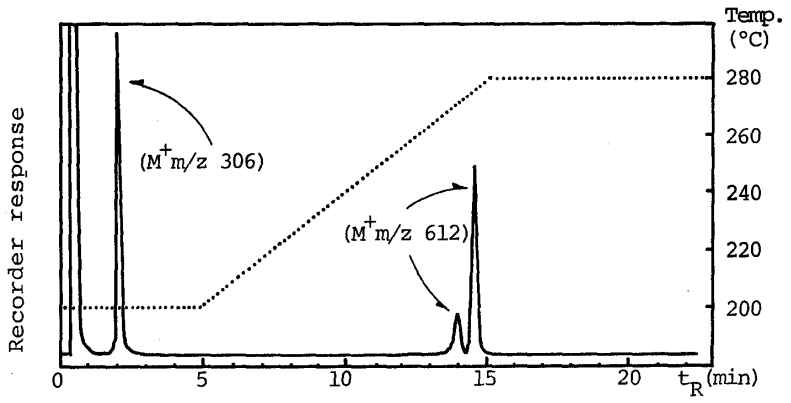


Fig. 1 Gas Chromatogram of Methyl β-L-threo-Pentopyranos-4-uloside as TMS Derivative

Column: 1.5% OV-1 on Shimalite W (1m x 3mm i.d.)

It must be noted that brominolysis of the stannylene intermediate (2) caused oxidation only at C-4, whereas acylation of the same intermediate exclusively gave 3-O-acylate.[3] We are tentatively considering the cyclic mechanism shown in Chart 3 for this oxidation, which explains why only the axial hydroxyl group was oxidized.

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2) a) S. David, C. R. Acad. Sci., 278(C), 1051(1974); b) S. David and A. Thieffry, J. Chem. Soc., Perkin Trans. I, 1979, 1568.

3) Y. Tsuda, Md. E. Haque, and K. Yoshimoto, Chem. Pharm. Bull., 31, 1612(1983).

4) 6: Colorless needles from AcOEt. IR(ν_{max}^{KBr} cm^{-1}): 3300, 1640. ^{1}H-NMR(pyr-d_5): δ 5.31(1H, d, J=14.5 Hz, C_5-H), 5.22(1H, d, J=2.8 Hz, C_1-H), 5.14(1H, d, J=8.2 Hz, C_3-H), 4.66(1H, d, J=14.5 Hz, C_5-H), 4.36(1H, dd, J=2.8 and 8.2 Hz, C_2-H), 3.49(3H, s, OCH_3). Anal. Calcd for $C_6H_{11}NO_5$: C, 40.68; H, 6.26; N, 7.91. Found: C, 40.52; H, 6.22; N, 7.78.

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6) 9: IR(ν_{max}^{KBr} cm^{-1}): 3440, 1655, 1548. ^{1}H-NMR($CDCl_3$): δ 6.36(1H, d, J=8.8 Hz, -NH-), 5.12(1H, dd, J=4.1 and 10 Hz, C_3-H), 5.00(1H, d, J=3.5 Hz, C_1-H), 4.67(1H, dd, J=3.5 and 10 Hz, C_2-H), 4.60-4.48(1H, m, C_4-H), 4.02(1H, dd, J=2 and 12.5 Hz, C_5-H), 3.56(1H, dd, J=2 and 12.5 Hz, C_5-H), 3.47(3H, s, OCH_3), 3.16(6H, s, $-SO_2CH_3$ x 2), 2.09(3H, s, -OAc).

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