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Preliminary communication

The stereochemistry of the reduction of 1,6-anhydro-3,4-dideoxy-β-D-*glycero*-hex-3-enopyranos-2-ulose (levoglucosenone) with lithium aluminium hydride

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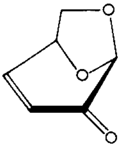
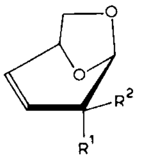
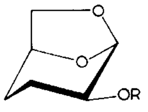
Shafizadeh and Chin have recently reported[1] a laboratory-scale preparation of 1,6-anhydro-3,4-dideoxy-β-D-*glycero*-hex-3-enopyranos-2-ulose (levoglucosenone) (**1**) and have described several additions to the carbonyl group of **1**. We have carried out related work, but disagree with the configurational assignments made by Shafizadeh and Chin[1] for some of their products. For instance, they suggested that reduction of **1** with lithium aluminium hydride yields principally (84%) 1,6-anhydro-3,4-dideoxy-β-D-*erythro*-hex-3-enopyranose (**2**), whereas we have assigned this product as 1,6-anhydro-3,4-dideoxy-β-D-*threo*-hex-3-enopyranose (**3**) on the basis of the following chemical evidence.

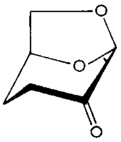

1



2 R1 = OH, R2 = H
3 R1 = H, R2 = OH
4 R1 = H, R2 = OTs
8 R1 = Me, R2 = OH
9 R1 = OH, R2 = Me



5 R = Ts
7 R = H


6

The enol **2** {m.p. 53–54°, $[\alpha]_D$ −236° (*c* 1, chloroform)} has been prepared by two unequivocal routes by Köll *et al.*[2], who converted it into the C-2 epimer **3** {m.p. 65–66.5°, $[\alpha]_D$ −35.3° (*c* 1, chloroform)} by an oxidation–reduction($NaBH_4$) sequence. We find that reduction of **1** with lithium aluminium hydride in ether affords a product (> 80%) having m.p. 67–69°, $[\alpha]_D$ −34° (*c* 1, chloroform), which is clearly **3**. Toluene-*p*-sulphonylation of **3** gave **4**, m.p. 74–75°, $[\alpha]_D$ −41° (*c* 1, chloroform), which, on catalytic hydrogenation of the carbon–carbon double bond, yielded 1,6-anhydro-3,4-dideoxy-2-*O*-

toluene-*p*-sulphonyl-β-D-*threo*-hexopyranose (**5**), m.p. 85–86°, [α]$_D$ –80° (*c* 1, chloroform). Compound **5** was also obtained by reduction of 1,6-anhydro-3,4-dideoxy-β-D-*glycero*-hexopyranos-2-ulose[3] (**6**) with lithium aluminium hydride and sulphonylation of the resulting alcohol **7**. The sulphonate **5** has been prepared independently by Czech workers[3,4], by routes that leave little doubt as to the configuration at C-2; lit.[4], m.p. 83–85°, [α]$_D$ –82° (*c* 0.66, chloroform)*. The foregoing evidence establishes that reduction of **1** with lithium aluminium hydride gives principally **3**, arising from attack of hydride ion on the less-hindered side of the carbonyl group. The absence of spin coupling between H-1 and H-2 was cited by Shafizadeh and Chin[1] as evidence for the "*trans* disposition" of these atoms in the product that they obtained on reduction of **1** with lithium aluminium hydride. However, Köll *et al.*[2] observed small spin-couplings between H-1 and H-2, and between H-1 and H-3, in the ^{1}H-n.m.r. spectra of **2** ($J_{1,2}$ 1.6, $J_{1,3}$ 1.8 Hz) and **3** ($J_{1,2}$ 2.5, $J_{1,3}$ 2.2 Hz). The small couplings measured are compatible with the structures assigned. Finally, we point out that the reductions of **1** and **6** with sodium borohydride give **3**[2] (95%) and **7**[3] (89%), respectively.

Such Grignard reagents as methylmagnesium iodide would also be expected to add from the less-hindered side of the carbonyl group of **1**, to yield **8** rather than **9**. This is contrary to the findings recently reported[1].

New compounds gave elemental analyses and spectroscopic data compatible with the structures assigned.

ACKNOWLEDGMENTS

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REFERENCES

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*The corresponding β-D-*erythro* derivative has m.p. 84–86°, [α]$_D$ –42° (*c* 0.8, chloroform)[4]; although the melting points of the two sulphonates are virtually identical, the [α]$_D$ values readily distinguish between them.