Preliminary communication

An efficient and regioselective synthesis of acyclic C-nucleosides from mesoionic compounds

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During the past few decades, much effort has been directed toward the development of synthesis routes to C-nucleosides, and 1,3-dipolar cycloadditions to carbohydrate dipolarophiles constitute an easy and versatile pathway¹⁻³. Although data on the reactivity of mesoionic heterocycles⁴⁻⁷ are abundant, to our knowledge, there has been no report on cycloadditions with sugar electron-attracting olefins and we now report on this topic.

3-Methyl-2-(4-nitrophenyl)-4-phenyl-1,3-oxazolium-5-olate⁸ (1) reacted regioselectively with (*E*)-3,4,5,6,7-penta-*O*-acetyl-1,2-dideoxy-1-*C*-nitro-D-galacto-(2) and -D-manno-hept-1-enitol⁹ (3) (acetic anhydride, 7 days, room temp.) to give the pyrrole derivatives 4[†] {69%; m.p. 150–152°, $[\alpha]_D - 78°$ (c 0.5, chloroform)} and 5 {65%; m.p. 84–86°, $[\alpha]_D + 53°$ (c 0.5, chloroform)}, respectively, presumably via 6 which loses carbon dioxide and nitrous acid¹⁰, and aromatises.

The structures of 4 and 5 were established through the selective irradiation of phenyl protons and subsequent magnetisation transfer to H-4 (\sim 12%). Explanation of the regiochemical course of this reaction requires further study.

Deacylation of 4 and 5 with methanolic sodium methoxide gave the acyclic C-nucleosides 1-methyl-2-(4-nitrophenyl)-3-(D-galacto- (6) {66%; m.p. 168-170°, $[\alpha]_D - 67^\circ$ (c 0.5, pyridine)} and 3-(D-manno-pentitol-1-yl)-5-phenylpyrrole (7) {73%; m.p. 98-100° (dec.), $[\alpha]_D - 53^\circ$ (c 0.5, ethanol)}, respectively, and the oxidative degradation of the pentahydroxypentyl chain of these compounds yielded the 3-formyl derivative 8, m.p. 148-149° (from ethanol).

The structures assigned to 4-8 accord with the spectral data (u.v., i.r., ¹H-and ¹³C-n.m.r.).

The above C-3 pyrrole nucleosides, now available from accessible mesoionic compounds, were obtained¹¹ previously by reaction of 1-alkyl(aryl)amino-1-deoxy-

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^{*}Satisfactory elemental analyses were obtained for 4-7.

D-fructoses with 1,3-dicarbonyl compounds. The scope and limitations of the new procedure are being studied further.



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