x-O-*n*-alkyl-itols. Substrate Structure and Alkyl Chain Position Influences on Their Liquid Crystalline Properties

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We prepared the hereafter series of x-O-*n*-alkyl galactitol, glucitol, mannitol and xylitol derivatives by reducing the corresponding x-O-*n*-alkyl-monosaccharide precursors.

Alkyl chain is noted $R = n - C_nH_{2n+1}$ with $n = 6$ to 12. Studied parameters are: length (n) and position (x) of alkyl chain number and orientations of hydroxyle groups.

The liquid crystalline phase studies show, as for their monosaccharidic precursors, that transition phase temperatures increase either with the alkyl chain length or with the OH group number increasing. Nevertheless, the X-position of the alkyl chain and the relative OH group orientations have generally higher influence than those observed for their heterocyclic analogs.

Sugar Nitronates: Versatile Intermediates for the Preparation of Chiral Bicyclic Systems

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Recently we have disclosed an asymmetric variant of the tandem [4 + 2]/[3 + 2] cycloaddition of nitroalkenes starting from a carbohydrate-appended heterodiene. Its reaction with ethyl vinyl ether (EVE) gave rise to a single diastereoisomer in 86% yield and whose structure was unequivocally determined by X-ray diffractometry. Our previous attempts, however, to isolate the intermediate nitronates were unsuccessful. We reasoned that such elusive species could be trapped *in situ* in the presence of a second dipolarophile, thereby enabling the preparation of diversely functionalized bicyclic systems. With these premises we have now performed asymmetric cycloadditions with EVE and an electron-withdrawing alkene such as methyl acrylate, acrylonitrile, or methyl vinyl ketone in ethanolic solution. The latter alkenes captured the sugar nitronate releasing the corresponding cycloadducts as crystalline solids in high yields. The reactions are regiospecific, exhibit a pronounced facial diastereoselectivity, and the major products can be obtained as pure diastereoisomers by recrystallization. As expected for an inverse electronic demand cycloaddition, the deficient alkenes alone did not react with the nitroalkene. This ensures that the initial Diels-Alder reaction will always occur with the electron-rich vinyl ether.

Synthesis and Hydrogenolysis of Dioxolane Type Diphenylmethylene and Fluoren-9-ylidene Carbohydrate Acetals Containing a Neighbouring Substituted Hydroxyl Function

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Hydrogenolysis of dioxolane-type diphenylmethylene and fluoren-9-ylidene acetals containing a free OH group in the vicinity of the *equatorial* side of the dioxolane ring resulted exclusively in *axial* diphenylmethyl or fluoren-9-yl ethers with chloroalane (AlH_2Cl) as the reagent.

Series of dioxolane-type diphenylmethylene and fluoren-9-ylidene acetals of hexoses containing adjacent *O*-alkyl, deoxy or hydroxy functions were prepared and hydrogenolysed with the $LiAlH_4$-$AlCl_3$ reagent. The hydrogenolysis resulted in all cases a mixture of the corresponding *axial* and *equatorial* ethers.

The observed direction of ring-cleavage was discussed.

Synthesis of α,β-unsaturated Lactones Linked to Sugars. Configurational Determination by N.O.E.

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In this work we present the synthesis of bioactive sugar derivatives containing in their structure an α,β-unsaturated lactone. The spirolactones were synthesised by a Reformatsky type reaction of the appropriate carbonyl compounds with ethyl bromomethylacrylate and activated zinc.

The configuration of the new stereogenic centre was determined by N.O.E. experiments.

Synthetic Approach to Pyrazole Sugar Derivatives

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In this work we report the synthesis of the pseudo-C-nucleosides by two different procedures. The starting material used was a pentodialdofuranose and the chain elongation was accomplished by Reformatsky and Wittig reactions. Construction of the pyrazole ring was possible by reaction with a hidrazine derivative followed by cyclization or by 1,3-dipolar cycloaddition with diazometane and treatment with chlorine.

The bioactivity of the compounds was tested against *Musca Domestica* and the results obtained show that they produce some effect in their nervous system.

Synthesis of Angucycline Antibiotics Bearing C-glycosidically Linked Oligosaccharides

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The quinoide angucycline antibiotics form an interesting group of natural products due to their broad spectrum of biological activities which include antibacterial, cytostatic, and enzyme inhibiting effects as well as activity in the inhibition of platelet aggregation. A large number of angucyclines bear a *C*-