Addition of Nitryl Iodide to Unsaturated Carbohydrate Derivatives

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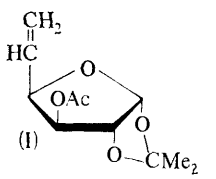
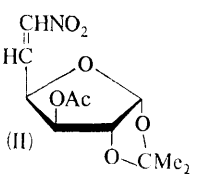
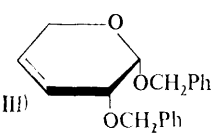
THERE is considerable interest in the addition of pseudo-halogens to olefins as a method of stereospecific introduction of nitrogen functions into organic compounds. Thus, iodine isocyanate (INCO) adds stereospecifically *trans* to open-chain and cyclic olefins and *trans*-diaxially to steroid olefins to form β-iodo-isocyanates.[1] Similarly, iodine azide (IN_3) has been shown to add in a highly stereospecific manner to many unsaturated systems; terminal olefins form adducts in which the azido-function is at the 2-position,[2] unlike nitryl chloride (NO_2Cl) which adds to an unsymmetrical terminal olefin to give the 2-chloro-1-nitroalkane.[3] We report preliminary results on the addition of the pseudo-halogen[4] nitryl iodide (NO_2I) to unsaturated sugars. The reagent is produced *in situ* by the reaction of silver nitrite and iodine in ether solution.



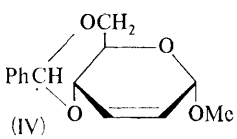
(I)



(II)



(III)



(IV)

5,6-Dideoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hex-5-enose[5] was converted into the 3-*O*-acetyl derivative (I), which was treated with nitryl iodide in ether, to give predominantly an iodo-*C*-nitro-adduct and another compound. The adduct was unstable on standing, but could be dehydrohalogenated by sodium hydrogen carbonate in boiling benzene to the known 3-*O*-acetyl-5,6-dideoxy-1,2-*O*-isopropylidene-6-*C*-nitro-α-D-*xylo*-hex-5-enose (II)[6] thereby establishing the position of the nitro-function. The double bond in compound (II) was selectively reduced with sodium borohydride in ethanol to yield 5,6-dideoxy-1,2-*O*-isopropylidene-6-*C*-nitro-α-D-*xylo*-hexose, m.p. 103·5—104°, $[\alpha]_D$ $-15 \pm 2°$ (*c*, 0·6 chloroform). Such reductions, in the carbohydrate field, have been achieved[7] by hydrogenation over palladium black.

Addition of nitryl iodide to benzyl 2-*O*-benzyl-3,4-dideoxy-α-D-*glycero*-pent-3-enoside (III)[8] gave a crystalline adduct which on dehydrohalogenation with sodium hydrogen carbonate in boiling benzene yielded a cyclic, unsaturated nitro-sugar derivative. The position of the nitro-function has not yet been established. Methyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-*erythro*-hex-2-enoside (IV)[9] has resisted the addition of nitryl iodide in many solvents. Addition to the β-D-isomer is being attempted.

Thus is achieved a simple preparation of unsaturated nitro-sugars. These highly reactive compounds are susceptible to many nucleophilic addition reactions of use in the synthesis of different carbohydrate derivatives.[10]

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