Addition of Iodine Azide to Unsaturated Sugars

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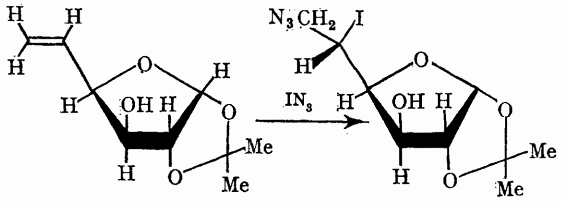
THE addition of pseudohalogens (for example, INCO,[1] IN_3,[2] NO_2Cl,[3] and NO_2I,[4]) to unsaturated sugars offers an attractive method for the stereospecific introduction of nitrogen functions into sugars and the adducts should be of considerable value in the synthesis of amino-sugars of biological interest. A recent communication[5] describing the addition of nitryl iodide (NO_2I) to unsaturated sugars prompts us to report some related additions with iodine azide (IN_3).

Iodine azide is generated *in situ* by the reaction of iodine monochloride with sodium azide in either acetonitrile or *NN*-dimethylformamide and it generally adds to terminal alkenes to form 2-azido-1-iodoalkanes, although *anti*-Markovnikov addition occurred with 3,3-dimethylbut-1-ene for steric reasons.[2] Reaction of 5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hex-5-enofuranose[6] (I) with iodine azide in acetonitrile afforded predominantly one crystalline adduct ($C_9H_{14}N_3IO_4$), m.p. 81—83°, $[\alpha]_D$ − 32° (*c* 1, in methanol), whose structure was established as 6-azido-5,6-dideoxy-5-iodo-1,2-*O*-isopropylidene-β-L-idofuranose (II) by *X*-ray crystallographic analysis. It is noteworthy that *anti*-Markovnikov addition takes place in this case also.



The adduct crystallised (ether–light petroleum, b.p. 40—60°) in the monoclinic space group $P2_1$, $a = 5{\cdot}86$, $b = 10{\cdot}20$, $c = 10{\cdot}80$ Å, and $\beta = 91{\cdot}2°$, $Z = 2$. Three-dimensional intensity data, recorded on equi-inclination Weissenberg photographs by use of Cu-K_α radiation and estimated visually, yielded a total of 829 independent structure amplitudes. The iodine atom was located from a Patterson synthesis and the remaining atoms were located from three-dimensional Fourier syntheses. Least-squares refinement of positional and thermal parameters led to generally satisfactory molecular dimensions (*R* 19·8%). Both the furanose and the dioxolan rings adopt "envelope" conformations which have C-4 and the acetal carbon atom displaced by *ca.* 0·5 Å in an *endo*- and *exo*-direction,† respectively, from the plane of the other four atoms.

The arrangement of atoms as viewed along the *a*-axis of the unit cell is shown in the Figure.

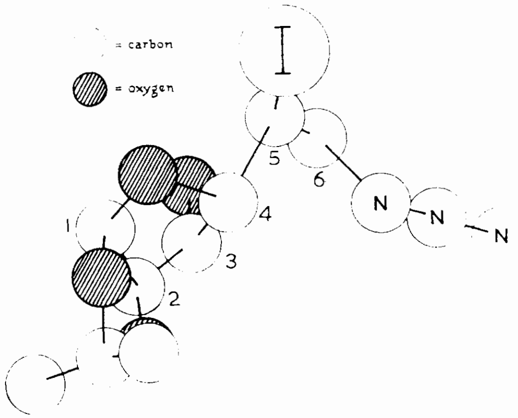


FIGURE. *Compound* (II) *viewed along the* a-*axis.*

3,4,6-Tri-*O*-acetyl-D-glucal[7] and 3,4,6-tri-*O*-acetyl-D-galactal[8] with iodine azide in acetonitrile gave good yields of non-crystalline adducts which are presumably 1-azido-2-iodo-derivatives by analogy[9] with other electrophilic additions to these alkenes that proceed through iodonium ions. The configurations of these adducts are being investigated. Ethyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside[10] and methyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside,[6] on the other hand, were unreactive towards iodine azide in either acetonitrile or *NN*-dimethylformamide; the latter alkene was also resistant to the addition of nitryl iodide in ether.[5]

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† The terms *endo* and *exo* have their usual meaning with respect to the trioxabicyclo[3,3,0]octane ring system.

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