The Solvolysis of Some Carbohydrate Nitrobenzene-*p*-sulphonates

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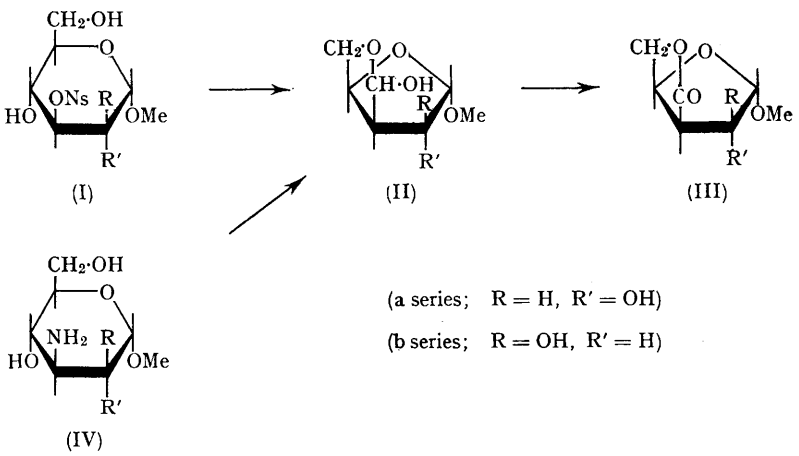
SULPHONATES of the secondary alcoholic groups of glycosides are relatively stable under neutral and acidic conditions.[1] Angyal and Stewart[2] have recently described several kinds of solvolytic reaction undergone by toluene-*p*-sulphonates of substituted inositols in boiling dimethylformamide. We now report that certain nitrobenzene-*p*-sulphonates of glycopyranosides undergo solvolysis in water to give products which have undergone sequential sulphonylation, debenzoylation, and partial acid hydrolysis. When it was heated at 100° in water in the presence of acetate buffer at pH5 it yielded the hemiacetal (IIa) of methyl 3-deoxy-3-formyl-α-D-xylofuranoside, m.p. 95°, $[\alpha]_D$ + 68° → 78·5° (final, H_2O), identical with the product of deamination of methyl 3-amino-3-deoxy-α-D-glucoside (IVa) with nitrous acid.[4] Identity was confirmed by oxidation with bromine



ring contraction. Methyl α-D-glucoside 3-nitrobenzene-*p*-sulphonate (Ia), m.p. 146° (decomp.), $[\alpha]_D$ + 122° (Me_2CO), was prepared from methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-glucoside[3] by to give the γ-lactone, (IIIa) m.p. 81—83°, $[\alpha]_D$ + 244° (0·01N-NaOH), $\nu_{max.}$ 1761 cm.$^{-1}$. In similar fashion the mannoside derivative (Ib), m.p. 145° (decomp.), $[\alpha]_D$ + 45·7° (pyridine), was

[1] R. S. Tipson, *Adv. Carbohydrate Chem.*, 1953, **8**, 107.
[2] S. J. Angyal and T. S. Stewart, *Proc. Chem. Soc.*, 1964, 331.
[3] E. J. Bourne, A. J. Haggard, and J. C. Tatlow, *J. Chem. Soc.*, 1953, 735.
[4] S. Inoue and H. Ogawa, *Chem. and Pharm. Bull.* (*Japan*), 1960, **8**, 79.

prepared by equatorial monosulphonylation of methyl 4,6-*O*-benzylidene-α-D-mannoside,[5] followed by mild acid hydrolysis. Solvolysis gave methyl 3-deoxy-3-formyl-α-D-lyxofuranoside as the hemiacetal (IIb), m.p. 94°, $[\alpha]_D$ + 32° (H_2O), which also resulted from the treatment of the 3-amino-3-deoxymannoside (IVb)[6] with nitrous acid. Bromine oxidation in this case gave a syrupy γ-lactone (IIIb), $\nu_{max.}$ 1773 cm.$^{-1}$

In the examples described the solvolysis of the nitrobenzenesulphonate follows closely the deamination of the corresponding amino-compound with nitrous acid. The scope of the reaction is now being investigated. Satisfactory analytical data were obtained for all the crystalline compounds reported.

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[5] J. G. Buchanan and J. C. P. Schwarz, *J. Chem. Soc.*, 1962, 4770.
[6] A. C. Richardson, *J. Chem. Soc.*, 1962, 373.