Acid *versus* Base Hydrolysis of a Disulphonylated Hexitol. 1,4,3,6-Dianhydro-D-Iditol (D-Isoidide) *versus* 2,3:4,5-Dianhydro-D-Iditol

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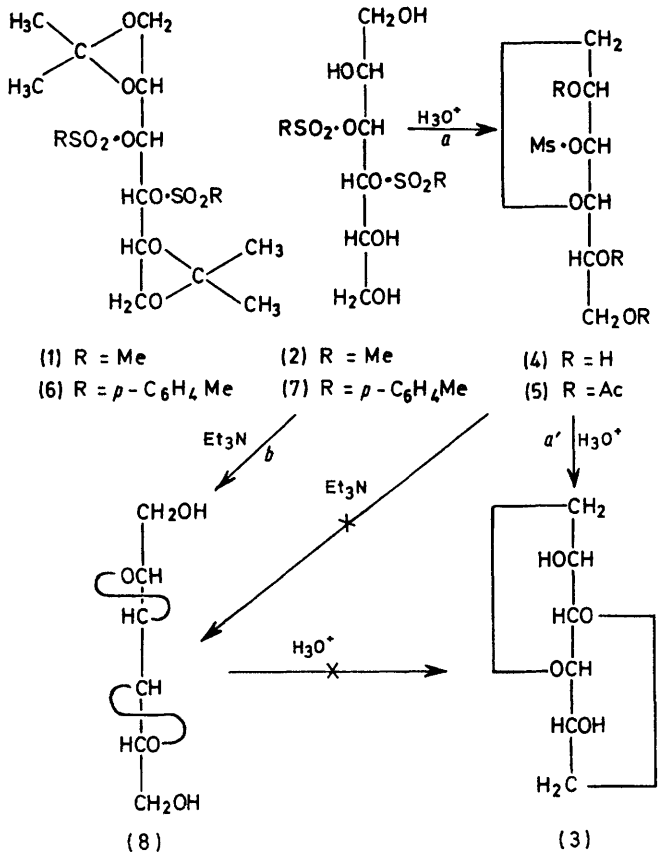
Summary Whereas acid hydrolysis of 3,4-di-*O*-methylsulphonyl-D-mannitol (**2**) produces 1,4-anhydro-3-*O*-methylsulphonyl-D-talitol (**4**) and thereafter 1,4:3,6-dianhydro-D-iditol (**3**), base hydrolysis of the ester (**2**) gives isomeric 2,3:4,5-dianhydro-D-iditol (**8**) exclusively.

SULPHONIC esters are normally regarded as being prone to base-catalysed reaction but resistant to acid hydrolysis.[1] However, there is reason[2] to suspect that the latter generalization is less correct, though acid hydrolysis of sulphonic esters has remained relatively unexplored.[3] We report here the acid- and base-catalysed hydrolysis of a disulphonylated hexitol, which proceeds rapidly in either medium and gives quantitative amounts of different isomeric products.

We attempted to deacetonate compound (**1**) by hydrolysis in water containing ion-exchange resin (H^+). However, the product obtained after hydrolysis for 1 h was not the mannitol (**2**),[4] but 1,4:3,6-dianhydro-D-iditol (D-isoidide) (**3**) whose structure was confirmed by the spectra and optical rotations of its diacetate† and dimesylate.[5,6]

If heating of the suspension of compound (**1**) in water containing the resin was stopped immediately upon dissolution, compound (**2**) comprised *ca.* 90% (n.m.r.) of the syrupy hydrolysate. Continuation of reflux for 5 min beyond dissolution afforded compound (**4**) characterised as the crystalline triacetate (**5**)†, m.p. 103—104°; $[\alpha]_D^{23}$ +9·52 ($CHCl_3$). Continuation of reflux for 30 min beyond dissolution gave compound (**3**). The course of the transformations was readily monitored by n.m.r. spectroscopy.[7]

† This compound gave correct elemental analysis and spectroscopic data.



Deacetonation of compound (**6**) has been reported[8] to give compound (**7**) which when saponified with barium methoxide for 2 h does not give the dianhydro-hexitol (**3**) as claimed[4] but instead the isomer (**8**). We have confirmed this result and found that the transformation could be accomplished more conveniently by treating compound (**2**) with Et_3N–MeOH–H_2O for 0·5 h at room temperature. Thus, acid hydrolysis (paths $a + a'$) of compound (**2**) gives (**3**) and no (**8**) while base hydrolysis (path b) gives (**8**) and no (**3**). There are no organic side products in either hydrolysis.

The bis-oxiran (**8**) when refluxed for 0·5 h in the presence of acid gives a number of products,‡ none of which is the iditol (**3**). Hence compound (**8**) is not an intermediate in the conversion of (**2**) into (**3**). Similarly compound (**4**) is not an intermediate between (**2**) and (**8**), since it is not affected by treatment with triethylamine for 30 min.

Hydrolysis of the ditosylate (**6**) in 70% acetic acid at 70 °C for 3 h goes beyone the tetrol (**7**) state also. T.l.c. of the hydrolysate showed three components, one of which had the same R_F as compound (**3**). It therefore appears that Wiggins[4] must have unwittingly achieved his synthetic objective (**3**) in the first step, as the result of prolonged acid hydrolysis of the starting material (**6**). The subsequent 'saponification' was therefore superfluous since compound (**3**) is not formed by treatment of the tetrol (**7**) with base.

It is noteworthy that acid-catalysed cleavage of a sulphonate ester appears to be invariably accompanied by formation of an oxolone ring,[9] whereas base-catalysed cleavage invariably results in an oxiran.

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‡ Some of these appear from paper chromatography to be hexitols. They could be D- and/or L-mannitol, or D- and/or L-allitol depending upon the site of oxiran scission.

[1] (*a*) R. S. Tipson, *Adv. Carbohydrate Chem.*, 1953, **8**, 143; (*b*) D. H. Ball and F. W. Parrish, *ibid.*, 1968, **23**, 233.
[2] For example, H. Ohle and E. Dickhauser, *Ber.* 1925, **58**, 2593; G. J. Robertson and D. Gall, *J. Chem. Soc.*, 1937, 1600; J. K. N. Jones, P. W. Kent, and M. Stacey, *ibid.*, 1947, 1341; S. S. Brown and G. M. Timmis, *ibid.*, 1961, 3656.
[3] J. Defaye, *Adv. Carbohydrate Chem.*, 1970, **25**, 203.
[4] L. F. Wiggins, *J. Chem. Soc.*, 1947, 1403.
[5] F. J. Hopton and G. H. S. Thomas, *Canad. J. Chem.*, 1969, **47**, 2395.
[6] H. G. Fletcher, jun., and R. M. Goepp, jun., *J. Amer. Chem. Soc.*, 1949, **68**, 939.
[7] The 60 MHz spectrum is deceptively simple. For a detailed discussion of the 100 MHz spectrum, see ref. 5.
[8] R. S. Tipson and A. Cohen, *Carbohydrate Res.*, 1968, **7**, 232.
[9] P. A. J. Gorin, *Canad. J. Chem.*, 1963, **41**, 2417; R. Ahluwahlia, S. J. Angyal, and M. H. Randall, *Carbohydrate Res.*, 1967, **4**, 478; P. W. Austin, J. G. Buchanan, and R. M. Saunders, *J. Chem. Soc.* (*C*), 1967, 372; J. Defaye and J. Hildesheim, *Tetrahedron Letters*, 1968, 313.