# 1,4-Migration of a Methoxy-group during a Benzoate Displacement Reaction: 4-*O*-Methyl-L-lyxose

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THE benzoate displacement of sulphonate ester groups has found wide application in carbohydrate chemistry.[1] Simple displacement does not always occur and recent communications have described variations, *e.g.* olefin and epoxide formation.[1] We now report a case of methoxy-group migration.

Treatment of the dimethylacetal (I) (obtained from 2,3,5-tri-*O*-benzyl-D-ribofuranose)[2] with tetra-n-butylammonium benzoate in *N*-methylpyrrolidone[3] did not give the expected 4-*O*-benzoyl-L-lyxose derivative (II). Instead a syrupy isomeric compound was obtained which was identified

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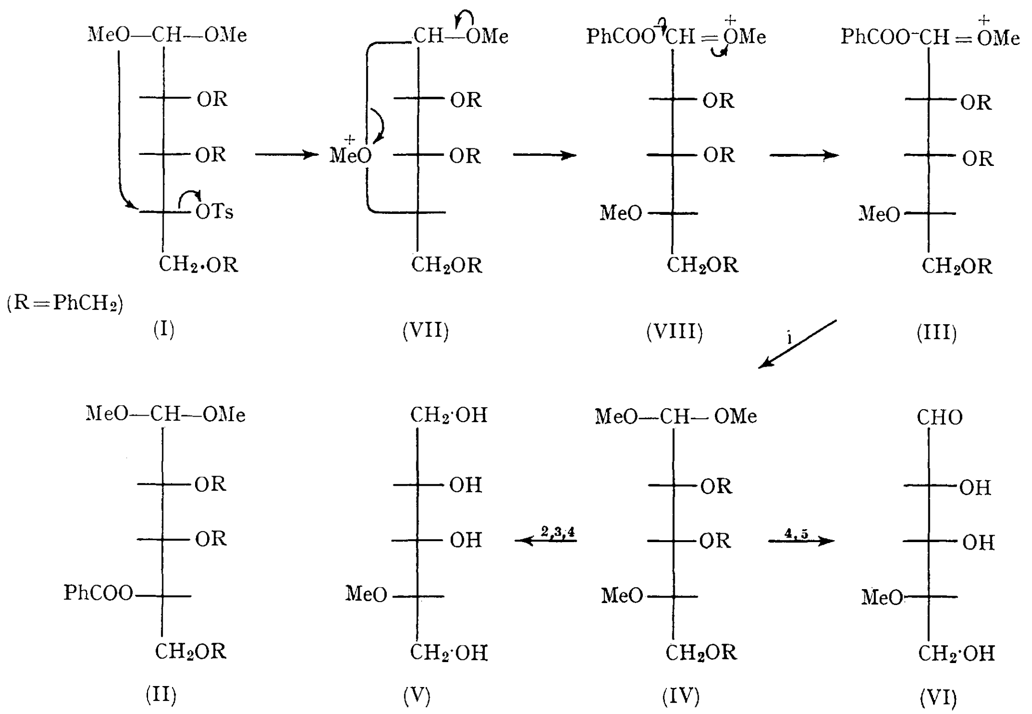
[1] S. J. Angyal and T. S. Stewart, *Proc. Chem. Soc.*, 1964, **331**, and references therein.

[2] R. Barker and H. G. Fletcher, *J. Org. Chem.*, 1961, **26**, 4605.

[3] N. A. Hughes and P. R. H. Speakman, *J. Chem. Soc.*, 1965, 2236.

as 1-*O*-benzoyl-2,3,5-tri-*O*-benzyl-4-*O*-methyl-L-lyxose methylhemiacetal (III). Two diastereoisomers are possible for this structure, due to asymmetry at C-1, and the product may well be a mixture of the two.



1. HCl-MeOH 2. $H_2SO_4$-aqueous acetone 3. $NaBH_4$ 4. $H_2$-Pd 5. $H_2SO_4$-$H_2O$

The structure (III) was proved as follows. Methanolysis gave 2,3,5-tri-*O*-benzyl-4-*O*-methyl-L-lyxose dimethylacetal (IV) which was converted as shown into 4-*O*-methyl-L-lyxitol (2-*O*-methyl-L-arabinitol) (V), identified by comparison with an authentic sample synthesised as described for the known enantiomorph.[4] 4-*O*-Methyl-L-lyxose (VI) was also obtained from the acetal (IV) as shown and characterised as the diethyldithioacetal which was compared with the enantiomorph prepared from methyl 2,3-*O*-isopropylidene-α-D-lyxopyranoside[5] by standard methods.*

The migration of a methoxy-group appears to be the result of favourable participation[7] by the methoxy-group in the solvolysis of the tosylate (I) producing a five-membered cyclic oxonium ion (VII). This cyclic ion can be opened up by a mesomeric effect from the second methoxy-group to give the new oxonium ion (VIII) which is then attacked by a benzoate ion; the possibility of direct attack by a benzoate ion on the cyclic ion (VII) also exists. A 1,2-methoxy-group migration was recently reported when 1,3,4,6-tetra-*O*-acetyl-2-*O*-methyl-D-glucopyranose was obtained in small yield from methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo-α-D-mannopyranoside.[8]

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* A similar synthesis of 4-*O*-methyl-D-lyxose from ethyl 2,3-*O*-isopropylidene-α-D-lyxopyranoside was recently reported.[6]

[4] J. C. Sowden, M. L. Oftedahl, and A. Kirkland, *J. Org. Chem.*, 1962, **27**, 1791.
[5] P. W. Kent and P. F. V. Ward, *J. Chem. Soc.*, 1953, 416.
[6] J. Piotrovsky, J. P. Verheijden, and P. J. Stoffyn, *Bull. Soc. chim. belges*, 1964, **73**, 969.
[7] B. Capon, *Quart. Rev.*, 1964, **18**, 49.
[8] R. U. Lemieux and B. Fraser-Reid, *Canad. J. Chem.*, 1964, **42**, 539.