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Preliminary communication

The direct preparation of 1′,6,6′-trideoxysucrose from sucrose *via* 6-*O*-mesitylenesulphonyl-α-D-glucopyranosyl 1,6-di-*O*-mesitylenesulphonyl-β-D-fructofuranoside*

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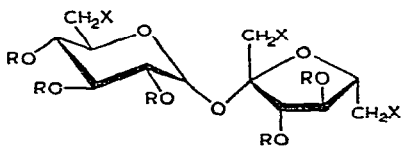
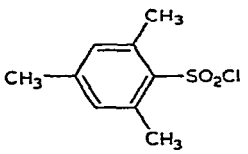
Trimolar tosylation of sucrose (1) affords 1′,6,6′-tri-*O*-tosylsucrose (2) in 23% yield after column chromatography[2]. Recently[3], mesitylenesulphonyl chloride (3) was shown to be more selective than toluene-*p*-sulphonyl chloride, particularly towards vicinal diol systems. We report herein on the selective mesitylenesulphonylation of sucrose, whereby the trimesitylenesulphonate can be isolated directly in high yield, thus obviating the need for chromatography.



1 R = H, X = OH
2 R = H, X = OTs
4 R = H, X = OMes
7 R = Ac, X = OMes
8 R = Ac, X = Cl
9 R = H, X = Cl
10 R = H, X = H
11 R = Ac, X = H



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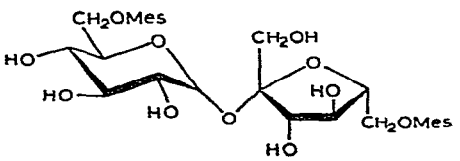

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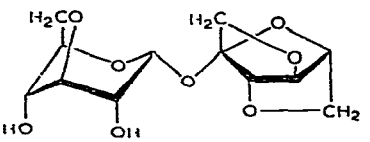

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Mes = mesitylenesulphonyl

*Sucrochemistry: Part XXI. For Part XX, see Ref. 1.

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Treatment of sucrose (**1**) in anhydrous pyridine with 3 mol. of mesitylenesulphonyl chloride[3] at −5 to 0° for 6 days gave one major and several minor products (t.l.c.). Concentration of the reaction mixture and conventional extraction of the residue into chloroform gave 6-*O*-mesitylenesulphonyl-α-D-glucopyranosyl 1,6-di-*O*-mesitylenesulphonyl-β-D-fructofuranoside (**4**, 40%), m.p. 135° (dec.) (from acetone–chloroform at 35°), $[\alpha]_D$ +43° (*c* 1, methanol). More **4** (8%) was obtained from the mother liquors after chromatography on silica gel. A slower-moving fraction, which was shown by n.m.r. spectroscopy to be a mixture of isomeric disulphonates, gave, on fractional crystallization, a pure disulphonate, m.p. 129–130°, $[\alpha]_D$ +67.5° (*c* 1, methanol). On the basis of its reactions and spectral data for the hexa-*O*-acyl derivatives, this compound was formulated as 6-*O*-mesitylenesulphonyl-α-D-glucopyranosyl 6-*O*-mesitylenesulphonyl-β-D-fructofuranoside (**5**).

The trisulphonate **4** was characterised by its conversion with hot methanolic sodium methoxide into known[2] 3,6-anhydro-α-D-glucopyranosyl 1,4:3,6-dianhydro-β-D-fructofuranoside (**6**).

The high yield and ease of isolation of **4** makes it an attractive intermediate for the preparation of sucrose derivatives modified at the primary positions, and, as an example, its conversion into the hitherto unknown 1′,6,6′-trideoxysucrose (**10**) is described. Treatment of the penta-acetate (**7**) of **4** with lithium chloride in *N*,*N*-dimethylformamide containing a trace of iodine, at 140° for 18 h, gave the trichloride **8** in high yield, m.p. 127° (from ethanol), $[\alpha]_D$ +58° (*c* 1, chloroform). Deacetylation (Zemplén) of **8** gave amorphous 1′,6,6′-trichloro-1′,6,6′-trideoxysucrose (**9**), $[\alpha]_D$ +56.5° (*c* 1, methanol); lit.[4] $[\alpha]_D$ +52.5° (acetone). The location of the chlorine substituents was shown by ^{13}C-n.m.r. spectroscopy, since the three primary carbons resonated ~ 16 p.p.m. upfield from the corresponding atoms in sucrose[1]. Reductive dechlorination (ethanol–Raney nickel–potassium hydroxide[5]) of **9** gave syrupy 1′,6,6′-trideoxysucrose (**10**), the penta-acetate (**11**) of which had m.p. 170–172°, $[\alpha]_D$ +58° (*c* 1, chloroform).

The structure of **11** was confirmed by the following n.m.r. data (100 MHz, C_6D_6, *signifies that the assignment was confirmed by decoupling): H-1 τ 4.39 (d, $J_{1,2}$ 3.5 Hz), H-2 4.98 (q, $J_{2,3}$ 10.5 Hz), H-3 4.20 (q, $J_{3,4}$ 9.5 Hz), H-4 5.00 (t, $J_{4,5}$ 9.5 Hz), H-5* 5.70 (m), H-6* 8.84 (d, $J_{5,6}$ 6.0 Hz), H-1′ 8.57 (s), H-3′ 4.54–4.77 (m), H-5′* 6.05 (m), H-6′* 8.60 (d, $J_{5',6'}$ 6.0 Hz).

ACKNOWLEDGMENT

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