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Note

Reductive desulfonylation of carbohydrate *p*-toluenesulfonates with sodium in liquid ammonia

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Reductive desulfonylation of carbohydrate *p*-toluenesulfonates has been previously accomplished with sodium amalgam[1a], Raney nickel[1b], and lithium aluminum hydride[1c,2]. These methods were, however, either not of general applicability or were not selective for the cleavage of the S–O bond[2]. The mode of the attack of the reagent frequently depended on the position of the *p*-tolylsulfonyl group in the sugar molecule and on the nature of the solvent used[2]. Thus, side reactions[1,2] or difficulties in the purification of reaction products[3] imposed a limitation in the use of these methods.

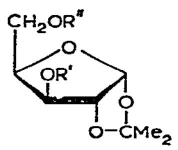
Denney and Goldstein[4] had previously found that the reduction of cyclohexyl *p*-toluenesulfonate with sodium in liquid ammonia proceeds with S–O bond cleavage exclusively, *i.e.* that neither cyclohexane nor cyclohexene was formed during the reaction. Based on these findings, we have studied the reductive desulfonylation of mono- and di-*p*-toluenesulfonates of several furanosides. We have found that in all cases the reductive desulfonylation with sodium and liquid ammonia was very selective for cleavage of the S–O bond.

Table I summarizes the results obtained for several carbohydrate *p*-toluenesulfonates.

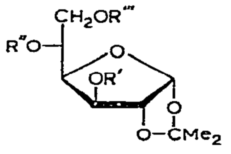
TABLE I

DESULFONYLATION OF VARIOUS CARBOHYDRATE *p*-TOLUENESULFONATES

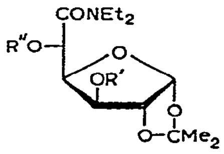
Compound	*Yield of desulfonylated product* (%)
1,2-*O*-Isopropylidene-5-*O*-*p*-tolylsulfonyl-α-D-xylofuranose[5] (1)	70
1,2-*O*-Isopropylidene-3,5-di-*O*-*p*-tolylsulfonyl-α-D-xylofuranose[6] (2)	65
1,2-*O*-Isopropylidene-6-*O*-*p*-tolylsulfonyl-α-D-glucofuranose[7] (3)	66
6-*O*-Benzoyl-1,2-*O*-isopropylidene-3,5-di-*O*-*p*-tolylsulfonyl-α-D-glucofuranose[8] (4)	68
5-*O*-Acetyl-*N*,*N*-diethyl-1,2-*O*-isopropylidene-3-*O*-*p*-tolylsulfonyl-α-D-glucofuranuronamide[9] (5)	73



1 R' = H; R'' = Ts
2 R' = R'' = Ts



3 R' = R'' = H; R''' = Ts
4 R' = R'' = Ts; R''' = Bz



5 R' = Ts; R'' = Ac

EXPERIMENTAL

*Desulfonylation of 1,2-*O*-isopropylidene-5-*O*-*p*-tolylsulfonyl-α-*D*-xylofuranose* (**1**). — A solution of 3.44 g (0.01 mole) of **1** in abs. tetrahydrofuran (10 ml) was added over a 20-min period to a stirred solution of 1.6 g (0.07 equiv.) of sodium in dry liquid ammonia (100 ml) at −80°. After stirring for 2 h at −80° and 1 h at −33°, ethanol (4–5 ml) was added to the reaction mixture until the blue color disappeared, at which point solid ammonium chloride (*ca.* 5 g) and water (5 ml) were added. The reaction mixture was kept overnight at room temperature to remove the excess of ammonia, and the residual solution was diluted with ethanol (300 ml) and saturated with carbon dioxide. The precipitate of sodium hydrogen carbonate was filtered off, washed several times with small portions of ethanol, and the combined filtrates were evaporated to dryness *in vacuo*. The dry residue was dissolved in boiling chloroform (*ca.* 200 ml) and the undissolved material was removed by filtration. The solution was evaporated to dryness to give a yellowish, oily product which was chromatographed on silica gel (E. Merck, Darmstadt, grain size < 0.08 mm). Elution with 85:15 benzene–methanol afforded 1.33 g (70%) of pure 1,2-*O*-isopropylidene-α-D-xylofuranose.

*Desulfonylation of 1,2-*O*-isopropylidene-3,5-di-*O*-*p*-tolylsulfonyl-α-*D*-xylofuranose* (**2**). — A solution of **2** (2.37 g; 4.75 mmoles) in abs. tetrahydrofuran (10 ml) was added at −80° to a solution of sodium (2.3 g; 0.1 mole) in liquid ammonia (*ca.* 100 ml). The reaction mixture was worked up as described above to yield 0.62 g (69%) of 1,2-*O*-isopropylidene-α-D-xylofuranose.

*Desulfonylation of 1,2-*O*-isopropylidene-6-*O*-*p*-tolylsulfonyl-α-*D*-glucofuranose* (**3**). — Compound **3** (1.87 g; 5 mmoles) was desulfonylated as described above. Chromatography yielded 0.73 g (66%) of 1,2-*O*-isopropylidene-α-D-glucofuranose, and 0.116 g (11%) of 6-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose.

*Desulfonylation of 6-*O*-benzoyl-1,2-*O*-isopropylidene-3,5-di-*O*-*p*-tolylsulfonyl-α-*D*-glucofuranose* (**4**). — Treatment of 3.16 g of **4** as described above yielded 0.75 g (68%) of pure 1,2-*O*-isopropylidene-α-D-glucofuranose, m.p. 160°.

*Desulfonylation of 5-*O*-acetyl-*N,N*-diethyl-1,2-*O*-isopropylidene-3-*O*-*p*-tolylsulfonyl-α-*D*-glucofuranuronamide* (**5**). — Treatment of **5** (300 mg) as described above yielded, after chromatography on silica gel, 130 mg (73%) of *N*,*N*-diethyl-1,2-*O*-isopropylidene-α-D-glucofuranuronamide.

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