

Preliminary communication

Catalytic transfer hydrogenation of 1,3-dioxolanes

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Benzylidene acetals are important protecting groups in sugar chemistry¹, which are readily removed² by hydrogenolysis in the presence of Pd/C. Selective deacetalation may be achieved by hydrolysis and acetolysis³. These properties, together with the variety of preparative methods and the use of benzylidene derivatives in structural modifications of carbohydrates⁴, have made them valuable in synthetic organocarbohydrate chemistry.

The selective hydrolysis of benzylidene acetals constitutes an important route to partially protected derivatives of carbohydrates, but this approach has limitations. For example, the benzylidene groups in 2,3:4,6-di-*O*-benzylidene- α -D-mannopyranoside are removed at similar rates during acid hydrolysis⁵.

We now report on the selective removal of 2-phenyl-1,3-dioxolane groups by catalytic transfer hydrogenation. This technique has been used for the cleavage of *O*-benzyl groups in carbohydrate derivatives, using formic acid⁶ or cyclohexene⁷ as the hydrogen donor, and benzylidene substituents are readily⁶ or partly removed⁷ under these conditions. Recently, we found⁸ that catalytic transfer hydrogenation of methyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene- α -D-gluco- and - α -D-galacto-pyranoside with ammonium formate as a hydrogen donor and Pd/C as the catalyst gave methyl 4,6-*O*-benzylidene- α -D-gluco- and - α -D-galacto-pyranoside in yields of 90% and 93%, respectively. We now report examples which show that the 2-phenyl-1,3-dioxane ring is more stable than the 2-phenyl-1,3-dioxolane ring, and selective removal of five-membered acetal rings may be achieved.

Typically, a solution of acetal (0.2 mmol) and ammonium formate (100 mg) in methanol (5–10 mL) was boiled under reflux in the presence of 10% Pd/C (400 mg). The reaction was monitored by t.l.c. and, when complete, the catalyst was removed, the filtrate was concentrated, and the residue was subjected to column chromatography on silical gel. The reactions were complete within 30–40 min and the products were obtained in yields of 75–98%.

The results in Table I suggest that the method may be of general value in the synthesis of partially protected sugars.

TABLE I

CATALYTIC TRANSFER HYDROGENATION OF BENZYLIDENE ACETALS ^a

<i>Starting material</i>	<i>Product</i>	<i>Yield</i> ^b (%)
1,2- <i>O</i> -Benzylidene- α-D-glucofuranose	D-Glucose	97
2,3:4,5-Di- <i>O</i> -benzylidene- β-D-fructopyranose	D-Fructose	98
Methyl (<i>exo</i> -Ph)-2,3:4,6-di- <i>O</i> -benzylidene-α-D-mannopyranoside	Methyl 4,6- <i>O</i> -benzylidene- α-D-mannopyranoside	86
1,3:2,4:5,6-Tri- <i>O</i> -benzylidene- D-glucitol ^c	1,3:2,4-Di- <i>O</i> -benzylidene- D-glucitol	75

^a All compounds were characterised by m.p., $[\alpha]_D$, and ¹H-n.m.r. data. ^b Pure isolated product.

^c A ~1:2 mixture of *endo*- and *exo*-isomers.

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