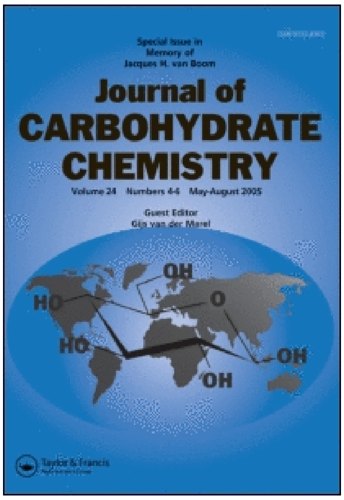

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Communication

ISOMERIZATION AND CLEAVAGE OF ALLYL ETHERS OF CARBOHYDRATES BY TRANS-[$Pd(NH_3)_2Cl_2$]

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Allyl ethers are widely used for the "temporary" protection of hydroxy groups in carbohydrates.[1] The allyl group is conveniently removed by isomerization and subsequent cleavage of the labile prop-1-enyl group.[2] The rearrangement of allyl ethers to prop-1-enyl ethers is readily achieved by treatment with potassium t-butoxide in dimethyl sulfoxide, using tris(triphenylphosphine)rhodium chloride, palladium on activated charcoal and by an ene reaction with diethylazodicarboxylate.[3] Prop-1-enyl ethers are readily cleaved under acidic conditions, ozonolysis followed by alkaline hydrolysis, reaction with alkaline permanganate solution, or treatment with mercuric chloride in the presence of mercuric oxide.[2,4] The isomerization of allyl ethers to prop-1-enyl ethers can also be carried out in the presence of palladium on carbon or complex bis(benzonitrile)palladium(II) chloride.[5] Recently, Bruce and Roshan-Ali[6] showed that derivatives of allyl phenyl ether are smoothly cleaved by this complex. This has made it possible to remove the protecting group in a one-pot oper-

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ation. We have now investigated the effect of palladium catalysts on the isomerization and cleavage of the allyl group in carbohydrate derivatives.

In order to compare the effect of the catalysts, the reaction of methyl 4,6-O-benzylidene-2,3-di-O-allyl-α-D-glucopyranoside with a number of complexes of palladium was investigated,[7] the best results being obtained by using trans-[$Pd(NH_3)_2Cl_2$] (1) as the catalyst.[8] In the presence of (1) allyl ethers isomerize to prop-1-enyl ethers (mixture of trans 40% and 60% cis isomer).

The rate of reaction strongly depends upon the structure of the substituents. For example, 6-O-allyl-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose (2) was converted to 6-O-prop-1-enyl ether (2a) after 4 h in 30% yield, whereas the isomerization of allyl 6-O-allyl-α-D-galactopyranoside (3) was complete after 1 h, thus showing that bulky groups impede the isomerization.

Under the proposed conditions cleavage of prop-1-enyl ethers was effected by refluxing ethers with 1 in tert-butyl alcohol for several hours. Thus, methyl 4,6-O-benzylidene-2,3-di-O-allyl-α-D-gluco-(7), β-D-gluco-(8), α-D-galacto- (9), and β-D-galactopyranoside (10) were readily converted into methyl 4,6-O-benzylidene-α-D-gluco- (7a), B-D-gluco- (8a), α-D-galacto- (9a), and β-D-galactopyranoside (10a), respectively. We have shown that the prop-1-enyl aglycon is considerably more stable to the action of 1 than other prop-1-enyl groups in carbohydrate molecules. When allyl tetra-O-acetyl-α-D-galactopyranoside (5) was treated with 1, TLC showed a conversion of the starting material into a new product, prop-1-enyl tetra-O-acetyl-α-D-galactopyranoside (5a) within 6 h, with no further change over 24 h. Acidic hydrolysis of the product (removal of the prop-1-enyl group) yielded a product with a similar mobility to that of 2,3,4,6-tetra-O-

TABLE 1. Isomerisation of Allyl Ether and Removal of the Ether Group in Carbohydrate Derivatives Catalysed by trans-$[Pd(NH_3)_2Cl_2]$.

Starting compound [a)]	Product [b)]	Yield [c)] (%)	Reaction time (h)	cis:trans product ratio
2	2a	30	4	d)
3	3a	91	1	d)
4	4a	94	0.7	60:40
4	4b	90	6	-
5	5a	96	6	65:35
6	6a	89	36	55:45
7	7a	90	12	-
8	8a	88	14	-
9	9a	92	18	-
10	10a	90	8	-

(a) Allyl ethers were obtained by the alkylation of sugars in a catalytic two-phase system.[10] (b) Table 2 provides data for the new compounds. The results concerning known product are in agreement with literature data. For compounds 3-10(a) satisfactory elemental analyses were obtained. (c) Yield of pure isolated product. (d) The relative ratio of cis- and trans-isomer was not determined.

acetyl-D-galactopyranose. Allyl 2,3,4-tri-O-acetyl-6-O-allyl-α-D-galactopyranoside (6), under the same conditions gave prop-1-enyl 2,3,4-tri-O-acetyl-α-D-galactopyranoside (6a). Therefore, prop-1-enyl aglycone is stable to the action of the palladium catalyst for 24 h, thus allowing the removal of other allyl groups in the same molecule without deprotection of the anomeric hydroxyl group. Monovinyl ethers of 1,2-diols[9] and prop-1-enyl ethers of carbohydrates[4] have been

TABLE 2: Physical and NMR Data for prop-i-enyl derivatives of carbohydrates

Compound	M.p.(^{o}C)	α_{D}^{20}	^{1}H-NMR (ppm)
3a	62-66	+63.8(MeOH)	($D_2$0,TSP-d_4):6.40-5.85(m,2H,0-C$\underline{H}$=), 5.20 ($H_{anomeric}$), 1.56(m,6H,-C$\underline{H}_3$);
4a	syrup	+124 (MeOH)	(methanol-d_4,TMS):cis- 6.25(dq,1H,0-C$\underline{H}$=, J=6.5Hz, 1.6Hz), 5.16($H_{anomeric}$), 4.63 (dq,1H,=C$\underline{H}$-, J=7Hz, 6.5Hz), 1.67(dd,3H,-C$\underline{H}_3$, J=7Hz, 1.6Hz); trans- 1.60(dd,3H,-C$\underline{H}_3$, J=7Hz, 1.5Hz);
5a	88-90	+142($CHCl_3$)	($CDCl_3$,TMS):cis- 6.16(dq,1H,0-C$\underline{H}$=, J=6Hz, J=1.5Hz), 5.60($H_{anomeric}$), 2.18 and 2.11 and 2.08 and 2.03)s, 3H, -COC$\underline{H}_3$), 1.67(dd,3H,-C$\underline{H}_3$, J=6.6Hz, 1.5Hz); trans- 1.58(dd,3H,-CH_3, J=6.5Hz, 1.5Hz);
6a	syrup	+144($CHCl_3$)	($CDCl_3$,TMS):cis- 6.42-6.00(m,1H,0-C$\underline{H}$=), 5.58 ($H_{anomeric}$), 3.62(2H,H-6,H-6), 3.23(br.s,0$\underline{H}$), 2.19 and 2.11 and 2.05(s,3H,-COC$\underline{H}_3$), 1.67 (dd,3H,-C$\underline{H}_3$, J=6.7Hz, 1.5Hz), trans- 1.58 (dd,3H,-C$\underline{H}_3$, J=6.7Hz, 1.2Hz).

shown to cyclize to acetals in the presence of an acidic catalyst. We have found that allyl derivatives of carbohydrates, with unprotected hydroxyl groups in a suitable position, can be transformed directly into propylidene acetals in a one-pot operation by treatment with 1 in boiling tert-butyl alcohol. Thus allyl-α-**D**-galactopyranoside (4) isomerises after 1 h, and may be cyclised to give 1,2-O-propylidene-α-**D**-galactopyranose (4b), a useful synthetic intermediate.

In a typical experiment, methyl 4,6-O-benzylidene-2,3-di-O-allyl-α-**D**-glucopyranoside (7) (543 mg, 1.5 mmol), trans-[Pd(NH_3)Cl_2] (1) (106 mg, 0.5 mmol), tert-butyl alcohol (25 mL) is refluxed until TLC indicates complete cleavage of the allyl ether (12 h). The catalyst is filtered off and washed with the methanol. The filtrate is concentrated and product (7a) is isolated from the residue by column chromatography on silica gel.

The ease of isomerizing allyl ethers to prop-1-enyl ethers, as well as the selective cleavage or cyclisation of the prop-1-enyl group indicates that (1) in tert-butyl alcohol may be a useful reagent for the preparation of selectively substituted derivatives of carbohydrates, and it is this subject that is being investigated.

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