

The Allyl Ether as a Protecting Group in Carbohydrate Chemistry. Isomerisations with Tris(phenyl)phosphine-rhodium(I) Chloride

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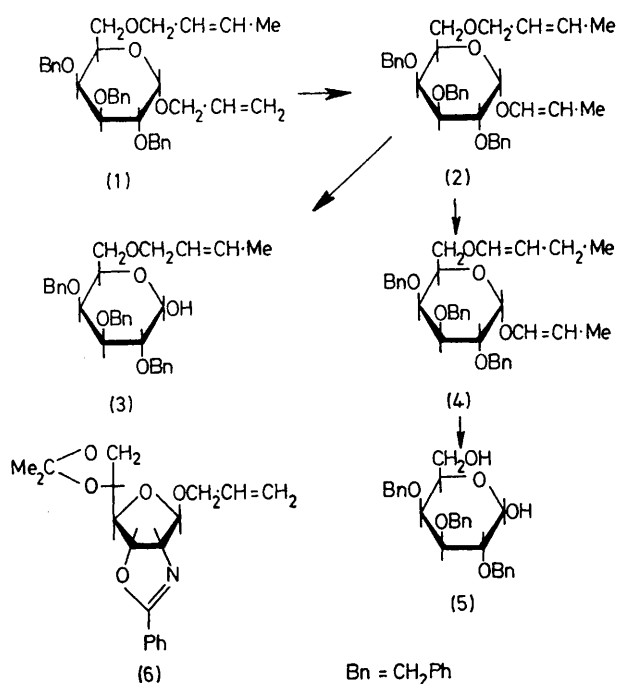
Summary The isomerisations of allyl, 2-methylallyl, and but-2-enyl groups by tris(phenyl)phosphine-rhodium(I) chloride are compared with the reactions of these groups with potassium *t*-butoxide in dimethyl sulphoxide.

In previous publications¹⁻⁴ we have shown that the allyl, 2-methylallyl, and but-2-enyl groups are useful protecting groups in the carbohydrate series and have compared their behaviour with potassium *t*-butoxide in dimethyl sulphoxide. Recently it has been shown^{5,6} that tris(phenyl)phosphine-rhodium(I) chloride catalyses the isomerisation of allyl ethers to prop-1-enyl ethers under neutral conditions. We have compared the rates of isomerisation of allyl, 2-methylallyl, and but-2-enyl groups into the corresponding vinyl ethers, with the rhodium complex and have shown that under our conditions the 2-methylallyl group is isomerised at a slightly lower rate than the allyl group whereas the but-2-enyl group is isomerised at a significantly lower rate than the allyl group. By comparison, the but-2-enyl group is cleaved³ at a higher rate and the 2-methylallyl group is isomerised at a much lower rate⁴ than the allyl

group is isomerised by potassium *t*-butoxide in dimethyl sulphoxide.

The conditions used are important since Corey and Suggs⁵ using ethanol-water (9:1) at reflux achieved *ca.* 95% conversion (apparently an equilibrium state) of allyl to prop-1-enyl ethers in 3 h, whereas Golborn and Scheinmann⁶ using benzene as solvent achieved *ca.* 50% conversion in 35 h. We have used a mixture of ethanol-benzene-water (7:3:1) as solvent (to improve the solubility of our compounds) and otherwise the conditions of Corey and Suggs.⁵ 6-*O*-Allyl-1,2:3,4-di-*O*-isopropylidene- α -D-galactopyranose⁷ was converted (*ca.* 95%) into the prop-1-enyl ether in 1 h under these conditions whereas the corresponding 6-*O*-but-2'-enyl ether³ was isomerised (*ca.* 95%) into a mixture of the 6-*O*-but-1'-enyl ether (*ca.* 95%) (hydrolysed by HgCl₂ in the presence of HgO² to give 1,2:3,4-di-*O*-isopropylidene- α -D-galactopyranose) and another product presumed to be the 6-*O*-but-3'-enyl ether (since it was unaffected by HgCl₂ or by potassium *t*-butoxide in dimethyl sulphoxide) in 24 h. If the rhodium complex was added after the reaction mixture had reached reflux temperature then the

isomerisation of the allyl to the prop-1-enyl group was *ca.* 95% complete within 10 min.



The isomerisation of the but-2-enyl ether is of interest in connection with the synthesis of plasmalogens which are derivatives of 1-*O*-alk-*cis*-1'-enyl-L-glycerol.⁸ However it

has been shown⁶ that the but-1-enyl ethers produced by isomerisations of this type [using dichlorobis(benzonitrile)-palladium(II)] are a mixture of *cis*- and *trans*-isomers in a ratio of *ca.* 60:40.

The practical significance of the large rate difference in the isomerisations of the allyl and but-2-enyl groups was investigated when both groups were present in the same molecule. When allyl 2,3,4-tri-*O*-benzyl-6-*O*-but-2'-enyl- α -D-galactopyranoside (1) (prepared by the benzylation of allyl 6-*O*-but-2'-enyl- α -D-galactopyranoside³) was treated with the rhodium complex *ca.* 95% conversion into a major product (2) occurred within 2 h. The total product was treated with HgCl₂² to convert the major product into the free sugar (3) [under these conditions the minor product (4) gave the diol (5)] which was isolated in 60% yield after chromatography on neutral alumina. It was characterised by reduction with sodium borohydride and subsequent treatment with potassium *t*-butoxide in dimethyl sulphoxide to cleave³ the but-2-enyl group, to give the known⁷ crystalline 2,3,4-tri-*O*-benzyl-D-galactitol.

Trisphenylphosphinerhodium(I) chloride can abstract carbon monoxide from aldehydes⁹ but the free sugar (3) and 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose¹ were not affected by the rhodium complex under the above conditions in 24 h and it therefore appears that the catalyst can be used for the isomerisations of allyl groups in free sugars. The phenyloxazoline group of compound (6) was also stable to the isomerisation conditions in contrast to its behaviour with potassium *t*-butoxide in dimethyl sulphoxide.¹⁰

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