The Allyl Ether as a Protecting Group in Carbohydrate Chemistry. Isomerisations with Tristriphenylphosphinerhodium(I) Chloride

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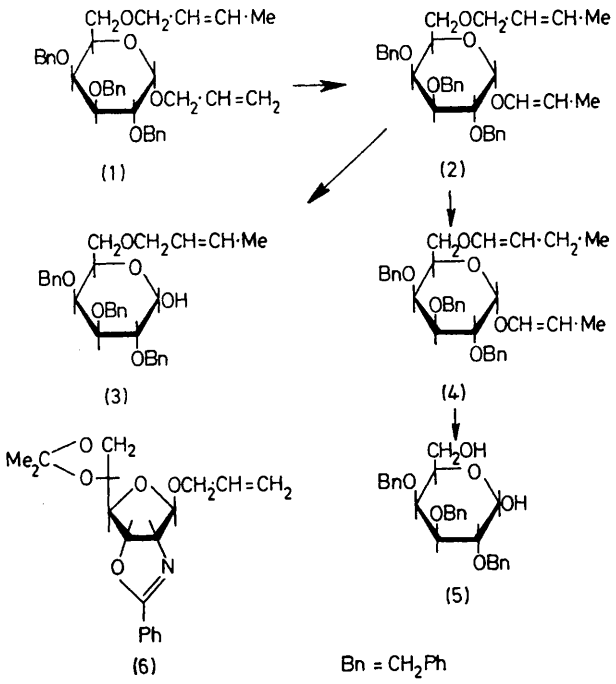
Summary The isomerisations of allyl, 2-methylallyl, and but-2-enyl groups by tristriphenylphosphinerhodium(I) chloride are compared with the reactions of these groups with potassium t-butoxide in dimethyl sulphoxide.

IN previous publications[1-4] 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 tristriphenylphosphinerhodium(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-methyl-allyl, 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 cleaved[3] at a higher rate and the 2-methylallyl group is isomerised at a much lower rate[4] than the allyl group is isomerised by potassium t-butoxide in dimethyl sulphoxide.

The conditions used are important since Corey and Suggs[5] 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 Scheinmann[6] 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-galactopyranose[7] was converted (*ca.* 95%) into the prop-1-enyl ether in 1 h under these conditions whereas the corresponding 6-*O*-but-2′-enyl ether[3] was isomerised (*ca.* 95%) into a mixture of the 6-*O*-but-1′-enyl ether (*ca.* 95%) (hydrolysed by $HgCl_2$ in the presence of HgO[2] 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 $HgCl_2$ 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 shown[6] 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-galactopyranoside[3]) was treated with the rhodium complex *ca.* 95% conversion into a major product (**2**) occurred within 2 h. The total product was treated with $HgCl_2$[2] 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 cleave[3] the but-2-enyl group, to give the known[7] crystalline 2,3,4-tri-*O*-benzyl-D-galactitol.

Tristriphenylphosphinerhodium(I) chloride can abstract carbon monoxide from aldehydes[9] but the free sugar (**3**) and 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose[1] 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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