

The Allyl Ether as a Protecting Group in  
Carbohydrate Chemistry

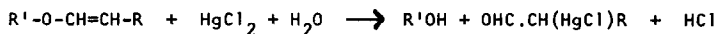
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We have previously described (1) the application of the allyl ether as a protecting group in carbohydrate chemistry. The allyl group is conveniently removed by alkaline isomerisation to the cis-prop-1-enyl group and subsequent hydrolysis with dilute acid. In the case of carbohydrate derivatives containing other acid-labile groupings we have used ozonolysis or oxidation with alkaline permanganate for the selective removal of the prop-1-enyl group.

With a view to finding other non-acidic conditions for the removal of the prop-1-enyl group we investigated the action of mercuric salts with these derivatives. Mercuric salts are known (2) to react with vinyl ethers as shown and by applying this reaction



in the presence of mercuric oxide (to maintain a neutral medium) we have developed a rapid and convenient method for the preparation of carbohydrate derivatives from the prop-1-enyl ethers. The method is of particular value for the preparation of free sugars containing acid labile groupings, from the corresponding prop-1-enyl glycosides.

For example, mercuric chloride (500 mg.) in acetone-water (10 ml., 4:1) was added to a stirred mixture of prop-1'-enyl 4,6-O-benzylidene- $\alpha$ -D-galactopyranoside (500 mg.), mercuric oxide (500 mg.) and acetone-water (10 ml., 4:1). After 5 min., thin-layer chromatography showed complete conversion of the starting material into a product. The mercuric oxide was filtered off, sodium hydrogen carbonate (1 g.) was added to the filtrate and hydrogen sulphide was passed through the solution to precipitate the excess of mercuric salts. After filtration and evaporation of the

solvents, the residue was extracted with hot methyl ethyl ketone and 4,6-0-benzylidene-D-galactose [m.p. 192-194°;  $[\alpha]_D^{25} + 97^\circ$  ( $c$  0.47 in water) - final value] crystallised from the extract on cooling. This compound has previously been isolated (3) from the mixture of compounds obtained by the action of benzaldehyde on D-galactose in the presence of zinc chloride.

In a similar way 2,3-di-0-benzyl-4,6-0-benzylidene-D-galactose [m.p. 153-155° (from benzene);  $[\alpha]_D^{23} + 78^\circ$  ( $c$  0.5 in chloroform)] was obtained from prop-1'-enyl 2,3-di-0-benzyl-4,6-0-benzylidene- $\alpha$ -D-galactopyranoside in excellent yield.

Sodium borohydride reduction of the 2,3-di-0-benzyl-4,6-0-benzylidene-D-galactose gave 2,3-di-0-benzyl-4,6-0-benzylidene-D-galactitol [m.p. 157-159° (from methanol);  $[\alpha]_D^{23} + 41^\circ$  ( $c$  1.02 in chloroform)] required for synthetic studies in connection with the sphingolipids. This method for the conversion of the prop-1-enyl glycosides into the corresponding free sugars and subsequent borohydride reduction should provide a convenient route for the preparation of many substituted alditols.

3-0-Prop-1'-enyl-1,2:5,6-di-0-isopropylidene-D-glucose and methyl 4,6-0-benzylidene-2,3-di-0-prop-1'-enyl- $\alpha$ -D-glucopyranoside were readily converted into 1,2:5,6-di-0-isopropylidene-D-glucose and methyl 4,6-0-benzylidene- $\alpha$ -D-glucopyranoside respectively by the mercuric chloride-mercuric oxide procedure.

Satisfactory analytical figures were obtained for all the compounds described.

#### References

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