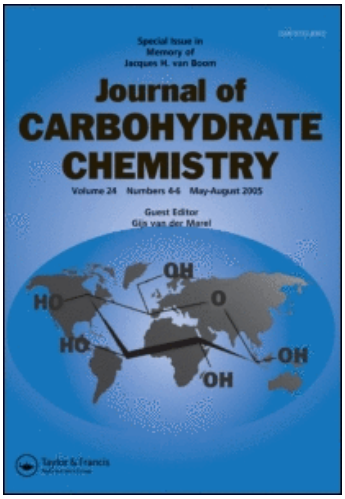

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Unexpected Formation of A 4,6-*O*-Propylidene Derivative from Galactose and Allyl Alcohol in the Presence of Amberlyst^{R}15

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COMMUNICATION

UNEXPECTED FORMATION OF A 4,6-*O*-PROPYLIDENE DERIVATIVE FROM GALACTOSE AND ALLYL ALCOHOL IN THE PRESENCE OF AMBERLYST^{R}15

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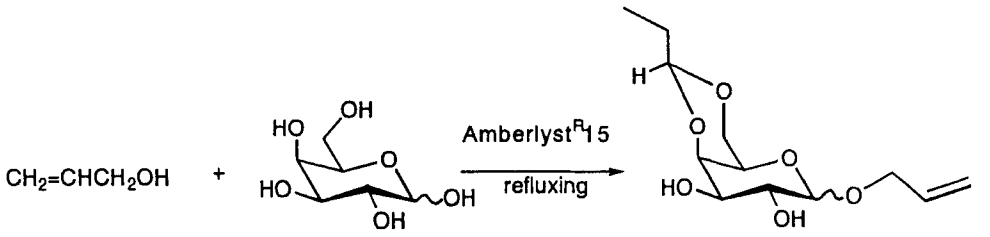
Allyl ethers are convenient and widely used protecting groups in synthetic carbohydrate chemistry.[2] One of the attractive reactions of the allyl ether group is its ready isomerization into a prop-1-enyl ether function under basic or metal-mediated conditions.[2-4] In our research projects to extend galactosyltransferase reactions to the enzymic syntheses of βGal 1,1-linked sugars,[5] 1-*O*-allyl galactopyranoside was needed as a key synthetic intermediate. Anhydrous cation exchange resin (Amberlyst^{R}15:Rohm & Haas Co.) was chosen as the acidic catalyst owing to its ease of handling and removal. In this paper we report an unexpected result of this reaction which gave allyl 4,6-*O*-propylidene galactopyranoside from galactose and Amberlyst in refluxing allyl alcohol.

On treatment of galactose (200 mg) and Amberlyst (100 mg) in allyl alcohol (5 mL) at 100-110 ℃, TLC analysis (silica gel, acetonitrile:water, 10:1) indicated that the allyl glycosylation was completed within 15 min, affording allyl D-galactopyranoside.



SCHEME

When the reaction was continued for an additional hour, less polar products appeared on the TLC. After 3 hours at 100 ℃, yields of the new products reached about 30-40% of the allyl glycoside as analyzed by TLC. Initially these were assumed to be diallylated derivatives in which another OH group at C-2, C-3, C-4 or C-6 was transferred into an allyl ether group. These products were isolated as an anomeric mixture in 30% yield based on galactose by extraction with ethyl acetate and chromatographic purification on silica gel. The ^{1}H NMR spectrum (FIGURE), however, revealed a unique structure different from the expected di-*O*-allylated derivative. The signals at 0.96 ppm (3H, t, CH_3), 1.69 ppm (2H, m, -CH_2-) and 4.65 ppm (1H, t, -*O*-CH-*O*-) indicated the presence of a propylidene function and those at 5.95 ppm (1H, m, -CH=C-) and at 5.2-5.4 ppm indicated the presence of an allyl ether. The signals at 5.00 ppm (d, $J_{1,2}$=3.5 Hz) and 4.45 ppm (d, $J_{1,2}$=8.0 Hz) could be assigned as anomeric protons of α- and β-glycosides, respectively. This information as well as ^{1}H NMR analysis of the chromatographically purified di-*O*-benzylated derivative enabled us to assigne the structure of the reaction products as allyl 4,6-*O*-propylidene-D-galactopyranoside (α/β = *ca.* 3/2).

The above results allowed us to assume that allyl alcohol was isomerized to propanal under acidic conditions with Amberlyst®15, even though there are only a few reports on the acid catalyzed isomerization of allyl alcohols or allyl ethers.[6] In order to confirm this assumption allyl alcohol was refluxed with Amberlyst for 3 hours, and evidence for the isomerization checked by ^{1}H NMR spectroscopy. The NMR

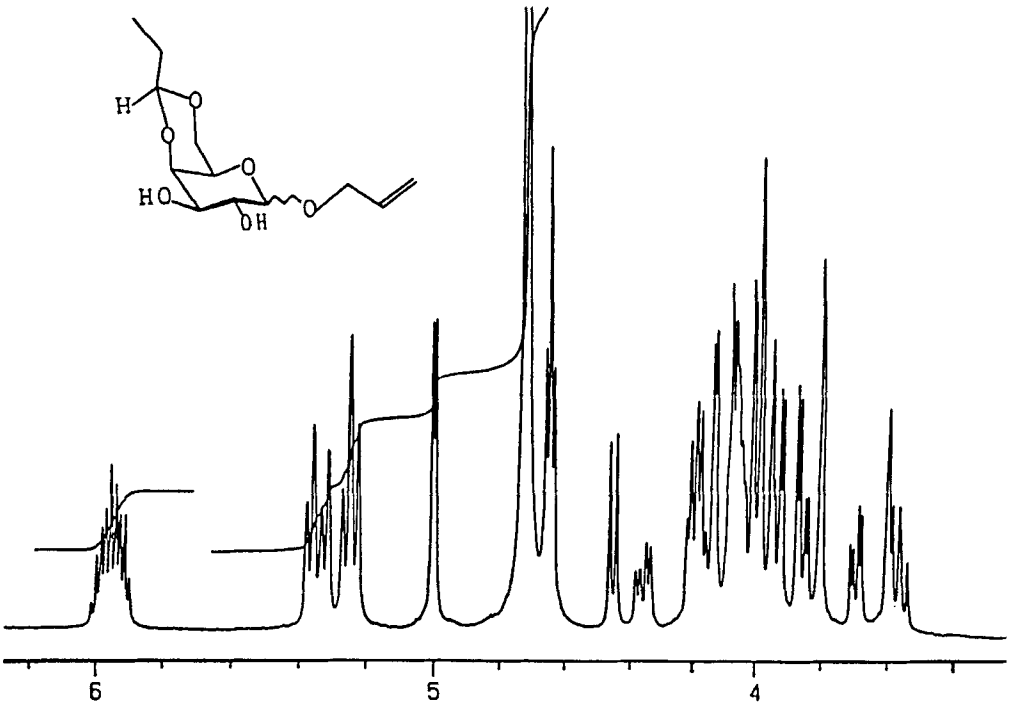


FIG. 400 MHz ^{1}H NMR Spectrum in D_2O.

spectrum was compared with that of the standard solution containing allyl alcohol (80%) and propanal (*ca.* 20%) which were preliminarily heated for 30 min at 80 ℃ with Amberlyst^{R}15. The spectra showed that 3-5% of allyl alcohol was converted into propanal existing in the form of 1,1-diallyloxy propane which should be the propylidene donor in the observed reaction. The result also indicated that the 4,6-*O*-propylidene group tolerated the acidic conditions, though most of allyl alcohol was still found to remain in the reaction mixture.

In order to extend this novel reaction, glucose was subjected to the same reaction and similarly afforded allyl 4,6-*O*-propylidene glucopyranosides (α/β = *ca.* 2/1) in 30% yield.

In conclusion, allyl 4,6-*O*-propylidene galactopyranoside was found to be derived from galactose and allyl alcohol in the presence of Amberlyst^{R}15. The results

may show the potential of allyl alcohol to be used both for the allyl glycosylation and propylidenation[7] in acidic media. The mechanism should be evaluated in more detail since the isomerization of allyl alcohol under acidic conditions is unexpected and rather unusual. Alternatively, a quite different reaction mechanism may be possible.

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7. T. Bieg and W. Szeja[4b] have reported the preparation of 1,2-*O*-propylidenene α-D-galactopyranoside from allyl α-D-galactopyranoside *via* isomerization of the allyl ether by *trans*-$[Pd(NH_3)Cl_2]$ in *tert*-butyl alcohol.