*Carbohydrate Research*, 42 (1975) C4–C5

**Preliminary communication**

# On the partial acetylation of 1,6-anhydro-β-D-galactopyranose: silica gel-promoted interconversion of the 2,3- and 2,4-diacetates

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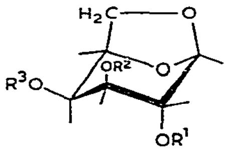
(Received April 14th, 1975; accepted for publication, May 2nd, 1975)

The partial acetylation of 1,6-anhydro-β-D-galactopyranose (**1**) and its 2-acetate (**2**) with acetic anhydride in pyridine has been reported to give the 2,3-diacetate (**3**) in yields of 41% and 54%, respectively[1]. The factors governing the relative reactivities of hydroxyl groups are not at present sufficiently known[2] and other factors, besides conformational effects, were invoked to explain the preferential reactivity sequence ax HO-3 > eq HO-4. We recently found[3], however, that partial acetylation of **1** and **2** with acetic anhydride–pyridine gave a mixture of **3**, m.p. 114–116°, $[\alpha]^{25}_{D}$ −0.5° (chloroform) (25% from **1** and 40% from **2**), and syrupy 2,4-di-*O*-acetyl-1,6-anhydro-β-D-galactopyranose (**4**), $[\alpha]^{26}_{D}$ −8.5° (25% from **1** and 40% from **2**), which were later used in the syntheses of 4-*O*- and 3-*O*-α- and -β-D-galactopyranosyl-D-galactoses[4]. The structures of diacetates **3** and **4** were determined by n.m.r. spectroscopy. The chemical shifts of the various protons and the signal pattern in the low-field region of the spectra were sufficiently different to permit detection of each diacetate (**3** and **4**) in diacetate mixtures. For **3**, the signal for H-3 was a multiplet at $\tau$ 4.92 ($J_{3,4}$ 5.5, $J_{2,3}$ ~$J_{1,3}$ ~$J_{3,5}$ 1.5 Hz), and that for H-4 was a wide triplet at $\tau$ 5.83 ($J_{4,3}$ 4.5 Hz). In the spectrum of **4**, the multiplet assigned to H-3 appeared at $\tau$ 5.90, and the H-4 triplet at $\tau$ 5.00. Signals assigned to H-2 resonated at $\tau$ 5.25 (**3**) and 5.20 (**4**), and could also be differentiated.



1 $R^1 = R^2 = R^3 = H$
2 $R^1 = Ac, R^2 = R^3 = H$
3 $R^1 = R^2 = Ac, R^3 = H$
4 $R^1 = R^3 = Ac, R^2 = H$
5 $R^1 = R^2 = R^3 = Ac$

The acetylation products were isolated by column chromatography on silica gel[1,3], and we have now observed that either **3** or **4** gives a 1:1 mixture of **3** and **4** when passed through a silica gel column, when kept overnight in solution in contact with silica gel, or when adsorbed for several hours on a silica gel t.l.c. plate before development. As acyl migration clearly takes place during the isolation process, the relative reactivities of the hydroxyl groups in **1** and **2** cannot be inferred from the amounts of **3** and **4** isolated by the above procedure[1,3]. However, the relative proportions of diacetates **3** and **4** can be determined from the integrated intensities of the signals for H-2 and H-4 of **4** and for H-3 of **3**, in the n.m.r. spectra of acetylation mixtures. By this method, we found that, in contrast to previous results[1], the main diacetate of the partial acetylation of **1** and **2** was the 2,4-derivative **4**; the 2,3-diacetate **3** was also formed, but in variable and smaller proportions according to the acetylation conditions. When the partial acetylation of **1** was carried out under the conditions reported by Shapiro *et al.*[1], the n.m.r. spectrum of the acetylation mixture indicated that diacetates **4** and **3** were present in a ratio 5:1. Under these conditions, triacetate **5** was the main acetylation product. Similarly, partial acetylation of **2** gave diacetates **4** and **3** in the ratio 3:1, with triacetate **5** being formed in smaller proportion.

Kinetic studies on the partial acetylation of **1** and **2** are presently being carried out.

## ACKNOWLEDGMENTS

The authors thank Professor A. Alemany for helpful discussions, Miss M. D. Casado for recording the n.m.r. spectra, and the Ministerio de Educación y Ciencia for a scholarship (M. E. Ch-F).

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