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Ruthenium-Catalysed Epimerisation of Carbohydrate Alcohols as a Method to Determine the Equilibria for Epimer Interconversion in Hexopyranosides

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Ruthenium-catalysed epimerisation of secondary carbohydrate alcohols was used to determine the thermodynamic equilibrium between non-anomeric epimers of partially protected glucose, mannose and allose derivatives. A cyclopentadienylruthenium catalyst was used to epimerise each of two pure epimeric alcohols in two separate experiments. The epimerisation reactions were run until the same ratio of epimers was obtained from the two experiments.

Introduction

Transition metal complexes can catalyse the redox interconversion of alcohols and ketones in reactions that are conceptually related to, but mechanistically distinct from, the classical Meerwein–Ponndorf–Verley–Oppenauer reaction,[1] with transition metal hydrides being formed as intermediates.[2] An oxidation–reduction (dehydrogenation–hydrogenation) sequence results in the racemisation (or epimerisation) of alcohols. Beyond its basic importance, the homogeneous catalytic hydrogen-transfer redox reaction has also been coupled with other concepts in organic chemistry to give methods for alcohol functionalisation, as for example with enzymatic kinetic resolution to give a dynamic kinetic resolution,[3] or for the formation of C–N, C–O or C–C bonds by a sequence of oxidation–activation, coupling and re-reduction.[4] In particular, dynamic kinetic resolution based on the racemisation (or epimerisation) of secondary alcohols with ruthenium catalysts **1a**–**c** (Figure 1) has found many applications in enantioselective synthesis.[3] The catalyst **1c**, activated with *t*BuOK, has been shown to have exceptional reactivity, racemising, for example, 1-phenylethanol with $t_{1/2} < 2$ min at room temp. with 0.5 mol-% catalytic loading.[5] Hence this catalyst was chosen for the study described in this paper. The reaction mechanism of racemisation of secondary alcohols by catalyst **1c** has been studied in some detail,[6–8] and an overview is given in Scheme 1.

Carbohydrates are a cheap, renewable raw material, and so are of great interest for the future from the point of view of green chemistry.[9] They are also very rich in alcohol functionality, so the reactivity, and especially the catalytic reactivity, of carbohydrate alcohols is an important area for research. The Oppenauer oxidation is not used for carbohydrate alcohols,[10,11] and judging by earlier reports in the literature, secondary carbohydrate alcohols appear to be very unreactive towards oxidation by transition-metal complex-catalysed hydrogen transfer: it has been shown that the anomeric hemiacetal of carbohydrates may be oxidised to the lactone by rhodium or ruthenium complexes operating by a hydrogen-transfer mechanism, without affecting unprotected secondary hydroxy groups, confirming their low reactivity.[14–19] One paper does describe low-yielding oxidation of OH-5 in a glucofuranose derivative by dehydrogenation with a $RuH_2(PPh_3)_4$ catalyst.[19] Also, with *heterogeneous* catalysts some reactivity has been reported.[20,21]

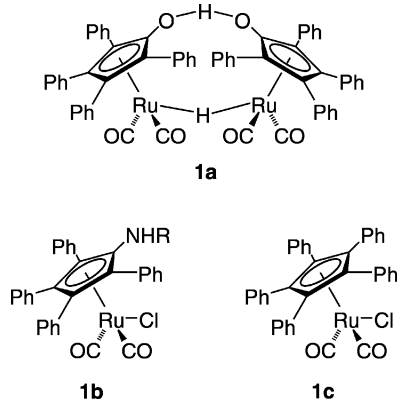

Figure 1. Ruthenium complexes used in the racemisation or epimerisation of secondary alcohols.

The reason for this low reactivity is probably primarily electronic in origin: The transfer of hydride from the alcohol C atom to the metal centre is rate-determining for electron-deficient alcohols.[28] It is known that electron-

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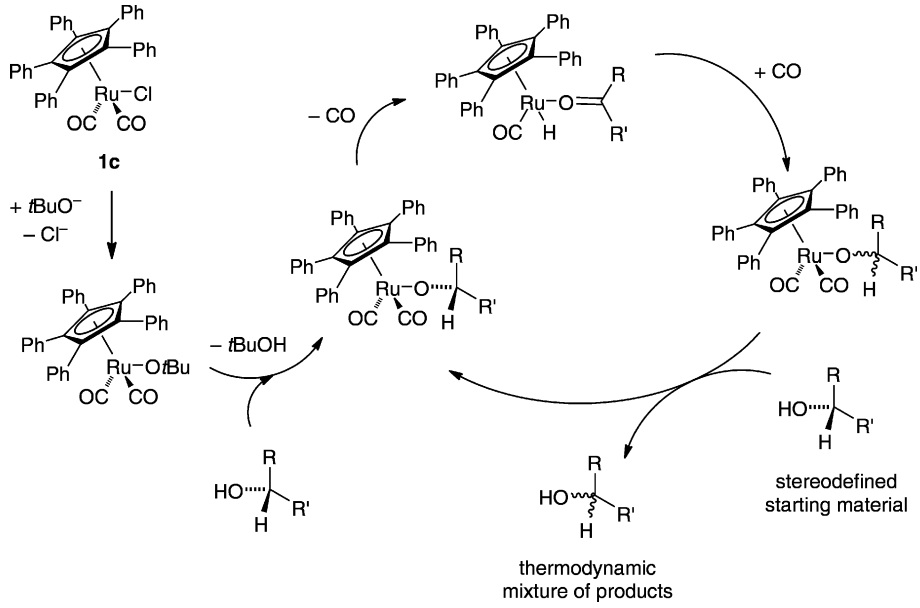


Scheme 1. Mechanistic overview of the epimerisation/racemisation reaction as catalysed by the ruthenium complex **1c**.

withdrawing substituents on the alcohol moiety disfavour this process,[28] and the polyoxygenated nature of the carbohydrate means that secondary alcohol functionalities are expected to be electron-deficient and their dehydrogenation to be slow. Steric arguments against coordination of the alcohol to the metal are almost certainly less important: secondary carbohydrate alcohols are sterically hindered, but bulky *tert*-butoxide is known to be a ligand during the activation of the ruthenium epimerisation catalyst complex **1c** (Scheme 1).[7] The presence of multiple Lewis basic coordination sites in carbohydrates may also play some role in their low reactivity towards redox catalysts.

In this paper, we describe the ruthenium-catalysed epimerisation of secondary carbohydrate alcohols. Using this reaction, we are able to experimentally address the position of equilibrium and hence the relative stabilities of different hexopyranosides, as well as a hexofuranose derivative. Measurement of the equilibrium configuration of secondary hydroxy groups (i.e. not the anomeric position) around the pyranose ring, and thus the relative thermodynamic stabilities of the different pyranoside configurations, is a matter of fundamental importance, especially given the importance of carbohydrates, and pyranosides in particular, in nature. However, it is not a straightforward task, and information about non-anomeric configurational equilibria has been obtained only in some special cases. An enzyme, UDP-glucose-4′-epimerase, catalyses the reversible interconversion of (anomerically locked) α UDP-glucose and α UDP-galactose, allowing a direct measurement of the relative stabilities of α-glucose and α-galactose derivatives.[29] The equilibrium constant has been estimated to be $K \approx 3$ in favour of the α-glucose derivative. On unprotected sugars, the molybdenum-catalysed Bilik reaction[30] and nickel-mediated reactions[31] interconvert 2-epimeric aldoses by carbon-skeleton-rearrangement mechanisms. The equilibrium ratio of free glucose and mannose as measured by the Bilik procedure is 2.5:1 (using 0.05 equiv. catalyst),[30] whereas the nickel-catalysed route gives a ratio around 1.4:1–1.7:1 (using 1 equiv. catalyst).[31] In these C-2 epimerisation reactions,[30–32] a free hemiacetal is required, meaning that as well as the interconversion of C-2 epimers (and possibly other side-reactions), the situation is complicated by (rapid) equilibration of the anomers at C-1.

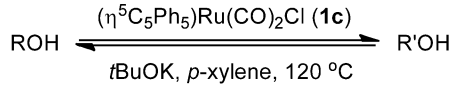
Results and Discussion

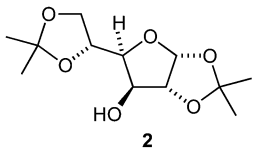
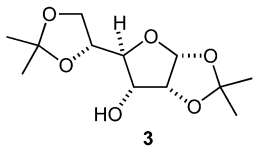
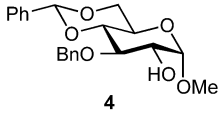
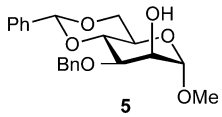
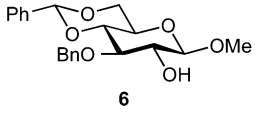
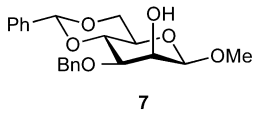
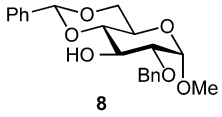
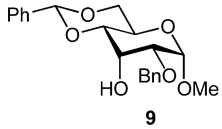
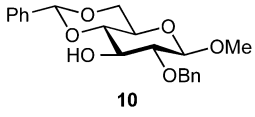
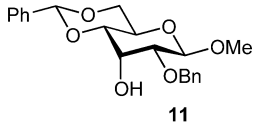
We began by examining the reactivity of a readily available model secondary carbohydrate alcohol, the mono-unprotected furanose derivative diacetone glucose **2**, and its C-3 epimer **3**, with ruthenium catalyst **1c** (activated with *t*BuOK). Despite the very high reactivity of this catalyst in the epimerisation of secondary alcohols,[5] no reaction was seen with the carbohydrate alcohol **2** in toluene after several hours at room temperature.

Nevertheless, heating the carbohydrate alcohol **2** with the catalyst did result in some epimerisation, and after long reaction times at high temperature (120 °C), with a change of solvent to *p*-xylene, significant reaction was seen, giving a 70:30 mixture of diastereomers **2** and **3**, as judged by the ^{1}H NMR spectrum of the crude product mixture. Repeating the reaction starting from the C-3 epimer **3** gave the same mixture of diastereomers, indicating that the thermodynamic equilibrium for the epimerisation reaction had been reached (Table 1, entry 1). We went on to examine a series of pairs of epimeric secondary mono-unprotected pyranoside alcohols. Each of the alcohols **4**–**11**[33] were exposed to the epimerisation catalyst in *p*-xylene at 120 °C (Table 1, entries 2–5).

In most cases (Table 1, entries 1, 2, 4 and 5) the same product composition, within experimental error, was reached from both directions (i.e., starting from each of the

Table 1. Reactions were carried out with (η^5-C_5Ph_5)Ru(CO)$_2$Cl (**1c**) (0.05 equiv.), *t*BuOK (0.06 equiv.) in *p*-xylene at 120 °C for the times stated.



Entry	ROH	R'OH	Outcome from ROH[a]	Outcome from R'OH[a]
1	 **2**	 **3**	From **2** (24 h): **2**:**3**, 70:30	from **3** (24 h): **2**:**3**, 70:30
2	 **4**	 **5**	From **4** (24 h): **4**:**5**, 45:55	from **5** (48 h): **4**:**5**, 45:55
3	 **6**	 **7**	From **6** (120 h): **6**:**7**, 93:7[b]	from **7** (72 h): **6**:**7**, 88:12[b]
4	 **8**	 **9**	From **8** (120 h): **8**:**9**, 89:11[b]	from **9** (120 h): **8**:**9**, 89:11[b]
5	 **10**	 **11**	From **10** (48 h): **10**:**11**, 74:26	from **11** (72 h): **10**:**11**, 73:27

[a] Ratio determined by integration of signals in the ^{1}H NMR spectrum of the crude reaction product mixture. [b] Two additional portions of catalyst (0.05 equiv. each) were added during the reaction as thermodynamic equilibrium between the interconverting epimers was not reached with the initial amount (0.05 equiv.) of catalyst: starting from **6** with only 0.05 equiv. catalyst, after 48 h the ratio **6**/**7** was 95:5; starting from **7** with only 0.05 equiv. catalyst, after 96 h the ratio **6**/**7** was 55:45; starting from **8** with only 0.05 equiv. catalyst, after 48 h the ratio **8**/**9** was 95:5; starting from **9** with only 0.05 equiv. catalyst, after 120 h the ratio **8**/**9** was 62:38.

two epimers) indicating that equilibrium had been reached (Figure 2). In one case (Table 1, entry 3), equilibrium was not reached from at least one direction, but the diastereomeric ratio of **6**/**7** was 93:7 and 88:12 when starting from **6** or **7**, respectively, indicating that a diastereomeric mixture close to the equilibrium composition had been reached. The reactions were quite clean: by-product formation was minimal. The catalyst is apparently deactivated under the harsh reaction conditions and long reaction times used; for two of the pairs of interconverting epimers (viz **6**–**7** and **8**–**9**), the same composition was not reached from both directions with 0.05 equiv. catalyst, but the addition of further catalyst at intervals during the reaction induced further reaction and progress towards equilibrium (Table 1, entries 3 and 4).

The alcohols with OH-2 free (**4**–**7**, Table 1, entries 2 and 3) equilibrate between *gluco* and *manno* configurations. Entry 2 clearly shows that the α-*manno*-configured alcohol **5** has a similar stability to the α-*gluco*-configured alcohol **4**

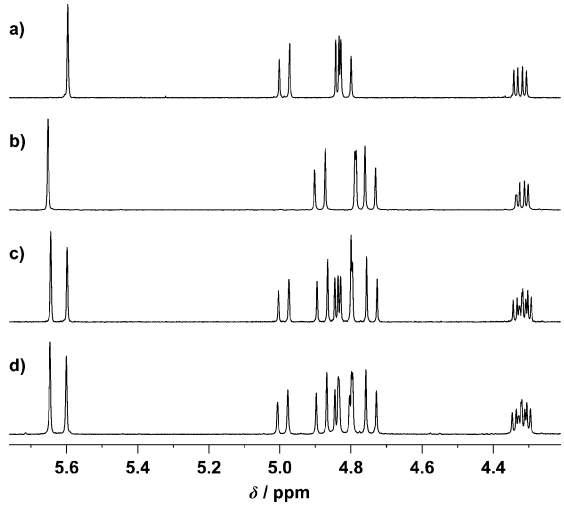


Figure 2. Extracts of the 400 MHz ^{1}H NMR spectra of a) isolated **4**; b) isolated **5**; c) crude product mixture from epimerisation starting from **4**; d) crude product mixture starting from **5**.

($K_{393\,K} \approx 0.8$). In fact, the equilibrium is shifted slightly in favour of the *manno* derivative. This is a counterintuitive result if diaxial interactions are the main consideration. However, on the top face of a pyranoside ring, diaxial interactions are lower in energy than those in a cyclohexane due to the absence of axial substituents on the ring oxygen and also due to the slightly distorted ring pucker. For the β-*gluco*–β-*manno* interconversion (Table 1, entry 3), equilibrium was not reached, but we can say that here the β-*gluco* alcohol **6** is more stable than the β-*manno* alcohol **7** with the equilibrium constant in the range $7 \leq K_{393\,K} \leq 13$. The difference between the behaviour of the α (**4** and **5**) and β (**6** and **7**) pairs is a manifestation of the Δ2 effect, which refers to the observed greater difference in stability of the α over the β anomer for mannose than for glucose.[34–36] This has been explained as being due to destabilisation of the β-*manno* configuration due to the close proximity of three oxygen atoms (O-1, O-2 and O-5) or by an enhanced stabilisation of α-*manno* configuration due to the 180° angle between neighbouring dipoles (C1–O1 and C2–O2).

The pyranoside alcohols with OH-3 free (**8**–**11**, Table 1, entries 4 and 5) equilibrate between *gluco* and *allo* configurations. Entry 5 shows that at equilibrium, the β-*allo*-configured alcohol **11** is less stable than the β-*gluco* alcohol **10** with an equilibrium constant of $K_{393\,K} = 2.8 \pm 0.2$. In entry 4, equilibrium was reached after addition of a total of 0.15 equiv. of the catalyst, and the α-*allo* alcohol **9** is less stable than the α-*gluco* alcohol **8** with an equilibrium constant of $K_{393\,K} = 8.1 \pm 0.5$. Hence for both anomers the *gluco* configuration is more stable than the *allo*, but the difference in stability is greater between the α compounds (**8** and **9**) than the β compounds (**10** and **11**), which is consistent with a steric clash between the axial OH-3 and the axial anomeric oxygen in the α-*allo* compound **9** that is not present in the β-*allo* derivative **11**.

In their experiments on the epimerisation of unprotected methyl glycopyranosides with Raney nickel, Koch and Stuart,[24,25] and later Perlin,[22] observed that thermodynamic equilibrium was not reached (i.e. the same composition of the product mixture was not reached starting from each of the components – indeed the same mixture was not seen starting from any two of the components tested), but it is noteworthy that significant α-Glc→α-Gal and α-Glc→α-Man epimerisation away from the α-glucoside was seen. This observation, along with the data from the skeletal rearrangement reactions[30,31] (see above) and now our result for the α-Glc–α-Man equilibrium position, is at odds with an assumption that α-*gluco* is obviously the most stable configuration for glycopyranosides.

Conclusions

The results described in this article represent one of the first reports of the reaction of secondary carbohydrate alcohols in transition-metal complex-catalysed hydrogen-transfer redox reactions.[19] The epimerisation reaction is expected to give a thermodynamic mixture of products, and indeed this was seen in most cases, while in one case, a diastereomeric mixture close to the equilibrium composition was obtained. The reaction requires somewhat forcing conditions, but the carbohydrate derivatives appear to be stable and by-product formation was minimal. Equilibrium constants are expected to change with temperature and solvent, and the protecting group pattern and the presence of between 5 and 15 mol-% of the catalytic complex may also influence the position of equilibrium to some extent. Hence the values obtained here cannot be treated as absolute. Nevertheless, as far as we are aware, the thermodynamic equilibrium positions of α-*gluco* vs. α-*manno*, of β-*gluco* vs. β-*manno*, or of *gluco* vs. *allo* interconversions have not been measured experimentally before, which lends the results reported here some significance.

Experimental Section

General Procedures for Epimerisation: All epimerisation reactions were carried out under dry argon atmosphere using standard Schlenk technique. All syringes used were purged with Ar three times before use. All glassware was flame-dried and left to cool to room temp. in a desiccator and then placed under Ar. Addition of extra ruthenium complex (η^5-C_5Ph_5)Ru(CO)$_2$Cl (**1c**) was carried out under an argon atmosphere in a glove box. The *p*-xylene was dried with sodium wire. Dry THF was obtained from a VAC solvent purifier. Ruthenium complex (η^5-C_5Ph_5)Ru(CO)$_2$Cl (**1c**) was synthesised according to a literature procedure.[8]

For Carbohydrate Alcohols that were Solids: The carbohydrate alcohol (37 mg, 0.10 mmol) and (η^5-C_5Ph_5)Ru(CO)$_2$Cl (**1c**) (3.2 mg, 0.005 mmol, 0.05 equiv.) were added to a flame-dried Schlenk tube (10 mL), which was purged with Ar three times. *p*-Xylene (1 mL) was added by syringe and the resulting solution was stirred under Ar at room temp. for 10 min. *t*BuOK (12 μL of a 0.5 M solution in THF, 0.006 mmol, 0.06 equiv.) was then added, and the solution typically immediately changed colour from pale yellow to orange-yellow. After 10 min, the reaction mixture was submerged in an oil-bath at 120 °C and left to stir for 24, 48, 72 or 120 h. After this time, the reaction mixture was allowed to cool to room temp., transferred to a round-bottomed flask (rinsing with CH_2Cl_2) and concentrated in vacuo. The crude reaction product was dried on a vacuum pump and then analysed by ^{1}H NMR spectroscopy.

For Carbohydrate Alcohols that were Oils: The carbohydrate alcohol was dissolved in the appropriate volume of *p*-xylene to give a 0.1 M stock solution, and then stirred over molecular sieves (4 Å) for 3 h. (η^5-C_5Ph_5)Ru(CO)$_2$Cl (**1c**) (3.2 mg, 0.005 mmol, 0.05 equiv.) was added to a flame-dried Schlenk tube (10 mL), which was purged with Ar three times. The *p*-xylene solution (1 mL) of the carbohydrate alcohol was added to this tube by syringe, and the resulting solution was stirred under Ar at room temp. for 10 min. *t*BuOK (12 μL of a 0.5 M solution in THF, 0.006 mmol, 0.06 equiv.) was then added, and the solution typically immediately changed colour from pale yellow to orange-yellow. After 10 min, the reaction mixture was submerged in an oil-bath at 120 °C and left to stir for 24, 48, 72 or 120 h. After this time, the reaction mixture was allowed to cool to room temp., transferred to a round-bottomed flask (rinsing with CH_2Cl_2) and concentrated in vacuo. The crude reaction product was dried on a vacuum pump and then analysed by ^{1}H NMR spectroscopy.

Procedure for the Addition of Extra Catalyst: The reaction mixture was allowed to cool to room temp. Additional ruthenium complex (η^5-C_5Ph_5)Ru(CO)$_2$Cl (**1c**) (3.2 mg, 0.005 mmol, 0.05 equiv.) was added under an argon atmosphere in a glove box. The reaction vessel was sealed and removed from the glove box. Additional *t*BuOK (12 μL, 0.5 M in dry THF, 0.006 mmol, 0.06 equiv.) was then added to the reaction mixture. The reaction mixture was left to stir at room temp. for 10 min and was then submerged in an oil-bath at 120 °C and left to stir. This procedure was repeated as required.

Acknowledgments

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[21] Extensive epimerisation of the hydroxy groups of unprotected glycosides has been observed over Raney nickel after several days at 100 °C,[22–25] and also under hydrogenation conditions over copper chromite under high pressure at 180 °C (along with reduction products).[26] It has been suggested that these reactions go by dehydrogenation/re-hydrogenation mechanisms. In the heterogeneous oxidation (dehydrogenation) of carbohydrates over platinum, the primary C-6 is oxidised, and the unprotected secondary alcohols are unaffected.[27].
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