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Hydrosilylation conditions applied on alkenyl benzylated xyloses: selective reduction and isomerization

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In the presence of triethylsilane and different transition metal catalysts, the main reactive pathways observed from benzylated xyloses bearing an unsaturated tether were the reduction and the isomerization of the double bond without debenzylation of the sugar moiety. Copyright © 2009 John Wiley & Sons, Ltd.

Keywords: pentosides; hydrosilylation; reduction; isomerization; palladium; platinum

Introduction

Over recent years we have pursued a research program dedicated to the valorization of D-xylose and L-arabinose,[1,2] i.e. pentoses readily accessible from wheat straw and bran.[3] In this context, we have recently reported the surfactant properties of D-xylose derivatives obtained by glycosylation with unsaturated alcohols as shown in Scheme 1.[4]

On the other hand, the synthesis and use of glycodendrimers is a growing research topic.[5] In this context, carbosiloxane-based glycodendrimers have shown interesting biological properties.[6] This led us to envisage the synthesis of such compounds via hydrosilylation with triethylsilane of the double bond of the above D-xylose derivatives. Such reaction is usually catalyzed by various transition metals[7] and we chose to use palladium and platinum complexes. Since it is known that hydrosilanes can react with alcohols under Pd[8,9] and Pt[10] catalysis, the reactions were carried out from benzylated substrates.

Experimental

All experiments were carried out under an argon atmosphere in distilled solvents. $PdCl_2(MeCN)_2$ [11] and dicyclopentadienedichloroplatinum (II)[12] were prepared as described in the literature. $Pd(PPh_3)_4$, Speier's catalyst CPA ($H_2PtCl_6 \cdot 6H_2O$) and Karsted's catalyst in toluene solution are commercially available and were used as received.

^1H and ^{13}C NMR spectra were recorded on an AC 250 Bruker in $CDCl_3$ as solvent with TMS as reference for ^1H spectra and $CDCl_3$ (δ7.0) for ^{13}C spectra. All experiments (MS and HRMS) were performed on a hybrid tandem quadrupole/time-of-flight (Q-TOF) instrument, equipped with a pneumatically assisted electrospray (Z-spray) ion source (Micromass, Manchester, UK) operated in positive mode. The electrospray potential was set to 3 kV in positive ion mode (flow of injection 5 μl/ min) and the extraction cone voltage was usually varied between (30 and 90 V).

Pd-catalyzed Reactions

Method A

In a Schlenk tube containing a solution of $PdCl_2(MeCN)_2$ (0.05 equiv.) and PPh_3 (0.05 equiv.) in THF (1 ml) were successively added the alkene diluted in THF (1 ml) and triethylsilane (1.5 equiv.). The resulting mixture was heated for 20 h at 70 °C, then filtered over Celite® and concentrated under reduced pressure. The product was purified by chromatography using petroleum ether–ethyl acetate 95 : 5 as eluting mixture and the residue was analyzed by ^1H NMR.

Method B

The substrate was dissolved in DMF (2 ml). Triethylsilane (1.5 equiv.) and $Pd(PPh_3)_4$ (0.02 equiv.) were successively added and the resulting mixture was heated at 115 °C for 5 h. After filtration over Celite® and concentration under reduced pressure, the residue was purified by chromatography (eluting mixture : petroleum ether/ethyl acetate 95 : 5) and the residue was analyzed by ^1H NMR.

Pt-catalyzed Reactions

Method C

After dissolving the substrate (0.1 mmol) in THF (1.5 ml), triethylsilane (1.5 equiv.) and CPA or Speier catalyst (0.05 equiv.), previously activated in isopropanol, were successively added drop-wise. The resulting mixture was heated at 70 °C for 20 h, then filtered over Celite® and concentrated under reduced pressure. After purification by chromatography (eluting mixture petroleum ether–ethyl acetate 95 : 5), the residue was analyzed by ^1H NMR.

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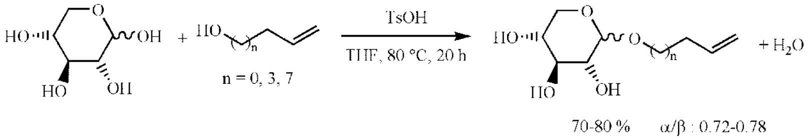
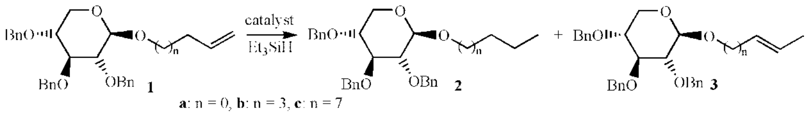


Scheme 1. Glycosylation of D-xylose.



Scheme 2. Reactions of pentosides with Et_3SiH in the presence of different catalysts.

Method D

A similar procedure was used to that described above, with respectively the substrate (0.2 mmol) in THF (2 ml), triethylsilane (1.5 equiv.) and $PtCp_2Cl_2$ (0.05 equiv.).

Method E

A similar procedure was used to that described above with respectively the substrate (0.2 mmol) in THF (2 ml), triethylsilane (1.5 equiv.) and Karsted's catalyst (0.02 equiv.).

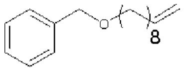
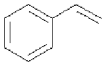
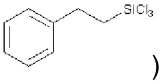
Results and Discussion

Benzylated alkenyl pentosides **1a–1c** (Scheme 2) were obtained from the corresponding polyols using benzyl bromide and NaH in DMSO.

The first experiments were carried out using allyl 2,3,4-tri-*O*-benzyl-D-xylopyranoside (**1a**) as the substrate and a 1 : 1 mixture of $PdCl_2(MeCN)_2–PPh_3$ [13] as the catalyst in THF (Table 1, entry 1). Heating this mixture at 70 °C for 20 h led to the complete consumption of the substrate. After filtration over Celite® to remove the catalyst, the crude reaction mixture was analyzed by mass spectroscopy. This analysis showed the absence of the expected hydrosilylation product; the only identified product was the reduction product **2a** (Scheme 2). Switching to $Pd(PPh_3)_4$ as the catalyst and DMF as the solvent at 110 °C[14] did not induce the hydrosilylation reaction but led to the formation of a mixture of **2a** and the isomerization product **3a** (Scheme 2; Table 1, entry 2). Under similar experimental conditions, the hex-1-enyl-2,3,4-tri-*O*-benzyl-D-xylopyranoside (**1b**) and the dec-1-enyl-2,3,4-tri-*O*-benzyl-D-xylopyranoside (**1c**) afforded also a mixture of the corresponding **2** and **3** without production of hydrosilylation products (Table 1, entries 3–6). It seems interesting, however, to note that the **2 : 3** ratios depend greatly on the reaction conditions and the length of the alkenyl tether.

The presence of the sugar moiety seems to have a real effect on the orientation of the reaction, mechanisms of hydrogenation and isomerization being predominant towards the one relative to hydrosilylation. However, in fact, while reactions performed on 10-benzyloxy-dec-1-ene and on styrene or octene led respectively to either hydrogenated and isomerized adducts or hydrosilylated ones (Table 1, entry 7 vs entries 8 and 9), the reactivity is probably influenced in the presence of the oxygen atom as a potential poisoning weak ligand. Furthermore, while hydrosilanes are used for debenzylation of $PhCO_2Bn$ in the presence of $PdCl_2$ and Et_3N in

Table 1. Pd-catalyzed reactions

Entry	Substrate	Method[a]	Conversion (%)[b]	**2:3**[b]
1	**1a**	A	100	100 : 0
2	**1a**	B	100	80 : 20
3	**1b**	A	100	53 : 47
4	**1b**	B	100	20 : 80
5	**1c**	A	100	74 : 26
6	**1c**	B	66	18 : 48
7[c]		B	52	7 : 45
8[d]		B	100	-/-()
9[e]	1-Octene (C_8H_{16})	B	100	-/-(n-$C_8H_{17}SiEt_3$)

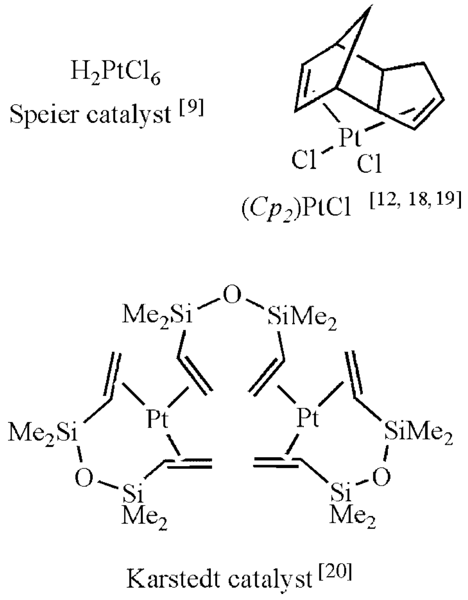
[a] Method A: substrate (0.1 mmol), $PdCl_2(MeCN)_2$ (0.05 equiv.), PPh_3 (0.05 equiv.), Et_3SiH (1.5 equiv.), THF (2 ml), 70 °C, 20 h. Method B: substrate (0.1 mmol), $Pd(PPh_3)_4$ (0.02 equiv.), Et_3SiH (1.5 equiv.), DMF (2 ml), 110 °C, 5 h.

[b] **2** and **3** were identified by mass spectroscopy and ^1H NMR, the ratios were determined by ^1H NMR.

[c] 0.4 mmol of substrate.

[d] Tsuji *et al.*[14] Cl_3SiH instead of Et_3SiH.

[e] Tsuji *et al.*[14]



Scheme 3. Pt catalysts.

Table 2. Pt-catalyzed reactions

Entry	Substrate	Method[a]	Conversion (%)[b]	**2 : 3**[b]
1	**1a**	C	100	100 : 0
2	**1a**	D	100	100 : 0
3	**1a**	E	100	80:20[c]
4	**1b**	C	100	82 : 18
5	**1b**	D	100	100 : 0
6	**1b**	E	100	55 : 45
7	**1c**	C	100	100 : 0
8	**1c**	D	100	90 : 10
9	**1c**	E	100	20 : 80

[a] All reactions have been carried out using 0.1 mmol of substrate, 1.5 equiv. of Et_3SiH and the Pt catalyst (0.02–0.5 equiv.) in THF (1.5 ml) at 50 or 70 °C for 20 h. Method C: Speier catalyst (0.05 equiv.), 70 °C, 20 h. Method D: $(Cp_2)PtCl_2$ (0.02 equiv.), 70 °C, 20 h. Method E: Karsted catalyst (0.02 equiv.), 70 °C, 20 h.

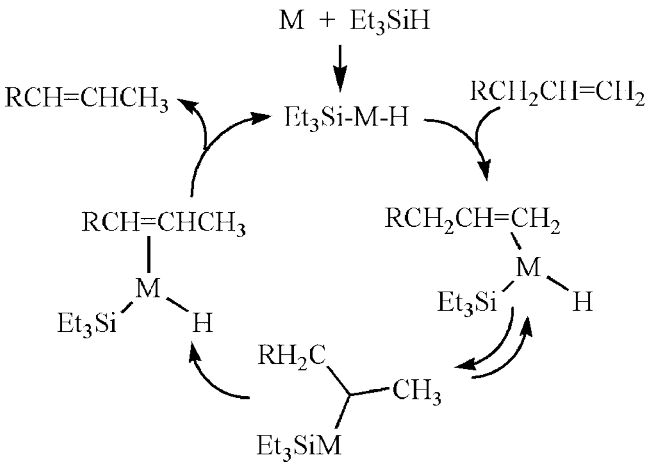
[b] See Table 1.

[c] Traces of a hydrosilylation adduct have been detected by mass spectroscopy.

methanol,[15] the absence of debenzylation of the sugar moiety is here noteworthy even when reduction of the double bond takes place as the major transformation.

As platinum complexes are often used to induce hydrosilylation reactions,[16] we carried out subsequent experiments using the Pt^{IV}, Pt^{II} and Pt^0 catalysts shown in Scheme 3.

As indicated by the results summarized in Table 2, all these catalysts mediated the complete transformation of the substrates but, unfortunately, without formation of hydrosilylation compounds, except from **1a** which, in the presence of the Karstedt catalyst, provided traces of the hydrosilylated derivative (entry 3). Except for this compound, the only identified compounds were the reduction and isomerization products. As with the Pd catalysts, the **2 : 3** ratios depended on the reaction conditions and the length of the alkenyl tether.



Scheme 4. Mechanism of isomerization.

Comments concerning the formation of the reduction and isomerization products are required. According to literature,[9,19,21,22] the reaction of Et_3SiH with transition metals (M) can lead to the generation of Et_3SiMH and hydrogen. Thus, some metal-catalyzed hydrogenation of the C=C bond can occur. The used experimental conditions are, however, not able to induce the hydrogenolysis of the benzyloxy groups. In fact, the literature reports examples of the selective Pd-catalyzed hydrogenation of C=C bonds in the presence of such protective groups.[23] The isomerization occurs probably via the addition of Et_3SiMH to the double bond (Scheme 4).[9] The subsequent β-H elimination can afford the isomerization product.

In conclusion, the reaction of the unsaturated pentosides **1a**–**1c** with triethylsilane in the presence of various Pd and Pt catalysts led mainly to the hydrogenation and isomerization of the terminal double bond.

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