J.Serb.Chem.Soc. 68 (10)719–722(2003)
JSCS – 3091

UDC 577.164.1+66.095.12+547.81:66.097
Short communication

SHORT COMMUNICATION

Vitamin B_{12}-catalyzed synthesis of some peracetylated alkyl β-D-xylopyranosides

ZORICA D. PETROVIĆ*, DEJAN ANĐELKOVIĆ and LJILJANA STEVANOVIĆ

Department of Chemistry, Faculty of Science, University of Kragujevac, Radoja Domanovića 12, P. O. Box 60, 34000 Kragujevac, Serbia and Montenegro

(Received 28 March, revised 30 May 2003)

Abstract: The vitamin B_{12}-catalyzed glycosylation reaction of brominated β-D-xylose peracetate with alkanols ROH (C_1-C_8) has been studied. The catalytically active species in this reaction was cob(I)alamin, obtained by chemical reduction of Vitamin B_{12} with $NaBH_4$ (Co(III) to Co(I)). The reaction was carried out with 2 mol% of vitamin B_{12}, with respect to xylosyl bromide **1**, under argon at room temperature. Under these conditions, peracetylated C_1-C_8-alkyl β-D-xylopyranosides (**3a**–**3f**) were obtained in moderate yield (55–70 %). In all cases 3,4-di-*O*-acetyl-D-xylal (**4**) was obtained, as the product of reductive elimination of peracetylated xylosyl bromide (15–25 %).

Keywords: alkyl β-D-xylopyranosides; brominated β-D-xylose peracetate; glycosylaton; vitamin B_{12}.

INTRODUCTION

Vitamin B_{12} is a "pigment of life" and coenzyme which promotes a series of biochemical transformations *in vivo*.[1] It is also a chiral and nontoxic reagent in organic chemistry which has been applied as catalyst for various types of reactions.[2] The catalytically active species in these reactions is cob(I)alamin obtained by electrochemical or chemical reduction (with activated Zn dust or with $NaBH_4$) of vitamin B_{12} (cyanocob(III)alamin) in two consecutive one-electron reductions:

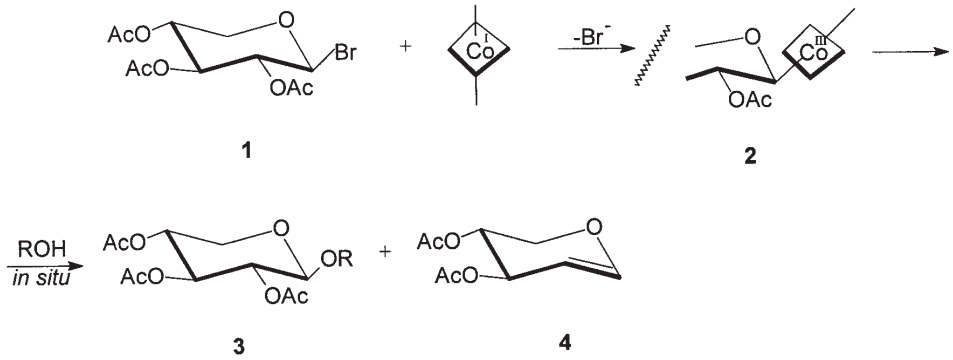
$$\text{Co(III)} \xrightarrow{+1e^-} \text{Co(II)} \xrightarrow{+1e^-} \text{Co(I)}$$

The cob(I)alamin, obtained in this way, is a very powerful nucleophile[3] and reacts rapidly with alkyl halides to form organocob(III)alamins (from kinetic studies Schrauzer *et al.*[4] concluded that the rate law corresponds to an S_N2 type substitution at the carbon). Finally, cleavage of the Co–C bond of this intermediate affords the products of the reactions: reductive C–C bond formation, reductive elimination, hydrogenation, oxidation, substitution[5] depending on the structure of the substrates and the reaction conditions.

* Author for corespondence

RESULTS AND DISCUSSION

In recent years we have studied the reactons of organic halides catalyzed by vitamin B_{12}[6–8] and glycosylation reactions of xylose peracetate.[9] In continuation of these investigations, the behavior of brominated β-D-xylose peracetate in the B_{12}-catalyzed glycosylation reaction** has been examined. The reaction was started with 2 mol% of vitamin B_{12}, with respect to xylosyl bromide **1**, and with $NaBH_4$, as the reducing agent. Then xylosyl bromide, dissolved in the corresponding alkanol ROH, was added *in situ* to the reaction mixture under argon at room temperature. The obtained xylosecob(III)alamin **2**



Scheme 1.

gave with C_1-C_8 alkanols ROH (**a**–**f**) the peracetylated alkyl β-D-xylopyranosides **3a**–**3f** which were isolated by flash chromatography (yield 55–70 %) and characterized by spectroscopic methods (Scheme 1, Table I). Their ^{1}H and ^{13}C-NMR data are in agreement with their assigned structures.[9] In all cases 3,4-di-*O*-acetyl-D-xylal (**4**) was obtained (15–25 %), as the product of reductive elimination of peracetylated xylosyl bromide.

TABLE I. Vitamin B_{12}-catalyzed reaction of brominated β-D-xylose peracetate with alkanols ROH

ROH ($CH_3(CH_2)_nOH$)	*n*	Products[a]	Yield/%[b]
a	0	**3a**	70
b	1	**3b**	66
c	2	**3c**	62
d	3	**3d**	60
e	6	**3e**	58
f	7	**3f**	55

[a]Structures were determined on the basis of ^{1}H-NMR and ^{13}C-NMR spectral data.
[b]Isolated yields

** Glycosylation reactions of mono-or disaccharides are particularly interesting in the synthesis of biodegradable surfactants, detergents and emulsifiers; mainly alkylpolyglucosides have been prepared.[10]

EXPERIMENTAL

General methods

Column chromotography was carried out on Merck silica gel (particle size 0.04–0.06 mm) using toluene and ethyl acetate as eluents. Thin layer chromatography (TLC) was performed on Merck TLC silica gel 60 F_{254} aluminium sheets. The spots were visualized by spraying with 10 % sulfuric acid in ethanol and subsequent heating. NMR spectra were recorded on a Varian Gemini 200 (200 MHz) or Bruker AC 250 (250 MHz) in $CDCl_3$ with TMS as the internal standard.

General procedure for the synthesis of alkyl β-D-xylopyranosides

A 100 cm^3 flask under Ar, containing 30 cm^3 of alkanol ROH (C1-C8; **a**–**f**), was charged with 0.16 g (0.12 mmol) of vitamin B_{12} and 0.09 g (2.4 mmol) of $NaBH_4$, wrapped around a magnetic stirrer bar. After stirring for 30 min the color changed from red to dark green (which is a sign that the Co(III) from the vitamin B_{12} had been reduced to Co(I)). Then, tri-*O*-acetyl-D-xylopyranosyl bromide (2.58 g, 8 mmol), previously prepared from peracetylated xylose by means of the classical HBr procedure, dissolved in alkanol ROH was added to this mixture. The color immediately changed to red (xylose-Co(III)). After stirring for 20 h at room temperature, the dark red mixture was washed with ice brine and extracted with dichloromethane (3 × 25 cm^3). The combined organic phases were washed twice with water (2 × 25 cm^3), filtered over Celite and evaporated *in vacuo*. The resulting syrup was purified by dry column chromatography (silica gel 60 (Merck), toluene/ethyl acetate) giving the products **3a**–**3f** (in yields ranging from 55 – 70 % based on peracetylated β-D-xylose) which were characterized by spectroscopic methods. In all cases 3,4-di-*O*-acetyl-D-xylal (**4**) was obtained in yields of 15–25 %.

Methyl 2,3,4-tri-O-*acetyl-β-D-xylopyranoside (**3a**β)*. This compound was obtained, according to the previous procedure, using methanol (30 cm^3), vitamin B_{12} (0.16 g; 0.12 mmol), $NaBH_4$ (0.09 g; 2.4 mmol) and tri-*O*-acetyl-D-xylopyranosyl bromide (2.58 g, 8 mmol). The reaction period was 20 h. The usual work-up followed by removal of excess MeOH and purfication by dry-flash chromatography afforded 1.54 g of **3a**β (70 % with respect to the starting **1**), as a colourless viscous oil.

^{1}H-NMR ($CDCl_3$), 200 MHz; δ = 4.42 (*d*, H-1), 4.87–5.01 (*dd*, H-2), 5.12 (*dd*, H-3), 4.90 (X part of the ABX spectra, H-4), 3.31 (A part of the ABX spectra, H-5a), 4.07 (B part of the ABX spectra, H-5b), 3.47 (*s*, H-1a), 1.99, 1.99, 2.00, 2.00 (4*s*, $OCOCH_3$), 1.57 (*m*, H-2), 1.28 (*m*, $-(CH_2)_n-$), 0.88 (*t*, $-(CH_2)_nCH_3$) ppm; ^{13}C-NMR ($CDCl_3$, 50 MHz): δ = 100.6 (C-1), 71.4 (C-2), 70.8 (C-3), 69.2 (C-4), 61.9 (C-5), 68.8 (C-1'), 31.3 (C-2'), 18.9 (C-3'), 13.6 (C-4') ppm.

1-Butyl 2,3,4-tri-O-*acetyl-β-D-xylopyranoside (**3d**β)*. This compound was obtained, according to the previous procedure, using 1-butanol (30 cm^3), vitamin B_{12} (0.16 g; 0.12 mmol), $NaBH_4$ (0.09 g; 2.4 mmol) and tri-*O*-acetyl-D-xylopyranosyl bromide (2.58 g, 8 mmol). The reaction period was 20 h. The usual work-up followed by removal of the excess BuOH and purfication by dry-flash chromatography afforded 1.5 g of **3d**β (60 % with respect to the starting **1**), as a colourless viscous oil.

^{1}H-NMR ($CDCl_3$), 200 MHz: δ = 4.42 (*d*, H-1), 4.87–5.01 (*dd*, H-2), 5.12 (*dd*, H-3), 4.90 (X part of the ABX spectra, H-4), 3.31 (A part of the ABX spectra, H-5a), 4.07 (B part of the ABX spectra, H-5b), 3.40 (*dt*, A part of the ABX_2 spectra, H-1a), 3.77 (*dt*, B part of the ABX_2, H-1b), 1.99, 1.99, 2.00, 2.00 (4*s*, $OCOCH_3$), 1.57 (*m*, H-2'), 1.28 (*m*, $-(CH_2)_2-$), 0.88 (*t*, $-(CH_2)_nCH_3$) ppm; ^{13}C-NMR ($CDCl_3$, 50 MHz): δ = 100.6 (C-1), 71.4 (C-2), 70.8 (C-3), 69.2 (C-4), 61.9 (C-5), 68.8 (C-1'), 31.3 (C-2'), 18.9 (C-3'), 13.6 (C-4') ppm.

3,4-Di-O-*acetyl-D-xylal* (***4***). This compound was obtained, according to the previous procedure, as a side product (0.3 g; 20 % with respect to the starting **1**). NMR characteristics of this yellow oil was identical with those of a commercial sample.

ИЗВОД

СИНТЕЗА НЕКИХ ПЕРАЦЕТИЛОВАНИХ АЛКИЛ –β-D-КСИЛОПИРАНОЗИДА КАТАЛИЗОВАНА ВИТАМИНОМ B_{12}

ЗОРИЦА Д. ПЕТРОВИЋ*, ДЕЈАН АНЂЕЛКОВИЋ и ЉИЉАНА СТЕВАНОВИЋ

Институт за хемију, Природно-математички факултет, Универзитет у Крагујевцу, Радоја Домановића 12, п. пр. 60, 34000 Крагујевац

C_1-C_8-Алкил -β-D-ксилопиранозиди (**3a**-**3f**) су синтетизовани у реакцији гликозилације бромида перацитиловане D-ксилозе **1** и алканола ROH (C_1-C_8) катализованој витамином B_{12}. Каталитички активна врста - Co(I) јон је добивен редукцијом витамина B_{12} помоћу $NaBH_4$. Реакција је изведена са 2 mol% витамина B_{12}, у односу на полазни бромид, на собној температури и под аргоном. Споредни производ ове рекације, 3,4-ди-*O*-ацетил-D-ксилал, настао је редуктивном елиминацијом полазног бромида у приносу од 15–20 %.

(Примљено 28. марта, ревидирано 30. маја 2003)

REFERENCES

1. J. Retey, J. A. Robinson, *Stereospecificity in Organic Chemistry and Enzymology*, Verlag Chemie, Weinheim, 1982, p. 185, and references cited therein
2. R. Scheffold, G. Rytz, L. Valder, in *Modern Synthetic Methods*, Vol. 3, R. Scheffold, Ed., Wiley, New York, 1983, p. 355, and references cited therein
3. P. K. Das, H. A. O. Hill, J. M. Pratt, R. J. P. Williams, *Biochim. Biophys. Acta* **161** (1967) 646
4. G. N. Schrauzer, E. Deutch, *J. Am. Chem. Soc.* **91** (1969) 3341
5. R. Scheffold, S. Abrecht, R. Orlinski, H. R. Ruf, P. Stamouli, O. Tinembart, L. Walder, C. Weymuth, *Pure Appl. Chem.* **59** (1987) 363
6. Z. D. Petrović, S. Konstantinović, R. Scheffold, S. Milosavljević, *Ind. J. Chem.* **36B** (1999) 765
7. Z. Petrović, Z. Bugarčić, Lj. Marjanović, S. Konstantinović, *J. Mol. Cat. A: Chem.* **142** (1999) 393
8. Z. Petrović, B. Mojsilović, Z. Bugarčić, *J. Mol. Cat. A: Chem.* **170** (2001) 267
9. S. Konstantinović, Z. Petrović, A. Spasojević, B. Mojsilović, *Ind. J. Chem.* **40B** (2001) 614
10. D. E. Koeltzow, A. D. Urfer, *J. Am. Oil. Chem. Soc.* **61** (1984) 1651, and references cited therein.