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Catalytic Osmylation of Allyl D-Glucopyranoside

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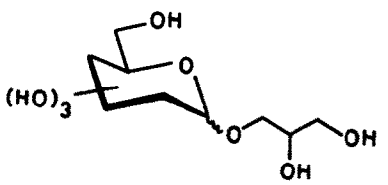
Abstract: Catalytic osmylation of allyl D-glucopyranoside leading to the formation of glycosyl glycerol derivatives is described.

Glycosyl glycerols (**1**) are the valuable part structures of several biologically active natural products[1]. The new class of gluco-sulpholipids, isolated from cyano bacteria and possessing an interesting anti-AIDS activity, perhaps testify the importance of glycosyl glycerols[2]. The general route[3] of condensing glycosyl halides with a 2,3-disubstituted glycerol, particularly the commonly used 2,3-O-isopropylideneglycerol is fraught with many difficulties, the foremost being the epimerization[4] of the glycerol unit under conditions of the reaction. Although many modifications have been suggested, a search to develop a simple protocol is still continuing.

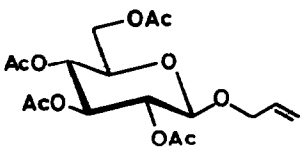


1

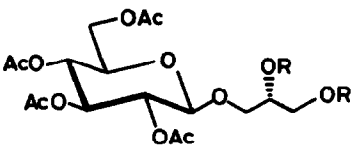
Catalytic osmylation is undoubtedly the most powerful tool to convert olefins into the corresponding vicinal diols[5]. The importance of this reaction has greatly increased by the use of cinchona alkaloids as chiral auxiliaries, the modification pioneered by Sharpless[6]. In light of the foregoing discussions, we examined (Table) catalytic osmylation of allyl D-glucopyranoside derivatives to develop a simple methodology for glycosyl glycerols. Since the allyl group is directly linked to the sugar substrate, we expected this reaction to be stereoselective[7].

Allyl 2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside (**2**) was prepared by the known procedure[8]. Subsequent catalytic osmylation (entry 1) of **2** with osmium tetroxide (0.004 eq) and N-methyl morpholine N-oxide (1.5 eq) in aq. acetone (1:9) at 0° gave a mixture of diol (**3a/3b**) in 95% yield. Surprisingly, the ^{1}H-nmr spectrum of it (**3a/3b**) did not resolve, however, the corresponding acetonide derivative (**4a/4b**) revealed distinctly separated signals for the anomeric protons (H-1). Based on the integration over H-1, the ratios of diastereomers **3a/3b** and **4a/4b** were calculated as 65:35. At this juncture it was not possible to predict correct stereochemistry of the major product. However, to determine this we monotritylated the mixture of **3a/3b** with trityl chloride (1.2 eq) and pyridine followed by conventional acetylation to give a mixture of **5a/5b**. Comparison of the ^{1}H-nmr spectrum, particularly, the anomeric signals, with those reported[9] for the individual molecules **5a** and **5b** conclusively proved that the parent compound **3a** was formed predominantly. We therefore, anticipated that the osmylation of **2** in the prese-

nce of the matching dihydroquinidine-p-chlorobenzoate may enhance the diastereofacial selectivity (observed - 75:25 for **3a/3b**, entry 2) whereas, there would be a decrease in selectivity (observed - 55:45 for **3a/3b**, entry 3) with mismatching dihydroquinine-p-chlorobenzoate. It is pertinent to mention that the cinchona alkaloids had a marginal effect on the stereochemical outcome of this reaction.

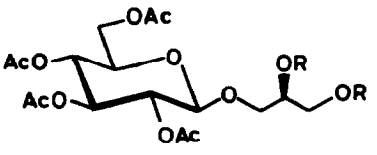


2



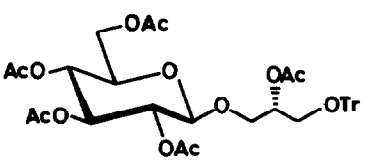
3a R=H

4a R=CMe$_2$

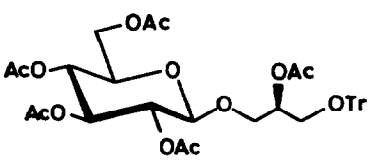


3b R=H

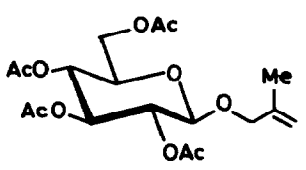
4b R=CMe$_2$



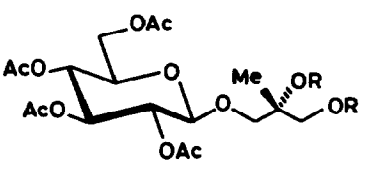
5a



5b

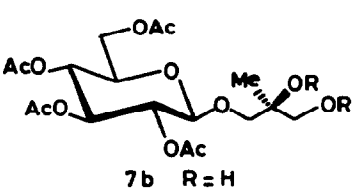


6



7a R = H

8a R = CMe$_2$

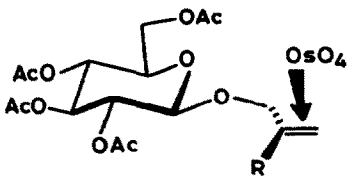


7b R = H

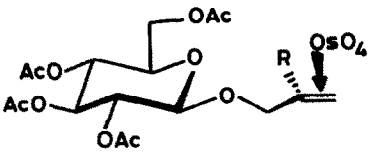
8b R = CMe$_2$

We also examined the catalytic osmylation of 2-isobutenyl tetra-O-acetyl-β-D-glucopyranoside (**6**) with a view to evaluate the effect of methyl substituent on its stereoselectivity. The synthesis of **6** in 75% yield was carried out by treating 2,3,4,6-tetra-O-acetyl D-glucosyl bromide with methallyl alcohol in the presence of mercuric cyanide and mercuric bromide[10]. The osmylation (entry 4) of **6** at 0° followed by isopropylidenation of the resulting diol (**7a/7b**) gave the acetonide (**8a/8b**). The ^{1}H-nmr spectrum revealed 67:33 mixture of **7a/7b** based on the integration over H-1. When the above reaction was conducted in the presence of dihydroquinidine-p-chlorobenzoate (entry 5), we observed good enhancement in the diastereofacial selectivity 82:18.

The allyl β-D-glycoside exists in two conformations A and B. Our results indicated that the confirmation A is a preferred one. Because the approach of osmium tetroxide from the face opposite to that of preexisting anomeric oxygen seems most probable, compound **3a** has formed as a major product. This could also explain the favourable but moderate influence of dihydroquinidine-p-chlorobenzoate on the stereoselectivity of catalytic osmylation. However,

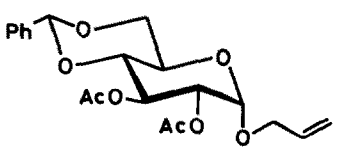
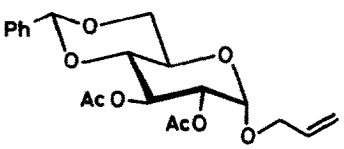


A



B

Table

Entry	Substrate	Chiral auxiliary	Ratio[a]
1	2	-	65:35
2	2	Dihydroquinidine-p-chloro benzoate[c]	75:25
3	2	Dihydroquinine-p-chloro benzoate[c]	56:44
4	6	-	67:33
5	6	Dihydroquinidine-p-chloro benzoate[c]	82:18
6[b]		-	52:48
7		Dihydroquinidine-p-chloro benzoate[c]	56:44

a Based on the integration over H-1 signals.

b Synthesised by the reported procedure - H.P. Wessel, J. Carbohydr. Chem., 7, 263 (1988).

c Reaction carried out with the slow addition of substrate.

to our surprise catalytic osmylation of allyl α-D-glucopyranoside did not show much diastereofacial selectivity (entry 6,7).

In conclusion, catalytic osmylation of allyl glucoside could prove to be a simple and efficient methodology for obtaining glycosyl glycerol derivatives. Efforts to achieve more respectiable selectivity during osmylation perhaps by employing other chiral auxiliaries[11] and the enzymatic hydrolysis of glycosyl glycerol derivative to provide the most valuable C_3 chiral building blocks are now under study in these laboratories.

References and Footnotes:

1. a) W Lennarz, Adv Lipid Res. **4**, 209 (1966); b) L D Bergelson, Vspekhi Sovrem biologii, **64**, 355 (1967); c) N Shaw, Bacteriol Rev, **34**, 365 (1970).
2. K R Gustafson, J H Cardellina II, R W Fuller, O S Weislow, R F Kiser, K M Snader, G M L Batterson, M R Boyd, J Natl Cancer Instt, **81**, 1254 (1989).
3. a) H Paulsen, Angew Chem Int Ed Engl, **21**, 155 (1982); b) R R Schmidt, Angew Chem Int Ed Engl, **25**, 212 (1986).
4. C A A Van Boeckel, G M Visser & J H Van Boom, Tetrahedron, **41**, 4557 (1985).
5. V Van Rheenan, R C Kelley and D Y Cha, Tetrahedron Lett, 1973 (1976).
6. a) E N Jacobsen, I Marko, W S Mungall, G Shroder and K B Sharpless, J Am Chem Soc, **110**, 1968 (1988); b) B B Lohray, T H Kalantar, B M Kim, C Y Park, T Shibata, J S M Wai and K B Sharpless, Tetrahedron Lett, **30**, 2041 (1989).
7. a) J K Cha, W J Christ and Y Kishi, Tetrahedron, **40**, 2247 (1984); b) J S Brimacombe and A K M S Kabir, Carbohydrate Res. **150**, 35 (1986); c) S Jarosz, Carbohydrate Res. **183**, 209 (1988); d) A V Rama Rao, M K Gurjar and S V Joshi, Tetrahedron Asymmetry, **1**, 697 (1990).
8. H M Flowers, Methods in Carbohydrate Chemistry, **6**, 474 (1972).
9. T Ogawa, K Katano and M Matsui, Carbohydrate Res, **70**, 37 (1979).
10. Compound **6** was prepared as follows: To a stirred solution of methallyl alcohol (1.0 g, 14 mmol), molecular sieves 4A (2.0 g), mercuric cyanide (2.7 g) and mercuric bromide (1.0 g) in dry CH_2Cl_2 was added freshly prepared 2,3:4,6-tetra-O-acetyl-D-glucopyranosyl bromide (5.0 g, 12 mmol). After 18 h, the reaction mixture was worked up and the residue chromatographed on silica gel using ethyl acetate pet ether (1:10) as eluent to afford 2-isobutenyl 2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside (3.8 g, 75%), $[\alpha]_D$ -25.04 (c 1.0, $CHCl_3$). ^{1}H-nmr ($CDCl_3$: 200 MHz) data: α 1.64 (s, 3H), 2.00, 2.03, 2.05, 2.09 (4s, 12H), 3.64 (m, 1H), 4.00, 4.21 (ABq, 2H, J = 12.4 Hz), 4.10 (dd, 1H, J = 3.0 and 8.3 Hz), 4.27 (dd, 1H, J = 4.2, 8.3 Hz), 4.49 (d, 1H, J = 8.3 Hz), 4.92 (m, 2H), 4.99 (t, 1H, J = 9.2 Hz), 5.05 (t, 1H, J = 9.2 Hz). 5.19 (t, 1H, J = 9.2 Hz); ^{13}C-nmr : 170.591, 170.197, 169.324, 169.184, 140.437, 113.311, 98.989, 72.735, 71.593, 71.134, 68.327, 61.813, 20.491, 19.057.
11. a) E J Corey, Pure Appl Chem. **62**, 1209 (1990); b) T Oishi and M Hirama, J Org Chem. **54**, 5834 (1989); c) K Tomioka, M Nakajima and K Koga, J Am Chem Soc. **109**, 6213 (1987).

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