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Metathesis of Ω-Unsaturated Glucosides with Chloro-Aryloxide Complexes of Tungsten, as a New Way Leading to Unsaturated Bolaamphiphiles

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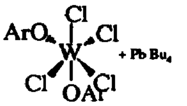
Abstract: Glucosides of unsaturated alcohols, bearing different protecting groups at glucose units underwent catalytic metathesis affording bolaamphiphiles with good yields. Tungsten aryloxo-complexes (**1** and **2**) were found to be superior catalysts for this process.

Metathesis is a well known catalytic process, intensively studied for thirty years, because of their numerous practical applications[1-3]. It was applied mainly to acyclic, and cyclic olefins, and in few cases also for olefins bearing single functional groups[4,5] (e.g. esters, ethers, thioethers, nitriles). It seemed to be very interesting to extend the scope of this reaction to polyfunctional compounds, such carbohydrates. The method appears as very simple synthetic way leading to bolaamphiphiles. During last few years this group of compounds have met growing interest because of their unusual properties as surfactants and high ability to form monolayer membranes[6]. They are also used for studying mechanisms of membrane processes[7], as well as some enzymatic reactions[8,9]. The practical use of these compounds is expected to grow in the near future. Among others, one of the most interesting classes of bolaamphiphiles is the neutral one (non-charged hydrophilic parts) containing carbohydrate units at both ends of the long aliphatic chain.



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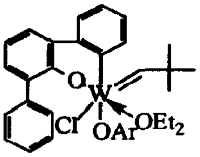


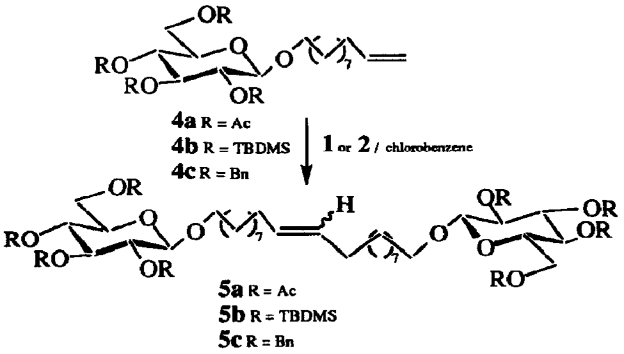
2

Ar = 2, 6 - diphenylphenyl

We have recently developed a new generation of chloro-aryloxide complexes of tungsten, **1** and **2** which are among the most active catalysts in metathesis of olefins bearing functional groups (e.g. esters, thioethers, phosphoranes)[10,11]. The most active and stereoselective catalyst **2** is a cyclo metallated aryloxo (chloro) neopentylidene tungsten complex[5,12].

Since these catalysts tolerate a wide range of functional groups, especialy esters, and since the ligand environment around the tungsten atom is extremely bulky (o, o'- diphenyl phenoxy) it was logical to test these complexes with unsaturated carbohydrates, namely ω-unsaturated glucosides. Appropriate protecting groups for sugar residue were used to avoid deactivation of the oxophilic catalysts with a d^0 configuration. For this reason a series of substrates **4a,b,c** with acetyl esters, t-butyldimethylsilyl ethers and benzyl ethers as protecting groups was prepared by classical glycosylation[13] of 10-undecen-1-ol by tetra-O-acetyl-*gluco*pyranosyl bromide **3** in the presence of the silver triflate, following by deprotection and reprotection procedures[14,15].

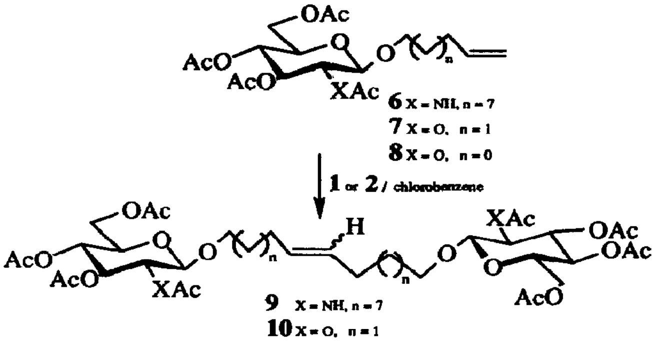
Substrates **4a,b,c** in the presence of catalysts **1** or **2** in chlorobenzene at 80°C under argon gave expected metathesis products and ethylene.



Acetyl esters and silyl ethers were found to be superior to benzyl ethers, which can deactivate the catalyst resulting in lower yields despite a higher catalyst / substrate ratio (see Table).

To explore the scope of this reaction, we employed the aminosugar derivative **6** and 4-pentenyl and allyl glucosides **7** and **8** as other substrates[18]. Catalysts **1** and **2** were also active for the substrate containing acetamido functional group. For pentenyl glucoside **7**, results obtained were as good as for the undecenyl one, but allyl glucoside **8** did not give any product at all. As we thought, in the case of allyl glucoside **8** as well as the benzyl protected substrate **4c**, catalysts were deactivated by complexation of the metal to the ether oxygen atoms. For the silylated substrate **4b** the steric hindrance was large enough to prevent complexation to tungsten.

For the substrate **4b**, the catalyst developed by Mol, (Re_2O_7 / Al_2O_3 - SiO_2 /Pb Bu_4)[4], gave no metathesis product.



All purified reaction products were separated by column chromatography, and were characterised by their ^{1}H and ^{13}C NMR spectra: proton and carbon atoms signals of terminal double bond for substrates were replaced in the spectra of products by signals of symetrically substituted olefins (results are summarized in Tables 1 and 2).

Table 1: Catalytic metathesis of carbohydrate-containing substrates:

Substrate	Catalyst	Catalyst/substrate ratio	Reaction time hrs	Reaction temp °C	Product	Yield %
4a	**2**	1:10	12	80	**5a**	64
4a	**1**	1:5	12	80	**5a**	52
4b	**1**	1:12	12	65	**5b**	51
4b	**2**	1:12	12	65	**5b**	92
4c	**1**	1:5	12	80	**5c**	37
4c	**2**	1:15	12	80	no reaction	0
6	**1**	1:10	12	80	**9**	62
7	**1**	1:20	6	80	**10**	65
8	**1**	1:8	12	80	no reaction	0

Table 2: NMR data for olefinic protons and carbon atoms (ppm)

	Substrate					Product	
	Hα and Hα'	Hβ	Cα	Cβ		Hα = Hβ	Cα = Cβ
4a	5.08-4.87m	5.82	114.4	139.3	**5a**	5.38 bt	130.5
4b	5.06-4.92	5.81	113.8	139.5	**5b**	5.37	130.4
4c	4.99-4.91	5.82	114.2	139.4	**5c**	5.39 bt	130.3
6	5.07-4.90	5.81	114.7	139.6	**9**	5.36 bt	130.3
7	5.02-4.85	5.71	115.0	137.7	**10**	5.38 bt	129.9
8	5.33-5.15	5.85	116.2	136.8	--	--	--

In conclusion, the catalytic metathesis process was for the first time applied to sugar derivatives . Catalysts **1** and **2** appeared to be very effective in the presence of numerous functional groups. As result, an efficient method leading to unsaturated bolaamphiphiles was developed.

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References and notes:

1. Calderon, N; Chen, H. Y; Scott, K. W. *Tetrahedron Lett.* **1967**, 3327.
2. Ivin, K. J; *Olefin Metathesis*, Academic Press, London, **1983**.
3. Chevalier, P.; Sinou, D. Descotes, G.; *J. Organomet .Chem.* **1976**, *113*, 1-9
4. Mol, J. C. *J. Mol Cat.* **1991**, 145-162.
5. Couturier, J-L; Tanaka, K; Leconte, M; Basset, J-M; Ollivier, J. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 112-115.
6. Fuhrhop, J-H; Bach, R. *Adv. in Supramolecular Chem.* **1992**, vol. 2, 25-63.
7. Munoz, S; Mallen, J; Nakano, A; Chen, Z; Cay, I; Echegoyen, L; Gokel, G. W; *J Am. Chem. Soc.* **1993**, *115*, 1705-1711.
8. Ats, S-C; Lehman, J; Petry, S. *Carbohydr. Res.* **1994**, *252*, 325-332.
9. Ats, S-C; Lehman, J; Petry, S. *Carbohydr. Res.* **1992**, *233*, 125-139.
10. Quignard, F.; Leconte, M.; Basset, J-M.; Hsu, L-Y.; Alexander, J. J.; Shore, S. G. *Inorg. Chem.* **1987**, *26*, 4272-4277.
11. Couturier, J-L; Paillet, Ch; ; Leconte, M; Basset, J-M; Weiss, K. *Angew. Chem. Int. Ed; Engl.* **1992**, *31*, 628-631.
12. Quignard, F; Leconte, M; Basset, J-M. *J. Mol. Cat.* **1986**, *36*, 13-29.
13. Hanessian, S; Banoub, J. *Carbohydr. Res.* **1977**, *53*, C-13.
14. The glycosylation was carried out in dichloromethane at rt., and afforded the β-glucoside as the only product, in 62% yield.
15. Acetyl esters were removed by the Zenplen method, and reprotections were carried out by standard procedures [16,17].
16. Corey, E. J; Venkateswarlu, A. *J. Am. Chem. Soc.* **1972**, *94*, 6190-6193.
17. Fletcher, H. G. *Methods Carbohydr. Chem.* **1963**, vol. 2, 166-167.
18. Glycosylations were done by the same procedure as for **4b** using 4-penten-1-ol, and allyl alcohol respectively.

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