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AN EFFICIENT ROUTE TO HOMOLOGATED PYRANOSIDIC CONJUGATED ENALS

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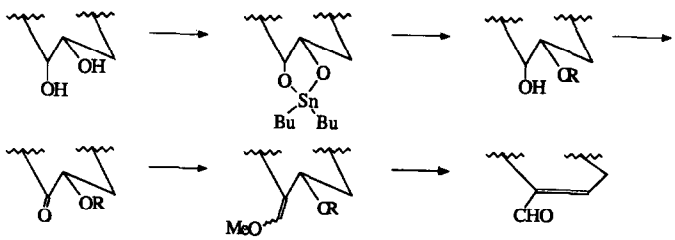
Abstract : Mild acidic treatment of pyranosidic α-alkoxy vinyl ethers affords homologated conjugated enals ready for hetero Diels-Alder reactions and for C-glycoside synthesis.

The use of carbohydrates as chiral building blocks for the synthesis of natural products implies a choice of the sugar derivative[1,2] on the basis of easy accessibility, latent functionalities, and versatility. Extension of the scope of carbohydrates as suitable building blocks relies on the development of convenient key intermediates capable of meeting these requirements. In this context, we have recently reported homologated pyranosidic conjugated enals[3] and shown their versatility in cycloaddition reactions[3,4]. A recent paper by Lipshutz et al.[5] prompts us to report now an additional methodology allowing simple access to previously unknown homologated pyranosidic conjugated enals complementing the ones already described[3,5].

The method proposed now allows the over-all transformation, as shown below, of a cis-diol[6] into a conjugated enal by taking advantage of the implications of the stannylene procedure[7]. As expected,



when subjected to mild acidic treatment, α-alkoxy vinyl ethers 1 - 5 are readily transformed into the corresponding homologated conjugated enals 6 - 10[8] in excellent yields. Access to such pyranosidic α-alkoxy vinyl ethers is provided by a Wittig-Horner reaction of the corresponding α-alkoxy uloses or by hetero Diels-Alder reaction of former conjugated enal systems[3]. Compounds 4 and 5 result from this approach[3].

Besides the potential of the new homologated conjugated enals for hetero Diels-Alder reactions, compounds 9 and 10, containing a 1,5-dicarbonyl system, appear to be interesting building blocks for alkaloid synthesis and 8 and 9 as starting materials for C-glycosides[9].

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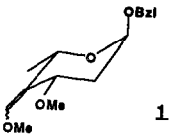
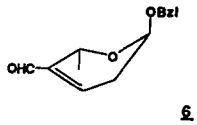
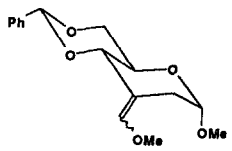
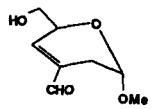
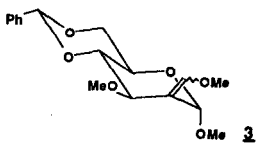
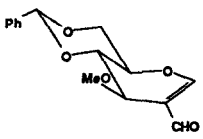
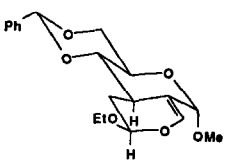
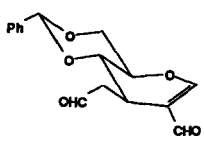
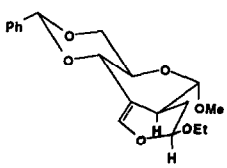
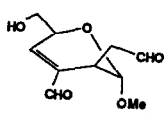
2 - S. Hanessian, "Total Synthesis of Natural Products, The Chiron Approach", Pergamon Press, Oxford, 1983.

3 - J.C. Lopez, E. Lameignère and G. Lukacs, J. Chem. Soc. Chem. Commun., 514, 1988.

Substrate	Yield	Product	$[\alpha]_D^{22}$ $CHCl_3$
 1	71% (a)	 6	-101° (C=0.6)
 2	88% (b)	 7	+32° (C=0.23)
 3	89% (a)	 8	+105° (C=0.6)
 4	93% (a)	 9	+111° (C=0.26)
 5	91% (b)	 10	+93° (C=0.44)

(a): Treatment with pyridinium hydrochloride 0.1 M in pyridine, 25°C, 12 h.
(b): Treatment with 20% AcOH in water , 25°C , 1 h.

4 - J.C. Lopez, E. Lameignère and G. Lukacs, J. Chem. Soc. Chem. Commun., 706, 1988.

5 - B.H. Lipshutz, S.L. Nguyen and T.R. Elworthy, Tetrahedron, 44, 3355, 1988.

6 - This method complements our previous publication[3] which, based on an epoxide opening by a dithiane, can be visualized as the transformation of a trans-diol into a homologated conjugated enal.

7 - S. David and S. Hanessian, Tetrahedron, 41, 643, 1985.

8 - All new compounds gave satisfactory microanalytical results.Yields indicated correspond to isolated pure products.NMR spectra were measured in $CDCl_3$ solution.Characteristic chemical shifts are given relative to internal TMS.Mass spectra were measured by chemical ionization. 6 , syrup, MH^+ 233, ^1H NMR : 5.10 (dd,1H,$J_{1,2ax}$ = 3 Hz, $J_{1,2eq}$ = 1 Hz,H-1), 6.78 (m,1H,H-3), 9.46 (s,1H,CHO) ; 7, syrup, MH^+173, ^1H NMR : 5.10 (bs,1H,H-1), 6.78 (bs,1H,H-4), 9.57 (s,1H,CHO) ; 8, mp 75 - 78°C, MH^+ 277, ^1H NMR : 7.46 (s,1H,H-1), 9.45 (s,1H,CHO) ; 9, syrup, MH^+ 289, ^1H NMR : 7.36 (s,1H,H-1), 9.40 (s,1H,CHO), 9.80 (s,1H,CHO) ; 10, syrup, MH^+ 215, ^1H NMR : 4.86 (2s,2H,H-1,H-4), 9.56 (s,1H,CHO), 9.90 (s,1H,CHO).

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