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A Levoglucosenone-Derived Symmetrical Chiron

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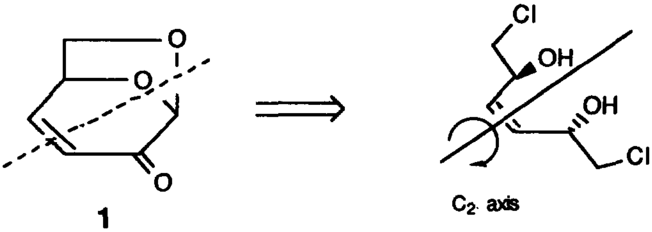
Abstract : Levoglucosenone, a readily available pyrolysis product of cellulose, has been converted to a symmetrical allylic bis chlorhydrin.

Molecules having C_2 symmetry are of current interest for their synthetic applications [1]; in this note, a method for converting a readily available pyrolysis product of cellulose into a chiron of C_2 symmetry is disclosed.

Levoglucosenone, 1 [2-4], can be conveniently obtained by simple pyrolysis of cellulose [5-10]. Medium Performance Liquid Chromatography [11] has been found to be particularly useful for the purification of the crude pyrolysate, thus allowing rapid isolation at the bench of gram quantities of pure 1 [12]. Considering the broken line drawn on its formula, it can be seen that appropriate functional group manipulations could in principle yield a functionalized C_2 symmetrical synthon.



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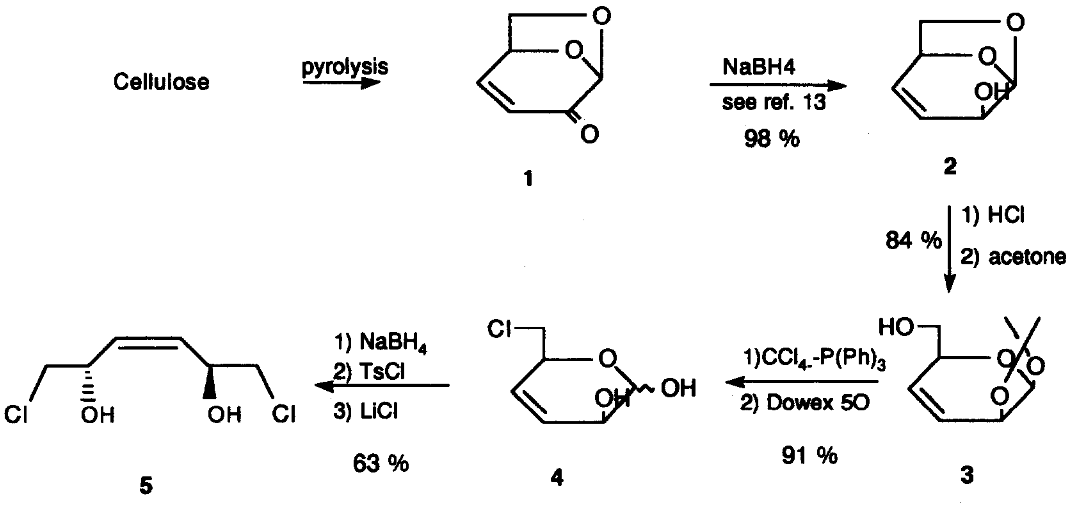
Since stereoselective reduction of the carbonyl group of 1 was known [13] to afford almost quantitatively the alcohol 2, this became an appropriate starting point for our purpose. Hydrolysis of 2 (0.5 M HCl, 100 °C, 40 min) afforded an hemiacetal but, as selective chlorination of its primary hydroxyl group failed, protection (acetone, $CuSO_4$, 15 days) was introduced to give 3 . Chlorination (CCl_4, $(C_6H_5)_3P$, pyridine, RT, 2 h) now proceeded smoothly and produced, after deprotection of the acetal (Dowex 50W X8, THF -H_2O, 60 °C, 8 h), the desired chloride 4.

Reduction of the aldehyde (excess $NaBH_4$, -20°C, pH adjustment to 7 before isolation), followed by selective tosylation [14] of the primary hydroxyl group (1.2 equiv. TsCl, pyr, -20 °C), and displacement by chloride (10 equiv. LiCl , DMF, Ar, 90 °C, 7 h) gave 5 . It is of interest to note that despite the cis configuration of the double bond, no pyran derivatives, from internal displacement of the tosylate, could be observed.

As expected from its symmetry, 5 displayed only three lines in its ^{13}C -nmr spectrum [15] . The good overall yield of this synthesis (over 45 % from 1) and the ready availability of levoglucosenone [12] make this approach to a C_2 [16] chiron particularly attractive.



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12. Cellulose, pretreated with phosphoric acid (3 % w/w), was pyrolyzed (270 °C, 10 kPa) for 20 minutes; after washing the crude pyrolysate with aqueous sodium bicarbonate, MPLC (see ref. 11) on silica gel 60 H (15 nm particle size) was performed. Elution with dichloromethane afforded pure 1 without the need for further purification in *ca.* 4 % yield (which is within the range of literature ones : see ref. 5-9); the whole process takes only 2-3 hours.
13. Shafizadeh, F.; Furneaux, R.H.; Stevenson, T.T.; *Carbohydr. Res.*, **1979**, 71, 169-191.
14. In contrast to other intermediates, this tosylate was too fragile to be characterized and was immediately used without purification.
15. 5 : colorless oil, $[\alpha]^{D}_{25}$ - 13° (c =1.9, CHCl$_3$). ^{13}C-nmr (75 Mhz, CDCl$_3$): 132.2 (C-3 and C-4), 68.4 (C-2 and C-5), 49.1 (C-1 and C-6). ^{1}H-nmr (300 MHz- CDCl$_3$) : an ABMX system with resonances centered at 5.65, 4.7 and 3.55 ppm; upon irradiation of the 4.7 ppm resonance, this collapses to a singlet for the vinylic protons and an AB sytem for the methylenes.
16. For related chirons and synthetic applications see *inter alia* : Kuszmann, J.; Sohar, P.; *Carbohydr. Res.*,**1980**, 83, 63-72. Köll,P.; Kopf, J.; Metzger, J.O.; Schwarting, W.; Oelting, M.; *Liebigs Ann. Chem.* ,**1987**, 199-204. Dureault,A.; Tranchepain,I.; Depezay, J.-C.; *Synthesis*, **1987**, 491-493. Machinaga, N.; Kibayashi, C.; *Tetrahedron Lett.*, **1990**, 31,3637-3640. ; Kammerer, J.; Rihs, G.; Prinzbach, H.; *Angew. Chem., Int. Ed. Engl.*, **1990**, 29, 1038-1040. Takano, S.; Iwabuchi, Y. Ogasawara, K.; *J. Chem. Soc., Chem. Commun.*, **1991**, 820- 821. Machinaga, N.; Kibayashi, C.; *Synthesis*, **1992**, 989-994. Marzi, M.; Minetti. P.; Misiti. D.; *Tetrahedron*, **1992**, 48, 10127-10132.

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