Synthesis of Carbohydrate-Derived Acylsilanes

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Abstract: Syntheses of some new acylsilanes derived from carbohydrates are described using a nucleophilic displacement of a leaving group (iodide, triflate) by 2-lithio-2-trimethylsilyl-1,3-dithiane, followed by a dithioketal deprotection.
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Acylsilanes are versatile molecules which have attracted much attention in organic synthesis these last two decades.[1] Various methods of synthesis are available in the literature, but there is still a need for complementary methodologies, particularly for polyfunctionalized acylsilanes. One of the more classical methods is that simultaneously described by the groups of Brook and Corey, based on the umpolung strategy.[2] It consists in the silylation of an acyl anion equivalent derived from the thioacetalization of an aldehyde. We have recently described a new general method for the synthesis of functionalized acylsilanes (β-hydroxy, α,β-unsaturated and β-oxo-acylsilanes) by the opening of an epoxide with a silylcarbonyl anion equivalent: 2-lithio-2-trimethylsilyl-1,3-dithiane (LTD).[3] This strategy was successfully applied to the synthesis of glucose-derived acylsilanes. We now report the synthesis of acylsilanes derived from xylose and arabinose by reaction of LTD with electrophilic sugar derivatives such as iodides and triflates.
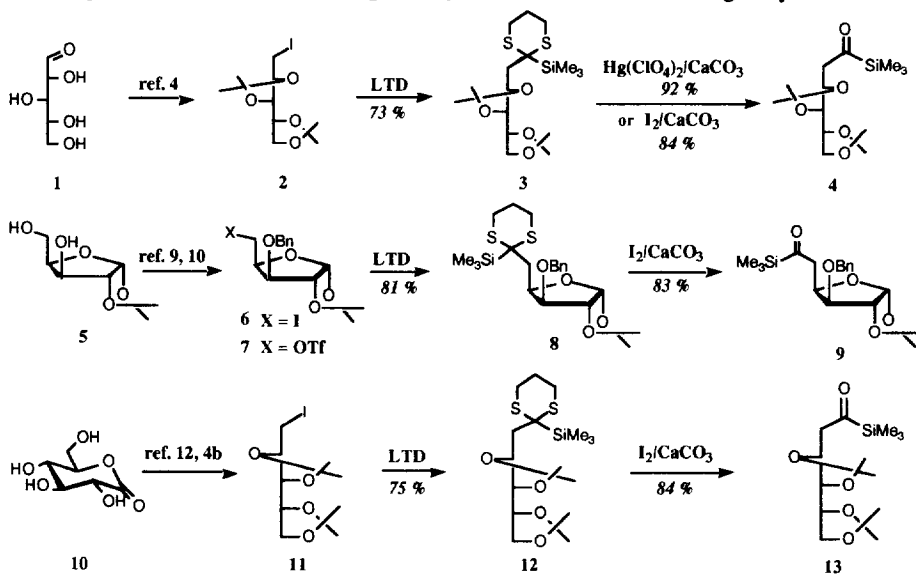
Xylose derived acylsilanes

From D-xylose. The substitution of an iodide by LTD was first attempted with 1-iodo-1-deoxy-2,3:4,5-di-*O*-isopropylidene-D-xylitol **2**, prepared from D-xylose **1**.[4] Reaction of **2** with LTD gave efficiently the silyl dithioketal **3** which was converted smoothly into the corresponding acylsilane **4**[5] by reaction with mercuric perchlorate[6a] or diiodine[6b] in a buffered medium. These conditions do not induce any removal of the isopropylidene groups. The iodine method was generally prefered owing to the high toxicity of mercuric salts.

From xylitol. The same reaction pathway was used with racemic compound **2** obtained in two steps from xylitol[7,8,4b] and gave the corresponding racemic acylsilane **4**.

From 1,2-O-isopropylidene-D-xylofuranose. Starting from this commercially available compound **5**, we have performed the synthesis of another xylose-derived acylsilane having the acylsilane functionality attached on C-5. First, a similar iodide substitution was attempted on compound **6**,[9] but the reaction took a different path.

The access to the acylsilane was achieved by reaction of LTD with the 5-*O*-triflyl derivative **7**,[10] giving the dithioketal analog **8** which on treatment with I_2-$CaCO_3$ was transformed into the target acylsilane **9**.[11]

Arabinose-derived acylsilanes

From D-glucono-1,5-lactone. Compound **11**[4b] was prepared from D-glucono-1,5-lactone **10**,[12] a very cheap starting material. Then, the sequence described above led to the acylsilane **13**.[13] Compound **13** as well as its L-enantiomer could be obtained from D- and L-arabinose according to the procedure applied to D- xylose.

Summary: Various acylsilanes can be synthesized from easily available starting sugars such as glucose,[3] xylitol, xylose, arabinose or gluconolactone. These acylsilanes are interesting synthons for further transformations which are under investigation.[14]

<div align="center">References and notes</div>

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