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Synthesis of New Functionalized bis-Acylsilanes. β-Hydroxy- and β-oxo-bis-acylsilanes.

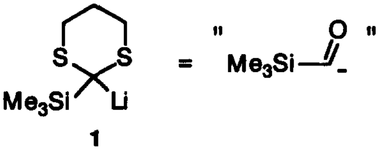
Jean-Philippe Bouillon and Charles Portella*

Laboratoire "Réactions Sélectives et Applications". Associé au CNRS (UMR 6519)
Université de Reims. Faculté des Sciences. B.P. 1039, 51687 Reims Cedex 2. France.

Dedicated to the memory of Zdenek Janousek

Abstract. The syntheses of new bis-acylsilanes from 2-lithio-2-trimethylsilyl-1,3-dithiane and epichlorohydrin or the diepoxide of buta-1,3-diene are reported. 3-Hydroxy- and 3-oxo-1,1-bis(trimethylsilyl)pentan-1,5-dione were prepared from epichlorohydrin whereas the 3,4-dihydroxy-bis-acylsilane derived from the diepoxide had a low stability and led to (5-trimethylsilylfuran-2-yl)acetyltrimethylsilane. © 1997 Elsevier Science Ltd.

Acylsilanes[1] exhibit a versatile chemistry combining the usual properties of the ketones and some specific properties essentially due to the oxygenophilicity (Brook rearrangement)[2] and fluorophilicity[3] of silicon. We have recently described the synthesis of functionalized acylsilanes and their application to sugar derived acylsilanes.[4,5] These syntheses were based on the reaction of the silylcarbonyl anion equivalent **1** with electrophilic substrates such as epoxy-[4] or halo- and triflate-derivatives.[5] On the other hand, the synthesis of some bis-acylsilanes, compounds which have not yet been extensively studied, have appeared in recent reports.[6-9] In particular, a paper related to reductive reactions of acylsilanes, including bis-acylsilanes,[8] prompted us to report some of our results concerning this family of compounds. We have been involved for some years in the chemistry of acylsilanes in connection with both organofluorine[10-12] and carbohydrate[4,5,13] chemistry, and are currently extending our investigations toward various types of bis-acylsilanes reactivity. This preliminary report deals with the synthesis of β-hydroxy- and β,γ-dihydroxy-bis-acylsilanes **6** and **10**, and of the β-oxo-bis-acylsilane **7**.

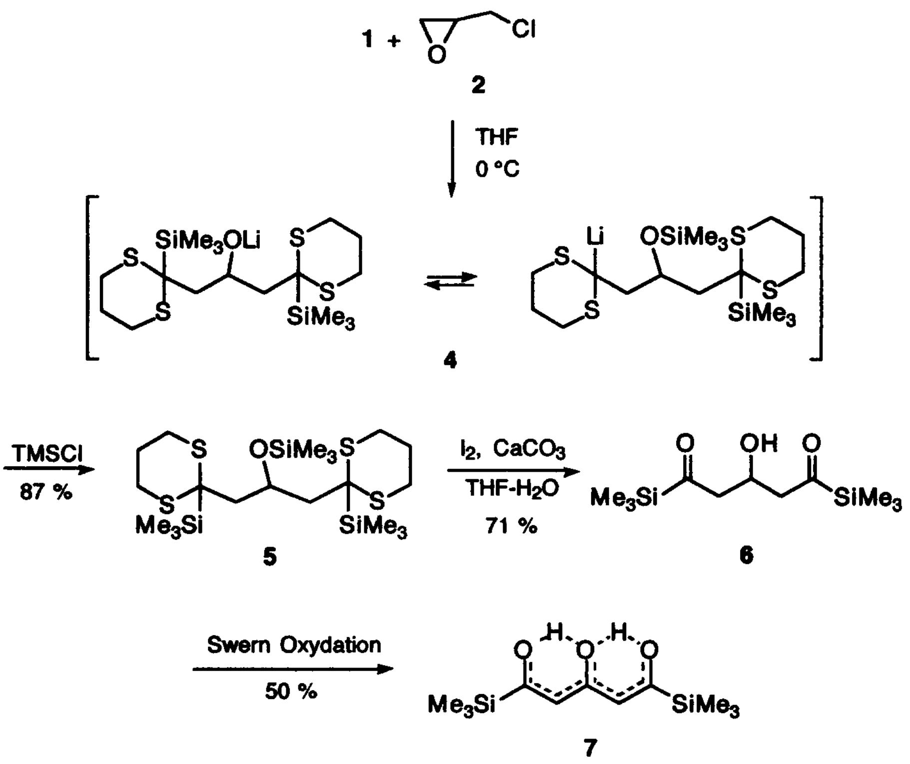


1

Using the above mentioned strategy of introduction of the silylcarbonyl moiety, we have reacted the reagent **1** with epichlorohydrin **2** and with the *meso* buta-1,3-diene diepoxide **3**. Reaction of **1** with **2** (0.5 eq.), in the conditions depicted in the scheme 1 related to our reported procedure,[4] led effectively (87%) to the silyloxy

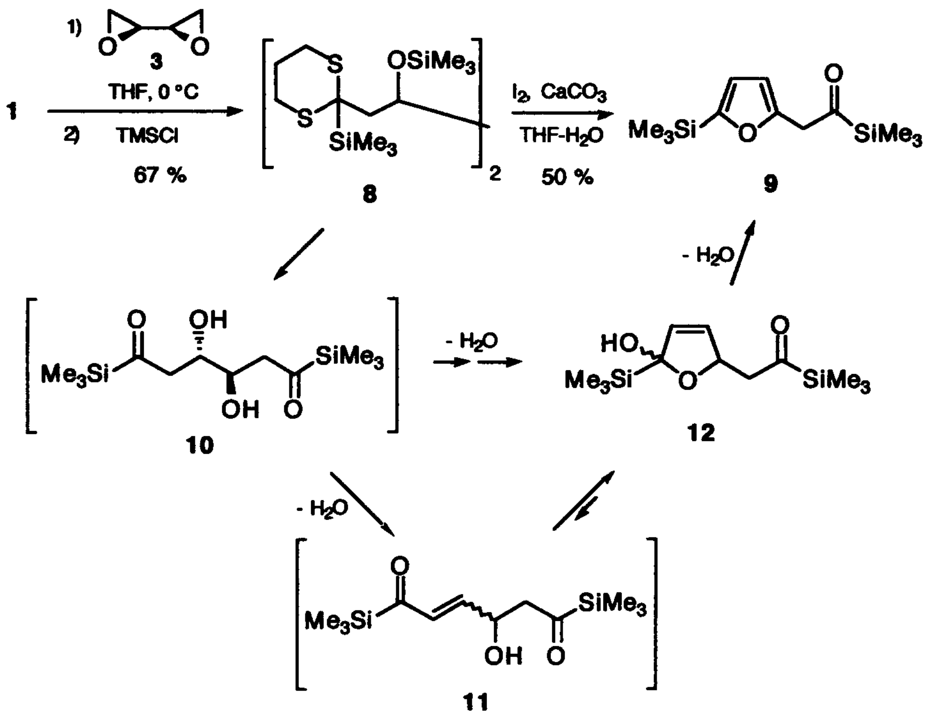
Fax: 33 3 26 05 31 66. E-mail: charles.portella@univ-reims.fr

bis-TMS-1,3-dithiane **5** (Scheme 1). Before the final work-up, the addition of TMSCl overcame the problem of intramolecular silicon transfer to oxygen by trapping either of the equilibrated intermediates **4**.[4] Treatment of **5** with iodine in the presence of calcium carbonate gave the β-hydroxy-bis-acylsilane **6** in 71% yield.[14,15] Swern type oxidation of **6** led to the corresponding β-oxo-bis-acylsilane **7** (50 %). As previously observed for simple β-oxo-acylsilanes,[4] compound **7** is completely displaced toward the enol form, as demonstrated by the IR, ^{1}H- and ^{13}C-NMR spectra.[16]



Scheme 1

A similar reaction sequence was applied to the diepoxide **3** (Scheme 2). The bis-TMS-1,3-dithiane **8** was isolated in 67% yield (accompanied by a minor amount of hydroxy (6%) and dihydroxy (9%) analogues). Interestingly, the dethioketalization using the above conditions gave the furan derived acylsilane **9** directly in 50% yield.[17] We were not able to detect any trace of the expected bis-acylsilane **10**. In an experiment with a shorter reaction time, we isolated a 90/10 mixture of **9** and a product whose ^{1}H- and ^{13}C-NMR spectra seemed to be consistent with the structure **12**.[18] The latter is actually the hemiketal form of the bis-acylsilane **11**, itself being the result of a first dehydration of the expected dihydroxy derivative **10**, although the reverse sequence -intramolecular hemiketalisation-dehydration- would also give **12**. Aromatization to the furan derivative **9** constituted the driving force of the further dehydration of **12**.



Scheme 2

The new compounds **6**, **7** and **9** are representative of the chemistry of bis-acylsilanes. For example, the highly functionalized silyl derivative **9** is obtained in a two steps procedure from commercially available 2-TMS-1,3-dithiane and **3**. The optimization of this reaction sequence as well as further synthesis and reactions of bis-acylsilanes are currently under investigation.

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References and notes

1. Reviews : Ricci, A.; Degl'Innocenti, A. *Synthesis* **1989**, 647-660.
   Page, P.C.B.; Klair, S.S.; Rosenthal, S. *Chem. Soc. Rev.* **1990**, *19*, 147-195.
   Cirillo, P.F.; Panek, J.S. *Org. Prep. Proc. Int.* **1992**, *24*, 555-582.
   Nàjera, C.; Yus, M. *Org. Prep. Proc. Int.* **1995**, *27*, 385-456.
2. Brook, A.G. *Acc. Chem. Res.* **1974**, *7*, 77-84.
   Reich, H.J.; Holtan, R.C.; Bolm, C. *J. Am. Chem. Soc.* **1990**, *112*, 5609-5617, and refs therein. See also refs 10-13.
3. Degl'Innocenti, A.; Pike, S.; Walton, D. R. M., Seconi, G.; Ricci, A; Fiorenza, M. *J. Chem. Soc., Chem. Commun.* **1980**, 1201-1202.
   Schinzer, D.; Heathcock, C. H. *Tetrahedron Lett.* **1981**, *22*, 1881-1884.
   Ricci, A.; Degl'Innocenti, A.; Chimichi, S.; Fiorenza, M.; Rossini, G.; Bestmann, H. J. *J. Org. Chem.* **1985**, *50*, 130-133
   Page, P. C. B.; Rosenthal, S.; Williams, R. V. *Tetrahedron Lett.* **1987**, *28*, 4455-4456.
4. Plantier-Royon, R.; Portella, C. *Synlett* **1994**, 527-529.
5. Plantier-Royon, R.; Portella, C. *Tetrahedron Lett.* **1996**, *37*, 6113-6114.
6. Capperucci, A.; Degl'Innocenti, A.; Faggi, C.; Ricci, A. *J. Org. Chem.* **1988**, *53*, 3612-3614.
7. Degl'Innocenti, A.; Capperucci, A.; Bartoletti, L.; Mordini, A.; Reginato, G. *Tetrahedron Lett.* **1994**, *35*, 2081-2082.
8. Chuang, T.-H.; Fang, J.-M.; Jiaang, W.-T.; Tsai, Y.-M. *J. Org. Chem.* **1996**, *61*, 1794-1805.
9. Brook, A.G.; Anderson, D.G.; Duff, J.M.; Jones, P.F.; MacRae, D.M. *J. Am. Chem. Soc.* **1968**, *90*, 1076-1078.
10. Dondy, B.; Portella, C. *J. Org. Chem.* **1993**, *58*, 6671-6674.
11. Doussot, P.; Portella, C. *J. Org. Chem.* **1993**, *58*, 6675-6680.
12. Brigaud, T.; Doussot, P.; Portella, C. *J. Chem. Soc., Chem. Commun.* **1994**, 2117-2118.
13. Brigaud, T.; Lefebvre, O.; Plantier-Royon, R.; Portella, C. *Tetrahedron Lett.* **1996**, *37*, 6115-6116.
14. All new compounds gave satisfactory analysis.
15. Selected data for **6** : IR (film, cm^{-1}) : 3500-3300 (OH), 1640 (CO); ^1H NMR ($CDCl_3$) δ (ppm/TMS) : 0.21 ($SiMe_3$), 2.79 (dd, J = 5.9 Hz, J = 1.1 Hz, CH_2); ^{13}C NMR ($CDCl_3$) δ (ppm/TMS) : 63.0 (CHOH), 249.0 (CO).
16. Selected data for **7** : IR (film, cm^{-1}) : 1557; ^1H NMR ($CDCl_3$) δ (ppm/TMS) : 5.45 (s, =CH), 13.78 (brs, OH); ^{13}C NMR ($CDCl_3$) δ (ppm/TMS) : 191.1 (CO), 194.4 (CO).
17. Selected data for **9** : IR (film, cm^{-1}) : 1645 (CO); ^1H NMR ($CDCl_3$) δ (ppm/ TMS) : 6.15 (d, J = 3.1 Hz, =CH), 6.58 (d, J = 3.1 Hz, =CH); ^{13}C NMR ($CDCl_3$) δ (ppm/TMS) : 241.6 (CO).
18. Selected data for **12** : ^1H NMR ($CDCl_3$) δ (ppm/ TMS) : 3.12 (d, J = 7.2 Hz, CH_2), 4.33 (dd, J = 7.3 Hz, J = 7.2 Hz, CH), 6.06 (d, J = 3.1 Hz, =CH), 6.55 (d, J = 3.1 Hz, =CH); ^{13}C NMR ($CDCl_3$) δ (ppm/TMS) : 238.9 (CO).

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