Pergamon

Tetrahedron Letters 40 (1999) 1885–1886

TETRAHEDRON
LETTERS

A Facile Synthesis of 2,6-Bis-trialkylsilyl-4H-pyranes from 1,5-Bis-acylsilanes.

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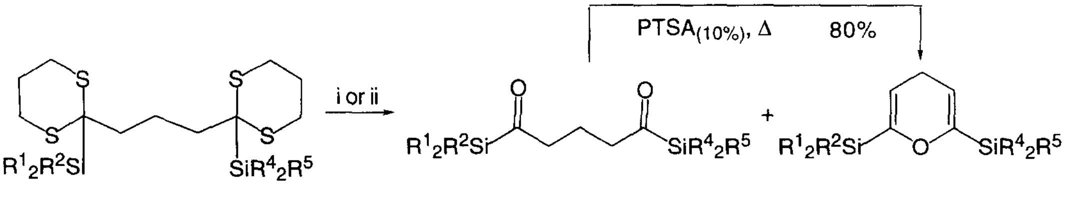
Received 7 December 1998; accepted 6 January 1999

Abstract. The new 2,6-bis-trialkylsilyl-4H-pyranes were easily prepared from 1,5-bis-dithianes via a two steps sequence of dethioketalization and cyclodehydration in the presence of a catalytic amount of p-toluenesulfonic acid. © 1999 Elsevier Science Ltd. All rights reserved.

We have recently undertaken a research programme on the chemistry of bis-acylsilanes (bis-AC), a class of compounds with interesting reactivity, but rather little studied so far.[1,2] An easy aldol cyclization has already been reported when the linker between the two acylsilane functions is an enolizable chain comprised of 4 or 5 carbon atoms.[2,3] We report here that bis-AC with a three methylene chain linker, the 1,5-bis-acylsilanes **2a-f**, are very efficiently converted into 2,6-bis-trialkylsilyl-4H-pyranes **3a-f**, a new type of substituted pyrane.

The 1,5-bis-AC **2a-f** were synthesized according to the classical procedure,[1-3] *via* the corresponding bis-dithiane intermediates **1a-f** (Scheme 1 and 2). After oxidative dethioketalization of the bis-TMS derivative **1a**, the isolation of the expected bis-AC **2a** proved to be difficult, because spontaneous transformation into **3a** occured during the solvant evaporation, whatever the methodology used for deblocking the dithianyl system (MeI or HgO). The bis-AC **2a** could be isolated in good yield (83%) if solvant was removed with care, at temperatures below 20°C. Moreover, addition of a catalytic amount of p-toluenesulfonic acid (PTSA) allowed a complete conversion into the bis-TMS pyrane **3a** (yield 80%) during a simple Kugelrohr distillation under vaccuum (Scheme 1). The same difficulty to obtain good yields of the mixed TMS-DPMS bis-AC **2b** came from its easy cylodehydration into the corresponding 4H-pyrane **3b**.



R^1, R^2, R^4, R^5 = Me : **1a**
R^1, R^2, R^5 = Me, R^4 = Ph : **1b**

2a : 83%[4]
2b : 59%[4]

3a : 5%[4]
3b : 21%[4]

i : MeI, $CaCO_3$, MeCN-H_2O, reflux ; ii : HgO, BF_3OEt_2, celite, THF-H_2O, 25°C

Scheme 1[5]

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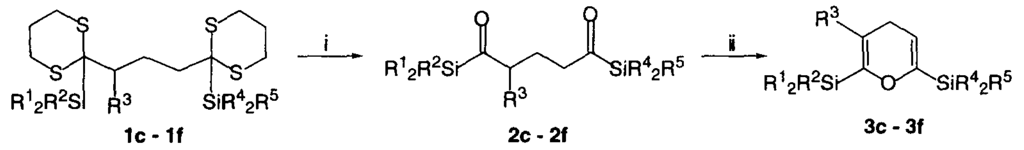
PII: S0040-4039(99)00066-0

The 1,5-bis-AC with a more crowded silicon (compounds **2c**, **2f**) or with a α-methyl substituent (compounds **2d**, **2e**) are easily isolated in good yields in the presence of a mercuric salt (Scheme 2, Table). Their cyclodehydration is facile and efficient under acid catalysis. Some representative examples are reported in the Table.



i : $Hg(ClO_4)_2.xH_2O$, $CaCO_3$, THF/H_2O ii : $PTSA_{(10\%)}$, Δ

Scheme 2[5]

Table. Synthesis of Bis-acylsilanes 2c-f and Dihydropyranes 3c-f

Bis-dithiane	R^1	R^2	R^3	R^4	R^5	Bis-acyl-silane	Yield (%)	Dihydro-pyrane	Yield[a] (%)[b]
1c	Me	ᵗBu	H	Me	ᵗBu	**2c**	100	**3c**	89 (89)
1d	Me	Me	Me	Me	Me	**2d**	79	**3d**	50[c]
1e	Me	ᵗBu	Me	Me	ᵗBu	**2e**	84	**3e**	91 (81)
1f	Me	ᵗBu	H	Et	Et	**2f**	77	**3f**	94 (75)

[a] Yield of **3c-f** from **2c-f**. [b] Yield of **3c-f** from **1c-f**. [c] Conversion of **2d** : 78%.

These 2,6-bis-trialkylsilyl-4H-pyranes **3a-f** seem to be unprecedented. Only 2-trimethylsilyl-4H-pyranes prepared by metallation-silylation of the corresponding 4H-pyranes, have been reported.[6] Several examples in the related family of 2-trialkylsilyl-dihydropyranes were described. They were generally prepared by metallation-silylation procedure,[7] by cyclisation of haloacylsilanes[8] or by cycloaddition between an enamine and trimethylsilylvinylketone.[9] Reduction of 1,5-bis-AC bearing two trimethylsilyl or diphenylmethylsilyl groups with samarium diiodide or tributylstannane were reported to give 2,6-bis-trialkylsilyl-dihydropyranes,[3] but the corresponding 4H-pyranes were not mentionned, even during the preparation (using a similar procedure) of the starting 1,5-bis-AC. The TMS derivative **2a** tends to cyclized spontaneously into **3a** in our hands.

In summary, the cyclodehydration of 1,5-bis-acylsilanes **2a** and **2c-f** is an easy and quantitative transformation leading to bis-silylated-4H-pyranes **3a** and **3c-f**, interesting new organosilicon compounds whose reactivity is currently under investigation.

References and notes

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4. The yields reported in the Scheme 1 were the best results, but these yields were difficultly reproducible owing to the easy conversion into **3** (**2a**: 30%-83%; **2b**: 26%-59%; **3a**: 5%-33%; **3b**: 21%-53%).
5. All new compounds gave satisfactory analysis (IR, MS, ^1H and ^{13}C NMR).
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