Reactions of Hexamethyldisilathiane with Silyl Acetals: a General Access to Thioformylsilanes

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Abstract: Reaction of several silylated acetals with hexamethyldisilathiane (HMDST) in the presence of $CoCl_2$•$6H_2O$ affords a simple, novel and general entry to thioformylsilanes, directly trapped *in situ* as their Diels-Alder cycloadducts.

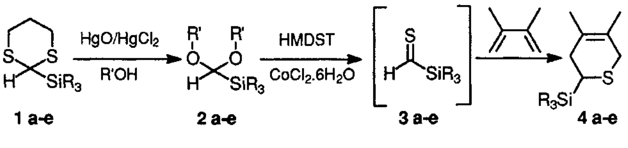
Acylsilanes are well-known compounds that have been shown useful as intermediates in synthetic organic chemistry.[1] They participate in regio- and stereoselective processes that allow the synthesis of a number of polyfunctionalized molecules. Preparation of silyl enolethers,[2] diastereoselective aldol condensations,[3] the synthesis of β–hydroxysilanes[4] and the stereoselective synthesis of vinylsilanes[5] are just a few examples of their valuable reactivity.

The chemistry of formylsilanes, on the other hand, although extremely attractive, has only recently received important contributions from the work of Silverman[6] and Katritzky[7] and with the synthesis of the first stable formylsilane, triisopropylformylsilane, by Soderquist,[8] thus opening the doors to its fascinating chemistry.

Our long dated interest in the chemistry of acylsilanes,[9] and, more recently, in the synthesis of thiocarbonyl containing compounds,[10] coupled with the mentioned development of synthetically useful routes to formylsilanes, led us to undertake an investigation toward the synthesis of an even more reactive class of compounds, thioformylsilanes. To the best of our knowledge only one example of such compounds has been reported in the literature, thioformyltrimethylsilane, through the Vedejs' photolytical fragmentation of phenacylsulfides.[11]

In this connection our recently developed hexamethyldisilathiane based thionation procedure[12] of carbonyl compounds, due to its intrinsic mildness, appeared well suited for the synthesis of thioformylsilanes, and could have afforded a possible general entry to these compounds.

Direct thionation of tri(isopropyl)formylsilane, prepared according to Soderquist procedure,[8] proved somewhat troublesome, probably as a consequence of the reported high instability and reactivity of formyl silanes, leading only to intractable material.



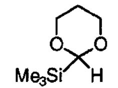
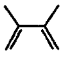
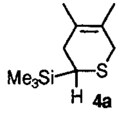
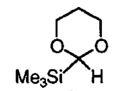
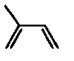
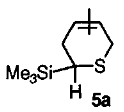
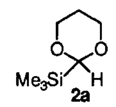
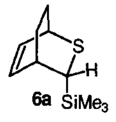
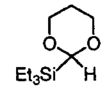
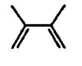
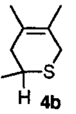
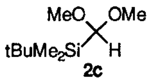
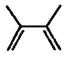
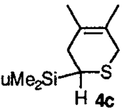
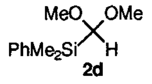
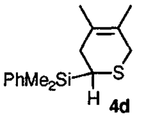
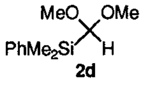
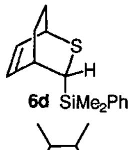
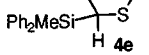
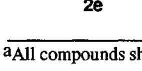
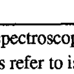
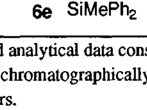
a R = Me, R' = -$(CH_2)_3$-
b R = Et, R' = -$(CH_2)_3$-
c R = tBuMe$_2$ R' = -$(CH_2)_3$-
d R = PhMe$_2$ R' = Me
e R = Ph$_2$Me R' = Me

Scheme 1

Consequently we reasoned that the corresponding silyl acetals **2**, precursors of formylsilanes, could also behave, upon treatment with hexamethyldisilathiane, as good precursors of the wanted thioaldehydes. Recent findings from this laboratory pointed out that benzaldehyde dimethylacetal can be easily converted into the corresponding thiobenzaldehyde upon treatment with HMDST and $CoCl_2$•$6H_2O$.[13]

In this communication we want to report our recent results toward the development of a general route for the synthesis and the chemical trapping of a variety of thioformylsilanes. Thus, for instance, when 2-trimethylsilyl-1,3-dithiane **1a** was treated with $HgCl_2$/HgO in refluxing methanol, the corresponding acetal **2a** could be obtained in good yield (Scheme 1). Subsequent exposure of this acetal to HMDST and $CoCl_2$•$6H_2O$ in acetonitrile led to the corresponding thioaldehyde **3a** that could be isolated as oligomeric material, thus showing that the thioformylsilane had indeed been generated, but, irrespective of the steric hindrance of the silicon moiety, it was not stable in the monomeric form. When the same reaction was repeated in the presence of 5 fold excess of a suitable trapping agent such as of 2,3-dimethylbutadiene, the silyldihydrothiopyran **4a** could be smoothly obtained in satisfactory yield, thus confirming that the synthesis of thioformylsilanes was possible[14] (Scheme 1).

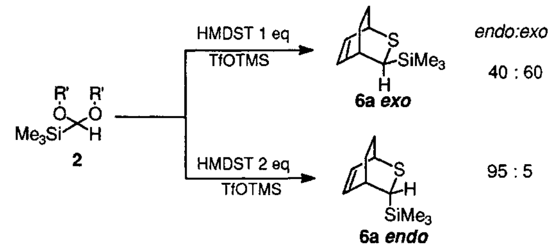
Table. Synthesis of thioformylsilanes.

Acetal	Diene	Product[a]	Yield[b]
 **2a**		 **4a**	41
 **2a**		 **5a**	37[c]
 **2a**		 **6a**	64
 **2b**		 **4b**	51
 **2c**		 **4c**	41
 **2d**		 **4d**	56
 **2d**		 **6d**	58
 **2e**		 **4e**	62
 **2e**		 **6e**	54

[a]All compounds showed spectroscopical and analytical data consistent with the assigned structure. [b]Yields refer to isolated, chromatographically pure materials. [c]Isolated as a mixture of the two regioisomers.

Results of this study are summarised in the Table. This reaction can be performed on a wide range of formylsilanes, thus showing the generality of the methodology. Both 1,3-dioxanes **2a,b** and dimethoxy derivatives **2c-e** can be satisfactorily used as starting materials, the choice simply depending on the volatility of the obtained acetals. Trapping with dimethylbutadiene afforded the Diels-Alder cycloadducts in good yields, showing that these silyl thioaldehydes are quite reactive, in comparison with the aliphatic ones, which have been reported to be rather inert in Diels-Alder reactions. Interestingly, when using cyclohexadiene as the trapping agent, we were not able to detect even traces of the *exo* isomer in the crude reaction mixtures, with the exception of the trimethylsilyl derivative **6a**, whose reaction mixture was composed by a 95 : 5 ratio of *endo/exo* isomer, as determined by NMR on the crude.

Furthermore, when the Lewis acid used was the more oxophilic $CF_3SO_3SiMe_3$ (TfOTMS), the reaction proved to proceed as well and, as already observed in the case of thioaldehydes, a stereodefined entry to both the *endo* or the *exo* isomer could be developed.



Scheme 2

Thus, when using 2 equivalents of HMDST, a 95 : 5 ratio of *endo*: *exo* isomers was obtained, while when using 1 equivalent of HMDST the selectivity was shifted toward the *exo* isomer. It should be underlined that in this last case (1 eq. of HMDST), in contrast to what is observed with thioaldehydes, only a slight prevalence of the *exo* compound can be detected (Scheme 2).

Thus, in conclusion, treatment of silyl acetals with HMDST in the presence of $CoCl_2 \cdot 6H_2O$ affords a general and mild procedure for the synthesis of highly reactive thioformylsilanes, whose reactivity is currently under investigation in our laboratories.

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14. A solution of 50 mg (0.31 mmol) of 2-trimethylsilyl-1,3-dioxane **2a** in 0.35 mL of acetonitrile was treated under inert atmosphere with 127 mg (1.55 mmol) of 2,3-dimethyl-1,3-butadiene, 110 mg (0.62 mmol) of hexamethyldisilathiane and a solution of 74 mg (0.31 mmol) of $CoCl_2 \cdot 6H_2O$ in 2 mL of acetonitrile. The reaction was stirred at room temperature in the dark for 24h and monitored by GC/MS. After extraction with ether, the mixture was treated with saturated NH_4Cl, water and brine. Drying over Na_2CO_3 and removal of the solvent under vacuum afforded the crude product which was purified by tlc (petroleum ether) to obtain 25.4 mg of pure product.^1H NMR ($CDCl_3$) δ (ppm): 0.09 (s, 9H), 1.66 (bs, 3H), 1.70 (bs, 3H), 1.86-2.80 (m, 3H), 2.62 - 2.78 (bd, 1H), 3.20 - 3.38 (bd, 1H). ^{13}C NMR ($CDCl_3$) δ (ppm): -3.4, 19.8, 20.2, 25.8, 31.7, 33.5, 123.5, 127.5. MS (%): 200 (M^+, 2), 185 (1), 127 (3), 94 (100), 73 (42), 67 (11), 45 (12). Anal. Calcd. for $C_{10}H_{20}SSi$: C, 59.93; H, 10.06. Found: C, 59.76; H, 10.34.