Pergamon

Tetrahedron Letters 42 (2001) 763–766

TETRAHEDRON
LETTERS

Formation of silanethiols by reaction of silanes with carbonyl sulfide: implications for radical-chain reduction of thiocarbonyl compounds by silanes

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Received 16 October 2000; accepted 15 November 2000

Abstract—Carbonyl sulfide reacts with organosilanes at 60–85°C, in the presence of a radical initiator, to give the corresponding silanethiols. Triphenylsilane is confirmed as an excellent replacement for tributyltin hydride in the Barton–McCombie deoxygenation of alcohols via their xanthates under mild conditions. Reduction of xanthates by silanes can produce COS as a by-product, leading to the in situ formation of silanethiol that will then act as a protic polarity-reversal catalyst for the reduction. © 2001 Elsevier Science Ltd. All rights reserved.

We have reported previously that the radical-chain reduction of alkyl bromides and chlorides by triethylsilane (TES) and by some other simple silanes [Eq. (1)] is promoted by thiols.[1] The function of the thiol is to act as a protic polarity-reversal catalyst[2] for the propagation step (2) and, in the presence of thiol, this direct hydrogen-atom transfer process is replaced by the cycle of more rapid reactions (3) and (4). Without a thiol catalyst under the same conditions, very little reduction of the alkyl halide takes place. Radical-chain reduction of *S*-methyl dithiocarbonate (xanthate) esters by TES [Eq. (5)] initiated by dicumyl peroxide in refluxing octane also involves the overall reaction (2) as a propagation step but, somewhat surprisingly, yields of RH are almost as high in the absence of an added thiol catalyst as in its presence.[1] To account for this result, it was suggested that a thiol (possibly Et_3SiSH) is formed in situ by side reactions, thus obviating the need to add a separate thiol catalyst.[1]

$$\mathrm{RHal+Et_3SiH \rightarrow RH+Et_3SiHal} \tag{1}$$

$$\mathrm{R^{\bullet}+Et_3SiH \rightarrow RH+Et_3Si^{\bullet}} \tag{2}$$

$$\mathrm{R^{\bullet}+XSH \rightarrow RH+XS^{\bullet}} \tag{3}$$

$$\mathrm{XS^{\bullet}+Et_3SiH \rightleftharpoons Et_3Si^{\bullet}+XSH} \tag{4}$$

$$\mathrm{ROC(=)+Et_3SiH \rightarrow RH+Et_3SiSC(=O)SMe} \tag{5}$$

The Si–H bond in triphenylsilane (TPS) is weaker than that in TES[3,4] and we have now shown that radical-chain reduction of xanthates by TPS occurs at 60°C in dioxane in the presence of di-*tert*-butyl hyponitrite[5] (TBHN) as initiator; again the reduction does not usually require an added thiol catalyst. Thus, treatment of the xanthate **1** (1.0 mmol) with TPS (1.5 mmol) and TBHN (5 mol% based on **1**) in dioxane for 2.5 h at 60°C afforded the 3-deoxyglucofuranoside **2** in 90% yield after a simple chromatographic work-up. Barton and co-workers[6] have shown previously that diphenylsilane functions similarly to bring about the reduction of **1** under mild conditions and, most recently, they have reported[7] that a phosphine–borane (especially $Bu_3P \rightarrow BH_3$) can also serve as the hydrogen-atom donor[8] to mediate this reaction. It could be argued that the C-3-centred radical derived from **1** is especially electrophilic, rendering it particularly reactive in direct hydrogen-atom abstraction from the silane or the phosphine–borane. However, we find that cholestanyl xanthate **3** is also efficiently (85% isolated yield) reduced to cholestane **4** by TPS at 60°C in dioxane under the conditions described for the reduction of **1**;[9] when 5 mol% triphenylsilanethiol (Ph_3SiSH, TPST) was added at the start of this reaction the yield was raised only marginally to 90%.

Keywords: silicon and compounds; thiols; radicals and radical reactions; deoxygenation; catalysis.

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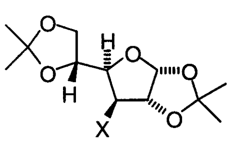
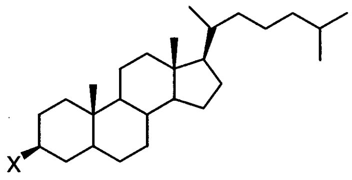
PII: S0040-4039(00)02109-2



1 X = OC(=S)SMe
2 X = H



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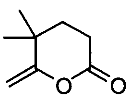

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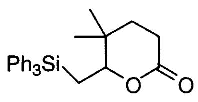

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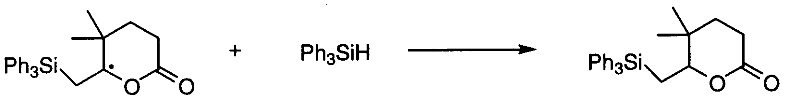
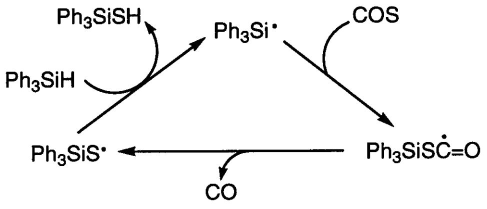
Radical-chain hydrosilylation of the methylene lactone **5** with TPS to give **6** is strongly promoted by TPST, which in this case acts as a polarity–reversal catalyst for reaction (6).[10] In the present work, treatment of **5** (1.0 mmol) with TPS (1.1 mmol), in the presence of TBHN and TPST (both 5 mol% based on **5**) in dioxane (2 cm^3) at 60°C for 2.5 h, led to quantitative formation of **6** as determined by ^{1}H NMR spectroscopy; in the absence of thiol the conversion of **5** was $\leq$1%. However, when the thiol was replaced by the xanthate **1** (10 mol%) conversion of **5** to **6** was 94%, showing that **1** or (more likely) something derived from it acts as an efficient catalyst for reaction (6). The initial sulfur-containing product from the reduction of a xanthate by TPS is $Ph_3SiSC(=O)SMe$ but, under our conditions, it is likely[11] that this will undergo partial or complete thermal decomposition during the course of the hydrosilylation to give carbonyl sulfide (COS) according to Eq. (7).[12] In fact, we find that the hydrosilylation of **5** is very effectively catalysed by COS when ca. 20 mol% of this is bubbled slowly through the reaction mixture, using a motor-driven syringe, and conversion to **6** under these conditions was $\geq$98%. We reasoned that carbonyl sulfide should react with TPS by a radical-chain mechanism to give TPST and carbon monoxide, through the propagation cycle shown in Scheme 1, and that the silanethiol would then serve as the active catalyst. In the present paper we report that this reaction does indeed take place rapidly and that a number of other organosilanes can be converted to silanethiols by treatment with COS.



(6)



Scheme 1.

$$Ph_3SiSC(=O)SMe \longrightarrow Ph_3SiSMe + COS \qquad (7)$$

A solution of TPS and TBHN (5 mol%) in dry dioxane was stirred and heated under argon at 60°C, while a slow stream of COS was bubbled through the liquid. After 2.5 h the solvent was removed by evaporation and the

Table 1. Thiols prepared by the reaction of carbonyl sulfide with silanes or triphenylgermane in dioxane

Entry	Silane[a]	Initiator (mol%)	Conditions[b] (Temp./°C)	Thiol (isolated yield%)	Lit. ref. for thiol
1	Ph_3SiH	TBHN (5)	A (60)	Ph_3SiSH (87)	[13]
2	Ph_3SiH	AIBN (5)	A (85)	Ph_3SiSH (40)	[13]
3	Ph_3SiH	DLP (5)	A (80)	Ph_3SiSH (76)	[13]
4	α-$NpPh_2SiH$	TBHN (5)	A (60)	α-$NpPh_2SiSH$ (83)	This work[14]
5	$(o\text{-}MeC_6H_4)_3SiH$	TBHN (5)	A (60)	$(o\text{-}MeC_6H_4)_3SiSH$ (82)	[16]
6	$MePh_2SiH$	TBHN (5)	A (60)	$MePh_2SiSH$ (78)	[16]
7	Bu^tPh_2SiH	TBHN (10)	B (60)	Bu^tPh_2SiSH (63)	[17]
8	Me_2PhSiH	TBHN (5)	A (60)	$Me_2PhSiSH$ (72)	[16]
9	Pr^i_3SiH	TBHN (10)	B (60)	Pr^i_3SiSH (74)	[18]
10	Bu^tOPh_2SiH	TBHN (10)	B (60)	Bu^tOPh_2SiSH (32)[c]	This work
11	$(Bu^tO)_2PhSiH$	TBHN (5)	A (60)	$(Bu^tO)_2PhSiSH$ (10)[c]	This work
12	$(Bu^tO)_3SiH$	TBHN (5)	A (60)	$(Bu^tO)_3SiSH$ (ca. 5)[c]	[19]
13	Ph_2SiH_2	TBHN (10)	B (60)	$Ph_2Si(SH)_2$[d] (49)	This work
14	Ph_3GeH	TBHN (5)	A (60)	Ph_3GeSH[e] (78)	This work
15	Ph_3GeH	DLP (5)	A (80)	Ph_3GeSH[e] (85)	This work

[a] Scale generally 5–15 mmol; concentration ca. 0.5 M for reactions at atmospheric pressure and ca. 1 M for reactions under pressure.

[b] A = COS bubbled through the reaction mixture; B = COS pressure 2.5 bar above atmospheric.

[c] Yield estimated by ^{1}H NMR spectroscopy; thiol not isolated in a pure state.

[d] Bp 118–120°C at 0.05 mmHg.

[e] Mp 107–109°C.

residue was shown by NMR spectroscopy to consist mainly of TPST (96%) together with a trace of unreacted silane. In the absence of TBHN but under otherwise identical conditions, no conversion of TPS to TPST was detectable, confirming the radical-chain nature of the reaction. Several other organosilanes and triphenylgermane were converted to the corresponding metalloidal thiols by the same method and the results are collected in Table 1. In some cases yields were improved if the reaction was carried out in a thick-walled glass bottle under a pressure of COS ca. 2.5 bar above atmospheric. Azobis(isobutyronitrile) (AIBN) and dilauroyl peroxide (DLP) were investigated as alternative initiators (at 80–85°C) and sometimes gave better results than TBHN. In this context, it must be borne in mind that use of TBHN leads to the production of *tert*-butyl alcohol which may react with some of the metalloidal thiols to replace the SH group by a Bu^tO group and liberate H_2S.

The yield of silanethiol drops rapidly as the phenyl groups in TPS are replaced sequentially with *tert*-butoxy groups (entries 10–12). Attachment of an electronegative oxygen atom to silicon probably strengthens the Si–H bond and decreases the electron density at the hydrogen atom, making the latter less readily abstracted by the electrophilic silanethiyl radical (cf. Scheme 1). It is also likely to render the silicon atom in the corresponding silyl radical 'harder' and less thiophilic, reducing the rate of its addition to the C=S group in carbonyl sulfide.

Triphenylgermane reacts with COS in a similar way to the silanes and gives the germanethiol in essentially quantitative yield (entries 14 and 15). This thiol also functioned as an effective protic polarity-reversal catalyst for the radical-chain addition of triphenylsilane to the methylene lactone **5** and complete (≥98%) conversion to the adduct **6** was obtained in its presence (5 mol%) under the conditions described above for catalysis by TBST.

We conclude that (i) simple organosilanes, in particular triphenylsilane, are excellent, relatively cheap and environmentally-sound replacements for tributyltin hydride in Barton–McCombie-type deoxygenations via xanthate esters, (ii) the possible role of thiols generated in situ from thiocarbonyl compounds should always be considered in mechanistic discussions of their reactions with metallic or metalloidal hydrides and (iii) COS reacts with organosilanes under mild conditions to provide a convenient and clean method for the synthesis of silanethiols. As demonstrated by the reaction of triphenylgermane with COS, it seems likely that the method can be extended to the preparation of other metallic and metalloidal thiols.

Acknowledgements

We thank the EPSRC for financial support.

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5.3%. Satisfactory spectroscopic and analytical data were obtained for all other new compounds, unless stated otherwise.

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