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LETTERS

Preparation of silanethiols by reaction of silanes with triphenylphosphine sulfide and with alkanethiols

Yudong Cai and Brian P. Roberts*

Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK

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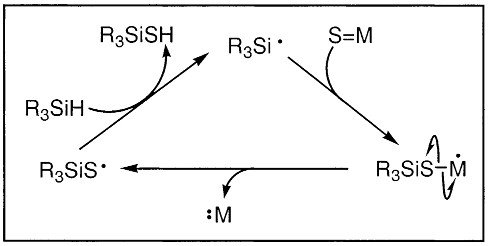
Abstract—Silanes react with triphenylphosphine sulfide by a radical-chain mechanism to give the corresponding silanethiols in good yield. Silanethiols are similarly formed when silanes react with *tert*-dodecanethiol. Enantiomerically pure (*S*)-$Bu^tMePhSiH$ gave racemic silanethiol with $Ph_3P{=}S$, but with *tert*-dodecanethiol silanethiol with an ee up to 60% has been obtained, although in low chemical yield. © 2001 Elsevier Science Ltd. All rights reserved.

Organosilanethiols (R_3SiSH) now have a number of applications in organic chemistry. Triphenylsilanethiol[1] and triisopropylsilanethiol[2] function as H_2S equivalents for the synthesis of alkanethiols and thioethers, when C–S bond formation can be accomplished by radical or heterolytic pathways. The silanethiols $(Me_3Si)_3SiSH$[3] and $(Me_3Si)_2MeSiSH$[4] have been used as homolytic reducing agents for alkyl halides and silanethiols [in particular Ph_3SiSH and $(Bu^tO)_3SiSH$] have been used as protic polarity-reversal catalysts to promote the overall abstraction of electron-rich hydrogen by one nucleophilic radical to produce a second nucleophilic radical.[5]

We have reported recently[6] that silanes react by a radical-chain mechanism with carbonyl sulfide to give silanethiols and carbon monoxide (Scheme 1; M = CO) in good yield when the other groups attached to silicon are alkyl or aryl. However, poor yields are obtained when alkoxy groups are attached to silicon.



Scheme 1.

The many similarities between phosphines and carbon monoxide, together with the high affinity of silicon for bonding to the electronegative sulfur atom, suggested that phosphine sulfides might serve as sulfur-transfer reagents in place of the carbonyl sulfide (Scheme 1; $M = PR_3$). The reaction of COS proceeds via an intermediate thioacyl radical **1**, while addition of the silyl radical to $R_3P{=}S$ would give an intermediate thiophosphoranyl radical[7] **2**, α-scission of which could yield the phosphine and a silanethiyl radical.[8,9]

$R_3SiS\text{-}\dot{C}{=}O$ **1** $R_3SiS\text{-}\dot{P}R_3$ **2**

In the present paper we report that silanethiols can indeed be prepared by the radical-chain reaction of silanes with phosphine sulfides and that this reaction is more tolerant of the presence of alkoxy groups attached to silicon than is the corresponding reaction with COS. While this work was in progress, a report by Chatgilialoglu and co-workers[11] appeared in which these authors described the reduction of phosphine sulfides and selenides with tris(trimethylsilyl)silane to give the parent phosphine. Although, the silicon-containing products of these reactions were not examined, it was thought that the intermediate radical $(Me_3Si)_3SiX^\bullet$ (X = S or Se) rearranged by a 1,2-shift of a trimethylsilyl group from Si to X more rapidly than it abstracted hydrogen from the silane.

Keywords: silicon and compounds; phosphorus and compounds; thiols; radicals and radical reactions.

* Corresponding author.

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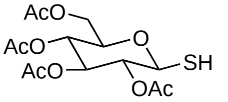
When a dioxane solution containing triphenylsilane and triphenylphosphine sulfide (1.2 equiv.) was heated for 2.5 h at 60°C under argon, in the presence of di-*tert*-butyl hyponitrite[12] (TBHN; 5 mol% based on silane) as a thermal source of initiating *tert*-butoxyl radicals, 97% of the silane was converted into triphenylsilanethiol (as judged by ^{1}H NMR spectroscopy). Essentially no silanethiol was formed in the absence of the initiator, confirming the radical-chain nature of the reaction. The same result was achieved using azobis(isobutyronitrile) (AIBN) at 85°C or in refluxing octane (bath temperature 140°C, internal temperature ca. 130°C) as solvent with 2,2-di-*tert*-butylperoxybutane[13] (DBPB) as initiator. The results are summarised in Table 1.

Tributylphosphine sulfide and methyldiphenylphosphine sulfide were less effective sulfur-transfer reagents than triphenylphosphine sulfide (entries 4 and 5), perhaps because the presence of alkyl groups attached to phosphorus increases the basicity of the corresponding phosphine and consequently reduces the rate of P–S bond cleavage in the intermediate thiophosphoranyl radical. Triphenylphosphine sulfide also reacts with $MePh_2SiH$ and with racemic $Bu^tMePhSiH$ to give high yields of the corresponding silanethiols (entries 6–8), although the (*S*)-enantiomer[14] of the latter silane gave extensively (at 60°C) or completely racemic (at 130°C) product, showing that the configuration of the pyramidal intermediate silyl radical $Bu^tMePhSi^\bullet$ is scrambled during the reaction (entries 9 and 10).[15] The (*S*)-silane also gave completely racemic silanethiol when treated with COS in dioxane at 60°C, under the conditions described previously.[6]

In contrast to the low yield obtained from its reaction with COS,[6] Bu^tOPh_2SiH was efficiently converted to the silanethiol by reaction with $Ph_3P{=}S$ (entries 11–13), especially at higher temperatures. The separation of the silanethiol from the triphenylphosphine produced was facilitated by addition of elemental sulfur to the reaction mixture, to affect its conversion back to the polar and relatively insoluble $Ph_3P{=}S$.[16,17]

We have reported previously that the glucosidic thiol **3** undergoes efficient desulfurisation at C-1 to give **4** when heated at 60°C in dioxane in the presence of triphenylsilane (1.2 equiv.) and TBHN (5 mol% based on silane).[18] It was pointed out that triphenylsilanethiol was also a product of the reaction, although this compound was not isolated. We now report that this reaction, which shows promise as a method for the desulfurisation of aliphatic thiols, can also provide an efficient route to silanethiols. The propagation cycle of the proposed radical-chain mechanism is shown in Scheme 2, although the S_H2 reaction of the silyl radical with the thiol to displace an alkyl radical might take place via a discrete sulfuranyl radical intermediate.[19]



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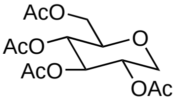

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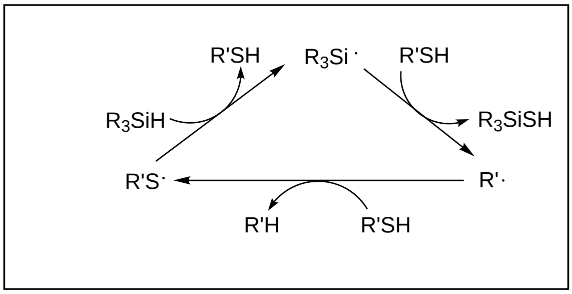

Scheme 2.

Table 1. Thiols prepared by the reaction of phosphine sulfides with silanes

Entry	Silane[a]	Phosphine sufide	Conditions[b]	Initiator (bath temp./°C)	Solvent[c]	Product[d] (conversion %)
1	Ph_3SiH	Ph_3PS	A	TBHN (60)	D	Ph_3SiSH (97)
2	Ph_3SiH	Ph_3PS	A	AIBN (85)	D	Ph_3SiSH (97)
3	Ph_3SiH	Ph_3PS	A	DBPB (140)	O	Ph_3SiSH (98)
4	Ph_3SiH	$MePh_2PS$	A	TBHN (60)	D	Ph_3SiSH (57)
5	Ph_3SiH	Bu_3PS	A	TBHN (60)	D	Ph_3SiSH (11)
6	$MePh_2SiH$	Ph_3PS	A	TBHN (60)	D	$MePh_2SiSH$ (93)
7	$MePh_2SiH$	Ph_3PS	A	AIBN (85)	D	$MePh_2SiSH$ (95)
8	$Bu^tMePhSiH$	Ph_3PS	B	DBPB (140)	O	$Bu^tMePhSiSH$ (97)[e]
9	(*S*)-$Bu^tMePhSiH$	Ph_3PS	B	TBHN (60)	D	$Bu^tMePhSiSH$ (86)[f]
10	(*S*)-$Bu^tMePhSiH$	Ph_3PS	B	DBPB (140)	O	$Bu^tMePhSiSH$ (97)[g]
11	Bu^tOPh_2SiH	Ph_3PS	A	TBHN (60)	D	Bu^tOPh_2SiSH (53)
12	Bu^tOPh_2SiH	Ph_3PS	A	AIBN (85)	D	Bu^tOPh_2SiSH (54)
13	Bu^tOPh_2SiH	Ph_3PS	B	DBPB (140)	O	Bu^tOPh_2SiSH (95)[h]

[a] Scale 1–10 mmol; concentration ca. 0.5 M; reaction time 2.5 h.

[b] A = 1.2 equiv. phosphine sulfide and 5 mol% initiator based on silane; B = 1.5 equiv. phosphine sulfide and 7.5 mol% initiator based on silane.

[c] D = dioxane; O = octane.

[d] Conversion estimated by ^{1}H NMR spectroscopy.

[e] Isolated yield 73%; bp 98–100°C/2 mmHg.

[f] ee = 7%, retention of configuration at Si assumed.

[g] ee = 0%.

[h] Isolated yield 72%; bp 112–114°C/0.02 mmHg.

Table 2. Thiols prepared by the reaction of alkanethiols with silanes

Entry	Silane[a]	Alkanethiol[b]	Initiator[c] (bath temp./°C)	Solvent[d]	Product[e] (conversion %)
1	Ph_3SiH	TDT	TBHN (60)	D	Ph_3SiSH (94)[f]
2	Ph_3SiH	TDT	AIBN (85)	D	Ph_3SiSH (95)
3	Ph_3SiH	$PhCH_2SH$	TBHN (60)	D	Ph_3SiSH (51)
4	(*S*)-$Bu^tMePhSiH$	TDT	TBHN (60)	D	$Bu^tMePhSiSH$ (41)[g]
5	(*S*)-$Bu^tMePhSiH$	TDT[h]	TBHN (60)	D	$Bu^tMePhSiSH$ (16)[i]
6	(*S*)-$Bu^tMePhSiH$	TDT	DBPB (140)	O	$Bu^tMePhSiSH$ (49)[j]
7	(*S*)-$Bu^tMePhSiH$	TDT[h]	DBPB (140)	O	$Bu^tMePhSiSH$ (27)[k]
8	Bu^tOPh_2SiH	TDT	TBHN (60)	D	Bu^tOPh_2SiSH (12)
9	Bu^tOPh_2SiH	TDT	AIBN (85)	D	Bu^tOPh_2SiSH (5)
10	Bu^tOPh_2SiH	TDT	DBPB (140)	O	Bu^tOPh_2SiSH (15)

[a] Scale generally 1.0 mmol; concentration ca. 0.5 M.

[b] 1.05 equiv. of alkanethiol based on silane, unless stated otherwise.

[c] 5 mol% initiator based on silane.

[d] D = dioxane; O = octane.

[e] Estimated by ^1H NMR spectroscopy.

[f] Isolated yield 75%.

[g] ee = 29%, retention of configuration at silicon assumed.

[h] 2.0 equiv. of alkanethiol.

[i] ee = 60%.

[j] ee = 3%.

[k] ee = 23%.

When a dioxane solution containing triphenylsilane and *tert*-dodecanethiol[20] (1.05 equiv.) was stirred and heated at 60°C under argon, in the presence of TBHN (5 mol% based on silane), the silane was smoothly converted to triphenylsilanethiol (94% by NMR); the results are summarised in Table 2. No reaction occurred in the absence of initiator and, as for sulfur transfer from $Ph_3P{=}S$, AIBN was equally effective as initiator (entry 2). Although benzyl mercaptan has a relatively weak C–S bond, this reagent gave lower yields of silanethiol than TDT (entry 3), perhaps because of the presence of benzylic CH groups that lead to side reactions and to inhibition of the radical-chain process.[21] Although the yields of silanethiol from (*S*)-$Bu^tMePhSiH$ were lower than those obtained from the reaction of $Ph_3P{=}S$ under similar conditions (entries 4–7), the $Bu^tMePhSiSH$ produced was not racemic and showed an ee up to 60% (entry 5). These observations imply that the silyl radical reacts with TDT more rapidly than with the phosphine sulfide under comparable conditions. Although increasing the amount of TDT used to 2 equiv. led to the expected increase in ee of the silanethiol produced (entries 5 and 7), the chemical yield was reduced considerably. When attempting to understand these results, it must be borne in mind that the overall rate of a radical-chain reaction does not depend simply on the rate of any single propagation step. Furthermore, the mechanisms of both types of sulfur-transfer reaction are likely to be more complex in detail than shown in Schemes 1 and 2. For example, the addition of the silyl radical to $R_3P{=}S$ (Scheme 1) may be reversible under the reaction conditions and abstraction of hydrogen from TDT by the silyl radical is also likely to be reversible (Scheme 2).

The radical-chain reaction between Bu^tOPh_2SiH and TDT gives low yields of the corresponding silanethiol and is not synthetically useful (entries 8–10).

We conclude that the reaction of silanes with triphenylphosphine sulfide constitutes a useful method for the preparation of silanethiols, especially when the latter are liquids and thus readily isolated from solid by-products. So far, the reaction of aliphatic thiols with silanes is more limited in scope, but can be useful for the preparation of solid silanethiols (especially if these are water sensitive) and might perhaps be developed into a method for the synthesis of homochiral silanethiols.

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9. The phosphoranyl radical $[Bu^tOPBu_3]^\bullet$ undergoes α-scission to give butyl radicals so rapidly that it is not detectable by EPR spectroscopy even at −100°C.[8,10] In contrast, the EPR spectrum of the thiophosphoranyl radical $[(Bu^tO)_3SiSPBu_3]^\bullet$, generated by photolysis of the bis(tri-*tert*-butoxysilyl) disulfide in the presence of tributylphosphine, is readily detectable [a(P) 614.5 G, a(6 H) 3.2 G, g 2.0079 in cyclopropane at −73°C]. There was no spectroscopic evidence for cleavage of this thiophosphoranyl radical to give butyl radicals at even higher temperatures and the spectrum of $[(Bu^tO)_3SiSPBu_3]^\bullet$ was still readily detectable at +23°C.[10] It seems likely that the

unpaired electron in the thiophosphoranyl radical is confined to the PS σ* orbital[7] and such a structure would have a tendency to fragment by P–S bond cleavage, rather than by loss of a butyl radical.[8]

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15. The enantiomeric purity of *tert*-butylmethylphenylsilanethiol could not be determined directly and it was converted to $\mathrm{Bu^tMePhSiSCH_2CO_2Et}$ by stirring with ethyl bromoacetate and potassium carbonate in benzene at room temperature. The ee of the resulting ester was determined by HPLC using a Chiralcel-OD column (Daicel Chemical Industries) and eluting with hexane–isopropyl alcohol (99.5:0.5).
16. *Representative procedure*: *tert*-Butoxydiphenylsilane (1.28 g, 5.0 mmol), triphenylphosphine sulfide (2.21 g, 7.5 mmol), DBPB (50% w/w in mineral oil, 0.18 g, 0.38 mmol) and dry octane (10 $\mathrm{cm^3}$) were placed in a dry, argon-filled flask, containing a magnetic stirrer bar and equipped with a condenser. The flask was then immersed in an oil bath, pre-heated to 140°C, and the reaction mixture was stirred for 2.5 h and then allowed to cool to room temperature. The excess sulfide was removed by filtration and the filter cake was washed thoroughly with light petroleum. The solvents were removed from the filtrate under reduced pressure and benzene (8 $\mathrm{cm^3}$) and powdered sulfur (0.16 g, 5.0 mmol) were added to the residue. The mixture was stirred at room temperature for 2 h, the benzene was removed by rotary evaporation and light petroleum was added to the residue to precipitate triphenylphosphine sulfide. After cooling to −10°C to complete precipitation, the $\mathrm{Ph_3PS}$ was removed by filtration. The solvent was evaporated from the filtrate under reduced pressure and the residue was distilled to give *tert*-butoxydiphenylsilanethiol (1.04 g, 72%) as a colourless oil, bp 112–114°C/0.02 mmHg. NMR (500 MHz for ^{1}H, 125.7 MHz for ^{13}C, $\mathrm{CDCl_3}$ solvent); δ_H 0.51 (1 H, s, SH), 1.38 (9 H, s, Bu^t), 7.36–7.71 (10 H, m, Ph); δ_C 31.9, 75.6, 127.8, 130.1, 134.3, 136.9. MS (EI, 70 eV) 288 (M^+, 1.3), 273 (2.4), 255 (4.2), 45 (100%). IR (KBr disc) 2558 $\mathrm{cm^{-1}}$ (SH str.). Found: C, 66.4; H, 6.9. $\mathrm{C_{16}H_{20}OSSi}$ requires C, 66.6; H, 7.0%.
    tert-Butylmethylphenylsilanethiol was prepared in a similar way from racemic *tert*-butylmethylphenylsilane as a colourless oil, bp 98–100°C/2 mmHg. δ_H −0.11 (1 H, s, SH), 0.62 (3 H, s, Me), 0.97 (9 H, s, Bu^t), 7.37–7.65 (5 H, m, Ph); δ_C −2.6, 19.1, 26.1, 127.7, 129.7, 134.5, 135.4. MS (EI, 70 eV) 210 (M^+, 5), 153 (M^+–Bu^t, 100%). IR (KBr disc) 2562 $\mathrm{cm^{-1}}$ (SH str.). Found: C, 62.9; H, 8.7. $\mathrm{C_{11}H_{18}SSi}$ requires C, 62.8; H, 8.6%.
17. Attempts to use triphenylphosphine to *catalyse* the reaction between triphenylsilane and elemental sulfur to give the silanethiol were unsuccessful. It seems likely that triphenylsilyl radicals react with sulfur in preference to $\mathrm{Ph_3PS}$ under these conditions, leading to chain inhibition.
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20. This is the isomeric mixture of tertiary thiols as obtained from Aldrich.
21. Methyl thioglycolate ($\mathrm{MeO_2CCH_2SH}$) gave results similar to those obtained using TDT. Thus, with triphenylsilane, otherwise under the conditions of Table 2, entry 1, conversion to $\mathrm{Ph_3SiSH}$ was 98% and the isolated yield was 84%. An advantage of using methyl thioglycolate is that the methyl acetate produced as a by-product is very easily removed by evaporation.