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Insertion of dimethylsilylene into the sulphur–hydrogen bond of trialkoxysilanethiols *

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Abstract

The first example of silylene insertion into a S–H bond in solution is described. The trialkoxysilanethiols, significantly more acidic than carbon thiols, were found to be efficient trapping agents for photochemically-generated dimethylsilylene. Chemical evidence for insertion products is presented. A surprisingly high yield of products of insertion of more than one Me₂Si unit was observed. In contrast, when alkyl mercaptans and thiophenol were employed no formal insertion products were found. A mechanism of the insertion reaction involving initial interaction of sulphur lone pair of electrons with an empty p orbital of silylene followed by a proton shift is proposed, and supported by EHT and *ab initio* calculations of orbital interactions and the deprotonation energy of mercaptans and silanethiols.

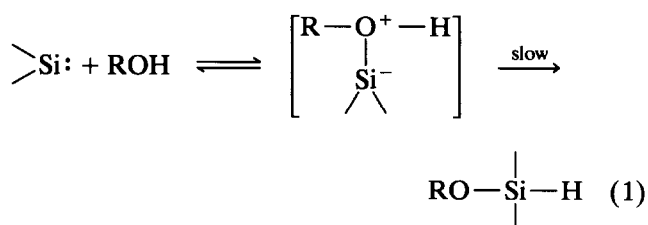
1. Introduction

Divalent compounds of elements of Group 14 have attracted considerable interest in recent years [1–3]. One focus of current studies is the elucidation of mechanisms of reactions of short-lived molecules containing divalent carbon, silicon and germanium atoms. These electron-deficient neutral species undergo many unusual reactions, which in the case of silylenes and germlylenes have led to the formation of whole new types of compound. Comparison of the behaviour of carbenes with those of the silicon and germanium analogues reveal how the mechanistic principles developed for organic chemistry must be modified to deal with bond-making and bond-cleavage processes for the elements lying further down the Periodic Table.

In view of the increasingly important role of silylenes in chemistry and materials science, it is not surprising that considerable interest attaches to study typical re-

actions of these species and their analogues. Silylenes, like carbenes, readily undergo insertion into a variety of σ -bonds [4]. Carbene insertion reactions are generally thought to occur in a single step without activation [5], but extensive research on silylene insertions has shown that there are important differences in the mechanisms of silylene and carbene insertions.

The insertion reactions of silylene into homonuclear and heteronuclear single bonds have been studied both by examination of the products formed and by kinetic studies of the disappearance of silylene in the presence of trapping agents containing reactive single bonds [6]. Several silylene insertions into N–H, O–H, F–H, P–H, S–H, and Cl–H bonds have been observed [1,4], but only Weber *et al.* have suggested detailed mechanisms based on experimental results. They proposed that insertion of dimethylsilylene into the O–H bond involves a two-step process (eqn. (1)) [7,8]:



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* We dedicate this paper to Professor M.G. Voronkov, the recipient of Doctor Honoris Causa degree from our University, one of whose lasting achievements is to have greatly enhanced the understanding of organosilicon–sulphur chemistry as the field developed rapidly under his influence.

The reaction involves initial interaction of an oxygen lone pair of electrons with the empty 3p orbital of silylene to give a stable zwitterionic-complex, for there is a significant barrier to the rearrangement to give the final product. The barrier was indicated by calculation to be the hydrogen migration step [9], and this was supported by the isotope effect found by Weber and Steele [8]. The calculated rearrangement barrier (22 kcal/mol) was large enough to suggest that the intermediate complexes might be spectroscopically observable [9]. Subsequently, West and his associates [10], in a study of the reactions of silylene with Lewis bases in 3-methylpentane matrices, reported the first spectroscopic observation of a silylene-alcohol complex. Further support for the facile complex formation between dimethylsilylene and compounds containing lone pairs of electrons was provided by kinetic studies involving 266 nm laser flash photolysis [6,11]. Comparisons of the relative reactivities of dimethylsilylene toward methanol *vs.* Et₃SiH as revealed by the product ratio from static photolyses with that obtained by direct kinetic studies involving laser flash photolysis, suggests that the discrepancy can be readily explained in terms of the reversibility formation of the complex between the silylene and the alcohol. Furthermore, the rate constants for ethanol, 2-propanol and tert-butanol with free dimethylsilylene are close to one another [11] and this could be attributed to the fact that the alcohols behave as Lewis bases. Thus, the increasing number of alkyl substituents in the alcohols causes enhancement in their lone-pair donating capability, and this compensates for increase in steric hindrance. That the alcohols do not function as proton donors (Brønsted acids – interacting with filled 3p orbital) is supported by the fact that ethers are as reactive toward the silylenes as the alcohols.

The aim of this study was to examine the insertion of dimethylsilylene, photogenerated from dodecamethylcyclohexasilane, into the S–H bond of trialkoxysilanethiols. To the best of our knowledge there is only one previous example of insertion of silylene into S–H bond, namely the reaction of SiH₂ with H₂S in the gas phase reported by Margrave [12].

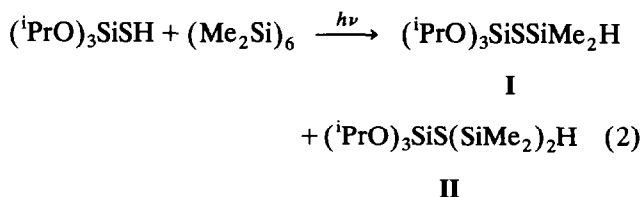
Although, the calculated energy barrier for the hydrogen shift in the complex H₂Si···SH₂ is quite small [9] and silylene–donor adducts with sulphur compounds are known [13], the lower basicity of the sulphur atom compared with oxygen could be a potential disadvantage and lower the case of silylene insertion into the S–H bond. We were able to avoid this problem because of our extensive knowledge of the unusual nature of trialkoxysilanethiols, which we found to be much more acidic [14] than their carbon counterparts.

We thus decided to use these compounds as potential trapping agents for dimethylsilylene.

2. Results and discussion

Dimethylsilylene was generated by UV (254 nm) photolysis of dodecamethylcyclohexasilane, prepared by a published method [15]. The silylene precursor was irradiated with a low-pressure mercury lamp in n-hexane solution under dry argon at room temperature. The photolysis was carried out in the presence of a 10-fold molar excess of selected trialkoxysilanethiols made as previously described [16].

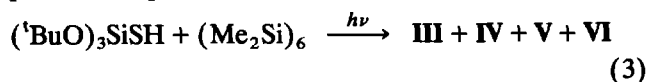
In the case of tri-*i*-propoxysilanethiol, after 2 h irradiation analysis of the photolysate by GLC showed that the concentration of thiol had decreased and two new compounds had been formed. (The silanethiol itself was shown to be inert to prolonged irradiation under the same conditions.) Insertion of dimethylsilylene proceeded smoothly to give, in good yield, two identified products **I** and **II** in the ratio 5:1, as shown in eqn. (2):



The formation of **I** represents the first clear observation of silylene insertion into an S–H bond. The high yield of **II** was rather unexpected; one possibility is that the increasing concentration of **I** provided an efficient new trapping agent, possessing an Si–H bond, and further free silylene formed could insert into this bond. However, having in mind the very complex mechanism of photodegradation of (Me₂Si)₆ we cannot exclude a radical process. The photochemical behaviour of cyclic polysilanes was shown, experimentally [17] and theoretically [18], to be very complex and so photochemical fission of dodecamethylcyclohexasilane may not always act as a clean source of singlet dimethylsilylene. Furthermore, when reaction (2) was carried out with a smaller excess of thiol (3:1) the product ratio was only 3:1. The available results do not justify speculation about the role of Me₂Si fragments in the formation of **II**.

In order to find out how more bulky alkoxy substituents might influence the insertion of Me₂Si: into the S–H bond, we investigated the reaction of dimethylsilylene with tri-*t*-butoxysilanethiol. Under the same conditions the photolysis gave the product expected

from Me_2Si : into S-H insertion, along with three other products (eqn. (3)):



III: $(\text{}^t\text{BuO})_3\text{SiS}(\text{SiMe}_2)\text{H}$;
 IV: $(\text{}^t\text{BuO})_3\text{SiS}(\text{SiMe}_2)_2\text{H}$;
 V: $(\text{}^t\text{BuO})_3\text{SiS}(\text{SiMe}_2)_3\text{H}$;
 VI: $(\text{}^t\text{BuO})_3\text{SiS}(\text{SiMe}_2)_4\text{H}$

The yields of IV and VI were very low, but an unexpectedly high yield of V was detected (Table 1). Thus, if this type of product is formed in high yield, it must be due either to the suggested formation of $(\text{Me}_2\text{Si})_n$ fragments during photolysis of $(\text{Me}_2\text{Si})_6$ or to secondary reactions of silylene initially complexed with alkoxy-silanethiols containing oxygen lone pairs of electrons. Complexes of this nature are known to be far less reactive than the "free" silylene but this route cannot be ignored. With a decreasing ratio of thiol to silylene precursor the molar ratio of products III and V decreased.

The yields of the major products were similar for reactions (2) and (3) (Table 1), and we therefore decided to carry out the competition experiment under fixed photolysis conditions in the presence of an equimolar mixture of tri-*i*-propoxysilanethiol and tri-*t*-butoxysilanethiol. We found the relative rate constant for insertion of Me_2Si : into these two thiols to be 1.7. This indicates that bulky alkoxy groups attached to silicon atom do not have much effect on the reactivity of alkoxy-silanethiols toward silylene insertion. The high reactivity of alkoxy-silanethiols toward photogenerated Me_2Si : prompted us to investigate the behaviour of their carbon analogues and we chose thiophenol, *t*-butanethiol, and *n*-hexanethiol as model mercaptans. The photolysis was carried out under similar conditions in the presence of a 10-fold molar excess of the mercaptan. Analysis of the photolysates by GLC and IR spectroscopy showed that no products of insertion of Me_2Si : into the S-H bond were formed. However, the irradiation of the mixture resulted in the gradual disappearance of mercaptans and formation of the corresponding disulphides in significant amounts. It is un-

TABLE 1. Total yields of products of insertion of Me_2Si : into R-SH bonds

R	Molar ratio R-SH:(Me_2Si) ₆	Yield (%)	Molar ratio of products
$(\text{}^t\text{BuO})_3\text{Si-}$	10:1	76	III/V = 5
	3:1	41	III/V = 3
$(\text{}^i\text{PrO})_3\text{Si-}$	10:1	82	I/II = 4
	3:1	45	I/II = 1

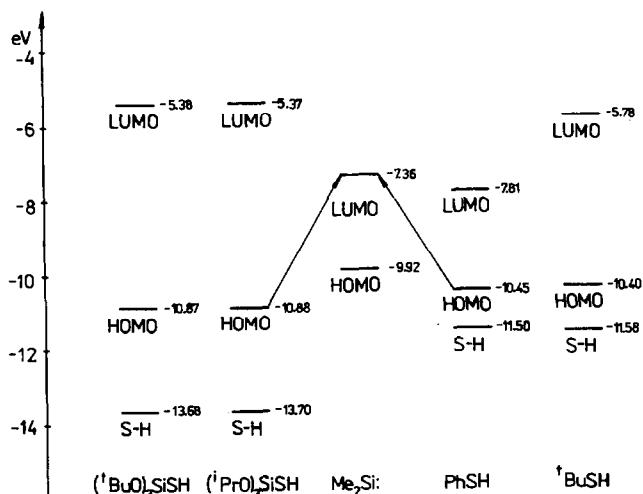


Fig. 1. Energy level diagram for trialkoxysilanethiols and mercaptans.

likely that the occurrence of photodecomposition of the organic thiols is the only reason for the absence of insertion of Me_2Si : into the S-H bond, and the lower acidity of mercaptans than of alkoxy-silanethiols, must be regarded as the likely cause.

In order to throw light on the differences in the reactivity of mercaptans and alkoxy-silanethiols we decided to employ the EHT method [19] for calculation of orbital interaction diagram for Me_2Si : and thiols. The calculated energy-levels (Fig. 1) indicate that interaction between the vacant p (LUMO) orbital of silylene and σ electrons of the S-H bond in thiols is clearly unfavourable.

On the other hand, the energy diagram for interaction of the LUMO of silylene and the HOMO of the thiols suggests that formation of an initial complex between the silylene and sulphur base is feasible. The HOMO electrons of $(\text{}^i\text{PrO})_3\text{SiSH}$ are localized in the sulphur p-orbital lying nearly perpendicular to the Si-S-H plane, while in the case of $(\text{}^t\text{BuO})_3\text{SiSH}$ the HOMO orbital seems to be more distorted due to nonbonding interactions with more bulky alkoxy substituents. The LUMO of Me_2Si :, perpendicular to the plane containing the other two orbitals on silicon, approaches the HOMO of silanethiol from the side where the overlap between the interacting orbitals is greatest.

The suggested geometry is in accord with that proposed by Rosenfield and Dunitz [20] for reactions of electrophiles with divalent sulphur.

Thus we believe that insertion of Me_2Si : into the S-H bond of a trialkoxysilanethiol involves initial formation of an ylid (donor-acceptor complex) followed

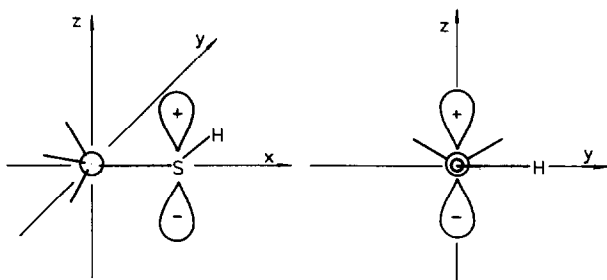
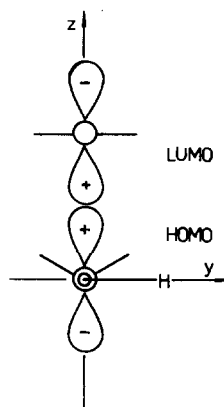
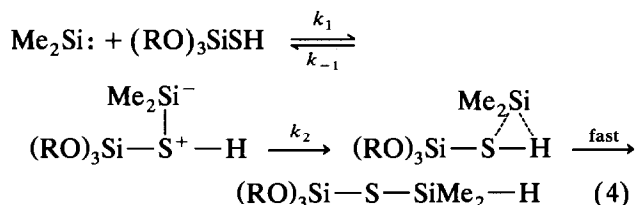
Fig. 2. HOMO orbital orientation for tri-*i*-propoxysilanethiol.

Fig. 3. Electronic interactions during silylene (LUMO) insertion into the S-H bond (HOMO).

by a proton shift *via* an asymmetrical high-energy transition state:



Under the conditions used, involving an excess of the thiol, the steady state treatment leads to eqn. (1):

$$\frac{d[\text{Product}]}{dt} \cong \frac{k_2 \cdot k_1}{k_1 + k_2} \cdot [:\text{SiMe}_2] \cdot [-\text{SH}] \cong k_2 \cdot [:\text{SiMe}_2] \cdot [-\text{SH}] \quad (1)$$

where:

$$\frac{d[\text{Product}]}{dt} = k_2 \cdot [\text{Ylid}]$$

$$\frac{d[\text{Ylid}]}{dt} = 0$$

$$k_1 \cdot [:\text{SiMe}_2] \cdot [-\text{SH}] = k_{-1} \cdot [\text{Ylid}] + k_2 \cdot [\text{Ylid}]$$

$$\frac{d[\text{Product}]}{dt} = \frac{k_2 \cdot k_1}{k_1 + k_2} \cdot [:\text{SiMe}_2] \cdot [-\text{SH}]$$

and

$$k_1 \approx k_{-1} \gg k_2$$

The nature and case of the formation of the sulphur-silylene complex [10,13] supported by the energy-level diagram presented above, seem now well understood. The difference between the subsequent product formation for alkoxy-silanethiols and mercaptans can be explained in terms of the importance of the S-H bond acidity. Thus, if the rate determining step of the insertion is the 1,2-proton transfer, the acidity of silanethiols will play a crucial role. In order to confirm this, the EHT and *ab initio* methods [19] were employed to calculate the deprotonation energies of mercaptans and silanethiols.

The calculated results lend strong support to the proposed mechanism of the insertion Me_2Si into the S-H bond, and show choice of the highly acidic trialkoxysilanethiols as potential trapping agents was justified.

In order to confirm the results obtained for silanethiols, we carried out competition experiments involving photolysis of $(\text{Me}_2\text{Si})_6$ in the presence of $(^i\text{PrO})_3\text{SiSH}$ and Et_3SiH . Using a 10-fold excess of both reagents we found the relative rates of insertion of dimethylsilylene into Et_3SiH and $(^i\text{PrO})_3\text{SiH}$ to be 1.2 ± 0.3 (average of three measurements). The silanes are widely recognized as useful and efficient reactive traps for the silylene, but the rather similar reactivity of trialkoxysilanethiols was rather unexpected. Furthermore, because the silanes are as good trapping agents as alcohols in nonpolar solvents [6,8], and complexation energies of silylene-Lewis base for H_2O and H_2S are close one to another, the high yield of the insertion product from trialkoxysilanethiols must be closely related to the S-H lability of the proton. Finally, we note that the high yield of products of insertion of more than one Me_2Si unit suggests that trialkoxysilanethiols may also be efficient traps for polysilane fragments formed during photolysis of $(\text{Me}_2\text{Si})_6$. Although no unambiguous evidence for this type of insertion has been reported in the light of our results and the

TABLE 2. The calculated deprotonation energies (ΔE) of mercaptans and silanethiols

Compound	ΔE (kJ mol ⁻¹)
$(^i\text{BuO})_3\text{SiSH}$	649.4
$(^i\text{PrO})_3\text{SiSH}$	648.9
$^t\text{BuSH}$	709.2
PhSH	707.9

knowledge of polysilane photodegradation, further study seems justified.

In conclusion, we have shown that owing to the high acidity of the S–H bond, trialkoxysilanethiols are effective trapping agents for photogenerated dimethylsilylene in solution.

3. Experimental details

Dodecamethylcyclohexasilane was prepared by a previously described method [15] as were the trialkoxysilanethiols [14]. Thiophenol, t-butanethiol, and n-hexanethiol (Merck) were distilled under dry argon before use. n-Hexane (HPLC grade, UV cut off at 204 nm) was distilled over Na. Argon was deoxygenated over Cu and dried over CaCl₂ and silica gel.

The static photolysis of (Me₂Si)₆ was carried out in a quartz tube equipped with a low-pressure mercury lamp TNN 15/32. The solutions were degassed by three freeze-pump-thaw cycles and then sealed under dry argon.

GLC analysis was carried out on a Willy Giede GCHF 18.3 instrument with flame ionization detector employing 1 m × 4 mm (i.d.) stainless steel column with 12.5% SE-30 on Chromosorb W/NAW (80–100 mesh) packing. n-Dodecane and n-decane were used as internal standards.

Linked GLC-MS was performed on a Finnigan-MAT 8230 mass spectrometer operating at ionizing energy of 20 eV and 70 eV. ¹H-NMR spectra were recorded on a Varian 360A spectrometer, and IR spectra on a Carl Zeiss Jena Specord 75 IR; values are reported in cm⁻¹ referenced to polystyrene. Kugelrohr distillation was employed for all vacuum separations.

3.1. Photolysis of dodecamethylcyclohexasilane in the presence of tri-*i*-propoxysilanethiol

Into the quartz photolysis tube equipped with a stopcock was introduced a solution of 0.554 g (1.59 mmol) of dodecamethylcyclohexasilane and 3.78 g (15.9 mmol) tri-*i*-propoxysilanethiol in 80 cm³ of n-hexane. The tube was degassed and filled with dry argon and the sample irradiated for 2 h with a mercury lamp. The mixture was analysed by GLC. Then the solvent was evaporated *in vacuo*, and the products were separated by Kugelrohr distillation. Decomposition of products was observed and attempts to prepare analytical samples failed. The products were analysed by GLC-MS and two products were identified: (a) (¹PrO)₃SiSiMe₂H (I): MS *m/e* (relative intensity) 296 (M⁺, 1), 295 (1), 281 (2), 253 (2), 205 (6), 163 (11), 121 (51); MS FD 296 (M⁺), (b) (¹PrO)₃SiS(SiMe₂)₂H (II): MS *m/e* 354 (M⁺, 1), 353 (1), 339 (3), 205 (7), 163 (14); MS FD 354 (M⁺). The products were in a 4:1 ratio.

When the ratio of (¹PrO)₃SiSH to (Me₂Si)₆ was lowered to 3:1, the product ratio I:II was 1:1.

3.2. Photolysis of dodecamethylcyclohexasilane in the presence of tri-*t*-butoxysilanethiol

A solution of 0.554 g (1.59 mmol) of dodecamethylcyclohexasilane and 4.45 g (15.9 mmol) of tri-*t*-butoxysilanethiol in 80 cm³ of n-hexane was photolysed for 2 h. The mixture was analysed by GLC and concentrated *in vacuo*, and the products were isolated by Kugelrohr distillation. Four products were found. (¹BuO)₃SiSiMe₂H (III): ¹H-NMR (C₆D₆) σ 0.56 (d, 6H), 1.56 (s, 27H), 5.06 (m, 1H); IR ν (Si–H) 2133 cm⁻¹; MS *m/e* (relative intensity) 338 (M⁺, 1), 247 (3), 225 (11), 169 (100); MS FD 338 (M⁺). (¹BuO)₃SiS(SiMe₂)₂H (IV): MS FD 396 (M⁺); (¹BuO)₃SiS(SiMe)₃H (V): MS FD 454 (M⁺); (¹BuO)₃SiS(SiMe)₄H (VI): MS FD 512 (M⁺). The total yield of products was *ca.* 76%; products III and V were present in a ratio of 5:1.

When the substrate ratio was 1:3, the ratio of products III and V was 3:1.

3.3. Competitive photolysis of dodecamethylcyclohexasilane with tri-*i*-propoxysilanethiol and tri-*t*-butoxysilanethiol

A solution of dodecamethylcyclohexasilane 0.558 g (1.60 mmol), tri-*i*-propoxysilanethiol 1.141 g (4.79 mmol), tri-*t*-butoxysilanethiol 1.355 g (4.84 mmol) in n-hexane (80 cm³) was photolysed for 2 h under the conditions described above. GLC analysis revealed that I and III were formed in a 1.7:1 ratio.

3.4. Photolysis of dodecamethylcyclohexasilane in the presence of an alkyl thiol or thiophenol

In separate experiments a solution in n-hexane (80 cm³) of dodecamethylcyclohexasilane 0.557 g (1.60 mmol) and t-butanethiol (15.9 mmol), n-hexanethiol (15.9 mmol), or thiophenol (15.9 mmol) was photolysed at 20°C for 2 h. Subsequent GLC analysis showed that the corresponding disulphides had been formed, and no other products were found. IR spectroscopy showed that no Si–H bonds were present.

3.5. Competition photolysis of dodecamethylcyclohexasilane with tri-*i*-propoxysilanethiol and triethylsilane

A solution of dodecamethylcyclohexasilane 0.139 (0.4 mmol), tri-*i*-propoxysilanethiol 0.995 g (4.18 mmol), triethylsilane 0.484 g (4.17 mmol) in n-hexane (20 cm³) was irradiated as above for 2 h. The yield of insertion products was then determined by GLC analysis. GLC-MS analysis was also carried out to confirm that the products were identical with authentic samples. The analysis indicated the formation of I and triethyldimethyldisilane in a 1.2:1 ratio.

Acknowledgment

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