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Contributions to the chemistry of silicon–sulphur compounds

LI *. The insertion of sulphur into Si–Si bonds of permethylpolysilanes

B. Becker and W. Wojnowski
Institute of Inorganic Chemistry and Technology, Technical University, 80-952 Gdańsk (Poland)

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Abstract

The cyclic hexasilane $(Me_2Si)_6$ (**1**) and the linear polymeric $(Me_2Si)_x$ react with elemental sulphur at 190–200 °C much slowly than $(Me_2Si)_5$. Reaction of **1** gives initially the insertion product $(Me_2Si)_6S$, and hence $(Me_2Si)_5S$, $(Me_2Si)_4S_2$, and finally hexamethyl-1,3-dithiacyclopentasilane, $(Me_2SiS)_3$, and $(Me_2SiS)_2$. These last three products are also formed in the reaction of sulphur with the linear polymer. The mechanism of sulphur insertion into the polysilane molecule is discussed; and it is suggested that the polysilane acts as a nucleophile so that its reactivity is related principally to its electron-donating ability. A pathway involving several sulphur insertions and dimethylsilanethione eliminations is proposed.

The reaction provides a convenient method for preparation of the cyclic species $(Me_2SiS)_n$ with $n = 2$ or 3.

Introduction

Some years ago one of us briefly reported the insertions of sulphur and selenium into the Si–Si bond [2] of a cyclic polysilane, decamethylcyclopentasilane, and showed them to give the new six-membered ring species $(Me_2Si)_5S$ and $(Me_2Si)_5Se$, respectively. Subsequently the insertion of sulphur into octamethylcyclotetrasilane [3], 2,2,3,3,4,4,5,5-octamethyl-1-thiacyclopentasilane [4], octaethylcyclotetrasilane [5], decaethylcyclopentasilane [5], and hexa-t-butylcyclotrisilane [6] were described. Recently a synthesis of disilathiiranes from disilenes and sulphur [7] was reported.

Lower cyclic polysilanes $(R_2Si)_n$ with $n = 3–5$ are usually regarded as strained ring systems, and the degree of strain is often used to account for the increasing

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[*] For part L see ref. 1.

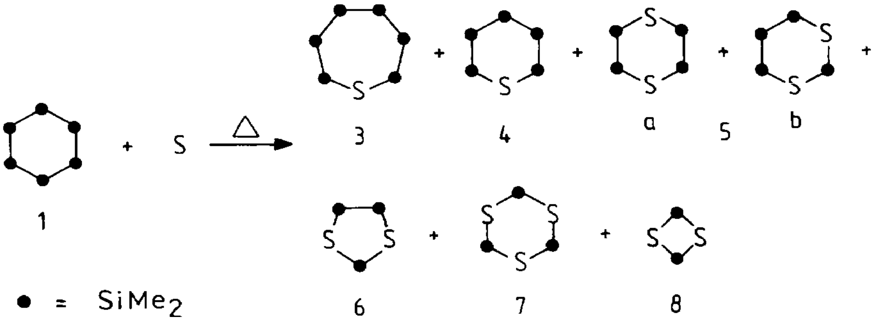
reactivity of these compounds with decreasing ring size [2–8]. The concept seems to be valid also for lower cyclic disilanes; e.g. octamethyl-1,2-disilacyclobutane undergoes sulphur insertion at 60 °C [9] whereas with hexamethyldisilane a temperature of 320 °C is required [10].

The conditions used previously [2] for the reaction of sulphur with 1 : 1 mixture of $(Me_2Si)_5$ and $(Me_2Si)_6$ favoured the formation of $(Me_2Si)_5S$. No attempts have been made to check if indeed the "ring strain" is indispensable for the sulphur reaction with polysilanes.

We report here on the reaction of sulphur with dodecamethylcyclohexasilane $(Me_2Si)_6$ and the linear polymeric permethylpolysilane $(Me_2Si)_x$ which, although unstrained, reacts at a temperature as low as 190 °C.

Results

In an earlier study [2], when a solution containing 1 mmol of dodecamethylcyclohexasilane, $(Me_2Si)_6$ (**1**) and 1 mmol decamethylcyclopentasilane, $(Me_2Si)_5$ (**2**), in decalin was refluxed for 6 h with 1.1 equivalents of sulphur, **2** reacted quantitatively, to give $(Me_2Si)_5S$, and **1** did not react at all. In the experiments described below, reaction of **1** was carried out with an excess of S at 190–350 °C in the absence of solvent. Under these conditions **1** was found to react with sulphur even at 190 °C, although at this temperature the reaction was slow (see Scheme 1).



Scheme 1

Products **4**, **7** and **8** were identified gas chromatographically by comparison of their retention times with those of authentic samples and by subsequent GC/MS analysis. Product **6** was isolated pure and identified by its NMR and MS spectra, which agreed well with those reported previously [11,12]. Products **5a,b** and **3** were identified from their GC/MS spectra. In the case of **5** the molecular ion *m/e* 296 was readily detected, but the observation of the fragmentation pattern different from that reported for octamethyl-1,4-dithiacyclohexasilane **5a** [4] suggests that two isomeric compounds, **5a** and octamethyl-1,3-dithiacyclohexasilane (**5b**), are present. In the case of dodecamethyl-1-thiacycloheptasilane (**3**) which is a new compound, the fragmentation was similar to that for **4**, with the molecular ion (*m/e* 380) showing the expected isotope pattern.

The reaction conditions and the yields of products are summarized in Table 1.

Product **3**, the initial product of sulphur insertion into the cyclosilane ring, was found in only small amounts. Only traces of **4** and **5** were detected.

Table 1

The reaction of $(\mathrm{Me_2Si})_6$ (**1**) with sulphur. Conditions and yields of products

Run	Temp. (°C)	Time (h)	S/**1** [a] ratio	Products (%) [b]				Unchanged **1** (%) [b]
				3	**6**	**7**	**8**	
1	350	14	6	–	–	88	12	–
2	300	14	6	–	–	88	12	–
3			3	–	19	34	4	43
4	250	10	6	–	11	71	13	5
5			3	5	20	32	–	43
6 [c]	200	10	6	5	22	22	4	46
7 [c]			3	5	20	17	1	57
8 [c]	190	10	6	3	9	5	1	82
9 [c]			3	2	4	2	1	91

[a] Sulphur in g-atom, **1** in mol. [b] The yields are derived from the GLC peak areas and are based on the number of equivalents of available $\mathrm{Me_2Si}$ groups. [c] Traces of **4** and **5a,b** were also detected by GLC.

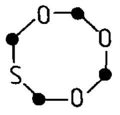
The reaction rate was low at 190 °C but markedly faster at 200 °C. The amount of sulphur used did not appreciably influence the overall reaction course. Even at 300 °C some **1** remained even when the amount of sulphur used was three times as large as was necessary for insertion of one sulphur atom into the $\mathrm{Si_6}$ ring. Three main products, **6**, **7** and **8** were formed. Two of them, **7** and **8**, are known to be in rapid thermal equilibrium [13].

When **6** was heated with sulphur for 5 h at 250 °C 28% of **7** was formed, (when **6** was heated alone under these conditions it was recovered unchanged).

When **1** was heated with sulphur in presence of a large excess of hexamethyltrisiloxane (**9**), some unchanged **1** remained along with the products shown in eq. 1.

$$\begin{array}{l} \mathbf{1} + 6\,\mathrm{S} + 20\,\mathbf{9} \xrightarrow[14\ \mathrm{h}]{200\,^{\circ}\mathrm{C}} \mathbf{3}\ (11\%) + \mathbf{4}\ (1\%) + \mathbf{5}\ (5\%) + \\ \qquad\qquad \mathbf{6}\ (29\%) + \mathbf{7}\ (3\%) + \mathbf{8}\ (4\%) + \mathbf{10}\ (17\%) \end{array} \tag{1}$$

Compound **11**, which would be performed by dimethylsilylene insertion into the Si–O bond of **9**, was not observed.



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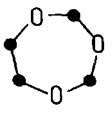

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The outcome of reactions of **1** with sulphur in decalin as a solvent did not significantly differ from those in absence of solvent, although the yields, especially of **6** and **7**, were greater (see Table 1, run 8) (eq. 2):

$$\begin{array}{l} \mathbf{1} + \mathrm{S} \xrightarrow[6.5\ \mathrm{h}]{190\,^{\circ}\mathrm{C}} \mathbf{3}\ (6\%) + \mathbf{4,5}\ (\text{traces}) + \mathbf{6}\ (8\%) + \mathbf{7}\ (3\%) \\ \qquad\qquad\qquad {\scriptstyle +5\,\mathrm{S}}\Big\downarrow{\scriptstyle 7\,\mathrm{h},\,190\,^{\circ}\mathrm{C}} \\ \qquad \mathbf{3}\ (4\%) + \mathbf{4,5}\ (\text{traces}) + \mathbf{6}\ (34\%) + \mathbf{7}\ (45\%) \end{array} \tag{2}$$

When we repeated the experiment described in ref. 2, in which an equimolar mixture of **1** and $(\mathrm{Me_2Si})_5$ (**2**) was treated with 1.1 equivalent of sulphur, we found that after 6 h at 190 °C, when no **2** remained, in addition to **4** small quantities (combined overall yield less than 5%) of **5**, **6** and **7** were present. When the reaction was continued for a further 6 h the concentration of **6** increased slightly at the expense of **4**.

A mixture of **1** and **2** (0.8/1 molar ratio) was then heated with 1, 2.5, and 5 equivalents (based on **2**) of sulphur at 190 °C for 6 h without solvent. The results are summarized in eq. 3. GC analysis showed that the amount of **1** remained constant in all cases.

$$\mathbf{2} \left\{ \begin{array}{l} \xrightarrow{1\ \mathrm{S}} \mathbf{4}\ (6\%) + \mathbf{6}\ (12\%) + \mathbf{7}\ (5\%) \\ \xrightarrow{2.5\ \mathrm{S}} \mathbf{4}\ (22\%) + \mathbf{6}\ (46\%) + \mathbf{7}\ (12\%) + \mathbf{8}\ (3\%) \\ \xrightarrow{5\ \mathrm{S}} \mathbf{4}\ (10\%) + \mathbf{6}\ (54\%) + \mathbf{7}\ (27\%) + \mathbf{8}\ (8\%) \end{array} \right. \qquad (3)$$

One run involving use of one equivalent of S was stopped after 1.5 h. In addition to unchanged **1** and residual **2**, the compounds **4** (8%), **5** (4%), and **6** (10%) were present. No **7** was detected.

No study of the reaction of elemental sulphur with linear polysilanes has previously been reported. We used the linear, insoluble polymer $(Me_2Si)_x$ formed as a by-product during the synthesis of cyclic polysilanes [14,15]. When a mixture of this polymer and sulphur ($Me_2Si/S = 1/1$) was heated at 250 °C for 9 h the only detectable products were the cyclic species **7** and **8**, the combined yield being quantitative. The polymer remained practically unchanged when exposed on its own to similar conditions.

The polymer was then treated with sulphur at 200 °C for 10 h; half of the polymer remained and only two products were found, **7** (38%) and, unexpectedly, **6** (12%).

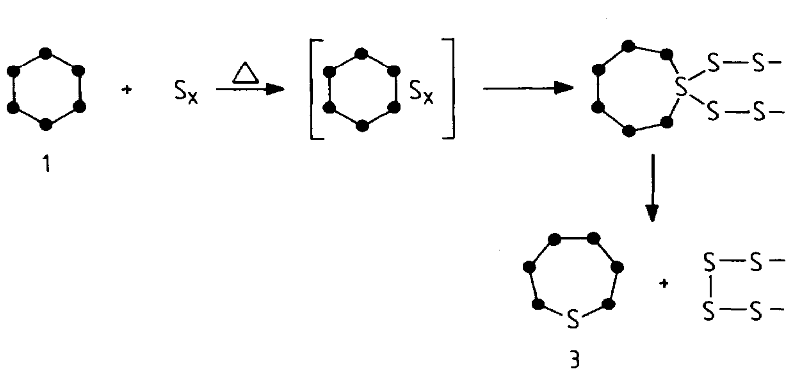
Discussion

The results show that $(Me_2Si)_6$ reacts, though more slowly, with sulphur under conditions (190 °C) in which $(Me_2Si)_5$ (**2**) was known to react [2]. The reactivities of $(Me_2Si)_6$ and the polymeric $(Me_2Si)_x$ are comparable. The much greater reactivities of $(Me_2Si)_5$ (**2**) and $(Me_2Si)_4$ (**12**) [3] may arise from increased ring strain [2–4].

The four-membered ring of octamethyl-1,2-disilacyclobutane, although it has only one Si–Si bond, readily undergoes sulphur insertion at 60 °C [9], while $Me_3SiSiMe_3$ [16] and $Et_3SiSiEt_3$ [17] do not react with sulphur even at 200–215 °C. It is evident that three-, four- and five-membered sila-cycles are very reactive, but ring strain is not essential for reaction, since the six-membered **1** and the linear dimethylsilylene polymer are unstrained but also react.

The σ-conjugation in silicon chains [18,19] results in a higher electron-donating ability (with a low ionization potential, near or below 8 eV [20,21]). The oxidation potentials of a series of peralkylcyclopolysilanes $(R^1R^2Si)_n$ ($n = 3$–7) [22] showed that the electron-donating ability increases with decreasing ring size. For linear permethylpolysilanes the electron-donating ability increases with the increasing chain length [23].

Polysilanes [24–27], and also 1,2-disilacycloalkanes [28], form charge transfer (CT) complexes with tetracyanoethylene (TCNE). The ionization potential (*IP*) of tetramethyl-1,2-disilacyclopentane, as estimated from CT spectra [25,28], is about



Scheme 2

8.3 eV, and for tetramethyl-1,2-disilacyclobutane even lower value is expected. The *IP* of hexamethyldisilane is significantly higher, 8.69 eV [20]. We thus relate the reactivity of polysilanes to the electron-donating ability of the molecule. The reactivity may also be increased when the reaction results in formation of a new species with more favourable geometry (e.g. ring expansion of small cycles).

We assume that the first step of the reaction between polysilane and sulphur is the formation of a CT complex (polysilane as a donor) followed by an insertion of one sulphur atom with formation of a sulfurane-like transition state, which after rearrangement at the central sulphur atom dissociates to the thiacyclopolysilane and another sulphur molecule (see Scheme 2).This mechanism resembles that proposed for peracid oxidation of di- and poly-silanes [29]. It is relevant to note that Steudel [30,31] recently suggested hypervalent sulphur species as intermediates in the interconversion reactions in/and between sulphur and polysulphides.

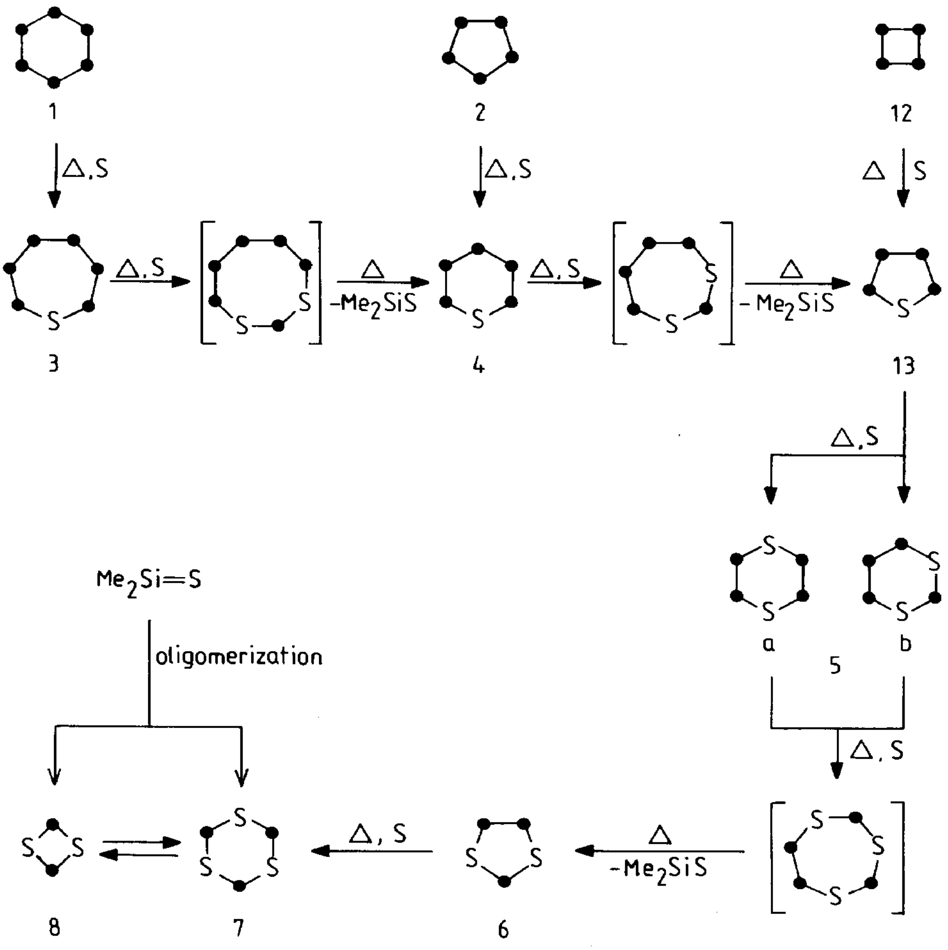
The insertion of sulphur into the Si–Si bond is sensitive to steric factors. Thus $(Me_2Si)_5$ [2] is more reactive than $(Et_2Si)_5$ [5], and the reactivities of $(t\text{-}Bu_2Si)_3$ [6] and $(Me_2Si)_4$ [3] are comparable.

The reactions of $(Me_2Si)_6$ with sulphur in no case gave high yields of **3** and usually only traces of **4** and **5** were detected. From the products **1** seems to be less reactive toward sulphur than **3**, **4** and **5**. Only **6** shows similar reactivity, and it can be obtained in higher yield. The presence of sulphur does not interrupt the σ-bond conjugation in silicon–sulphur backbone chains [27], and this should also be the case for silicon–sulphur cycles. Indeed **6** (which is completely unstrained according to force field (MM2) calculations) is more reactive than hexamethyldisilane, although less reactive than the cyclopentasilane **2**.

Taking account of our results and those reported previously for **2** [2] and **12** [3,4], we suggest the sequence shown in Scheme 3 for the reactions of cyclic permethylpolysilanes with sulphur.

The pathway depicted predicts that **1** and the smaller-ring cyclic polysilanes **2** and **12** should all give the same final products **6**, **7** and **8**. (We showed that **1** and **2** do, indeed, give these products.)

Hengge and Schuster [4] tried to prepare **5a** directly from **12** and sulphur but obtained mixtures. They also tried use of octamethylthiacyclopentasilane (**13**), but concluded that at higher temperature and with longer reaction time **5a** probably isomerizes to **5b**, and **7** and **8** are formed. The results obtained by Carlson and West

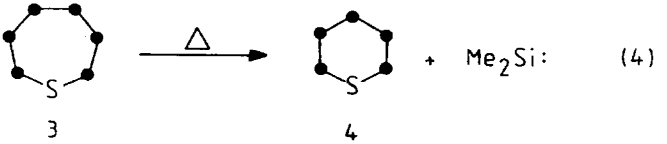


Scheme 3

[5] for reactions involving octaethylcyclotetrasilane are in good agreement with Scheme 3.

The insertion of sulphur into **1**, **2**, **12**, **13** and **6**, which gives **3**, **4**, **13**, **5** and **7**, respectively, is well documented, but the observed stepwise degradation requires additional discussion.

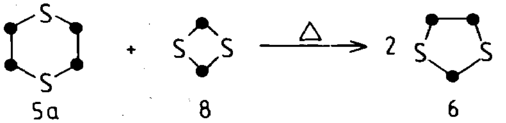
1. Thermally induced elimination of silylene (for example from **3**, eq. 4) seems



unlikely, since we did not observe even traces of the expected Me_2Si-insertion product **11** when hexamethylcyclotrisiloxane (**9**) was present in great excess as a trapping agent. More significantly, the yields of **4**, **5**, **6**, and especially **3**, were not decreased compared with those in the experiment in absence of **9** (Table 1, run 6; eq. 1), although the yield of **7** was significantly reduced and the silanethione insertion product **10** was formed.

Compound **6** was found to be thermally stable, but for other thiasilacycles thermal elimination of silylene, although unlikely (**3**, **4**, **5** and **6** did not decompose during routine GC analyses even though the temperature of injection chamber was 250–280 ° C), cannot be excluded. Dimethylsilylene can react with sulphur to give silanethione much more rapidly than it inserts into the Si–O bond of **9** [32] or the Si–S bond of other thiasilacycle such as **3** [33]. Recently a fast reaction of germylene with elemental sulphur at −10 ° C was reported [34].

2. The formation of **6** could be explained in terms of a redistribution between the cyclic species **5a** and **8** (eq. 5). Similar redistribution between 1,1,2,2-tetramethyl-


5a 8 6

(5)

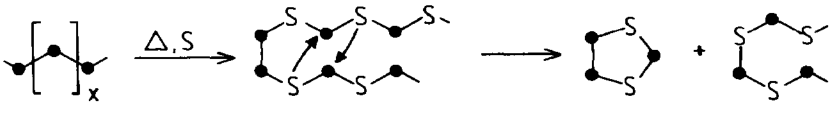
1,2-disila-3,6-dithiacyclohexane and **8** was found to proceed rapidly at 215 ° C, giving **6** and 1,1-dimethyl-1-sila-2,5-dithiacyclopentane [11].

Compound **5a** did not react with **7** or **8** during several days at 70 ° C, but in the presence of pyridine as catalyst product **6** was formed in 75% yield at 70 ° C after 3 d [12]. This route, does not, however, explain either the formation of **4** from **1** (or **5** from **1** and **2**) nor the observed [5] accumulation of the ethyl analogue of **5a** rather than the anologue of **5b** in the reaction of $(Et_2Si)_4$ with elemental sulphur.

3. Insertion of sulphur into thiacyclopolysilane, followed by thermally-induced ring contraction to the more stable cycle and silanethione, provides the simplest explanation. Cyclic thiapolysilanes, of the type suggested as the reaction intermediate are unknown, but they cannot be excluded from consideration, at least as short-lived species.

The product of $Me_2Si{=}S$ insertion, **10**, was formed in the experiment with **9** as trapping agent (eq. 1). This result does not unambiguously confirm the formation of silanethione as a key intermediate, since it is known that **7** alone can react with **9** to give **10** [35].

The suggestion that **4**, **6** and **13** can be formed as a result of ring contraction of their precursors (Scheme 3) with simultaneous elimination of silanethione is supported by fact that the linear polymeric $(Me_2Si)_x$ when heated with sulphur also gave **6**, which might be formed by ring closure of an appropriate silicon–sulphur chain containing some intact Si–Si bonds, as in Scheme 4:



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Scheme 4

Recently Sakurai et al. [36] reported on the photochemical extrusion of $Me_2Si{=}S$ from dibenzo-1,3-disila-2-thiacycloheptadiene.

It is known that cyclic polysilanes are oxidized in stepwise fashion by perbenzoic acids [37–39], finally giving products of oxygen insertion into all of the Si–Si bonds. Si–Si bonds adjacent to oxygen are more susceptible to further oxidation than others. Peracid oxidations proceed well at ambient temperature, but Alnaimi and

Weber [38] noted that dodecamethyl-pentaoxa-hexasilacycloundecane undergoes a facile thermal elimination of hexamethylcyclotrisiloxane (**9**) with formation of hexamethyl-1,3-dioxa-2,4,5-trisilacyclopentane, which is an oxa-analogue of **6**.

The reaction of polysilane with sulphur may be of use in synthesis. Permethylpolysilanes can serve as convenient sources of cyclic disilthianes **7** and **8**; for this use can be made of the mixture of various dimethylsilyl species obtained by coupling of dimethyldichlorosilane with alkali metals [15,18]. After the reaction with stoichiometric quantity of sulphur (based on Me_2Si) at about 250 °C, the final result is always the same, that is, only disilthianes **7** and **8** are formed.

In comparison with the standard route involving reaction of Me_2SiCl_2 with hydrogen sulphide [40,41], the method proposed above has some important advantages:

1. Some $SiMe_2$-species (e.g. polymer) are now commercially available and are easier to handle than Me_2SiCl_2.
2. The use of hazardous H_2S is avoided.
3. The reaction is very easy to perform, and gives very high yields.

Since elemental silicon can be regarded as a three-dimensional silicon-substituted polysilane, the insertion of sulphur into the Si–Si bond has been known for a long time, since Berzelius [42] synthesized silicon disulphide from the elements in 1824.

Experimental

Dodecamethylcyclohexasilane (**1**), decamethylcyclopentasilane (**2**), and dimethylsilylene polymer were obtained as described previously [14]. The crude polymer was breed from soluble contaminats by extraction with hexane in a Soxhlet apparatus.

Decalin, benzene, and hexane were dried over Na.

Gas-chromatographic analyses (FID) were performed on 1 m × 4 mm SE-30 column (10% on Chromosorb W NAW, 80–100 mesh) with Ar as a flow gas. The temperature was programmed in the range 100–250 °C (8 °C/min). Yields were based on the peak areas.

Linked GC/Mass spectroscopy (70 eV) was carried out with a Varian 711 Mat spectrometer. A 1.5 m × 3 mm OV-1 (3% on Supelcoport, 80–100 mesh) column was used.

NMR spectra were recorded on Varian 360A spectrometer (60 MHz) in CCl_4 with TMS as internal standard.

The reactions were usually performed on a 1 mmol scale of **1** (or 1 mmol of **2** mixed with 0.8 mmol of **1**) in evacuated sealed glass ampoules ($V \approx 2$ cm^3), which were kept in an electric oven (±1 °C). Light was excluded. The reactions were stopped by cooling, and the contents of ampoules dissolved in benzene then analysed by chromatography.

Reactions in decalin (10 cm^3) were performed on the same scale in a 25 ml flask equipped with a magnetic stirrer, a condenser, and an argon inlet.

Some experiments with **1** were carried out on larger scale, as described below.

A mixture of 8.7 g (25 mmol) of **1** and 4.8 g (150 mg-atom) of sulphur was placed in a 15 cm^3 glass ampoule which was then evacuated and sealed and kept for 11 h at 200 °C. The tube was cooled and opened, and the contents dissolved in 15 cm^3 of hexane, and 2.7 g (84.5 mg-atom) of residual sulphur was filtered off. The filtrate was examined by GLC. In addition to unchanged **1**, the following products were detected: **3** (7%), **4** (2%), **5** (1%), **6** (16%), **7** (19%) and **8** (1%). The hexane was then evaporated from the solution and the residue kept for one day at 0 ° C. About 4 g (11.5 mmol) of unreacted **1** separated. The liquid residue was twice distilled, and 1.2 g (10%) of **6** was obtained. B.p. 110–113 ° C/15 mmHg; ^{1}H NMR (δ) 0.45 (s,12H), 0.60 (s,6H).

The products **4**, **7** and **8** were identified by GLC comparison with authentic samples [2,40,41]. For **3**, **4**, **5**, **6** and **7** by GC/MS the following ions were observed [m/e (abundance)]:

3: 380(6) [M], 365(7) [$M-\mathrm{Me}$], 321(2) [$M-\mathrm{Me_2SiH}$], 307(3) [$\mathrm{Me_9Si_5S}$], 263(2) [$M-\mathrm{Me_2SiH}-\mathrm{Me_2Si}$], 249(6) [$\mathrm{Me_7Si_4S}$], 191(3) [$\mathrm{Me_5Si_3S}$], 174(37) [$\mathrm{Me_6Si_3}$], 159(9) [$\mathrm{Me_5Si_3}$], 131(11) [$\mathrm{Me_5Si_2}$], 129(7) [$\mathrm{(SiCH_2)_2Me_3}$], 116(54) [$\mathrm{Me_4Si_2}$], 101(10) [$\mathrm{Me_3Si_2}$], 99(7) [$\mathrm{(SiCH_2)_2Me}$], 73(100) [$\mathrm{Me_3Si}$].

4: 322(7) [M], 307(8) [$M-\mathrm{Me{=}Me_9Si_5S}$], 263(9) [$M-\mathrm{Me_2SiH}$], 249(5) [$\mathrm{Me_7Si_4S}$], 191(6) [$\mathrm{Me_5Si_3S}$], 174(5) [$\mathrm{Me_6Si_3}$], 159(4) [$\mathrm{Me_5Si_3}$], 131(11) [$\mathrm{Me_5Si_2}$], 129(5) [$\mathrm{(SiCH_2)_2Me_3}$], 116(69) [$\mathrm{Me_4Si_2}$], 101(8) [$\mathrm{Me_3Si_2}$], 99(6) [$\mathrm{(SiCH_2)_2Me}$], 73(100) [$\mathrm{Me_3Si}$].

5a,b: 296(6) [M], 281(4) [$M-\mathrm{Me}$], 237(3) [$M-\mathrm{Me_2SiH}$], 223(6) [$M-\mathrm{Me}-\mathrm{Me_2Si}$], 207(3) [$\mathrm{Me_6Si_3SH}$], 191(5) [$\mathrm{Me_5Si_3S}$], 180(2) [$\mathrm{Me_4Si_2S_2}$], 165(16) [$\mathrm{Me_3Si_2S_2}$], 163(4) [$\mathrm{Me_5Si_2S}$], 147(9) [$\mathrm{Me_3Si_2CH_2S}$], 133(7) [$\mathrm{Me_3Si_2S}$], 131(11) [$\mathrm{Me_5Si_2}$], 116(100) [$\mathrm{Me_4Si_2}$], 101(8) [$\mathrm{Me_3Si_2}$], 73(73) [$\mathrm{Me_3Si}$].

6: 238(96) [M], 223(100) [$M-\mathrm{Me}$], 165(42) [$\mathrm{Me_3Si_2S_2}$], 163(46) [$\mathrm{Me_5Si_2S}$], 147(11) [$M-\mathrm{Me_2SiSH{=}Me_3Si_2CH_2S}$], 133(8) [$\mathrm{Me_3Si_2S}$], 131(4) [$\mathrm{Me_5Si_2}$], 73(83) [$\mathrm{Me_3Si}$].

7: 270(13) [M], 255(52) [$M-\mathrm{Me}$], 180(10) [$\mathrm{Me_4Si_2S_2}$], 165(100) [$\mathrm{Me_3Si_2S_2}$], 75(18) [MeSiS], 73(38) [$\mathrm{Me_3Si}$).

*Reaction of **6** with sulphur*

A mixture of 60 mg of **6** (0.25 mmol) and 10 mg of sulphur (0.31 mg-atom) was heated in a sealed evacuated glass ampoule for 5 h at 250 ° C. GLC analysis showed that 28% of **7** had been formed. In a control experiment, **6** was recovered unchanged after being heated alone under the same conditions.

*Reaction of **1** with sulphur in the presence of $(Me_2SiO)_3$ (**9**)*

A mixture of 58 mg of **1** (0.167 mmol), 32 mg of sulphur (1 mg-atom), and 740 mg of **9** (3.33 mmol) in an evacuated, sealed ampoule was kept for 14 h at 200 ° C. GLC analysis revealed the following products: **3** (11%), **4** (1%), **5** (5%), **6** (29%), **7** (3%), **8** (4%) and 2,2,4,4,6,6,8,8-octamethyl-1,3,5-trioxa-7-thiacyclooctane (**10**) (17%). **10** was identified by a GLC comparison with an authentic sample prepared as described previously [35].

Reaction of $(Me_2Si)_x$ polymer with sulphur

1. A mixture of the polymer (58 mg) and sulphur (32 mg) was heated in a sealed evacuated ampoule for 9 h at 250 ° C. The partly solid product mixture was completely soluble in benzene. Two products were found, **7** (88%) and **8** (12%).

2. A mixture of the polymer (58 mg) and sulphur (32 mg) was kept as above for 10 h at 200 ° C. Benzene was added and the residual polymer (29 mg) filtered off. GLC analysis of the solution showed two products, **6** (12%) and **7** (38%).

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