NOVEL 2,4-DISILATHIETANE RING SYSTEM FROM [2 + 2]CYCLOADDITION OF 1,1-DIMETHYL-1-SILAETHYLENE, $Me_2Si=CH_2$, TO DIMETHYLSILANTHIONE, $Me_2Si=S$. PERTURBATION MOLECULAR ORBITAL (PMO) STUDY ON REACTIVITY OF INTERMEDIATES WITH A DOUBLE-BONDED SILICON ATOM *

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(Received October 18th, 1983)

Summary

Copyrolysis of 1,1-dimethyl-1-silacyclobutane (I) with both hexamethylcyclotrisilthiane (II) and tetramethylcyclodisilthiane (III) at 560°C involves 1,1-dimethyl-1-silaethylene, $Me_2Si=CH_2$ (IV), and dimethylsilanthione, $Me_2Si=S$ (V), intermediates and yields the following cycloaddition products: the new 2,2,4,4-tetramethyl-2,4-disilathietane (VI), 1,1,3,3-tetramethyl-1,3-disilacyclobutane (VII), and III. Six-membered cyclocarbosilthianes, 1,1,3,3,5,5-hexamethyl-2-thia-1,3,5-trisilacyclohexane (VIII) and 1,1,3,3,5,5-hexamethyl-2,4-dithia-1,3,5-trisilacyclohexane (IX) have also been derived by inserting IV and V into the Si–S bond of VI.
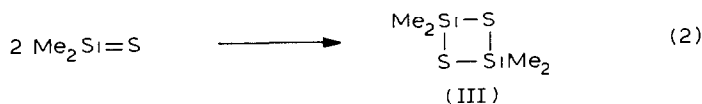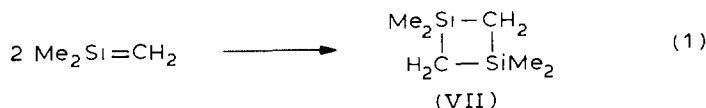
Copyrolysis of I with thietane (X) also results in four- and six-membered cyclocarbosilthianes, the major product being VI. This is discussed in terms of dimethylsilanthione formation via [2 + 2]cycloaddition of IV to thioformaldehyde (XI) followed by [4 → 2 + 2]cyclodecomposition of the 2-silathietane intermediate. A perturbation molecular orbital study of [2 + 2]cycloaddition involving intermediates IV, V, and XI has shown that IV reacts more readily with V and XI than it cyclodimerizes. Dimerization of V is the most prominent reaction.

Introduction

[2 + 2]Cycloaddition is known to be a frequent reaction of unstable intermediates containing a double-bonded silicon atom [1–3]. In the absence of effective traps it

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* The paper is dedicated to Professor M. Kumada with whom we had several valuable discussions in the A.V. Topchiev Institute.

proceeds to cyclodimerize. Thus, 1,1-dimethyl-1-silaethylene (IV) and dimethyl-silanthione (V) give rise to 1,1,3,3-tetramethyl-1,3-disilacyclobutane (VII) and tetra-methylcyclodisilthiane (III), respectively (eqs. 1 and 2):

$$2 \ Me_2Si=CH_2 \longrightarrow \begin{array}{c} Me_2Si-CH_2 \\ | \quad\quad | \\ H_2C-SiMe_2 \end{array} \quad\quad (1)$$
$$(VII)$$

$$2 \ Me_2Si=S \longrightarrow \begin{array}{c} Me_2Si-S \\ | \quad\quad | \\ S-SiMe_2 \end{array} \quad\quad (2)$$
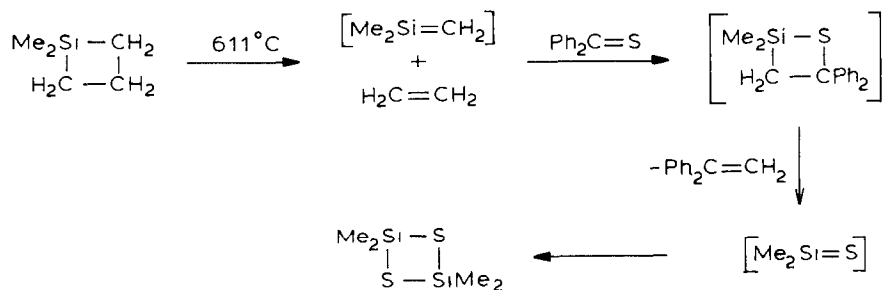$$(III)$$

Silaalkenes react with carbonyl, thiocarbonyl, and azomethine compounds via a [2 + 2]cycloaddition [4 → 2 + 2]cycloelimination sequence [1–3], but little is known about [2 + 2]cycloaddition of silaalkenes to Si=X intermediates, in particular, to Si=S compounds. For instance, in the copyrolysis of I with thiobenzophenone [4] (Scheme 1) IV changes into V and a stable dimer III is obtained. Despite the participation of both Si=C and Si=S intermediates (IV and V) no reaction products of eq. 3 are observed.
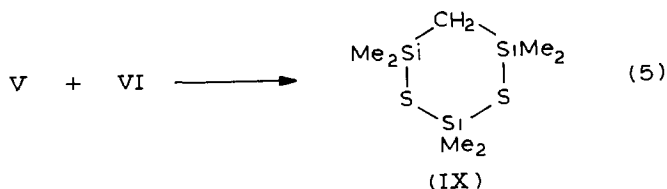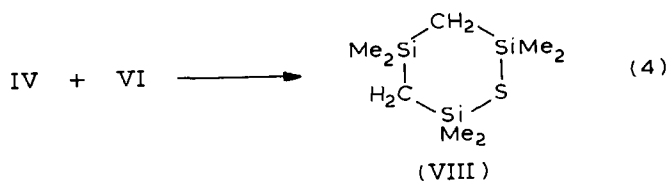
$$IV \ + \ V \longrightarrow \begin{array}{c} Me_2Si-CH_2 \\ | \quad\quad | \\ S-SiMe_2 \end{array} \quad\quad (3)$$
$$(VI)$$
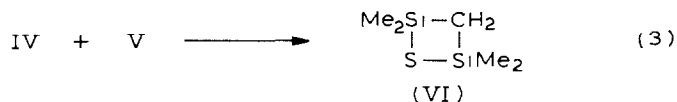
In search of [2 + 2]cycloaddition reactions between Si=C and Si=S intermediates we have studied the copyrolysis of I (a source of IV [5]) with hexamethylcyclotri-silthiane (II) and tetramethylcyclodisilthiane (III) (both are sources of V [6,7]) as well as of I with thietane (X) (a source of thioformaldehyde (XI) [8]), and have succeeded in preparing 2,2,4,4-tetramethyl-2,4-disilathietane (VI), a new heterocyclic system with silicon and sulfur atoms. In addition, six-membered cyclocarbosilthianes were obtained by insertion reactions (eqs. 4 and 5):

Since the study involves several types of unsaturated intermediate ($Me_2Si=CH_2$,

$$\begin{array}{ccc} Me_2Si-CH_2 \\ | \quad\quad | \\ H_2C-CH_2 \end{array} \xrightarrow{611°C} \begin{bmatrix} Me_2Si=CH_2 \\ + \\ H_2C=CH_2 \end{bmatrix} \xrightarrow{Ph_2C=S} \begin{bmatrix} Me_2Si-S \\ | \quad\quad | \\ H_2C-CPh_2 \end{bmatrix}$$

$$\begin{array}{c} Me_2Si-S \\ | \quad\quad | \\ S-SiMe_2 \end{array} \longleftarrow \quad\quad [Me_2Si=S]$$

with the step labeled $-Ph_2C=CH_2$ descending between them.

SCHEME 1

IV + VI $\longrightarrow$ [structure VIII] (4)

(VIII)

V + VI $\longrightarrow$ [structure IX] (5)

(IX)

Me$_2$Si=S, and H$_2$C=S), their reactivities in different [2 + 2]cycloaddition reactions were examined using the perturbation molecular orbital (PMO) theory.

Results

Gas-phase pyrolysis of hexamethylcyclotrisilthiane

We checked the gas-phase pyrolysis of II for production of dimethylsilanthione at 560°C, that is in a temperature range used for the selective generation of IV from I in a flow system. As with liquid phase thermolysis (200°C) [6], the only product of gas-phase pyrolysis of II was the four-membered cyclosilthiane III. The intermediacy of V was confirmed by trapping it with 1,1,3,3-tetramethyl-2-oxa-1,3-disilacyclopentane (Scheme 2).

[Scheme 2 structures] $\xrightarrow[-\text{III}]{560°C}$ [Me$_2$Si=S] $\longrightarrow$ [structures]
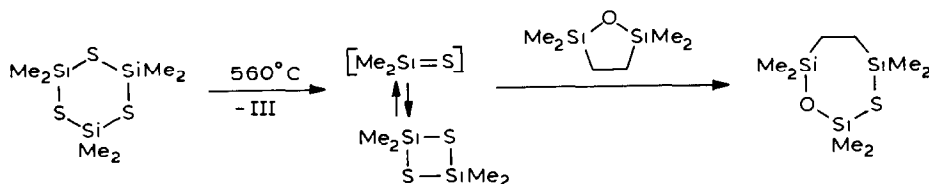
SCHEME 2

Hexamethylcyclotrisilthiane is completely transformed into III upon gas-phase pyrolysis and, therefore, it was used to prepare III instead of distilling II in an H$_2$S stream [9,10].

*Copyrolysis of 1,1-dimethyl-1-silacyclobutane with hexamethylcyclotrisilthiane*

Copyrolysis of two mixtures containing I and II in approximate ratios of 5/1 and 1/1 was studied at 560°C. For the 5/1 mixture, the pyrolysate ingredients, as identified by the GS/MS method, were the four- and six-membered cyclocarbosilthianes VI, VIII, and IX in a 3.9/2/1 ratio. In addition, a dimer of VI, i.e. 1,1,3,3,5,5,7,7-octamethyl-2,6-dithia-1,3,5,7-tetrasilacyclooctane (XII) was present, and the formation of III was supressed. In the copyrolysis of the 1/1 mixture, the ratio of VI, VIII, and IX was 10.5/1/14 and III was present in an amount of 32.3%. Correspondingly, the concentration of VII decreased from 23.6% to zero, see Table 1.
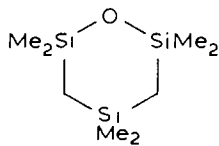
TABLE 1

COPYROLYSIS OF 1,1-DIMETHYL-1-CYCLOBUTANE WITH CYCLOSILTHIANES II AND III AND WITH THIETANE. COMPOSITION OF PRODUCTS CONTAINING Si–CH$_2$–Si AND Si–S–Si GROUPINGS

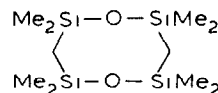| Starting mixture	(mmol)	Copyrolysis products (mol%)						
		VII	VI	III	VIII	IX	II	XII
I + II	(2.7/2.6)	–	10.5	32.3	1.0	18.0	4.0	–
	(4.8/0.89)	23.6	22.0	–	12.8	5.6	--	1.8
I + III	(5.0/1.0)	48.6	17.2	–	6.5	0.4	–	–
I + X	(10.9/2.97)	35.0	27.0	--	6.0	0.4	–	0.5

Since cyclocarbosilthianes and cyclosilthianes are hydrolytically unstable, their several hydrolysis products (XIII–XX) were also observed.
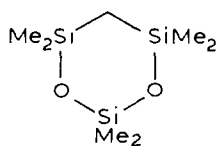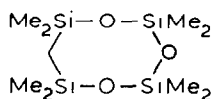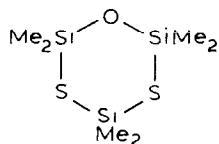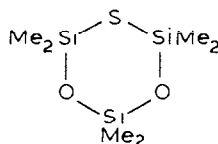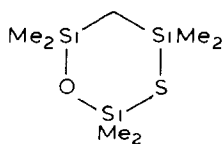
(XIII)   (XIV)   (XV)

(XVI)   (XVII)   (XVIII)
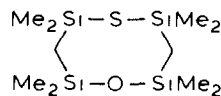
(XIX)   (XX)

The chromatograms of the copyrolysis products are shown in Figs. 1 and 2. Their mass spectra are given in Table 2.

In the mass spectra of six-membered cyclosilthianes and cyclocarbosilthianes the intensities of the peaks of parent ions decrease with decrease in the number of sulfur atoms in the ring, being 18, 7.3, and 0.6% for II, IX, and VIII, respectively. A similar trend is observed for the four-membered heterocycles III and VI. The formation of the most abundant ion, of the $[P - 15]^+$ type, is due to the loss of a methyl group from the molecular ion. Further fragmentation of the $[P - 15]^+$ ion involves loss of the neutral molecules of IV or V; the loss of V being preferred (Scheme 3). Thus, in the mass spectrum of II the intensity of the $[P - 15]^+$ peak is (m/z 165) is 73%. The substitution of one sulfur atom by carbon (IX) lowered the intensity of this ion (m/z 147) to 44% and further substitution reduced the intensity to only 4% (m/z 129).

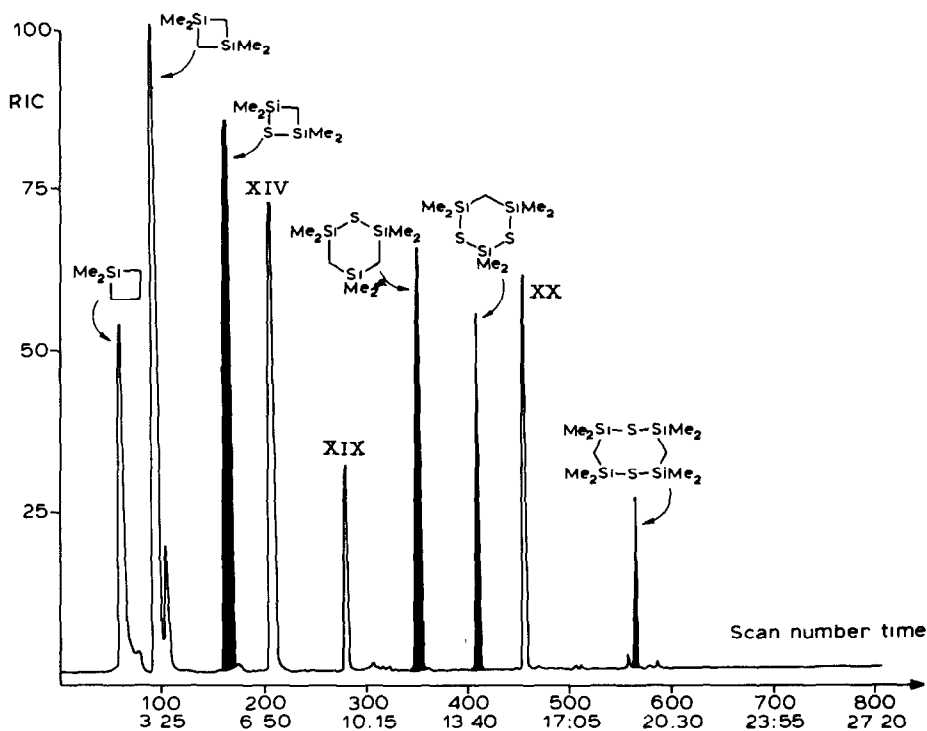Fig. 1. Chromatogram of the copyrolysis products of I and II (5.4/1 mixture), showing the reconstructed ion current (RIC) against scan number (100,200...) and scan time (min:s).
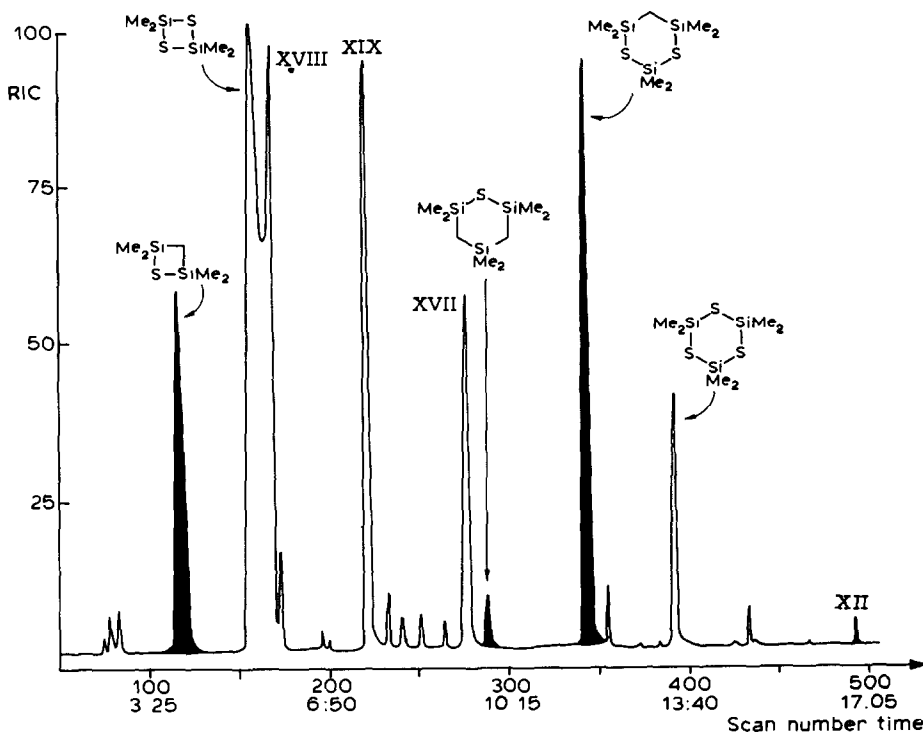

Fig. 2. Chromatogram of the copyrolysis products of I and II (1/1 mixture).

TABLE 2

MASS SPECTRA OF THE CYCLOSILTHIANES AND CYCLOCARBOSILTHIANES PRESENT IN THE PRODUCT MIXTURES FROM THE PYROLYSIS OF II AND THE COPYROLYSIS OF I WITH II AND WITH X; m/z (Relative intensities in %)[a]

Tetramethylcyclodisilthiane: 182(2.9), 181(2.9), 180(19.8)*, 168(1.0) 167(10.0), 166(9.0), *165(100.0)*, 151(1.5), 149(2.5), 135(5.3), 131 (1.2), 121(1.1), 91(2.6), 90(3.6), 89(2.0), 77(3.0), 76(1.7), 75 (18.9), 74(2.0), 73(30.2), 61(3.2), 60(1.2), 59(3.2), 58(1.8), 57 (1.2), 45(6.6), 44(1.7), 43(10.4), 42(2.1), 40(2.4).

2,2,4,4-Tetramethyl-2,4-disilathietane: 164(1.0), 163(1.4), 162(9.4)* 161(1.1), 149(5.5), 148(9.4), *147(100.0)*, 131(2.9), 177(1.4), 85 (1.7), 75(3.0), 73(3.2), 71(2.1), 69(1.2), 67(1.0), 66(2.0), 61(1.1) 60(1.0), 59(11.0), 58(3.5), 57(2.5), 55(2.2), 53(1.2), 45(11.7), 44(1.7), 43(2.8), 42(2.8).

1,1,3,3,5,5-Hexamethyl-2-thia-1,3,5-trisilacyclohexane: 234(0.6)*, 222(1.5), 221(9.0), 220(15.8), *219(100.0)*, 205(1.7), 204(2.0), 203 (10.0), 147(7.0), 133(1.1), 131(2.0), 129(3.8), 117(1.1), 115(1.5), 113(3.9), 103(1.6), 102(2.2), 101(2.0), 98(1.4), 85(3.0), 75(1.1), 74(1.1), 73(17.0), 72(2.8), 71(2.7), 59(12.8), 58(1.7), 57(1.2), 45(5.3), 44(2.7), 43(5.4).

1,1,3,3,5,5-Hexamethyl-2,4-dithia-1,3,5-trisilacyclohexane: 254(1.4) 253(1.6), 252(7.3)*, 240(2.1), 239(12.3), 238(14.0), *237(100.0)*, 221(4.6), 203(1.0), 149(4.0), 148(4.6), 147(44.1), 133(2.2), 131 (4.3), 117(1.1), 113(1.3), 91(1.0), 85(3.2), 75(3.5), 74(1.6), 73 (20.9), 72(3.4), 71(3.1), 59(9.5), 58(2 1), 57(1.7), 55(1.1), 45(5.6) 44(2.9), 43(6.2).

Hexamethylcyclotrisilthiane: 272(3.2), 271(3.5), 270(18.0)*, 258 (2.7), 257(20.9), 256(19.8), *255(100.0)*, 139(1.4), 167(9.4), 166 (9.9), 165(73.2), 151(2.7), 147(1.4), 135(3.2), 131(1.3), 91(3.5), 90(3.5), 89(1.4), 77(1.1), 75(15.3), 74(5.6), 73(59.3), 61(2.7), 59(4.3), 58(1.6), 45(11.3), 44(3.2), 43(10.2).
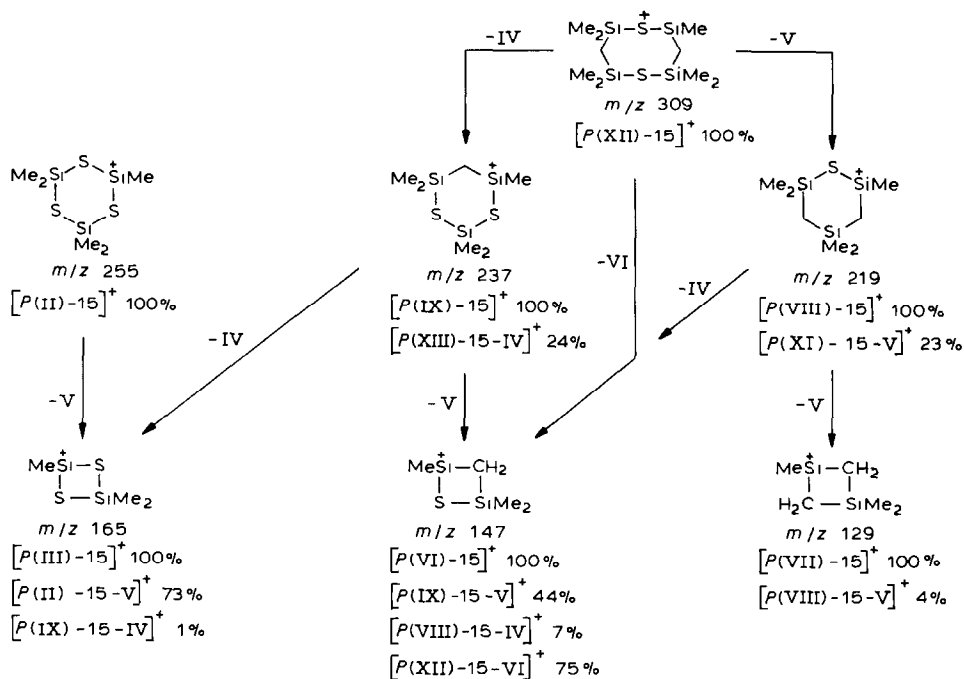
1,1,3,3,5,5,7,7-Octamethyl-2,6-dithia-1,3,5,7-tetrasilacyclooctane: 326(0.4), 325(0.4), 324(6.9)*, 312(4.7), 311(25.4), 310(28.0), *309 (100.0)*, 293(2.6), 239(4.3), 237(24.1), 221(15.6), 220(3.5), 219 (23.3), 203(3.9), 149(6.0), 148(8.2), 147(74.6), 133(2.2), 133(1.3) 85(2.6), 74(2.2), 73(36.2), 72(3.5), 71(1.7), 59(6.5), 45(4.3), 43(3.0).

[a] Asterisked peaks correspond to parent ions; peaks of $[P-15]^+$ ions are in italics.

TABLE 3

RELATIVE INTENSITIES OF THE $[P]^+$ AND $[P-15]^+$ ION PEAKS IN THE MASS SPECTRA OF HYDROLYZED COPYROLYSIS PRODUCTS OF I WITH II AND WITH X; m/z (%)

Compounds	$[P]^+$	$[P-15]^+$
1,1,3,3,5,5-Hexamethyl-2,4-dioxa-1,3,5-trisilacyclohexane (XIII)	220(0.3)	205(100.0)
1,1,3,3,5,5-Hexamethyl-2-oxa-1,3,5-trisilacyclohexane (XIV)	218(0.1)	203(100.0)
1,1,3,3,5,5,7,7-Octamethyl-2,6-dioxa-1,3,5,7-tetrasilacyclooctane (XV)	292(0.1)	277(100.0)
1,1,3,3,5,5,7,7-Octamethyl-2,4,6-trioxa-1,3,5,7-tetrasilacyclooctane (XVI)	294(0.1)	279(100.0)
1,1,3,3,5,5-Hexamethyl-2-oxa-4,6-dithia-1,3,5-trisilacyclohexane (XVII)	254(11.4)	239(100.0)
1,1,3,3,5,5-Hexamethyl-2,4-dioxa-6-thia-1,3,5-trisilacyclohexane (XVIII)	238(5.8)	223(100.0)
1,1,3,3,5,5-Hexamethyl-2-oxa-4-thia-1,3,5-trisilacyclohexane (XIX)	236(2.8)	221(100.0)
1,1,3,3,5,5,7,7-Octamethyl-2-oxa-6-thia-1,3,5,7-tetrasilacyclooctane (XX)	308(0.6)	293(100.0)

$$-IV \quad \underset{Me_2Si-S-SiMe_2}{\overset{Me_2Si-\overset{+}{S}-SiMe}{\diamondsuit}} \quad -V$$

$$m/z \ 309$$

$$\left[P(XII)-15\right]^+ 100\%$$

$$\underset{\underset{Me_2}{Si}}{\overset{S}{\underset{S}{\bigtriangleup}}} \begin{matrix} Me_2Si & \overset{S}{\diagdown} & \overset{+}{Si}Me \\ | & & | \\ S & & S \end{matrix}$$

m/z 255

$\left[P(II)-15\right]^+ 100\%$

$-IV$

$$\underset{S-SiMe_2}{\overset{MeSi-S}{\overset{+}{|}}}$$

m/z 165

$\left[P(III)-15\right]^+ 100\%$

$\left[P(II) -15 -V\right]^+ 73\%$

$\left[P(IX) -15 -IV\right]^+ 1\%$

$-V$

Me₂Si structure m/z 237

$\left[P(IX)-15\right]^+ 100\%$

$\left[P(XIII)-15-IV\right]^+ 24\%$

$-VI$

$-V$

$$\underset{S-SiMe_2}{\overset{MeSi-CH_2}{\overset{+}{|}}}$$

m/z 147

$\left[P(VI)-15\right]^+ 100\%$

$\left[P(IX)-15-V\right]^+ 44\%$

$\left[P(VIII)-15-IV\right]^+ 7\%$

$\left[P(XII)-15-VI\right]^+ 75\%$

$-IV$

Me₂Si structure m/z 219

$\left[P(VIII)-15\right]^+ 100\%$

$\left[P(XI)-15-V\right]^+ 23\%$

$-V$

$$\underset{H_2C-SiMe_2}{\overset{MeSi-CH_2}{\overset{+}{|}}}$$

m/z 129

$\left[P(VII)-15\right]^+ 100\%$

$\left[P(VIII)-15-V\right]^+ 4\%$

SCHEME 3. Fragmentation of $[P-15]^+$ ions in mass spectra of compounds II, VIII, IX and XII.

The loss of IV is less frequent and is observed only with VIII. The main fragmentation of the $[P-15]^+$ ion in the mass spectrum of the eight-membered cyclocarbosilthiane XII is related to the loss of the neutral molecule VI; the expulsion of IV and V also takes place.

Treatment with water of the copyrolysis products from the 5.4/1 mixture, yielded cyclocarbosiloxanes (Fig. 3), their mass spectra being identical to those of authentic samples [11]. The intensities of the parent and the $[P-15]^+$ ion peaks are given in Table 3, the latter ions being the more abundant. The formation of cyclocarbosiloxanes, upon hydrolysis, indicates the presence of cyclocarbosilthianes in the copyrolysis products. Indeed, XIV is the oxygen analog of VIII, etc. Hydrolysis of VI presumably yields 2,2,4,4-tetramethyl-2,4-disilaoxetane, an unstable intermediate which forms dimer XV [12].

Copyrolysis of 1,1-dimethyl-1-silacyclobutane with tetramethylcyclodisilthiane

Copyrolysis of a 5/1 mixture of I and III results in a similar mixture of products as the copyrolysis of I with II (Fig. 4). However, the relative ratios of the cyclocarbosilthianes VI, VIII, and IX are different, being 43/16/1. No starting cyclosilthiane is present among the products because of its complete conversion into V, followed by reaction with IV, resulting in VI. Predominant formation of 2,4-disilathietane, VI, as well as a greater amount of VIII than IX, suggests the importance of reactions 3–5, rather than of 6.
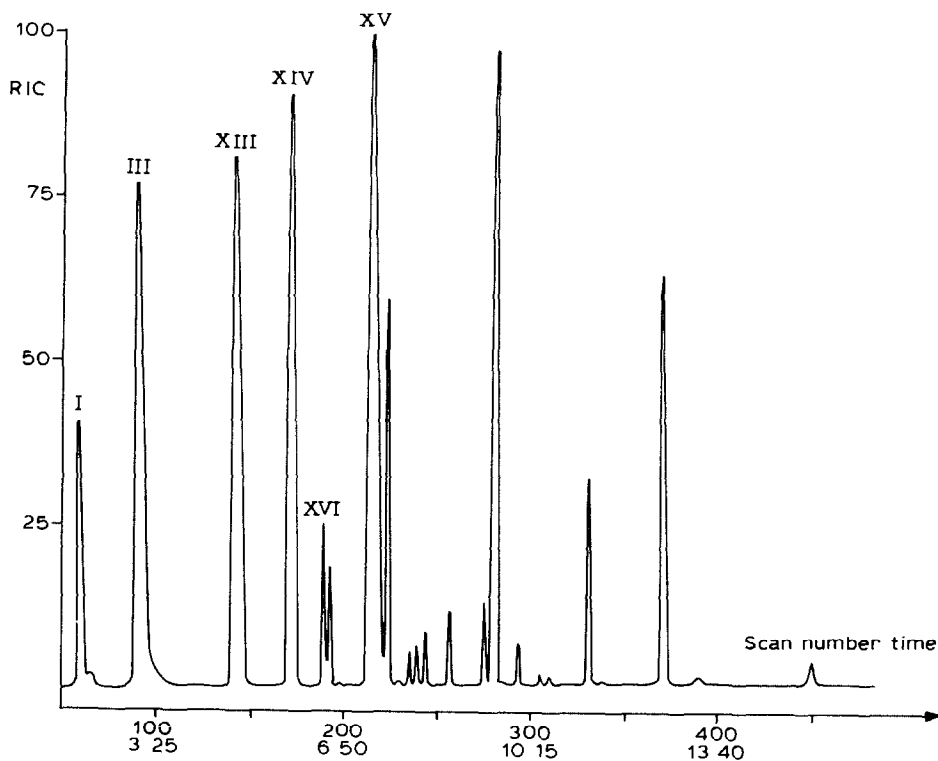
IV + III → IX   (6)

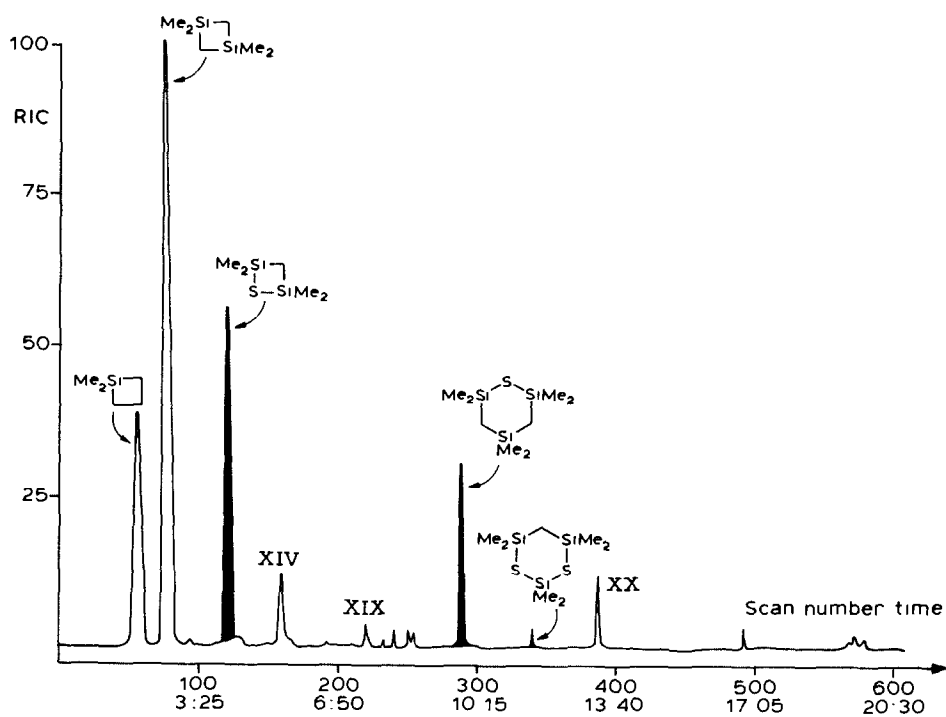Fig. 3. Chromatogram of the hydrolysed copyrolysis products of I and II.

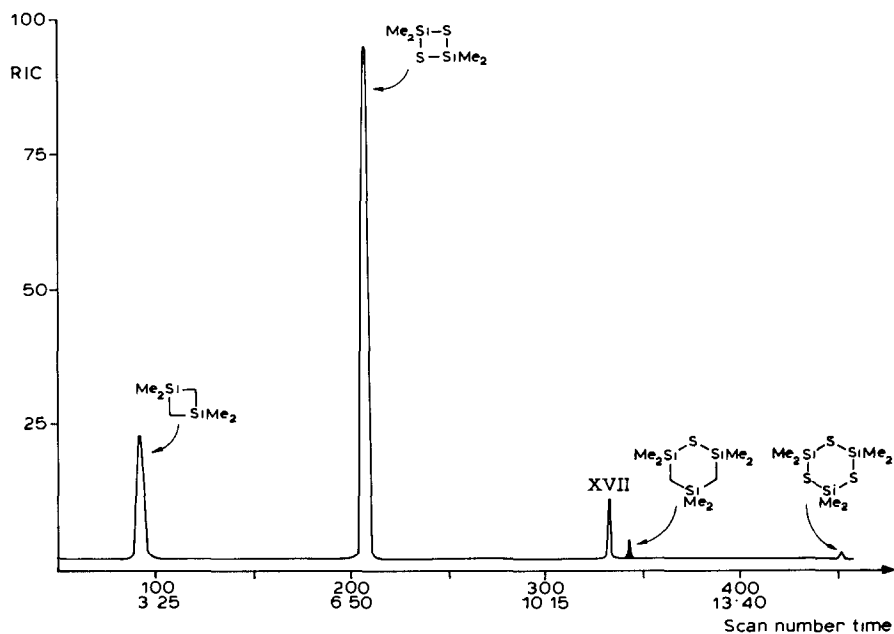Fig. 4. Chromatogram of the copyrolysis products of I and III.

Fig. 5. Chromatogram of the copyrolysis products of II and VII.

Copyrolysis of hexamethylcyclotrisilthiane with 1,1,3,3-tetramethyl-1,3-disilacyclobutane

In Fig. 5 is shown a chromatogram of the copyrolysis products from a mixture of II and VII (1/1 mol ratio). Like pyrolysis of II alone, the major product is the four-membered cyclosilthiane III. Disilacyclobutane VII seems not to decompose to produce the intermediate IV (absence of VI). Moreover, VII is not readily involved with silanthione V (reaction 7), as only traces of the insertion product VIII are found.

$$V + VII \rightarrow VIII \tag{7}$$

Copyrolysis of 1,1-dimethyl-1-silacyclobutane with thietane

The formation of four- and six-membered cyclocarbosilthianes from 1,1-dimethyl-1-silaethylene and dimethylsilanthione, generated in a process similar to one shown in Scheme 1, have been observed; thietane being used as the source of thioformaldehyde [8]. A chromatogram of the copyrolysis products of I and X (mol ratio 3.7/1) is shown in Fig. 6. The ratio of the cyclocarbosilthianes VI, VIII, and IX was 68/15/1. Tetramethylcyclodisilthiane, previously described as the main product of the copyrolysis of I with thiobenzophenone [4] was not found.

PMO study of the reactivity of intermediates with double-bonded silicon atom

The copyrolysis which has been described, involves the intermediacy of 1,1-dimethyl-1-silaethylene and dimethylsilanthione. In addition, thioformaldehyde takes part in the copyrolysis of I with X. Because of the significance of [2 + 2]cycloaddition reactions in the further transformations of the unsaturated intermediates, we examined their theoretical reactivities by the PMO method [13]. As well as 1–3, the reactions 8–14 have also been taken into account.
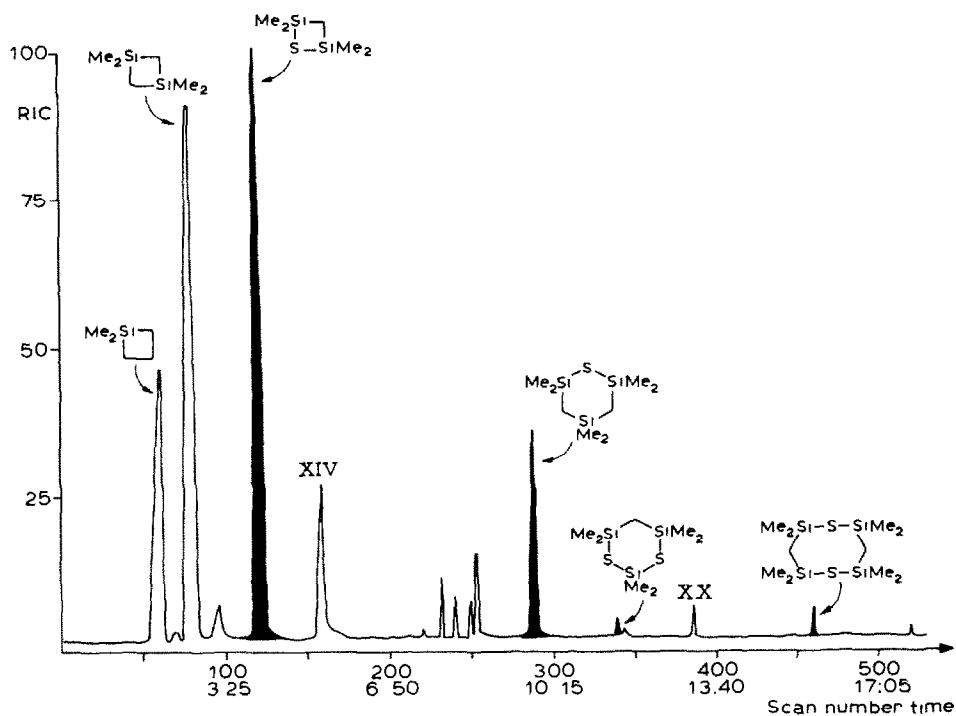
Fig. 6. Chromatogram of the copyrolysis products of I and X.

The PMO energy, $E(\text{PMO})$, was used as a measure of reactivity; $E(\text{PMO}) = E(\text{C}) + E(\text{CT})$, where $E(\text{C})$ is the Coulombic energy and $E(\text{CT})$ the charge transfer energy, both were calculated as described in refs. 13 and 14. Interatomic distances, atomic charges, orbital energies, MO coefficients and integrals, γ, were calculated using CNDO/2 approximations on an sp-basis (Table 4).
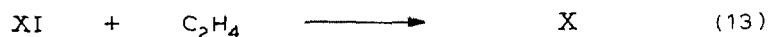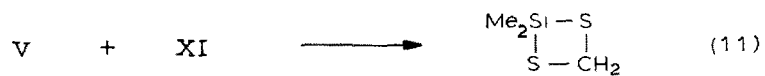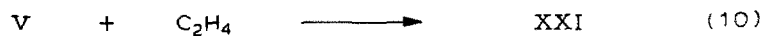
$$\text{IV} \quad + \quad \text{C}_2\text{H}_4 \quad \longrightarrow \quad \text{I} \qquad (8)$$

$$\text{IV} \quad + \quad \text{XI} \quad \longrightarrow \quad \begin{array}{c} \text{Me}_2\text{Si} - \text{CH}_2 \\ | \qquad | \\ \text{S} - \text{CH}_2 \end{array} \qquad (9)$$

$$\text{V} \quad + \quad \text{C}_2\text{H}_4 \quad \longrightarrow \quad \text{XXI} \qquad (10)$$

$$\text{V} \quad + \quad \text{XI} \quad \longrightarrow \quad \begin{array}{c} \text{Me}_2\text{Si} - \text{S} \\ | \qquad | \\ \text{S} - \text{CH}_2 \end{array} \qquad (11)$$

$$\text{XI} \quad + \quad \text{XI} \quad \longrightarrow \quad \begin{array}{c} \text{H}_2\text{C} - \text{S} \\ | \qquad | \\ \text{S} - \text{CH}_2 \end{array} \qquad (12)$$

$$\text{XI} \quad + \quad \text{C}_2\text{H}_4 \quad \longrightarrow \quad \text{X} \qquad (13)$$

$$\text{C}_2\text{H}_4 \quad + \quad \text{C}_2\text{H}_4 \quad \longrightarrow \quad \begin{array}{c} \text{H}_2\text{C} - \text{CH}_2 \\ | \qquad | \\ \text{H}_2\text{C} - \text{CH}_2 \end{array} \qquad (14)$$
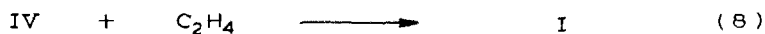
TABLE 4

INTERATOMIC DISTANCES (r(X=Y)) Å, ATOMIC CHARGES (Q(X),Q(Y)), BOND ORDERS (W(X=Y)) [a], HOMO AND LUMO OF MOLECULES R_2X=Y (R = H, Me; X = C, Si; Y = H_2C, S)

Molecules	r(X=Y) (Å)			Charges ($\bar{e}$)		W(X=Y)	HOMO	LUMO
	CNDO/2 calculation	Experimental	Ab initio calculation	Q_X	Q_Y			
Me_2Si=CH_2	1.892	[b]	1.715[c] 1.728[c]	0.344	−0.202	1.89	π	π^*
Me_2Si=S	2.190[d]	–	[e]	0.525	−0.351	1.59	$1p$	π^*
H_2C=S	1.707	1.611[f]	1.613[f]	0.094	−1.133	1.99	$1p$	π^*
H_2C=CH_2	1.307	1.337[g]	1.314[i]	−0.018	−0.018	2.0	π	π^*

[a] Wiberg bond order [17]. [b] X-ray r(Si=C) value in $(Me_3Si)_2$Si=C(O$SiMe_3$)Ad, 1.764 Å [18]. [c] r(Si=C) in refs. 19 and 20. [d] Approximate r(Si=S) values, 1.993 Å [16]. [e] r(Si=S) value in H_2Si=S, 1.945 Å [21]. [f] Ref. 22. [g] Ref. 23. [i] Ref. 24.

Considering the maximal overlapping principle and the probability of a tricentric transition state for [2 + 2]cyclodimerization reactions [15], the E(CT) for reactions 1, 8, and 14 were calculated for the approach of molecules shown in Fig. 7B. Other reactions were calculated for the approaches shown in Figs. 7C and 7D. Since antiparallel orientation of molecular dipoles provides an attractive interaction between molecules (positive values of E(C)$_\leftrightarrows$) it was used for calculations of E(CT)
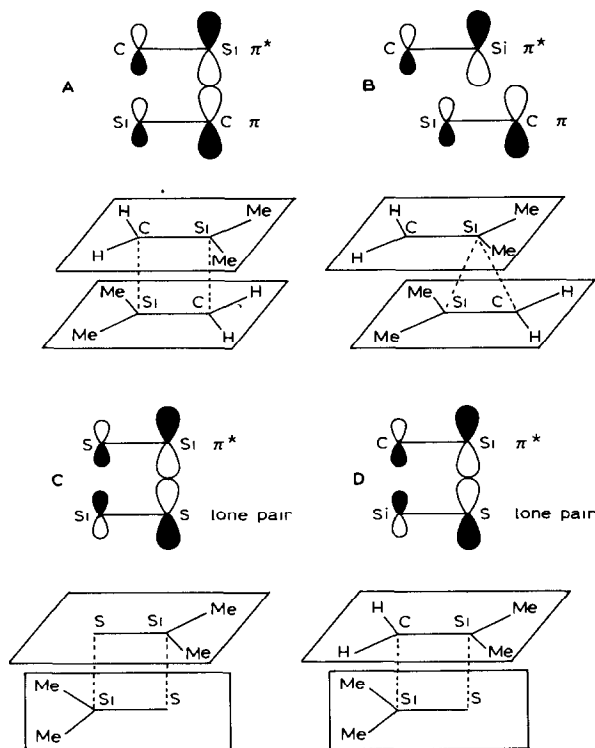

Fig. 7. MO representation of [2 + 2]cycloaddition of Si=C and Si=S intermediates.

TABLE 5

$E(C)$, $E(CT)$ AND $E(PMO)$ ENERGIES (kcal/mol) FOR {2+2]CYCLOADDITION REACTIONS INVOLVING INTERMEDIATES IV, V, XI AND ETHYLENE

Reagents		$E(C)_{\rightarrow}^{\rightarrow}$	$E(C)_{\rightleftarrows}$	$E(CT)$	$E(PMO)$	Reaction
$Me_2Si=CH_2$	$Me_2Si=CH_2$	−4.60	0.50	5.69	6.19	1
$Me_2Si=S$	$Me_2Si=S$	−11.2	5.14	18.2	23.3	2
$Me_2Si=S$	$Me_2Si=CH_2$	−7.0	2.06	11.4	13.4	3
$Me_2Si=CH_2$	$H_2C=CH_2$	0.53	0.53	0.39	0.92	8
$Me_2Si=CH_2$	$H_2C=S$	−0.40	1.55	19.0	20.6	9
$Me_2Si=S$	$H_2C=CH_2$	0.64	0.64	2.56	3.20	10
$Me_2Si=S$	$H_2C=S$	−1.04	2.43	5.25	7.68	11
$H_2C=S$	$H_2C=S$	−0.53	0.21	4.03	4.24	12
$H_2C=S$	$H_2C=CH_2$	−0.15	−0.15	2.25	2.10	13
$H_2C=CH_2$	$H_2C=CH_2$	−0.14	−0.14	0.26	0.12	14

and $E(PMO)$. In Table 5 are given the values of $E(C)$, $E(CT)$, and $E(PMO)$ for an intermolecular distance of 3 Å, for which mutual perturbation of CNDO/2 wave functions may be neglected.

Discussion

The product distribution for the copyrolysis of 1,1-dimethyl-1-silacyclobutane with both hexamethylcyclotrisilthiane and tetramethylcyclodisilthiane seems to be in fairly good agreement with Scheme 4. Indeed, stoichiometric quantities of the intermediates IV and V are consumed, producing 2,4-disilathietane, VI, whereas an excess of IV or V yields either 1,3-disilacyclobutane, VII, or cyclodisilthiane, III. Another reaction is the insertion of IV and V into the Si–S bond of VI, yielding the
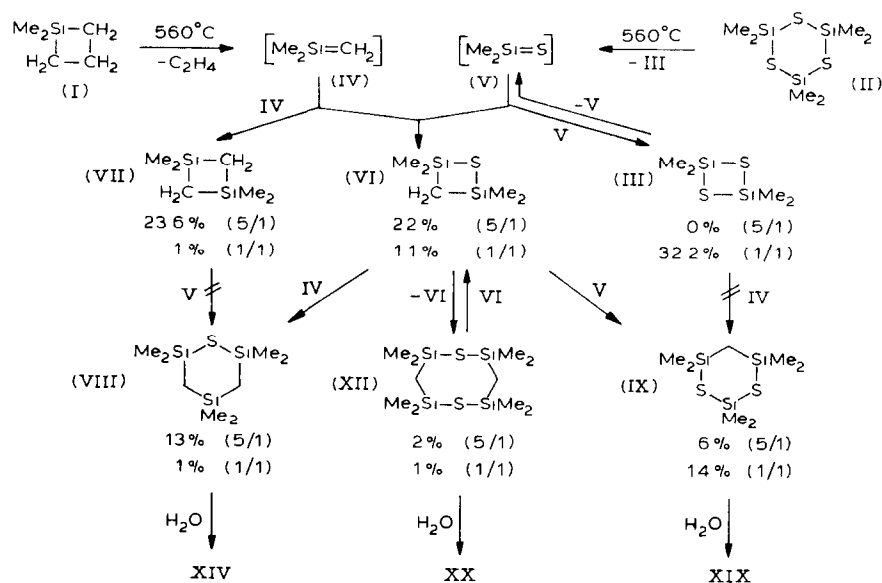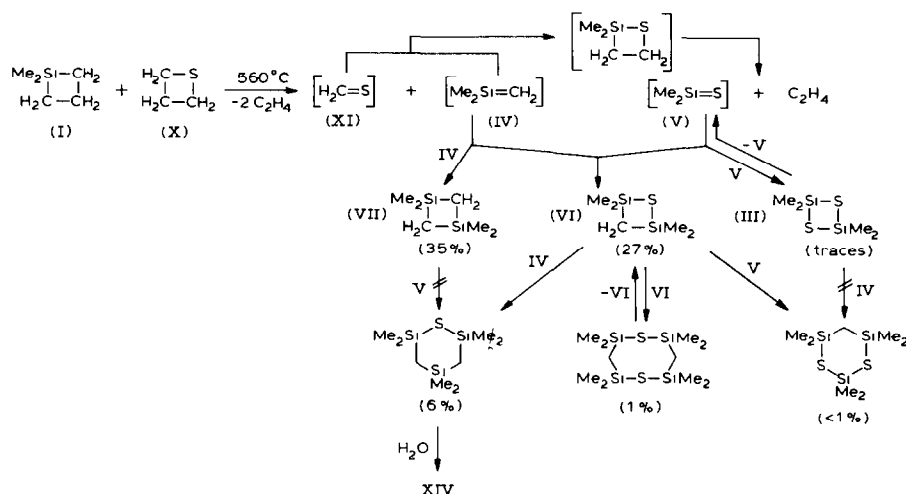

SCHEME 4

six-membered cyclocarbosilthianes VIII and IX. An alternative pathway for the formation of IX (eq. 6) is less preferable because molecule III dissociates completely into the monomeric form V at the pyrolysis temperature.

The five-fold increase in the concentration of I doubles the relative amount of VI in the products. Correspondingly, the VII content increased from zero to 23.6%, but the relative amount of III falls from 32.3% to zero. There is also a rise in the concentration of VIII and a decrease in the concentration of IX, but their total content remains almost unchanged.

Copyrolysis of I with X is interpreted in terms of the intermediacy of IV, V, and

SCHEME 5

XI (Scheme 5). The primary intermediates IV and IX produce dimethylsilanthione via the [2 + 2]cycloaddition, [4 → 2 + 2]cycloelimination sequence. Excessive amounts of IV trap V, yielding VI. In addition, IV inserts into the Si–S bond of VI giving VIII. Thus, the only reaction of V in the copyrolysis of I with X in a 3.7/1 mol ratio is [2 + 2]cycloaddition to give VI.

The other possible reaction of V, that is cyclodimerization and insertion into the Si–S bond of VI, does not compete with the trapping of V by excess of IV. These results differ from those on the copyrolysis of I with thiobenzophenone [4], where no cyclocarbosilthianes have been observed. This discrepancy is apparently due to the excess of thiobenzophenone compared to dimethylsilaethylene. Indeed, even a stochiometric amount of Si=C and C=S compounds is sufficient to transform IV completely into V. This emerges from the study of the gas-phase pyrolysis of 3,3-dimethyl-3-silathietane [16], a reaction giving stoichiometric quantities of IV and XI and which ends with the formation of tetramethylcyclodisilthiane.

Generally, the distribution of pyrolysis products is in good agreement with the predictions of the reactivity of the intermediates by the PMO method. It is seen from Table 5 that cyclodimerization of V is the fastest reaction. Somewhat slower are the [2 + 2]cycloadditions of IV to both XI and V; cyclodimerization of IV is an even less rapid reaction. Ethylene exhibits the lowest reactivity towards the intermediates IV, XI, and V.

In addition, the mechanism of [2 + 2]cycloaddition reactions involving intermediates V and XI may differ from that involving IV and ethylene because of the difference in their orbital structures. Ethylene and 1,1-dimethyl-1-silaethylene have π-type HOMO and π^*-type LUMO, whereas dimethylsilanthione and thioformaldehyde have lp-type HOMO and π^*-type LUMO. Therefore, [2 + 2]cycloaddition of ethylene to IV and cyclodimerization of both silaalkenes and olefins proceed as non-concerted processes (Fig. 7A). On the contrary, cycloaddition of IV to both V and XI, as well as cyclodimerization of V and XI, may occur as concerted reactions when the orientations shown in Figs. 7C and 7D is achieved.

According to theory, reaction 9 is the most important pathway for copyrolysis of 1,1-dimethyl-1-silacyclobutane with thietane (Scheme 5) and this involves the intermediate 2-silathietane. Further, [4 → 2 + 2]cyclodecomposition of 2-silathietane produces the dimethylsilanthione intermediate which, with IV, is consumed mainly via reaction 3. The excess of IV suppresses the fast dimerization of V (eq. 2). Despite the fact that cyclodimerization of IX is assumed to be a medium rate reaction no dithiane XXIII has been detected. Presumably, this is due to the fast [4 → 2 + 2]cyclodecomposition of XXIII under the pyrolysis conditions (a reverse reaction to 12).

In the copyrolysis of I with both II and III the intermediates IV and V were generated independently. The distribution of reaction products is due to the competition of [2 + 2]cycloaddition reactions 1–3, rather than of 8 and 10.

It is evident that the [2 + 2]cycloaddition of 1,1-dimethyl-1-silaethylene to dimethylsilanthione is the common reaction of compounds with double-bonded silicon atom which makes possible the preparation of the novel 2,4-disilathietane ring system.

Experimental

The starting materials, 1,1-dimethyl-1-silacyclobutane [25], 1,1,3,3-tetramethyl-1,3-disilacycbutane [26], 1,1,3,3-tetramethyl-2-oxa-1,3-disilacyclopentane [10], hexamethylcyclotrisilthiane [10], and thietane [27], were synthesized by the methods described earlier. Tetramethylcyclodisilthiane was obtained by the gas-phase pyrolysis of II.

The pyrolyses were carried out in a stream of dry helium (flow rate, 25 ml/min) at 560°C, using a flow reactor consisting of a quartz tube, 14 mm in diameter and 270 mm long, placed into an electric furnace. The starting materials were fed in at a rate of 0.02 ml/min. The pyrolysate was collected in a trap cooled in liquid nitrogen.

The product analysis was carried out with FINIGAN 4021 and LKB 2091 GC/MS systems. The 30 m long glass capillary columns SE-54 and SE-30 were used. The rate of programmed temperature increase over the range 50–250°C was 8°/min and the ionization energy was 70 eV.

Gas-phase pyrolysis of hexamethylcyclotrisilthiane
Liquid II (0.71 g, 2.63 mmole) gave III, 0.45 g (95% yield) as needle-shaped crystals. Mass: m/z (%): $[P]^+$ 180(24), $[P-15]^+$ 165(100). IR (10 K, Ar matrix, cm^{-1}): 443s, 563s, 684vs, 784s, 830s, 837vs, 1248m, 1253s. The molecular and crystal structures of III were determined [28].

Copyrolysis of hexamethylcyclotrisilthiane with 1,1,3,3-tetramethyl-2-oxa-1,2-disilacyclopentane

A mixture of II (0.38 g, 1.4 mmole) and 1,1,3,3-tetramethyl-2-oxa-1,3-disilacyclopentane (1.2 g, 7.5 mmole) produced 1.2 g pyrolysate containing 71.2% of unchanged oxadisilacyclopentane. Also present and identified, were II (16.4%) and 1,1,3,3,5,5-hexamethyl-2-oxa-4-thia-1,3,5-trisilacyclopentane (7.2%). Mass spectrum of the oxathiatrisilacycloheptane: $[P]^+$ 250(11.96), $[P - 15]^+$ 235(100).

Copyrolysis of 1,1-Dimethyl-1-silacyclobutane with hexamethylcyclotrisilthiane

Two mixtures of I and II, with 5.4/1 and 1/1 mol ratios, were pyrolyzed. White needle-shaped crystals were formed at the interface on cooling the pyrolysis products with liquid nitrogen, and dissolved in the liquid phase of the pyrolysate on defreezing the trap. The 5.4/1 mixture (0.48 g, 4.8 mmole of I and 0.24 g, 0.89 mmole of II) gave 0.51 g of pyrolysate. Identified products were I (8.9%), VI (22%), VII (23.6%), VIII (12.8%), IX (5.6%), and XII (1.8%). In addition, the hydrolysis products of cyclocarbosilthianes XIV (11.8%), XIX (1.8%), and XX (7.6%) were present. The mass spectra are given in Tables 2 and 3, and the chromatogram is shown in Fig. 1.

During the pyrolysis of the 1/1 mixture (0.27 g, 2.7 mmole of I, and 0.7 g, 2.6 mmole of II) 0.8 g of pyrolysis products were isolated. Their composition was as follows: III (32.2%), VI (10.5%), VIII (1.0%), IX (18.0%), XVII (6.7%), XVIII (12.9%), and XIX (10.9%).

Hydrolysis of the copyrolysis products of 1,1-dimethyl-1-silacyclobutane and hexamethylcyclotrisilthiane

Water (10 ml) was added to the pyrolysate 1.2 g obtained from the 5/1 mixture of I and II, H_2S being eliminated during the reaction. The mixture was stirred for 10 h and left overnight. The organic layer was extracted with pentane and dried; 0.8 g of hydrolysate was obtained. The GC retention times were compared with those of authentic samples of the cyclocarbosiloxanes synthesized previously [11]. The following cyclocarbosiloxanes were identified: XIII (20.2%), XIV (17.2%), XVI (3.2%), and XV (28.2%). The chromatogram is shown in Fig. 3 and the mass spectra are given in Table 3.

Copyrolysis of 1,1-dimethyl-1-silacyclobutane with tetramethylcyclodisilthiane

A mixture of I (0.5 g, 5m mole) and III (0.18 g, 1.0 mmole) produced 0.5 g of a pyrolysate composed of I (18.2%), VII (48.6%), VI (17.2%), VIII (6.5%), and IX (0.4%). The hydrolysis products XIV (3.8%), XIX (0.5%), and XX (1.4%) were also present. The chromatogram is shown in Fig. 4, and the mass spectra are given in Tables 2 and 3.

Copyrolysis of hexamethylcyclotrisilthiane with 1,1,3,3-tetramethyl-1,3-disilacyclobutane

The needle-shaped crystals produced from a mixture of II (071 g, 2.6 mmole) and VII (0.38 g, 2.6 mmole) were dissolved in pentane and analyzed. The composition of the pyrolysis products (0.8 g) was as follows: VII (22.0%), III (70.0%), VIII (1.0%), II (0.5%), and XVII (4.0%). The chromatogram is shown in Fig. 5.

Copyrolysis of 1,1-dimethyl-1-silacyclobutane with thietane

A mixture of I (1.09 g, 10.9 mmole) and X (0.22 g, 2.97 mmole) produced 0.91 g of liquid pyrolysate and needle-shaped crystals. The pyrolysate composition was as follows: I (18.0%), VI (27%), VIII (6.0%), IX (0.4%), XII (7.0%), XIV (7.0%), and XX (0.5%). The chromatogram is shown in Fig. 6.

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