Journal of Organometallic Chemistry, 214 (1981) 145—154
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

THERMAL ISOMERIZATION AND DECOMPOSITION OF 3,3-DIETHYL-2,4-DIMETHYL-3-SILATHIETANE

L.E. GUSEL'NIKOV *, V.M. SOKOLOVA, E.A. VOLNINA, V.G. ZAIKIN, N.S. NAMETKIN

A.V. Topchev Institute of Petrochemical Synthesis, USSR Academy of Sciences, Moscow (U.S.S.R.)

M.G. VORONKOV *, S.V. KIRPICHENKO and V.V. KEIKO

Institute of Organic Chemistry, Siberian Division of the USSR Academy of Sciences, Irkutsk (U.S.S.R.)

(Received January 13th, 1981)

Summary

Pyrolysis of 3,3-diethyl-2,4-dimethyl-3-silathietane (I) has been studied at temperatures from 300 to 530°C using the pulse pyolytic GC-MS method. Decomposition of I proceeds with the elimination of ethane, ethylene, propylene, butadiene, *cis*- and *trans*-but-2-ene, and also with the loss of atomic sulphur. Isomerization into sulphur-containing unsaturated compounds is the main transformation process of I. The intermediacy of 1,1-diethyl-2-methyl-1-silaethylene and diethylsilathione is also discussed.

Introduction

The interest in the study of gas-phase pyrolysis of four-membered heterocycles is motivated by the formation of reactive element—carbon double-bonded intermediates as a result of the splitting "in half" typical for them. Thus, pyrolysis of oxetane [1] and thietane [2] yields formaldehyde and thioformaldehyde, respectively, and of azetidine [3] under similar conditions gives rise to methyleneimine which is stable only at low temperatures. Pyrolysis of monosilacyclobutanes [4] is a known method of generating silaalkenes: unstable intermediates with silicon—carbon double $p_\pi—p_\pi$ bonds. Decomposition of four-membered heterocycles with silicon—nitrogen [5], silicon—oxygen [6], and silicon—sulphur [7] bonds has been described. They are themselves, however, the intermediate products formed in copyrolysis of monosilacyclobutanes and imines, carbonyl or thiocarbonyl compounds, respectively. Decomposition "in half" is typical also for 1,1-dimethyl-1-germacyclobutane [8] and 1-methyl-

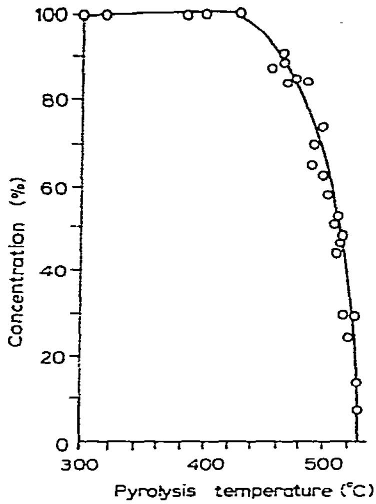


Fig. 1. Concentration of 3,3-diethyl-2,4-dimethyl-3-silathietane vs. pyrolysis temperature (residence time 12 sec).

2,2-diphenyl-2-germaazetidine [9]. But nothing is known about the gas-phase transformations of four-membered heterocyclic compounds containing N, O or S in the ring at position 3 to the silicon atom.

The present report discusses the pyrolysis of 3,3-diethyl-2,4-dimethyl-3-silathietane (I) — the first representative of compounds of 3-silathietane series [10].

Results

Figure 1 shows the decomposition curve showing a decrease in I as the pyrolysis temperature is increased. The chromatograms of pyrolysis products

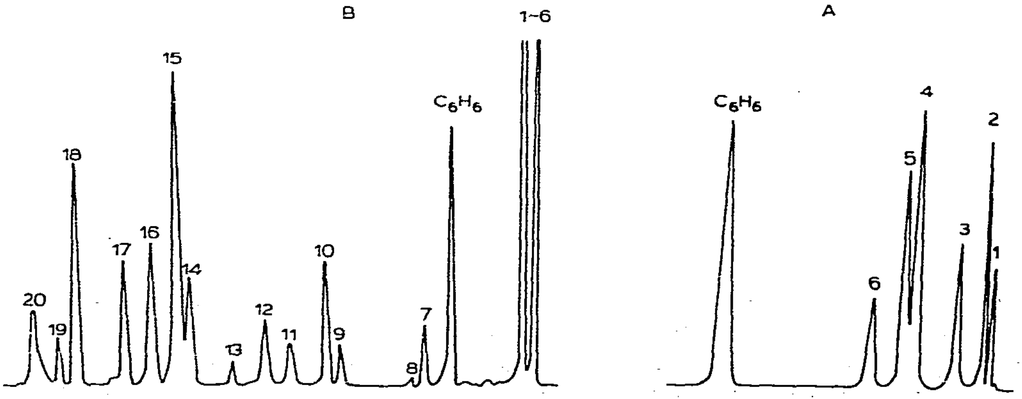


Fig. 2. GC of 3,3-diethyl-2,4-dimethyl-3-silathietane pyrolysis products at 510°C. Columns: A, alumina; B, 7% E-301; temperature programming (6°C/min) from 25°C; peaks 3 and 6 have been magnified by 3 times, 7-12 and 17-20- by 10 times; peaks 1 and 2 have been reduced by 3.3 times, peak 16 by 3 times.

TABLE 1

COMPOSITION AND TYPE OF IONS IN THE MASS SPECTRA OF PULSE PYROLYSIS PRODUCTS OF I AT 510°C

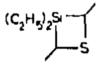
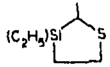
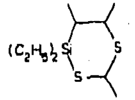
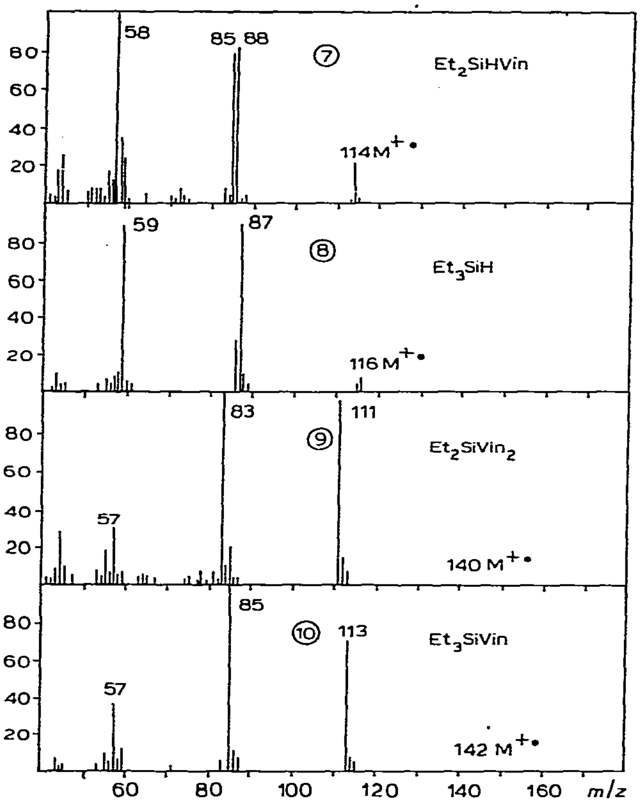
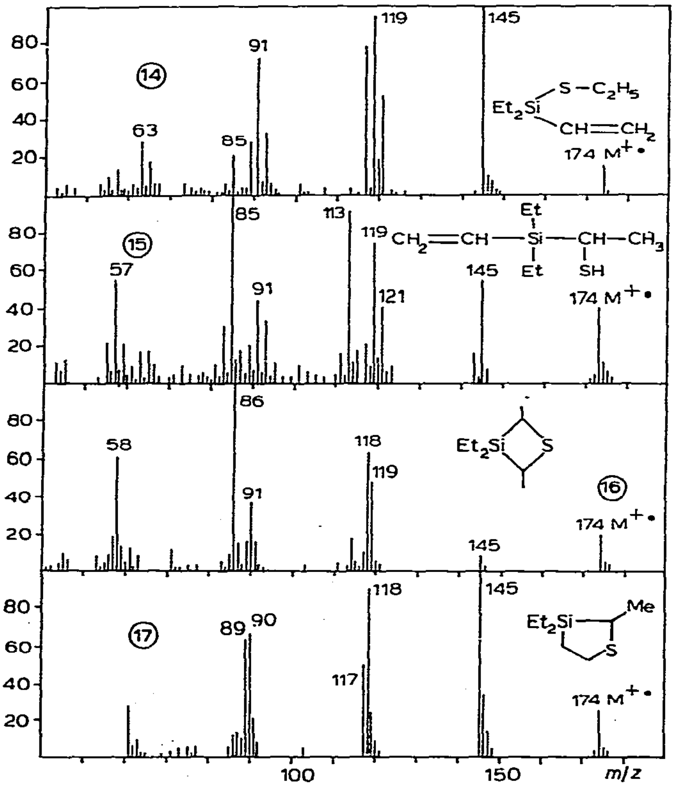
Peak number	*m/z*	Relative intensity	Composition	Ion type	Deduced structure of product
7	114	20	$[C_6H_{14}Si]^{+\cdot}$	$M^{+\cdot}$	$(C_2H_5)_2Si(H)CH{=}CH_2$
	86	82	$[C_4H_{10}Si]^{+\cdot}$	$[M-C_2H_4]^{+\cdot}$	
	85	78	$[C_4H_9Si]^+$	$[M-C_2H_5]^+$	
	57	100	$[C_2H_5Si]^+$	$[M-C_2H_5-C_2H_4]^+$	
8	116	7	$[C_6H_{16}Si]^{+\cdot}$	$M^{+\cdot}$	$(C_2H_5)_3SiH$
	115	4	$[C_6H_{15}Si]^+$	$[M-H]^+$	
	87	81	$[C_4H_{11}Si]^+$	$[M-C_2H_5]^+$	
	59	100	$[C_2H_7Si]^+$	$[M-C_2H_5-C_2H_4]^+$	
9	140	—	$[C_8H_{16}Si]^{+\cdot}$	$M^{+\cdot}$	$(C_2H_5)_2Si(CH{=}CH_2)_2$
	111	93	$[C_6H_{11}Si]^+$	$[M-C_2H_5]^+$	
	83	100	$[C_4H_7Si]^+$	$[M-C_2H_5-C_2H_4]^+$	
10	142	2	$[C_8H_{18}Si]^{+\cdot}$	$M^{+\cdot}$	$(C_2H_5)_3SiCH{=}CH_2$
	113	72	$[C_6H_{13}Si]^+$	$[M-C_2H_5]^+$	
	85	100	$[C_4H_9Si]^+$	$[M-C_2H_5-C_2H_4]^+$	
	57	33	$[C_2H_5Si]^+$	$[M-C_2H_5-2\ C_2H_4]^+$	
14	174	17	$[C_8H_{18}SiS]^{+\cdot}$	$M^{+\cdot}$	$(C_2H_2)_2(CH_2{=}CH)SiSC_2H_5$
	145	100	$[C_6H_{13}SiS]^+$	$[M-C_2H_5]^+$	
	121	54	$[C_4H_{13}SiS]^+$	$[M-C_4H_5]^+$	
	119	97	$[C_4H_{11}SiS]^+$	$[M-C_2H_5-C_2H_2]^+$	
	117	79	$[C_4H_9SiS]^+$	$[M-C_2H_5-C_2H_4]^+$	
	91	74	$[C_2H_7SiS]^+$	$[M-C_2H_5-C_2H_2-C_2H_4]^+$	
15	174	12	$[C_8H_{18}SiS]^{+\cdot}$	$M^{+\cdot}$	$(C_2H_5)_2(CH_2{=}CH)SiCH(SH)CH_3$
	173	40	$[C_8H_{17}SiS]^+$	$[M-H]^+$	
	145	52	$[C_6H_{13}SiS]^+$	$[M-C_2H_5]^+$	
	119	74	$[C_4H_{11}SiS]^+$	$[M-C_2H_5-C_2H_2]^+$	
	113	92	$[C_6H_{13}Si]^+$	$[M-H-CH_3CHS]^+$	
	85	100	$[C_4H_9Si]^+$	$[M-H-CH_3CHS-C_2H_4]^+$	
	57	55	$[C_2H_5Si]^+$	$[M-H-CH_3CHS-2\ C_2H_4]^+$	
16	174	14	$[C_8H_{18}SiS]^+$	$M^{+\cdot}$	
	146	3	$[C_6H_{14}SiS]^{+\cdot}$	$[M-C_2H_4]^{+\cdot}$	
	145	9	$[C_6H_{13}SiS]^+$	$[M-C_2H_5]^+$	
	119	57	$[C_4H_{11}SiS]^+$	$[M-C_4H_7]^+$	
	118	67	$[C_4H_{10}SiS]^{+\cdot}$	$[M-C_4H_8]^{+\cdot}$	

TABLE 1 (*continued*)

Peak number	m/z	Relative intensity	Composition	Ion type	Deduced structure of product
	114	17	$[C_6H_{14}Si]^{+\cdot}$	$[M-CH_3CHS]^{+\cdot}$	
	90	35	$[C_2H_6SiS]^{+\cdot}$	$[M-C_4H_8-C_2H_4]^{+\cdot}$	
	89	56	$[C_2H_5SiS]^{+}$	$[M-C_2H_5-2\ C_2H_4]^{+}$	
	86	100	$[C_4H_8Si]^{+\cdot}$	$[M-CH_3CHS-C_2H_4]^{+\cdot}$	
	58	62	$[C_2H_6Si]^{+\cdot}$	$[M-CH_3CHS-2\ C_2H_4]^{+\cdot}$	
17	174	28	$[C_8H_{18}SiS]^{+\cdot}$	$M^{+\cdot}$	
	146	34	$[C_6H_{14}SiS]^{+\cdot}$	$[M-C_2H_4]^{+\cdot}$	
	145	100	$[C_6H_{13}SiS]^{+}$	$[M-C_2H_5]^{+}$	
	118	62	$[C_4H_{10}SiS]^{+\cdot}$	$[M-2\ C_2H_4]^{+\cdot}$	
	90	32	$[C_2H_6SiS]^{+\cdot}$	$[M-3\ C_2H_4]^{+\cdot}$	
18	234	13	$[C_{10}H_{22}SiS_2]^{+\cdot}$	$M^{+\cdot}$	
	205	52	$[C_8H_{17}SiS_2]^{+}$	$[M-C_2H_5]^{+}$	
	145	100	$[C_6H_{13}SiS]^{+}$	$[M-C_2H_5-CH_3CHS]^{+}$	
	103	77	$[C_3H_7SiS]^{+}$	$[M-C_2H_5-CH_3CHS-C_3H_6]^{+}$	
	75	65	$[CH_3SiS]^{+}$	$[M-C_2H_5-CH_3CHS-C_3H_6-C_2H_4]^{+}$	


58
85 88
⑦
$Et_2SiHVin$
114 M+•
59
87
⑧
Et_3SiH
116 M+•
83
111
⑨
Et_2SiVin_2
57
140 M+•
85
⑩
113
Et_3SiVin
57
142 M+•
80
60
40
20
60
80
100
120
140
160
m/z


119
145
91
⑭
63
85
$Et_2Si(S-C_2H_5)(CH=CH_2)$
174 M+•
85
113
119
$CH_2=CH-Si(Et)(Et)-CH(SH)-CH_3$
⑮
57
145
91
121
174 M+•
86
58
118
119
Et_2Si
S
91
⑯
174 M+•
145
118
145
Me
Et_2Si
S
⑰
89
90
117
174 M+•
80
60
40
20
100
150
m/z

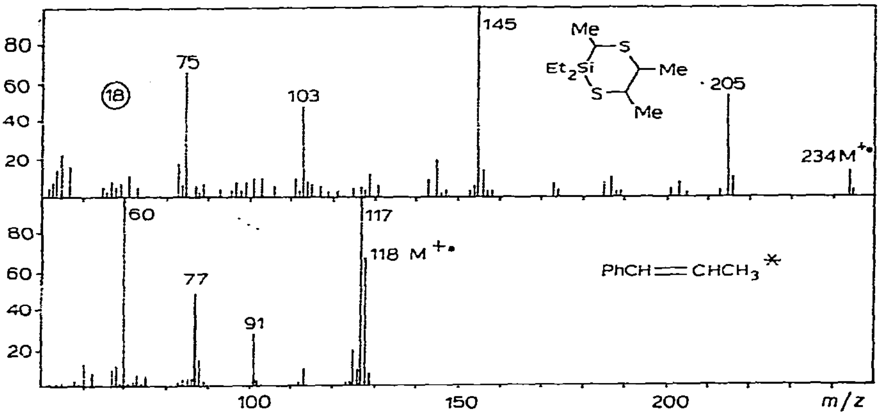


Fig. 3. Mass spectra of components shown in chromatogram in Fig. 2, and their probable structures (*Mass spectrum of β-methylstyrene formed in copyrolysis of I with benzaldehyde).

obtained by the pulse pyrolytic gas chromatography-mass spectrometry (GC-MS) method using benzene as standard are shown in Fig. 2. The gaseous products (1, ethane; 2, ethylene; 3, propylene; 4, *trans*-but-2-ene; 5, *cis*-but-2-ene; 6, buta-1,3-diene) were identified by gas chromatography. Compounds 8, 10, and 17 were identified by comparing their mass spectra with those of standard substances. The structures of products 7, 9, 14, 15, and 18 were deduced from fragmentations of ions in their mass spectra. We did not succeed in determining the structure of compounds 11—13 and 19, which are present in negligible amounts, and 20. Figure 3 shows the mass spectra of products 7—10 and 14—18, and their probable structures. The most typical ions for them and their compositions are given in Table 1. The yields of products are given in Table 2.

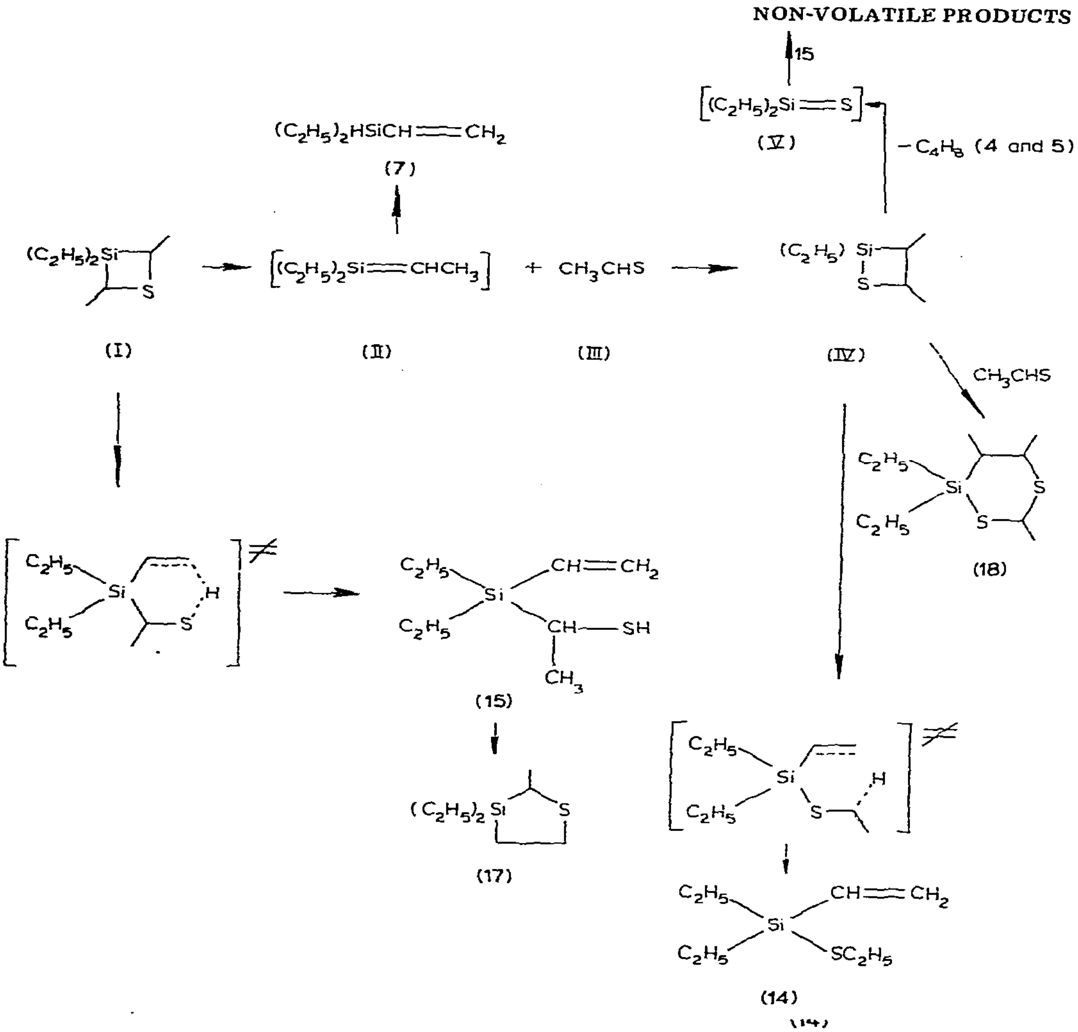
Discussion

As is seen from Fig. 1, decomposition of I starts at 440°C and conversion is practically complete at 530°C. The pyrolysis products of I may be divided into three groups. Compounds 1—10 obtained through decomposition reactions are classed into group I. Group II contains isomerization products 14, 15 and 17, and the unidentified components constitute group III.

The formation of a number of pyrolysis products can be explained (Scheme 1) in terms of initial decomposition of I "in half" into the intermediates 1,1-diethyl-2-methyl-1-silaethylene (II) and thioacetaldehyde (III). Thus, compound 7 possibly indicates an isomerization of II which is similar to that observed earlier by Kreeger and Shechter [11] upon pyrolysis of trimethylsilyldiazomethane. The intermediacy of II is confirmed also by copyrolysis of I and benzaldehyde, which yields α-methylstyrene (pseudo Wittig reaction [6,7]). Insertion into the Si—S bond of the intermediate 2,2-diethyl-3,4-dimethyl-2-silathietane (IV) yields 18. Subsequent decomposition of IV "in half" is responsible for the formation of intermediate diethylsilathione (V) and *cis*- and *trans*-but-2-enes.

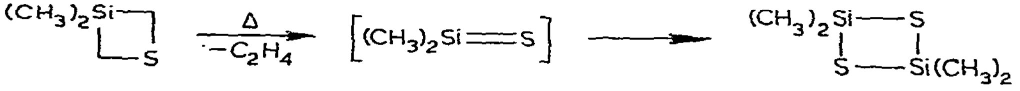
However, we did not succeed in detecting the cyclodimerization product of V, apparently due to concurrent reactions of V with thiols which are also

SCHEME 1



formed. In this respect, of much interest is the pyrolysis of 3,3-dimethyl-3-silathietane (Scheme 2) which gives rise mainly to the dimer of dimethylsilathione *.

SCHEME 2



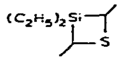
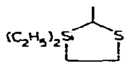
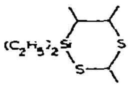
The formation of 15, to which we assign the structure of vinyldiethyl(1-mercaptoethyl)silane, is probably associated with the primary homolytic cleavage of the C—S bond in the ring of I; it is followed by 1,5-migration of a hydrogen

---

* This part of the work was carried out with E.N. Suslova.

TABLE 2

YIELD OF PRODUCTS (in moles) FOR 100 moles OF TRANSFORMED I AT 510°C (RESIDENCE TIME 12 sec, CONVERSION 65.4%) [a]

Product	Peak number	Yield
C_2H_6	1	17.3
C_2H_4	2	48.3
C_3H_6	3	3.0
trans-C_4H_8	4	19.4
cis-C_4H_8	5	17.7
C_4H_6	6	2.7
$(C_2H_5)_2SiH(CH{=}CH_2)$	7	0.72
$(C_2H_5)_3SiH$	8	0.13
$(C_2H_5)_2Si(CH{=}CH_2)_2$	9	0.62
$(C_2H_5)_3SiCH{=}CH_2$	10	2.1
Not identified	11	0.90
Not identified	12	0.94
Not identified	13	0.29
$(C_2H_5)_2Si(CH{=}CH_2)SC_2H_5$	14	17.4
$(C_2H_5)_2(CH_2{=}CH)SiCH(SH)CH_3$	15	47.4
	16	—
	17	2.0
	18	2.6
Not identified	19	0.6
Not identified	20	2.7
		186.8

[a] The yields of products 7—20 have not been corrected.

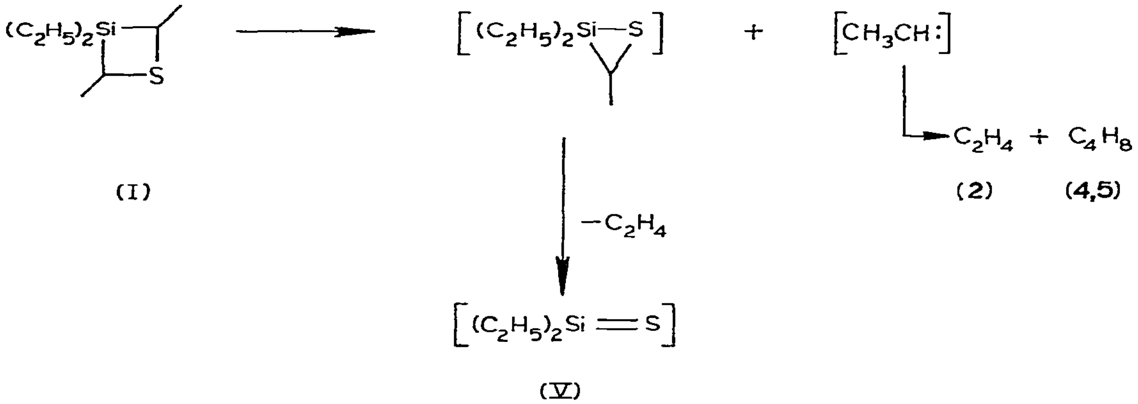
atom in a biradical. The isomer 14, which is assumed to have the structure of vinyldiethyl(ethylthio)silane, is formed in a similar manner from IV via initial cleavage of the C—C bond. Apparently, isomerization of I into 14, 15, and 17 (the latter is probably the intermolecular cyclization product of 15) proceeds more readily than a similar process that takes place upon pyrolysis of 1,1,3-trimethyl-1-silacyclobutane [13] or 1,1,2-trimethyl-1-silacyclobutane [14].

The formation of products 1—3, 6, 8—10 is not reflected in Scheme 1. In addition, large amounts of ethylene are found, which is possibly formed in two different ways. The first one involves elimination of methylcarbene which is promoted by the 1,3-transannular interaction of silicon with sulphur atoms in I; the resultant product, 2-silathiirane, decomposes further to form ethylene and V via [3 → 2 + 1]-cycloelimination (Scheme 3). The other way involves decomposition of a $C_2H_5^{\cdot}$ radical. The large amount of ethane formed suggests involvement of ethyl radicals in the pyrolysis of I.

The mechanism of the formation of butadiene is less obvious and is probably associated with secondary decomposition of 14 and 15.

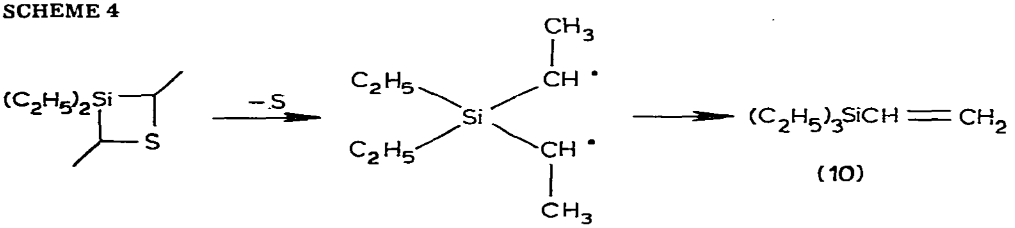
Among the products 7—10 formed by the loss of the sulphur atom, triethyl-

SCHEME 3



vinylsilane is the main constituent and is formed as a result of biradical intramolecular disproportionation (Scheme 4).

SCHEME 4



The yields of the products, which are given in Table 2, were used to estimate the contribution of isomerisation and decomposition processes upon pyrolysis of I. One hundred moles of I were found to be required to produce 186.8 moles of volatile pyrolysis products at 510°C. This includes 78.4 moles of silicon-containing products (11—13, 14 and 20), of which 66.8 moles (85%) are accounted for by 14, 15 and 17 isomers of I. Taking into consideration that the total amount of C_2—C_4 products amounts to 108.4 moles, it may be concluded that the silicon-containing decomposition products of I are mainly used to form non-volatile products that cannot be detected by GLC.

A certain correlation exists between pyrolysis and electron impact fragmantation processes of I [15]. An intense peak from the rearrangement of the diethylsilathione ion, m/z 118, which is formed by the loss of C_4H_8 from the molecular ion, is observed in the mass spectrum of I [15]. Besides, cleavage of the four-membered ring "in half" gives rise to 1,1-diethyl-2-methyl-1-silaethylene ion, m/z 114, and acetaldehyde. Another rearrangement ion, m/z 119 ($Et_2\overset{+}{S}iSH$) is also abundant in the mass spectrum of I. Although a similar decomposition is not observed upon pyrolysis, it suggests a hydrogen atom migration from the methyl group to sulphur.

Experimental

Materials

3,3-Diethyl-2,4-dimethyl-3-silathietane synthesized by the procedure described in the literature [10] is a mixture of *E* and *Z* isomers in the ratio 1 : 1.

Pyrolysis

Pyrolysis of I was studied in a quartz pulse microreactor 27 cm long and 0.9 cm in diameter which was a part of a chromatographic system consisting of two chromatographic columns and two flame ionization detectors connected in parallel (through a flow divider). The pyrolysis products C_1—C_6 (right up to benzene which was used as internal standard) were isolated on a column (3 mm X 3 m) packed with alumina. A similar column packed with 7% E-301 was used for separating the remaining components.

The second column was used also when pyrolysis of I was studied by pyrolytic GC-MS with a LKB 2091 instrument.

References

1 D.A. Bitter and W.D. Walters, J. Amer. Chem. Soc., 77 (1955) 1429.
2 A. Jones and P.P. Lossing, J. Phys. Chem., 71 (1967) 4111.
3 V.V. Volkova, L.E. Gusel'nikov, V.N. Perchenko, V.G. Zaikin, E.I. Eremina and N.S. Nametkin, Tetrahedron Lett., (1978) 577.
4 L.E. Gusel'nikov and N.S. Nametkin, Chem. Revs., 79 (1979) 529.
5 C.M. Golino, R.D. Bush and L.H. Sommer, J. Amer. Chem. Soc., 96 (1974) 614.
6 C.M. Golino, R.D. Bush, D.W. Roark and L.H. Sommer, J. Organometal. Chem., 66 (1974) 29.
7 L.H. Sommer and J. McLick, J. Organometal. Chem., 101 (1975) 171.
8 N.S. Nametkin, L.E. Gusel'nikov, R.L. Ushakova, V.Yu. Orlov, O.V. Kuzmin and V.M. Vdovin, Dokl. Akad. Nauk SSSR, 194 (1970) 1096.
9 M. Riviers-Baudet, P. Riviers and J. Satge, J. Organometal. Chem., 154 (1978) C23.
10 M.G. Voronkov, T.J. Barton, S.V. Kirpichenko, V.V. Keiko and V.A. Pestunovich, Izv. Akad. Nauk SSSR, Ser. Khim., (1976) 710.
11 H.L. Kreeger and H. Shechter, Tetrahedron Lett., (1975) 2061.
12 M.G. Voronkov, S.V. Kirpichenko, E.N. Suslova and V.V. Keiko, Zh. Obsh. Khim., 50 (1980) 2387.
13 L.E. Gusel'nikov, N.S. Nametkin and N.N. Dolgopolov, J. Organometal. Chem., 169 (1979) 165.
14 T.J. Barton, G. Marquarlt, J.A. Kilgeur, J. Organometal. Chem., 85 (1975) 317.
15 L.E. Gusel'nikov,V.V. Volkova, V.G. Zaikin, N.A. Tarasenko, A.A. Tischenkov, M.G. Voronkov and S.V. Kirpichenko, J. Organometal. Chem., 215 (1981) 9.