EXPERIMENTAL

The ^1H NMR spectra were obtained on a Tesla BS-467 (60 MHz) instrument and the ^{13}C and ^{29}Si spectra on a Jeol FX-90 (90 MHz).

Reactions of (II) with unsaturated compounds were brought about by heating equimolar mixtures of reagents [containing 0.5 mole % Rhacac $(CO)_2$ in a sealed ampul for 5-10 h at 100-150°C]. The reaction products were separated by vacuum distillation.

CONCLUSIONS

1-Hydrosilatrane does not react with monosubstituted ethylenes (or acetylenes) either in the presence of platinum or rhodium complexes or upon initiation of the reactions using organic peroxides, UV irradiation, or thermal methods. By contrast, 2-methyl-6-ethyl-1,3-dioxa-6-aza-2-silacyclooctane readily takes part in hydrosilylation of the indicated unsaturated compounds when Rhacac $(CO)_2$ is present.

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PYROLYSIS OF 8,8-DIMETHYL-8-SILA-2,3,4,5-TETRATHIABICYCLO[4.3.0]NONANE

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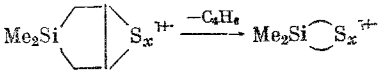
UDC 541.11:542.92:547.1'128

We have reported earlier that under electron-impact conditions the decomposition of the bicyclic silicon-containing polysulfide 8,8-dimethyl-8-sila-2,3,4,5-tetrathiabicyclo[4.3.0]-nonane (I), containing a Si atom in the ring joined to the polysulfide ring, proceeds in two directions [1]. The simpler route is the gradual elimination of the S atoms until the formation of 1,1-dimethylsilacyclopent-3-ene. Besides this, the decomposition is accompanied by a skeletal rearrangement with the ejection of C_4H_6 from the ring and migration of the S atoms to the Si atom with the formation of silacyclosulfanes and dimethylsilanethione:



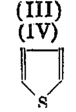
$x = 1-4.$

Based on the frequently encountered analogy between thermal and mass-spectrometric decomposition of organic compounds, we have studied the thermal decomposition of the cyclic tetrasulfide (I).

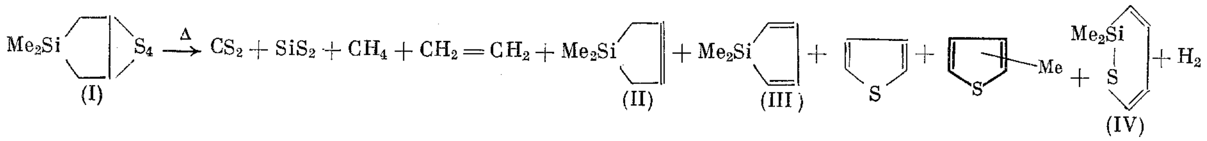
The pyrolysis of (I) was performed in a pulsed pyrolytic system with a residence time in the reaction zone of 11-13 sec. The thermolysis products were separated and identified by conventional GLC/mass spectrometry. The composition of the reaction mixtures obtained in the decomposition of the polysulfide (I) in the temperature interval 400-600°C and the characteristic ions present in the mass spectra of the pyrolysis products are given in Table 1.

A. V. Topchiev Institute of Petrochemical Synthesis, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 902-905, April, 1986. Original article submitted November 20, 1984.

TABLE 1. Composition of the Pyrolysate (%) and Characteristic Ions in the Mass Spectra of the Pyrolysis Products of Compound (I)

Pyrolysis product	Pyrolysis temp., °C			Characteristic ions, m/z
	400	500	600	
CH_4+C_2H_4	1,2	2	3	16 $M^{+\cdot}$, 28 $M^{+\cdot}$
CS_2	0,7	6	12	76 $M^{+\cdot}$, 44 $[CS]^+$
(II)	6,4	1,5	–	112 $M^{+\cdot}$, 97 $[M-CH_3]^+$
(III)	–	–	1,3	110 $M^{+\cdot}$, 95 $[M-CH_3]^+$
(IV)	2,6	4	3,8	See Fig. 1b
	–	6	14,5	84 $M^{+\cdot}$, 58 $[M-C_2H_2]^+$
2 (3)-Methylthiopene	–	–	1,5	98 $M^{+\cdot}$, 97 $[M-H]^+$
$(Me_2SiO)_{3-4}$	1	1,6	3,6	207 $[M-CH_3]^+$, 281 $[M-CH_3]^+$
Conversion, %	12,2	23	44	

It was found that the pyrolysis of compound (I) leads to the formation of the following compounds:



The thermal decomposition of compound (I) starts at 400°. The main reaction products are 1,1-dimethylsilacyclopent-3-ene (II) and 1,1-dimethyl-1-sila-2-thiacyclohexa-3,5-diene (IV), whereby the silane (II) is the product which is characteristic for the mass-spectral decomposition of the polysulfide (I). Evidently, the first pyrolysis act is the elimination of the highly reactive molecules of S_4 and the silane (II), the further interaction of which follows the scheme

$$(I) \xrightarrow{\Delta} (II) + [S_4] \rightarrow CS_2 + SiS_2 + CH_2 = CH_2 + H_2$$

Compound (IV) is generated probably by the dehydrogenation of the silane (II), followed by the reaction of the diene (III) with the active sulfur S_4 which is enhanced by the strong polarization of the Si–C bond by the action of the sulfur molecules [2]

$$(II) \xrightarrow[-H_2]{\Delta} (III) \xrightarrow{[S_4]} (IV) + [S_3]$$

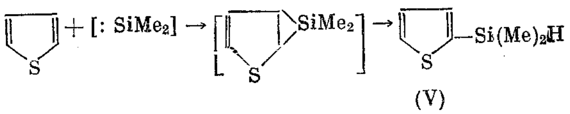
An analogous introduction of sulfur via the Si–C bond with widening of the ring has been described for silacyclobutane [3] and silacyclopropanes [4].

However, compound (IV) can be formed also by the synchronous elimination of S atoms from (I) and migration of one of the atoms to the Si atom

$$(I) \xrightarrow{\Delta} (IV) + [S_3] + H_2$$

This is supported by the negligible increase in the amount of (IV) in the mixture when the pyrolysis temperature is increased to 500° and by the further decrease in the concentration of the diene (IV) at 600°. In the case of an intermolecular formation of (IV) its content in the mixture should sharply increase with increasing temperature, due to an increase in the conversion of the polysulfide (I) as well as due to the strain imposed on the five-membered Si-containing ring.

It must be pointed out that compound (IV) is isomeric with dimethylhydrosilylthiophene (V); the appearance of this compound could be expected from the reaction of thiophene with the intermediate active particle $[Me_2Si:]$:



However, the mass spectrum of the reference sample of compound (V) (Fig. 1a), which contains the characteristic peak of $[M - H]^+$, does not correspond to the spectrum of its isomer,

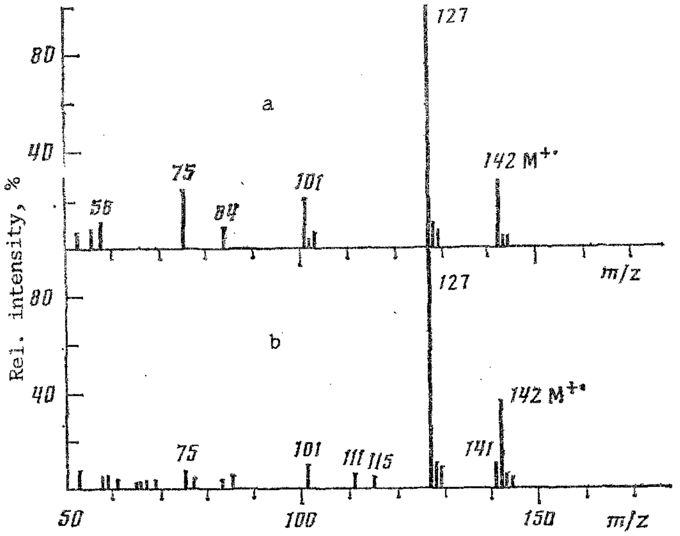
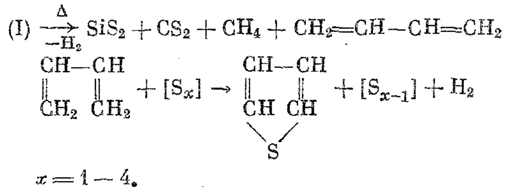


Fig. 1. Mass spectra of a) dimethylhydrosilylthiophene and b) 1,1-dimethyl-1-sila-2-thiacyclohexa-3,5-diene.

obtained in the pyrolysis (Fig. 1b); this confirms the above-mentioned mechanism of formation of (IV).

An increase in thermolysis temperature to 500 and 600° leads to a decrease in the content of (II). The yield of CS_2 sharply increases. Besides this, large amounts of thiophene are formed, and at 600° of its homolog methylthiophene. The absence of thiophene in the pyrolysis products of (I) at 400° indicates that it is generated via the intermediate formation of butadiene which reacts further with sulfur:

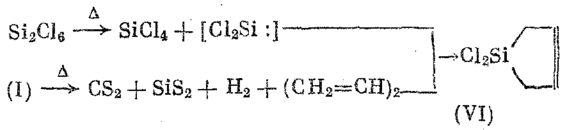


$$\text{(I)} \xrightarrow[-H_2]{\Delta} SiS_2 + CS_2 + CH_4 + CH_2{=}CH{-}CH{=}CH_2$$

$x = 1 - 4.$

The formation of methylthiophene includes obviously the migration of the methyl radical from the Si atom to one of the C atoms of the cyclopentane fragment. It must be pointed out that the amount of active sulfur formed in the course of the pyrolysis is not sufficient to convert H_2 into H_2S.

The ejection of butadiene and the attack of the Si atom by the S atoms take place synchronously, without the intermediate formation of dimethylsilylene. This is confirmed by the absence of an adduct of the active particle [Me_2Si:] with 2,3-dimethylbutadiene in the copyrolysis of the latter with (I) at 600°. The intermediate formation of butadiene in the thermal decomposition of (I) is also confirmed by the formation of 1,1-dichlorosilacyclopent-3-ene (VI) in the copyrolysis of (I) with hexachlorodisilane which decomposes above 500° into [:$SiCl_2$] and $SiCl_4$ [5]



$$Si_2Cl_6 \xrightarrow{\Delta} SiCl_4 + [Cl_2Si:]$$

$$\text{(I)} \xrightarrow{\Delta} CS_2 + SiS_2 + H_2 + (CH_2{=}CH)_2$$

(VI)

Evidently, the formation of certain amounts of thiophene from active sulfur and ethylene must not be excluded. The presence of cyclosiloxanes $(Me_2SiO)_{3-4}$ (see Table 1) among the pyrolysis products of (I) is due to the presence of traces of atmospheric oxygen in the microreactor.

It must be pointed out that SiS_2 could not be detected by mass spectrometry; it was identified as a nonvolatile, dark-gray film on the surface of the microreactor which hydrolyzed in air with the evolution of H_2S.

EXPERIMENTAL

The polysulfide (I) was synthesized according to [6]. The thermal conversions of (I) were studied with the use of a quartz pulsed microreactor (150 mm long, diameter 6 mm) in a stream of helium from which traces of water and oxygen had been removed by passage through a molecular sieve and heated copper powder. The microreactor was connected directly to the chromatographic column of an LKB-2091 GLC/mass spectrometer. The saturated solution of (I) in benzene was injected into the reactor with a 0.2-μl microsyringe through a self-sealing washer of the sample inlet.

The reaction products were separated on a stainless steel column (3m × 3mm), packed with polyethylene glycol adipate on Spherochrom as the stationary phase, and using helium as the carrier gas. The chromatograms were obtained with temperature programming (5 deg/min) from 30 to 250°; the temperature of the evaporator was 250°C. The mass spectra were recorded at an ionizing-electron energy of 70 eV, an emission current of 50 μA, and a temperature of the ion source and the molecular separator of 200°C.

CONCLUSIONS

The main products of the pyrolysis of 8,8-dimethyl-8-sila-2,3,4,5-tetrathiabicyclo-[4.3.0]nonane at 400° are 1,1-dimethylsilacyclopent-3-ene and 1,1-dimethyl-1-sila-2-thiacyclohexa-3,5-diene, and at 600° carbon disulfide and thiophene; silacyclopentene is the sole reaction product, characteristic for the mass-spectrometric decomposition of the initial tetrasulfide.

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EQUILIBRIUM CH ACIDITY OF Ni(II) COMPLEXES OF SCHIFF'S BASES OF AMINO ACIDS WITH S-2-N-(N'-BENZYLPROLYL)AMINOBENZALDEHYDE AND S-2-N-(N'-BENZYLPROLYL)AMINOBENZOPHENONE

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The CH acidity of amino acids determines many chemical properties of these compounds. Their transamination, the formation of a C—C bond, etc. occur through the intermediate formation of carbanions of amino acids in nature. The enzymes of the pyridoxal series [1-4] are responsible for these conversions. The final stage is the formation of Schiff's bases in which the α-proton of the amino acid fragment is labile and is split off under the action of bases, giving a carbanion which further reacts with electrophiles as in the following scheme [2]:

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. L. Ya. Karpov Physicochemical Institute, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 905-909, April, 1986. Original article submitted November 2, 1984.

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