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MASS SPECTROMETRIC INVESTIGATION OF SILICON-CONTAINING CYCLIC POLYSULPHIDES

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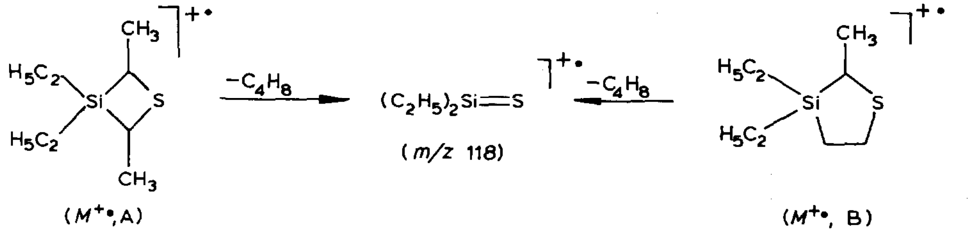
Summary

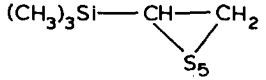
The electron impact-induced decomposition of cyclic polysulphides prepared by the cycloaddition reaction between S_x and trimethylvinylsilane (1-trimethylsilyl-2,3,4,5,6-pentathiacycloheptane (I), 1-methyl-3-trimethylsilyl-2,5-dithiacyclopentane (II), 1,4-di(trimethylsilyl)-2,3,6-trithiacycloheptane (III), 1,4-di(trimethylsilyl)-2,3,6,7-tetrathiacyclooctane (IV) and 1,1-dimethyl-1-silacyclopentene (8,8-dimethyl-8-sila-2,3,4,5-tetrathiabicyclo[4.3.0]nonane (V), 6,6,13,13-tetramethyl-6,13-disila-2,3,9,10-tetrathiatricyclo[9.3.0.$0^{4,8}$]tetradecane (VI) and 7,7,14,14-tetramethyl-7,14-disila-2,3,4,10,11-pentathiatricyclo[10.3.0.$0^{5,9}$]pentadecane (VII)) has been studied. The major fragmentation pathway of the compounds I–IV, containing a silicon atom in the side chain trimethylsilyl group, results in the formation of the $[(CH_3)_3SiCHCH_2S]^{+\cdot}$ ions. Skeletal rearrangements associated with the migration of sulphur atoms to silicon and the loss of C_4H_6 appeared to be characteristic of polysulphides V–VII which contain silicon atom in annelated cycle. The $[(CH_3)_2SiS_2]^{+\cdot}$ and $[(CH_3)_2Si{=}S]^{+\cdot}$ ions are the final products of the rearrangements.

Introduction

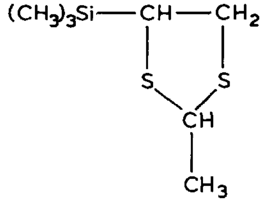
Recently [1,2], some of us have shown that the cycloaddition reaction between S_8 and linear or cyclic olefins in the presence of $Fe_3(CO)_{12}$ resulted in the formation of cyclic polysulphides. In particular, polysulphides I–IV and V–VII were obtained from trimethylvinylsilane and 1,1-dimethyl-1-sila-3-cyclopentene, respectively. From theoretical and practical points of view, it was of interest to study the behaviour of these polysulphides under electron impact conditions since the presence of silicon and sulphur atoms in the same molecule could lead to skeletal rearrangements whose recognation is necessary for rational interpretation of the mass spectra. Recent examples of such rearrangements were found in the case of 1,1-diethyl-2,4-dimethyl-1-sila-3-thiacyclobutane (A) and 1,1-diethyl-2-methyl-1-sila-3-thiacyclopentane (B), the molecular ions of which readily lose a C_4H_8 molecule at the expense of cyclic carbon atoms to yield the diethylsilathione ion-radical [3,4]:



The present paper discusses the electron impact mass spectra of polysulphides I–VII having a silicon atom out of the sulphur-containing cycle.



(I)



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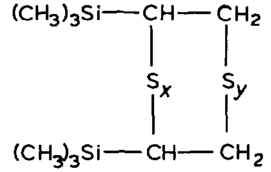
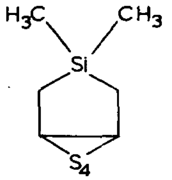


(III : $x = 2$, $y = 1$;
IV : $x = 2$, $y = 2$)



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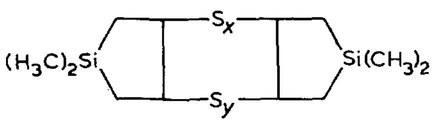


(VI : $x = y = 2$;
VII : $x = 2$, $y = 3$)

Results and discussion

The compounds under study may be subdivided into two groups. The first group includes the monocyclic polysulphides I–IV containing a silicon atom in the side chain trimethylsilyl group. The second one includes bi- (V) and tri-cyclic compounds (VI, VII) containing a silicon atom in an annelated ring. The mass spectral data for compounds I–IV obtained at 70 eV are given in Table 1. The 70 eV mass spectra of compounds V–VII are presented in Fig. 1. Metastable ions corresponding to some characteristic transitions for compounds I–VII are given in Table 2.

The mass spectra of the polysulphides I–IV prepared from trimethylvinylsilane show pronounced $M^{+\cdot}$ peaks and the base peaks for the $(CH_3)_3Si^+$ (m/z 73) ions characterising the side chain trimethylsilyl group. It is interesting to note that the $[M - CH_3]^+$ ions arising usually at the expense of the $(CH_3)_3Si$ group are insignificant or absent at all in these cases.

Under electron impact, all the compounds I–IV afford the common characteristic ion of mass 132 (**a**) corresponding to formula $(CH_3)_3SiC_2H_3S$. The ions **a** can have a number of structures among which the structures of trimethylsilylthiirane, trimeth-

TABLE 1

CHARACTERISTIC IONS IN THE MASS SPECTRA OF CYCLIC POLYSULPHIDES I–IV (m/z, relative abundance in %)

Ions	I	II	III	IV
$M^{+\cdot}$	260(13)	192(16)	296(6)	328(3)
$[M-\mathrm{CH_3}]^+$	–	177(2)	281(1)	–
$[M-\mathrm{S}]^+$	228(2)	–	–	–
$[M-2\mathrm{S}]^+$	196(81)	–	–	–
$[M-3\mathrm{S}]^+$	164(12)	–	–	–
$[M-\mathrm{S_2CH{=}CH_2}]^+$	–	–	205(8)	–
$[M-\mathrm{Me_3SiCHCH_2(S)}]^+$	–	–	164(6)	196(26)
$[M-2\mathrm{S}-\mathrm{CH_3}]^+$	181(2)	–	–	–
$[M-2\mathrm{S}-\mathrm{Me_3Si}]^+$	123(9)	–	–	–
$[M-\mathrm{Me_3SiCH{=}CH_2}-\mathrm{CH_3}]^+$	–	–	149(4)	–
$[\mathrm{Me_3SiCHCH_2(S)}]^{+\cdot}$ (**a**)	132(98)	132(37)	132(12)	132(42)
$[\mathrm{Me_2\overset{+}{Si}CHCH_2(S)}]$	117(27)	117(21)	117(14)	117(15)
$[\mathrm{CH_2CHS_2}]^+$	91(16)	91(4)	91(32)	91(15)
$[\mathrm{Me_2SiCH{=}CH_2}]^+$	85(12)	85(3)	85(10)	85(7)
$[\mathrm{Me_3Si}]^+$	73(100)	73(100)	73(100)	73(100)
$[\mathrm{S_2}]^+$	64(42)	–	–	–
$[\mathrm{CH_2CHS}]^+$	59(52)	59(14)	59(13)	59(17)
$[\mathrm{CH{=}S}]^+$	45(73)	45(14)	45(13)	45(18)

ylsilylthioacetaldehyde and methyl(trimethylsilyl)thioketone seem to be most probable.

In the case of I, the ion **a** may arise both from successive elimination of four sulphur atoms and the two-stage loss of S_2 from the molecular ions. Elimination of

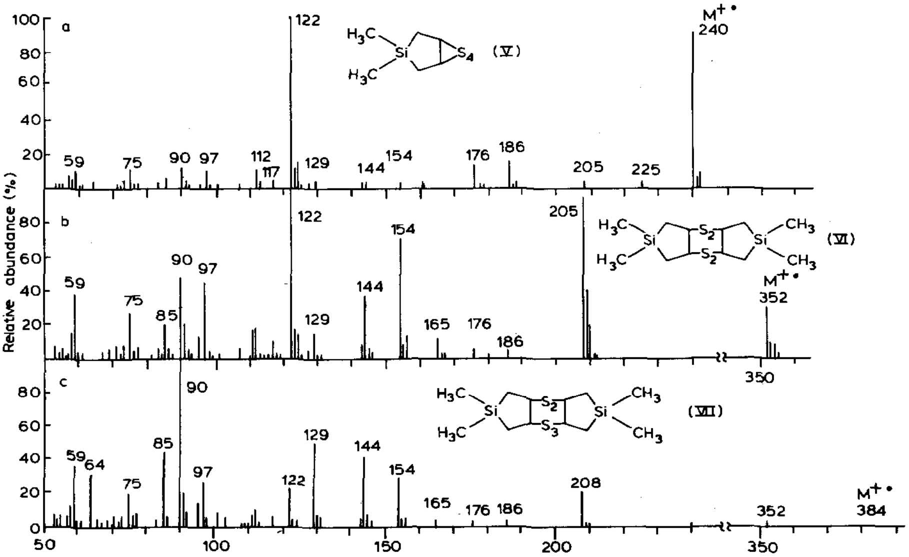
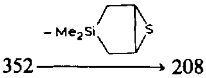


Fig. 1. The mass spectra of: a) 8,8-dimethyl-8-sila-2,3,4,5-tetrathiabicyclo[4.3.0]nonane; b) 6,6,13,13-tetramethyl-6,13-disila-2,3,9,10-tetrathiatricyclo[9.3.0.0^{4,8}]tetradecane; c) 7,7,14,14-tetramethyl-7,14-disila-2,3,4,10,11-pentathiatricyclo[10.3.0.0^{5,9}]pentadecane.

TABLE 2

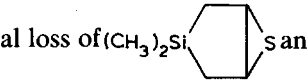
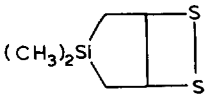
METASTABLE TRANSITIONS OBSERVED IN THE MASS SPECTRA OF POLYSULPHIDES I–VII

Compound	Observed m^*	Transition
I	147.7	$260 \xrightarrow{-2S} 196$
	103.4	$260 \xrightarrow{-3S} 164$
	88.9	$196 \xrightarrow{-2S} 132$
II	90.8	$192 \xrightarrow{-CH_3CHS} 132$
III	142.0	$296 \xrightarrow{-S_2CH{=}CH_2} 205$
	90.9	$296 \xrightarrow{-Me_3SiCHCH_2S} 164$
IV	117.1	$328 \xrightarrow{-Me_3Si\text{-}CHCH_2S} 196$
	88.9	$196 \xrightarrow{-S_2} 132$
	40.4	$132 \xrightarrow{-CHCH_2S} 73$
V	144.2	$240 \xrightarrow{-C_4H_6} 186$
	129.0	$240 \xrightarrow{-S_2} 176$
	84.6	$176 \xrightarrow{-C_4H_6} 122$
VI	122.9	
	114.0	$208 \xrightarrow{-C_4H_6} 154$
VII	114.0	$208 \xrightarrow{-C_4H_6} 154$
	115.6	$144 \xrightarrow{-CH_3} 129$

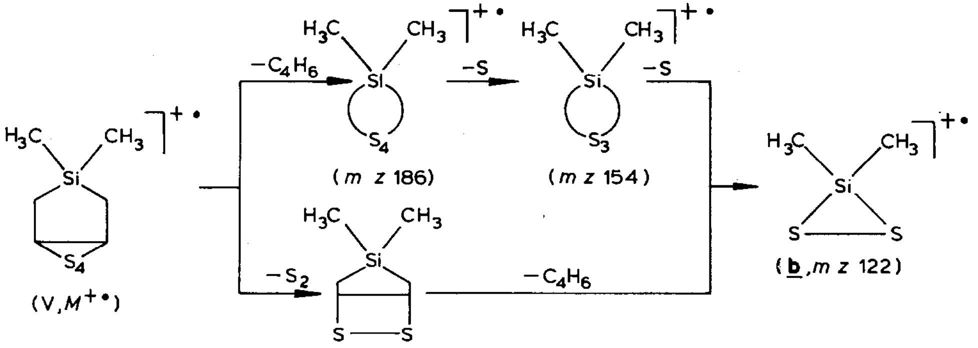
thioacetaldehyde is the only fragmentation path of the compound II leading to the ion **a**. For the polysulfides III and IV, this ion may originate directly from the molecular ions. In this series, however, another process is realized which involves the initial loss of the neutral species $(CH_3)_3SiC_2H_3S$ (the formation of the *m/z* 164 and 196 ions, respectively) followed by the elimination of S and S_2 respectively.

It should be noted that no pronounced skeletal rearrangements are encountered in the fragmentation of the compounds I–IV. The formation of the ions $[\mathbf{a} - CH_3]^+$ (*m/z* 117), $[C_2H_3S_2]^+$ (*m/z* 91), $(CH_3)_2\overset{+}{Si}CH{=}CH_2$ (*m/z* 85), $[C_2H_3S]^+$ (*m/z* 59) and $[CHS]^+$ (*m/z* 45) may be also due to simple cleavages.

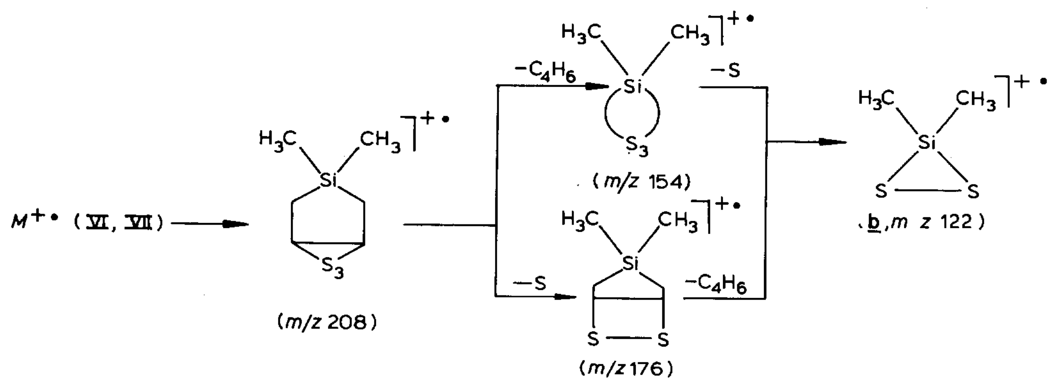
A comparison of the mass spectra of compounds V–VII (Fig. 1) shows that they are qualitatively similar to each other below the peak at *m/z* 208. This gives evidence that their main fragmentation pathways are identical. The stability of the molecular ion is the highest for bicyclic polysulfide V and decreases sharply for the tricyclic compounds VI and VII.

The simplest fragmentation mode of V involves the stepwise elimination of four sulphur atoms from the molecular ion to yield the ions of masses 208, 176, 144 and 112. The same peaks are also observed in the mass spectra of compounds VI and VII. In this case, however, their occurance is due to initial loss of  and  from the molecular ions, respectively.

An interesting feature of the electron impact-induced fragmentation of V–VII (containing silicon and sulphur atoms in the neighbouring cycles) is the skeletal rearrangement associated with the transfer of sulphur to the silicon atom and the loss of a hydrocarbon species C_4H_6 from cycle. In the case of V, such a rearrangement is realized both in the molecular ion and in the $[M - S_2]^{+\cdot}$ (m/z 176) ion. The ion of mass 186 thus formed in the former case readily eliminates two sulphur atoms. The two parallel processes give rise to the ion **b** (m/z 122), which is the base peak in the spectrum of V:



The ion **b** (m/z 122) is also the base peak in the spectrum of VI and is of moderate intensity in the spectrum of VII. It is likely that two pathways lead to this ion starting from the ion of mass 208:



Ion **b** undergoes further decomposition due to the loss of a sulphur atom giving rise to the dimethylsilathione ion-radical $[(CH_3)_2Si{=}S]^{+\cdot}$ (m/z 90). Differences in the intensity of this ion in the spectra of compounds V–VII suggests that the dimethylsilathion ion-radical may originate from such a process but also from other fragmentation pathways.

The lower mass ranges of the spectra of V-VII demonstrate the pronounced ions $[S_2SiCH_3]^+$ (m/z 107) and $CH_3\overset{+}{S}i{=}S$ (m/z 75) which are also formed from ions **b**.

Experimental

Syntheses of compounds I–IV was reported previously [1,2]. Syntheses of compounds V–VII will be published elsewhere. The compounds studied (except II) were obtained as crystalline solids, which after recrystallization (ethanol) had m.p. 59 (I), 80 (III), 138 (IV), 84.5–85 (V), 192–193 (VI) and 194–195°C (VII). Compound II had b.p. 62–63°C/1 Torr, n_D^{20} 1, 5150.

The mass spectra were obtained on an LKB-2091 instrument by using the direct inlet system for I and III–VII (evaporation temp. 50–100°C) and the heated inlet system for II at 200°C. The operating conditions were 70 and 12 eV electron energy, 25 μA emission current and 200°C ionization chamber temperature.

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