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Abstract

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MASS SPECTRA AND STRUCTURE OF SILICON-CONTAINING VINYLACETYLENES

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The study of the mass spectra of vinylacetylene and its homologs made it possible to establish a relationship between the intensities of the molecular and certain fragment ions and the structure of the hydrocarbons (^{1}).

In the spectra of vinylacetylene and its nearest homologs, the molecular ions have the greatest intensity. With an increase in the alkyl radicals, a sharp decrease in the intensity of the molecular ion and an increase in the intensity of fragment ions are observed; among these, the ion with mass 39 attracts attention. In the spectra of all enyne hydrocarbons not containing a tert-butyl radical, two maxima are observed for the ions $C_3H_x^+$ and $C_6H_x^+$. Enyne hydrocarbons containing a tert-butyl radical decompose differently under the influence of electron impact. If it is located at a double bond in the β-position to a triple bond, then an intense $C_4H_9^+$ ion with mass 57 appears in the spectrum. When a tert-butyl radical is present at a triple bond, its cleavage does not occur. The principal direction of the decomposition process of the molecular ion becomes the successive detachment of methyl groups.

In light of these data, the study of the mass spectra of enyne silicon hydrocarbons was of undoubted interest. We investigated the mass spectra of four silicon-containing enynes: 1-trimethylsilylbut-3-yn-1-ene (I), 1-trimethylsilyl-3-methylbut-3-yn-1-ene (II), 1-trimethylsilylpent-3-yn-1-ene (III), and 1-triethylsilylbut-3-yn-1-ene (IV).

In contrast to vinylacetylene hydrocarbons, the process of dissociative ionization of their silicon-containing analogs proceeds in an exclusively selective manner (Table 1).

The molecule of trimethylsilylbutenyne (I), under the influence of electron impact, undergoes decomposition predominantly with cleavage of one methyl radical: the molecular ion with mass 124 has a low intensity, whereas the ion with mass 109 accounts for 48% of the total ion current

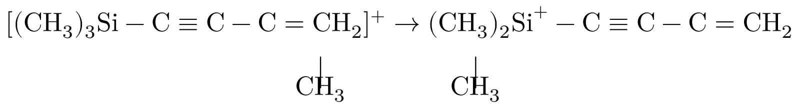
$$[(CH_3)_3Si - C \equiv C - CH = CH_2]^+ \longrightarrow (CH_3)_2Si^+ - C \equiv C - CH - CH_2$$

124 (13.5%) 109 (100%)

Further decomposition proceeds with the formation of silicon-containing ions with masses 93, 83, 81, 79, 69, and 55 and intensities from 3 to 15%, by successive cleavage of CH, CH_2, or CH_3 groups. The presence of silicon in the indicated ions is beyond doubt, since in the spectrum each of them corresponds to a characteristic grouping of peaks associated with the presence of three isotopes of silicon.

The decomposition of the two nearest homologs of (I), silicon hydrocarbons (II) and (III), proceeds according to an analogous scheme: the most stable ions for both homologs proved to be the ions with mass 123, arising upon cleavage from the molecular-

of a methyl radical from the molecular ion



$$[(CH_3)_3Si - C \equiv C - \underset{\overset{|}{CH_3}}{C} = CH_2]^+ \rightarrow (CH_3)_2Si^+ - C \equiv C - \underset{\overset{|}{CH_3}}{C} = CH_2$$

138 (7.8%) 123 (100%)

$$[(CH_3)_3Si{-}C \equiv C{-}CH = CH{-}CH_3]^+ \rightarrow (CH_3)_2Si^+{-}C \equiv C{-}CH = CH{-}CH_3$$

138 (5.4%) 123 (100%)

Further decomposition in the case of (II) and (III) is even less pronounced than in the case of (I): ions of mass 123 account for 68–71% of the total ion intensity.

In the spectrum of the saturated analog of (I)—trimethylbutylsilane—the most intense ions are $(CH_3)_3Si^+$ with mass 73. Decomposition with elimination of methyl groups is expressed much more weakly; this direction of decomposition is represented in the spectrum by $(CH_3)_2Si^+H$ ions with mass 59. The remaining ions in the spectrum of trimethylbutylsilane have very low intensity.

Table 1

Mass spectra of enynylsilanes *

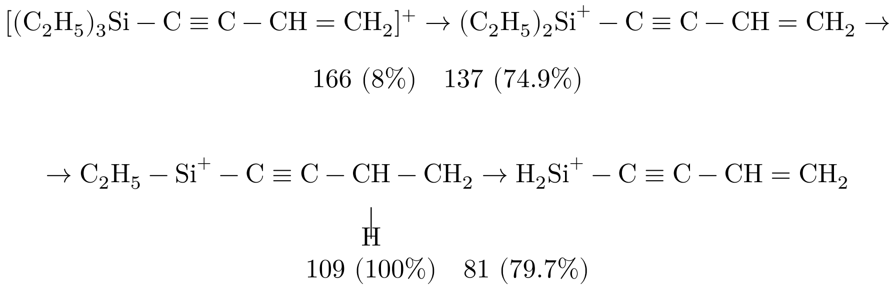
Ion masses	(I)	(II)	(III)	(IV)	Ion masses	(I)	(II)	(III)	(IV)
15	1,1	–	–	–	80	–	–	–	6,6
26	–	–	–	2,6	81	3,5	–	–	79,7
27	–	–	–	7,4	82	–	–	–	7,9

Ion masses	(I)	(II)	(III)	(IV)	Ion masses	(I)	(II)	(III)	(IV)
28	2,7	–	–	8,3	83	7,7	1,8	2,2	5,6
29	–	–	1,2	6,1	93	2,9	1,9	1,0	2,4
39	1,1	–	–	2,0	95	1,0	–	2,0	2,4
41	–	–	–	5,3	97	–	3,2	–	–
42	1,1	–	–	–	107	1,0	1,1	–	4,4
43	15,1	–	–	10,4	108	–	–	–	1,9
44	3,3	–	6,5	4,3	109	100,0	–	–	100,0
45	1,7	1,2	–	–	110	3,8	–	–	11,5
46	–	–	1,3	–	111	–	–	–	3,8
53	10,7	3,2	3,4	18,3	121	–	5,3	–	–
54	1,3	–	–	5,5	122	–	5,6	–	–
55	5,4	1,8	1,2	18,4	123	–	100,0	100,0	–
56	–	–	–	1,9	124	13,5	–	3,6	–
57	–	–	–	5,5	125	1,1	–	–	–
66	2,7	1,2	–	1,4	137	–	–	–	74,9
67	6,6	4,5	2,7	4,9	138	–	7,8	5,4	7,8
69	14,0	2,4	3,1	13,7	139	–	–	–	2,8
77	2,6	–	–	3,0	166	–	–	–	8,0
79	6,4	–	–	20,2					

* The table does not include ionic peaks with intensities below 1%.

The mass spectrum of triethylsilylbutenyne (IV) is characterized by a deeper process of decomposition of the molecular ion. The most intense in the spectrum (IV) are silicon-containing ions with masses 137, 109, and 81.

The main direction of the dissociative ionization process of (IV) can be expressed by the scheme:



$$[(C_2H_5)_3Si - C \equiv C - CH = CH_2]^+ \rightarrow (C_2H_5)_2Si^+ - C \equiv C - CH = CH_2 \rightarrow$$

166 (8%) 137 (74.9%)

$$\rightarrow C_2H_5 - Si^+ - C \equiv C - \underset{\overset{|}{H}}{CH} - CH_2 \rightarrow H_2Si^+ - C \equiv C - CH = CH_2$$

109 (100%) 81 (79.7%)

Ions 166, 137, 109, and 81 account for 55% of the total ion current.

As can be seen from the schemes presented, the initial stage of dissociation for all silicon-containing vinylacetylenes is the same: an alkyl radical is split off from the silicon atom. Further, in the case of (IV), successive elimination of ethylene molecules occurs.

The validity of the proposed decomposition scheme for (IV) is confirmed by the detection in the spectrum of the corresponding metastable ions. As is known, the presence of the latter may serve as evidence for definite stages of the decomposition process.

The decomposition $C_8H_{13}Si^+ \to C_6H_9Si^+$ should be accompanied by the formation of a metastable ion with fractional mass 86.7 $\left(m_A^* = \frac{m^2}{m_i}\right)$ (^{6}). Indeed, in the spectrum of (IV) there is a peak at 86.7 with an intensity of 1.3% of the maximum.

The decomposition $C_6H_9Si^+ \to C_4H_5Si^+$ gives an ion present in the spectrum with mass 60.1 and intensity 0.7%.

It is interesting to note that in the decomposition of (IV) an ion of mass 109 is formed, apparently isomeric with the ion of the same mass arising in the dissociation of (I). The transformations observed in the interaction of silicon-containing enynes with electrons have a certain similarity to some chemical reactions of tetraalkylsilanes. In the thermal cracking of tetraalkylsilanes, formation of trialkylsilanes and olefins is observed (^{3},^{4}). Under the action of sulfuric acid on organosilicon compounds containing $(CH_3)_3Si$ groups, one methyl group is split off (^{5}).

Comparison of the mass spectra of enynic hydrocarbons and their silicon-containing analogs makes it possible to establish certain analogies and differences associated with the replacement of carbon by silicon.

tert-Butyl and trimethylsilyl radicals at the triple bond behave identically; they are not split off as a whole, and decomposition proceeds with detachment of methyl groups. However, in the case of silicon hydrocarbons, predominantly one methyl group is detached, and the most intense ions in the spectrum are those whose formation is accompanied by hydrogen migration. In the case of similarly constructed enynic hydrocarbons, the demethylation process is not limited to one methyl group, but proceeds further and is accompanied by dehydrogenation with formation of the ion $C_7H_7^+$, which apparently has the structure of the tropylium ion (^{6}).

If the molecule contains no multiple bonds (for example, trimethylbutylsilane and 2,2-dimethylhexane), then processes of elimination of trimethylsilyl and tert-butyl radicals take place.

All the trialkylsilylalkenynes investigated were prepared from trialkylchlorosilanes and magnesium bromovinylacetylenes by M. D. Stadnichuk, for which the authors express their gratitude to him.

The investigation was carried out on an MS-1 instrument with the previously described improvements.

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