*Polish J. Chem.*, **75**, 429–441 (2001)

# Mass Spectrometric Investigation of Tautomers of N-Substituted 4-Iminopentan-2-ones in the Gas Phase*

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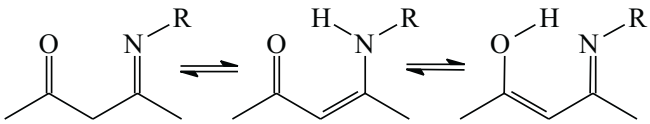
*(Received September 11th, 2000; revised manuscript November 29th, 2000)*

Mass fragmentation of 4-iminopentan-2-one N-substituted with organosilicon group suggests that in the gas phase upon electron ionization (EI) conditions only 4-imino-2-keto tautomer occurs. The simultaneous occurrence of 4-aminopent-3-en-2-keto tautomeric form was ruled out on the basis of mass fragmentation of some alkylaromatic derivatives of 4-aminopent-3-en-2-one.

**Key words:** tautomer investigation, electron ionization mass spectrometry, ketoimine

Selective stationary phases for complexation gas chromatography have recently been intensively examined [1,2]. The problem of their preparation is the modification of silica with silanes having both alkoxy groups (*i.e.* – $OC_2H_5$) and groups capable of specific, characterized by electron–donor properties interactions with adsorbate molecules. Bidentate Schiff bases, *e.g.* N-substituted with silyl groups iminoketonate derived from acetyloacetone have been successfully used as chemically bonded chelates [3].

Iminoketonate can coexist in three tautomeric forms (*a-c*).



(*a*) (*b*) (*c*)

In complexation gas chromatography, the separation mechanism consists in the formation of metastable complexes either of organic type or with cations of transition metals. In this case it is necessary to determine, which of the tautomeric forms is dominant. In solutions, only 4-aminopent-3-en-2-one (tautomer *b*) has been found to occur commonly [4]. Also tautomer (b) is present in the crystalline state, if R is an aromatic substituent [5]. Yet in the gas phase, on the ground of electron ionization mass spectra, tautomer (a) has been found to occur commonly [6].

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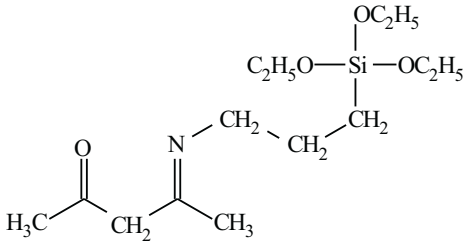
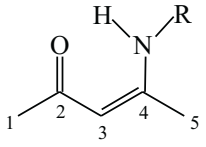
* In memory of Adam S. Płaziak (1948–1998).
Mass Spectrometric Behaviour of Acyclic Polydentate Ligands and Its Complexes. Part III. For parts I and II see [6] and [8], respectively.

In this paper results of EI mass spectrometric behavior of 4-(3-triethoxysilylpropylimino)pentan-2-one (compound **1**) are given. Compound **1**

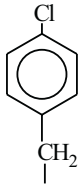


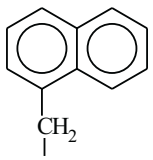
is used for preparing phases for complexation gas chromatography. Our previous research proved that mass spectrometry is a proper method to determine the structure of tautomers [6]. For rejection or confirmation of possibility of the formation of tautomer (b) we have examined model compounds with a series of alkylaromatic derivatives of 4-aminopent-3-en-2-one (compounds **2**–**6**):

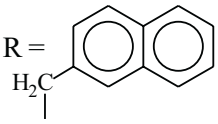


**2**. R = 

**3**. R = 

**4**. R = 

**5**. R = 

**6**. R = 

## RESULTS AND DISCUSSION

Low-resolution mass spectra of triethoxysilylalkyl derivates of ketoimine (compound **1**) and alkylaromatic derivatives of 4-aminopent-3-en-2-one as the model compounds (compounds **2**–**6**) are shown in Figure 1. High-resolution data are presented in Table 1. The spectra of metastable ions are summarized in Table 2.

For the evaluation of fragmentation pathways of molecular ions for compounds **1**–**6** linked scan analyses in B/E mode were used. For compound **1** molecular ion $M^{+\bullet}$ (m/z = 303) fragmentation of organosilicon substituent at nitrogen and fragmentation of carbon chain derived from ketoimine group are observed. In the mass fragmentation pathways of compound **1** dominant are the fragments characteristic of the organosilicon group decompositon [7].

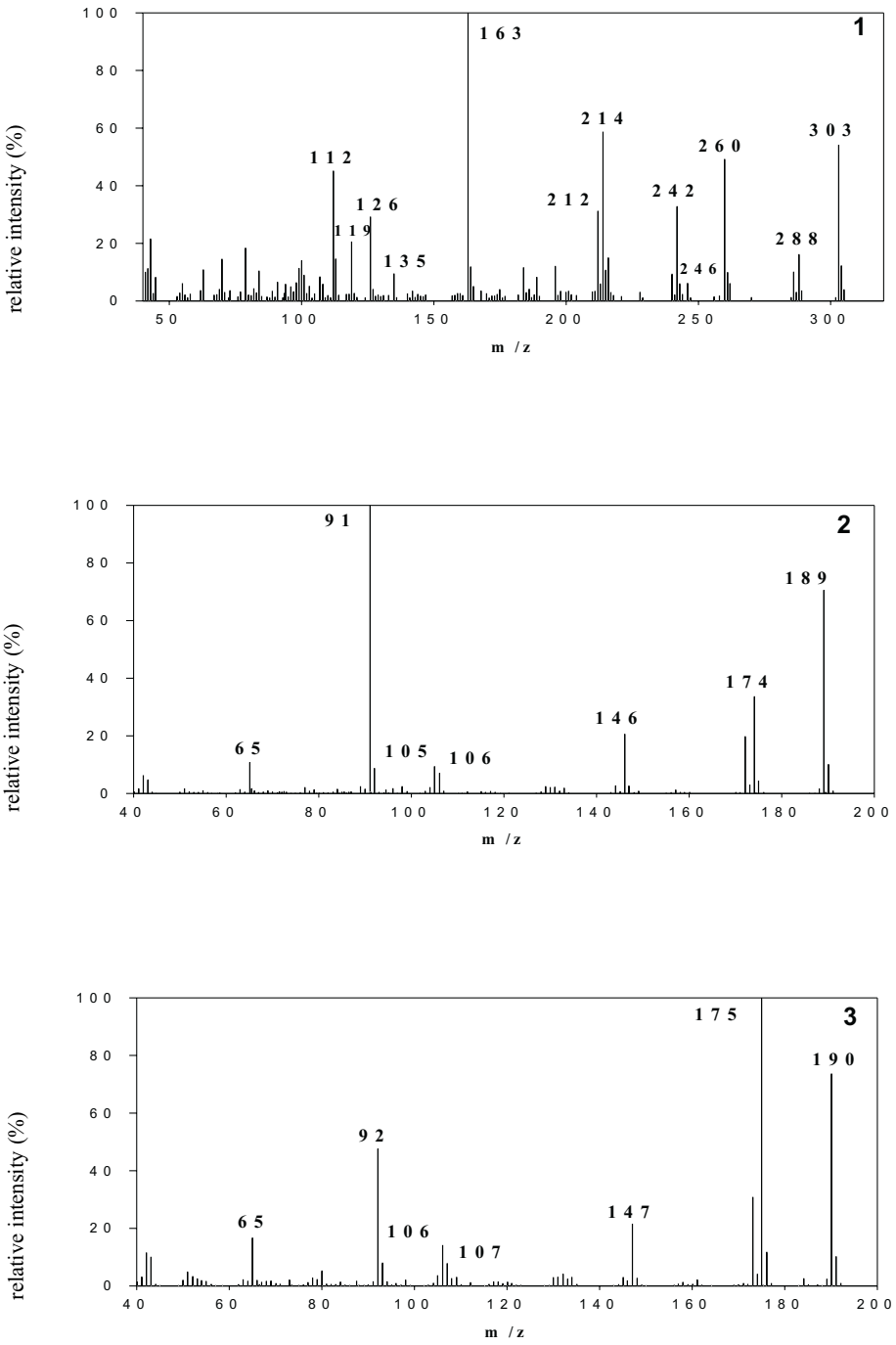



**Figure 1.** Low resolution mass spectra of compounds **1**–**6** (continuation on next page).

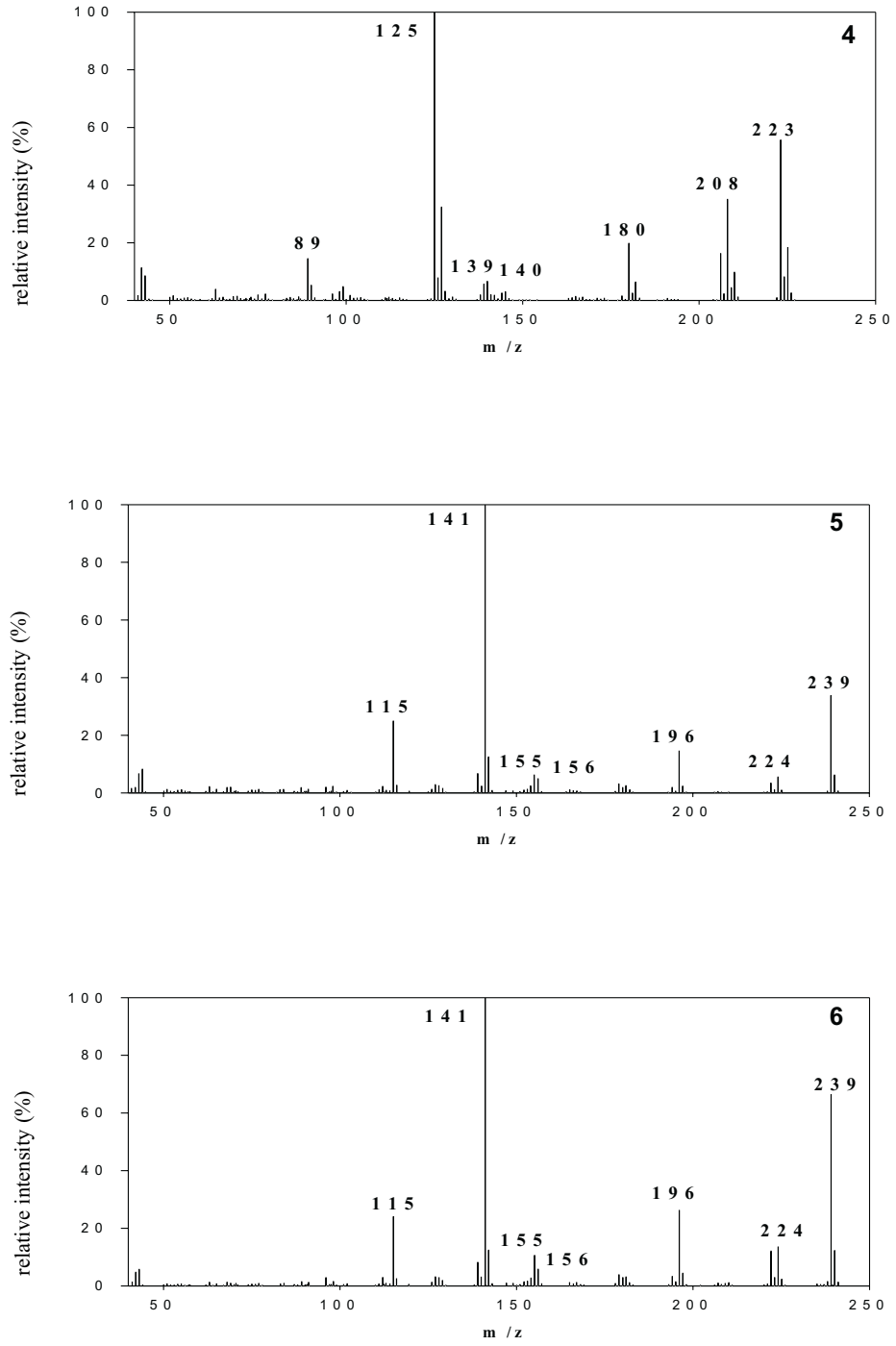



**Figure 1.** Low resolution mass spectra of compounds **1**–**6**.

**Table 1.** High-resolution data of compounds **1**–**6**.

| Cpd. | m/z Calculated | m/z Obtained | Error (ppm) | Composition |
|---|---|---|---|---|
| **1** | 303.18658 | 303.18813 | 5.1 | $C_{14}H_{29}NO_4Si$ |
| | 288.16312 | 288.16195 | 4.1 | $C_{13}H_{26}NO_4Si$ |
| | 260.16820 | 260.16949 | 5.0 | $C_{12}H_{26}NO_3Si$ |
| | 246.15254 | 246.15208 | 1.9 | $C_{11}H_{24}NO_3Si$ |
| | 242.12125 | 242.12211 | 3.6 | $C_{11}H_{20}NO_3Si$ |
| | 214.12633 | 214.12542 | 4.2 | $C_{10}H_{20}NO_2Si$ |
| | 212.11069 | 212.11024 | 2.1 | $C_{10}H_{18}NO_2Si$ |
| | 163.07905 | 163.07827 | 4.7 | $C_6H_{15}O_3Si$ |
| | 135.04774 | 135.04822 | .5 | $C_4H_{11}O_3Si$ |
| | 126.09189 | 126.09308 | 9.4 | $C_7H_{12}NO$ |
| | 119.05283 | 119.05364 | 6.8 | $C_4H_{11}O_2Si$ |
| | 112.07624 | 112.07621 | 0.3 | $C_6H_{10}NO$ |
| **2** | 189.11537 | 189.11561 | 1.3 | $C_{12}H_{15}NO$ |
| | 174.09189 | 174.09349 | 9.2 | $C_{11}H_{12}NO$ |
| | 146.09697 | 146.09681 | 1.1 | $C_{10}H_{12}N$ |
| | 106.06567 | 106.06616 | 4.6 | $C_7H_8N$ |
| | 105.07043 | 105.07011 | 3.0 | $C_8H_9$ |
| | 91.05478 | 91.05399 | 8.7 | $C_7H_7$ |
| **3** | 190.11061 | 190.11109 | 2.5 | $C_{11}H_{14}N_2O$ |
| | 175.08714 | 175.08610 | 6.0 | $C_{10}H_{11}N_2O$ |
| | 147.09222 | 147.09265 | 2.9 | $C_9H_{11}N_2$ |
| | 107.06092 | 107.06195 | 9.6 | $C_6H_7N_2$ |
| | 106.06567 | 106.06462 | 9.9 | $C_7H_8N$ |
| | 92.05003 | 92.05056 | 5.8 | $C_6H_6N$ |
| **4** | 223.07639 | 223.07595 | 2.0 | $C_{12}H_{14}NO_{35}Cl$ |
| | 208.05292 | 208.05390 | 4.7 | $C_{11}H_{11}NO_{35}Cl$ |
| | 180.05800 | 180.05658 | 7.9 | $C_{10}H_{11}N_{35}Cl$ |
| | 140.02670 | 140.02533 | 9.8 | $C_7H_7N_{35}Cl$ |
| | 139.03145 | 139.03117 | 2.0 | $C_8H_8{}^{35}Cl$ |
| | 125.01580 | 125.01520 | 4.8 | $C_7H_6{}^{35}Cl$ |
| **5** | 239.13101 | 239.13101 | 0.0 | $C_{16}H_{17}NO$ |
| | 224.10754 | 224.10716 | 1.7 | $C_{15}H_{14}NO$ |
| | 196.11263 | 196.11217 | 2.3 | $C_{14}H_{14}N$ |
| | 156.08133 | 156.08202 | 4.4 | $C_{11}H_{10}N$ |
| | 155.08607 | 155.08561 | 3.0 | $C_{12}H_{11}$ |
| | 141.07042 | 141.07070 | 2.0 | $C_{11}H_9$ |
| **6** | 239.13101 | 239.13174 | 3.0 | $C_{16}H_{17}NO$ |
| | 224.10754 | 224.10722 | 1.4 | $C_{15}H_{14}NO$ |
| | 196.11263 | 196.11310 | 2.4 | $C_{14}H_{14}N$ |
| | 156.08133 | 156.08086 | 3.0 | $C_{11}H_{10}N$ |
| | 155.08607 | 155.08675 | 4.4 | $C_{12}H_{11}$ |
| | 141.07042 | 141.06959 | 5.9 | $C_{11}H_9$ |

**Table 2.** Spectra of metastable ions of compounds **1**–**6**.

| **B/E** | parent ion<br>m/z(%) | detected daughter ions<br>m/z(%) |
|---|---|---|
| **1** | 303 (100) | 288(2) 260(3) 246(1.5) 242(0.5) 214(1) 163(1) 126(0.5) 112(0.5) |
| | 163 (100) | 135(0.5) 119(1) |
| **2-6** | $[M]^{+\cdot}$(100) | $[M-15]^{+}$(5-10) $[M-43]^{+}$(5-10) $[M-83]^{+}$(1-2) $[M-84]^{+}$(1-2) $R^{+}$(1-3) |
| **$B^2E$** | daughter ion<br>m/z(%) | detected parent ions<br>m/z(%) |
| **1** | 242(100) | 303(0.5) 288(4.5) |
| | 214(100) | 303(0.5) 260(3) 242 (1) |
| | 212(100) | 257(2.5) 242(1.5) |
| **2-6** | $[M-83]^{+}$(100) | $[M]^{+\cdot}$(0.5-1) $[M-15]^{+}$(0.5-1) $[M-43]^{+}$(0.5-1) |
| | $[M-84]^{+}$(100) | $[M]^{+\cdot}$(0.5-1) $[M-15]^{+}$(0.5-1) $[M-43]^{+}$(5-8) |

**Fragmentation of the organosilicon group:** As a result of elimination of ethanol molecule from ions $[M-15]^{+}$ and $[M-43]^{+}$ (ions formed by the elimination of methyl and acetyl radicals, respectively as we have described previously [6]) even-electron ions of m/z = 242 and m/z = 214 are obtained, respectively. As it results from the $B^2/E$ spectra, these ions also come directly from the molecular ion, while ion of m/z = 214 comes also from the ion of m/z = 242 as a result of a carbon monoxide molecule elimination. Suggested structures of these ions are presented in Figure 2.

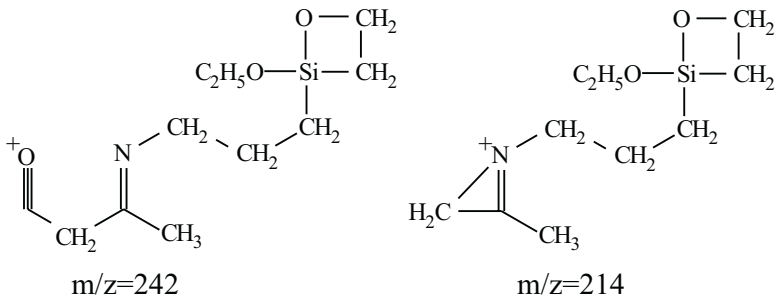



**Figure 2.** Suggested structures of ions at m/z = 242 and m/z = 214.

As it results from the $B^2/E$ spectrum, the ion of m/z = 242 is the parent ion for the ion of m/z = 212, which comes into existence in consequence of the elimination of formaldehyde molecule. The ion of m/z = 212 comes also from the ion of m/z = 257, intensity of which is very low on a normal low resolution mass spectrum (Figure 1) but is of crucial importance to fragmentation. The peak at m/z = 257 corresponds, most likely, to the ion coming from the molecular ion as a result of ethanol molecule elimination and because of further fragmentation, eliminating ethoxyl radical, we ob-

tain an even-electron ion of m/z = 212. According to this interpretation, the ion has two different structures (a and b) depending on the ion they come from (Figure 3). These structures have, however, the same empirical formula.

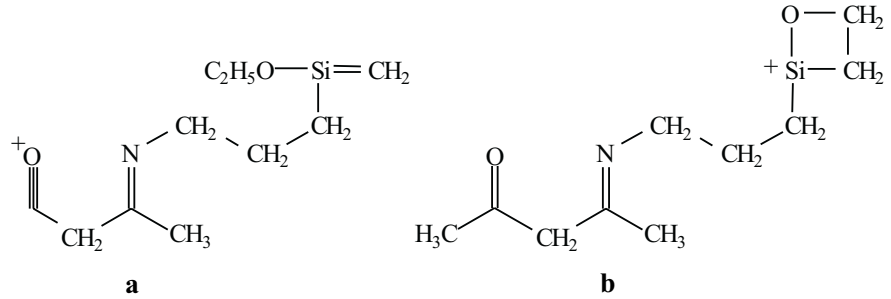



**Figure 3.** Structures of ion at m/z = 212: a) structure formed as a result of the elimination of formaldehyde molecule from ion at m/z = 242; b) structure formed as a result of the elimination of ethoxyl radical from ion at m/z = 257.

The following fragmentation pathways of the described compound are associated with simple cleavage of single bonds in organosilicon group, which leads to the formation of respective even-electron ions (Figure 4).

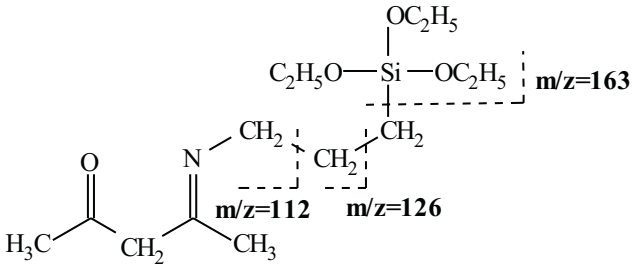



**Figure 4.** Fragmentation of compound **1** *via* simple cleavages of single bonds in organosilicon group.

As a result of cleavage of the C–Si bond, an ion of m/z = 163 is formed. It has relative abundance of 100% and the point of its further fragmentation (B/E spectrum) is the elimination of a molecule of mass equal to 44 (oxirane or acetaldehyde), forming an ion of m/z = 119 or the elimination of ethylene forming an ion of m/z = 135 (Figure 5).

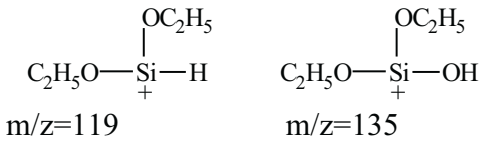
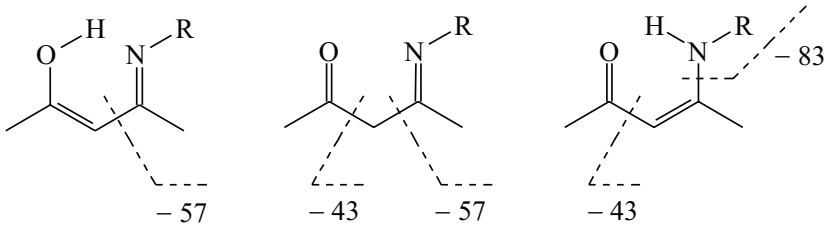



**Figure 5.** Daughter ions created from ions at m/z = 163.

**Fragmentation of carbonic chain of the ketoimine group:** As a result of cleavage of the C–C bonds of the ketoimine group in the carbon chain derived from acetylacetone the $CH_3CH_3^{\bullet}$, $CH_3CO^{\bullet}$ and $CH_3COCH_2^{\bullet}$ radicals are eliminated, which leads to the formation of even-electron ions of m/z = 288 ($[M-15]^+$), m/z = 260 ($[M-43]^+$) and m/z = 246 ($[M-57]^+$), respectively. This pathway of fragmentation has already been observed for 4-(arylimino)pentan-2-ones and the presence of even-electron ions $[M-43]^+$ and $[M-57]^+$, yet without $[M-83]^+$ ion (m/z=220), indicates the dominance of tautomer 4-iminopentan-2-on (tautomer a) [6], as it is shown in Figure 6.



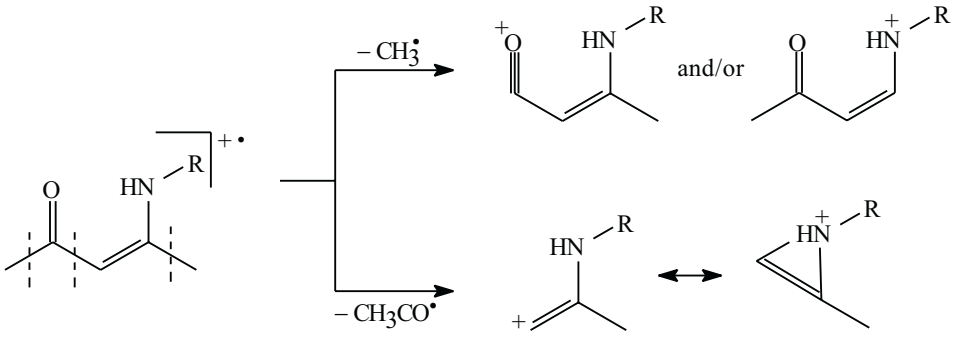

4-Iminopent-2-en-2-ol (tautomert c) | 4-Iminopentan-2-one (tautomer a) | 4-Aminopent-3-en-2-one (tautomer b)

**Figure 6.** Expected fragmentation pathways of three different isomers.

The ion $[M-43]^+$ is very abundant in the mass spectrum of compound **1** (Figure 1), which permits to exclude the tautomer 4-iminopent-2-en-2-ol. Yet the ion $[M-57]^+$ has only 7% of relative abundance, which may also mean that the ion $[M-43]^+$ derives from tautomer 4-aminopent-3-en-2-one. Although the appearance of an intensive peak, coming from $[M-83]^+$ ion at m/z = 220, should be then expected (Figure 6). In order to confirm this hypothesis we have prepared and investigated a series of alkylaromatic derivatives of 4-aminopent-3-en-2-one (compounds **2**–**6**). These compounds were chosen, because when alkylaryl substituent at nitrogen atom is present, significant peaks at m/z = $[M-83]^+$, *i.e.* for 4-(N-benzylamino)pent-3-en-2-one and 4-(N-(2′-furylmethylene)-amino)pent-3-en-2-one [6], are observed in mass spectra. For selected model compounds the fragmentation of alkylaryl group is relatively poor, which enables to observe the fragmentation of carbon chain of ketoimine group more thoroughly. For compounds **2**–**6** four types of decomposition of the molecular ions have been identified: (i) simple cleavages of the C–C bonds providing even-electron ions at m/z = $[M-15]^+$ and $[M-43]^+$, (ii) cleavages of the C–N bonds leading to the formation of even-electron ions of substituent R+, (iii) cleavages of the C–N bonds leading to the formation of even-electron ions at m/z = $[M-83]^+$, (iv) rearrangement resulting in producing even-electron ions at m/z = $[M-84]^+$.

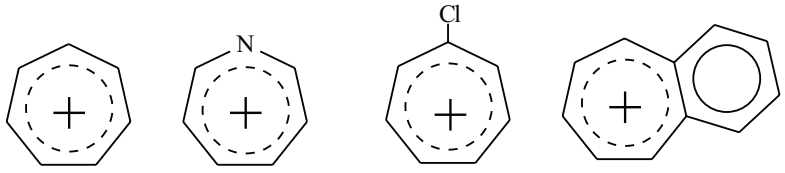
**Simple cleavages of the C–C bonds: the formation of ions containing quaternary nitrogen atom:** The loss of $CH_3^{\bullet}$ and $CH_3CO^{\bullet}$ radicals yielding $[M-15]^+$ and $[M-43]^+$ even-electron ions have been observed in the whole series of compounds **2**–**6** as a result of simple cleavages of the C(1)–C(2) and/or C(4)–C(5), C(2)–C(3) bonds, respectively.

This fragmentation pattern was observed also in the linked scan B/E mass spectra for molecular ions of compounds **2**–**6**; daughter ions created after cleavages of above mentioned bonds were recorded. As indicated in Scheme 1, loss of $CH_3^{\bullet}$ radical can occur from both ends of 4-aminopent-3-en-2-one. The cleavage of the C(1)–C(2) bond produces $[M\text{-}15]^+$ ion containing tertiary oxygen atom and cleavage of the C(4)–C(5) bond yields the ion containing quaternary nitrogen atom. In general, the rupture of such bonds has been commonly observed during mass fragmentation of aliphatic ketones including acetylacetone and acetylacetonate complexes of a number of metal cations and aryliminopentan-2-ones [6,8,9]. The rupture of the C(2)–C(3) bonds can produce even-electron ions containing quaternary nitrogen as well. The elimination of $CH_3^{\bullet}$, $CH_3CO^{\bullet}$ radicals is shown in Scheme 1.



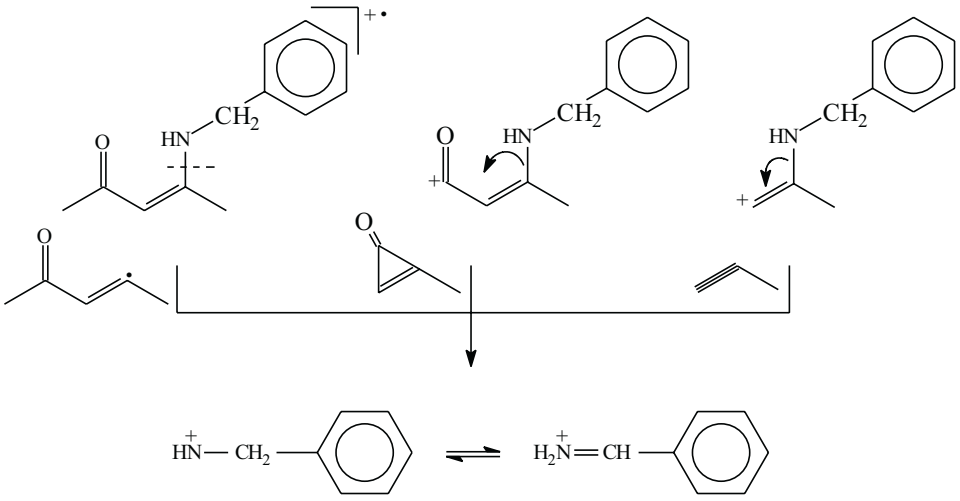

**Scheme 1.** Formation and suggested structures of ions formed *via* simple cleavage of C-C bonds.

**Cleavage of the C–N bond: the formation of ions of alkylaryl substituents:** As a result of N–$C_{sp3}$ bond rupture, the even-electron ion of $R^+$ (where R = alkylaryl substituent, **2**–**6**) is formed. Peaks corresponding to $R^+$ ions have 50–100% abundance in the all low-resolution spectra; this high abundance was already explained by a skeletal rearrangement, occurring exclusively in the alkylaryl derivatives [10]. The formation of tropylium ion after the cleavage of N–$C_{sp3}$ bond was observed as well [11]. The $R^+$ stands for tropylium ion in the case of compound **2** and its analogues – compounds **3**–**6**.



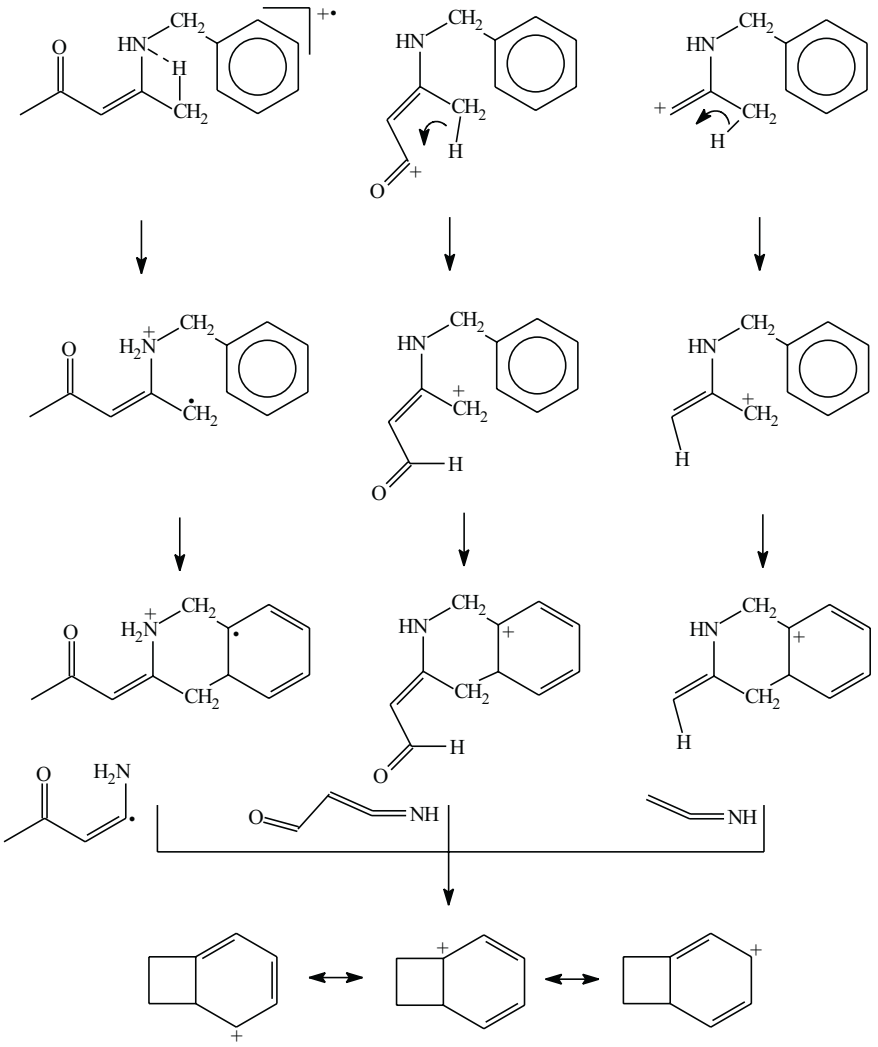

**Cleavages of the C–N bonds leading to even-electron ions at m/z = $[M\text{-}83]^+$:** In all low resolution spectra of all studied compounds a peak at m/z = $[M\text{-}83]^+$ is clearly seen. This ion is present in the linked scan B/E of molecular ions as well. Linked scans $B^2/E$ of $[M\text{-}83]^+$ ion enabled to detect $[M]^{+\bullet}$, $[M\text{-}15]^+$ and $[M\text{-}43]^+$ ions as its parent

ions. The molecular formulae of $[M-83]^{+\bullet}$ fragment ion corresponds to R substituent plus NH group for all investigated compounds. The mechanism of the formation of $[M-83]^{+}$ ion from three different parent ions in the mass spectrum of compound **2** is presented in Scheme 2. Such phenomena, resulting from the rupture of N–$C_{sp2}$ single bond, were already described [11,12]. The fragmentation pathways and structures of ions for compounds **3**–**6** are analogous.




**Scheme 2.** Formation and suggested structures of $[M-83]^{+}$ ion for compound **2**.

**Rearrangement resulting in producing $[M-84]^{+}$ ion:** Except for the peak of $[M-83]^{+}$ ion, formed as the result of a simple cleavage of the N–$C_{sp2}$ single bond, a peak of $[M-84]^{+}$ ion is observed in the mass spectra. However, on the basis of high resolution results we can say that it is not the $[M-83]^{+}$ minus hydrogen atom. The molecular formulae of $[M-84]^{+}$ ion for all compounds studied corresponds to R substituent plus methylene group. This ion is formed from $[M]^{+\bullet}$, $[M-15]^{+}$ and $[M-43]^{+}$. In the molecular ions a transfer of the H–atom to nitrogen atom of amino group is possible. In the $[M-15]^{+}$ and $[M-43]^{+}$ ions H–transition to C(2) and C(3) carbons is also possible, as H-transfer from methyl group to the carbenium ion has been already observed [13]. In the intermediate structures free-radical addition or electrophilic addition to aromatic ring can proceed. The proposed fragmentation mechanism of the formation of $[M-84]^{+}$ ion for compound **2** is shown in Scheme 3. Analogous formation pathways are possible also for compounds **3**–**6**. A similar fragmentation pathway was observed for 4-(arylimino)pentan-2-ones, but charge retention was on the other side, producing even electron ion at m/z = $[84]^{+}$ [6].



**Scheme 3.** The formation pathway and suggested structures of $[M-84]^+$ ion for compound **2**.

## CONCLUSIONS

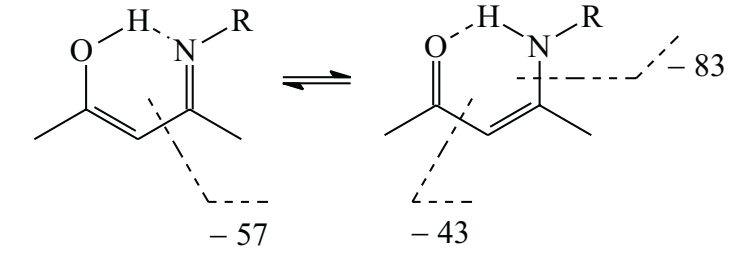
The point of fragmentation pathways for 4-(3-triethoxysilylpropylimino)pentan-2-on (compound **1**) is the cleavage of organosilicon group. At the same time there are both a simple rupture of single bonds (C–C or C–Si) and elimination of neutral molecules of organic compounds, which includes the transition of hydrogen atom. Such fragmentation is characteristic of such a kind of organosilicon compounds [7].

The point of ketoimine group fragmentation is the rupture of single carbon–carbon bonds of the chain deriving from acetylacetone. The presence of even-electron ions $[M-43]^+$ and $[M-57]^+$ indicates that in the gas phase, *i.e.* upon EI conditions, compound **1** occurs in 4-iminopentan-2-on form (tautomer a) (Figure 6), like it has

been observed for 4-(arylimino)pentan-2-ones [6]. The presence of $[M-43]^+$ peak in the mass spectrum excludes the possibility of occurrence of tautomer (c) (4-iminopent-2-en-2-ol), yet the absence of $[M-83]^+$ and the presence of $[M-57]^+$ peak excludes the occurrence of tautomeric form (b) (4-aminopent-3-en-2-one).

The investigation of some alkylaromatic derivatives of 4-aminopent-3-en-2-one (compounds **2**–**6**) as model compounds indicates that in the gas phase the presence of fragment ions $[M-43]^+$ and $[M-83]^+$ and the absence of $[M-57]^+$ in mass spectra recorded by us is characteristic only of the tautomeric form (b) (Figure 6). Another possibility of the formation $[M-43]^+$ and $[M-83]^+$ ions should be also taken into consideration. Fast intramolecular H-transfer can proceed between isomers of 4-iminopent-2-en-2-ol and 4-aminopent-3-en-2-one, but in this case a simple cleavage of single C(3)–C(4) bond producing even electron ion at m/z = $[M-57]^+$ should be clearly seen [6].

The absence of such a cleavage seems to confirm our conclusion.




4-Iminopent-2-en-2-ol 4-Aminopent-3-en-2-one

## EXPERIMENTAL

Low-resolution mass spectra were recorded on an AMD 402 two-sector mass spectrometer (AMD Intectra, Germany) of B/E geometry. High-resolution data were obtained on the same instrument using a V/E high resolution scan. Elemental composition of the ions were determined with an error of less than 10 ppm in relation to perfluorokerosene (Fluka, Switzerland) at resolving power of 10000. Metastable ions were recorded on the same instrument using link scans (B/E, $B^2/E$). Compounds were introduced into the mass spectrometer using a direct insertion probe in EI mode (70 eV, 0.5 mA total emission current) with accelerating voltage of 8 kV, a source temperature of 200°C and an inlet temperature of 70–150°C.

*Synthesis*: All amines, except benzylamine (from Fluka) and 3-aminopropyltriethoxysilane (from Gelest) were prepared from the corresponding methylarenes. The methylarene (50 mmol) was dissolved in carbon tetrachloride (50 ml) and N-bromosuccinimide (55 mmol) and benzoic peroxide (50 mg) was added. This solution was refluxed for over 2 h. Then, after cooling, the precipitate of succinimide was filtered off and the solvent was removed on a rotary evaporator. The crude benzylbromide derivative was used without a purification. The bromoderivate was dissolved in isopropanol (25 ml), to which phthalimide-DBU salt (50 mmol) was added. The solution was heated under reflux for over 1 h. After cooling, the precipitate of N-substituted phthalimide was filtered off. To the suspension of the obtained imide in methanol (50 ml) hydrazine hydrate (100%) was added (50 mmol) and this solution was refluxed for over 3 h. Then concentrated hydrochloric acid (10 ml) was dropped for 10 min and the mixture was refluxed for 1 h. Methanol was evaporated and a solution of NaOH (10%) was added (30 ml). The amine was extracted three times with ether, the organic layer was dried over magnesium sulfate and the solvent was removed on a rotary evaporator. The amines were used to synthesis of imines without a purification. To the solution of the obtained amine in benzene (25 ml), 2,4-pentanedione (40 mmol) and *p*-toluenesulfonic acid (10 mg)

were added and the mixture was heated in Dean-Stark apparatus until water was produced. The solvent was evaporated and the resulting oily product was purified by flash column chromatography (silica gel; hexane-diethyl ether 1:1 v/v). The yields of imines were over 80% in relation to methylarene. The triethoxysilyl derivate was prepared according to the same procedure and, after removing the solvent, the product was distilled under reduced pressure (138–140°C/0.5 mmHg), with yield of 70%.

*$^{13}$C NMR chemical shifts [ppm]*: All $^{13}$C NMR spectra were recorded on a Varian Gemini 2000 spectrometer at operating frequency 75.063 MHz in $CDCl_3$ (c = 0.1 mol*dm$^{-3}$) and TMS as an internal standard. Compound **1**: 7.4, 18.1, 18.5, 23.7, 28.5, 45.3, 58.2, 94.9, 162.8, 194.3, $^{29}$Si NMR: –46.3 ppm; Compound **2**: 18.8; 28.9; 46.7; 95.9; 126.7; 127.4; 128.8; 138.1; 163.1; 195.3; Compound **3**: 18.3; 28.6; 45.0; 96.0; 120.9; 146.9; 149.4; 162.1; 195.2; Compound **4**: 18.8; 28.9; 46.0; 96.1; 128.0; 128.9; 133.2; 136.6; 162.8; 195.6; Compound **5**: 18.7; 28.9; 44.3; 95.9; 122.2; 123.9; 125.3; 125.7; 126.3; 127.9; 128.7; 130.4; 133.1; 133.4; 162.9; 195.1; Compound **6**: 19.0; 29.0; 49.9; 96.0; 124.7; 125.0; 125.8; 126.2; 127.5; 127.7; 128.5; 132.6; 133.2; 135.4; 163.0; 195.3;

Acknowledgment

We express our appreciation of the discussion with Dr. M. Stobiecki. B. Gierczyk and R. Frański extend their thanks to the Foundation for Polish Science for fellowships.

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