MASS SPECTRA OF HETEROAROMATIC DERIVATIVES OF SILICON, GERMANIUM, AND TIN* (REVIEW)

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A review summarizing material on the mass spectrometry of furyl and thienyl derivatives of the Group IVB elements.

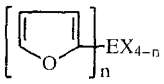
Results of studies of the mass spectra of alkyl and aryl derivatives of Group IVB elements have been summarized in review [1] and monographs [2-4]; however, they did not take account of studies of the mass spectra of heterocyclic derivatives of silicon, germanium, and tin.

We set a goal of explaining the features of the fragmentation of furyl and thienyl derivatives of silicon, germanium, and tin – heteroanalogs of the corresponding phenyl derivatives. The results of our work are summarized in the present review.

COMPOUNDS OF THE R_nEX_{4-n} TYPE

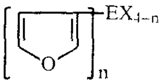
The mass spectra of phenyl derivatives of the Group IVB elements are characterized by the rather high intensity of the molecular ion (which, however, decreases from the 60% of the maximum peak of Ph_4Si [5] to the 5% of Ph_4Ge and 0.2% of Ph_4Sn [6, 7]) compared to the intensity of the molecular ion of the correspondingly alkyl derivatives.

We have studied the mass spectra of furyl (I-III) and thienyl (IV) derivatives of the Group IVB elements, heteroanalogs of the corresponding phenyl derivatives, and the mass spectra of 2-(4,5-dihydrofuryl)silanes (V).



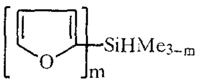
I

X = H, Me, Cl, Br, OEt



II

X = H, Me



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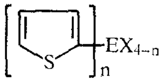

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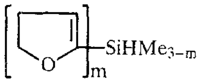

V

X = H, Me, Cl, Br, OEt, CH_2Cl

I, II, IV E = Si, Ge, Sn; n = 1-4; m = 1-3

Replacement of the CH═CH grouping by an O or S heteroatom, which is a π-donor and σ-acceptor, leads to a restructuring of the aromatic system, in contrast to $EPh_4^{+\bullet}$, because of the donor capability of the O and S heteroatoms stabilizes the $ER_4^{+\bullet}$ molecular ion (R = 2-furyl, 2-thienyl, E = Si, Ge, Sn) by redistributing the positive charge over the entire heteroaromatic ring.

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*Dedicated to Professor A. R. Katritsky in connection with his 65th birthday.

Latvian Institute of Organic Synthesis, Riga LV-1006. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, 891-898, July, 1993. Original article submitted June 10, 1993.

0009-3122/93/2907-0754$12.50

TABLE 1. Ratio of Intensities of $[M-R]^+$ and $[M-X]^+$ Ion Peaks to $M^{+\bullet}$ in the Mass Spectra of R_nEX_{4-n} Compounds

$$\frac{I_{[M-R]^+}}{I_{M^{+\cdot}}}=A; \qquad \frac{I_{[M-X]^+}}{I_{M^{+\cdot}}}=B$$

n	X	E = Si		E = Ge		E = Sn	
		A	B	A	B	A	B
R = 2-furyl							
4		0,1	—	0,8	—	7,1	—
3	H	0,1	0,1	0,4	0,4	—	—
3	Me	0,1	0,7	0,4	2,9	—	—
3	OEt	0,1	0,2	—	—	—	—
3	Cl	—	—	0,3	0,8	—	—
3	Br	—	—	0,3	3,5	—	—
2	H	0,2	0,3	0,3	0,3	—	—
2	Me	0,2	1,9	0,4	3,9	4,0	25,0
2	OEt	—	0,4	—	—	—	—
2	Cl	—	—	0,3	2,5	—	—
2	Br	—	—	0,2	4,3	—	—
1	H	0,1	1,1	—	—	—	—
1	Me	0,3	6,7	—	8,3	1,0	8,3
1	OEt	—	0,7	—	—	—	—
1	Br	—	—	0,7	4,3	—	—
R = 3-furyl							
4		1,0	—	2,2	—	1,8	—
3	H	0,8	0,6	—	—	—	—
3	Me	0,3	3,1	2,5	14,3	1,4	16,7
2	H	0,2	1,2	—	—	—	—
2	Me	0,5	4,5	1,6	11,1	3,1	14,7
1	Me	0,5	5,8	1,4	9,1	2,4	14,3
R = 2-thienyl							
4		0,3	—	4,0	—	1,1	—
3	H	0,3	0,2	1,9	0,6	—	—
3	Me	0,2	2,1	0,9	6,3	1,4	16,7
3	OEt	0,2	0,3	—	—	—	—
3	Cl	0,3	0,1	0,4	1,0	—	—
3	Br	—	—	1,1	6,7	—	—
2	H	0,1	0,6	0,5	0,6	—	—
2	Me	0,2	2,9	1,2	14,3	1,2	16,7
2	OEt	0,3	0,5	—	—	—	—
2	Cl	0,3	0,2	0,2	1,8	—	—
2	Br	—	—	0,5	5,9	—	—
1	H	—	0,7	—	0,7	—	—
1	Me	0,3	4,3	0,8	11,1	0,6	12,5
1	OEt	—	0,6	—	—	—	—
1	Cl	0,2	0,7	0,1	2,3	—	—
1	Br	—	—	0,3	5,0	—	—

The stability of the molecules to electron impact; i.e., the fraction of the total ion current due to molecular ions, decreases threefold on going from silicon to germanium and tin [8]. A decrease in the number of hetaryl groups in the R_nEMe_{4-n} molecules also leads to a reduction of the molecular ion peak (Fig. 1).

The fragmentation of molecular ions of the R_nEX_{4-n} type of compound is characterized by the splitting off of one of the substituents, leading to the appearance of the even electron ions $[M-R]^+$ or $[M-X]^+$. The participation of the π-electron

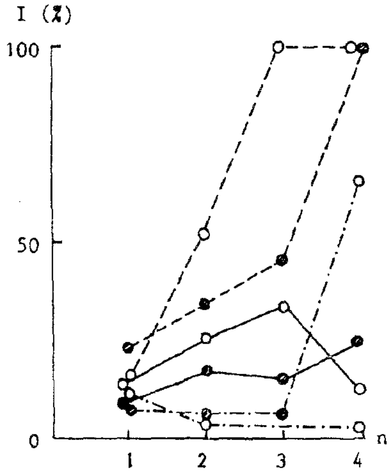


Fig. 1. Changes in the intensity of the molecular ion peak in the mass spectra of R_nEMe_{4-n} compounds as a function of the number of hetaryl groups, n. R) 2-Furyl (open circles), 2-thienyl (filled circles); E) Si (dashed line), Ge (solid line), Sn (dot-dashed line).

system of the heterocycle and the unshared pair of electrons of the O or S heteroatom in localizing the charge makes it easier to split off substituent X than hetaryl substituent R [9-11].

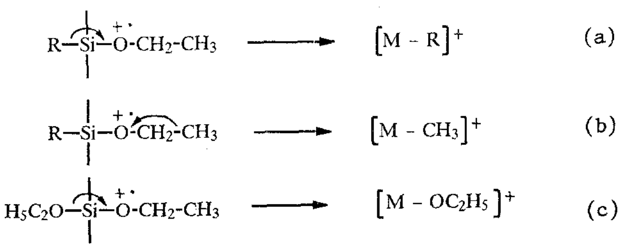
In the fragmentation of the majority of Group IVB compounds by electron impact, the positive charge is localized primarily on the fragment containing element E, and ions containing the element make up the major part of the total ion current [1]. This is confirmed only in part for the compounds we have studied. In the mass spectra of R_4E compounds, a notable portion of the total ion current consists of odd electron, rearranged ions of benzofuran or benzthiophene and $R_2^{+\bullet}$ ions (difuryl or dithienyl) [12, 13].

The rearranged ions mentioned are also observed in the fragmentation of R_nEX_{4-n} compounds (X = H, CH_3, C_2H_5, n = 2, 3), which are characterized by the rearrangement processes, and also by the splitting off of substituent X, leading to an ion peak of maximum intensity [10, 13-15].

A comparison of the mass spectra of 2-furylsilanes, III, and dihydrofurans, V, shows that the stability of molecular ions of III is higher than the stability of molecular ions corresponding to compounds V thanks to the decreased probability of delocalization of positive charge due to the weakened degree of conjugation in compounds V [16]. At the same time, because of the additional delocalization of charge over several heterocycles, the stability of the molecular ion is found to increase with increasing number of dihydrofuryl groups in the molecule.

The more prevalent splitting off of the dihydrofuryl radical compared to the methyl radical in compounds V in contrast to the corresponding furyl analogs is also evidence of the weakening of the interaction of the heterocycle with the silicon atom in dihydrofurylsilanes. Replacement of hetaryl R groups in compounds I and IV by ethoxy groups leads to the appearance of new paths of mass spectrometric fragmentation related to the possibility of localizing charge on the oxygen atom of the ethoxy group, which facilitates the rupture of three different bonds: the C–C in the ethoxy group, and the Si–O and Si–R groups [17] (scheme 1)

Scheme 1

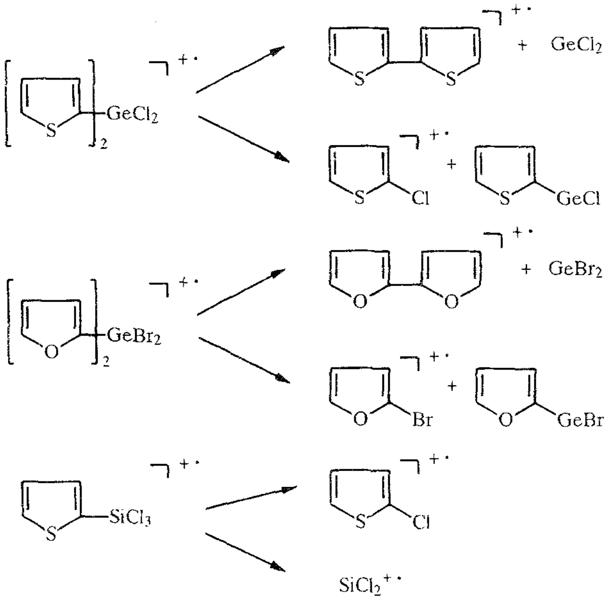


As the number of ethoxy groups decreases, the importance of the splitting off of an ethoxy group is lowered (path b). Unlike the corresponding phenyl derivatives, which are characterized by strong loss of phenyl substituents, this path appears only weakly in the fragmentation of compounds I and IV. This is evidence of a definite role of the interaction between the silicon atom and the heterocycle in charge delocalization.

Rearranged, odd electron ions along with the even electron ions are characteristic of the mass spectra of furyl- and thienylethoxysilanes [17, 18].

The stability of the devalent state of element E (especially germanium) determines the fragmentation of hetaryl(halogen)silanes and -germanes. This is manifested in the ejection of $EHal_2$ and REHal, neutral species with a high ionization potential, and leads to the formation of highly rearranged ions [9, 13], as well as abundant $EHal^+$ ions.

Scheme 2

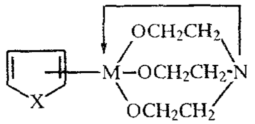


The changes in the nature of fragmentation introduced by the replacement of the hetaryl groups, R, by substituent X in R_nEX_{4-n} compounds are basically determined by the E−R and E−X bond energies. The stability of the corresponding bonds is characterized by the ratio of the intensities of the $[M-R]^+$ and $[M-X]^+$ ions to the intensity of the molecular ion (Table 1) [19]. A comparison of the data presented affords a qualitative comparison of the E−X and E−R bond strengths: $Si-Cl > Si-C_{hetaryl} > Si-C_{2\text{-furyl}} > Si-C_{3\text{-furyl}} > Si-C_{2\text{-thienyl}} > Si-C_{phenyl} > Si-H > Si-OEt > Si-Me$.

As the metallic properties are strengthened on going from silicon to germanium and tin, the localization of positive charge on atom E, the lowering of the energy to break the E−C bond, and also the increase in the specific weight of the splinter ions in the spectrum acquire a more pronounced character.

HETARYLSILATRANES AND GERMATRANES

The interaction discussed in the previous section, of a π-donor, heteroaromatic ring with a Group IVB element, leading to the delocalization of positive charge also is manifested in the mass spectra of hetarylsilatranes VIa and germatranes, VIb.



VIa, b

VI a M = Si, b M = Ge; X = O, S

The mass spectra of the alkyl- and arylsilatranes studied, for molecules of which N → Si donor-acceptor interaction is characteristic, are characterized by the low stability of the molecular ion and the stability of the $[M-R]^+$ ions thanks to the drive of the five-coordinate, positively charged silicon atom to go to the four-coordinate state [20].

The mass spectra of germatranes are also characterized by the low stability of the molecular ion, but, unlike the silatranes, fragmentation of the molecular ion takes place analogously to a cyclic amine, which is evidence of the susceptibility of the unshared pair of nitrogen electrons to electron impact; i.e., of the absence of a donor-acceptor interaction of the unshared pair of nitrogen electrons with the germanium atom [21].

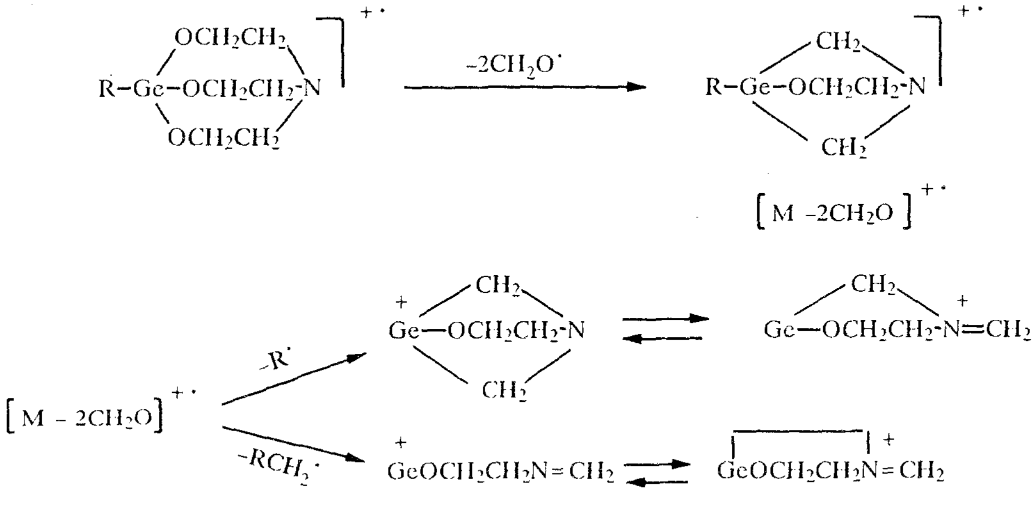
The mass spectra of compounds VIa, unlike alkyl- and arylsilatranes, are characterized by the high intensity of the molecular ions and the decisive role of ions arising from the rupture of bonds in the silatrane skeleton [22]. The pecularities of the fragmentation of VIa are apparently due to the participation of the unshared pair of oxygen or sulfur electrons of substituent R in the delocalization of charge. The redistribution of electron density leads to an increase in the strength of the Si–R bond. The participation of oxygen or sulfur atoms in the delocalization of charge is apparent in the difference in stability of the molecular ion, depends on the interaction of heterocycle R with the silicon atom: The intensity of the molecular ion peaks of the 2-hetaryl derivatives is greater than that of the 3-hetaryl derivatives, but is insignificant for furylsilatrane because of the disruption of the conjugation with the methylene bridge.

Fragmentation of compounds VIb, as of their alkyl and phenyl analogs, is determined by the position of the nitrogen atom as the center of localization of positive charge [22, 23]. As a result of a two-fold-α-rupture (relative to the nitrogen), a $[M-2CH_2O]^+$ ion is formed, which then is transformed into two, very intense ions, the stability of which is determined by the localization of charge on the nitrogen atom (scheme 3).

The nature of the fragmentation of compounds VIb is evidence of the absence of a donor-acceptor interaction in these molecules in the gas phase.

In order to obtain additional information about the transannular interaction, milder methods of ionization were used: chemical ionization and fast atom bombardment [23, 24]. With compounds VIa, where the unshared pair of nitrogen electrons take part in forming a coordinate bond, the molecular ion $M^{+\bullet}$ is formed in the mass spectra produced with chemical ionization and fast atom bombardment. With compounds VIb, on the other hand, the absence of a coordinate bond leads to protonation of the nitrogen atom and the preponderant formation of MH^+ ions.

Scheme 3



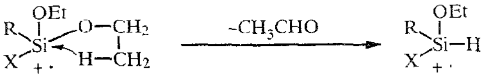
With chemical ionization and fast atom bombardment, $[M-R]^+$ ion peaks are present in the mass spectra of compounds VIa and VIb, being more intense for VIa compounds. These data indicate the presence of a weak donor-acceptor interaction in the VIa compounds under these conditions and the absence of such in the VIb compounds.

REARRANGEMENT PROCESSES ON THE FRAGMENTATION OF HETARYL DERIVATIVES OF SILICON, GERMANIUM, AND TIN UNDER ELECTRON IMPACT

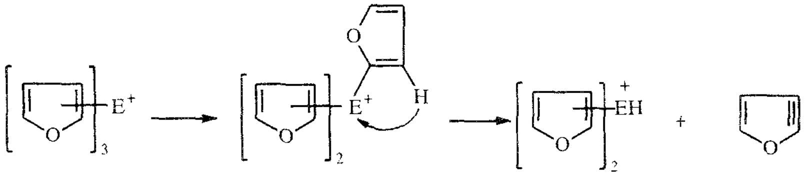
The role of rearrangement processes in the fragmentation of R_nEX_{4-n} type compounds is determined by the reduction of the bond energies on going from silicon to germanium and tin. This role is most obvious for silicon derivatives.

Some of the observed hydrogen rearrangements come about through the migration of a hydrogen atom to the cation-radical center on atom E. The elimination of an acetaldehyde molecule from an ethoxy group in $R_nSi(Ge)X_{4-n}(X = OC_2H_5)$ [17] (scheme 4) and of dehydrofuran, C_4H_2O, from the $R_4Si(Ge)^{+\bullet}$ molecular ion [12] (scheme 5) and in the fragmentation of R_3SiCH_2Cl [25] takes place this way.

Scheme 4



Scheme 5

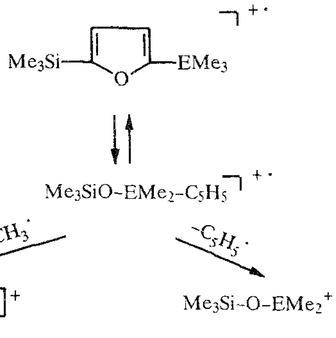


Migration of hydrogen to the oxygen atom causes the elimination of a C_2H_4 molecule from $R_nSi(OC_2H_5)_{4-n}$ [17].

A shift of charge from the Group IVB element to the heteroaromatic ring is the reason that on the fragmentation of molecular ions of $RnEX_{4-n}$ (n = 2, 3, 4) one hetaryl group migrates to another, and rearranged $R_2^{+\bullet}$ ions appear with a high intenisty [8, 12, 13, 17]. In this, the E−X bond energy is of great significance; i.e., the relatively low $E-CH_3$ bond energy allows the methyl group to be split off and hinders rearrangement; conversely, the high E−Hal bond energy facilitates the formation of $R_2^{+\bullet}$.

In the fragmentation of 2,5-bis(trimethylsilyl)furan and of its monogermyl and monostannyl analogs, a specific rearrangement is observed [26]. The formation of $[M-C_5H_5]^+$ occurs, which can only be explained by a rearrangement with the formation of a siloxane bond, Si−O−Si, as a result of the opening of the furan ring (scheme 6).

Scheme 6

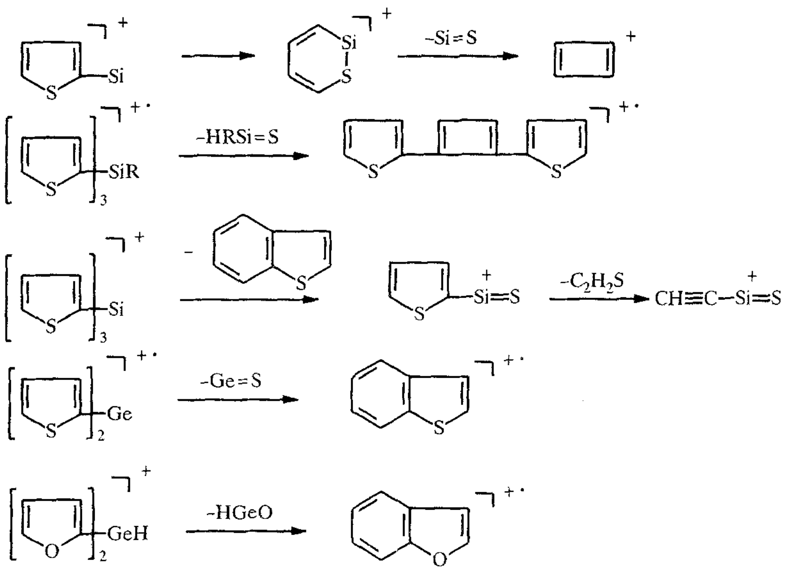


E = Si, Ge, Sn

The essential factors in the rearrangement are the relatively low energy for breaking open the furan ring and the case of migration of the trimethylsilyl group (no rearrangement is observed in the case of the bisgermyl and biscarbon analogs).

Another type of skeletal rearrangement in the heteryl derivatives of Group IVB elements is characterized by the migration of the element to the heteratom of the ring and the formation of a species containing an E=O or E=S double bond. Here, both neutral and ionized species of this type are formed [12, 13] (scheme 7).

Scheme 7



The existence of the rearrangement products discussed under the conditions of fragmentation by electron impact is shown by element analysis of the ions with high resolution, and by scanning the metastable ions.

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