Journal of Organometallic Chemistry, 384 (1990) 257–261
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20422

Chemical ionization and fast atom bombardment mass spectra of 1-hetero-aryl-silatranes and -germatranes

S. Rozite, I. Mažeika, A. Gaukhman, N.P. Erchak, L.M. Ignatovich and E. Lukevics *
Institute of Organic Synthesis, Latvian Academy of Sciences, Latvia, Riga (U.S.S.R.)

(Received September 5th, 1989)

Abstract

Chemical ionization (CI) and fast atom bombardment (FAB) mass spectra of hetero-aryl (furyl, thienyl) derivatives of silatranes and germatranes were studied. These methods have advantages over electron impact ionization for studying intramolecular donor–acceptor interactions in silatranes and germatranes. The products of germatrane fragmentation provide evidence in favour of a sample-matrix interaction under FAB. FAB appears to be a preferable analytical method for studying silylethyl derivatives of silatranes.

Introduction

On the basis of the fragmentation pattern under electron impact (EI), Bochkarev and co-workers have demonstrated the existence of a N→Si transannular bond in silatranes in the gaseous phase [1] and absence of the analogous bond, N→Ge, in germatranes [2]. The difference in the degree of transannular interaction must also be reflected in the mass spectra obtained by other ionization methods. The CI and FAB mass spectra of the hetero-aryl derivatives of silatranes Ia–Ie, germatranes IIa–IIe and the corresponding phenyl analogues If and IIf were studied.

$\mathrm{R}\overleftarrow{\mathrm{E}(\mathrm{OCH_2CH_2})_3\mathrm{N}}$

(I: E = Si, II: E = Ge; R = 2-furyl (a), 3-furyl (b), furfuryl (c), 2-thienyl (d), 3-thienyl (e), phenyl (f)).

Results and discussion

Both CI and FAB mass spectra mainly contain peaks of even-electron cations (quasi-molecular ions) formed as a result of protonation (CI, FAB) or addition of reagent gas molecules (CI). The formation of fragment ions almost always occurs by

0022-328X/90/$03.50

Table 1

Characteristic peaks (m/z, %) in the CI mass spectra of silatranes Ia–Ie and germatranes IIa–IIe [a]

Ion	Ia	Ib	Ic	Id	Ie
$M^{+\cdot}$	241(12)	241(8)	–	257(12)	257(7)
MH^+	242(8)	242(8)	256(85)	258(7)	258(3)
$[M-R]^+$	174(28)	174(31)	174(48)	174(35)	174(32)
$[(M-R)NH_3]^+$	191(100)	191(100)	191(100)	191(100)	191(100)
	IIa	IIb	IIc	IId	IIe
$M^{+\cdot}$	287(14)	287(14)	301(16)	303(16)	303(14)
MH^+	288(100)	288(100)	302(100)	304(100)	304(100)
$[M-R]^+$	220(11)	220(3)	220(22)	220(9)	220(3)
$[(M-R)NH_3]^+$	237(47)	237(7)	237(22)	237(34)	237(6)

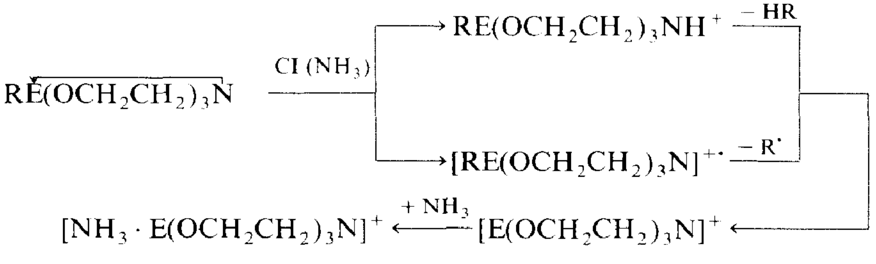
[a] m/z values are given for ^{74}Ge.

elimination of neutral molecules from the even-electron quasi-molecular ions. The mass spectra of non-polar compounds differ only slightly from EI mass spectra; the quasi-molecular ions MH^+ appear if the compound under study contains proton-acceptor groups [3].

The formation of a particular type of ion ($M^{+\cdot}$, MH^+ or $(M+NH_4)^+$) under CI (NH_3) is determined by the affinity of the respective compound to protons [4]. Reagent gas $H^+(NH_3)$ can protonate organic compounds whose proton affinity exceeds 205 kcal/mol.

As expected, the formation of molecular ions and protonated molecular ions in CI spectra (Table 1) proves the different extent of the N→Si(Ge) interaction. The molecular ion $M^{+\cdot}$ is predominantly formed in silatranes where the lone electron pair of the N atom participates in the formation of the coordination bond, while the absence of the N→Ge bond in germatranes leads to protonated MH^+ ions with maximum intensity. Furfurylsilatrane Ic is an exception, as there is no molecular ion peak in its mass spectrum, but the MH^+ ion peak exceeds 85% of the maximum value. This observation, as well as differences in the EI mass spectra [5], can be explained by disturbances in charge delocalization on the molecular ion owing to isolation of the hetero-aryl group from the silatrane system by a methylene group.

Further decomposition of the $M^{+\cdot}$ and MH^+ ions under CI conditions involves loss of the R substituent. $[M-R]^+$ ion and $[(M-R)NH_3]^+$ adduct ion peaks appear in the spectra (Scheme 1). Adduct ion formation appears to be a more advantageous process: $I_{[M-R]^+} < I_{[(M-R)NH_3]^+}$ holds true for all spectra. The adduct ion corresponds to the main peak in the spectra of silatranes Ia–Ie.



Scheme 1

Table 2

Characteristic peaks (m/z, %) in the FAB mass spectra of silatranes Ia–If and germatranes IIa–IIf [a]

Ion	Ia	Ib	Ic	Id	Ie	If
$M^{+\cdot}$	241(19)	241(11)	255(5)	257(9)	257(10)	251(4)
MH^+	242(6)	242(5)	256(22)	258(5)	258(10)	252(13)
$[M-R]^+$	174(100)	174(95)	174(100)	174(100)	174(100)	174(100)
$[M-H]^+$	240(18)	240(8)	–	256(9)	256(5)	–
$(HOCH_2CH_2)_3NH^+$	–	150(100)	150(17)	–	–	–
	IIa	IIb	IIc	IId	IIe	IIf
MH^+	288(7)	288(8)	302(58)	304(30)	304(31)	298(100)
$[M-R]^+$	220(55)	220(13)	220(100)	220(43)	220(36)	220(46)
$(HOCH_2CH_2)_3NH^+$	150(100)	150(100)	150(86)	150(100)	150(200)	150(95)
Others	247(11)	247(7)	261(5)			

[a] m/z values are given for ^{74}Ge; peak intensities take into account the contribution of all germanium isotopes.

The FAB mass spectra (ionizing gas: argon; matrix liquid: thioglycerol) of silatranes are characterized by intense $[M-R]^+$ fragment ion peaks (Table 2). As in the case of CI, the molecular ion peaks are more intense than those of MH^+ ions (compounds Ie, If are exceptions to the rule). The reduced intensity of the molecular ion in the spectrum of furfurylsilatrane Ic in comparison with furyl- and thienyl-silatranes has also been observed in EI spectra [5]. Germatranes IIa–IIf have no $M^{+\cdot}$ ion peaks in FAB spectra and the intensity of the MH^+ ion peaks is higher than that of the corresponding silatranes I. The unusually high intensity of MH^+ ions of furfuryl- and phenyl-germatranes should be noted (cf. IIc, IIf): if the $M^{+\cdot}$ peak intensity of Ic in the EI spectra is equal to 8% of the maximum $[M-R]^+$ peak value, the intensity of the quasi-molecular MH^+ ion peak reaches 58% in FAB spectra (Table 2).

The existence of intense peaks with m/z 150, the peak of the protonated molecular ion of triethanolamine $(HOCH_2CH_2)_3NH^+$, is a typical feature of FAB mass spectra. A similar fragmentation accompanied by silatrane ring cleavage is described in ref. 6. The reaction of silatrane hydrolysis is allegedly caused by argon atom bombardment. The substitution of some ligands (halogen, phenyl) for matrix radicals induced by FAB can be observed in the spectra of some coordination compounds of transition metals [7,8]. An ion with m/z 150 occurs in all the germatranes IIa–IIf and only two silatranes, Ib and Ic, tested. In some FAB spectra, we also found peaks with m/z 247 (cf. IIa, IIb) and 261 (cf. IIc). The isotope pattern indicates the presence of one germanium atom in these ions, and the difference of 14 m.u. corresponds to the mass difference between substituents R in compounds IIa, IIb and IIc. High-resolution mass spectra of these ions under FAB failed to give reliable results because of the absence of a suitable mass standard. In the FAB mass spectra of germatranes using glycerol as a liquid matrix, we could not find ions with m/z 247 (or 261) or ions analogous to them. This may be because of the increase in acidity of thioglycerol compared with glycerol and, like triethanolamine formation, this is, in our opinion, indicative of germatrane solvolysis in thioglycerol under FAB.

Because of the limited possibilities of charge delocalization on silylethyl derivatives of silatrane III, their EI mass spectra are of little informative value: along with

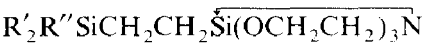
Table 3

Characteristic peaks (m/z, %) in the FAB mass spectra of silylethylsilatranes IIIa–IIIh

Ion	IIIa	IIIb[a]	IIIc	IIId	IIIe	IIIf	IIIg	IIIh
$M^{+\cdot}$	317	431	327	327	343	379	411	399
	(3)	(1)	(2)	(1)	(26)	(3)	(5)	(2)
MH^+	318	–	328	328	344	380	412	400
	(3)		(2)	(1)	(18)	(2)	(3)	(1)
$[M-H]^+$	316	429	326	326	342	378	410	398
	(10)	(1)	(6)	(4)	(55)	(5)	(4)	(4)
$[M-R'(R'')]^+$	286	364	312	312	328	364	328	384
	(26)	(19)	(5)	(6)	(6)	(2)	(100)	(1)
			260	260	260	312		322
			(62)	(31)	(21)	(100)		(76)
$[Si(OCH_2CH_2)_3N]^+$	174	–	174	174	174	174	174	174
	(100)		(100)	(100)	(100)	(84)	(100)	(100)

[a] m/z 150(100), $(HOCH_2CH_2)_3NH^+$.

a weak molecular ion peak, the spectrum contains only an intense $[Si(OCH_2CH_2)_3N]^+$ silatranyl cation peak with m/z 174 [5].

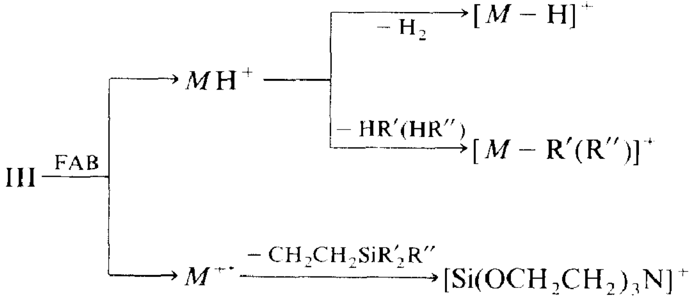


$R'_2R''SiCH_2CH_2Si(OCH_2CH_2)_3N$

(III)

($R' = R''$ = Et (a), 2-furyl (b),
R' = Me, R'' = 2-furyl (c), 3-furyl (d), 2-thienyl (e);
R'' = Me, R' = 2-furyl (f), 2-thienyl (g), phenyl (h))

A low-intensity molecular ion peak (1–5%, except for compound IIIe) is also observed in the FAB mass spectra. The weak peaks of the MH^+ ions suggest a lack of proton-acceptor sites in the molecule, i.e., the N atom is involved in the formation of the N→Si coordination bond. $[M - H]^+$ ion peaks are characteristic of the FAB mass spectra of silatrane III; this type of ion is also characteristic of silatrane I fragmentation (Table 3). The formation of $[M - H]$ ions should be considered in relation with the formation of $[M - R]^+$ ions: in our opinion, these ions result from the elimination of neutral molecules (H_2 or HR) from the MH^+ cation (Scheme 2). The predominant loss of the hetero-aryl substituent (in the form



Scheme 2

of furan or thiophen molecules), but not the loss of one methyl group (occurring during fragmentation under EI [5]), suggests a different mechanism of fragmentation under FAB. The participation of one of the silicon atoms in N→Si bonding weakens the neighbouring C–Si bond and causes charge localization preferably on the silatranyl cation $[Si(OCH_2CH_2)_3N]^+$ (87–100%).

Nonetheless, the FAB spectral data obtained allow us to determine both the molecular mass (existence of quasi-molecular MH^+ and $[M-H]^+$ ions) and the presence of substituents ($[M-R]^+$ ions) in silylethylsilatranes III more reliably than EI mass spectral data.

Experimental

CI mass spectra were obtained on a KRATOS MS-25 chromatomass spectrometer (reagent gas: NH_3).

FAB mass spectra were recorded on an AEI MS-50 instrument with a Ion. Tech. FAB 11NF source (bombarding gas: argon; matrix liquid: 2-thioglycerol).

Compounds I–III were obtained according to refs. 9–11.

References

1 V.N. Bochkarev, A.E. Chernyshev, V.Yu. Vitkovskiy, M.G. Voronkov, Zh. Obshch. Khim., 55 (1985) 1354.
2 A.E. Chernyshev, V.N. Bochkarev, Zh. Obshch. Khim., 57 (1987) 154.
3 C. Fenselau, R.J. Coller, Chem. Rev., 87 (1987) 501.
4 A.G. Harrison, Chemical Ionization Mass Spectrometry, CRC Press, Inc., Boca Raton FL, 1983, p. 156.
5 S. Rozite, I. Mažeika, A. Gaukhman, N. Erchak, L. Ignatovich, E. Lukevics, Metalloorg. Khim., in press.
6 L. Yan, W. Chai, G. Wang, G. Wu, K. Lu, Y. Luo, Org. Mass Spectrom., 22 (1987) 279.
7 B. Divisia-Blohorn, G. Kyriakakou, J. Ulrich, Org. Mass Spectrom., 20 (1985) 463.
8 J.M. Miller, A. Fulcher, Can. J. Chem., 63 (1984) 2308.
9 E. Lukevics, S. Germane, O.A. Pudova, N.P. Erchak, Khim.-Farm. Zh., 13 (1979) 52.
10 E. Lukevics, O.A. Pudova, J. Popelis, N.P. Erchak, Zh. Obshch. Khim., 51 (1981) 369.
11 E. Lukevics, L. Ignatovich, N. Porsiurova, S. Germane, Appl. Organomet. Chem., 2 (1988) 115.