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MASS-SPECTROMETRIC STUDY OF BENZOPYRIDOSILAAZEPINES AND -AZEPINONES

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The influence of various structural factors on the dissociative ionization of benzopyridosilaazepines and -azepinones has been investigated. It has been shown that the mass spectra can be used to identify isomeric benzopyridosilaazepinones with respect to the position of the amide fragment in the central heterocycle. The anomalously high intensity of the ion $[M - H]^+$ in the mass spectra of these compounds is attributed to fragmentation of the molecular ions from the open form.

The dissociative ionization of benzo[b,f]silepines [1] (nitrogen-free analogs of the substances investigated in the present article) has been reported earlier [1]. The mass-spectrometric characteristics of polycyclic compounds which contain the silaazepine fragment have so far not been studied. In the present work we have investigated fragmentation of the

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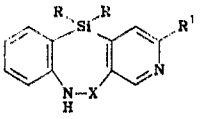
TABLE 1. Mass Spectra of Compounds I-V*

Compound	m/z values (relative intensity in %) †
I	241 (13), 240 (56), 239 (11), 227 (6), 226 (20), 225 (100), 223 (6), 210 (7), 209 (5), 198 (7), 197 (12), 196 (22), 185 (23), 182 (14), 181 (49), 167 (7), 166 (7), 164 (5), 163 (23), 162 (9), 149 (7), 146 (7), 135 (5), 120 (7), 119 (6), 105 (8), 83 (6), 57 (13); W_M = 9%
II	379 (32), 378 (98), 377 (10), 301 (30), 300 (30), 299 (100), 272 (10), 195 (8), 105 (6); W_M = 25%
III	255 (17), 254 (79), 253 (100), 240 (10), 239 (48), 211 (13), 196 (43), 169 (6), 167 (5), 135 (6), 119 (10); W_M = 14%
IV	255 (9), 254 (49), 253 (100), 252 (15), 240 (8), 239 (35), 211 (18), 196 (23), 134 (6), 120 (5); W_M = 12%
V	393 (35), 392 (100), 391 (91), 390 (5), 377 (9), 376 (8), 317 (5), 316 (17), 315 (52), 314 (26), 313 (8), 289 (8), 288 (23), 287 (68), 286 (5), 273 (5), 272 (10), 271 (16), 270 (8), 181 (10), 105 (10); W_M = 23%

*I) 5,5-Dimethyl-5-sila-5H,10H,11H-benzo[b]pyrido[4,3-e]-azepine; II) 3-methyl-5,5-diphenyl-5-sila-5H,10H,11H-benzo-[b]pyrido[4,3-e]azepine; III) 11-oxo-5,5-dimethyl-5-sila-5H, 10H,11H-benzo[b]pyrido[4,3-e]azepine; IV) 10-oxo-5,5-dimethyl-5-sila-5H,10H,11H-benzo[e]pyrido[3,4-b]azepine; V) 3-methyl-11-oxo-5,5-diphenyl-5-sila-5H,10H,11H-benzo[b]pyrido[4,3-e]-azepine and 3-methyl-10-oxo-5,5-diphenyl-5-sila-5H,10H,11H-benzo[e]pyrido[3,4-b]azepine.
†Peaks with intensities ≥5% are shown.

first representatives of a new group of nitrigen heterocycles (benzopyridosilaazepines) under the action of electron impact.*



I, III R=CH_3, R^1=H; II, V R=C_6H_5, R^1=CH_3; I, II X=CH_2, III, V X=CO

The mass spectra of the investigated compounds are given in Table 1. As expected [2], the resistance to decomposition (W_M) increases when the methyl group at the silicon atom is replaced by a phenyl group. However, in distinction from the dihydrosilaazaanthracenes and corresponding silaazaanthrones [3], W_M changes little in the transition from the benzopyridosilaazepines I, II to the benzopyridosilaazepinones III-V; this is evidently due to retention of the noncoplanar character of the molecule in the transition from compounds I, III to III-V.

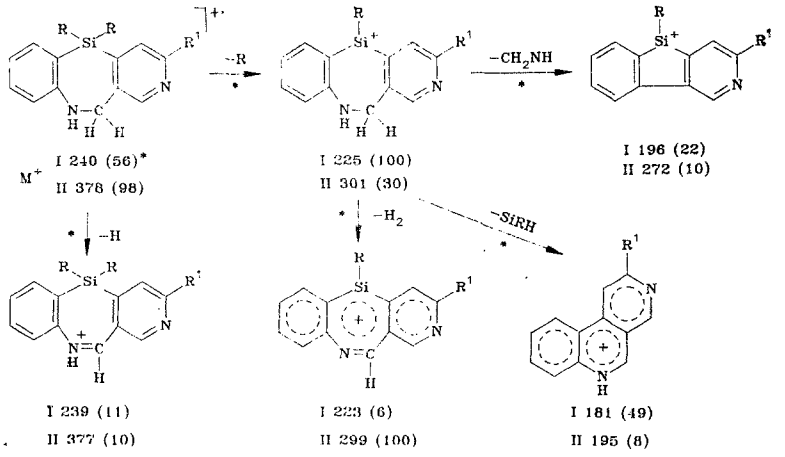
The molecular ions (M^+) of the silaazepines I, II decompose according to two routes (Scheme 1). The first route leads to the formation of ion peaks $[M - H]^+$ with similar intensities, due probably to the predominant splitting of a hydrogen atom from the methylene group [4]. The second route of fragmentation of compounds I, II leads to the elimination of the R substituent from the silicon atom, whereby in the case of the dimethyl-substituted compound I the ion peak $[M - R]^+$ has the maximum intensity.

The appearance of other fragment ions in the mass spectra of compounds I and II is due to the decomposition of the ion $[M - R]^+$. The fragmentation of this ion is characterized by the formation of the cation $[M - R - H_2]^+$ (Scheme 1; the process is confirmed by metastable ions). In the mass spectrum of compound I the intensity of this ion peak is insignificant, while in the spectrum of compound II its intensity is at a maximum (Table 1). Both mass spectra contain intensive peaks (~5%) of ions $[M - R - H_2]^+$ with two charges which is characteristic for aromatic polycyclic systems [5]. The mass spectra of the deutero-analogs of compounds I and II show that the hydrogen molecule which is splitting off contains the hydrogen atom of the NH group (the second hydrogen atom is due probably to the methylene group). All this leads to the assumption that the ion $[M - R - H_2]^+$ has the structure of the benzopyridosilaazepine cation (Scheme 1). The higher peak intensity of this ion in the mass spectrum of

*The structure of compound IV is shown in Scheme 2 (two pages hence). Compound V is a mixture of isomers (See Table 1.

compound II in comparison with I is due to the stabilizing effect of the phenyl group caused by its conjugation with the polycyclic system [2].

Scheme 1



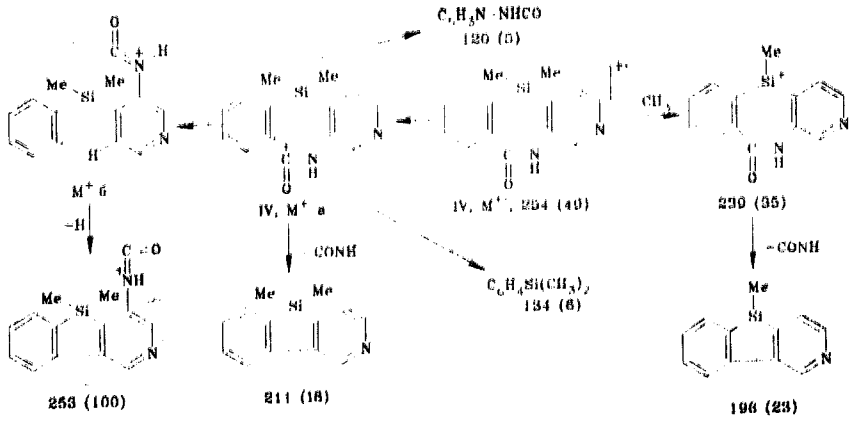
*(m/z values (% of maximum).

The second characteristic of the decomposition of the ion $[M - R]^+$ is the formation of a fragment that does not contain silicon, due to splitting of the particle SiRH (Scheme 1). This process is confirmed by metastable ions and by the measurment of the exact mass of this ionn in the mass spectrum of compound I (measured 181.0763, theory 181.0764, empirical formula $C_{12}H_9N_2$). Since in the mass spectra of compounds I and II, deuterated at the imino group, the ion peak $[M - R - SiRH]^+$ is shifted by one a.m. unit, it can be assumed that a hydrogen from the methylene, not the imino group, migrates to the silicon atom. This process is accompanied by the formation of highly stable ions which evidently have the structure of 3,6-phenanthroline with fully conjugated bonds (the latter assumption is confirmed by the presence of peaks of the corresponding ions carrying two charges). Another route for the fragmentation of the ion $[M - R]^+$, accompanied by narrowing of the central ring, is related to the elimination of the particle CH_2NH (Scheme 1).

The main decomposition routes that are characteristic for the azepines I and II occur also in the fragmentation of the silaazepines III-V. Nevertheless, the replacement of the methylene group in the seven-membered fragment of the molecule by a carbonyl group leads to some specific fragmentation features. In particular, regardless of the absence of a methylene group in the molecules of compounds III-V, the peak intensity of the ion $[M - H]^+$ is much higher than in the mass spectra of the silaazepines I and II. It must be pointed out that high-intensity peaks of the ions $[M - H]^+$ are not characteristic for the mass spectra of seven-membered lactams condensed with an aromatic ring [6]. Naturally, it can therefore be assumed that the moving force for the elimination of a hydrogen atom from M^+ of compounds III-V is the high stability of the fragments $[M-H]^+$ formed. The anomalously high peak intensity of the ions $[M-H]^+$ can be explained by fragmentation of lactams III-V from the open form of M^+. The existence of an open form of M^+ ions was postulated to explain the mass-spectrometric behavior of some oxygen- and silicon-containing polycyclic compounds [7]. In the ionization of compounds III-V the positive charge can be localized at the amide nitrogen [8] as well as at the oxygen atom of the carbonyl group [6]. In both cases the primary process in M^+ must bel the rupture of the both cases the primary process in M^+ must be the rupture of the bond between the carbonyl carbon and the pyridine (compounds III,V) or phenyl (compound IV) ring (β-rupture with respect to the heteroatom). In the open form of M^+ a separation into a cationic and a radical fraction takes place [8]. The existence of M^+ of the lactams III-V in an open form is confirmed by the elimination of a CONH particle already at the first stage of the decomposition : Scheme 2, Table 1). An analogous process which leads to narrowing of the central ring is observed in the fragmentation of compounds I and II only at the stage of the decomposition of the $[M - R]^+$ ion (Scheme 1).

The existence of M^+ of compounds III and IV in an open form is also confirmed by the formation of the following characteristic fragments: Ions are formed in the mass spectrum of compound III with m/z 119 and 135 which correspond to the rupture of the Si—C_{phenyl} bond; ions with m/z 120 and 134 are formed in the mass spectrum of compound IV that correspond to

Scheme 2



the rupture of the Si–C_{pyrid} bond (measured 120.0322, theory 120.0323, empirical formula $C_6H_4N_2O$; measured 134.0547, theory 134.0549, empirical formula $C_8H_{10}Si$; Scheme 2). These ion pairs can be used to establish the different arrangement of the amide fragment between the phenyl and pyridine rings.

Two routes are available for the formation of the $[M - H]^+$ ion from M^+ present in the open form *a*. The first assumes elimination of a hydrogen atom from the imide group and is based on the well-known fact that the fragment ion formed is stabilized by the isocyanate group [6, 9]. The second route for the formation of a stable $[M - H]^+$ ion is given by the possibility of rotation in the ion M^+ around the Si–C_{pyrid} bond (Scheme 2). Conformations can be formed in which splitting of an aromatic hydrogen atom will be accompanied by closure of a five-membered ring [10]. The $[M - H]^+$ ion formed has the stable structure of a silaazafluorene cation, with an isocyanate group at the $C_{(4)}$ atom, protonated via the nitrogen atom.

Thus, the different mass-spectrometric behavior of silaazepines and silaazepinones is due to the fact that fragmentation of the latter takes place predominantly in the open form of the molecular ion with the destruction of the polycyclic system. In the fragmentation of silaazepines the narrowing of the central seven-membered ring takes place only in the second stage of the decomposition.

EXPERIMENTAL

The mass spectra of compounds I-V and of their deutero-analogs were recorded on an LKB-9000 mass spectrometer at an ionizing potential of 70 V and a temperature of sample injection into the ion source of 50°. The accurate mass of the fragment ions was measured on an MS-30 instrument by the peak superposition method. Perfluorokerosene (PFK) was used as a standard. Compounds I-V were synthesized by the procedure given in [11]. Compounds I and II were deuterated in CH_3ONa solution with a 10-fold excess of CD_3OD by refluxing for 8 h. The purity and identity of the compounds was checked by TLC and IR and PMR data.

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