

MASS SPECTRA OF 9-SILA-9,10-DIHYDRO-3-AZAANTHRACENES AND THEIR DERIVATIVES

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Summary

Electron impact fragmentation of 18 compounds from the series of 9-sila-9,10-dihydro-3-azaanthracene has been studied. The formation of $[M - RH]^+$ ions where R is a substituent at the silicon atom is the main fragmentation route for siladihydroazaanthracenes. C(10)-Oxo derivatives lead to $[M - R']^+$ (maximum intensity ion) and $[M - R' - RH]^+$ ions. These regularities may be used for the identification and structural verification of the above compounds.

A specific feature of the mass spectra of siladihydroazaanthracenes is the randomisation of the hydrogen atoms at the C(10) position with the hydrogen atoms of the pyridine and benzene rings of the siladihydroazaanthracene ring.

Introduction

Dissociation of dihydrosilaanthracenes under electron impact has been studied in many papers [1–7]. A specific feature of these compounds is the appearance of the 9-methyl-9-silaanthracene cation during the dissociation of 9-chloro-9-methyl-9,10-dihydro-9-silaanthracene. But all attempts to synthesise of the corresponding neutral 9-methyl-9-silaanthracene, which could show aromatic properties, were unsuccessful.

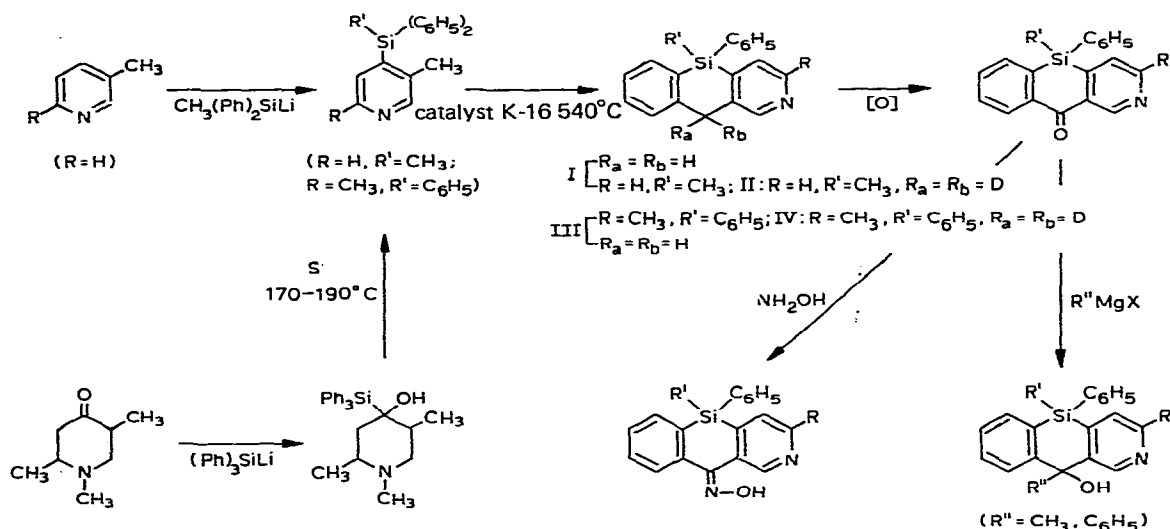
The fragmentation of a large number of siladihydroanthracenes with various substituents at the silicon atom and at C(10) (Br, Cl, H, COOCH₃, etc.) has been studied [3,6]. All the above compounds contain a hydrogen atom at the C(10) position, which in fact determines the fragmentation route, the formation of the corresponding silaanthracene cation. The fragmentation of compounds without a hydrogen atom at the C(10) position has not been studied. Earlier we performed the synthesis of the new organosilicon system 9-sila-9,10-dihydro-3-azaanthracene [8,9]. Several derivatives of siladihydroazaanthracene at the C(10) position, including ketones (V, VI), anthrols (VII–XIV) and

oximes (XV–XVIII) have been obtained. Here we report some of the specific features of the dissociative ionisation of these compounds.

Experimental

Siladihydroazaanthracenes and their derivatives were synthesized as shown in Scheme 1 [8,9]. Deuterated compounds (II, IV) of siladihydroazaanthracenes I

SCHEME 1



and III were obtained on heating 0.05 *N* solutions of the siladihydroazaanthracenes in the presence of sodium methylate in a sealed tube for 10 h [10]. NMR data showed that deuteration took place quantitatively. Mass spectra of the deuterio analogues of oxy compounds and oximes (VIII, X, XII, XIV, XVI, XVIII) were obtained by deuterium exchange of these compounds with methanol-*d* in the vapour phase, directly in the ionisation chamber.

Mass spectra * were measured on a standard MKh-1303 instrument, the direct inlet of samples into the ion source being used. The ionising voltage was 70 V and temperatures were as follows: 30°C (I, VII, VIII, XII), 40°C (IV, V, X); 60°C (II, III, IX, XIV, XV); 80°C (XI, XVII, XVIII); 100°C (VI); 120°C (XIII, XVI).

Results and discussion

Mass spectra of all the compounds I–XVIII show the molecular ion peak, its intensity depending on the nature of the functional groups at the C(10) position. The highest molecular ion stabilities W_m (0.15–0.30) are observed for compounds V, VI, XV–XVIII, containing C=O or C=N groups at the C(10) position. Replacement of a methyl substituent in compounds VIII and XV by a

* See Table 1.

TABLE 1

MASS SPECTRA OF 9-SILA-9,10-DIHYDRO-3-AZAANTHRACENES AND THEIR DERIVATIVES ^a

I:	287(2.1), 286(2.9), 273(14.2), 272(50), 245(2.8), 243(2.5), 218(2.1), 217(2.5), 211(8.3), 210(25.8), 209(100), 194(3.3), 193(2.5), 182(1.8), 181(1.8), 180(1.8), 167(5.8), 141(2.1), 105(6.7).
II:	289(1.7), 288(2.9), 287(0.8), 286(0.4), 275(11.1), 274(34.6), 273(12.3), 272(4.1), 247(2.5), 246(4.1), 245(3.3), 244(4.9), 243(3.7), 219(3.3), 218(4.1), 217(6.6), 212(5.3), 211(27.9), 210(100), 209(8.2), 196(6.9), 195(9.1), 194(4.9), 193(3.3), 182(6.9), 181(7.1), 180(5.7), 169(12.3), 168(14), 167(9.1), 141(9.8), 105(21.4).
III:	363(8.5), 362(10.8), 348(2.7), 324(1.8), 288(10.4), 287(11), 286(73), 285(100), 284(12), 283(13), 272(11), 271(24.8), 270(9.5), 259(12.6), 257(14.4), 243(15.8), 241(13.5), 215(22.5), 193(12.6), 182(10.8), 181(27.9), 180(20.2), 167(14.4), 165(18.9), 155(16.2), 152(12.3), 141(20.7), 129(11), 105(32).
IV:	365(2.2), 364(3.3), 363(3), 362(1.3), 350(0.6), 349(0.6), 324(0.7), 289(6.6), 288(20), 287(60), 286(100), 285(52), 284(3.7), 273(1.3), 272(2), 259(1.3), 258(2), 257(2.3), 244(3), 243(2.3), 216(3), 215(2), 193(1.7), 183(3.7), 182(4.3), 181(5.3), 180(4.3), 167(2), 165(2), 152(1.7), 143(2.7), 105(6.7).
V:	301(65), 300(2.9), 286(100), 283(3.5), 273(2), 272(1), 259(1.5), 258(2.5), 257(4.5), 255(3.5), 242(13.4), 241(10.9), 240(4.9), 230(35.), 224(5.9), 196(1.5), 181(3.5), 180(4), 165(3), 153(3.5), 105(4.9).
VI:	377(62), 376(4), 362(2.3), 360(1.1), 359(2.3), 349(1.7), 348(2.3), 334(1.1), 301(12), 300(100), 299(4), 286(2.3), 285(4), 272(3.4), 256(7.4), 241(1.7), 189(2.3), 188(4), 181(4.6), 105(2.8).
VII:	317(1.4), 316(1.9), 304(8.9), 303(28.7), 302(100), 300(0.5), 299(1), 290(1), 287(3.2), 286(9.6), 285(12.8), 284(46), 274(4.5), 242(7.5), 241(6.4), 240(10.8), 224(15), 222(8.2), 197(5), 180(6.4), 149(5.7), 105(7.4).
VIII:	318(1.6), 317(2), 316(0.7), 305(11.3), 304(30.6), 303(100), 302(43.3), 301(4.6), 290(2.7), 287(6.6), 286(16.6), 285(30.6), 284(43.3), 274(6.6), 243(6.6), 242(16), 241(18.7), 240(10.6), 225(15.3), 224(15.3), 222(19), 197(9), 180(8.7), 105(8.7).
IX:	379(11), 378(4), 365(10), 364(32), 362(4), 361(4.6), 348(3.3), 346(6.6), 316(2), 304(8), 303(29), 302(100), 301(17), 286(20), 285(15.3), 284(30.6), 283(11), 269(4.6), 258(4.6), 243(6), 242(14), 241(10.7), 224(6), 196(4.6), 182(4.7), 181(4), 105(10.6).
X:	380(7.5), 379(13), 378(4.7), 365(15.3), 364(34), 363(15.3), 362(7), 361(6), 349(17.6), 348(4.7), 347(7), 306(9.5), 304(37.6), 303(88.2), 302(100), 301(30.5), 287(33), 286(73), 285(47), 284(37.6), 274(31.7), 272(54.1), 270(13), 259(29.4), 258(16.4), 243(11.7), 242(23.5), 241(27), 240(23), 225(9.4), 224(11.7), 181(17.6), 105(20).
XI:	393(1.8), 392(1.2), 380(13), 379(47.8), 378(100), 365(3.1), 364(3.1), 363(1.3), 362(1.8), 361(3.1), 360(7.7), 317(6.8), 316(17.4), 302(2.8), 301(5.9), 300(13), 299(6), 298(8.7), 286(2), 285(2.2), 273(1.3), 272(3.4), 256(6.5), 238(4.4), 189(3.1), 181(2.8), 180(2.5), 150(2.4), 105(3.4).
XII:	394(1.4), 393(1.8), 381(8.3), 380(31.3), 379(100), 378(78), 365(4.1), 364(3), 363(1.8), 362(3.2), 361(5.5), 360(11), 318(5), 317(17), 316(13.8), 302(5), 301(12.4), 300(13), 299(5.5), 298(12), 287(6), 286(8.3), 285(13.4), 273(2.7), 272(5), 257(5) 256(8.7), 239(3.7), 189(4), 181(5), 150(3.2), 105(6.5).
XIII:	455(13), 454(1.8), 440(0.7), 439(1), 438(2.3), 437(2.3), 380(8.7), 379(33.3), 378(100), 377(7.8), 363(1.5), 362(2.7), 361(7.5), 360(9), 359(4.8), 349(0.7), 301(5), 300(10), 285(2), 272(2.5), 256(5.3), 181(2), 180(1.7), 105(2.5).
XIV:	456(17.5), 455(12.9), 439(2), 438(4.3), 437(4.3), 381(9.7), 380(30), 379(81.7), 378(100), 377(17.2), 363(3.2), 362(5.4), 361(13), 360(21.5), 359(9.7), 350(3.2), 349(1), 302(3.2), 301(11.8), 300(16), 287(3.2), 286(3.2), 285(5.4), 272(3.2), 257(3.2), 256(4.3), 181(3.2), 105(8.6).
XV:	316(100), 315(47), 302(17.8), 301(64.3), 300(38.6), 299(17), 286(14.3), 285(46.4), 284(14.3), 283(42.8), 270(2.8), 257(10), 256(23.5), 239(3.5), 238(5), 223(15.7), 207(10.5), 206(7), 198(11), 197(4.3), 196(5), 181(3.5), 180(5), 167(3.5), 165(3.5), 154(3.5), 137(7), 115(2.8), 105(7).
XVI:	317(70.9), 316(935.), 315(50), 302(58), 301(100), 300(87), 299(32), 287(29), 286(80.6), 285(96.7), 284(32), 283(35), 271(38.7), 270(50), 257(19.3), 256(50), 240(64), 224(19.3), 223(32), 208(19.3), 207(32), 206(16), 198(50), 197(38.7), 196(25.8), 181(32), 180(25.8), 167(25.8), 165(19.3), 154(19), 153(16), 137(19), 115(19), 105(50).

TABLE 1 (continued)

XVII: 392(100), 391(68), 377(27.3), 376(50), 375(25.5), 374(7.5), 363(3.8), 362(4.7), 361(5.6), 350(1.8), 349(2.8), 316(4.7), 315(9.4), 314(6.6), 300(9.4), 299(16.9), 297(12.3), 279(7.5), 272(7.5), 270(11.3), 257(7.5), 256(4.7), 243(2.8), 241(2), 206(9.4), 181(4.7), 149(3.8), 129(2.8), 111(6.6), 105(5.7).

XVIII: 393(69), 392(100), 391(57), 378(4.3), 377(8.5), 376(8.5), 375(11.4), 364(2.8), 363(4.8), 362(2.8), 350(1.4), 316(8.6), 315(7.1), 314(5.7), 301(5.7), 300(7), 299(5.7), 297(10), 279(4.3), 272(7), 271(7), 270(11.4), 257(8.6), 256(5.7), 243(5.7), 241(4.3), 221(8.6), 206(8.6), 181(11.4), 149(28), 129(10), 111(20), 105(21).

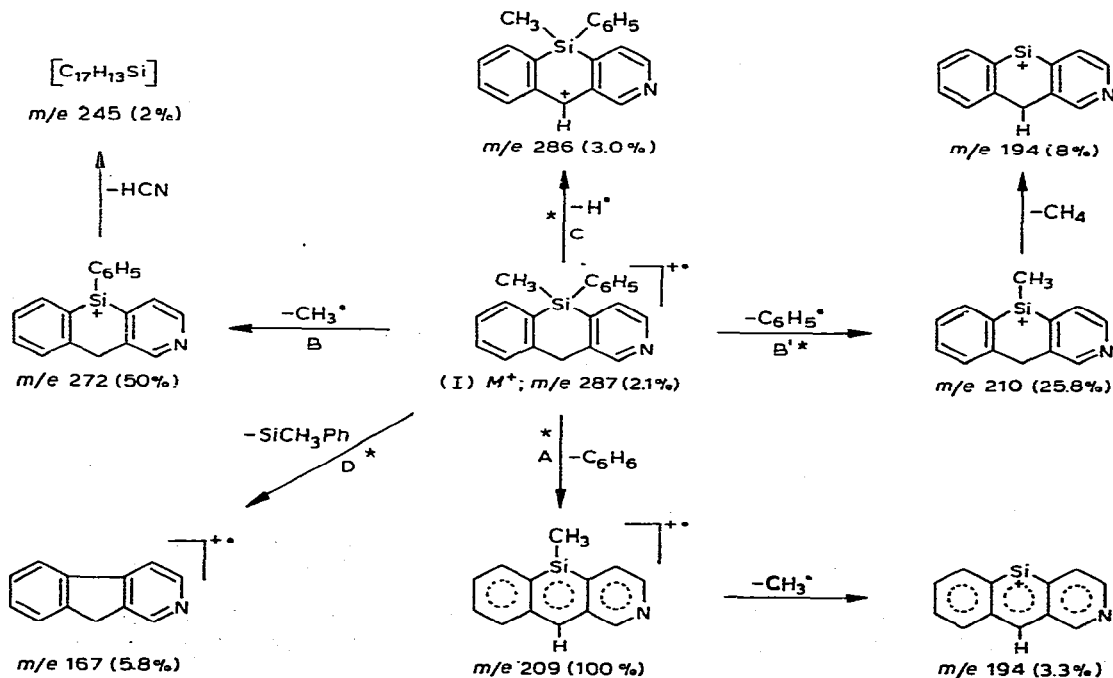
^a Mass of ions are given in m/e , their intensity is shown in (%) relative to the maximum intensity peak.

phenyl substituent as the silicon atom (XI, XVII), leads to a slight increase in W_m , 0.005 (VII), 0.007 (XI), 0.25 (XV), 0.28 (XVII), respectively. Dihydrosilaazaanthracenes I–IV and dihydrosilaazaanthrols VII–XIV show the lowest value for their molecular ion stability W_m (0.005–0.009).

9-Sila-9,10-dihydro-3-azaanthracenes (I–IV)

The dominating fragmentation route of compounds I–IV, as in the case of dihydrosilaanthracenes [6], is the abstraction of a benzene molecule with the formation of a $[M - C_6H_6]^+$ rearrangement ions (Scheme 2, Path A). Mass spec-

SCHEME 2



tra of deuterated compounds II and IV show a shift of one mass unit towards higher masses for $[M - C_6H_6]^+$ ion. This is in accordance with the migration of an hydrogen atom from the C(10) position to the phenyl radical leading to the formation of the ion $[M - C_6H_6]^+$. Absence of the fragment $[M - C_6H_6]^+$ in

the mass spectra of oxo derivatives V and VI confirms the proposed method of $[M - C_6H_6]^+$ ion formation. Elimination of the benzene molecule by M^+ ions is initiated by the formation of a fragment which has a stable silaazaanthracene cation-radical structure.

The second intensive fragmentation route of these compounds is the elimination of radicals at the silicon atom (Scheme 2, Path B). As a result the fragments $[M - R]^+$ are formed, where $R = CH_3$ (I and II) and $R = C_6H_5$ (III and IV). These fragments undergo a shift of two mass units towards higher masses in the mass spectra of deuterated compounds II and IV.

A specific feature of the fragmentation of 9-sila-9,10-dihydro-3-azaanthracenes (I–IV) is the presence of the $[M - H]^+$ ion, the intensity of which is higher than that of the molecular ion: $I_{[M-H]^+}/I_{M^+} = 3.5$, (Scheme 2, Path C). The ion $[M - H]^+$ is formed due to hydrogen abstraction from the C(10) position. This is explained by the comparatively low (0.10–0.28) ratio $I_{[M-H]^+}/I_{M^+}$ for compounds V and VI.

Mass spectra of the deuterated compounds II and IV show the presence of species $[M - H]^+$ in addition to the $[M - R]^+$ ion. Its formation may be explained by a randomisation process between the deuterium atoms at C(10) and the rest of the hydrogen atoms in the molecular ion II and IV. The appearance of ions $[M - C_6H_6]^+$ in mass spectra II and IV is explained likewise.

In addition to the above dissociation routes of I–IV, their molecular ions expel $SiR'R''$, where $R' = CH_3$, $R'' = C_6H_5$ for compounds I and II, and $R' = R'' = C_6H_5$ for III and IV. Fragments $[M - SiR'R'']$ are formed, possibly having a 2-azafluorene structure (Scheme 2, Path D).

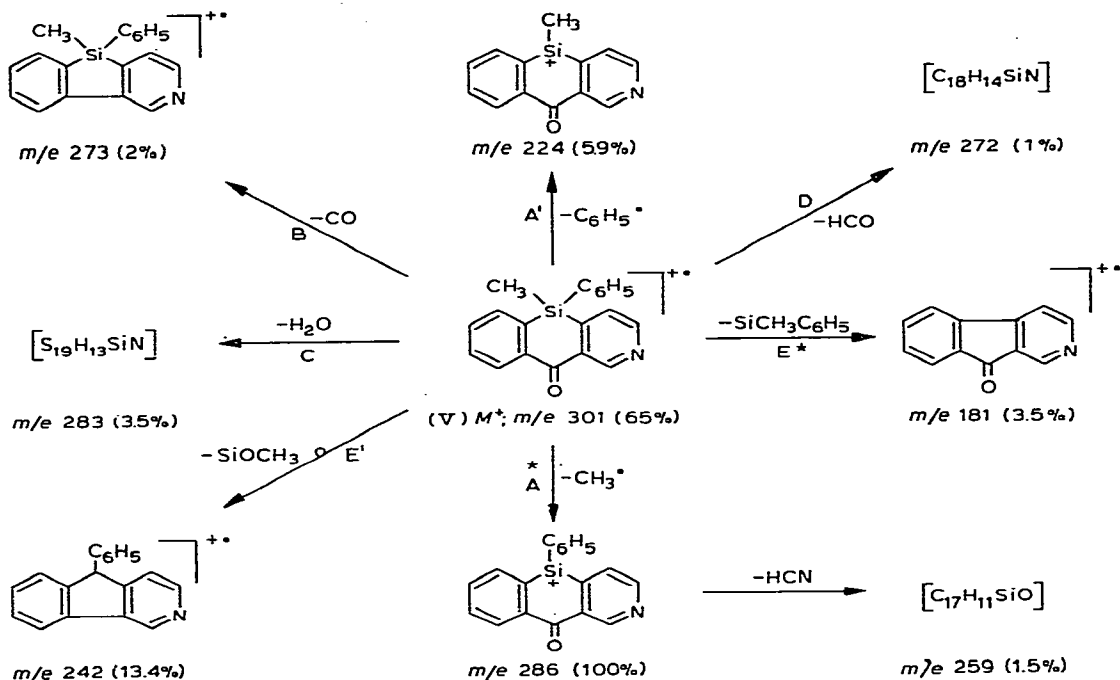
In comparison to the dissociative ionisation of compounds I and II, the dissociation of III and IV leads to a low intensity fragment $[M - CH_3]^+$, m/e 348. The presence of the CH_3 group at the carbon atom instead of at the silicon atom explains the low intensity of $[M - CH_3]^+$ ions. Further this fragment relative to the $[M - CH_3]^+$ ion in the mass spectra of I and II, readily expels C_6H_5 radical, leading to the fragment $[M - CH_3 - C_6H_5]$ m/e 271, which arises from the different hybridisation of the silicon atom in $[M - CH_3]^+$ ions of compounds I, II and III, IV.

9-Sila-9,10-dihydro-3-azaanthron (V, VI)

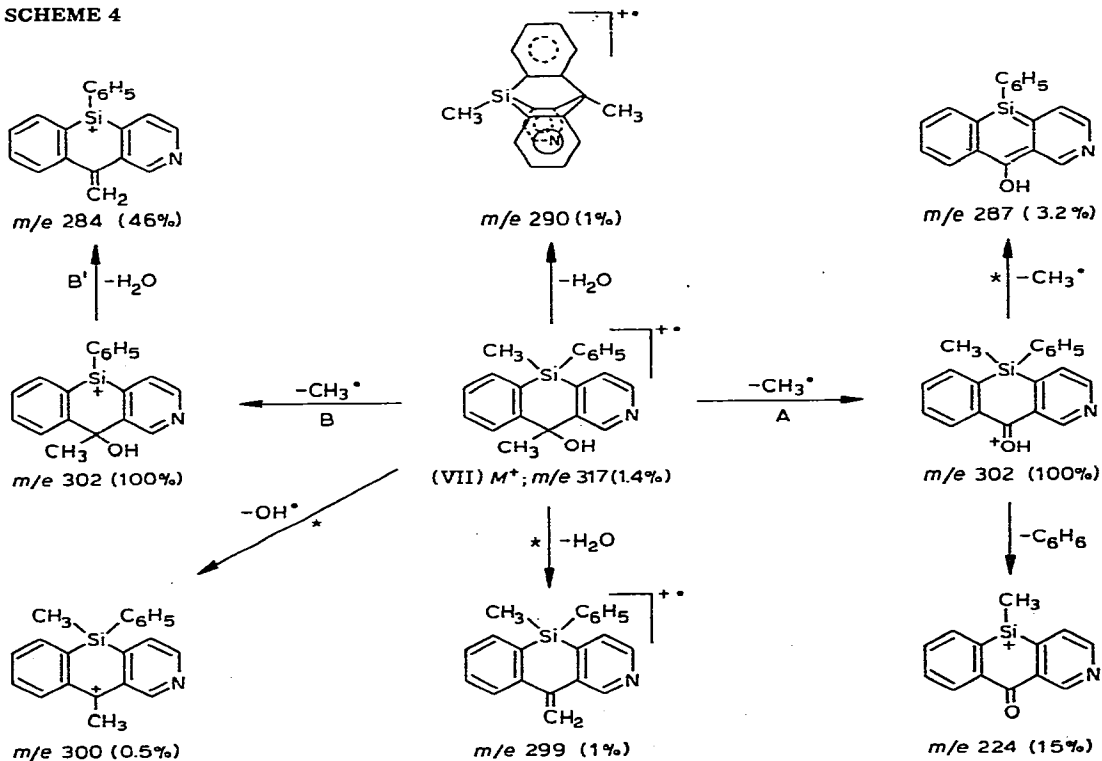
The main fragmentation route of ketones V and VI is the elimination of radicals R ($R = CH_3, C_6H_5$), attached to the silicon atom (Scheme 3, Path A). In contrast to the dissociative ionisation of compounds I–IV, mass spectra of V and VI do not consist of the rearrangement ion $[M - C_6H_6]^+$, which confirms the mechanism scheme of its formation due to hydrogen atom migration from the C(10) position. The molecular ions M^+ undergo complex rearrangement processes during their dissociation, the elimination of such species as CO, H_2O , HCO, $SiOCH_3$, $SiOC_6H_5$ (Scheme 3, Paths B, C, D, E) being observed in their mass spectra. The abstraction of the HCN molecule at the first and later stages takes place with low probability, peak ions such as $[M - HCN]^+$, $[M - SiOCH_3 - HCN]^+$, $[M - CH_3 - HCN]^+$ being of low intensity in the mass spectra of V and VI.

As in the case of the dissociative ionisation of compounds I–IV, the molecular ions of V and VI expel fragments $SiR'R''$ leading to $[M - SiR'R'']^+$ m/e

SCHEME 3



SCHEME 4



181 (Scheme 3, Path E), formation of which is confirmed by metastable peaks $m^* 109$ and $m^* 87$, respectively. The absence of a methyl group at the silicon atom in compound VI leads to the low intensity peak fragment $[M - \text{CH}_3]^+$ $m/e 362$ and an increase in the intensity of the peak ion $[M - \text{H}]^+$ $m/e 376$.

Silaazaanthrols-10 (VII–XIV)

Mass spectra of silaazaanthrols VII–XIV show maximum intensity ions $[M - \text{CH}_3]^+$ and $[M - \text{C}_6\text{H}_5]^+$ for compounds VII, VIII, XI, XII, and IX, X, XIII, XIV respectively. The dissociation of silaazaanthrols (VII–XIV) show a two-fold increase in the ratio $I_{[M-R]^+}/I_{M^+}$ (where $R = \text{CH}_3$ or C_6H_5) in comparison to that of compounds I and III. Such an increase indicates the elimination of CH_3 and C_6H_5 radicals from the C(10) position. This fact is in accordance with the fission of a β -bond relative to the oxygen atoms of the hydroxyl group (II) (Scheme 4, Path A).

The second route of the dissociative ionisation of the molecular ions VII–XIV is the loss of radicals situated at the silicon atom (Scheme 4, Path B) leading to $[M - \text{CH}_3]^+$ ion $m/e 364$, and fragment $[M - \text{C}_6\text{H}_5]^+$ $m/e 316$, in the mass spectra of IX and XI, respectively. This fragmentation path is further confirmed by the presence of a middle intensity peak fragment $[M - R - \text{H}_2\text{O}]^+$ where $R = \text{CH}_3$ (VII, VIII, XI, XII) and C_6H_5 (IX, X, XII, XIV).

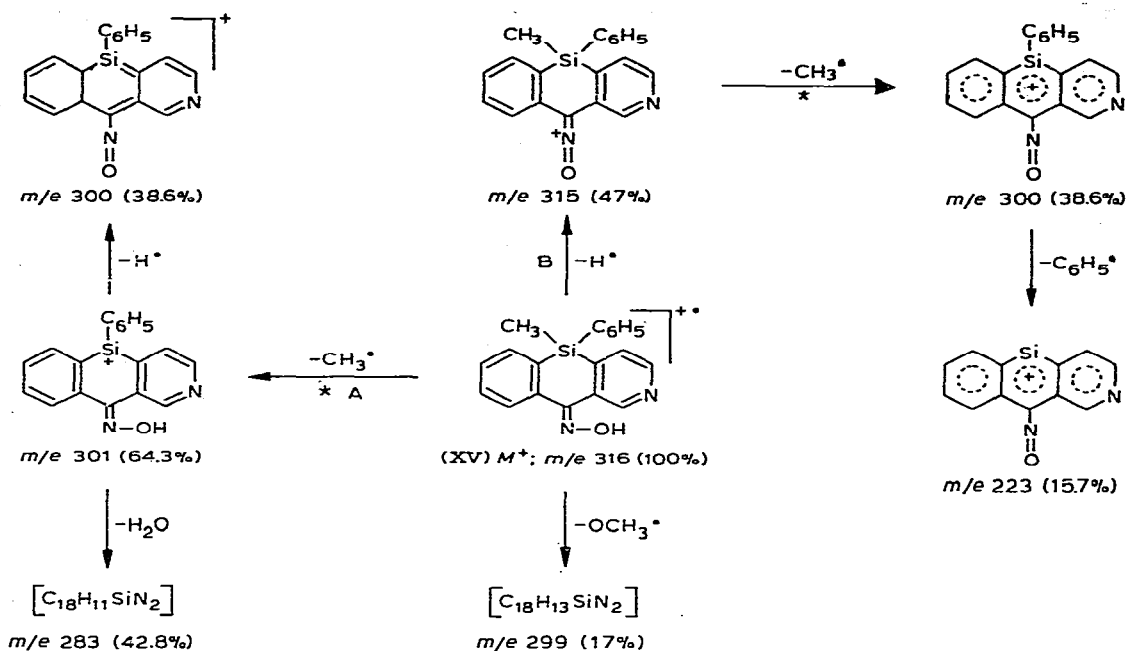
It is noteworthy that the presence of the OH group in silaazaanthrols, and its subsequent dissociation, does not lead to the active hydrogen atom migrating onto the C_6H_5 radical at the silicon atom with the formation of $[M - \text{C}_6\text{H}_6]^+$ rearrangement ion, as was the case for compounds I–IV. This fact is in accordance with the earlier assumption, that the appearance of the $[M - \text{C}_6\text{H}_6]^+$ ion is possibly due to the formation of a silaaromatic system of high stability. This is confirmed by the expulsion of a C_6H_6 molecule in the second stage of the dissociation of silaazaanthrols, leading to ions $[M - \text{CH}_3 - \text{C}_6\text{H}_6]^+$ $m/e 224$ (VII, VIII) and $m/e 300$ (XI, XII), and also ions $[M - \text{C}_6\text{H}_5 - \text{C}_6\text{H}_6]^+$ $m/e 224$ (IX, X) and $m/e 300$ (XIII, XIV) having the structure described above.

Other dissociative paths of the molecular ions VII–XIV lead to the ions $[M - \text{H}]^+$, $[M - \text{OH}]^+$ and $[M - \text{H}_2\text{O}]^+$, having relatively low intensity. The appearance of the latter ion may be explained by the elimination of hydrogen atom from the hydrocarbon radical situated at the C(10) position or at the silicon atom, along with the OH group (Scheme 4, Path C and D). Partial shifts of peak ions by one mass unit towards higher masses or absence of such a shift in the mass spectra of deuterated compounds VIII, X, XII and XIV confirm the formation of ions shown in Scheme 4.

Oxime-9-sila-9,10-dihydro-3-azaanthron-10 (XV–XVIII)

In contrast to the ketones V and VI, the dissociative ionisation of oxime XV–XVIII (Scheme 5, Path A), means that abstraction of radicals at the silicon atom is less probable. The ratio $I_{[M-\text{CH}_3]^+}/I_{M^+}$ for oximes XV and XVI and ketone V is 0.61 and 1.7 respectively; whereas for compounds XVII, XVIII and ketone VI the ratio is 0.13 and 1.59, respectively. Elimination of the hydrogen atom on the other hand leads to the formation of high intensity (approx. 3–6 times) $[M - \text{H}]^+$ ions (Scheme 4, Path B) in comparison to the same fragment in the mass spectra of V and VI.

SCHEME 5



Replacement of a CH₃ group by a C₆H₅ group at the silicon atom in oximes XV–XVIII, lowers the intensity (3–5 times) of peak ions $[M - R]^+$, $[M - H]^+$ and $[M - R - H_2O]^+$, where R is a substituent attached to the silicon atom. This distinguishes the mass spectral behaviour of oximes from their oxo derivatives V and VI. In addition, the mass spectra of compounds XV show fragment $[M - OCH_3]^+$ m/e 235, undergoing a shift of one mass unit towards a higher mass in the mass spectrum of the deuterated compound XVI. Its formation may be associated with the rearrangement of the molecular ion XV, similar to the Beckmann rearrangement for oximes [12]. Rearrangement ion m/e 299, corresponding to the loss of the OC₆H₅ species in the mass spectrum of compound XVII, has low intensity.

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