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MASS SPECTRA OF SILYLINDOLIZINES, DIHYDROSILANAPHTHOINDOLIZINE AND DIHYDROSILAAZAACEANTHRELENES

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Summary

The electron impact fragmentation of compounds from the series of silylindolizines, dihydrosilanaphthoindolizines, and dihydrosilaazaaceanthrelenes has been studied. For indolizines having an exocyclic silicon atom, carbomethoxy and benzoyl groups attached to the five membered ring, the loss of the OCH_3 species from the carbomethoxy groups and the hydrocarbon radical from the silicon atom takes place with almost equal intensity. In the case of dihydrosilanaphthoindolizines the expulsion of the OCH_3 group from the carbomethoxy substituents is the most pronounced fragmentation route; moreover, a sharp fall in the intensity of their molecular ion peak (about 5 times) is registered. The main fragmentation route during the dissociative ionisation of silaazaaceanthrelenes, in contrast to silylindolizines and silanaphthoindolizines, is the loss of the hydrocarbon radical attached to the nitrogen atom, and not the substituents at the silicon atom, or the OCH_3 species from the carbomethoxy groups. Such properties can be used for the purpose of structural analysis.

Introduction

The dissociative ionisation of indoles has been studied in detail [1]. The isomers of indoles, indolizines, have known mass spectrometry data [2,3], whereas any information regarding the mass spectral behaviour of indolizines having a triorganosilyl substituent, is absent.

The investigation of the fragmentation of these compounds is essential for the use of the mass spectroscopic method for structural analysis, especially for the identification of N-heteroaromatic systems having the same substituents, but, a slight difference in their structures. The present work is a contribution

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to the above question in the series of silylindolizines, dihydrosilanaphtho-indolizines and dihydrosilaazaaceanthrelenes.

Experimental

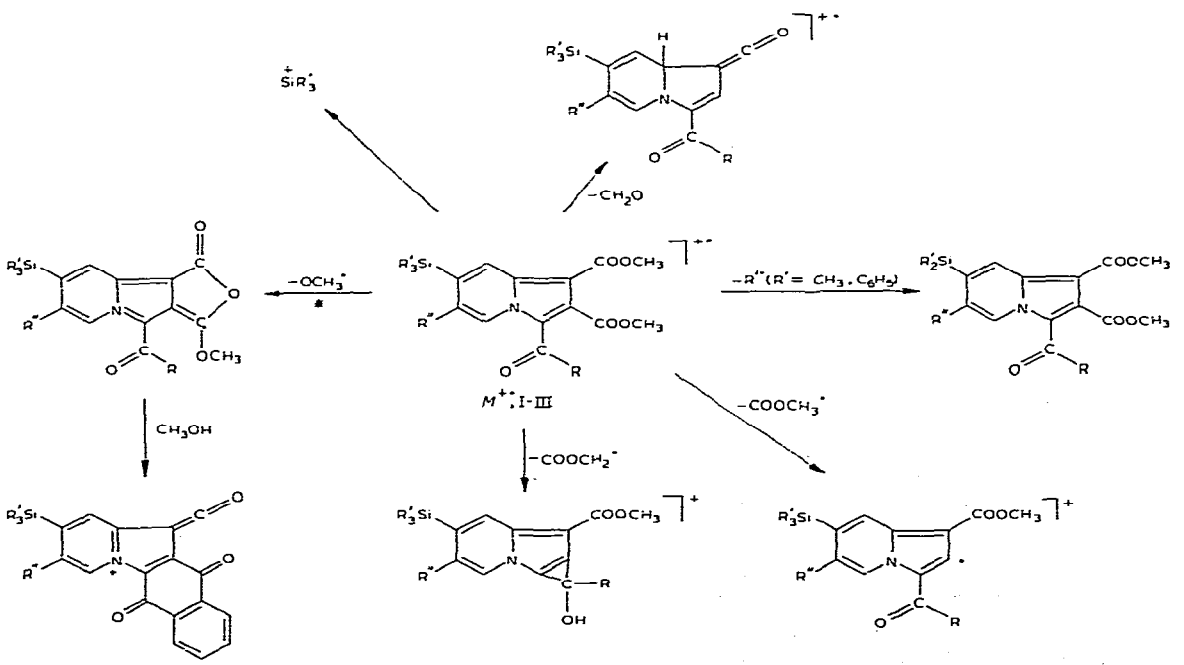
The synthesis of silyl-substituted indolizines, I—III, and dihydrosilanaphtho-indolizines, IV—VI, have been published [4]; synthesis of dihydrosilaazaace-anthrelenes VII—XII, has also been cited [5,6].

Mass spectra were measured on a CH-8 instrument. The ionising voltage was 70 V and temperatures were as follows: 40°C (I), 90°C (II, VII), 120°C (IV, V, VIII, X, XI, XII), 160°C (III, VI, IX).

Results and discussion

7-Triorganosilyl-substituted indolizines (I—III)

In the mass spectra of compounds I—III, the maximum intensity is seen for molecular ion peaks. The molecular ion stability (W_m) of indolizines I and II is approximately the same, independent of the nature of the substituents at the C(3) and C(6) positions of these compounds. This fact is probably explained by the presence of structural factors different in nature yet similar in their destabilising influence on the value W_m, in the molecules I and II. For indolizine I it is the benzoyl radical and for compound II the *ortho*-situated CH_3 and $SiPh_3$ groups. The above explanation is supported by the fairly low value of W_m for compound III (about 4 times), the molecules of which contain both these destabilising factors.



SCHEME 1

The dissociative ionisation of silylindolizines I—III takes place by a number of competitive routes (Scheme 1). The probability of realizing fragmentation routes depends on the nature of the hydrocarbon radical attached to the silicon atom and the absence or presence of an *ortho*-situated methyl radical relative to the SiR_3 group. The main fragmentation routes of compounds I—III are the loss of CH_3 radical from the silicon atom (I), as in the case of the dissociative ionisation of silyl-substituted pyridines [7] and dihydrosilaazaanthracenes [8], OCH_3 and $SiPh_3$ groups. In the mass spectra of compound I the intensity of the ion $(M - CH_3)^+$, *m/e* 394, is 8.8%, which is about is half the intensity of the fragment $(M - CH_3)^+$, *m/e* 378 (16.5%). Yet the probability of the expulsion of the methyl group, *K* (*K* equals the sum of the intensities of all the ions formed along this path, relative to the total ion current) is only 1.1 times higher than the probability of the loss of the OCH_3 radical (Table 1). A similar difference is observed for the intensities of the fragments $(M - C_6H_5)^+$ and $(M - OCH_3)^+$ and the probability of expulsion *K* in mass spectra of II and III.

The abstraction of an hydrocarbon radical from the silicon atom is the most intense process in the mass spectra of I. For substances II and III the same value is about 1.1—1.6 times less (Table 1). This indicates that the Si—Ph bond is comparatively stronger than the Si—CH_3 bond in the M^+ ions of the investigated indolizines.

The elimination of the OCH_3 group from compounds I and II, takes place with almost equal intensity, whereas for substance III, the value *K* for this process is about 3 times less. This is explained by the presence of a competitive process, that is the extreme ease of the loss of the $SiPh_3$ group. The ion $[M - OCH_3]^+$ which is formed in the case of indolizines I and III further loses a molecule of CH_3OH.

The absence of an intense peak of the ion $[M - OC_2H_5]^+$ in the mass spectrum of compound II is noteworthy. This fact shows that the probability of alkoxy group elimination depends on the position of the carboalkoxy group in the indolizine cycle. The experimental data show that the alkoxy group is most readily extracted from the C(1) and with a low intensity from the C(3) position.

The loss of the SiR_3 group in compounds II and III containing phenyl groups at the silicon atom takes place with extreme ease. The value *K* for this process is particularly high in the case of compound III, which is due to the presence of a benzoyl group instead of a carboethoxy one. The above process takes place with localisation of the positive charge totally on the silyl-containing fragment. Similar results were also obtained in the case of silyl-substituted pyridines [7]. As in the case of the dissociation of 1,2-dicarbomethoxy-substituted indolizines [2], compounds I—III readily lose the carbomethoxy groups.

In contrast to the dissociative ionisation of 1,2-dicarbo-methoxy-3-benzoyl-indolizine [2], the fragmentation of compounds I—III leads to the expulsion of a $COOCH_2$ species in the first stage. The loss of an analogous species $COOC_2H_4$ from the molecular ion of indolizine II takes place more readily (about 4 times). The $COOC_2H_4$ fragment is eliminated with a probability 4.9 times higher than that for the OC_2H_5 radical.

The fragmentation of compounds I and III also leads to the expulsion of the benzoyl radical; here the positive charge is localized on the above-mentioned

(Continued on p. 46)

TABLE 1

THE INTENSITY OF THE MOLECULAR ION PEAKS (I_M), THEIR STABILITY (W_M) AND DISSOCIATION PROBABILITY (K) [a] ALONG COMPETITIVE PATHS IN THE MASS SPECTRA OF COMPOUNDS I—XII (footnots see p. 45)

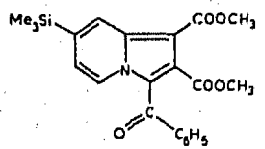
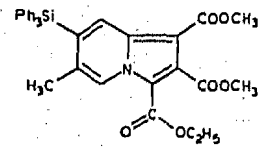
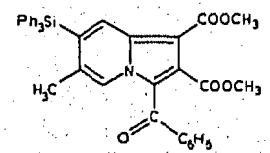
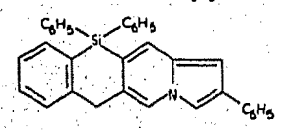
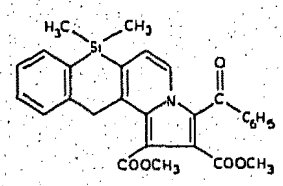
Compound	Formula	I_M (%)	W_M (%)	K (%) [b] $(M-OCH_3)^+$	$(M-R)^+$ R at Si	$(M-PhCO)^+$	$(M-COOCH_2)^+$	$(M-COOCH_3)^+$	$(M-CH_2O)^+$	$(M-C_6H_5)^+$
I		100	20.0	24.0	21.2	2.9	2.2	13.0	7.8	4.5
II		100	19.0	22.7	18.8	—	1.9	2.8	8.0	—
III		100	5.0	8.7	13.0	—	1.8	2.9	2.2	—
IV		100	47.8	—	10.0	—	—	—	—	—
V		16	2.2	50.0	0.1	26.0	—	0.4	—	0.6

TABLE 1 (continued)

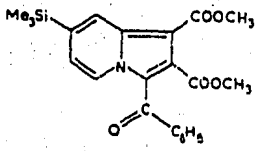
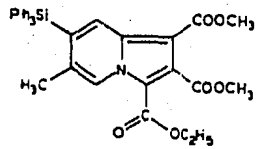
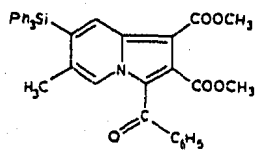
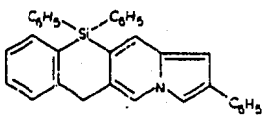
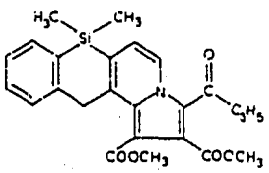
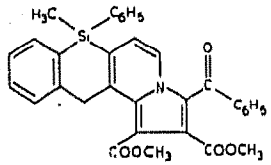
Compound	Formula	K (%) [b]							
		$(M-OC_2H_5)^+$	$(M-C_6H_6)^+$	$(M-COOC_2H_4)^+$	$(M-CH_3OH)$	$(M-H)^+$	SiR_3	$(M-HSiPh_2)^+$	$(M-SiPh_2)^+$
I		—	—	—	—	—	4.2	—	—
II		4.7	—	7.7	—	—	14.4	—	—
III		—	2.0	—	—	—	55.0	—	—
IV		—	28.2	—	—	1.8	—	9.3	2.9
V		—	—	—	25.2	—	—	—	—

TABLE 1 (continued)

THE INTENSITY OF THE MOLECULAR ION PEAKS (I_M), THEIR STABILITY (W_M) AND DISSOCIATION PROBABILITY (K) [a] ALONG COMPETITIVE PATHS IN THE MASS SPECTRA OF COMPOUNDS I–XII (footnots see p. 45)

Compound	Formula	I_M (%)	W_M (%)	K (%) [b] $(M-OCH_3)^+$	$(M-R)^+$ R at Si	$(M-PhCO)^+$	$(M-COOCH_2)^+$	$(M-COOCH_3)^+$	$(M-CH_2O)^+$	$(M-C_6H_5)^+$
VI		14	0.4	46.9	0.1	20.9	—	0.8	—	1.4

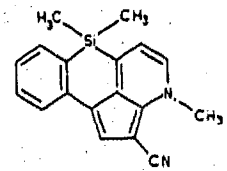
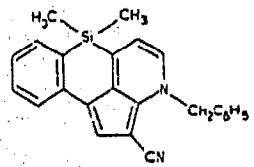
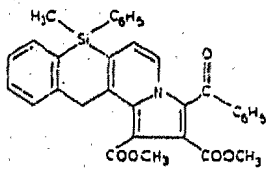
Compound	Formula	I_M (%)	W_M (%)	K (%) [b] $(M-H)^+$	$(M-R)^+$ R at Si	$(M-OCH_3)^+$	$(M-COOH)^+$
VII		100	43.0	—	—	—	—
VIII		81.0	11.0	—	—	—	—

TABLE 1 (continued)

Compound	Formula	K (%) [b]							
		$(M-OC_2H_5)^+$	$(M-C_6H_6)^+$	$(M-COOC_2H_4)^+$	$(M-CH_3OH)$	$(M-H)^+$	SiR_3	$(M-HSiPh_2)^+$	$(M-SiPh_2)^+$
VI		—	0.5	—	20.7	—	—	—	—

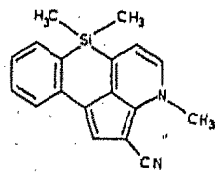
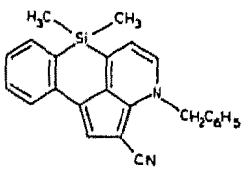
Compound	Formula	K (%) [b]				
		$(M-COOCH_3)^+$	$(M-HCOOH)^+$	$(M-CH_2O)^+$	$(M-SiMe_2)^+$	$(M-R)^+$ R at N
VII		—	—	—	10.1	46.6
VIII		—	—	—	—	85.5

TABLE 1 (continued)

THE INTENSITY OF THE MOLECULAR ION PEAKS (I_M), THEIR STABILITY (W_M) AND DISSOCIATION PROBABILITY (K) [a] ALONG COMPETITIVE PATHS IN THE MASS SPECTRA OF COMPOUNDS I–XII (footnots see p. 45)

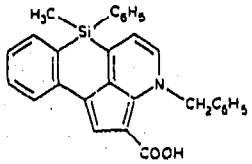
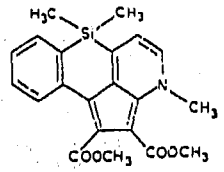
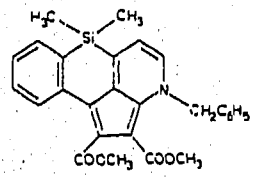
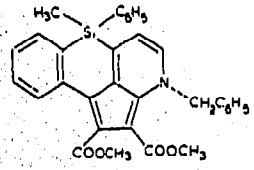
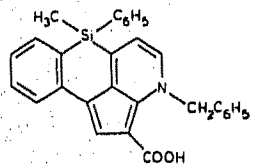
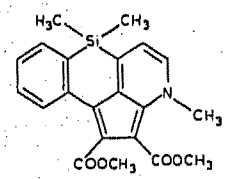
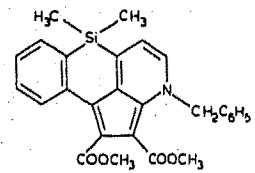
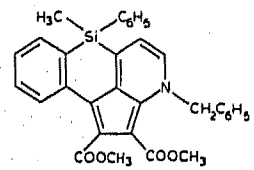
Compoud	Formula	K (%) [b]					
		I_M (%)	W_M (%)	$(M-H)^+$	$(M-R)^+$ R at Si	$(M-OCH_3)^+$	$(M-COOH)^+$
IX		97.0	14.5	1.5	R = Ph 2.1	—	73.0
X		100	26.3	—	—	10.6	—
XI		95	21.6	—	—	1.6	—
XII		100	24.0	—	—	7.4	—

TABLE 1 (continued)

Compound	Formula	K (%) [b]				
		$(M-COOCH_3)^+$	$(M-HCOOH)^+$	$(M-CH_2O)^+$	$(M-SiMe_2)^+$	$(M-R)^+$ R at N
IX		—	7.0	—	—	—
X		27.5	—	—	—	33.4
XI		13.9	—	—	—	63.7
XII		9.0	—	—	—	55.8

[a] The value K is calculated as the ratio of the sum of the intensities of all the ions formed along one of the fragmentation routes relative to the total ion current.
[b] Here the species eliminated by the ion M^+ in the first stages of its dissociation along competitive paths are represented.

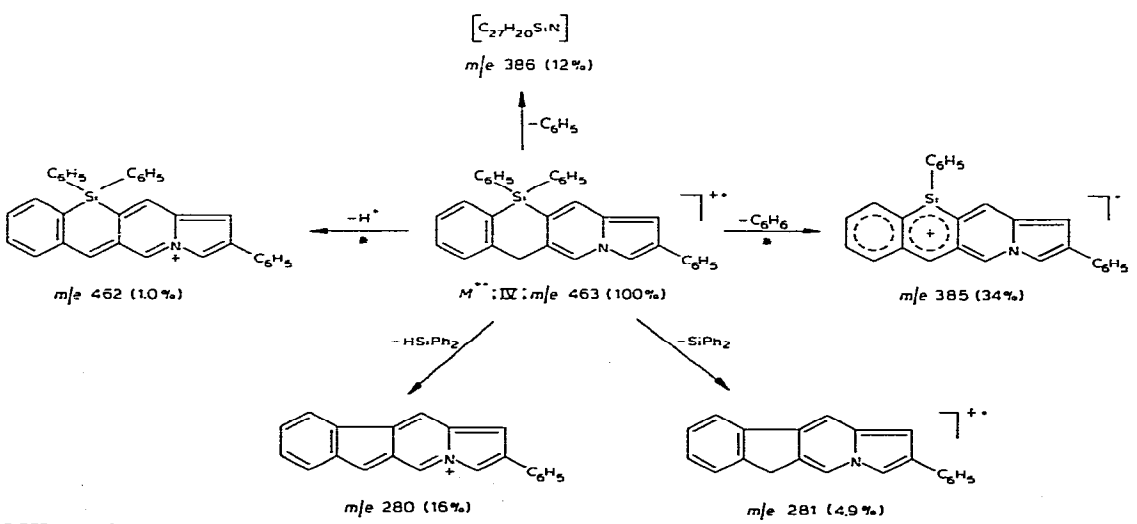
radical, and on the main part of the molecule. The formation of the ion $[M - PhCO]^+$ is not registered for mass spectra of indolizine III, whereas formation of the ion PhCO (27.2%) is observed.

In the mass spectra of indolizines II and III, as in the case of 3-methyl-4-silyl-substituted pyridines [7], an *ortho*-effect between the CH_3 and $SiPh_3$ substituents is observed. This leads to the elimination of a benzene molecule with the formation of a low intensity $[M - C_6H_6]^+$ ion.

Dihydrosilanaphthoindolizines (IV—VI)

In the mass spectra of compound IV, obtaining a phenyl group at the C(2) position, a maximum intensity molecular ion peak is observed. Compounds V and VI, having benzoyl and carbomethoxy groups in the pyrrole ring, show $I(M^+)$ as 16% and 14%, respectively. A low molecular ion intensity is also recorded for the dissociation of 2-methyl-9,9-diphenyl-9,10-dihydro-9-sila-3-azaanthracene (A) ($I(M^+) = 8.1\%$), which is the parent compound for the synthesis of compound IV. This indicates a noticeable stabilising effect of the indolizine moiety in the molecular ion of compound IV. The indolizine fragment decreases the mobility of the hydrogen atoms at the C(10) position. This deduction is supported by the sharp decrease in the formation of the ion $[M - H]^+$ in the mass spectra of compound IV in comparison to the above-mentioned dihydrosilaazaanthracene (A) ($I(M - H)^+/I(M^+)$ equals 0.03 and 1.3, respectively). The fall in the intensity of the ion $[M - C_6H_6]^+$ (about 2 times), which is formed as a result of the migration of a hydrogen atom from the C(10) position to the phenyl radical at the silicon atom, is explained likewise. The ion $[M - C_6H_6]^{+\cdot}$ is the dominating fragmentation route for compound IV (Scheme 2).

Other dissociative paths of the molecular ion of compound IV lead to the loss of the fragments C_6H_5, $Si(Ph)_2$, $HSi(Ph)_2$ (Scheme 2). The fragment $[M - HSiPh_2]^+$, *m/e* 280, is formed with greater probability than the fragment $[M -$



SCHEME 2

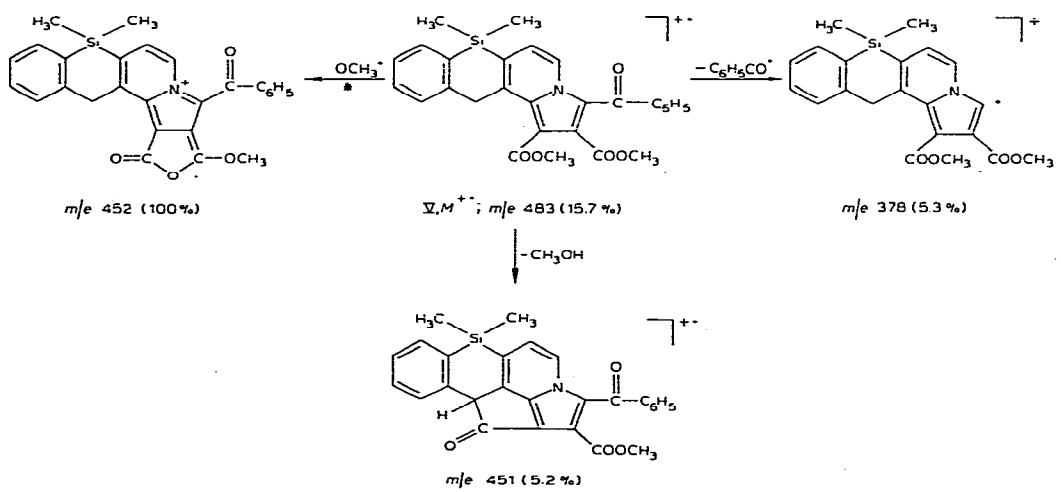
$SiPh_2]^+$. The mass spectra of compound A shows a reverse picture ($I(M - HSiPh_2)^+/I(M - SiPh_2)^+$ equals 0.7 for A and 3.2 for IV). These data demonstrate the comparatively high stability of the fragment $[M - HSiPh_2]^+$ formed during the dissociation of compound IV, due to the presence of a resonance-stabilised ion having a quaternary nitrogen atom.

The mass spectral behaviour of silanaphtoindolizines V and VI is determined by the presence of benzoyl and carbomethoxy groups in the indolizine fragment, and not the substituents attached to the silicon atom as was the case in compound IV, where the main fragmentation route was the loss of a benzene molecule and a phenyl radical due to the cleavage of the $Si—C_6H_5$ bond. In comparison to the indolizines I—III, the dihydrosilanaphtoindolizines V and VI show a sharp fall in the intensity of the molecular ion peak.

In contrast to compounds I—III, the dissociative ionisation of compounds V and VI is characterised by the pronounced elimination of the OCH_3 group from the molecular ions (Scheme 3). The probability of such a process is about 2 times higher in comparison to the silyl-substituted indolizines I and II and about 5 times in comparison to the fragmentation of indolizine III.

It is noteworthy that the loss of the OCH_3 group is also the main fragmentation route in case of the previously investigated 3-benzoyl-1,2-dicarbomethoxyindolizine [2]. As such, it is only the presence of an exocyclic triorganosilyl group in the indolizine cycle which decreases the intensity of the ion $[M - OCH_3]^+$, due to the appearance of a competitive process — the elimination of a hydrocarbon radical from the silicon atom.

The second unique feature of the dissociative ionisation of dihydrosilanaphthoindolizines V and VI in comparison to the silyl-substituted indolizines I and III is the comparatively easy loss of the benzoyl radical and a molecule of methanol. These two processes occur with equal intensity (about 21—26%) for both compounds. In the mass spectra of indolizines I and III ions $[M - PhCO]^+$ and $PhCO^+$ had low intensities and the fragment $[M - CH_3OH]^{+\cdot}$ is absent. The



SCHEME 3

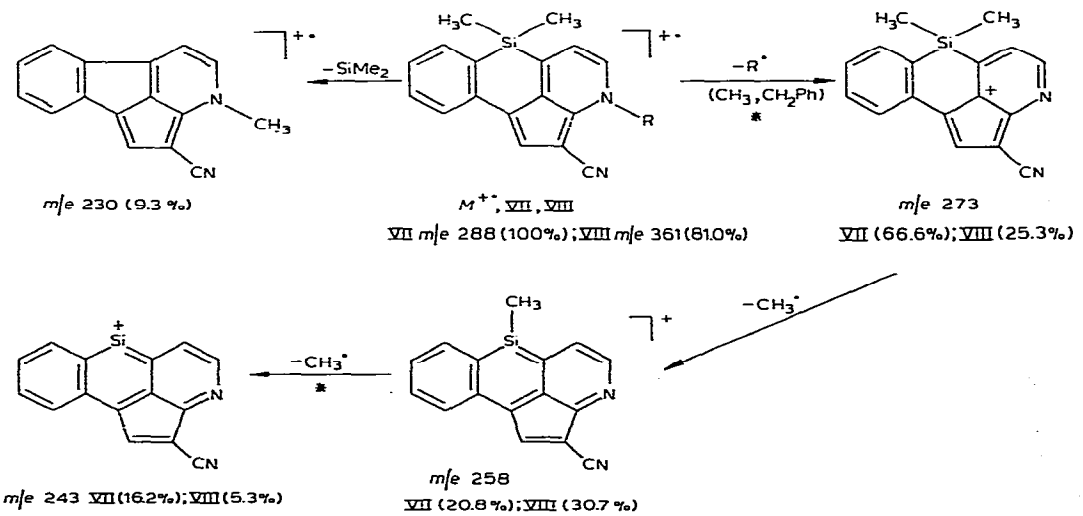
appearance of the latter during the dissociation of compounds V and VI is initiated by the migration of an hydrogen atom from the methylene group to the carbomethoxy radical at position 1, leading to the elimination of a CH_3OH molecule. As such, the formation of the ion $[M - CH_3OH]^{+\cdot}$ is due to the presence of methylene and carbomethoxy groups in *peri* positions of the molecules V and VI. At the same time, the dissociative ionisation of compounds V and VI does not lead to the ions $[M - COOCH_3]^+$ and $[M - COOCH_2]^+$, which had significant intensities in the mass spectra of compounds I—III.

Thus the dihydrosilanaphthoindolizines V and VI definitely differ in the course of fragmentation of the silyl-substituted indolizines I—III. The structural difference between compounds V and VI appears in the formation of the comparatively intense (about 2 times) peak ions $[M - Ph]^+$ and Ph^+ in the mass spectra of indolizine VI in comparison to the compound V. This is due to the elimination of $Ph^{\cdot}$, not only from the benzoyl group but also from the $SiCH_3$-C_6H_5 fragment during the dissociation of compound VI.

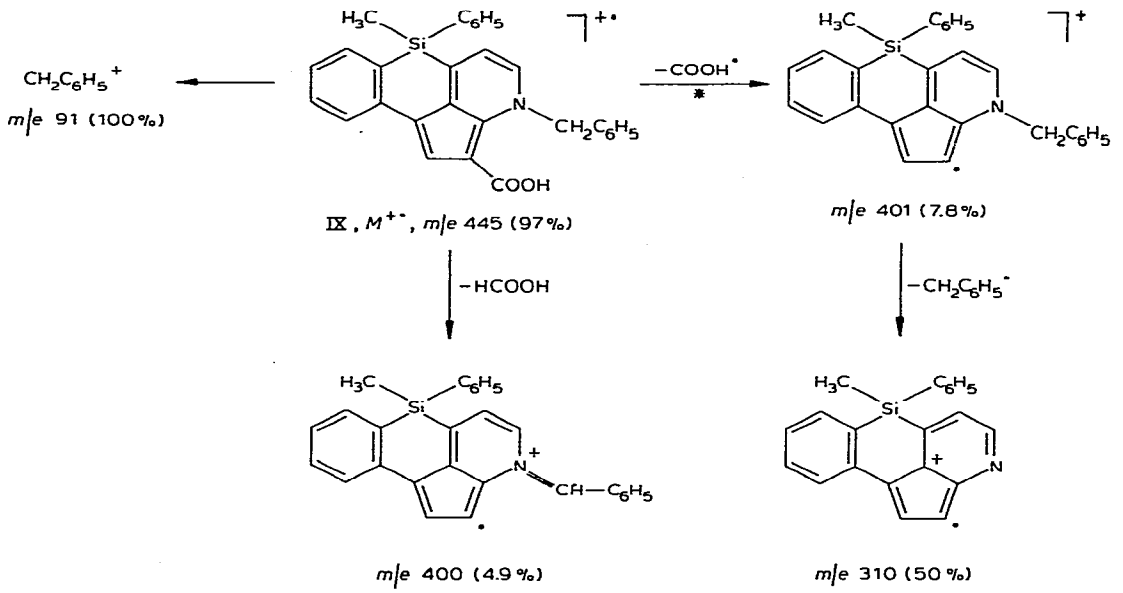
Dihydrosilaazaaceanthrelenes (VII—XIII)

The molecules of all these compounds contain a pseudoazulene fragment, represented by the NH-indenopyridine part of the molecule.

In the mass spectra of compounds VII and VIII, intense peaks of the molecular ions is observed. Their stability largely depends on the nature of the substituent at the nitrogen atom. In the case of the N-benzyl derivative the value W_M is 4 times less than that for the methyl-substituted compound VII. The absence of carbomethoxy and benzoyl groups in compounds VII and VIII (which in fact determine the large number of competitive fragmentation routes of the molecular ion of compounds I—III, V and VI) lead to a single path of the dissociative ionisation of compounds VII and VIII, i.e. the elimination of the substituent R (R = CH_3, CH_2Ph) situated at the nitrogen atom (Scheme 4). Fur-



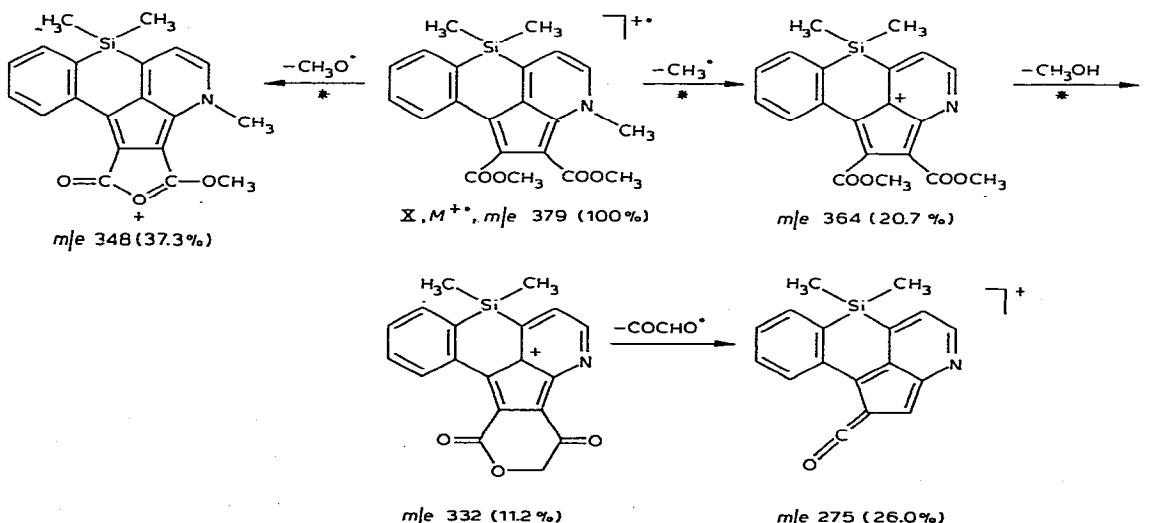
SCHEME 4



SCHEME 5

ther fragmentation of these compounds is determined by the consecutive loss from the ion $[M - R]^+$ of two CH_3 radicals attached to the silicon atom.

The fragmentation of pseudoazulene IX is accompanied, as in the case of compound VIII, by the appearance of an intense peak of CH_2Ph^+, *m/e* 91, whereas the ion $[M - C_6H_5CH_2]$ is not observed. The loss of this fragment may take place either from the molecular ion or from the ion $[M - COOH]^+$. The approximately similar molecular ion stabilities for compounds VIII and IX (Table 1) favour similar fragmentation pattern along their main fragmentation



SCHEME 6

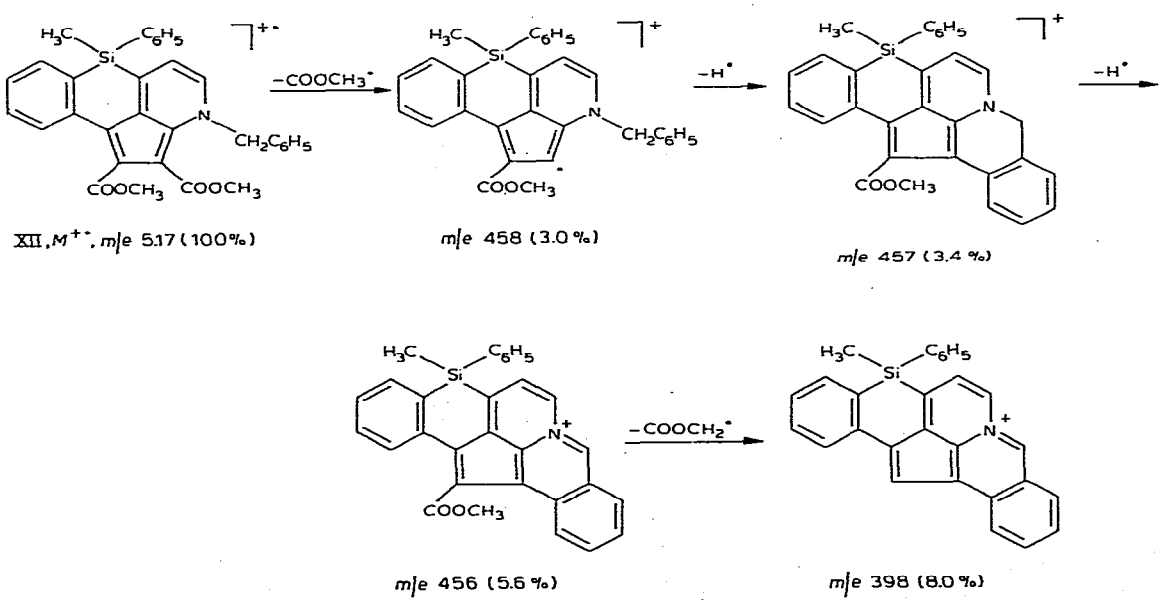
paths. It is also interesting to note that the molecular ion of compound IX loses the phenyl group more readily than a methyl group leading to the ions $[M - Ph]^+$, *m/e* 368 (4.2%), and $[M - CH_3]^+$, *m/e* 430 (0.3%) (Scheme 5).

The mass spectra of pseudoazulenes X—XII, in contrast to the dihydrosilanaphthoindolizines V and VI, show a maximum intensity molecular ion peak. The instability (W_M) depends on the nature of the substituents, either at the silicon or at the nitrogen atoms.

The main fragmentation of pseudoazulenes, as in the case of compounds VII and VIII, leads to the elimination of the substituent at the nitrogen atom and not the expulsion of radicals at the silicon atom (I—III) or loss of the OCH_3 species from the carbomethoxy groups (V and VI). The probability of the above process is about 2 times higher for compounds XI and XII, having a benzyl radical attached to the nitrogen atom, in comparison to the methyl group in compound X. A unique feature of the fragmentation of compounds X—XII is the comparatively easy loss of the carbomethoxy groups in comparison to those of indolizines I—III, V and VI (Scheme 6).

It is of interest to note one of the characteristic fragmentation paths of the benzyl-substituted pseudoazulenes XI and XII. After the elimination of a carbomethoxy group, the ion $[M - COOCH_3]^+$ consecutively expels two hydrogen atoms. This process, absent in the case of compound X, is explained by the cyclisation of the carbon atom of the phenyl radical in the benzyl substituent with the C(2) carbon atom, forming a six membered cycle (Scheme 7).

The presence of *ortho*-situated carbomethoxy groups in compounds X—XII lead to the elimination of a molecule of CH_3OH in the second stage of their fragmentation (Scheme 7). Compound X expels the fragment SiR'R" in the second stage (after the loss of a carbomethoxy group).



SCHEME 7

The presence of a methyl substituent at the nitrogen atom in compound X changes its fragmentation pattern in the later stages, in comparison to the compounds XI and XII. In contrast to compounds XI and XII, the ion $[M - CH_3OH]^{+\cdot}$ in mass spectra of X undergoes loss of the COCHO species (m/e 275), and the fragment $[M - COOCH_3]^+$ further loses the radicals $COOCH_3^\cdot$ and $OCH_3^\cdot$ (m/e 261 and 289, respectively).

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