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ELECTRON-IMPACT INDUCED FRAGMENTATION OF SOME 5,10-DIHYDROPHENAZASTANNINES

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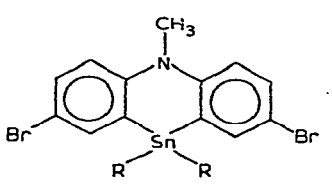
SUMMARY

The electron-impact induced fragmentation of four 5,10-dihydrophenazastannines [(I)–(IV)] was studied by low and high resolution mass spectrometry. Two of the compounds contain tin in the spiro position. To identify energetically favorable reaction paths, low electron-energy scans (12 eV) were taken along with 70 eV ones. The molecular ions fragment by consecutive ejection of the 10-substituents or, alternatively, by loss of R_2Sn. Subsequent fragmentation is accompanied by complex skeletal rearrangements and hydrogen migrations. An example of Sn–Br bond formation has been discovered. Ions of the phenanthridine type (*m/e* 179, $C_{13}H_9N$) are formed via enlargement of the center heterocyclic ring and rearomatization. Tentative mechanistic pathways are derived for all major fragmentation sequences on the basis of computer-aided correlation of metastable peaks, accurate mass measurements (elemental composition) and shifts resulting from specific deuterium labelling.

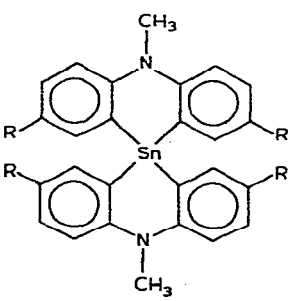
INTRODUCTION

As part of a study[1–4] undertaken to elucidate the electron-impact induced fragmentation reactions of heterocyclic organotin and organosilicon compounds, the mass spectra (Figs. 1–7) of four 5,10-dihydrophenazastannine derivatives [(I)–(IV)] were recorded and analyzed. Some of the findings were presented in a brief preliminary

SCHEME 1



(I), R = CH_3
(Ia), R = CH_3, H = D
(II), R = C_6H_5



(III), R = H
(IV), R = Br

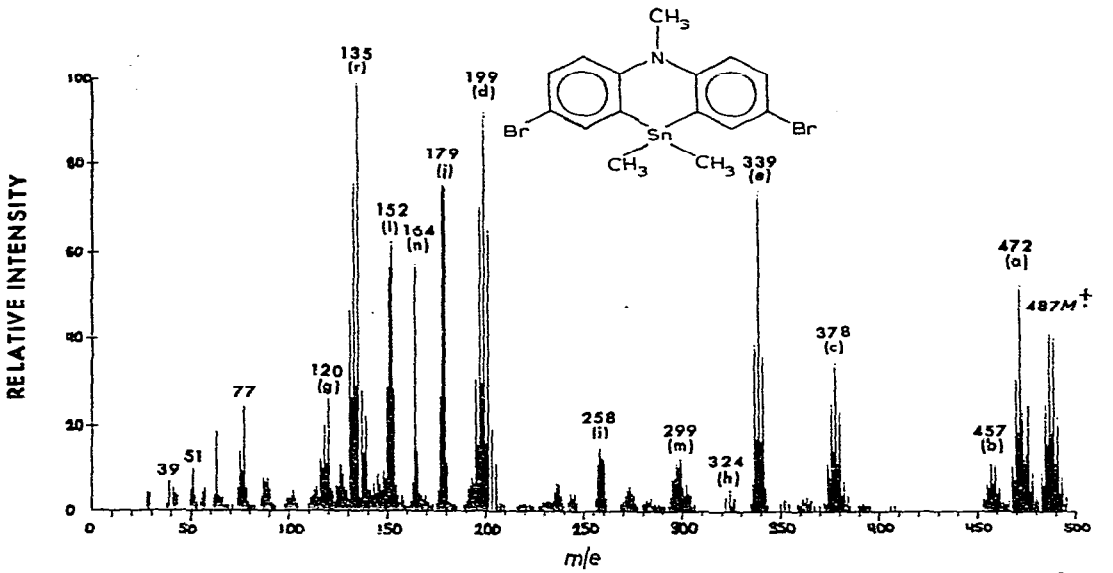


Fig. 1. Mass spectrum of 2,8-dibromo-5,10,10-trimethyl-5,10-dihydrophenazastannine taken at 70 eV.

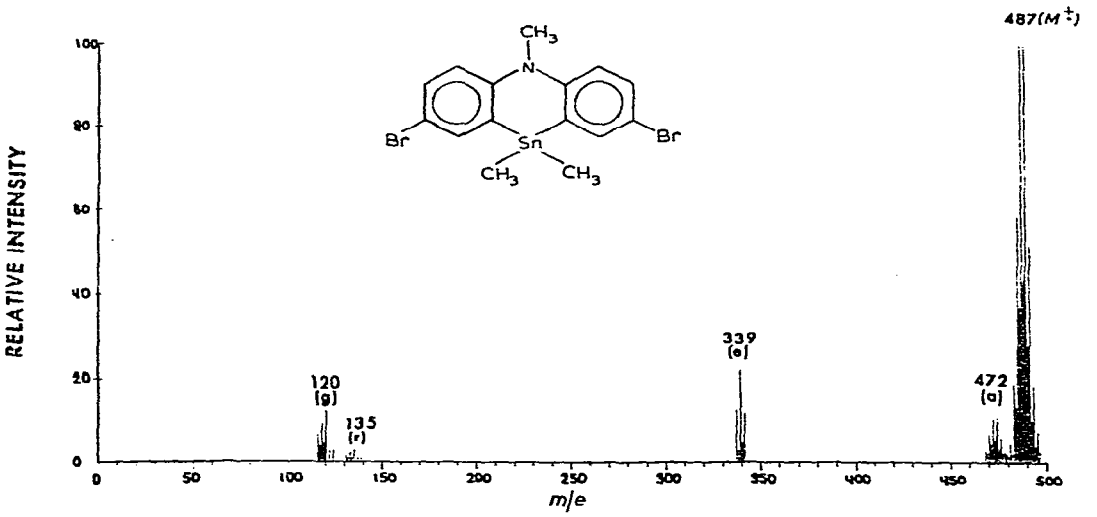


Fig. 2. Mass spectrum of 2,8-dibromo-5,10,10-trimethyl-5,10-dihydrophenazastannine taken at 12 eV.

report[5]. In two of the compounds [(III) and (IV)], tin is in the spiro position, three [(I), (II) and (IV)] contain bromine, and all four compounds have *N*-methyl substituents.

To identify the energetically most favorable fragmentation processes, 12 eV spectra were recorded along with 70 eV scans. To aid and secure interpretation, accurate masses and elemental compositions of all ions were determined for compound (I) by computer-coupled high resolution mass spectrometry[6]. The elemental compositions of selected ions in the mass spectrum of compound (I) are listed in Table 1. As-

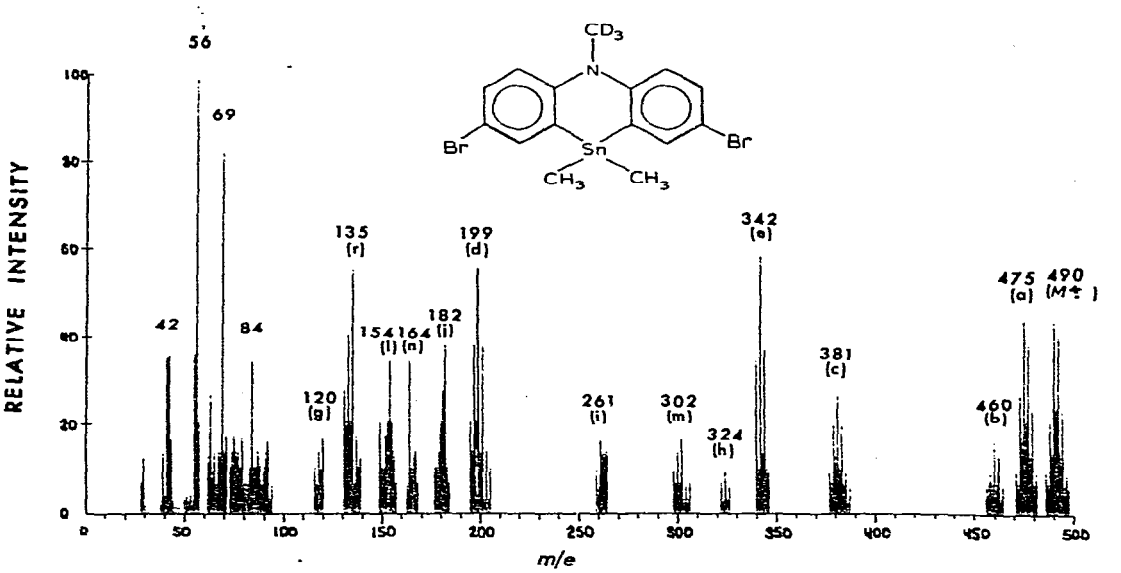


Fig. 3. Mass spectrum of 2,8-dibromo-5-(trideuteromethyl)-10,10-dimethyl-5,10-dihydrophenazastannine taken at 70 eV.

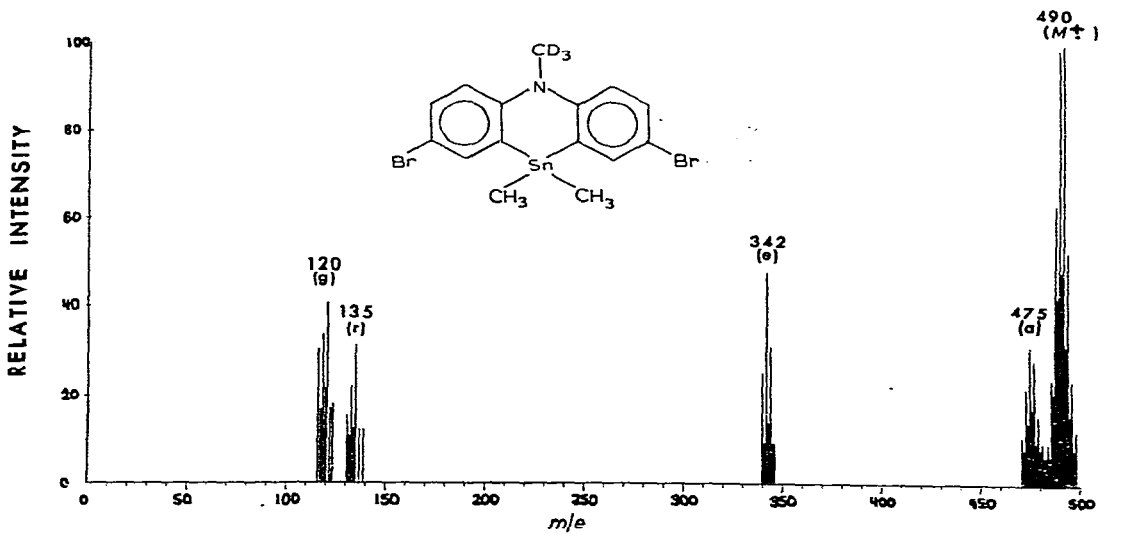


Fig. 4. Mass spectrum of 2,8-dibromo-5-(trideuteromethyl)-10,10-dimethyl-5,10-dihydrophenazastannine taken at 12 eV.

signments were confirmed, where possible, by identification of the appropriate metastable peaks[7] (Table 2). Additional details of the fragmentation mechanisms could be uncovered by specific isotope labelling: the N–CD_3 analogue of (I) [compound (Ia)] was prepared and the mass spectra compared using the Biemann shift technique[8].

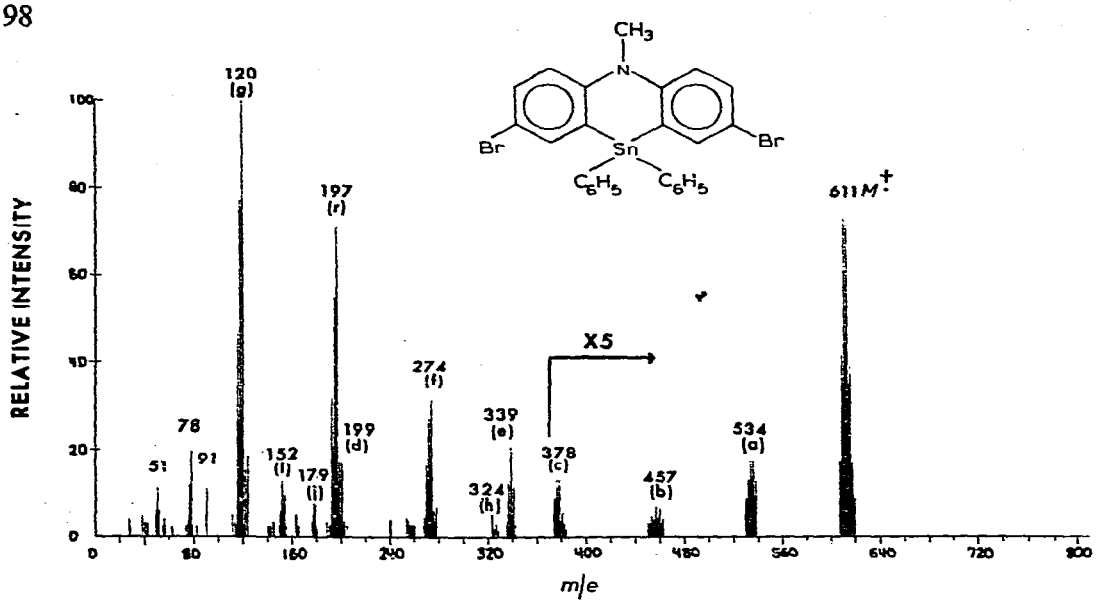


Fig. 5. Mass spectrum of 2,8-dibromo-5-methyl-10,10-diphenyl-5,10-dihydrophenazastannine taken at 70 eV.

TABLE 1

ACCURATE MASSES AND ELEMENTAL COMPOSITIONS[a] OF SELECTED IONS IN THE HIGH RESOLUTION MASS SPECTRUM OF COMPOUND(I)

Accurate mass measured (m/e)	*Elemental formula*	*Deviation from calculated m/e (nm)*
486.85682	$C_{15}H_{15}Br_2NSn$	−2.40
471.83393	$C_{14}H_{12}Br_2NSn$	−1.80
456.81096	$C_{13}H_9Br_2NSn$	−1.30
377.89345	$C_{13}H_9BrNSn$	−0.50
338.90676	$C_{13}H_9Br_2N$	−1.30
323.88673	$C_{12}H_6Br_2N$	+2.00
298.97787	$C_{13}H_9NSn$	+2.20
257.99379	$C_{13}H_9BrN$	+2.00
198.82006	BrSn	+1.70
179.07321	$C_{13}H_9N$	−0.20
164.05149	$C_{12}H_6N$	+1.50
152.06150	$C_{12}H_8$	−1.00
149.94929	C_2H_6Sn	+0.10
134.92669	CH_3Sn	+1.00
119.90212	Sn	+0.00
77.03935	C_6H_5	+0.20
76.03178	C_6H_4	+0.50
75.02283	C_6H_3	−0.50
41.04052	C_3H_5	+1.40

[a] Based on the following nuclidic masses:

C = 12.000000	^{79}Br = 78.918340	^{118}Sn = 117.902050
H = 1.007825	^{81}Br = 80.916340	^{120}Sn = 119.902200
N = 14.003074	^{116}Sn = 115.902190	

Search limited to $C_{100}H_{200}{}^{79}Br_2{}^{81}Br_2{}^{116}Sn_1{}^{118}Sn_1{}^{120}Sn_1$.

TABLE 2

METASTABLE IONS AND TRANSITIONS[a]

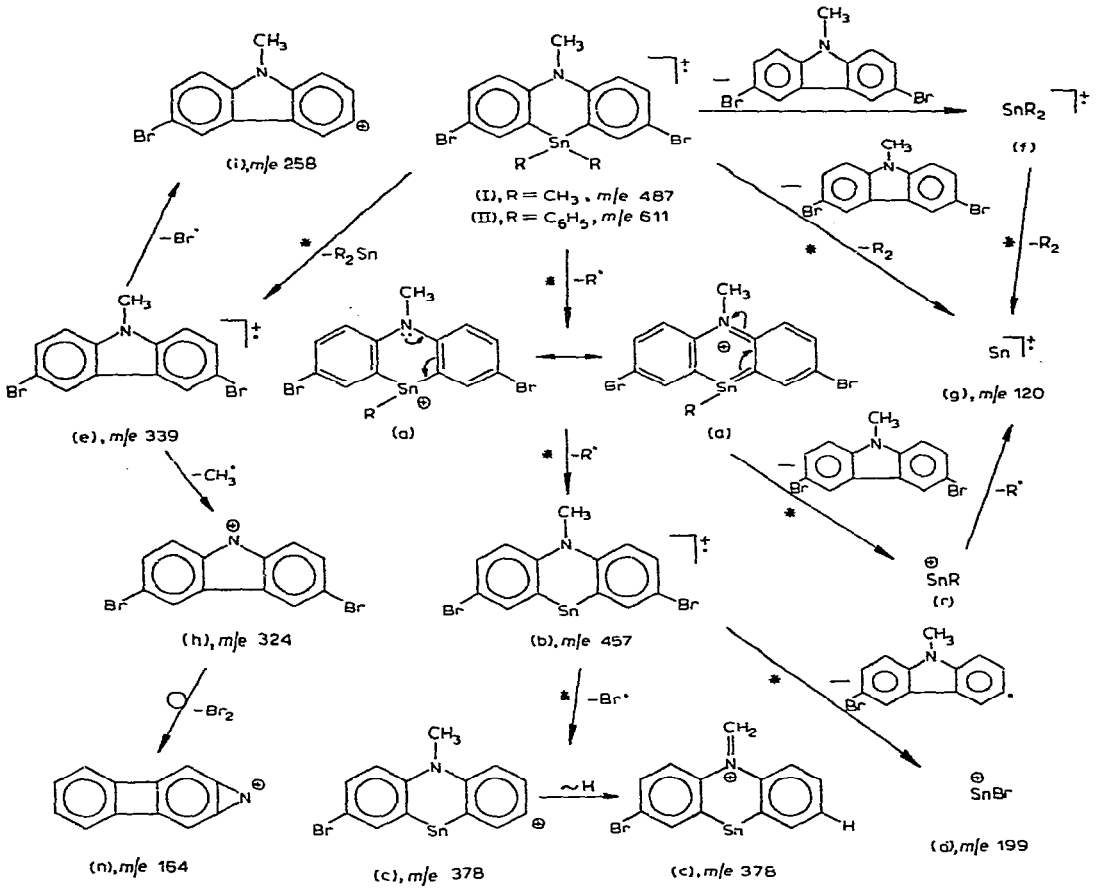
$m^*_{obs.}$	$m^*_{calcd.}$	Transition
Compound (I)		
457.50	457.46	$487 \xrightarrow{-CH_3^\cdot} 472$
442.50	442.48	$472 \xrightarrow{-CH_3^\cdot} 457$
312.50	312.66	$457 \xrightarrow{-Br^\cdot} 378$
236.00	235.98	$487 \xrightarrow{-C_2H_6Sn} 339$
177.00	177.01	$179 \xrightarrow{-H^\cdot} 178$
129.00	129.07	$179 \xrightarrow{-HCN} 152$
124.00	124.19	$258 \xrightarrow{-Br^\cdot} 179$
86.50	86.65	$457 \xrightarrow{-C_{13}H_9BrN^\cdot} 199$
38.50	38.60	$472 \xrightarrow{C_{13}H_9Br_2N} 135$
19.00		Unassigned
Compound (II)		
253.00		Unassigned
177.00	177.01	$179 \xrightarrow{-H^\cdot} 178$
110.00		Unassigned
72.50	72.67	$534 \xrightarrow{-C_{13}H_9Br_2N} 197$
52.50	52.55	$274 \xrightarrow{-C_6H_5\text{-}C_6H_5} 120$
34.20		Unassigned
23.50	23.56	$611 \xrightarrow{-C_6H_5\text{-}C_6H_5\ -C_{13}H_9Br_2N} 120$
Compound (III)		
188.00	187.97	$482 \xrightarrow{-C_{13}H_{11}N} 301$
179.00	179.01	$181 \xrightarrow{-H^\cdot} 180$
128.50	128.36	$180 \xrightarrow{-N{=}CH_2} 152$
109.00	108.84	$301 \xrightarrow{-Sn} 181$
68		Unassigned
47.60	47.84	$301 \xrightarrow{-C_{13}H_{11}N} 120$
Compound (IV)		
312.60	312.66	$457 \xrightarrow{-Br^\cdot} 378$
129.00	129.07	$179 \xrightarrow{-HCN} 152$

[a] Because of the many isotopes of tin, metastable peaks observed for tin-containing ions are wide. In Table 2, the values of $m^*_{obs.}$ correspond to the center of the broad peak. The values for $m^*_{calcd.}$ refer to the most abundant (^{120}Sn) tin isotope.

RESULTS AND DISCUSSION

The higher stability of phenazastannines as compared with phenoxastannines to electron impact is manifest by the fact that all phenazastannines investigated in this

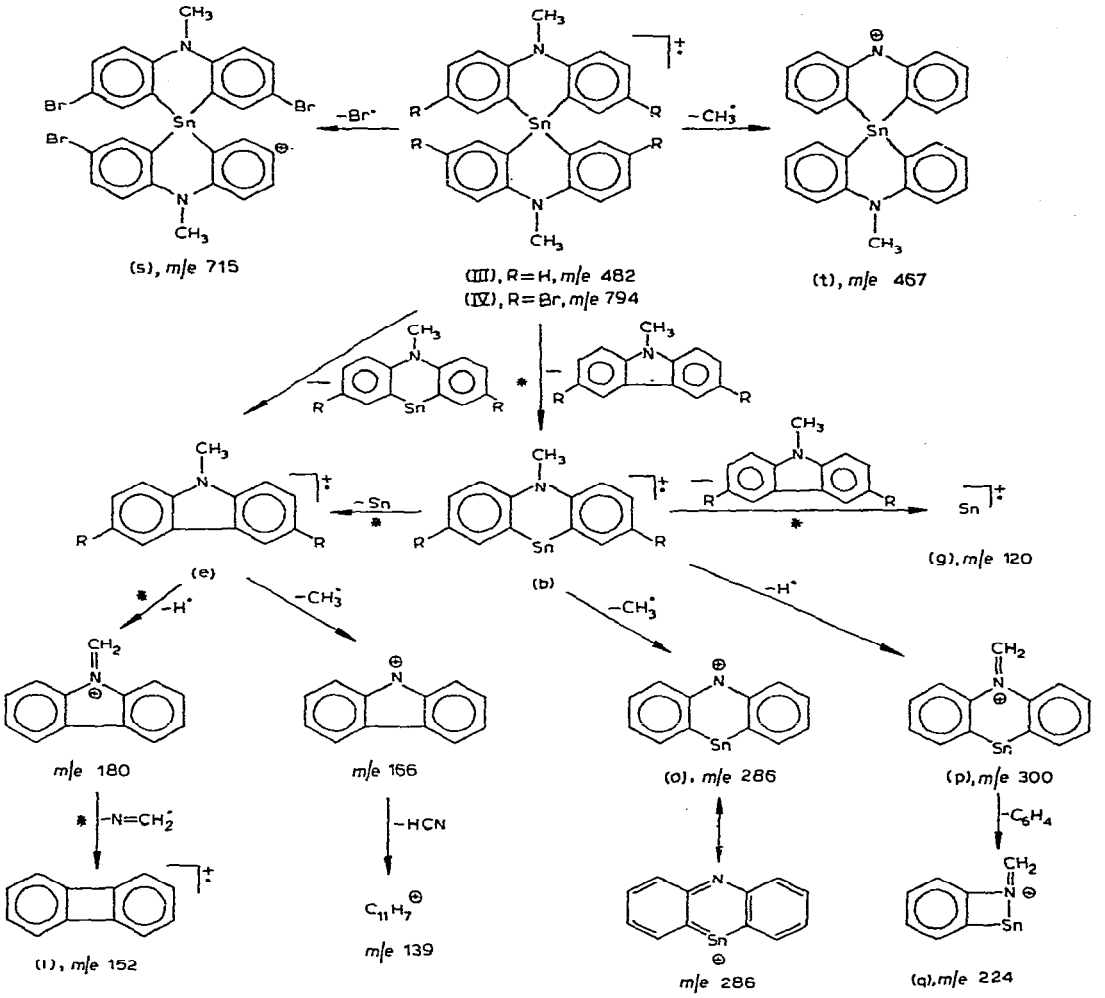
study exhibit parent ions* (*cf.*, Figs. 1 and 5–7) at 70 eV. At 12 eV, the parent ion becomes the most abundant peak ("base peak"). The predominant primary fragmentation step involves elimination of one of the *exocyclic* substituents on the tin atom in (I), (Ia) and (II), to form an even-electron ion (a) (Scheme 2). It is exclusively the *Sn*-methyl, rather than the *N*-methyl group, which is lost, as confirmed by the spectrum



SCHEME 2. *denotes fragmentations for which metastable peaks are present.

of the N–CD_3 analogue (Ia), showing a three-mass shift for $(M-R)^+$ from *m/e* 472 to *m/e* 475. For compounds (III) and (IV), in which the tin has no exocyclic substituent, alternative fragmentations take over: in the bromine-free compound (III) loss of an *N*-methyl group, while in (IV) ejection of bromine (Scheme 3) occurs. These observations can be explained qualitatively on the basis of the relative bond energies involved (C–N stronger than C–Br stronger than C–Sn)[9]. Moreover, the $(M-R)^+$ ion (a) is more abundant in (I) than in (II), reflecting the order of bond strengths (Sn phenyl > Sn methyl). However, the relative ease of occurrence of a particular mass spectrometric

* The term parent ion, as used in mass spectrometry, denotes the ionized molecule (molecular weight minus one electron).



SCHEME 3. *denotes fragmentations for which metastable peaks are present.

fragmentation among competing reactions is known (see *e.g.* ref. 10) to depend not only on the bond energies involved, but on other parameters, such as activation energy (ΔF^*), heat of formation (ΔH^*), of both the product ion and the neutral fragment eliminated, and steric factors, as well. The ability of an atom or group to stabilize the positive charge within the decomposing ion has a strong directing effect on mass-spectral fragmentation[11]. The ionization potential of tin being substantially lower than that of carbon, nitrogen or bromine[12], fragmentation of compounds (I)–(IV) can best be interpreted in terms of molecular ions electron-deficient on tin. The main driving force for the $M^{+\cdot} \rightarrow (M-R)^+$ transition is associated with strong stabilization of the product-ion. Charge-delocalization is possible by conventional resonance (*cf.*, Scheme 2) involving $p_\pi - p_\pi$ overlap between the tin and the aromatic rings within ion (a).

One of the subsequent fragmentation paths of ion (a) in compounds (I) and (II) involves the metastable supported elimination of the *second* R substituent, a generally unfavorable even- to odd-electron ion transition [(a) → (b)], which is completely ab-

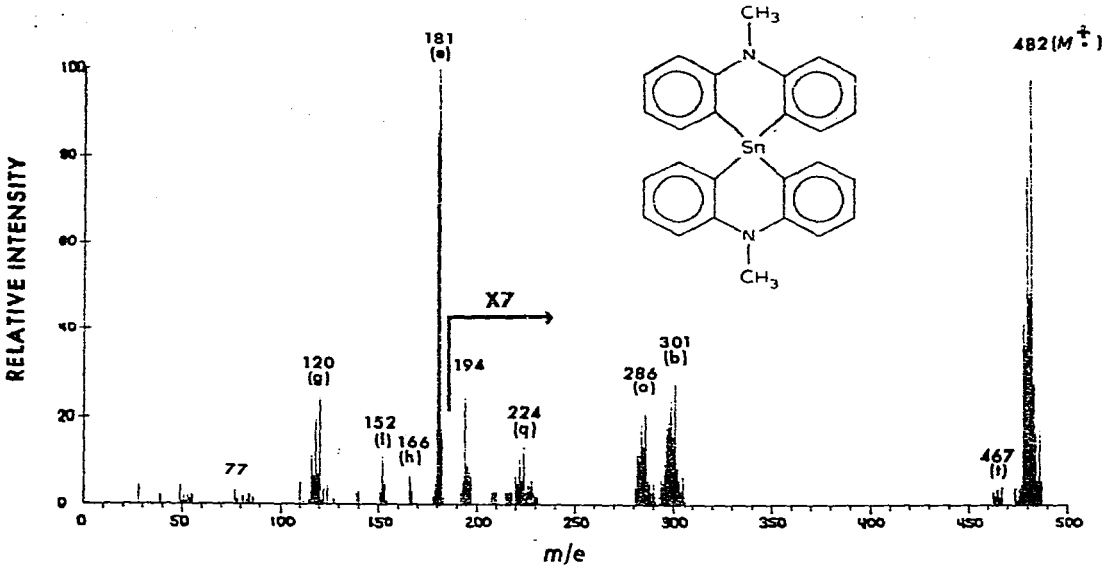


Fig. 6. Mass spectrum of 5,5′-dimethyl-10,10′-spirobis(5,10-dihydrophenazastannine) taken at 70 eV.

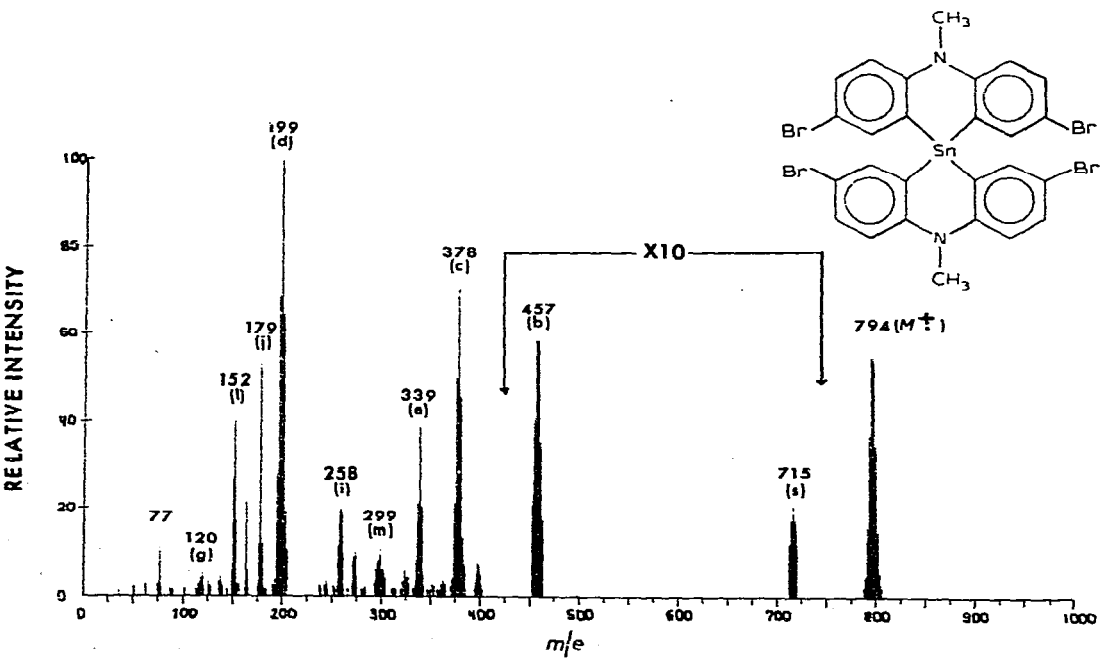
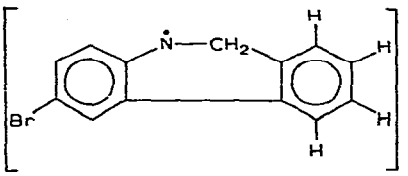


Fig. 7. Mass spectrum of 2,2′,8,8′-tetrabromo-5,5-dimethyl-10,10′-spirobis(5,10-dihydrophenazastannine) taken at 70 eV.

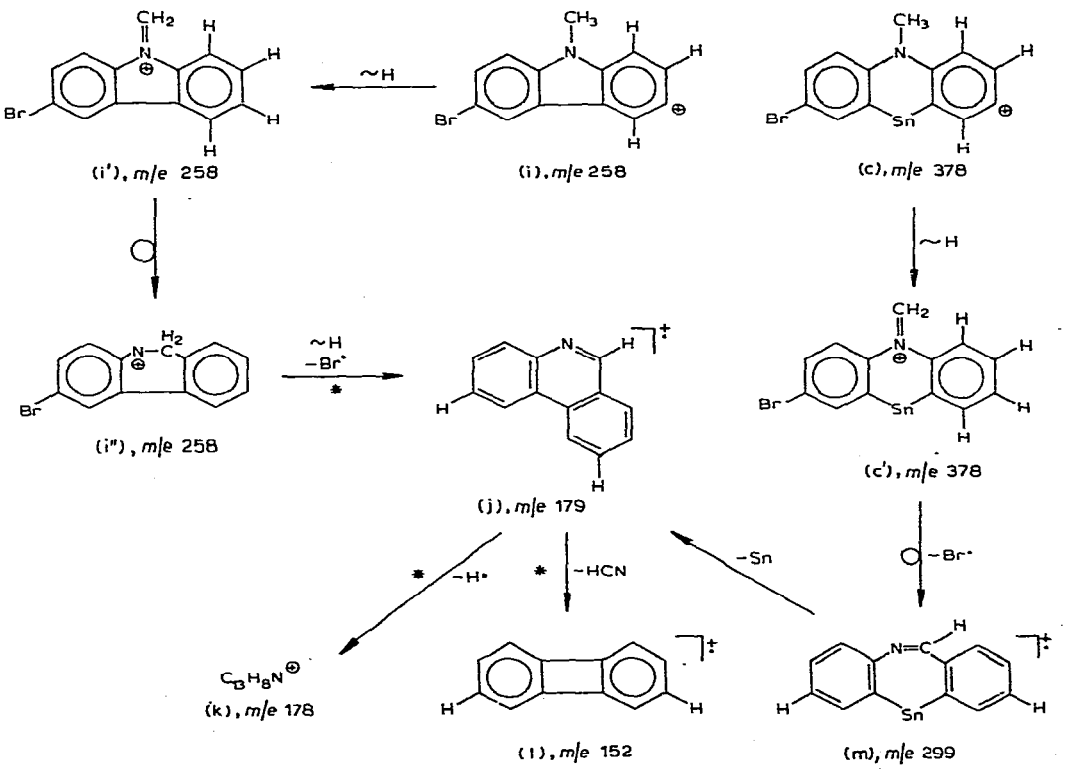
sent in the identically substituted 5,10-dihydrophenoxastannines[1,3]. Nitrogen, being more capable than oxygen of stabilizing the radical site by electron-sharing, lowers the activation energy of this reaction for compounds (I) and (II). Ion (b) is also prominent in spiro compounds (III) and (IV) at 70 eV.

Ion (b) (*m/e* 457) subsequently decomposes by ejection of a bromine radical [to (c), *m/e* 378] or, alternatively, by loss of $C_{13}H_9NBr^{\bullet}$ to (d), *m/e* 199. Both processes are supported by metastable peaks. High resolution mass measurements as well as the observed isotope pattern reveal that ion (d) is a single component, *viz.*, $(SnBr)^+$. The 457 → 199 transition involves *migration of a bromine atom from the aromatic ring to the metal.* Part of the driving force for this unusual and unexpected rearrangement is supplied by the formation of the strong $^+Sn–Br$ bond (appreciable double bond character). The process is probably accompanied by hydrogen migration from the *N*-CH_3 group to the aromatic ring and enlargement of the center ring, rendering the neutral fragment



more stable (resonance) (Scheme 2).

Alternative pathways of decomposition of the molecular ions of (I) and (II) include elimination of R_2Sn, dibromo-*N*-methylcarbazole and/or the combined loss



SCHEME 4. *denotes fragmentations for which metastable peaks are present.

of dibromo-*N*-methylcarbazole and R–R, to give ions (e) (*m/e* 339), (f) (*m/e* 150 and 274) or (g) (*m/e* 120), respectively. Ejection of a methyl group and of bromine compete in the further fragmentation of ion (e), resulting in ions (h) (*m/e* 324) and (i) (*m/e* 258), respectively (Scheme 2).

One of the most interesting and *a priori* not predictable features of the spectra of compounds (I), (II) and (IV) is a metal-free ion at *m/e* 179 (j), $C_{13}H_9N$ (single component by high resolution). According to a metastable peak at *m/e* 124.0 in the spectrum of (I), ion (i) is the precursor to (j) in that compound. Ion (j) shifts to *m/e* 182 in the *N*-CD_3 analogue, indicating that all three deuterium atoms are still incorporated in (j). Subsequent paths of decomposition of (j) (Scheme 4) are loss of H· to give ion (k), *m/e* 178 ($C_{13}H_8N$) and ejection of HCN [DCN in (Ia)] to give ion (l) *m/e* 152, $C_{12}H_8$. Ion (l), biphenylene, is shifted by *two mass units* to *m/e* 154 in the spectrum of the *N*-CD_3 analogue, indicating that two of the three deuterium atoms have migrated from the CD_3 group to the two aromatic rings.

A possible alternative pathway (not supported by metastable evidence) for the formation of ion *m/e* 179 (j) from *m/e* 378 [(c) or (c')] via ion (m) by consecutive elimination of bromine and tin is depicted in Scheme 4. The metal-containing but bromine-free ion (m) is appropriately shifted from *m/e* 299 to *m/e* 302 in the spectrum of (Ia).

Even-electron ion (h) (*m/e* 324) appears to lose Br_2, in a process accompanied by extensive skeletal rearrangement, to give rise to ion (n) (*m/e* 164), present in both the spectra of (I) and (II), and remaining unshifted in (Ia).

Ions (b), (c), (d), (e), (g), (i), (j), (l), (m) and (n) are all common to the spectra of both (I) and spiro compound (IV) (Schemes 2–4 and Figs. 1 and 7). The base peak in the spectrum of the bromine-free spiro compound (III) is *m/e* 181, formed by the consecutive loss of *N*-methylcarbazole and tin, as substantiated by metastable peaks at *m/e* 188.0 and 109.0. Subsequent decomposition of ion *m/e* 181 proceeds by two concurrent routes: loss of H· followed by elimination of CH_2N·, leading to ions *m/e* 180 and 152 respectively, and ejection of CH_3· (*m/e* 166) followed by loss of HCN (to give *m/e* 139), as reported previously by Bowie *et al.* in another connection[13].

Also unique to the spectrum of compound (III) is the resonance-stabilized even-electron ion (o), *m/e* 286, likely to originate from (b) by loss of the *N*-methyl group. A peak of appreciable abundance at *m/e* 224 (q) still contains tin. One possible path of formation is via (p) by loss of C_6H_4 (Scheme 3).

EXPERIMENTAL

The synthesis of the unlabelled organotin compounds has been described previously[14]. Freshly recrystallized pure samples have been used in this investigation. Labelled substrate (Ia) was synthesized from the corresponding diphenylamine according to the following procedure.

(Trideuteromethyl)bis(2,4-dibromophenyl)amine

To a solution of 1.51 g (0.035 moles, 55.6% oil) of sodium hydride in 25 ml of dry THF, 12.5 g (0.026 moles) of bis(2,4-dibromophenyl)amine in 200 ml of dry THF was slowly added dropwise with vigorous stirring and cooled in an ice bath. After the addition of the amine was completed the solution was refluxed overnight for 20 h. The solution was then allowed to cool to room temperature and then placed in an ice bath

and recooled to 0°. A solution of 5 g (0.035 moles) of trideuteromethyl iodide (CD_3I) in 25 ml of dry THF was slowly added dropwise with vigorous stirring. The solution was then allowed to warm to room temperature and refluxed overnight (20 h) with stirring. A precipitate had formed which was collected (10.5 g), and the filtrate was hydrolyzed by the slow addition of ice cold water. The layers were separated and the aqueous phase was extracted three times with 100 ml portions of ether. The organic layers were combined and dried. The solvent was removed by rotary evaporation leaving only a trace of a solid residue. The crude product (10.5 g) was recrystallized from toluene to give 9.1 g (70.3%) of white crystals, m.p. 142–144°.

2,8-*Dibromo*-5-(*trideuteriomethyl*)-10,10-*dimethyl*-5,10-*dihydrophenazastannine*(*Ia*)

A solution of 9.1 g (0.018 mole) of (trideuteromethyl)bis(2,4-dibromophenyl)-amine in 100 ml of ether at 0° under an atmosphere of nitrogen was treated with an n-hexane solution of n-butyllithium (30 ml, 0.044 mole), and the mixture was stirred for $1\frac{3}{4}$ h at 0°. Over a period of 30 min, 3.96 g (0.018 mole) of dimethyltin dichloride in 80 ml of ether was added dropwise to the ethereal solution at 0°. The solution was stirred for 20 h at room temperature. The solvent was distilled in *vacuo* (water-pump), dry toluene (200 ml) was added and the solution was refluxed overnight. The reaction mixture was then poured into ice water. The organic layer was separated, and the aqueous layer was extracted with three 100 ml portions of ether, the organic layers were combined and dried. The solvent was removed by rotary evaporation to give 8.60 g of a dark oil, which was taken up in hot ethyl acetate and treated with Norite, and filtered through a Silica Gel column. The solution was concentrated and placed in the freezer for one week to yield tan colored crystals melting at 94–104°. Recrystallization from n-hexane raised the m.p. to 120–122°. Yield 2 g.

The conventional ("low resolution") mass spectra were recorded on a Hitachi RMU-6D instrument at 70 and 12 eV and 50 μA, using the direct insertion probe, by Morgan-Schaffer Corp., Montreal. The high resolution data, in the form of an element map, were obtained on a CEC 21-110B doubly focusing mass spectrometer coupled with an IBM 1801 computer system. The metastable search was performed on a CDC 1600 computer using a time-sharing console. The program, similar to Rhodes' and Barber's[7], was written in the basic language. Final selection was made manually, utilizing intensity data.

ACKNOWLEDGEMENT

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