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ELECTRON-IMPACT INDUCED FRAGMENTATION OF SOME HETEROCYCLIC-TIN COMPOUNDS

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Summary

The electron impact induced fragmentation of a series of heterocyclic tin compounds: 10,10-dimethyl- and 10,10-diethylphenoxastannin, the corresponding dimethyl- and diethyltin twelve membered ring heterocycles, 10,10-dimethylphenothiastannin, 10,10-dimethylphenothiastannin 5,5-dioxide, 5,5-dimethyl-5,10-dihydrodibenzo[*b*,*e*]stannin and 10,10′-spirobiphenoxastannin, has been investigated. For the twelve membered ring compounds the results strongly support the structures given by Meinema and Noltes [2]. Primary fragmentation occurs by loss of an alkyl group, in accordance with the preferred tervalency of the tin ion. Further fragmentation pathways were established in each case by defocused metastable measurements and exact mass measurements. Loss of Sn-containing fragments is more common than in Sn-tetraalkyls because of charge stabilisation on the aromatic system.

Large differences were observed in molecular ion intensities of the various compounds investigated. Their intensities could be correlated with ionization potentials of the aromatic substituent. A theory attributing this to charge residence is put forward.

Introduction

Reaction of oxy-2,2′-bis(phenyllithium) with dialkyltin dichlorides is reported by Kupchik et al. [1] to give low yields of novel heterocyclic tin compounds, which were identified as dialkylphenoxastannins. Molecular weight determinations indicated these compounds to be dimeric, which was rationalized in terms of intermolecular tin—oxygen coordination.

Recent work in our laboratories has revealed that upon the attempted synthesis of dimethyl- and diethylphenoxastannins, along with the products

TABLE 3

NMR SPECTRA OF $X_2P(O)NMeAlEt_2$ [a]

Compound	X	P—N—CH_3	J(PNCH) [b]	$AlCH_2$	$AlCH_2C\underline{H}_3$	J(HCCH)	P—O—R	P—N—R	J(P—H_β)
Ib	MeO	7.60	16.5 (12.0)	9.78	8.60	7.5	6.75 d		11.3
IIb	EtO	7.55	17.2 (12.0)	9.73	8.58	7.5	6.20 dq, 8.98 t		7.5
IIIb	i-PrO	7.45	17.2 (11.2)	9.74	8.54	8.3	5.45 m, 8.83 d		
IVb	i-BuO	7.43	17.2 (12.0)	9.71	8.53	7.5	6.25 dd, 7.80—8.50 m 9.18 d		6.0
Vb	i-AmO	7.40	17.3 (12.0)	9.68	8.50	7.5	5.96 dt, 8.30—8.90 m 9.12 d		6.8
VIb	Me_2N	7.78	17.5 (10.5)	9.78	8.55	7.5		7.65 d	11.3
VIIb	Et_2N	7.55	17.3 (12.0)	9.73	8.50	7.5		7.08 dq, 9.05 t	9.8

[a] Chemical shift τ in ppm, coupling constant J in Hz; 10 to 15% solutions in benzene were used. [b] The value in parentheses shows J(PNCH) of the parent compound (Ia—VIIa)

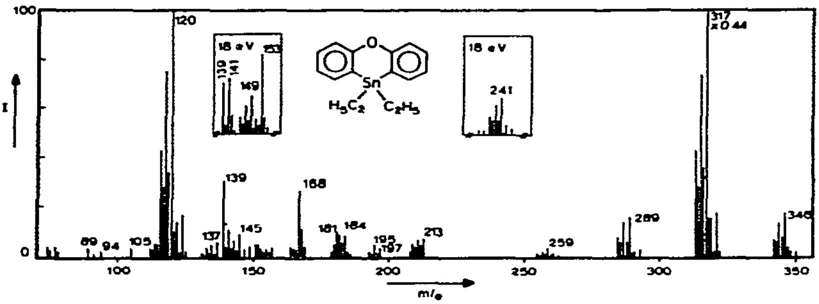

Fig. 2. Mass spectrum of 10,10-diethylphenoxastannin.

(i). Formation of a mono-coordinated Sn^+—R ion and the stable dibenzofuran molecule. This process is obscured in the ethyl compound at higher electron energies since an alternative competing fragmentation with a higher frequency factor, viz. formation of a Sn-three-coordinated ion at *m/e* 289* by loss of the stable C_2H_4 molecule, is available. At lower electron energies, however, Sn^+—C_2H_5 ions (*m/e* 149) are found in the spectrum (see Fig. 2).

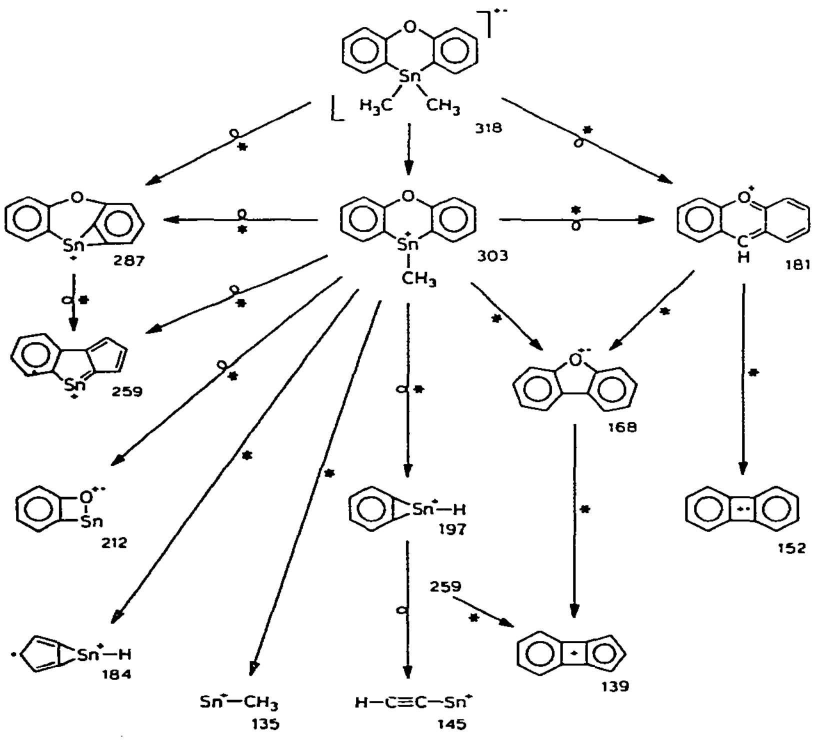

Fig. 3. Fragmentation pattern of 10,10-dimethylphenoxastannin. Note: Sn^{+} is formed from the ions at *m/e* 184, 197 and 212.

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[*] Reference to isotopic clusters is made throughout by use of the *m/e* value corresponding to the most abundant 120-tin isotope only.

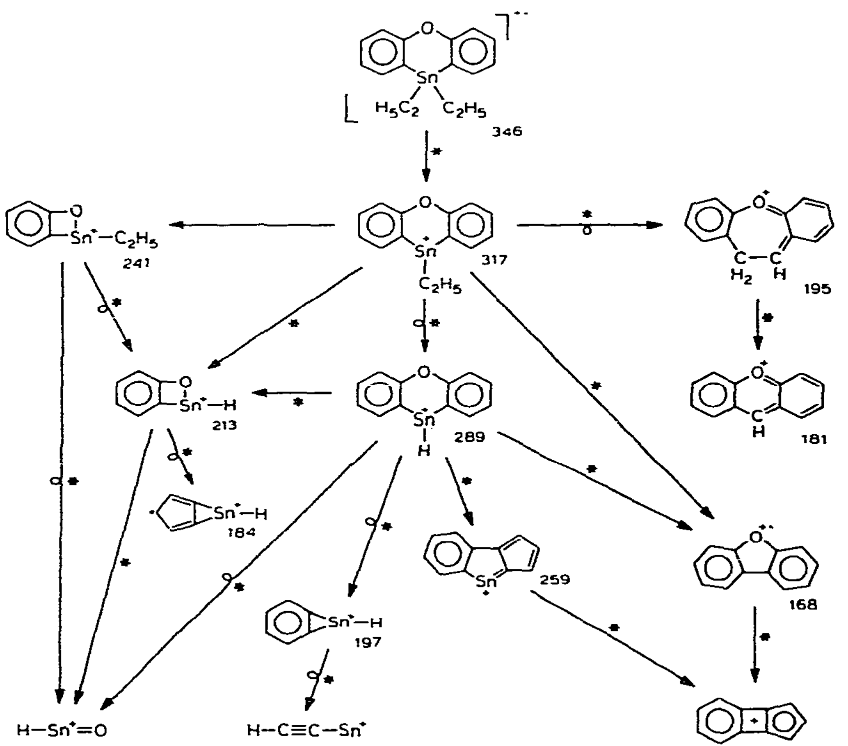

Fig. 4. Fragmentation pattern of 10,10-diethylphenoxastannin. Note: Sn$^{+\cdot}$ is formed from the ions at *m/e* 317, 289, 259, 213, 197 and 184.

(ii). Formation of a series of tin containing ions in generally small numbers. Some of these ions appear to be important intermediates in the formation of the abundant Sn$^{+\cdot}$ ions found in the spectra. However, not all are tin three- or mono-coordinated even-electron ions formed by elimination of stable molecules. Notable in this respect is the presence of relatively abundant $SnC_5H_4^{+\cdot}$ ions at *m/e* 184 (see Fig. 4 for a tentative formulation of ion structure), which decompose further into Sn$^{+\cdot}$ ions and cyclopentadiene neutrals. Furthermore, the dimethyl compound undergoes a rearrangement (migration of a CH_3 radical

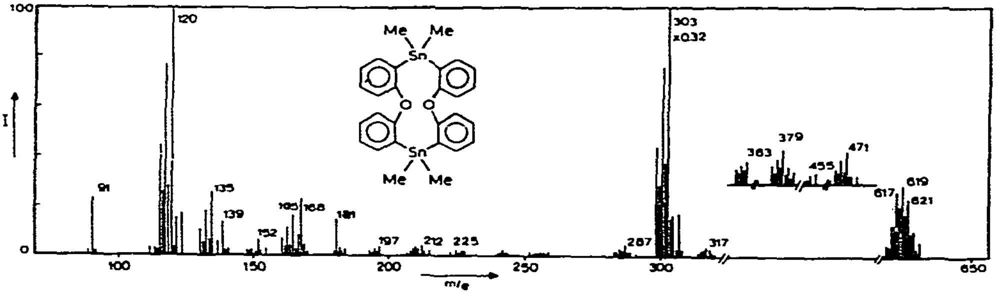

Fig. 5. Mass spectrum of the twelve-membered organotin-heterocycle $C_{28}H_{28}O_2Sn_2$.

to the phenyl ring) leading to the formation of a $C_7H_7^+$ (tropylium) ion and a tin two-coordinated neutral:

$(M-15)^+$ (*m/e* 303) → $C_7H_7^+$(*m/e* 91) + SnC_6H_4O(Mol.wt.212)

but in this reaction the positive charge can also reside at the tin containing fragment, which gives another odd electron fragment ion that also decomposes further into $Sn^{+\cdot}$ ions.

(iii). Formation of a series of non-metal containing ions. These ions are formed by initial loss of SnH_2 or the Sn—R radical*, the latter directly leading to the formation of the ionized heterocyclic substituent, i.e. dibenzofuran, which shows a fragmentation pattern resembling that of the free molecule [5]. The observation that metal-free ions are relatively abundant in the spectra of these compounds, whereas their abundance is very low in the spectra of simple tetraalkyltin compounds is not unexpected. Much better charge stabilisation should be possible with these heterocyclic substituents than with the alkyl groups.

Six- and twelve-membered ring compounds

The mass spectrum of the dimethyltin compound isolated by Kupchik is presented in Fig. 5. It closely resembles the spectrum considered by Lengyel to be that of the six membered ring, at least up to *m/e* 318. No high mass peaks were given in his spectrum. Our metastable measurements using the defocusing technique, however, clearly indicate that the peaks in the high mass region of Fig. 5 cannot be considered as impurities in the sample. Since Kupchik considered this compound to be dimeric dimethylphenoxastannin, we shall occasionally use the term "dimer" for this compound. The spectrum also resembles that of dimethylphenoxastannin, which is given in Fig. 1, be it that there are some notable differences:

(*i*). There is marked distinction in ion intensity between the molecular ion at *m/e* 318 from dimethylphenoxastannin and that at the same mass in the spectrum of the "dimer".

(*ii*). The ion intensity of the tin-containing ions at *m/e* 184 ($SnC_5H_4^{+\cdot}$) and *m/e* 145 ($Sn^+—C{\equiv}CH$), as well as the abundance of the dibenzofuran fragment ion at *m/e* 139, is greatly reduced in the spectrum of the "dimer".

(*iii*). In the spectrum of the "dimer" a tin containing isotopic cluster is present at *m/e* 165, which is not formed at all from the six membered ring compound. Lengyel suggested that this rearrangement ion was formed from the ion at *m/e* 318 via multiple bond cleavage and Sn—O bond formation:

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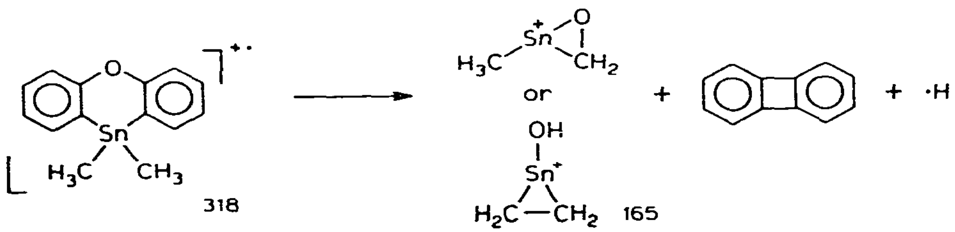
*Lengyel [3] reported that the ionized dibenzofuran molecule was formed by loss of $Sn(CH_3)_2$ from the ion at *m/e* 318. No evidence could be found however for this transition in either the six- or the twelve-membered ring compounds.

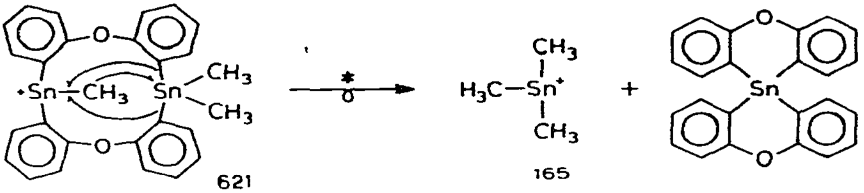


No metastable was found however by Lengyel to indicate the genesis of this ion. Exact mass measurements on the peaks at *m/e* 165 and 163 revealed however the following data:

$$\begin{cases} {}^{120}Sn(CH_3)_3 = 164.9725 \text{ (calc.)} \\ {}^{120}SnC_2H_5O = 164.9361 \text{ (calc.)} \end{cases} \quad \text{found:} \begin{cases} 164.9725 = {}^{120}SnC_3H_9 \ (\Delta = 0 \text{ ppm}) \\ 165.0704 = C_{13}H_9 \ (\Delta = 0 \text{ ppm}) \end{cases}$$

$$m/e \ 163 \text{ (found)} = 162.9729 = {}^{118}SnC_3H_9 \ (\Delta = 5 \text{ ppm})$$

so that the isotopic cluster has a different elemental composition from that suggested by Lengyel*. Furthermore a defocused metastable was found for the transitions $619^+ \rightarrow 165^+$ and $621^+ \rightarrow 165^+$ (found: 620). Since the identity of the isotopic cluster could be established by exact mass measurement to fit the formula $Sn_2C_{27}H_{25}O_2$, the isotopic distribution also being in very good agreement with the corresponding calculated value, the proposed genesis of the cluster at *m/e* 165 is:



The ion structure of the cluster at *m/e* 617 - 619 - 621 corresponds with loss of a $CH_3^{\bullet}$ radical from an undetected molecular ion of a twelve membered ring; it does not arise from a true dimer, which, apart from the convincing PMR evidence [2], also seems unlikely in the light of the observation that volatilisation of the six membered ring compound at the same much higher temperature necessary for volatilisation of the twelve membered ring causes no significant change in its spectrum.

The major initial fragmentation pathway of the $(M \overset{\bullet}{-} CH_3)^+$ ion in this compound consists of the formation of the stable tin three coordinated ion at *m/e* 303**, (also the major fragment ion in the spectrum of the 10,10-dimethyl-

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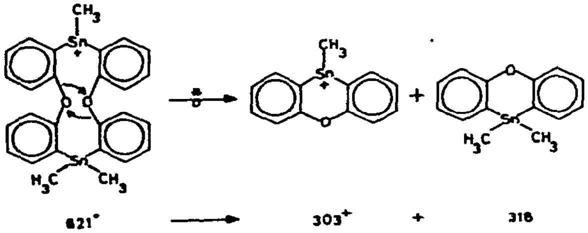
*The metal-free component is also found in the six membered ring.

**For this transition an intense metastable has been found by the defoc. technique. Furthermore, a broad metastable is seen in the spectrum at *m/e* 147 - 148 corresponding with the same transitions. This metastable was also observed by Lengyel but assigned to the transition 303 → 211; comparison of the defocused m^* intensities for both transitions makes the latter assignment less plausible.

phenoxastannin) and a neutral 10,10-dimethylphenoxastannin molecule*.



Further fragmentation proceeds predominantly from the ion at *m/e* 303, which accounts for the similarity of the spectra of both compounds in the lower mass region, although the internal energy distribution is probably somewhat less in the *m/e* 303 ions of the twelve membered ring. This is suggested by the relatively smaller abundance particularly of the ions at *m/e* 184 ($SnC_5H_4^{+\cdot}$), *m/e* 145 $(SnC_2H)^{+}$ and *m/e* 139 ($C_{11}H_7^{+}$) which are fragment ions whose formation requires a rather high activation energy, as is indicated by their relatively strong decrease in intensity in the low electron energy spectrum of the six membered ring.

A lower internal energy distribution of the *m/e* 303 ions from the twelve membered ring might well be expected, since the appearance potential of this ion (11.05 ev) is about 1.7 eV higher than that of the same ion from the six membered ring (9.40 eV). Incidentally the much higher *AP* for this ion in the twelve membered ring again makes the alternative dimer structure unlikely. Smaller fragment ions of diagnostic value in the high mass region are the one tin atom containing cluster at *m/e* 471 mainly composed of $SnC_{25}H_{19}O_2$ ions formed by metastable confirmed loss of $Sn(CH_3)_2$ from the $(M - 15)^+$ ion, the cluster at *m/e* 379, which is composed of $SnC_{19}H_{15}O$, $SnC_{18}H_{11}O_2$ and $^{118}Sn^{120}SnC_8H_{13}O_2$ ions (intensity ratio 2/1/1) for which no discrete transitions could be assigned (see below) and the cluster at *m/e* 363, which has the elemental composition $SnC_{18}H_{11}O$. The $SnC_{18}H_{11}O_2$ component of *m/e* 379 and the ions with *m/e* 363 might well have ion structures similar to the structures of ions at the same mass in 10,10′-spirobiphenoxastannin (see Fig. 13). This is further indicated by the finding of metastable transitions from *m/e* 455, which might have an ion structure analogous to the $(M - H)^+$ ion of the spiro compound.

The mass spectrum of the diethylphenoxastannin presented in Fig. 2 is also different from that published by Lengyel [3], the two spectra showing the same characteristic differences noted for the two dimethyl compounds. We believe that here, too, Lengyel dealt with a twelve membered ring compound. Again the six membered ring compound shows an intense molecular ion at *m/e* 346. This ion intensity appears to be very small in Lengyel's spectrum, where it is also accompanied by a cluster with one H-atom less. Furthermore, analogous to the case of the dimethyl compounds, the low electron energy spectrum of

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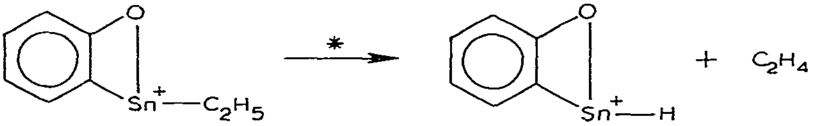
*The alternative fragmentation, in which the positive charge resides on the molecule and a radical is eliminated, is less favoured in view of the stabilities of ions and neutrals, as reflected in the low ion intensity of the *m/e* 318 ions in the spectrum. In so far as this reaction proceeds, it is accompanied by the reaction $(M - 15)^+ \rightarrow (318 - H)^+ + 304$, in which tin can be formally three coordinated in the ion and four coordinated in the neutral species.

diethylphenoxastannin more resembles the spectrum of the compound investigated by Lengyel. Not only because then ions whose formation requires a high activation energy have disappeared from the spectrum (e.g. the cluster at *m/e* 184), but also because now ions become more pronounced whose formation is competed by reactions of a higher frequency factor like the $Sn^+—C_2H_5$ ions at *m/e* 149 (see spectrum at page 207) or ions of which most decompose further at higher electron energies into smaller fragments. The latter is observed with the ions at *m/e* 241 (SnC_8H_9O). At low electron energies its presence is clearly discernable in the spectrum (see Fig. 2), in contrast to the electron energy normally used where it is also formed. Than it acts as an important intermediate for the formation of fragment ions at *m/e* 213:



which is supported by the presence of a very intense metastable (8% of daughter ion intensity).

Finally, the spectrum published by Lengyel also shows peaks which are not found in either the low or high eV spectrum of the six membered ring, viz. the Sn-containing cluster at *m/e* 179 and 207. These clusters whose formation and composition has not been treated by Lengyel might be composed of $SnHEt_2$ and $SnEt_3$ ions respectively, which would be in accordance with an analogous fragmentation of the dimethyl twelve-membered ring. Unfortunately a sample of sufficient purity was not available to check this supposition.

As has been mentioned already a very characteristic difference between the spectra of the six and the twelve membered ring compounds is the notable abundance of a molecular ion in the phenoxastannin while no molecular ions were detectable in the spectrum of the twelve membered ring. The small intensity of the ion at *m/e* 318, which is in fact a fragment ion of the twelve membered ring, was ascribed by Lengyel to be due to the abnormality of the Sn^V oxidation state, consistent with observations made on simple organotin derivatives [3].

There is indeed strong evidence that primary ionization of Group IVB tetraalkyl compounds results in the lack of one of the metal—carbon bond electrons. This leads to a molecular ion containing four coordinated tin which is unstable and therefore readily fragments. It is however not a priori very likely that this is also exclusively the case in compounds containing a heterocyclic moiety. Primary ionization in this type of compounds is likely to involve at least partially the removal of an electron from a molecular orbital determined by the heterocyclic moiety. Within the concept of charge localisation migration of the positive charge initially present on the substituent will depend upon the ability of the substituent to stabilise the positive charge.

Fragmentation of some related dimethyltin heterocycles

Since knowledge of the stability of molecular ions is especially of importance for structural elucidation of organometallic compounds we investigated this point in more detail. Therefore the mass spectra of some related dimethyl-

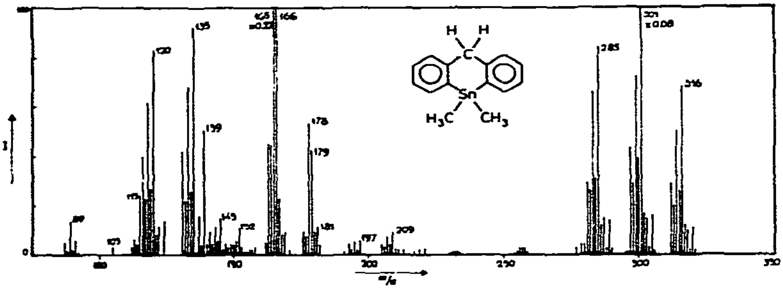


Fig. 6. Mass spectrum of 5,5-dimethyl-5,10-dihydrodibenzo[*b*,*e*]stannin.

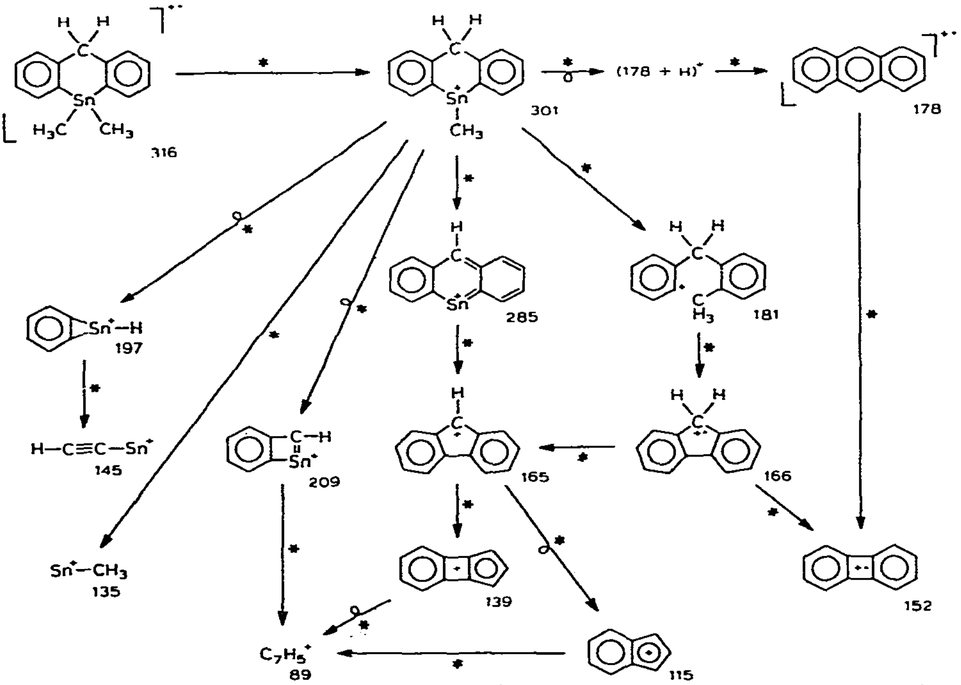


Fig. 7. Fragmentation pattern of 5,5-dimethyl-5,10-dihydrodibenzo[*b*,*e*]stannin. Note: $Sn^{+\cdot}$ is formed from the ions at *m/e* 301, 285 and 209.

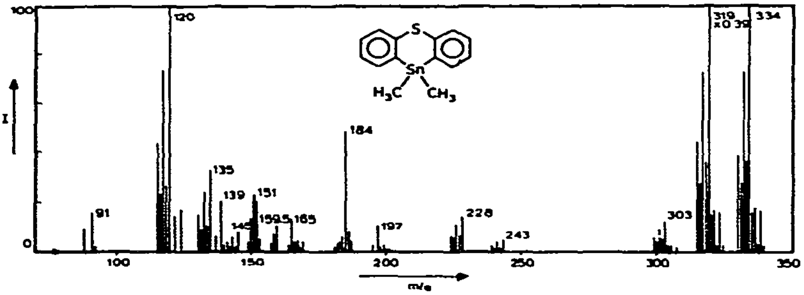


Fig. 8. Mass spectrum of 10 10-dimethylphenothiastannin.

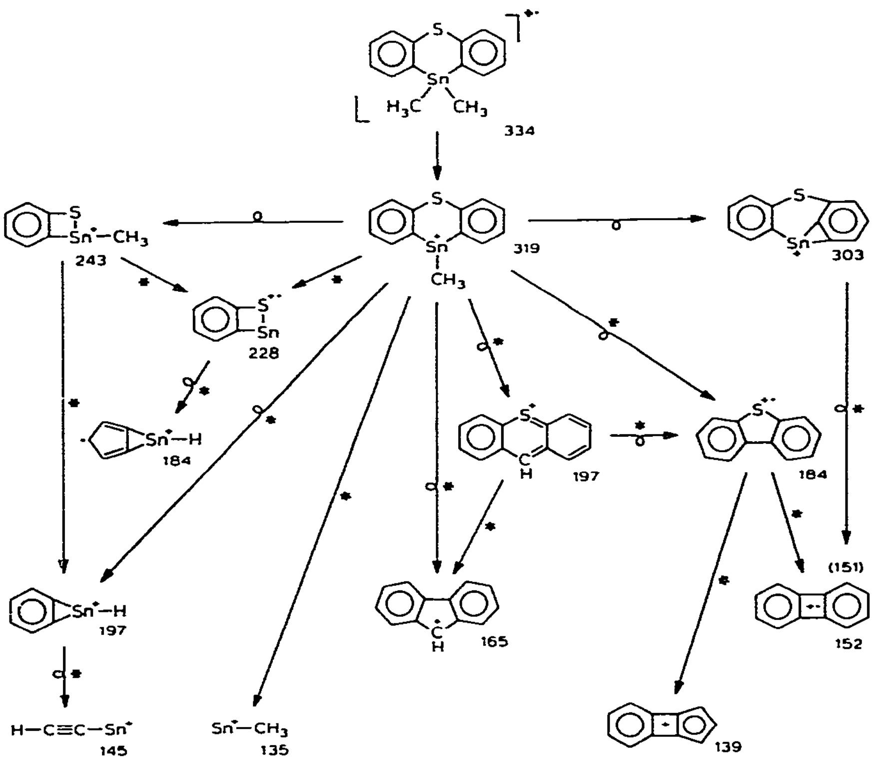


Fig. 9. Fragmentation pattern of 10,10-dimethylphenothiastannin. Note: Sn^{+} is formed from the ions at *m/e* 228, 197 and 184.

tin compounds in which the bridging oxygen atom has been replaced by —CH_2—, —S— and —SO_2—* were studied. The spectra of these compounds: 5,5-dimethyl-5,10-dihydrodibenzo[*b,e*]stannin, 10,10-dimethylphenothiastannin and 10,10-dimethylphenothiastannin 5,5-dioxide together with the corresponding fragmentation schemes** obtained from metastable measurements are presented in Figs. 6 - 11.

There are remarkable differences in intensity of the molecular ions, which will be discussed below, but comparison of the fragmentation patterns of these compounds shows that the principal routes of fragmentation outlined before for the oxygen containing compound are followed. In all cases fragmentation starts with loss of $\cdot CH_3$*** leading to a stable three coordinated tin containing ion, which in all cases carries about 50% of the total ion current. From this precursor ion fragmentation proceeds in the three ways described before.

The closest resemblance with the oxygen containing compound is seen in the spectrum of the *phenoxathiastannin*. Not only the fragmentation pathways

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*Variation of the bridging atom between the two phenyls was examined and not variation of the alkyl substituent since its influence on the intensity of molecular ions can be reasonably explained by differences in the Sn—C bond strength and the stability of the alkyl radical formed [6].

**All relevant elemental compositions of the ion structures proposed in the schemes have been obtained from exact mass measurements.

***The metastable transitions $318^{+} \rightarrow 181^{+}$ and $318^{+} \rightarrow 287^{+}$ are presumably corresponding with consecutive reactions.

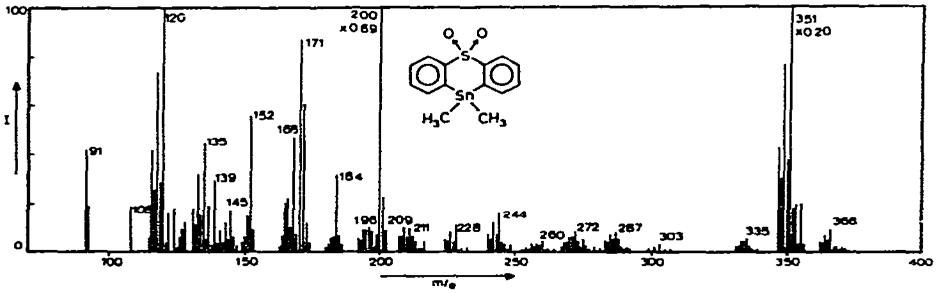

Fig. 10. Mass spectrum of 10,10-dimethylphenothiastannin 5,5-dioxide.

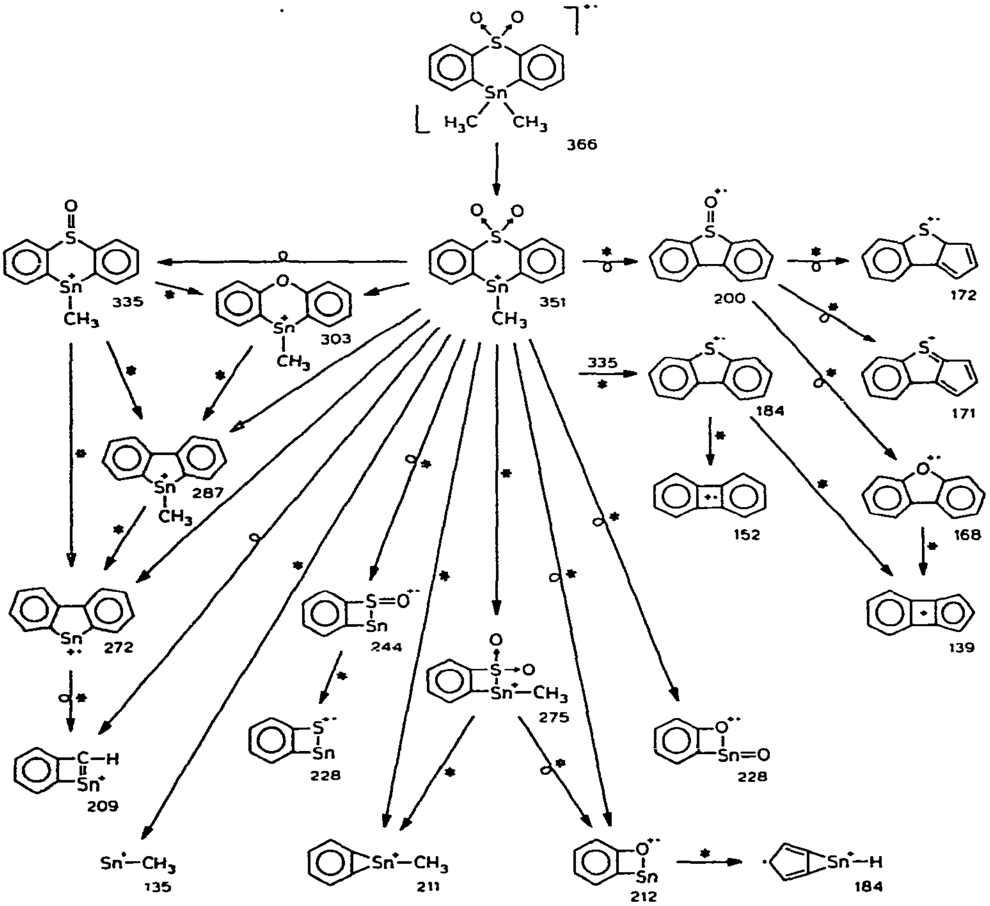

Fig. 11. Fragmentation pattern of 10,10-dimethylphenothiastannin 5,5-dioxide. Notes: $Sn^{+\cdot}$ is formed from the ions at *m/e* 287, 272, 211 and 196. Sn^{+}—CH_3 is also formed from the ions at *m/e* 287 and 211. Also metastable confirmed are the transitions 351 → 244 → 197 → 145.

but also the relative intensity distribution of corresponding ions are very much alike.

In the *dihydrodibenzostannin* the availability of hydrogen atoms at the $-CH_2-$group linking the two phenyls of the aromatic substituent, leads to an additional route of fragmentation to wit formation of the three-coordinated ion at *m/e* 285 and a stable CH_4 molecule. This process also occurs in the—O–, —S— and $-SO_2-$ compound but to a much lesser extent since then a hydrogen atom must be abstracted from the phenyl ring leading to a sterically unfavourable ion structure (see schemes). The ion at *m/e* 285 further fragments by loss of tin into the $(\text{fluorene-H})^+$ ion at *m/e* 165, which accounts for the fact that this ion has a considerably higher intensity than could be expected for the loss of H· from the ionized aromatic substituent fluorene [In the mass spectrum of fluorene itself the intensity ratio $M/M - 1$ is about 1.2 (ref. 5), in the spectrum of the tin compound it is approximately 0.2]. Loss of SnH_2 from the $(M - 15)^+$ ions is in this case not followed by a CH radical elimination since a stable aromatic entity, i.e., the anthracene molecular ion is formed. Finally in accordance with the expectation in this compound odd electron tin containing fragment ions are absent.

The behaviour of the *phenoxathiastannin dioxide* also fits the general rules outlined above but in contrast with the spectra discussed so far its spectrum is fairly complex. Because of nominal mass coincidence of ions containing one sulphur or two oxygen atoms e.g. the ions at *m/e* 228 which in fact are composed of these two types of ions (see Fig. 11) and the difficulties encountered in tracing the intensity distribution of isotopic clusters composed of several coinciding ions (e.g. the cluster at *m/e* 213 - 206 which appeared to be composed of SnC_7H_5, SnC_7H_7 and SnC_6H_4O ions*) elemental compositions of many ion structures presented in the scheme had to be determined. Since metastable measurements are performed at LR it was furthermore not always possible to determine an unambiguous precursor-daughter relationship in cases where different fragment ions of the same nominal mass may originate from the same precursor ion. Futhermore the spectrum shows an interesting difference with the other compounds with regard to the nature of the non-metal containing ions. In the —O—, —S— and $-CH_2-$ compounds one of the predominant fragmentation reactions consists of the formation of Sn^+CH_3 ions and the corresponding heterocyclic neutral molecule (dibenzofuran, dibenzothiophene and fluorene) but this process is in competition here with an analogous reaction in which the charge resides at the heterocyclic moiety and $Sn-CH_3$ radicals are formed. In the $-SO_2-$ compound however, the latter fragmentation hardly occurs as is indicated by the near absence of both molecular and fragment ions emanating from dibenzothiophene dioxide (the principal fragment ions of this compound are loss of SO as well as a successive elimination of two CO molecules from the molecular ion [7,8], processes which can be rationalized to occur after C—O bond formation in the molecular ion via a 1,2-phenyl shift). Formation of the ionized heterocyclic substituent apparently is an energetically less favourable process for the dioxide. This is reflected in the values we mea-

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*E.g. *m/e* 209 consists of a multiplet with the following principal components: 208.9583 = $C_7H_7{}^{118}Sn$ (Δ + 9.5 ppm), 208.9418 = $C_7H_5{}^{120}Sn$ (Δ + 2.5 ppm) and 208.9293 = $C_6H_4O{}^{117}Sn$ (Δ + 0.9 ppm).

sured for the ionization potentials of the heterocyclic substituents, dibenzothiophene dioxide having a considerably higher *IP* (9.28 eV) than the other three substituents dibenzofuran (8.77 eV), dibenzothiophene (8.44 eV) and fluorene (8.52 eV).

Nevertheless, non-metal containing ions are present in the spectrum but they are predominantly formed via Sn - O instead of C - O bond formation by loss of $O{=}Sn{\cdot}{-}CH_3$ radicals from the $(M - CH_3)^+$ and $(M - CH_3 - O)^+$ ions leading to the formation of intense dibenzosulphoxide ions at *m/e* 200 and dibenzothiophene ions at *m/e* 184 respectively. The former ions probably rearrange to a sulfenate ion structure and then lose CO/COH or elemental sulphur.

Fragmentation of the $(M - 15)^+$ ions into tin containing ions also shows a feature characteristic to the dioxide in that the complete hetero element moiety (the SO_2 molecule) can be eliminated, which accounts for the presence of the new ions at *m/e* 287 and 211.

Charge localization in the molecular ions

Despite the similarities of these four compounds in their fragmentation behaviour under electron impact the relative intensity of their molecular ions is greatly different; it descreases strongly in the order $-S- > -O- > -CH_2- > -SO_2$ (see Table 1). It is unlikely that this is due to the availability of alternative fragmentation pathways for the molecular ions of particularly the $-SO_2-$compound since metastable measurements indicate that in all cases fragmentation occurs nearly exclusively from the $(M - 15)^+$ ion. It is therefore in the first instance reasonable to consider the stability of the molecular ions with respect to their common initial fragmentation, viz.. $M^{+\cdot} \rightarrow (M - 15)^+ + CH_3^{\cdot}$. In an attempt to correlate the intensity of the molecular ions with the rate of the above mentioned fragmentation reaction, ionization and appearance potentials have been measured. The data are tabulated in Table 1 together with the relative abundances of molecular and $(M - 15)^+$ ions.

TABLE 1

ENERGETIC DATA OF SOME DIMETHYLTIN HETEROCYCLES

Compound	$M^{+\cdot}$		$(M - 15)^+$		
	Intensity (% t.i.c.)	*IP* (eV)	Intensity (% t.i.c.)	*AP* (eV)	*AP* − *IP* (eV)
10,10-Dimethylphenothiastannin	22	8.1	48	9.4	1.3
10,10-Dimethylphenoxastannin	12	8.1	56	9.4	1.3
5,5-Dimethyl-5,10-dihydro-dibenzo [*b*,*e*] stannin	4.4	8.6[a]	56	9.0	0.4
10,10-Dimethylphenothiastannin 5,5-dioxide	1.0	9.3[a]	50	9.6	0.3

[a] Although fairly reproducible, these *IP* values have to be considered as upper limits since they have been derived from molecular ions with a small intensity.

Invoking the simple rate expression of the quasi-equilibrium theory (QET) for the description of the unimolecular decomposition of ions:

$$k = \upsilon \left(\frac{E-E^0}{E}\right)^{s-1}$$

where υ = a frequency factor, E = the internal energy of the ions, E^0 = the activation energy and $s - 1$ = the effective number of vibrational degrees of freedom, leads to an explanation of the increased molecular ion intensity of the O, S compound vs. the CH_2 and SO_2 compounds. This difference is mainly caused by differences in E^0 values (reflected in the AP - IP values measured). An explanation on this basis of the relative intensity differences between especially the O and the S compounds meets with difficulties since E^0 values are identical while furthermore the differences in the number of effective oscillators and the frequency factors for these simple cleavage reactions are not likely to have so great an influence. It must be assumed that the internal energy distributions are not alike (including the possibility that differently populated separated electronic states exist), but unfortunately it is not easy to confirm this.

One specific approach is then to consider charge localization to take place before fragmentation instead of assuming dissipation of all energy above the ground level to be converted into vibrational energy prior to fragmentation [11 - 13]. The charge is then thought to be localized for several vibration periods in a distinct part of the molecule where it can trigger fragmentation, the average charge density being statistically maximized at the site of lowest ionization potential. The apparent charge residence time at a site is thus a function of the difference between local ionization potentials or in more tangible quantities the *IP* of model ions representing distinct parts in the molecule in competition for the charge. If these considerations are applied to the compound under investigation one might distinguish two such model ions viz. the aromatic substituent and the dimethyl—Sn entity. It is then expected that the primary fragmentation (loss of CH_3) is determined by the residence time of the positive charge at tin. Charge localization at the aromatic entity is not anticipated to lead to extensive fragmentation since the ionized aromatic substituent itself forms a stable entity under electron impact. The residence time at tin will be determined by the difference in ionization potential between the aromatic moiety, see Table 2 and the *IP* of the dimethyl—Sn entity. The latter is the same for all four compounds and might be estimated at 8.5 eV from the *IP* of $Sn(CH_3)_4$ [14,15].

TABLE 2

IP DATA OF PhXPh COMPOUNDS

X	*IP* (eV)
S[a]	8.4
O[b]	8.8
CH_2	9.4
SO_2	9.7

[a] The two lowest ionisation potentials derived from photo electron spectra are 7.8 and 9.1 eV for the sulfide and 8.0 and 8.9 eV for the ether. [b] Lit. value 8.82 eV, ref. [9].

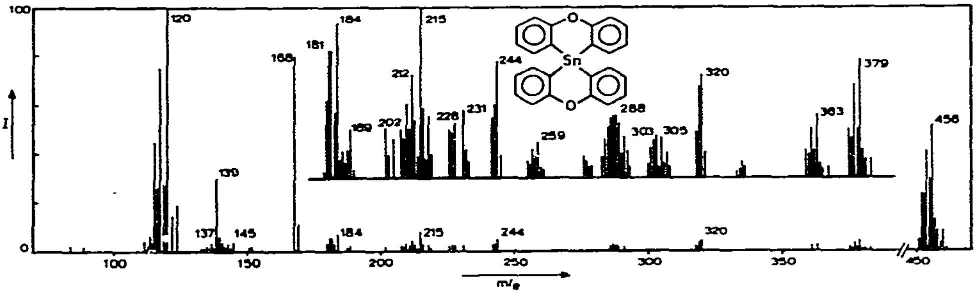

Fig. 12. Mass spectrum of 10,10'-spirobiphenoxastannin.

The difference in ionization potentials of the two parts of the molecule competing for the charge is indeed reflected in the differences in molecular ion intensities of the compounds under investigation. The *IP* differences indicate that in the sulfur compound charge localization is possible at the aromatic moiety in contrast to the dioxide where the high *IP* of the aromatic substituent will lead to charge localization mainly at the tin atom. The four-coordinated Sn^+ ions however do not have a stable configuration and will readily fragment into the tin three-coordinated ($M - CH_3$)-ions.

For the absence of molecular ions in the twelve membered ring compound we can not offer a straightforward explanation.

Fragmentation of 10,10'-spirobiphenoxastannin

Since we were interested to know whether the concept of charge localisation as a driving force for fragmentation also holds for tin compounds in which only heterocyclic moieties are present, we also examined the spectrum of 10,10'-spirobiphenoxastannin. The data for this compound are presented in Figs. 12 and 13.

Primary ionization can occur both at the substituent and perhaps also by removal of an electron from a Sn—C bond. Formation of an ion in which the charge resides at the metal atom, however, does in this case not contribute to the same extent to the instability of the molecular ions as in the dimethyl compound since the central metal atom is now linked by two bonds to the substituent.

The role of the $(M - 15)^+$ ion in the dimethyl compounds discussed before as the most important precursor ion is taken over in this compound by the molecular ion which then can be considered as an odd-electron tin three-coordinated ion. This dual function of the molecular ion is reflected in its abundant ion intensity.

Fragmentation of the molecular ion predominantly occurs by fission of the Sn—C bonds resulting in either the formation of dibenzofuran molecular ions (*m/e* 168) and phenoxastannin neutrals or two dibenzofuran neutrals leaving a very abundant $Sn^{+\cdot}$ ion.

Generally abundant $Sn^{+\cdot}$ ions may be expected in tin compounds with substituents which are linked by two bonds to the tin atom, since then fragmentation cannot easily result in the formation of three- or mono-coordinated even electron ions.

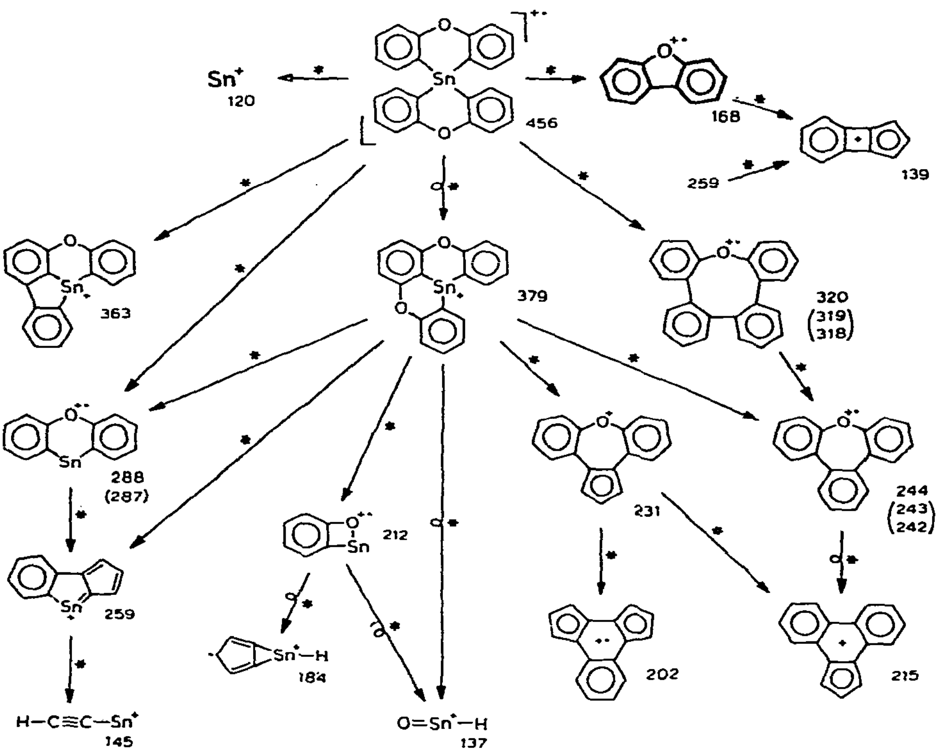

Fig. 13. Fragmentation pattern of 10,10'-spirobiphenoxastannin. Note: $Sn^{+\cdot}$ is also formed from the ions at *m/e* 379, 363, 288, 212 and 184.

Despite their relatively small abundance the formation of other ions has been traced in order to confirm the general rules outlined above and to obtain supporting evidence for the structure of corresponding ions in the spectra of the dimethyl compounds (discussed before) (see e.g. *m/e* 184, 212, 259, 288).

Experimental

The heterocyclic tin compounds investigated, 10,10-dimethyl- and 10,10-diethylphenoxastannin [2], the dimethyl twelve membered ring $Sn_2C_{28}H_{28}O_2$ [1,2], 5,5-dimethyl-5,10-dihydrodibenzo[*b,e*]stannin [16], 10,10-dimethylphenothiastannin [2], 10,10-dimethylphenothiastannin 5,5-dioxide and 10,10'-spirobiphenoxastannin [1] were synthesized according to procedures described in the literature.

Unless otherwise stated the measurements were performed using an AEI MS 902 mass spectrometer, normally operating at 70 eV electron energy, 8 kV ion accelerating voltage, 500 μA trap current and an ion chamber temperature varying from 50 - 70° for the volatile six-membered ring compounds to 130 - 150° for the twelve membered ring and the spiro-compound. Samples were admitted via the direct introduction system after evaporation of the solvent (chloroform) from the tip of a quartz sample probe. Spectra of the dimethyl- and diethylphenoxastannin were also obtained after introduction of these somples via the AGHIS (all glass heated inlet system) at 140°. Elemental compositions have been obtained from exact mass measurements at a resolving power of 20,000.

Ionization and appearance potentials have been measured using a gold—rhodium coated ion chamber [17] and a specially designed source supply, which allowed automatical scanning of a 10.00 V electron accelerating voltage range in about 35 sec. The electron accelerating voltage was displayed on a digital voltmeter. Measuring conditions were: I_{trap} 10 μA; V_{trap} 3.0 V; V_{repeller} 0 V; $V_{\mathrm{el.acc.}}$ 18.00 - 8.00 V and 16.00 - 6.00 V. *IP/AP* values have been calculated with Xenon as a calibrant gas using the method of Flesch and Svec [18] and incidentally also according to the method of Winters et al. [19].

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