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SUBSTITUENT EFFECTS IN THE ELECTRON-IMPACT INDUCED FRAGMENTATION OF PHENOXASTANNINS

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SUMMARY

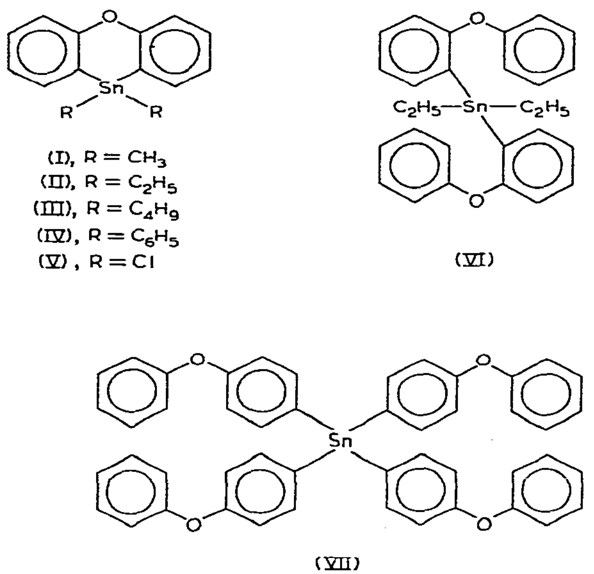
The common initial step in the electron-impact induced fragmentation of five Sn,Sn-disubstituted phenoxastannins (9-oxa-10-stanna-9,10-dihydroanthracenes) and two closely related acyclic organotin analogues is ejection of a metal-ligand as a radical. The subsequent break-down pattern, however, is markedly dependent on the nature of substituents. The propensity of tin to remain in the Sn^{IV} oxidation state is noted. Metastables indicate the competitive elimination of unusual neutral particles *e.g.*, C_6H_4 and C_6H_4O from fragment ions. Examples of Sn–O bond formation are presented. Complex skeletal and multiple hydrogen rearrangements involving C–C bond formation with concomitant loss of both heteroatoms [*e.g.*, transitions *m/e* 303→91, *m/e* 227→91 in (I) and *m/e* 289→153 in (II) and (III)] have been uncovered by accurate mass measurements and computer-aided correlation of metastable peaks. Complete "element maps", to determine the elemental composition of all ions, have been recorded for (III) and (VI). Low voltage (12 eV) studies were undertaken to identify the energetically favorable reaction paths.

INTRODUCTION

While the mass spectra of some simple tetraalkyl and tetraaryl derivatives of tin have been the subject of previous investigations[1-4], we are unaware of any previous detailed published report on electron-impact induced reactions of heterocyclic organotin compounds. As part of a continuing study[5-8] of the electron-impact induced fragmentation of heterocyclic organometallic compounds, the mass spectra (Figs. 1–5) of five 10,10-disubstituted phenoxastannins [(I)–(V)], were recorded and analyzed. The mass spectral fragmentation of the variously substituted tin heterocycles are compared and tentative fragmentation pathways suggested. For comparison, two closely related model substances *without* heterocyclic ring, *viz.*, diethylbis(*o*-phenoxyphenyl)tin (VI) and tetrakis(*o*-phenoxyphenyl)tin (VII) were included in this study (Figs. 6 and 7).

In view of the unique structure of these compounds, it was of considerable interest to examine their fragmentation, in order to determine what stable particles are eliminated after ionization in the mass spectrometer, what the energetically most favorable paths of decomposition are, to what degree a reversal of the preparative

SCHEME 1



(I), R = CH_3
(II), R = C_2H_5
(III), R = C_4H_9
(IV), R = C_6H_5
(V), R = Cl

(VI)

(VIII)

chemical reactions used in the synthesis occur. Furthermore, it was of interest to determine the effect of (*i*) the nature of substituents in position 10 and (*ii*) elimination of the central ring altogether [(VI) and (VIII)] will have on the general fragmentation pattern. Correlations between processes occurring in the mass spectrometer and in thermal reactions are also of interest.

The energetics of the fragmentation processes were studied by comparing 70 eV and 12 eV spectra. To aid interpretation, accurate masses and elemental com-

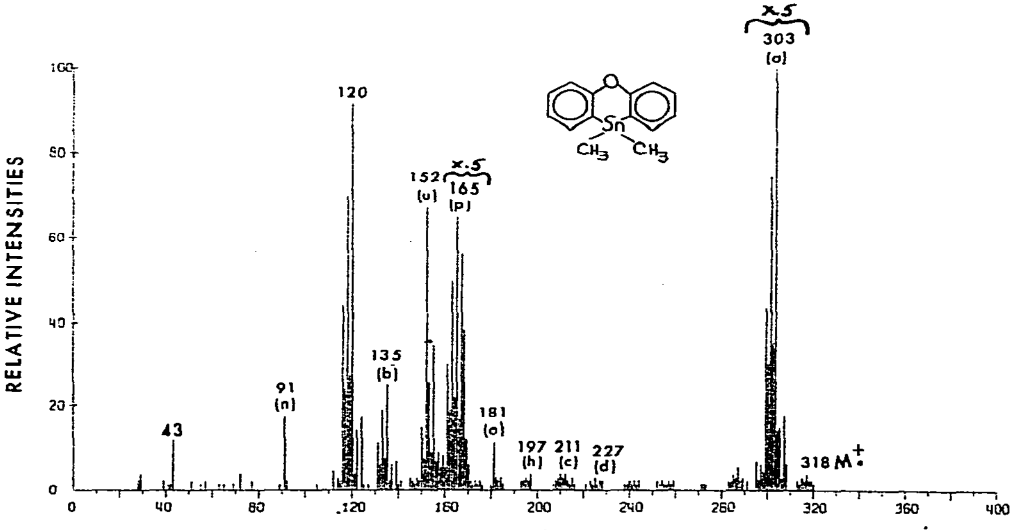


Fig. 1. Mass spectrum of 10,10-dimethylphenoxastannin taken at 70 eV

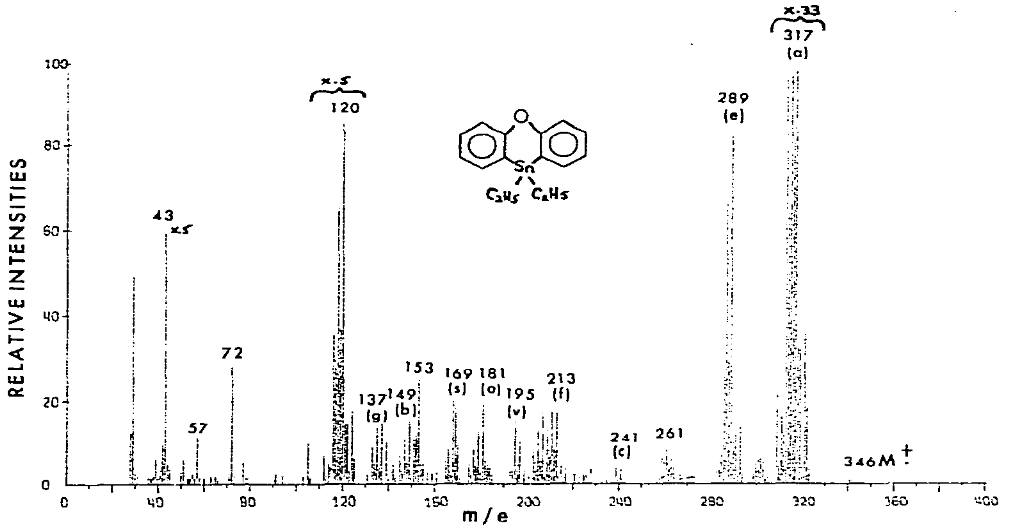


Fig. 2. Mass spectrum of 10,10-diethylphenoxastannin taken at 70 eV.

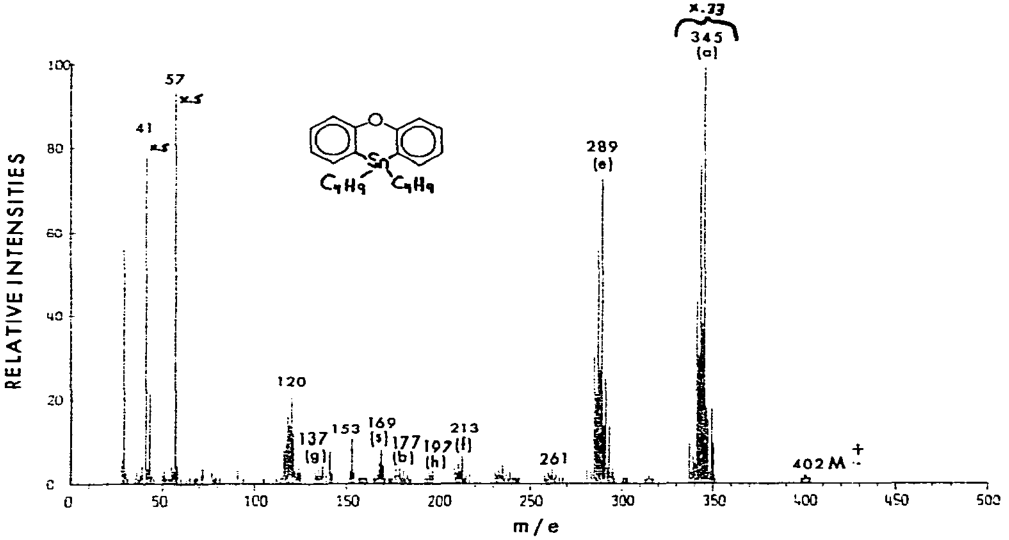


Fig. 3. Mass spectrum of 10,10-dibutylphenoxastannin taken at 70 eV.

positions of all ions were determined for compounds (III) and (VI) by recording complete high resolution spectra and processing the data through a computer in the form of "elemental maps"[9]. The elemental compositions of selected ions in the mass spectra of compounds (III) and (VI) are listed in Table 2. Some of the spectra exhibit a number of remarkably abundant doubly-charged ions. Doubly-charged ions occurring at a non-integral mass number are not included in the bar graphs.

Results of the present investigation indicate that some modes of fragmentation of the formally similar heterocycles containing both an oxygen and a σ-bonded tin atom are markedly dependent on the nature of the ligands attached to the metal.

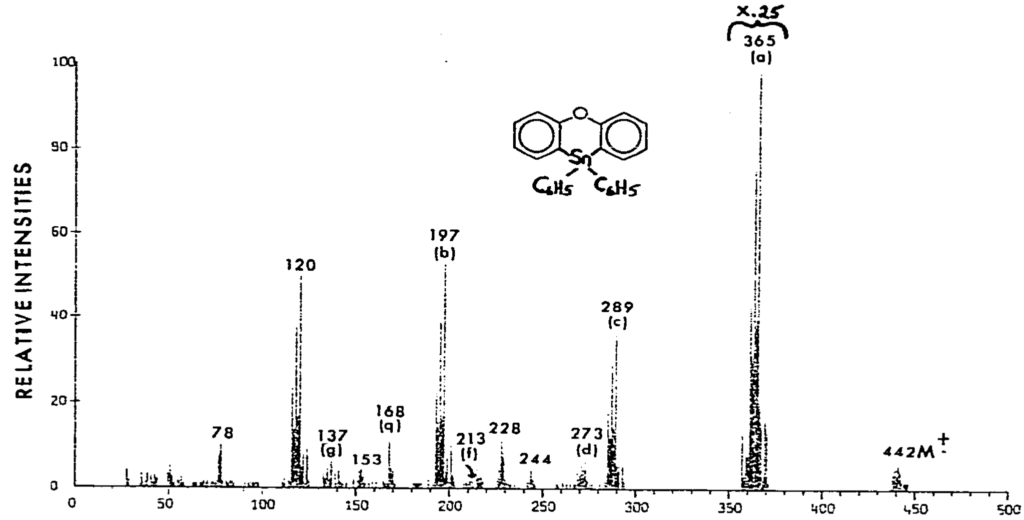


Fig. 4. Mass spectrum of 10,10-diphenylphenoxastannin taken at 70 eV.

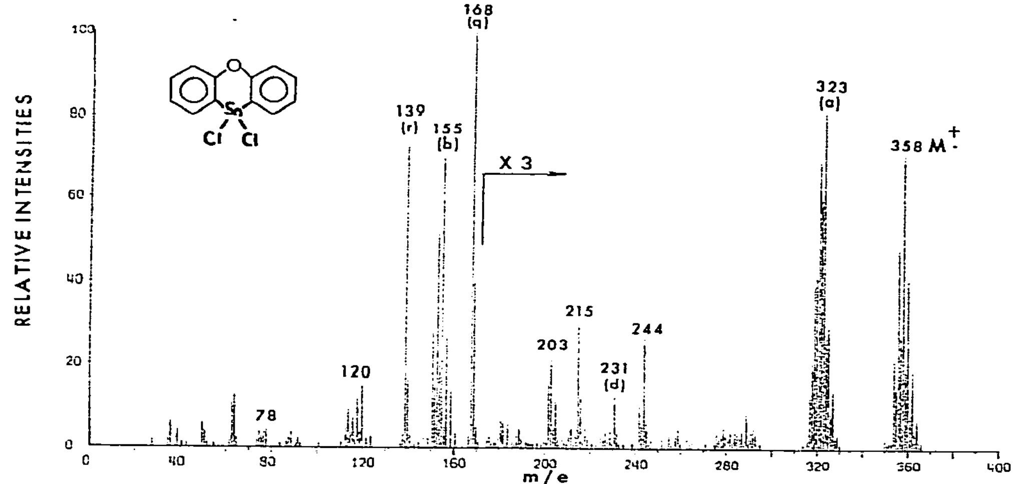


Fig. 5. Mass spectrum of 10,10-dichlorophenoxastannin taken at 70 eV.

Some elimination and skeletal rearrangement reactions, which are without precedent, have been found.

RESULTS AND DISCUSSION

A. Metal-containing ions

(1). *Molecular ion* $[Sn(R)_4]^{\cdot +}$. The molecular ions of all compounds are either absent or of very low abundance. This is consistent with earlier observations[10-13] made on simple organotin derivatives, and is due to the abnormality of the Sn^V oxidation state. The latter is also responsible for the fact that the spectra contain

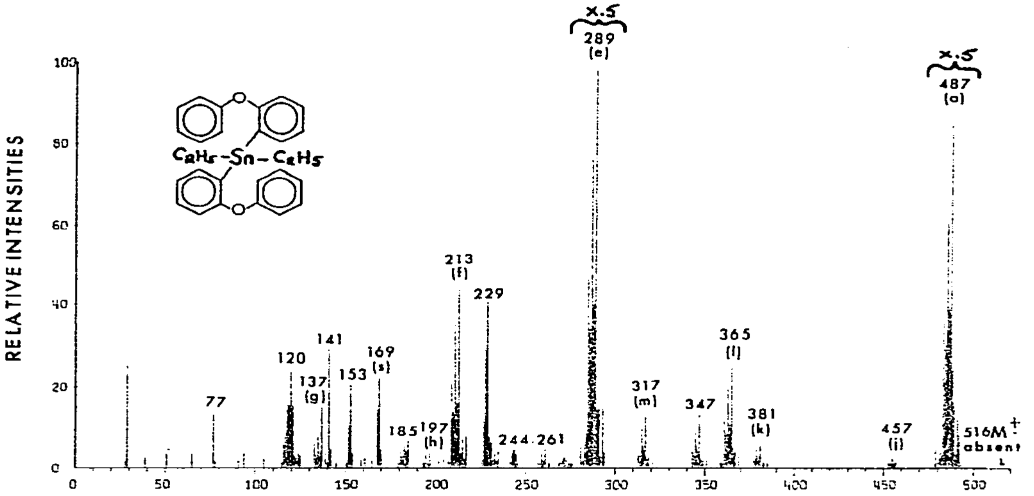


Fig. 6. Mass spectrum of diethylbis(*o*-phenoxyphenyl)tin taken at 70 eV.

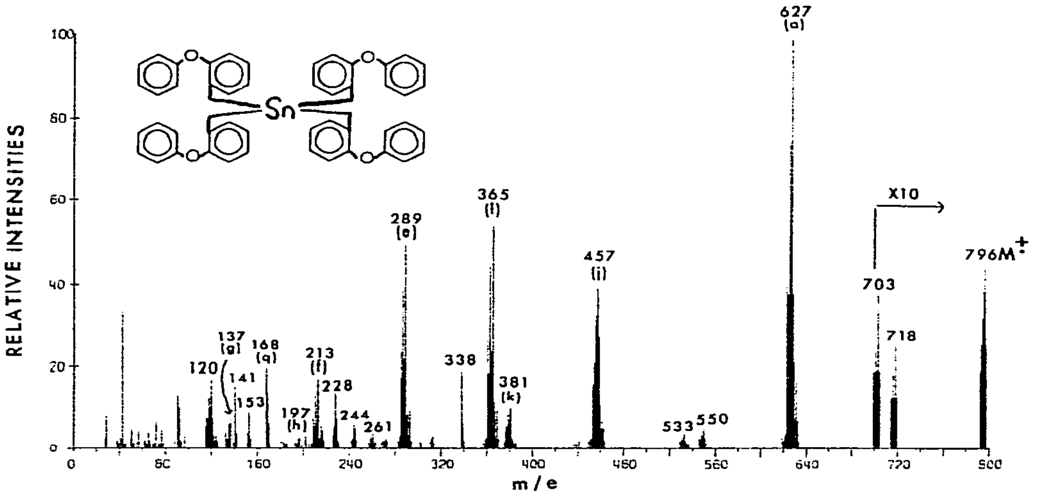


Fig. 7. Mass spectrum of tetrakis(*o*-phenoxyphenyl)tin taken at 70 eV.

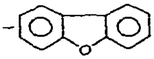
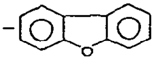
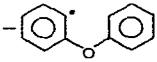
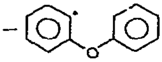
only a few odd-electron, metal-containing fragment ions with tetrasubstituted tin.

(2). *Metal IV oxidation state* $[Sn(R)_3]^+$. The predominant primary fragmentation pathway for all compounds investigated is the elimination of a radical from the molecular ion to form a trisubstituted (Sn^{IV}) metal ion (a). The reason for the overwhelming predominance of this fragmentation pathway in the tricyclic systems studied, is that the ion formed, $(M-R)^+$, contains the metal in the Sn^{IV} oxidation state, which is the most stable for tin[10,12]. The metal–aryl bond is much stronger than the metal–alkyl bond. In compound (VI), in which tin is attached to two alkyl and two aryl ligands, direct comparison of bond strengths is possible: the $(M-C_2H_5)^+$ peak in the spectrum of compound (VI) is about 100 times more abundant than the

(*Continued p.* 413)

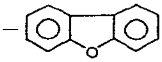
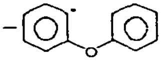
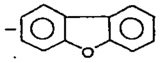
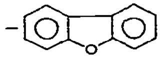
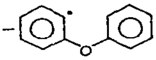
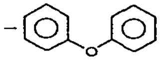
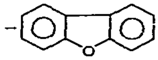
TABLE 1[a]

METASTABLE IONS AND TRANSITIONS

m^* obs.	m^* calcd.	Transition
Compound (I)		
147.0	146.93	 $303 \longrightarrow 211$
138.0	138.01	$140 \xrightarrow{-H^\bullet} 139$
108.0	108.12	$303 \xrightarrow{-SnH_2} 181$
93.0	93.15	$303 \xrightarrow{-SnCH_3^\bullet} 168$
60.0	60.15	 $303 \longrightarrow 135$
47.5	47.52	 $303 \xrightarrow{-CH_3^\bullet} 120$
36.5	36.48	$227 \xrightarrow{-SnO} 91$
27.0	27.33	$303 \xrightarrow{-C_6H_4OSn} 91$
Compound (II)		
263.0	263.47	$317 \xrightarrow{-H_2C{=}CH_2} 289$
164.0		Unassigned
151.0	151.01	$153 \xrightarrow{-H^\bullet} 152$
117.5	117.64	$169 \xrightarrow{-CO} 141$
99.0	98.83	$289 \xrightarrow{-Sn} 169$
81.0	81.00	$289 \xrightarrow{-SnO} 153$
50.0	49.83	 $289 \longrightarrow 120$
Compound (III)		
242.0	242.09	$345 \xrightarrow{-C_4H_8} 289$
189.0		Unassigned
157.0	156.99	$289 \xrightarrow{-C_6H_4} 213$
82.0	81.81	$345 \xrightarrow{-SnC_4H_9^\bullet} 168$
50.0	49.83	 $289 \longrightarrow 120$
29.5	29.49	$57 \xrightarrow{-CH_4} 4i$

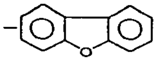
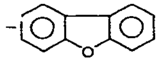
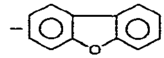
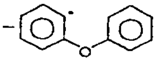
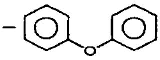
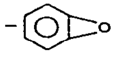
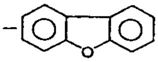
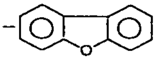
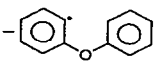
(*Continued*)

TABLE 1 (*continued*)

m^* obs.	m^* calcd.	Transition
Compound (IV)		
228.0	228.82	$365 \xrightarrow{-\mathrm{C_6H_4}} 289$
164.0		Unassigned
106.0	106.33	 $365 \longrightarrow 197$
50.0	49.83	 $289 \longrightarrow 120$
Compound (V)		
228.0		Unassigned
167.0	167.01	$169 \xrightarrow{-\mathrm{H}^{\bullet}} 168$
138.0	138.01	$140 \xrightarrow{-\mathrm{H}^{\bullet}} 139$
115.0	115.01	$168 \xrightarrow{-\mathrm{CHO}^{\bullet}} 139$
79.0	78.84	$358 \xrightarrow{-\mathrm{Sn(Cl)_2}} 168$
74.3	74.38	 $323 \longrightarrow 155$
59.5	59.82	$323 \xrightarrow[-\mathrm{CHO}^{\bullet}]{-\mathrm{SnCl}^{\bullet}} 139$
44.5	44.58	 $323 \xrightarrow{-\mathrm{Cl}^{\bullet}} 120$
Compound (VI)		
429.0	428.85	$487 \xrightarrow{-\mathrm{CH_3}\ -\mathrm{CH_3}} 457$
289.5	289.59	$347 \xrightarrow{-\mathrm{CH_3}\ -\mathrm{CH_3}} 317$
273.6	273.56	$487 \xrightarrow[-\mathrm{C_2H_6}]{-\mathrm{C_6H_4O}} 365$
263.5	263.47	$317 \xrightarrow{-\mathrm{H_2C{=}CH_2}} 289$
233.5	233.35	 $516 \longrightarrow 347$
206.0	206.34	 $487 \longrightarrow 317$
182.8	182.76	 $457 \longrightarrow 289$

(*Continued*)

TABLE 1 (*continued*)

m^* obs.	m^* calcd.	Transition
		
171.5	171.50	$487 \xrightarrow{-CH_3\ -CH_3} 289$
151.0	151.01	$153 \xrightarrow{-H^{\bullet}} 152$
144.0	143.67	$365 \xrightarrow{-SnO} 229$
		
119.0	119.08	$381 \longrightarrow 213$
118.0	117.64	$169 \xrightarrow{-CO} 141$
99.5	99.83	$289 \xrightarrow{-Sn} 169$
		
93.0	93.16	$487 \xrightarrow{-CH_3\ -CH_3\ -C_6H_4} 213$
82.0	82.30	$347 \xrightarrow{-Sn(C_2H_5)_2} 169$
81.0	81.00	$289 \xrightarrow{-SnO} 153$
		
50.0	49.83	$289 \longrightarrow 120$
Compound (VII)		
398.0		Unassigned
		
333.0	333.09	$627 \longrightarrow 457$
		
291.3	291.52	$457 \longrightarrow 365$
228.0–229.0	228.82	$365 \xrightarrow{-C_6H_4} 289$
		
182.0–183.0	182.76	$457 \longrightarrow 289$
		
119.0	119.08	$381 \longrightarrow 213$
117.7	117.64	$169 \xrightarrow{-CO} 141$
98.6	98.83	$289 \xrightarrow{-Sn} 169$
		
49.8	49.83	$289 \longrightarrow 120$

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[a] The metastable correlations were calculated by computer using a program similar to the one employed by Rhodes *et al.*[18]. Final assignments were made manually utilizing intensity data for m_1 and m_2.

TABLE 2

THE ELEMENTAL COMPOSITION OF SELECTED IONS IN COMPOUNDS (III) AND (VI)

Accurate mass measured (*m/e*)	Elemental composition	Deviation from calculated *m/e* (mmu)
Compound (III)		
402.09989	$C_{20}H_{26}OSn$	−0.60
345.02949	$C_{16}H_{17}OSn$	−0.50
288.96870	$C_{12}H_9OSn$	+1.20
212.93620	C_6H_5OSn	+0.00
196.94260	C_6H_5Sn	+1.30
184.94160	C_5H_5Sn	+0.30
176.97440	C_4H_9Sn	+1.80
169.06450	$C_{12}H_9O$	−0.70
168.05769	$C_{12}H_8O$	+0.20
153.07069	$C_{12}H_9$	+0.30
152.06320	$C_{12}H_8$	+0.60
141.07059	$C_{11}H_9$	+0.20
139.05479	$C_{11}H_7$	+0.00
136.90240	SnOH	−2.40
120.90940	SnH	−0.50
119.90310	Sn	+0.90
78.04569	C_6H_6	−1.20
77.03840	C_6H_5	−0.60
76.03120	C_6H_4	−0.00
57.06870	C_4H_9	−1.60
51.02249	C_4H_3	−0.90
43.05450	C_3H_7	−0.20
41.03900	C_3H_5	−0.00
Compound (VI)		
487.07300	$C_{26}H_{23}O_2Sn$	+1.00
457.02409	$C_{24}H_{17}O_2Sn$	−0.90
364.99780	$C_{18}H_{13}OSn$	−0.90
347.04819	$C_{16}H_9OSn$	+2.40
317.00009	$C_{14}H_{13}OSn$	+1.30
288.96700	$C_{12}H_9OSn$	−0.40
260.97230	$C_{11}H_9Sn$	−0.20
212.93610	C_6H_5OSn	−0.00
196.94110	C_6H_5Sn	−0.10
184.94330	C_5H_5Sn	+2.00
169.06419	$C_{12}H_9O$	−1.00
168.05749	$C_{12}H_8O$	+0.00
153.07090	$C_{12}H_9$	+0.50
152.06090	$C_{12}H_8$	−1.60
141.06880	$C_{11}H_9$	−1.50
139.05409	$C_{11}H_7$	−0.60
136.90340	SnOH	−1.40
120.90870	SnH	−1.20
119.90250	Sn	+0.30
92.02569	C_6H_4O	−0.40
78.04529	C_6H_6	−0.90
77.03809	C_6H_5	−0.90
76.03029	C_6H_4	−0.90

TABLE 3

MASS SPECTRA OF COMPOUNDS (I)–(VII) TAKEN AT 12 eV

Compound (I)		Compound (II)		Compound (III)	
m/e	Relative abundance (%)	*m/e*	Relative abundance (%)	*m/e*	Relative abundance (%)
299	54.4	168	25.0	285	10.9
300	45.5	169	15.5	286	9.1
301	81.8	170	31.0	287	18.2
302	45.5	309	5.1	288	10.9
303	100.0	310	1.7	289	25.4
304	27.3	311	3.4	290	5.4
305	27.3	312	3.4	291	9.1
306	9.0	313	44.8	292	1.8
307	27.3	314	32.7	293	5.4
		315	75.8	337	5.4
		316	37.9	338	1.8
		317	100.0	339	3.6
		318	17.2	340	3.6
		319	17.2	341	43.5
		320	3.4	342	32.8
		321	18.9	343	73.8
		322	5.1	344	38.2
				345	100.0
				346	18.2
				347	16.4
				348	5.4
				349	20.0
				350	5.4

Compound (IV)		Compound (V)		Compound (VI)	
359	2.5	168	100.0	343	34.8
360	2.5	169	19.4	344	26.1
361	43.4	170	9.6	345	52.2
362	31.9	354	21.6	346	30.4
363	76.2	355	12.9	347	69.6
364	40.9	356	38.7	348	17.4
365	100.0	357	21.6	349	17.4
366	22.1	358	58.2	350	8.7
367	16.3	359	21.6	351	17.4
368	4.1	360	35.5	483	47.8
369	17.2	361	9.7	484	43.4
370	4.9	362	19.4	485	78.3
438	3.3	363	6.4.	486	52.2
439	3.3	364	9.7	487	100.0
440	4.9			488	30.4
441	3.3			489	21.7
442	5.7			490	13.0
443	2.5			491	21.7
444	1.6				
445	0.8				
446	1.6				

(*Continued*)

TABLE 3 (*continued*)

Compound (VII)

m/e	Relative abundance (%)	*m/e*	Relative abundance (%)	*m/e*	Relative abundance (%)	*m/e*	Relative abundance (%)
361	38.9	455	72.2	552	5.6	702	9.3
362	33.3	456	46.3	553	3.7	703	14.8
363	68.5	457	87.0	554	5.6	704	7.4
364	37.0	458	27.8	619	5.6	705	5.6
365	88.9	459	16.7	620	3.7	714	7.4
366	22.2	460	9.3	621	5.6	715	7.4
367	16.7	461	16.7	622	5.6	716	9.3
368	5.6	462	7.4	623	44.4	717	7.4
369	16.7	529	3.7	624	42.6	718	11.1
370	5.6	530	3.7	625	75.9	719	5.6
377	7.4	531	5.6	626	55.5	720	3.7
378	5.6	532	3.7	627	100.0	792	7.4
379	9.3	533	7.4	628	42.6	793	9.3
380	7.4	546	11.1	629	22.2	794	14.8
381	12.9	547	11.1	130	11.1	795	12.9
451	5.6	548	18.5	631	18.5	796	18.5
452	9.3	549	12.9	632	9.3	797	9.3
453	40.7	550	24.1	699	7.4	798	5.6
454	35.2	551	9.3	700	7.4	799	3.7
				701	11.1	800	3.7

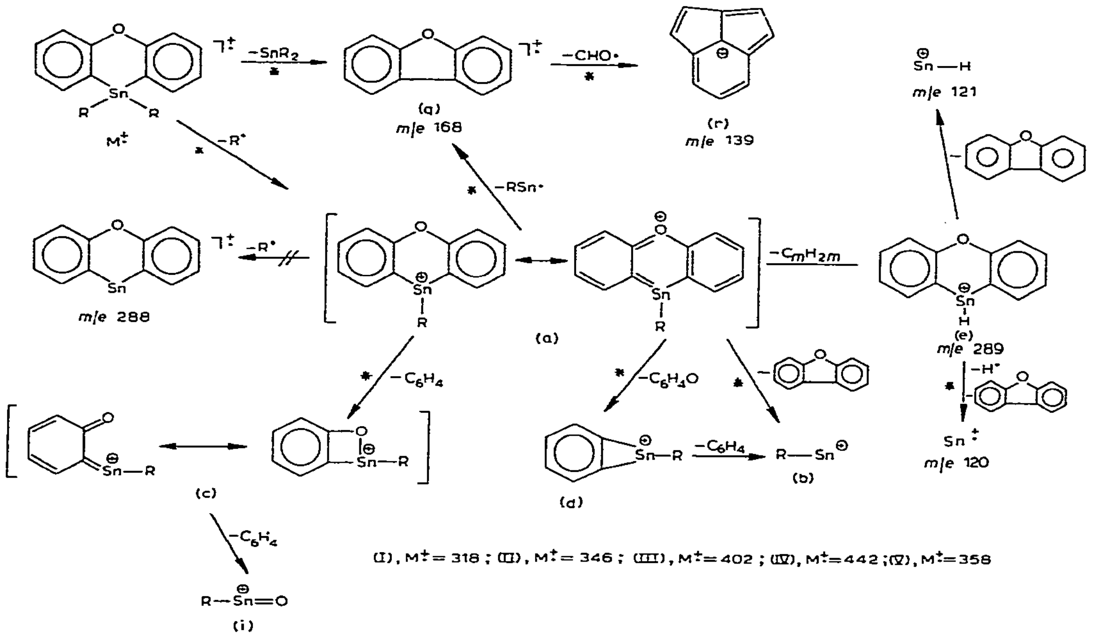
$(M-169)^+$ peak, corresponding to the loss of one of the aryl substituents. Where possible, then, an alkyl radical is eliminated preferentially.

Further fragmentation of ion (a) proceeds by elimination of neutral organic particles. The spectra show three major fragmentation reactions for the $(M-R)^+$ even-electron ion: when R is methyl or phenyl, [(I), (IV)] the neutral particles most readily lost are $C_{12}H_8O$ (dibenzofuran), C_6H_4 (benzyne?), and C_6H_4O to form ions (b), (c), and (d), respectively. If the metal ligands (R) contain two carbon atoms or more, as in the case of compounds (II) and (III), elimination of a neutral alkene moiety from the alkyl side chain with rearrangement of a hydrogen from carbon to tin is the predominant process, yielding ion (e), *m/e* 289. It has been postulated previously that the migrating hydrogen originates mainly from the β-carbon.

In this connection, it was interesting to investigate the spectra of compound (IV), in which no easily transferable hydrogen is available from the 10-substituents, the latter elimination thus being blocked. Subsequent fragmentation of ion (a) in compound (IV), therefore, takes different courses: loss of dibenzofuran and C_6H_4 (confirmed by metastables) predominates. By coincidence, ion (c) in the mass spectrum of compound (IV) occurs at the same mass (*m/e* 289) as ion (e) in (II) and (III).

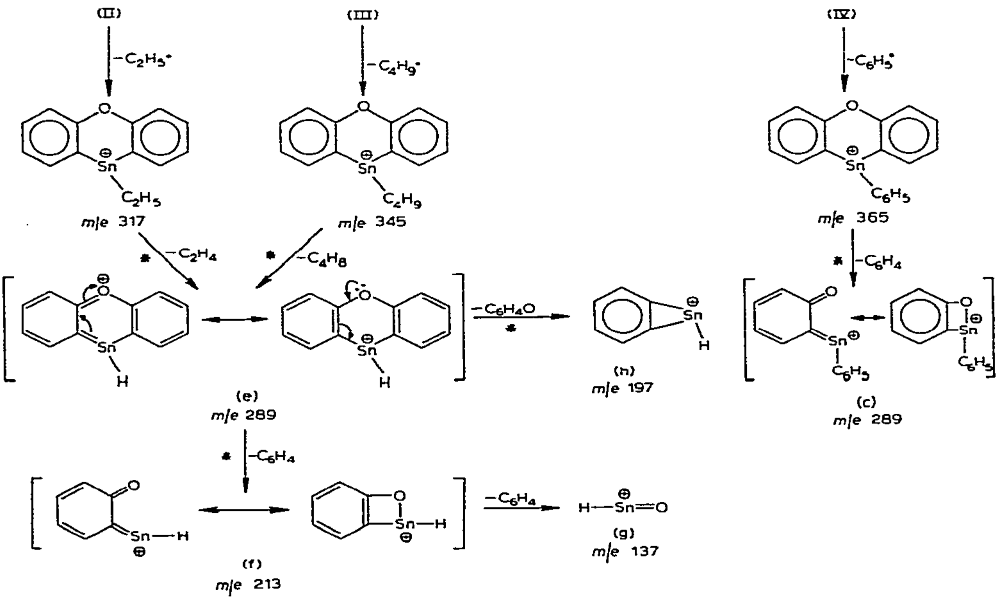
One of the pathways of the further fragmentation of ion (e) involves elimination of C_6H_4 to afford the resonance-stabilized ion (f), *m/e* 213. The formation of ion (f) requires fission of several bonds, compensated for by the formation of the Sn–O bond. The latter is facilitated by anchimeric assistance from the neighboring oxygen function. Ion (f) subsequently eliminates a second C_6H_4 particle yielding ion (g), *m/e*

SCHEME 2



* denotes fragmentations for which metastable peaks are present.

SCHEME 3

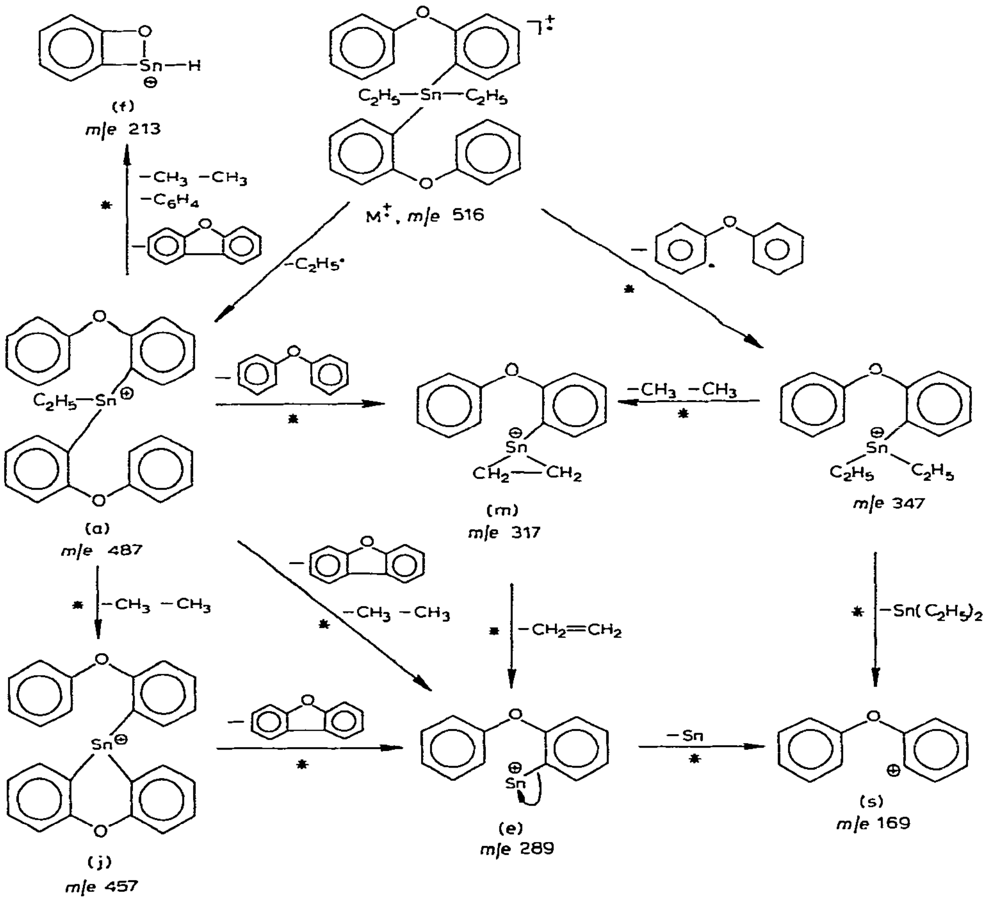


137, encompassing the strong[14] Sn=O double bond. Ion (e) can also afford ion (h), *m/e* 197, by loss of the neutral particle C_6H_4O.

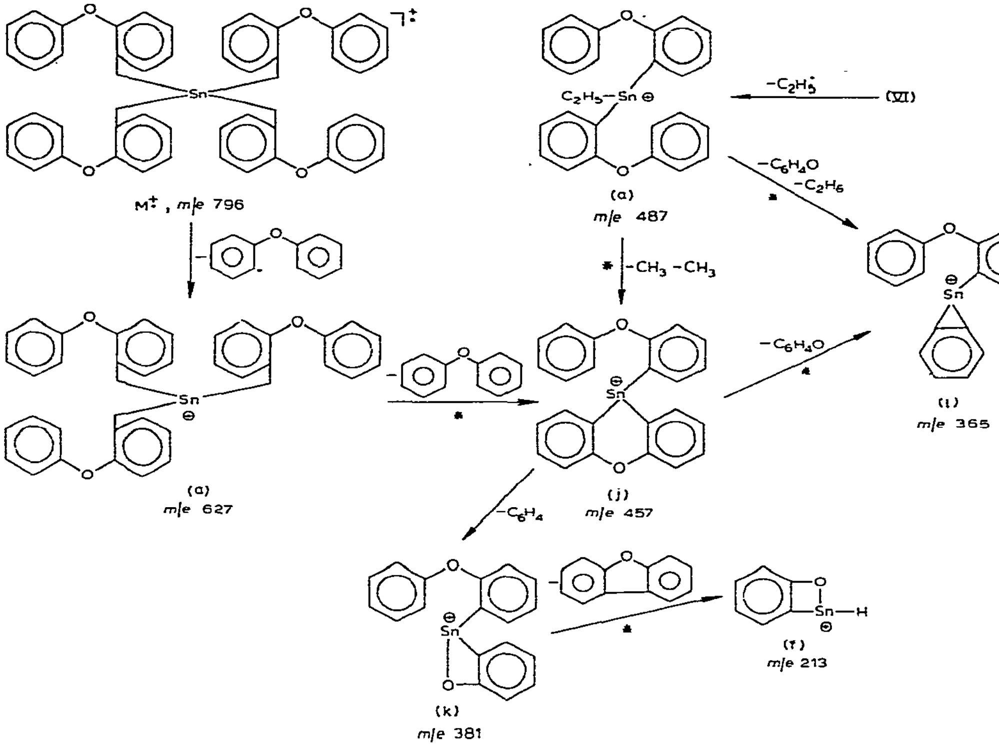
Ion (c), upon elimination of C_6H_4, yields $R{-}\overset{+}{Sn}{=}O$, (i), via a four-centered rearrangement, involving migration of oxygen from carbon to tin. One of the factors facilitating this remarkable rearrangement-elimination reaction is the high stability of the Sn^{IV} even-electron product ion. Elimination of C_6H_4 from ion (d) may lead to RSn^+ (b).

Finally, the $(M-R)^+$ ion in compound (VI) loses the elements of ethane (m^* at 429.0) to give ion (j), *m/e* 457, which in turn can undergo one of several elimination reactions entirely analogous to those previously discussed: it can eject the neutral particle C_6H_4 to form ion (k), *m/e* 381, or C_6H_4O to form ion (l), *m/e* 365, or it may eliminate the elements of dibenzofuran to afford ion (e), *m/e* 289, (Schemes 4–5). The latter further fragments in a manner previously discussed for compounds (II) and (III) (Scheme 3). The *m/e* 487 ion in compound (VI) can fragment alternatively by eliminating the elements of diphenyl ether to form ion (m), *m/e* 317. Interestingly, metastables indicate that transitions *m/e* 487→*m/e* 365 and *m/e* 487→*m/e* 213 occur partly in *one step*, involving simultaneous elimination of two and three neutral particles respectively.

SCHEME 4



SCHEME 5



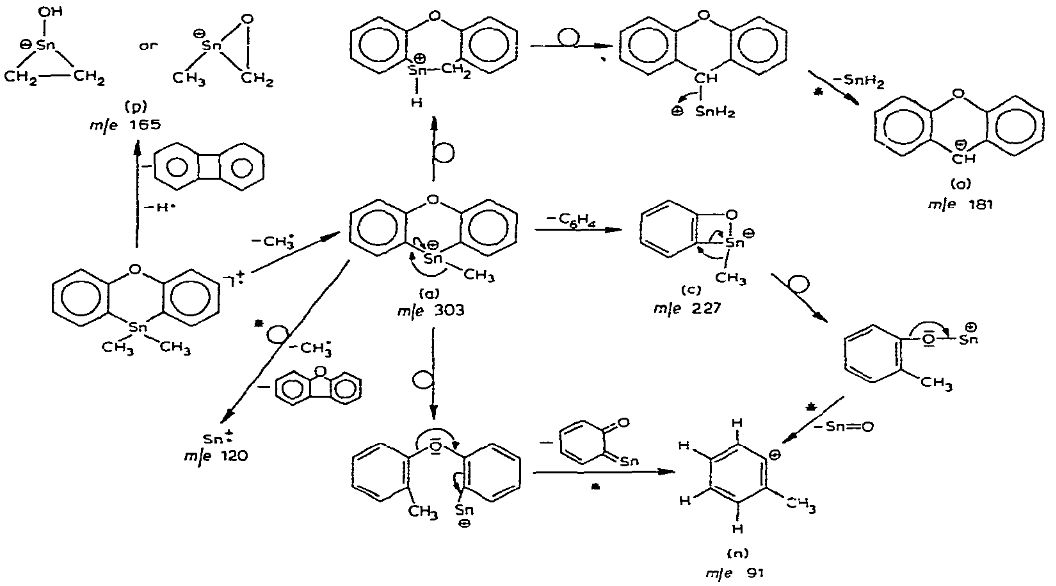
The fragmentation of compound (VII) also starts with the loss of a radical ($C_{12}H_9O^{\cdot}$), leading to ion (a), *m/e* 627. This ion, in turn, eliminates the elements of diphenyl ether to afford ion (j), *m/e* 457 [also present in compound (VI)], the subsequent fragmentation reactions of which are analogous to the ones depicted in Schemes 4 and 5 for compound (VI).

The spectra of 10,10-dimethylphenoxastannin (I) are marked by some strong ions, the formation of which requires extensive skeletal rearrangements. Such ions are, for example, *m/e* 91, 181, 120 and 165. Metastables identify at least two progenitors for ion *m/e* 91: even-electron ions *m/e* 303 $(M-CH_3)^+$ and *m/e* 227. Formation of *m/e* 91 from the former requires methyl migration from the metal to one of the phenyl rings followed by heterolytic C–O bond cleavage with concomitant ejection of C_6H_4OSn. Formation of *m/e* 91 from ion *m/e* 227 can be rationalized by a similar Sn→C methyl shift followed by elimination of SnO (Scheme 6).

Alternatively, the $(M-CH_3)^+$ ion (*m/e* 303) eliminates SnH_2, as confirmed by a metastable, to give a metal-free even-electron ion at *m/e* 181. A rationalization for this process, insertion of a CH_2 into a tin–phenyl bond with subsequent rearrangement of a second hydrogen atom to the metal, is depicted in Scheme 6.

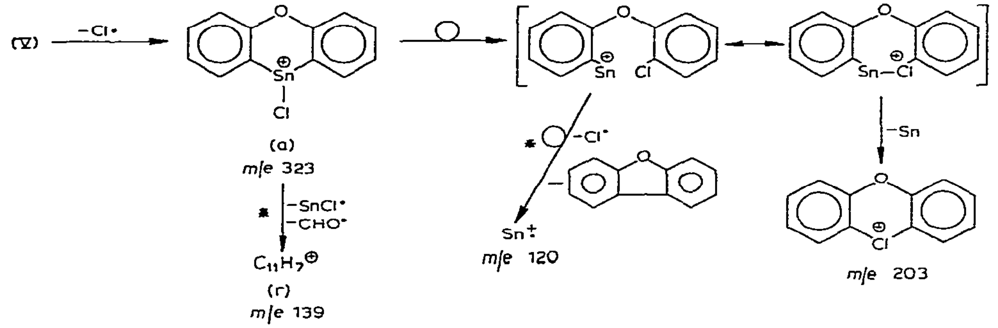
Metastable evidence (*cf.*, Table 1) indicates an additional decomposition path also requiring skeletal rearrangement for ion (a) in compounds (I) and (V): concomitant ejection of an R radical ($CH_3^{\cdot}$ and $Cl^{\cdot}$, respectively) and the elements of dibenzofuran (Schemes 6–7) to give the Sn-ion at *m/e* 120.

SCHEME 6



Arrows with loop indicate fragmentations accompanied by skeletal rearrangement

SCHEME 7



The fourth aforementioned rearrangement-ion, *m/e* 165, is metal-containing, as shown by the observed isotope pattern characteristic of tin. No metastable peak is present to indicate the genesis of this unique ion. Its formation must involve multiple bond cleavages and Sn–O bond formation.

(3). *Metal III oxidation state* $[Sn(R)_2]^{+\cdot}$. Isolated examples of the elimination neutral particles from the molecular ions of tin compounds resulting in an odd-electron tin-ion have been reported[10]. One example of this is the ejection of biphenyl from tetraphenyltin:

$$Ph_4Sn^{+\cdot} \rightarrow SnPh_2^{+\cdot} + Ph_2$$

Similar fragmentations are not found in the compounds investigated in this study, due to the very low abundance of Sn^V odd-electron ions themselves.

(4). *Metal II oxidation state* $(SnR)^+$. As expected from the known[12] stability of divalent tin species, there are moderately abundant Sn^{II} ions in our spectra. The progenitor of the RSn^+ peaks is the $(M-R)^+$ ion, as shown by metastables for compounds (I), (IV) and (V). The formation of SnH^+ ions in tin compounds with aromatic ligands has been noted in a previous investigation[11]. In the compounds of the present study, the SnH^+ ion originates from the *m/e* 289 (e) ion in a manner similar to the formation of the RSn^+ ion in compounds (I–V) (Scheme 2).

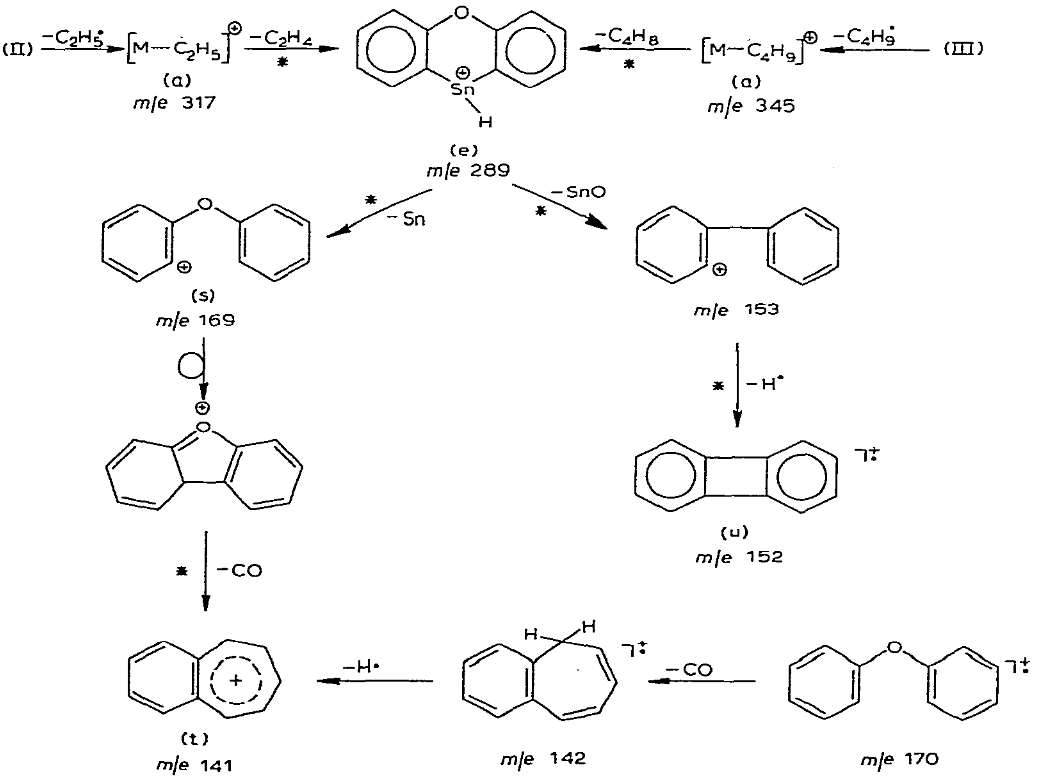
(5). *Metal I oxidation state* (*$Sn^{+\cdot}$*). The $Sn^{+\cdot}$ ion dominates many of the spectra recorded. No simple relationship between structure and abundance of the $Sn^{+\cdot}$ ion, could be found.

B. *Metal-free ions*

In contrast to other organometallic compounds (see for example, the recent review by Chambers, ref. 10), the spectra of the compounds discussed in this paper exhibit many abundant metal-free ions. This can be explained readily, as: (*i*) the second heteroatom (oxygen) stabilizes the positive charge and (*ii*) the two π-electron systems can form highly stable fused polycyclic aromatic ions.

The most notable of these metal-free ions is at *m/e* 168 (q), abundant in all compounds. This ion originates directly from the molecular ion by elimination of the neutral particle R_2Sn and can best be represented as (q) (Scheme 2), dibenzofuran. Ion (q) decomposes by the consecutive ejection of CO and H$^\cdot$ to form ion (r), *m/e* 139, as noted previously[15].

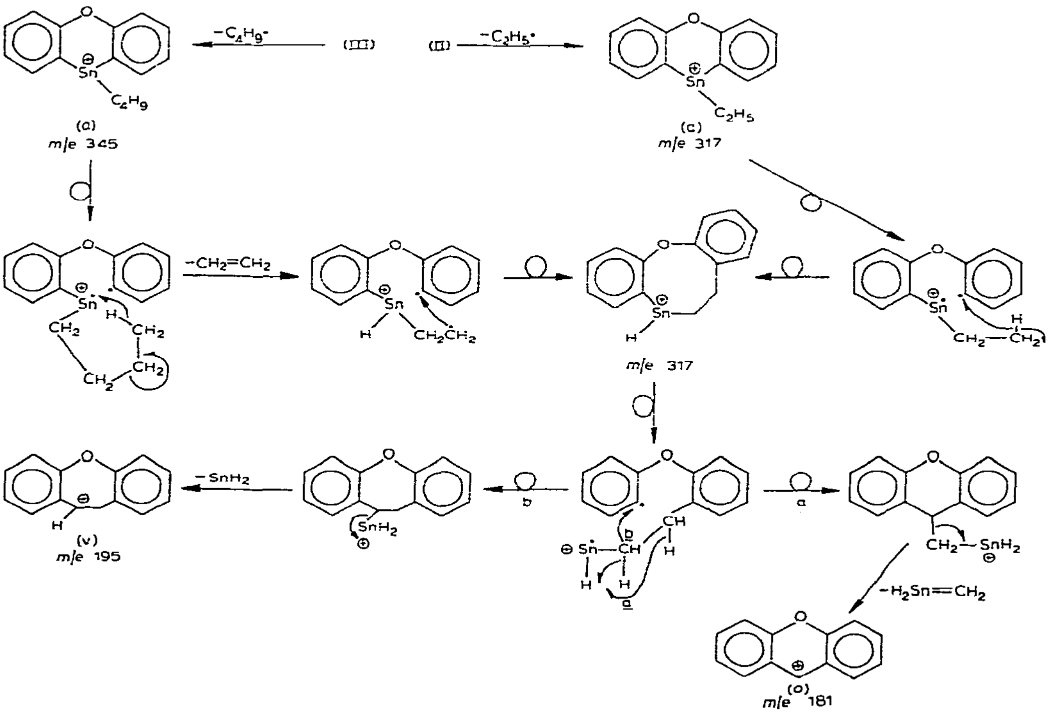
SCHEME 8



Another metal-free ion present in the spectra of compounds (II) and (III) and to a larger extent in compounds (VI) and (VII) is ion (s), *m/e* 169. This ion is derived from ion (e), *m/e* 289 by the loss of tin, and rearrangement of a hydrogen. Subsequent decomposition of ion (s) by elimination of CO yields the highly stable benzotropylium ion (t), *m/e* 141. The latter path is analogous to the mechanism discussed by Beynon[16] for the formation of ion *m/e* 141 from diphenyl ether. It should be noted that in compound (VI) ions *m/e* 168 and 169 are accompanied by the formation of *m/e* 170. The latter, formally diphenyl ether, must be formed by the rearrangement of one hydrogen from the ethyl ligands to the phenyl ring. The metastable-confirmed ejection of SnO from ion (e), *m/e* 289, leads to ion *m/e* 153, which subsequently loses a hydrogen radical to form ion (u), *m/e* 152.

There are some other oxygen-containing but metal-free even-electron ions in the spectra of compounds (II) and (III), the formation of which involves more complex skeletal rearrangement processes. Such ions are, for example, *m/e* 195 (v) and *m/e* 181 (o), formally $(M-RSnH_2)^+$ and $(M-RCH_2SnH_2)^+$, respectively. A reasonable mechanism accounting for these ions is depicted in Scheme 9: double hydrogen rearrangement from carbon to tin in ion $(M-R)^+$ (*m/e* 317) for compound (II), and the loss of ethylene from $(M-R)^+$ (*m/e* 345) for compound (III) followed by ring expansion and loss of SnH_2 or $H_2Sn{=}CH_2$ leads to ions *m/e* 195 and 181, respectively.

SCHEME 9



EXPERIMENTAL

The synthesis of the organotin compounds has been described previously[17].

The conventional ("low resolution") mass spectra were recorded on a Hitachi RMU-6D instrument at 70 eV and 12 eV and 50 μA, using the direct insertion method. The high resolution data, in the form of elemental map, were obtained on a CEC 21-110B doubly focusing mass spectrometer in conjunction with an IBM 1801 computer system.

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