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Tandem mass spectral studies of the fragmentation pathways of organotin compounds of general formula R_3SnR'

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Positive ion-electron impact (EI) mass spectra of organotin compounds of the type R_3SnR', where R = Ph, n−Bu, n−Pe and R′ = allyl, vinyl, H and Ph, have been recorded. The spectra were also examined by tandem mass spectrometry (MS-MS) in order to establish fragmentation reaction mechanisms for compounds bearing mixed substituents. Fragmentation patterns of six organotin compounds, based on precursor-product ion relationships are proposed. Significant differences were found in the reaction pathways of organotin compounds with different substituents. This technique has potential to predict the effect of substitution on the mass spectra of organotin compounds. Copyright © 2000 John Wiley & Sons, Ltd.

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1 INTRODUCTION

Conventional positive-ion electron impact (EI) mass spectra of organotin compounds of general formula R_3SnR' have been reported elsewhere.[1–5] These studies show some common features, namely the absence of any significant molecular ion and the high stability of R_3Sn^+ (for R = Me, Et, n-Pr, Ph) and /or RSn^+ (for R = n-Bu). Similar results were reported for a series of benzyltin derivatives, where the ease of cleavage of the Sn–R bond varies with the substituents, $PhCH_2$ = t-Bu > i-Pr > Et > Me.[6]

This current study extends the results of Chambers *et al.*[7] who proposed fragmentation pathways for the mass spectra of organotin compounds based mainly on metastable ion data. It was suggested that the decomposition modes of organotin compounds are greatly influenced by the odd or even bonding-electron character of an ion in its dissociation reactions.[8] Thus the even-electron ions, SnR_3^+ and SnR^+, are the most abundant, whilst parent ions decompose mainly by elimination of odd-electron neutral fragments. However, these studies were limited to producing fragmentation pathways either based on observed metastable ions or for which there was other substantiating evidence, but this approach resulted in some gaps in knowledge relating to dissociation of organotin compounds in the mass spectrometer. The advent of tandem mass spectrometry as an established analytical technique has enabled the speciation of organotin compounds through clear reaction pathways and dissociation modes.[9] In this method a precursor ion from an organometallic compound is selected using the first mass spectrometer; this ion is then collisionally dissociated in the reaction region and the resultant fragment ions are monitored by scanning with the second mass spectrometer. The nature and extent of fragmentation in the reaction region are influenced by the nature and pressure of the collision gas utilized and also by the kinetic energy of the selected ions. It is imperative to ensure similar analytical conditions in order to obtain reproducible results. The introduction of a heteroatom, especially a halogen, to produce compounds of general formula R_nSnX_{4-n}, has a dramatic effect on the corresponding positive-ion mass spectrum.[3,10] The effect of this substitution can be best illustrated by comparing the conventional EI spectra of Ph_3SnCl and Me_3SnCl.[11] The mass spectrum of Me_3SnCl shows the base peak at *m/z* 165 (Me_3Sn^+), whereas the most abundant ion of Ph_3SnCl is at *m/z* 154, corresponding to Ph_2^+ (i.e. biphenyl). A possible explanation for this is the stability of the Me_3Sn^+ ion, which could be due to the inductive effect of the methyl groups to the electron-deficient Sn^+ atom. In the case of Ph_3SnCl, two phenyl groups have undergone either

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Table 1 The organotin compounds used in this investigation[a]

	R		
R′	Phenyl	Butyl	Pentyl
Allyl	✓	✓	✓
Phenyl	✓		
Vinyl		✓	
Butyl		✓	
Hydride	✓		
Propyl		✓	

[a] All compounds were supplied by Aldrich Chemicals with the exception of Ph_3SnH, which was supplied by Lancaster Chemicals, All compounds were stated to be >93% pure. Compounds were used as received.

intramolecular rearrangement or radical reaction to form a very stable neutral species. A series of similar studies can be carried out by changing the nature of one of the substituent groups; for example, in compounds of the type R_3SnR', R′ can be alkyl, aryl, vinyl or allyl.

Positive-ion mass spectra and the fragmentation pathways of selected organotin compounds with mixed alkyl and/or aryl substituents were investigated to determine whether:

(1) the relative size of different substituents has any effect on resulting spectra;
(2) the nature of substituents (aromatic, aliphatic unsaturated) significantly changes the fragmentation/reaction pathways.

2 EXPERIMENTAL

Authentic samples of the organotin compounds listed in Table 1 were introduced into the mass spectrometer via the direct insertion probe. Mass spectra were first recorded under conventional EI conditions and subsequently in the precursor–product ion scan mode (MS–MS).

3 RESULTS

Each fragment ion occurs as a group of peaks (isotopic pattern) as a result of the six major tin isotopes. For simplicity the mass spectral fragmentation data are presented, in Table 2, in terms of the masses determined solely from the isotope ^{120}Sn. This approach allows the fragmentation data to be presented as a function of relative abundance, without duplication for the same fragment but with a different tin isotope.

Chambers *et al.*[7] and Gielen and Jurkschat[11] reported the elimination of a hydrocarbon radical from the molecular ion to produce R_3Sn^+ ions of high abundance. In this work this elimination was observed for the Ph_3SnR compounds whereas the alkyl analogues produced the RSn^+ ion at 100% relative abundance (RA), closely followed by R_2SnH^+, $RR'SnH^+$ and $RSnH_2{}^+$ with RA values ranging from 100 to 47%. For the series of compounds RSnR′ (R = butyl or pentyl) the nature of the dihydride is affected by R′. When R′ = phenyl or vinyl, the dihydride is $R'SnH_2^+$,whereas for the other species studied the results were those anticipated (viz. $RSnH_2^+$)on the basis of data from Chambers *et al.*,[7] who cited a relationship between the abundance of hydride ion formation and the number of tin–alkyl bonds present. In this investigation the relative abundance for all the $RSnH_2^+$compounds was in the range 80–100%.

The elimination of alkene groups has been observed in more cases than was expected from published results. Multiple alkene losses, for

Standard EI spectra	
Instrument:	VG Trio 3
Mass spectrometer:	Q1 only operating
Scan rate:	*m/z* 35–500 in 1 s
Resolution:	>1000
MS–MS spectra	
Instrument:	VG Trio 3
Q1	Set at *m/z* values selected from results of standard EI spectra
Q2 collision gas:	Argon at 3.2 mT
Q3 scanning	*m/z* 20–500 in 1 s
Resolution	>1000
Collision energy	6 eV

Table 2 EI mass spectral data for selected R_3SnR' compounds: mono-isotopic data from ^{120}Sn species

Pe_3SnPh	*m/z*	197	199	269	43	339	57	120	51
	RA (%)	100	87	71	70	47	11	8	3
Bu_3Sn(vinyl)	*m/z*	147	149	261	205	121	41	57	177
	RA (%)	100	90	76	66	54	38	14	8
Bu_3Sn(allyl)	*m/z*	177	121	119	120	291	41	235	57
	RA (%)	100	93	74	47	37	34	23	10
Ph_3SnH	*m/z*	351	51	197	77	120	78	50	154
	RA (%)	100	39	29	24	18	16	12	8
Ph_3Sn(allyl)	*m/z*	351	197	120	51	41	77	152	272
	RA (%)	100	64	29	26	23	14	7	5
Ph_4Sn	*m/z*	351	197	51	154	152	153	272	274
	RA (%)	100	33	32	26	15	14	12	11
Bu_4Sn	*m/z*	177	179	291	121	235	41	120	57
	RA (%)	100	98	71	63	62	43	30	27
Bu_3SnPr	*m/z*	179	177	221	121	235	277	165	291
	RA (%)	100	100	73	63	40	35	33	15

example from Pe_3SnPh and Bu_3SnR, have been identified and are cited in the appropriate fragmentation schemes. Some losses proposed by Chambers *et al.*[7] have now been confirmed.

3.1 Ph_3SnR'

The positive-ion EI mass spectra from Ph_3SnR' ($R' = H$, allyl, phenyl) all showed that the major fragmentation process occurred via cleavage of the R' group, giving rise to the stable ion Ph_3Sn^+. The main fragments formed are listed in Table 3. In all cases virtually no parent ion was detected. It was apparent that the three compounds produced very similar spectra as far as the major ions were concerned. However, one noticeable difference was the much lower relative abundance of *m/z* 154 (biphenyl) in the mass spectrum of the allyl derivative.

Table 3 EI mass spectral data[a] for selected Ph_3SnR' compounds

	R'		
Ion	H	Allyl	Pl
$[Ph_3SnR']^{+\cdot}$	—	√ (0.5)	√ (2)
$[Ph_3Sn]^+$	√ (100)	√ (100)	√ (100)[b]
$[Ph_2SnR']^+$	√ (8)	√ (2)	√ (100)[b]
$[PhSnR]^{+\cdot}$	—	√ (1)	√ (9)
$[Ph_2Sn]^{+\cdot}$	√ (7)	√ (3)	√ (9)
$[PhSn]^+$	√ (30)	√ (66)	√ (48)
$[Ph_2]^{+\cdot}$	√ (10)	√ (3)	√ (28)
$[Sn]^{+\cdot}$	√ (19)	√ (31)	√ (43)

[a] Values in parentheses are the relative abundances based on the ^{120}Sn ions.

[b] For Ph_4Sn, $Ph_3Sn^+ = Ph_2SnR'$ and $PhSnR = Ph_2Sn$.

The mass spectral data based on the tandem experiments showed that all four compounds investigated, after the initial loss of R', followed a similar reaction pathway. This pathway is summarized in Fig. 1. One feature which is noticeable in such a reaction pathway is the tendency of the fragment ion Ph_3Sn to undergo some rearrangement reaction and the subsequent loss of neutral species, namely benzene to form $PhSnC_6H_4^+$ (*m/z* 273), and Ph_2 (biphenyl, *m/z* 154) to form $PhSn^+$

This reaction pathway was confirmed by obtaining tandem mass spectral data based on the second most abundant tin isotope, ^{118}Sn. The difference of two mass units between ^{120}Sn and ^{118}Sn in the primary analyte is important where subsequent fragment losses may be either a neutral benzene molecule (mass 78) or a phenyl group (mass 77)

3.2 Bu_3SnR'

The mass spectra from Bu_3Sn R' (R' = allyl, vinyl, propyl, butyl) showed that the major fragmentation pattern processes occurred via formation of $BuSn^+$ and $BuSnH_2^+$ in Bu_4Sn, Bu_3Sn(allyl) and Bu_3SnPr but in the case of Bu_3Sn(vinyl) the major fragment ions were Sn(vinyl)$^+$ and SnH_2(vinyl)$^+$. The major fragments formed are listed in Table 4. In all cases very small or no parent ions were detected. One noticeable difference in this case was in the relative low abundance of the fragment $BuSnHR'$, when R' = allyl (1%) and when R' = butyl (62%), indicat-

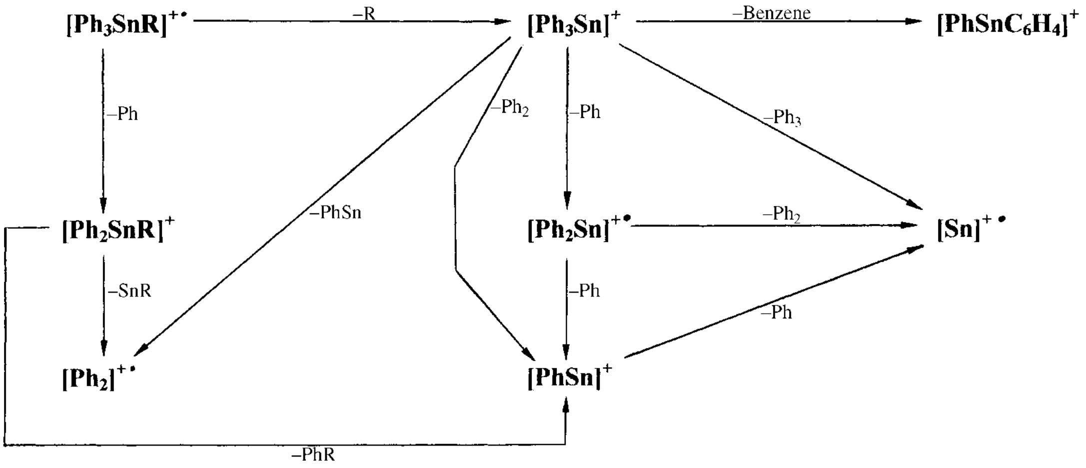

Figure 1 Fragmentation/reaction pathway for Ph_3SnR'.

ing the relative instability of the allyl-containing fragment.

The mass spectral data based on the tandem experiments showed that three of the compounds investigated (R′ = allyl, propyl, butyl), after initial loss of the R′ group, underwent consecutive loss of butene (*m/z* 56). In the case of the vinyl derivative, however, the formation of $Bu_2SnVinyl^+$ followed by consecutive loss of butene seems to be the preferred pathway. The reaction pathway for butyl, propyl and allyl derivatives is shown in Fig. 2, and that for the vinyl derivative in Fig. 3.

The reaction pathways for the four compounds were confirmed by obtaining tandem mass spectral data based on the second most abundant tin isotope, ^{118}Sn.

Table 4 EI mass spectra[a] for selected Bu_3SnR' compounds

	R′			
Ion	Vinyl	Allyl	Propyl	Butyl
$[Bu_3SnR']^{+\cdot}$	—	—	—	√ (1)
$[Bu_3Sn]^+$	√ (21)	√ (36)	√ (18)	√ (72)
$[Bu_2SnR']^+$	√ (79)	√ (9)	√ (35)	√ (72)
$[BuSnHR']^+$	√ (68)	√ (1)	√ (32)	√ (62)
$[Bu_2SnH]^+$	√ (2)	√ (24)	√ (40)	√ (62)
$[BuSnH_2]^+$	√ (6)	√ (80)	√ (100)	√ (98)
$[BuSn]^+$	√ (7)	√ (100)	√ (93)	√ (100)
$[SnH]^+$	√ (54)	√ (93)	√ (63)	√ (64)
$[Bu]^+$	√ (14)	√ (12)	√ (8)	√ (26)

[a] Values in parentheses are the relative abundances based on the ^{120}Sn ions.

[b] For R′ = butyl, $BuSn^+ = Bu_2SnR'^+$ and $Bu_2SnH^+ = BuSnHR'^+$.

3.3 Pe_3SnPh

The mass spectrum from phenyltripentyltin (Pe_3SnPh) showed that the major fragmentation processes occur via formation of $SnPh^+$ and $SnPhH_2^+$ (Table 2) and not via the formation of $PeSn^+$ and $PeSnH_2^+$. As in all the other organotin compounds investigated in this study, the molecular ion for this compound was not detected.

The mass spectral data based on the tandem experiment showed that after initial loss of the phenyl group Pe_3Sn^+ underwent consecutive loss of the neutral molecule, pentene (*m/z* 70). The reaction pathway for tripentylphenyltin is shown in Fig. 4.

4 DISCUSSION

The positive-ion EI mass spectra of the organotin compounds, $PhSnR'$ (R′ = H, allyl, phenyl) were dominated by formation of the fragment ion Ph_3Sn^+, which maintained the tin(IV) oxidation state. In contrast, in the EI mass spectrum of Ph_3SnCl the most abundant ion was at *m/z* 154 (biphenyl). This basic difference in the behaviour of these tin compounds in the mass spectrometer under similar experimental conditions is probably

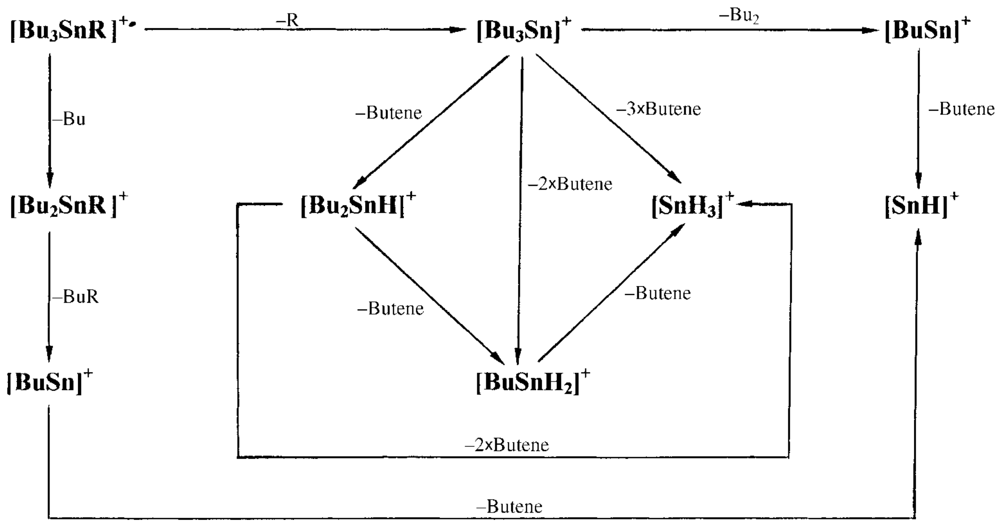

Figure 2 Fragmentation/reaction pathway for Bu_3SnR' (R' = allyl, butyl, propyl).

due to the relative electronegativites of the bonds Sn–Cl and Sn–C (in R′).

The positive-ion EI mass spectra of organotin compounds of general formula Bu_3SnR' (R' = vinyl, allyl, propyl, butyl) were not dominated by one particular fragment ion but were characterized by the presence of at least four different major fragment ions. This behaviour was not surprising, since the Sn–C bonds are of a similar nature, unlike Ph_3SnR', where a stabilizing effect is exerted by the benzene ring. On close examination, however, some discernible differences could be seen in the EI mass spectrum of Bu_3Sn (vinyl). For this compound the major fragments were Sn $(vinyl)^+$ and $SnH_2(vinyl)^+$, whereas for Bu_3Sn (allyl), Bu_3SnPr and Bu_4Sn the major fragments occurred at *m/z* 177 and 179 corresponding to $BuSn^+$ and $BuSnH_2{}^+$ respectively. A greater influence may be exerted by the double bond in the vinyl group, which is in close proximity to the Sn–C bond.

The possible effect of the presence of a double bond in an α position on stabilization of the resultant fragment ion was investigated by recording the mass spectrum of Pe_3SnPh. The fragmentation pathway of this compound is remarkably similar to that of Bu_3Sn (vinyl). In this case the unsaturation in the ring seems equivalent to the double bond in the vinyl group.

It is planned to investigate the relative effects of aryl and/or alkyl susbtituents on the mass spectra of

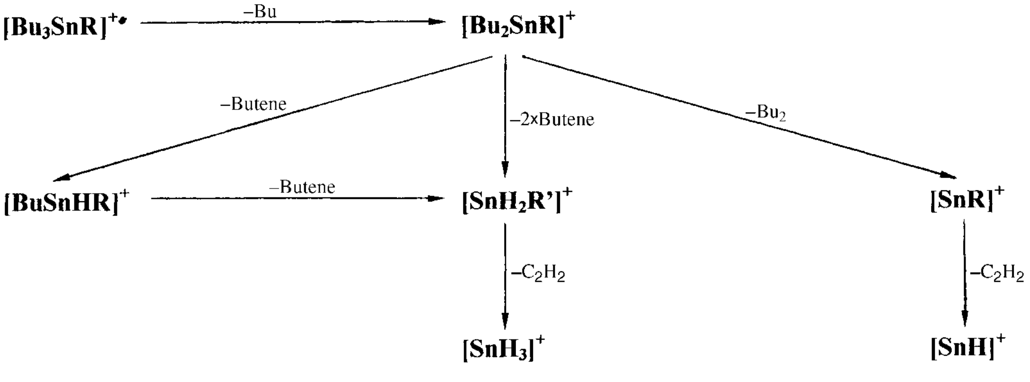

Figure 3 Fragmentation/reaction pathway for Bu_3SnR' (R' = vinyl).

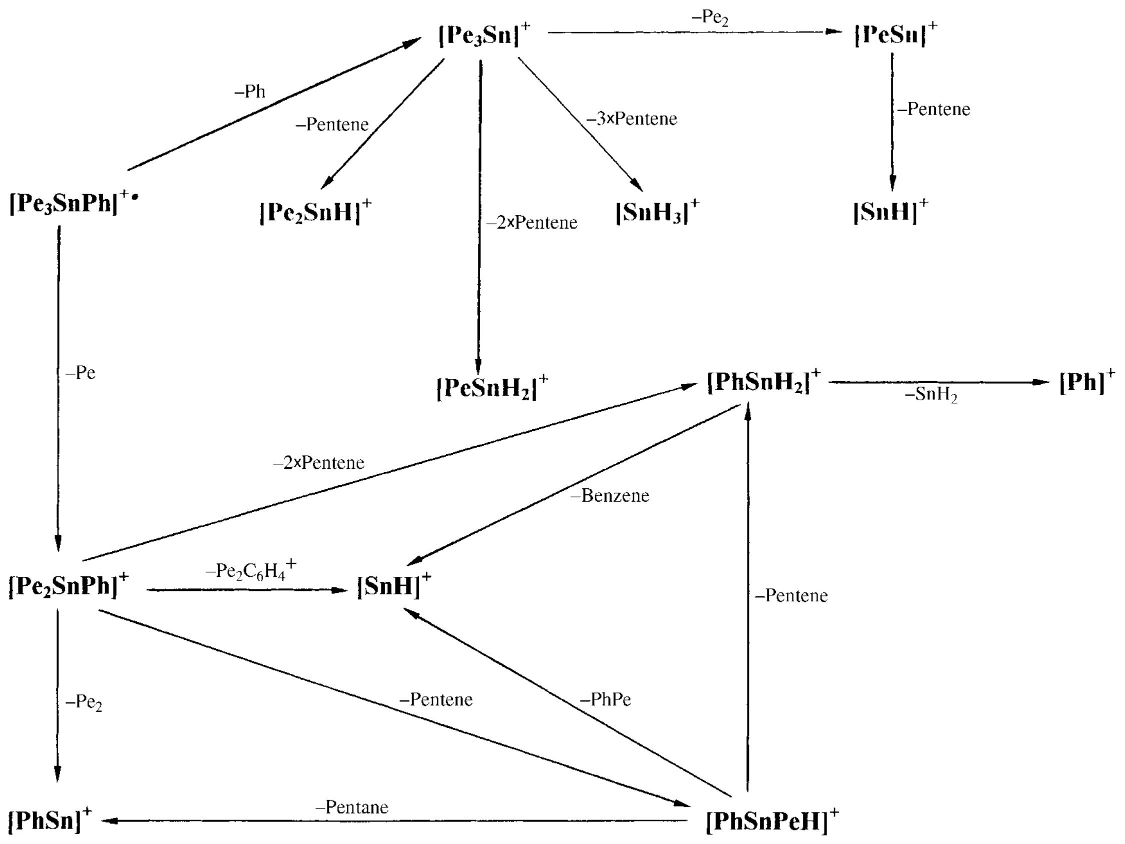

Figure 4 Fragmentation/reaction pathway for Pe_3SnPh.

compounds such as Ph_3SnBu, Ph_2SnBu_2 and $PhSnBu_3$ in order to study the roles of aromatic systems on mass spectral decomposition pathways.

REFERENCES

1. Gielen M, Mayence G. *J. Organomet. Chem.* 1968; **12**: 363.
2. Weben R, Visel F, Leusen K. *Anal. Chem.* 1980; **52**: 2299.
3. Lawson G, Ostah N. *Appl. Organomet. Chem.* 1993; **7**: 517.
4. Gielen M, Nasielski J. *Bull. Soc. Chim. Belg.* 1968; **77**: 5.
5. Gielen M, De Poorter B, Sciot MT, Topart J. *Bull. Soc. Chim. Belg.* 1968; **77**: 5.
6. Gielen M, Barthels MR, De Clercq M, Nasielski J. *Bull. Soc. Chim. Belg.* 1971; **80**: 89.
7. Chambers DB, Glockling F, Weston M. *J. Chem. Soc. (A)* 1967; 1759.
8. McLafferty FW. *Mass Spectrometry of Organic Ions.* Academic Press: London, 1963.
9. Lawson G, Ostah N. *N. Appl. Organomet. Chem.* 1993; **7**: 183.
10. Pierce J. *J. Am. Chem. Soc.* 1981; **103**: 2583.
11. Gielen M, Mayence G. *J. Organomet. Chem.* 1972; **46**: 281.
12. Gielen M, Jurkschat K. *Org. Mass Spectrom.* 1983; **18**: 224.