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Fragmentation and Rearrangement Processes in the Mass Spectra of Perhalogeno-aromatic Compounds. Part V.¹ Pentafluorophenyl Derivatives of Tin and Related Compounds

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The mass spectra of the compounds $(C_6F_5)_{4-n}SnR_n$ $(n = 1-3; R = Ph, Bu, and Me), [Me_3Sn]_2C_6X_4$ $(X = F and C_6F_5)_{4-n}SnR_n$ (R = 1-3; R = Ph, Bu, and Me)CI) and some related compounds have been studied. The basic features of the spectra are correlated with the nature and number of the hydrocarbon groups, and in the second type of compound, with the nature of the halogen and the ring position of the trimethyltin groups. In general, the mass spectra of compounds of the first type vary markedly with differing hydrocarbons, while increasing the hydrocarbon content shows no unusual features in the spectra. In compounds of the second type, the differences in the spectra of the fluorinated and chlorinated compounds are less obvious than the differences observed in the spectra of the 1,2- and 1,4-isomers. Halogen transfers to tin are common throughout leading to both neutral and charged tin-halogen species.

MASS spectrometric studies on pentafluorophenyl derivatives of Group IV 2,3 and Group V 1,3,4 elements are reported in earlier papers. Alkyl and aryl derivatives of tin have been studied using mass spectrometry by Chambers et al.,⁵ while Bowie and Nussey,⁶ have used deuterium labelling to study phenyl derivatives of Group IV. The modes of fragmentation of mixed pentafluorophenylalkyl/aryl derivatives of tin are reported here and discussed in relation to the aforementioned compounds. In addition, the effects of replacing fluorine by chlorine in $[Me_3Sn]_2C_6X_4$ derivatives are reported.

TABLE 1

Partial mass spectra of $(C_6F_5)_3$ SnR (abundance as % of total positive ion current)

Ion+	$R = C_6 H_5$	$R = C_4 H_9$	$R = CH_3$	$\begin{array}{c} R = \\ C_6 F_5 \end{array} *$		
(A) Tin-containing ions						
$(C_{6}F_{5})_{3}SnR \cdot (C_{6}F_{5})_{3}Sn \\ (C_{6}F_{5})_{2}SnR \cdot C_{12}F_{9}SnR \cdot (C_{6}F_{5})_{2}SnF \\ (C_{6}F_{5})_{2}SnF \\ (C_{6}F_{5})_{2}Sn \cdot (C_{6}F_{5})_{5}SnFR$	$ \begin{array}{r} 1 \cdot 8 \\ 2 \cdot 1 \\ 5 \cdot 1 \\ 0 \cdot 5 \\ 3 \cdot 6 \\ 3 \cdot 2 \end{array} $	8·4 1·6 3·9 0·5	6.5 17.2 11.3 3.3 8.9	$ \begin{array}{c} 7 \cdot 2 \\ 20 \cdot 6 \\ 10 \cdot 5 \\ 0 \cdot 2 \\ (10 \cdot 5) \end{array} $		
$(C_6F_5)SnF_2$ $(C_6F_5)Sn$ SnR SnF SnF Sn•	$ \begin{array}{c} 1 \cdot 3 \\ 5 \cdot 3 \\ 0 \cdot 8 \\ 20 \cdot 7 \\ 5 \cdot 5 \\ \hline 10 \ 0 \end{array} $	$ \begin{array}{r} 1 \cdot 4 \\ 1 \cdot 7 \\ 36 \cdot 5 \\ 2 \cdot 1 \\ \hline 56 \cdot 1 \end{array} $	$ \begin{array}{c} 2 \cdot 4 \\ 26 \cdot 6 \\ \hline 76 \cdot 9 \end{array} $	$ \begin{array}{r} (100) \\ 2 \cdot 8 \\ 1 \cdot 3 \\ 34 \cdot 9 \\ \hline 8 \cdot 0 \\ \end{array} $		
(D) Cignificant ion	49.9	90.1	76-2	88.0		
(b) $_{12}^{Signincant ion}$ $C_{18}F_{10}^{C}$ $C_{12}F_{8}^{C}$ $C_{12}F_{5}H_{5}^{C}$ $C_{12}F_{4}H_{4}^{C}$	0.2 0.1 1.3 4.9 0.9	0·3 0·1 2·1	1.2	0.8 0.1 0.5		
C ₆ F ₅ R	1·1 13·7 *	1.5 5.6 Ref. 2.	7·1 3·6	$2 \cdot 0$		

Some other aryl derivatives including partially fluorinated aromatic rings or fluorinated alkyl ring

substituents were studied and are discussed in terms of fluorine migration to tin atoms. While most spectra in each group of compounds have many characteristics in

TABLE 2

Partial mass spectra of $(C_6F_5)_2SnR_2$ (abundance as % of total positive ion current)

	R =	R =	$\mathbf{R} =$	$\mathbf{R} =$
Ion+	C_6H_5	C_4H_9	CH_3	(CH=CH ₂)
(A) Tin-containing	ions			
(C.F.) SnR.	0.8	3.6	8.4	
$(C_{e}F_{e})_{e}SnR$	4.8	26.4	38.6	$8 \cdot 2$
(C F), SnH		10.8		
$(C_{6}F_{5})_{2}Sn$				0.4
C ₁₂ F ₉ SnR∙	0.3		0.4	
$C_{6}F_{5}SnR_{2}$	$2 \cdot 3$	$1 \cdot 2$	$2 \cdot 5$	$5 \cdot 2$
C ₆ F ₅ SnRF	$4 \cdot 2$		15.1	4.8
C ₆ F ₅ SnHR		0.4		
C ₆ F ₅ SnR•	0.4			0.3
C_6F_5SnHF		0.2		
C ₆ F ₅ SnF·			0.9	0.3
C ₆ F ₅ Sn	$5 \cdot 5$	$4 \cdot 0$	3.5	8.1
$FSnR_2$	$1 \cdot 9$		$1 \cdot 2$	3.0
F_2SnR	_		0.9	0.5
SnR	$2 \cdot 7$		0.8	
FSn	15.5	7.4	21.5	20.9
Sn•	5.9	1.4	0.8	13.8
Total	44.3	$55 \cdot 4$	94.6	65.5
(B) Significant ion	s without t	in		
C ₁₂ F ₁₀ ·	0.1		0.2	0.3
$C_{12}F_8$			0.4	
$C_{12}F_5H_5$	0.3			
$C_{12}F_4H_4$	0.6			
C ₁₂ H ₁₀ ·	9.0			
C_6F_5	0.2	0.2	0.2	3.1
R	19.6	12.9	?	?

in common, some rather unusual transitions and fragmentations do occur.

(I) $(C_{\theta}H_{5})_{4-n}SnR_{n}$

Ion abundances are shown in Tables 1-3 and modes of fragmentation in Schemes 1-3; these are discussed below.

- ⁴ A. T. Rake and J. M. Miller, J. Chem. Soc. (A), 1970, 1881.
- ⁵ D. B. Chambers, F. Glockling, and M. Weston, J. Chem. Soc. (A), 1967, 1759. ⁶ J. H. Bowie and B. Nussey, Org. Mass Spec., 1970, **3**, 933.

¹ Part IV, A. T. Rake and J. M. Miller, Org. Mass Spec., 1970, 237.
 ² J. M. Miller, Canad. J. Chem., 1969, 47, 1613.
 ³ J. M. Miller, J. Chem. Soc. (A), 1967, 828.



 $\label{eq:Scheme 1} Scheme 1 \quad \mbox{Partial fragmentation of $(C_6F_5)_3SnR$} $$* Metastable observed in some $(C_6F_5)_nSnR_{4-n}$}$



SCHEME 2 Partial fragmentation of (C6F5)2SnR2

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SCHEME 3 Partial fragmentation of C6F5SnR3

TABLE 3

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Partial mass spectra of $C_6F_5SnR_3$ (abundance as % of total positive ion current)

C II

	1011	$\mathbf{r} = \mathbf{U}_6\mathbf{n}_5$	$\mathbf{r} = \mathbf{C}_4$	$H_9 K = CH_2$	ł
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	(A) Tin-containin	ng ions			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C _e F ₅ SnR ₃ •	0.3		3.3	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$C_{6}F_{5}SnR_{2}$	$6 \cdot 5$	9.5	27.3	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C ₆ F ₅ SnR•	0.7	6.0		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C ₆ F ₅ Sn	0.1	9.2	2.7	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	SnR_{a}	$8 \cdot 1$		4.4	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	FSnŘ,	$3 \cdot 5$		$6 \cdot 1$	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	SnR,•	$2 \cdot 8$	0.4	$1\cdot 3$	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	F ₂ SnR		1.0		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	SnR	$23 \cdot 1$	1.9	4.4	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	SnF	5.5	4.6	7.8	
Total $\overline{62 \cdot 0}$ $\overline{34 \cdot 6}$ $\overline{93 \cdot 3} *$ (B) Significant ions without tin $C_{12}H_{10} \cdot 19 \cdot 3$ R $10 \cdot 4$ $6 \cdot 9$ CU $5 \cdot 7$	Sn•	11.4	2.0	$2 \cdot 0$	
(B) Significant ions without tin $C_{12}H_{10}$ • 19.3 R 10.4 6.9 C U	Total	62.0	34.6	93.3 *	
$\begin{array}{ccc} C_{12}H_{10} \bullet & 19 \cdot 3 \\ R & 10 \cdot 4 & 6 \cdot 9 \\ C & U & 5 \cdot 7 \end{array}$	(B) Significant ic	ons without ti	n		
R 10·4 6·9	C. H.o.	19.3			
	R R	10.4	6.9		
C.H. 2.1	C.H.	5.7			
$C_{3}H_{5}$ 12.5	C,H,		12.5		
$C_{2}H_{5}$ 17.9	$\tilde{C_2H_5}$		17.9		
* Some ions not listed in this table. Please see text.	* Some ions	not listed in	this table.	Please see text.	

Bond Cleavage $\geq Sn-R^+ \longrightarrow \geq Sn^+ + R^+$.—Metastable transitions are observed in four cases for this type of elimination, although it is a transition common to all

$$\begin{array}{ll} (C_{6}F_{5})_{3}SnCH_{3}^{+*}\stackrel{*}{\longrightarrow} (C_{6}F_{5})_{3}Sn^{+}+CH_{3}^{*} & m^{*}=606 \\ (C_{6}F_{5})_{2}Sn(CH_{3})_{2}^{+*}\stackrel{*}{\longrightarrow} (C_{6}F_{5})_{3}SnCH_{3}^{+}+CH_{3}^{*} & m^{*}=454 \\ C_{6}F_{5})_{2}Sn(C_{4}H_{9})_{2}^{+*}\stackrel{*}{\longrightarrow} (C_{6}F_{5})_{2}SnC_{4}H_{9}^{+}+C_{4}H_{9}^{*} & m^{*}=460 \\ C_{6}F_{5}Sn(CH_{3})_{3}^{+*}\stackrel{*}{\longrightarrow} C_{6}F_{5}Sn(CH_{3})_{2}^{+}+CH_{3}^{*} & m^{*}=303 \end{array}$$

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compounds studied in this series as is evidenced by the abundances of the R_3Sn^+ ions ($R = C_6F_5$, C_6H_5 , C_4H_9 , C_2H_3 , and CH_3). Only one other elimination from the parent ion is supported by metastable evidence and the

$$C_{6}F_{5}Sn(CH_{3})_{3}^{+} \rightarrow C_{5}FSn(CH_{3})_{3}^{+} + CF_{4}$$
 $m^{*} = 179$

fragmentation patterns do not suggest any other eliminations from the molecular ions.

Elimination of C_6F_4 .—The neutral species, C_6F_4 , is often eliminated from three-co-ordinate tin ions. This elimination reaction necessitates transfer of a fluorine atom from the ring to the tin atom and must be regarded as the major source of $>Sn-F^+$ ions. Several metastable peaks support this transition. Although $>SnF^+$ ions are

So com	urce pound	Tra	ansition	Meta stab	a- le
(C ₆ F ₅) ₃ S	inC ₈ H₅	$(C_6F_5)_2$ SnF+ $\stackrel{*}{\longrightarrow}$	$-C_6F_5SnF_2^++C_6F_4$	m* —	223
(C ₆ F ₅) ₃ S	inC₄H ₉	(C ₆ F₅)₃Sn+ —	\leftarrow (C ₆ F ₅) ₂ SnF ⁺ + C ₆ F ₄	m * ==	360
(C ₆ F ₅) ₂ S	n(C ₆ H₅)₂	(C ₆ F ₅)₂SnC ₆ H ₅ + →	$\sim C_6 F_5 SnFC_6 H_5^+ + C_6 F_4$	m* =	276
(C ₆ F ₅) ₂ S	in(CH ₃) ₂	(C ₆ F ₅)₂SnCH ₃ + →	$\sim C_6F_5SnFCH_3 + C_6F_4$	m* =	220
$(C_{6}F_{5})_{2}S$	$in(C_2H_3)_2$	$(C_{6}F_{5})_{2}SnC_{2}H_{3}^{+}$	$-C_6F_5SnFC_2H_3+C_6F_4$	m* =	22 9

present for $C_6F_5SnR_3$ compounds, there is no metastable evidence for the elimination of C_6F_4 . However, this route is certainly the most feasible.

Bond Cleavage >Sn-R⁺ \longrightarrow >Sn⁺ + R[•].—While this type of elimination generally appears to be relatively uncommon, it is observed for three ions in this series of compounds. While the M₁ ions, having an even number

Source	Transition	stable
$(C_6F_5)_3SnC_4H_9$	$(C_6F_5)_2SnC_4H_9^+ \xrightarrow{*} (C_6F_5)_2Sn^{+} + C_4H_9^{+}$	m * = 4 05
$(C_6F_5)_2Sn(CH_3)_2$	$C_6F_5SnFCH_3^+ \xrightarrow{\bullet} C_6F_5SnF^{+} + CH_3^{\bullet}$	m* = 291
$C_6F_5Sn(C_4H_9)_3$	$C_6F_5Sn(C_4H_9)_2^+ \xrightarrow{*} C_6F_5SnC_4H_9^{+} + C_4H_9$	m* == 295
of electrons, ions, which i	are relatively abundant, the dau have an odd electron, are quite we n of $C = SnC + \frac{1}{2} \cdot (6^{\circ}/2)$	ghter M ₂ eak, with

the exception of $C_6F_5SnC_4H_9^{-1}$ (6%). Other $>Sn^+-$ Reactions.—Another common feature of these compounds, although not observed for $(C_6F_5)_4M$ compounds,² is the elimination of F• from $(C_6F_5)_2SnR$ ions, supported by the following metastable transitions.

Source	Transition	Meta- stable
$(C_6F_5)_3SnC_6H_5$ $(C_6F_5)_2Sn(C_6H_5)_2$	$(C_6F_5)_2SnC_6H_5^+ \xrightarrow{*} C_{12}F_9SnC_6H_5^{+} + F$	m* = 493
$(C_{6}F_{5})_{2}Sn(CH_{3})_{2}$	$(C_6F_5)_2$ SnCH ₃ + $\xrightarrow{*}$ C ₁₂ F ₉ SnCH ₃ + + F·	m* = 432

Again, the abundances of the odd-electron daughter ions are very low.

A rather unusual feature is the elimination of an RF neutral species from three-co-ordinate $\rm Sn^+$ ions. This elimination is observed only for $(\rm C_6F_5)_2\rm SnR_2$ compounds, with the exception of the butyl derivative. However, this may be due to the relative weakness of the precursor ions, $\rm C_6F_5\rm SnFR^+$, for $(\rm C_6F_5)_3\rm SnR$ and $\rm C_6F_5\rm SnR_3$ comcompounds. The following is a list of metastable

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transitions. In contrast to previous eliminations from

Source	Transition	Metastable
$(C_6F_5)_2$ Sn $(C_6H_5)_2$	$C_6F_5SnFC_6H_5^+ \xrightarrow{*} C_6F_5Sn^+ + C_6H_5F$	m* = 215
$(C_6F_5)_2$ Sn $(CH_3)_2$	$C_6F_5SnFCH_3^+ \xrightarrow{\bullet} C_6F_5Sn^+ + CH_3F$	m* = 257
$(C_6F_5)_2Sn(C_2H_3)_2$	$C_8F_5SnFC_2H_3^+ \xrightarrow{\bullet} C_8F_5Sn^+ + C_2H_3F$	m * == 247

three-co-ordinate tin, the daughter ions and neutral species contain an even number of electrons. Correspondingly, the relative abundances of these daughter ions are reasonably high. Another metastable transition involving three-co-ordinate tin ions is the elimination of the neutral SnF_2 species. This transition is observed only for the $(C_6F_5)_3SnR$ compounds in this series, although it is also evident for $(C_6F_5)_4Sn$.

$$\begin{array}{c} (C_6F_5)_3 \text{SnC}_6H_5 \\ (C_6F_5)_3 \text{SnC}_4H_9 \end{array} \right\} \ (C_6F_5)_2 \text{SnF}^+ \stackrel{\bullet}{\longrightarrow} C_{13}F_9^+ + \text{SnF}_2 \quad m^* = 223 \end{array}$$

 $(C_6F_5)_2Sn(C_4H_9)_2$ is unusual in the $(C_6F_5)_2SnR_2$ series in the sense that no $C_6F_5SnFC_4H_9^+$ ion is observed. It also loses butene in the following manner:

$$(C_{6}F_{5})_{2}SnC_{4}H_{9}^{+} \xrightarrow{*} (C_{6}F_{5})_{2}SnH^{+} + C_{4}H_{8} \quad m^{*} = 405 \cdot I$$

this is the only compound in this series to undergo a reaction of this type leading to an Sn-H bond.

Elimination of RR ($R = C_6H_5$ or C_6H_4 , C_6F_5 or C_6F_4).--No metastable evidence for transitions forming $C_{18}F_{12}^{+\bullet}$, $C_{12}F_{10}^{+\bullet}$, $C_{12}F_{8}^{+\bullet}$, $C_{12}F_{4}H_{4}^{+\bullet}$, $C_{12}H_{8}^{+\bullet}$, or $C_{12}H_{10}^{+}$ was observed. However, in the appropriate spectra, all these ions are present to a greater or lesser extent. In the $(C_6F_5)_3SnR$ compounds as well as $(C_6F_5)_2SnR_2$, when $R = CH_3$ or C_4H_9 , we observe $C_{12}F_{10}^{+*}$ and $C_{12}F_8^{+*}$, $C_{18}F_{12}^{+*}$ and $C_{18}F_{10}^{+*}$ being present only for the former series. These ions are also reported for $(C_6F_5)_4$ Sn. As expected, the abundances of these ions decrease as the relative proportion of C_6F_5 in the molecules decreases. For $(C_6F_5)_3SnC_6H_5$, the ion $C_{12}F_5H_5^{+}$, a mixed biphenylene, is unusually abundant, whereas it decreases for $(C_6F_5)_2Sn(C_6H_5)_2$ and is not evident in $C_6F_5Sn(C_6H_5)_3$. The ion $C_{12}H_{10}^{+*}$ is of major abundance in the spectrum of $(C_6H_5)_3SnC_6F_5$. There is no evidence for fused rings containing unequal amounts of F and H, in agreement with previous observations⁶ that no scrambling of hydrogens occurs between rings. The elimination of $C_{12}H_{10}$ is reported to be a major process for $M(C_6H_5)_4$ compounds,⁵ and although not indicated in the fragmentation schemes, our compounds presumably lose $C_{12}H_{10}$, $C_{12}H_5F_5$, and $C_{12}F_{10}$ neutral species. There was no evidence for elimination reactions of the type

$$SnR_3^+ \rightarrow SnR^+ + R_2$$
; or $SnR_2^+ \rightarrow Sn^{++} + R_2$

for CH₃, C₄H₉, or C₂H₃, although in all cases, there was a fairly large abundance of $R^{+\bullet}$.

Bond Cleavage in Disubstituted Tin Ions.—The only metastable transition observed for nominally two-coordinate ions is,

$$C_6F_5SnC_4H_9^{+} \rightarrow C_5F_5Sn^+ + C_4H_9^{+} \qquad m^* = 239$$

which is found in the mass spectrum of $C_6F_5Sn(C_4H_9)_3$. Undoubtedly, several other losses of one or two fragments from two-co-ordinate tin occur; these are shown in the suggested fragmentation schemes.

 $(CH_3)_3SnC_6F_5$.—This compound exhibited an unusual spectrum relative to the others in this series. The metastably supported loss of CF_4 from the molecular ion appears to be responsible for two series of ions, $(CH_3)_nSnC_5F^+$ (n = 3, 3, 1, 0) and $(CH_3)_nSnH_2C_5F^+$ (n = 2, 1, 0). These ions comprise *ca.* 16% of the total positive ion current. These types of ions are unique to this compound and do not appear in any other compound reported here. We offer no explanation of this unusual feature.

(II)
$$(Me_3Sn)_2C_6X_4$$
 (1,2- and 1,4-Isomers, $X = F$ or Cl)

Ion abundance measurements (Table 4) for these four compounds show few differences between the chlorinated

TABLE 4

Partial mass spectra of $(Me_3Sn)_2C_6X_4$. Tin-containing ions (abundances as % of total positive ion current)

`	/•	*		,
	1,2-Is	somer	1,4-Is	omer
Ion+	X = Cl	$\mathbf{X} = \mathbf{F}$	$\mathbf{X} = \mathbf{Cl}$	X = F
C.H.Sn.C.X.				4.8
C.H.Sn.C.X.	14.3	11.1	21.3	42.5
C.H. Sn.C.X.			0.1	0.5
C.H. Sn.C.X.	0.3	0.8		
C.H.Sn.C.X.	1.0	1.1	1.5	$2 \cdot 1$
C.H.Sn.C.X.			$\overline{0.5}$	1.5
C.H.Sn.C.X.	0.4	1.2	•••	- •
H.Sn.C.X.	• -		0.2	1.3
H.Sn.C.X.	0.4	0.8	• -	- 0
Sn C X .	0.2	0.3	0.1	0.2
$\operatorname{Sn}^{\circ} \operatorname{C}^{\circ} \operatorname{X}^{\circ}$	0.6	1.0	1.4	< 0.1
H Sn C X +	0.3	10	0.5	6.2
H SnC X	00		00	0.6
H SnC X				0.4
3 11 9 5 10 6 13 13 19 10 10 10 11 10 10 10 11 10 10 11 10 11 10 11	4.1	4.2	6.0	0.5
TH SnC Y		Ŧ 0	0.0	0.4
SnC X	1.6	1.3	1.8	0.8
TH SnC X .	10	1.0	10	0.7
Γ H Sp(X	9.4	0.0	9.0	9.9
C U SpC Y	0.4	0.9	0.4	0.4
TU SaC Y	1.5	0.4	2.9	9.1
$S_{n} S_{n} S_{n$	1.3	0.4	1.1	0.4
$\Gamma U S_n C \mathbf{V}_{\bullet}$	0.0		1.1	0.3
C U SaC Y	0.5		0.8	0.9
Cu Sac Y	0.6	1.1	1.0	
$S_{n} S_{n} S_{n$	1.9	0.4	9.7	
$\Gamma U Sn$	91.1	90.6	0.6	10.6
$\sim_3 \Pi_9 \Im \Pi$	21.1	29.0	9.0	10.0
CH Sn.	1*± 9.4	4.0	1.0	1.9
	0.9	4.9	1.9	1.9
$CU S_{n} V$	0.9	1.0	1.2	
CU Cn	7.4	15.9	4.9	2.1
$S_n \mathbf{V}$	15.9	10.0	19.7	4.8
Sur Sn.	1.7	2.1	1.0	0.4
511-	1.1	2.2	1.0	0.4
Total	88.1	90.2	91 ·5	92.7

and fluorinated species. The most obvious difference is the greater abundance of the ions $C_2H_6SnX^+$, $CH_3SnX_2^+$, and SnX^+ for the chlorinated species. The chlorine atom, being larger, more polarizable, and more weakly bonded to carbon than is fluorine, may as a result transfer to tin more readily than fluorine. Furthermore, the abundance of ions of the type $(CH_3)_nSnC_6X_m$ (n = 3, 2, 1,or 0 and m = 2 or 1), may indicate that elimination of Published on 01 January 1971. Downloaded by University of Reading on 28/12/2017 05:43:00

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chlorine from the aromatic ring is easier than the equivalent process for fluorine. A greater tendency for chlorine (compared to fluorine) migration to tin has also been observed in the thermal decomposition of perhalogenoaryltin compounds. For example, $(CH_3)_3SnC_6Cl_5$ gave $(CH_3)_3SnCl$ in 87% yield when heated at 300° for 4 hr.,⁷ whereas even at 400° $(CH_3)_3SnF_6F_5$ undergoes disproportionation to give $(CH_3)_4Sn.^8$

Ion abundance measurements show greater differences on comparison of the 1,2-isomers with the 1,4-isomers. The loss of CH_3 from the parent ion occurs more readily in the 1,4-compounds, particularly the fluoride. The 1,2-isomers lose a stable CH_4 moiety as well as C_2H_6 , whereas the 1,4-isomers lose CH_3 radicals and C_2H_6 . These are verified by metastable ion evidence.

Source
 Transition

$$m^*$$

 1,2-Chloro,
 $(CH_3)_6Sn_2C_6X_4^+ \cdot \star (CH_3)_5Sn_2C_6X_4^+ + CH_3^+ \cdot 512$
 446

 1,2-Chloro
 $(CH_3)_5Sn_2C_6X_4^+ \star (CH_3)_5Sn_2C_6X_4^+ + CH_3^+ \cdot 512$
 446

 1,2-Chloro
 $(CH_3)_5Sn_2C_6X_4^+ \star (CH_3)_5Sn_2C_6X_4^+ + CH_4^- \cdot 469$
 469

 1,2-Chloro
 $(CH_3)_5Sn_2C_6X_4^+ \star (CH_3)_5Sn_2C_6X_4^+ + CH_4^- \cdot 495$
 469

 All
 $(CH_3)_5Sn_2C_6X_4^+ \star (CH_3)_5Sn_2C_6X_4^+ + CH_4^- \cdot 418^- \cdot 3488$
 348

 All
 $(CH_3)_5Sn_2C_6X_4^+ \star (CH_3)_2SnC_6X_4^- \cdot 51.7 \cdot 59.1$
 51.7 - 59.1

 1,2-Chloro
 $C_4H_{11}Sn_2C_6X_4^+ \star (CH_3)_2SnC_6X_4^- \cdot 51.7 \cdot 59.1$
 35.6

 1,2-Chloro
 $(CH_3)_3Sn_2C_6X_4^+ \star (CH_3)_2SnC_6X_4^- \cdot 51.7 \cdot 59.1$
 35.6

 1,4-Fluoro
 $(CH_3)_3Sn_2C_6X_4^+ \star (CH_3)_2SnC_6X_4^+ \cdot 51.7 \cdot 59.1$
 402

 1,2-Chloro
 $C_2H_5Sn_2C_6X_4^+ \star (CH_3)_2Sn_2C_6X_4^+ \cdot 4.7 \cdot 451.7 \cdot 59.1$
 402

 1,2-Chloro
 $(CH_3)_3Sn_2C_6X_4^+ \star (CH_3)_2Sn_2C_6X_4^+ \cdot 4.7 \cdot 451.7 \cdot 59.1 \cdot 61.7 \cdot 59.1 \cdot 50.7 \cdot 50.1 \cdot 50.7 \cdot 50.7 \cdot 50.1 \cdot 50.7 \cdot 50.7 \cdot 50.1$

CH₃Sn₂C₆X₄⁺⁺ + CH₃· 386
,2-Chloro (CH₃)₃SnC₆X₂⁺
$$\stackrel{\bullet}{\longrightarrow}$$

(CH₃)₂SnC₆X₂⁺⁺ + CH₃· 278

The proximity of the tin atoms in the 1,2-isomers are responsible for the species containing CH_2 . We suggest the following structures to account for these ions:



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The loss of CH₄ to form an ion with a $-Sn^+=CH_2$ structure is discounted on the lack of evidence for this ion in the 1,4-isomers. The loss of 'C₄H₁₃ ' probably involves the simultaneous losses of neutral molecules and radicals. Possibilities include CH₄ or C₂H₆, and CH₃ or H ·. The fact that there is evidence for both simultaneous and stepwise routes, supports our interpretation.

The $(CH_3)_3Sn^+$ ion is three times more abundant in the 1,2-isomers than in the 1,4-isomers. This may be due in part to relief of strain on $Sn-C_{aryl}$ cleavage, a factor encouraging the loss of $(CH_3)_3Sn^+$ from $(CH_3)_5Sn_2C_6X_4^+$. The strain in 1,2-[$(CH_3)_3Sn]_2C_6Cl_4$ has been estimated to be *ca.* 20 kcal⁹ although ¹¹⁹Sn Mössbauer quadrupole splitting data for 1,2-[$(CH_3)_3Sn]_2C_6X_4$ types indicate that there is no significant loss of axial symmetry in these compounds.¹⁰ The higher abundances of $(CH_3)_2Sn^+$ and CH_3Sn^+ ions for these isomers are consistent with their formation from the $(CH_3)_3Sn^+$ as shown in the fragmentation schemes 4 and 5 which includes the metastable transition observed for all of these compounds.

$$(CH_3)_3Sn^+ \xrightarrow{*} (CH_3)_2Sn^{+} + CH_3 \cdot m^* = 136^{+}3$$

An unusual feature observed in all spectra is a rather strong, very broad (10 m.u.) metastable. The breadth makes measurement rather difficult, but best fits are obtained for the loss of *ca*. 60 a.m.u. from the $(p\text{-}CH_3)^+$ ion. As it is observed for both chlorinated and fluorinated species, it necessarily involves loss of only carbon and hydrogen. For the 1,4-isomers, simultaneous losses of two C_2H_6 species, or C_3H_8 and CH_4 , to give the $CH_3Sn_2C_6X_4^+$ ion seems a reasonable possibility. However, this daughter is not evident in the spectra of the 1,2-isomers, only $CH_2SnC_6X_4^+$ is observed, the origin of which has already been discussed.

Again, even-electron ions account for the bulk of the total positive ion current. As in the $(C_6F_5)_{4-n}SnR_n$ series, many metastable transitions involving evenelectron ions forming odd-electron daughter ions are observed.

Schemes 4 and 5 illustrate the fragmentation of the 1,2- and 1,4-isomers.

 $1-(CH_3)_3Sn-4-H-C_6F_4$ and $1-(CH_3)_3Sn-4-F-C_6H_4$.—Both species exhibit intense peaks due to a loss of CH_3 . from the parent ion. There is little similarity in ion abundances for the remaining ions (Table 5). As expected, the more highly fluorinated compound fragments to give a much larger abundance of ions containing tin-fluorine bonds, while the more highly hydrogenated compound exhibits greater abundances of $(CH_3)_nSn^+$ ions and $Sn^{+\cdot}$ ions. No fragments containing tin-hydrogen bonds were evident. A rather unusual ion, $SnCF^+$, was observed in the spectrum of $1-(CH_3)_3Sn-4-H-C_6F_4$.

⁷ T. Chivers and B. David, J. Organometallic Chem., 1968, **13**, 177.

⁸ T. Chivers, Ph.D. Thesis, Durham, 1964. ⁹ D. Seyferth and A. B. Evnin, J. Amer. Chem. Soc., 1967,

89, 1468.
 ¹⁰ T. Chivers and J. R. Sams, J. Chem. Soc. (A), 1970, 928.



Scheme 4 Partial fragmentation of $1,2-(CH_3)_6Sn_2C_6X_4$

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Furthermore, this ion was involved in the only metastable transition observed:

$$SnCF^+ \xrightarrow{*} Sn^{+} + CF^{+} m^* = 94.3$$

The presence of an abundant SnF^+ ion for 1-(CH₃)₃Sn-4-F-C₆H₄ indicates a lengthy migration of fluorine to tin, indicative of strong Sn-F affinity, relative to Sn-H. Migration of *p*-fluorine to the metal has previously been observed in the mass spectrum of *p*-FC₆H₄Mn(CO)₅.¹¹ The disparity in the abundances of the SnC₆X₄Y⁺ ions may arise from competing eliminations:



Step 1 is more favourable in the highly fluorinated species, step 2, more favourable in the highly hydrogenated species.

 $1-(CH_3)_3Sn-2-H-C_6Cl_4$.—The mass spectrum of this compound (Table 5) bears marked similarity to that observed for $1-(CH_3)_3Sn-4-H-C_6F_4$. There is again no evidence of tin hydride species being formed, but a large peak (*ca.* 28%) is observed for SnCl⁺, consistent with other chlorine-containing species studied in this work. Another series of ions SnCl_xH⁺, involving losses of Cl⁻ from the aromatic ring are present, but not observed for $1-(CH_3)_3Sn-4-H-C_6F_4$; this is further evidence in favour of weak C-Cl bonds relative to C-F bonds.

Two metastable transitions were observed in the spectrum.

$$(CH_3)_3SnC_6CI_4H^+$$
 $\stackrel{*}{\longrightarrow}$ $(CH_3)_2SnC_6CI_4H^+ + CH_3^*$ $m^* = 349$
 $SnC_6CI_4H^+$ $\stackrel{*}{\longrightarrow}$ $SnC_6CI_2H^+ + CI_2$ $m^* = 206$

 $1-(C_2H_5)_3$ Sn-3-CF₃-C₆H₄.—The mass spectrum (Table 6) of this compound indicates the presence of tin hydride species. Three metastable transitions indicate the formation of a tin-hydride species:

$$(C_{2}H_{5})_{2}SnC_{6}H_{4}CF_{3}^{+} \xrightarrow{\bullet} C_{2}H_{6}SnC_{6}H_{4}CF_{3}^{+} + C_{2}H_{4} \quad m^{*} = 269 \cdot 6$$

$$C_{2}H_{6}SnC_{6}H_{4}CF_{3}^{+} \xrightarrow{\bullet} H_{2}SnC_{6}H_{4}CF_{3}^{+} + C_{2}H_{4} \quad m^{*} = 241 \cdot 8$$

$$H_{2}SnC_{6}H_{4}CF_{3}^{+} \xrightarrow{\bullet} H_{2}SnC_{6}H_{3}CF_{2}^{+} + HF \quad m^{*} = 226 \cdot 5$$

The ion $C_2H_6SnC_6H_4CF_3^+$ probably has a tin-hydrogen bond and tin-ethyl bond, while $H_2SnC_6H_4CF_3^+$ must incorporate two tin-hydrogen bonds. However, it is not obvious whether the elimination of HF involves removal of a hydrogen atom from the tin or from the ring system. Since no ion corresponding to the loss of ¹¹ M. J. Mays and R. N. F. Simpson, J. Chem. Soc. (A). 1967, 1936



TABLE 5

Partial mass spectra of $Me_3SnC_6X_4Y$. Tin-containing ions (abundances as % of total positive ion current)

		-	,
	1,4-Isomer	1,2-Isomer	1,4-Isomer
	$\mathbf{X} = \mathbf{F}$	$\mathbf{X} = \mathbf{Cl},$	$\mathbf{X} = \mathbf{H}$.
Ion+	$\mathbf{Y} = \mathbf{H}$	$\mathbf{Y} = \mathbf{H}$	$\mathbf{Y} = \mathbf{F}$
C ₃ H ₉ SnC ₆ X ₄ Y·		0.5	0.7
$C_2H_6SnC_6X_4Y$	19.0	8.1	21.0
CH ₃ SnC ₆ X₄Y∙			$1 \cdot 0$
$SnC_{6}X_{4}Y$	3.4	$2 \cdot 3$	15.0
CH ₃ SnC ₆ X ₃ Y		0.5	
SnC ₆ X ₃ Ý		0.4	
SnC ₆ X ₂ Y		0.1	
SnC ₆ XY		1.5	
C ₃ H ₉ SnX·	$1 \cdot 2$		
C ₃ H ₉ Sn	$2 \cdot 0$	$2 \cdot 3$	$2 \cdot 0$
C ₂ H ₆ SnX	11.6	10.2	
C ₂ H ₆ SnY			1.4
C ₂ H ₆ Sn•			$2 \cdot 4$
CH _a SnX∙	1.8	$1 \cdot 9$	
CH ₃ SnY•			0.6
CH ₃ Sn	10.2	9.0	14.7
SnCX	5.6		
SnX	20.4	$28 \cdot 2$	
SnY			15.4
Sn	2.7	4.1	9.4
Tetal			
rotal	11.9	09.1	83·6

Тан	BLE 6
Partial mass spectrum o	of 1-(C ₂ H ₅) ₃ Sn-3-CF ₃ -C ₆ H ₄
$\operatorname{Ion^+}$	Abundance as % of total positive ion current
(A) Tin-containing ions	
$\begin{array}{c} (C_{2}H_{5})_{3}SnC_{6}H_{4}CF_{3}\cdot\\ (C_{2}H_{5})_{3}SnC_{6}H_{4}CF_{2}\cdot\\ (C_{2}H_{5})_{3}SnC_{6}H_{4}CF_{3}\cdot\\ C_{4}H_{6}SnC_{6}H_{4}CF_{3}\cdot\\ H_{2}SnC_{6}H_{4}CF_{3}\cdot\\ H_{2}SnC_{6}H_{4}CF_{3}\cdot\\ H_{2}SnC_{6}H_{3}CF_{2}\cdot\\ SnC_{6}H_{3}CF_{2}\cdot\\ C_{2}H_{5}Sn\cdot\\ SnF\cdot\\ SnH\cdot\\ Sn\cdot\end{array}$	$\begin{array}{c} 0.4 \\ 1.3 \\ 16.4 \\ 7.1 \\ 8.0 \\ 17.2 \\ 0.9 \\ 2.5 \\ 3.1 \\ 5.8 \\ 2.7 \\ 3.0 \end{array}$
Total	68.4
(B) Significant ions without	tin
$C_6H_5CF_2$ $C_6H_4CF_2$ · $C_6H_3CF_2$ C_8H_4CF	$ \begin{array}{r} 2 \cdot 6 \\ 1 \cdot 9 \\ 0 \cdot 7 \\ 10 \cdot 0 \end{array} $
C _a H ₅	2.6

 SnH_2 from $H_2SnC_6H_4CF_3^+$ is observed in the mass spectrum, it appears likely that the elimination of HF involves breaking a tin-hydrogen bond.

Ion abundance measurements indicate that the process of eliminating a C₂H₅ radical from the molecular ion is much more favourable than the loss of a fluorine radical. In reference to the other compounds in this work, it appears that the loss of a fluorine radical from the molecular ion occurs only for alkyl fluorines; never for aromatic fluorines. The quantity of SnF^+ ions observed also indicates that fluorine migration processes occur to some extent, even at extended distances. In contrast to the behaviour observed for 1-(C2H5)3Sn- $3-CF_3C_6H_4$, the mass spectrum of $C_6H_5CF_3$ shows an intense peak at m/e = 96 due to the ejection of CF₂ from the molecular ion.¹²

DISCUSSION

As found in previous work,1-5 even-electron ions are more abundant than odd-electron ions. Parent ions tend to eliminate an odd-electron neutral fragment, however, in contrast to earlier data on SnR₄ species,⁵ we find that SnR_3^+ and $XSnR_2^+$ ions often break down to odd-electron ions. In many cases, this elimination could not be attributed to the high stability of the neutral fragment. In the series $(C_6F_5)_{4-n}SnR_n$, the elimination of C_6F_5 and R from the molecular ion appeared to be strongly dependent upon the nature of R. In the compounds containing R₃Sn groups attached to an aromatic ring, the parent ion invariably eliminates R. neutral species rather than ring substituents.

Every spectrum shown a large abundance of ions containing SnF⁺ or SnCl⁺ species. Metastable evidence indicates that elimination of C_6F_4 is a dominant factor in producing tin-halide ions. Alternately, elimination

of SnF_2 neutral species from $(C_6F_5)_2SnF^+$ ions has metastable support. Furthermore, the unusual elimination of RF neutral species from $(C_6F_5)SnFR^+$ ions is shown to occur in $(C_6F_5)_2SnR_2$ compounds, but not other molecules.

The formation of $C_{18}F_{12}^{+}$ and $C_{18}F_{10}^{+}$ ions occurs only from the tris-pentafluorophenyl compounds; $C_{12}F_{10}^{+*}$ and $C_{12}F_8^{+*}$ ions forming from the bis-pentafluorophenyl compounds. Where $R = C_6H_5$, $C_{12}F_5H_5^{+}$, and C₁₂F₄H₄^{+•} ions occur, however, no ions unsymmetrical with regard to H and F content are observable. Despite the lack of metastable confirmation, polyphenylene ions are likely formed by a similar route to that postulated for Group V derivatives for which there is extensive metastable evidence.^{3,4} The thermal stabilities of these compounds are such, that at the source temperatures used, thermal decomposition cannot account for the polyphenylene ion formation.

The Sn⁺ ion was present in all spectra. No trend in abundances was evident in the compounds studied. It is of interest to note the absence of any SnH species in this series of perhalogenoaromatic compounds, with the single exception of the $(C_6F_5)_2SnH^+$ ion derived from $(C_6F_5)_2Sn(C_4H_9)_2.$

The parent ions were usually of low abundance, or absent as has been reported previously⁵ for a series of organo-stannanes. Unlike the pure hydrocarbon derivative for which a R₃Sn⁺ ion was usually the most abundant, the introduction of halogenocarbons often results in ions such as SnX being of similar or greater abundance than any R₃Sn⁺-type ion.

EXPERIMENTAL

Mass spectra were studied on an A.E.I. M.S.12 instrument operating at 70 eV and an accelerating voltage of 8 kV. All solids were introduced using a direct-insertion probe, the liquids via a heated inlet system.

Reported ion abundances are summed over all the isotopic contributions. The spectra, normalized to the base peak as 100% have been submitted to the Mass Spectrometry Data Center, AWRE, Aldermaston, England.

The compounds $(C_6H_5)_nSn(C_6F_5)_{4-n}$ and $(CH_3)_nSn(C_6F_5)_{4-n}$ were prepared as described by Chambers and Chivers; 13 $1,2-[(CH_3)_3Sn_2]C_6F_4,\ 1,4-[(CH_3)_3Sn_2]C_6F_4,\ \text{and}\ 1-(CH_3)_3Sn_2]C_6F_4$ 4-HC_6F_4 were prepared as described by Chivers.^{14} 1-(CH_3)_3Sn-4-FC_6H_4 (b.p. $62\text{--}63^\circ/1$ mm) was prepared from p-fluorophenylmagnesium bromide and trimethyltin chloride in diethyl ether. The butyl series was prepared as described by Pohlmann et al.15

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 ¹⁵ J. L. W. Pohlmann, F. E. Brinckman, G. Tesi, and R. E. Donadio, Z. Naturforsch., 1965, 20b, 1.

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