Mass Spectral Studies of Tetraorganotin (IV) Compounds Containing Long Chain Alkyl and Aryl Groups

[1]SADIQ-UR-REHMAN*, [2]MUHAMMAD AZIZ CHOUDHARY,
[3]SAQIB ALI AND [4]MOAZZAM HUSSAIN BHATTI
[1]*Department of Chemistry, The University of Azad Jammu and Kashmir Muzaffarabad-13100, Pakistan*
[2]*Department of Chemistry, Mirpur University of Science and Technology Mirpur, Pakistan*
[3]*Department of Chemistry, Quaid-i-Azam University, 45320 Islamabad, Pakistan*
[4]*Department of Chemistry, Allama Iqbal Open University, Islamabad, Pakistan*

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Summary: Tetraorganotin (IV) compounds having general formula $R_{4-x}SnR'_x$ where R = CH_3, *n*-C_4H_9, C_6H_5, $C_6H_5CH_2$, R′ = *n*-C_6H_{13} and x = 1 or 2, have been synthesized by the reaction of R_2SnCl_2 and R_3SnCl with appropriate amount of *n*-hexylmagnesium bromide, prepared *in situ* in dry ether. All the products were distilled under vacuum and thoroughly studied by mass spectrometric analysis to confirm their formation and fragmentation behavior. Molecular ion peaks were observed for some compounds with low relative abundance. The possible fragmentation pattern and data for all compounds have been discussed in detail.

Introduction

Organotin (IV) complexes may interact with biological systems in many different ways as, for instance, bactericides, fungicides, acaricides and industrial biocides [1]. In recent years, several investigations [2-4] to test their antitumor activity have been carried out. Organotin (IV) is well known to form complexes with ligands having oxygen [5-7], sulfur [8, 9] and nitrogen [10-12] donor sites.

In view of our continuous interest in synthesis and characterization [13-15], biological [16-18] and industrial [19] applications and X-ray crystal structure analysis [20-22] of organotin (IV) complexes, we have synthesized a series of organotin (IV) compounds containing long chain alkyl groups in addition to alkyl or aryl groups. In present work we report their mass spectral analysis along with possible fragmentation pattern whereas their synthesis and spectral characterization are reported elsewhere [23].

Results and Discussion

The mass fragmentation pattern of the individual compounds, with *m/z* values are given in Schemes 1-8 while the data for common fragments are reported in Table-1 and 2. In present work we are going to discuss mass fragmentation behavior of tetraorganotin (IV) compounds containing long chain alkyl groups. Usually, molecular ion peaks in most of the organometallic compounds are not observed by using EI technique [24] and we have observed a similar pattern except for compounds **I-III** and **IV** where M^+ of very low intensity are appeared. The

Table-1: Fragmentation Pattern and Relative Abundance of Common Ions Observed at 70 eV for $R_2SnR'_2$ Compounds.

Fragment Ions	(I) Int.(%) R = Bu	(III) Int.(%) R = Me	(V) Int.(%) R = Ph	(VII) Int.(%) R = Benzyl
$[R_2Sn(CH_2(CH_2)_4CH_3)_2]^+$	404(8)	320(1)	–	–
$[R_2SnCH_2(CH_2)_4CH_3]^+$	319(25)	235(100)	359(100)	387(5)
$[RSn(CH_2(CH_2)_4CH_3)_2]^+$	–	305(9)	–	381(16)
$[SnCH_2(CH_2)_4CH_3]^+$	–	205(3)	–	205(10)
$[RSn(CH_2(CH_2)_4CH_3)H]$	263(100)	221(10)	–	–
$[R_2SnH]^+$	235(28)	151(70)	275(53)	–
$[SnH^+/Sn^+]$	121(8)	121(3)	120(4)	120(4)
$[C_6H_5CH_2]^+$	–	–	–	91(61)
$[CH_3(CH_2)_4CH_2]^+$	85(3)	85(1)	85(4)	85(100)
$[CH_3(CH_2)_2CH_2]^+$	57(1)	–	57(5)	57(15)
$[CH_3CH_2CH_2]^+$	43(3)	–	43(16)	43(90)

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*To whom all correspondence should be addressed.

Table-2: Fragmentation Pattern and Relative Abundance of Common Ions Observed at 70 eV for R_3SnR' Compounds.

Fragment Ions	(II) Int.(%) R = Bu	(IV) Int.(%) R = Me	(VI) Int.(%) R = Ph	(VIII) Int.(%) R = Benzyl
$[R_3SnCH_2(CH_2)_4CH_3]^+$	376(5)	–	436(0.3)	–
$[R_2SnCH_2(CH_2)_4CH_3]^+$	319(100)	235(75)	–	387(5)
$[R_3Sn]^+$	291(31)	–	351(100)	393(9)
$[R_2Sn]^+$	–	150(28)	274(4)	302(5)
$[RSn]^+$	177(38)	135(31)	197(51)	211(21)
$[R_3SnH]^+$	–	166(3)	352(33)	–
$[R_2SnH]^+$	235(58)	151(100)	275(8)	–
$[SnH^+/Sn]^+$	121(33)	121(9)	120(6)	120(4)
$[C_6H_5CH_2]^+$	–	–	–	91(100)
$[CH_3(CH_2)_4CH_2]^+$	85(30)	85(5)	85(9)	85(60)
$[CH_3(CH_2)_2CH_2]^+$	57(91)	57(10)	57(10)	57(53)
$[CH_3CH_2CH_2]^+$	43(71)	43(10)	43(31)	43(58)

mass spectra of the representative compounds are given in Fig. 1 and 2.

*Di-n-butyl-di-n-hexyltin(IV), **I** and Tri-n-butyl-n-hexyltin(IV),* **II**

The possible fragmentation patterns for the compounds **I** and **II** are shown in Schemes 1 and 2. The molecular ion peaks of low intensities are observed in both compounds at *m/z* 404 and 376, respectively. In both compounds primary fragmentation involves loss of R (n-C_4H_9) or R′ (n-C_6H_{13}). However, in compound **I**, this fragmentation leads to the formation of more intense peaks at *m/z* 347 and 319 while loss of R (n-C_4H_9) in compound **II** forms base peak at *m/z* 319 and elimination of R′ (n-C_6H_{13}) gives peak at *m/z* 291 of intermediate intensity. Secondary fragmentation in both compounds may occur *via* loss of C_4H_8 or C_6H_{12} which follow β-hydrogen transfer mechanism [25]. In compound **I** base peak at *m/z* 263 observed due to $[RSnR'(H)]^+$ ion. Further fragmentation occurs due to stepwise loss of C_4H_8 or C_6H_{12} and ends to give $SnH]^+$ (121) at *m/z* 121. In compound **II**, 3rd route fragmentation occurs through loss of n-C_4H_{10} (RH) and C_4H_8 or C_6H_{12} *via* β-hydrogen transfer mechanism ending as $SnH]^+$ at *m/z* 121 (Scheme 2).

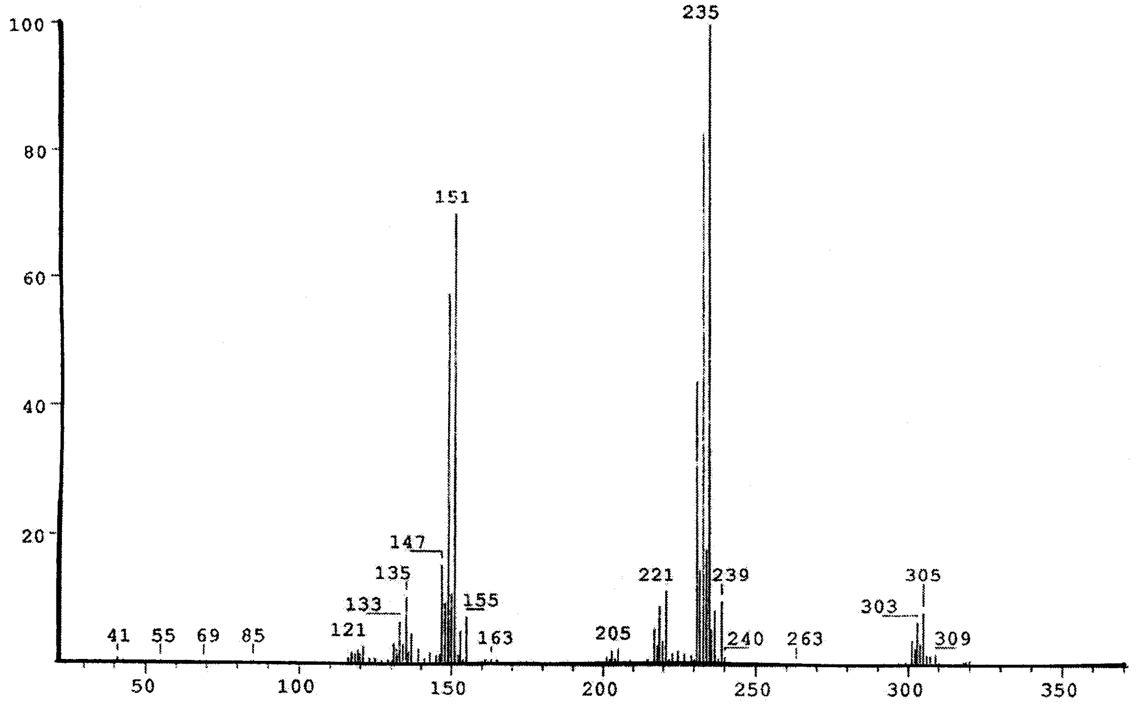


Fig. 1: Mass Spectrum of Dimethyl di-n-hexyltin (IV).

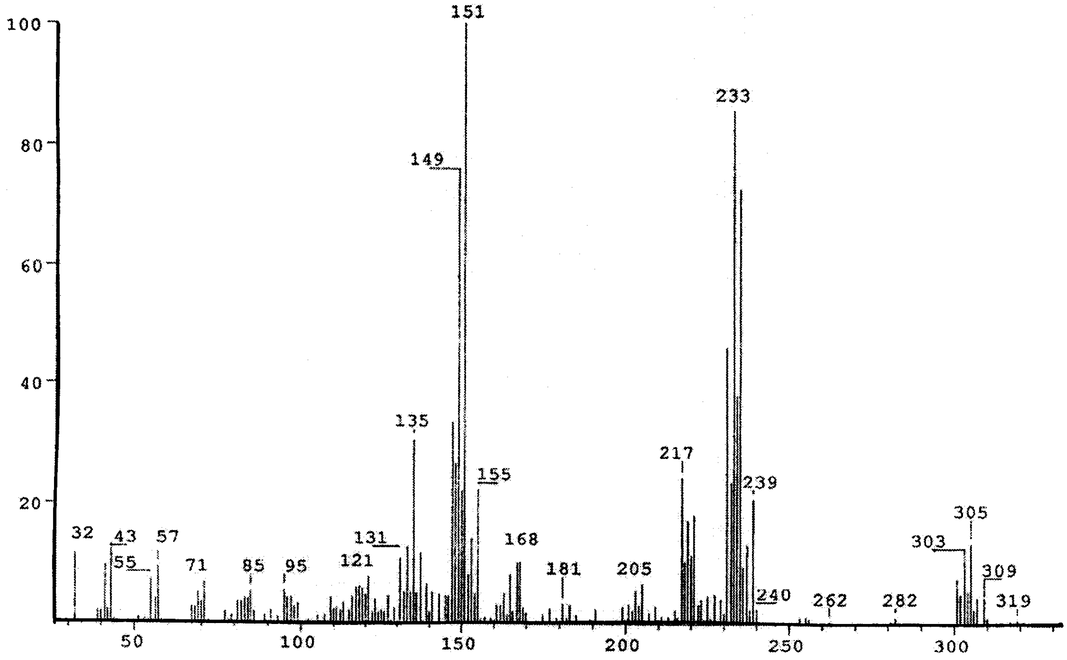
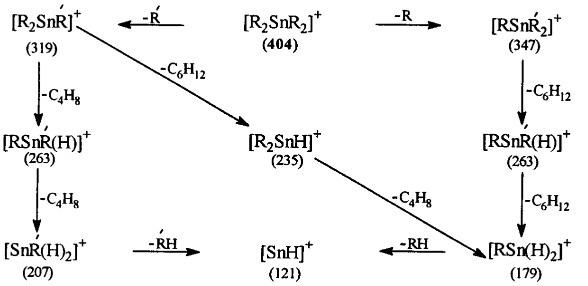
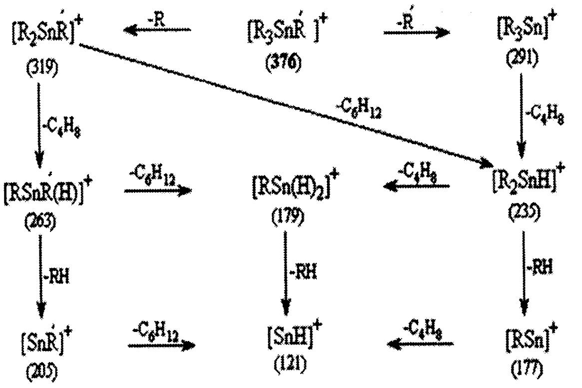


Fig. 2: Mass Spectrum of Trimethyl′-*n*-hexyltin (IV).



Scheme 1: Fragmentation Pattern for Compounds I and II.



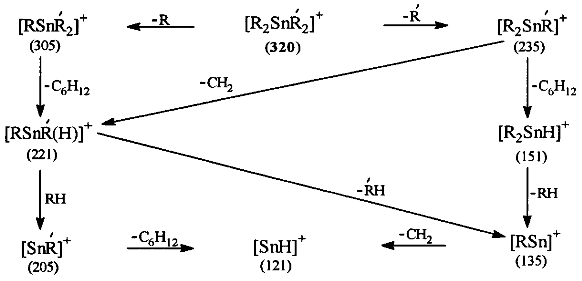
Scheme 2: Fragmentation Pattern for Compounds I and II When R = *n*-C_4H_9 and R′ = *n*-C_6H_{13}.

Peaks for R and R' are observed at *m/z* 57 and 85, respectively. Both R and R' further eliminate CH_2 group and give peaks at *m/z* 43 and 71, respectively. The common ions observed are reported in Table-1 and 2.

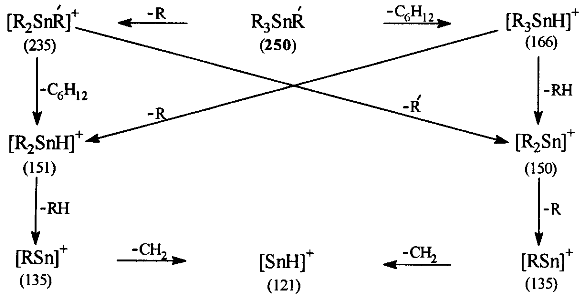
Dimethyl-di-n-hexyltin(IV), ***III*** *and Trimethyl-n-hexyltin(IV),* ***IV***

Schemes 3 and 4 show the fragmentation pattern of dimethyl- and trimethyl-*n*-hexyltin(IV) derivatives, respectively. The low intensity molecular ion peak is observed only in compound **III** but not in **IV**.

In compound **III** primary decomposition, like compound **I** and **II**, involves loss of R (CH_3) or R′ (*n*-C_6H_{13}). The elimination of CH_3 group ends into a fragment *m/z* 305 while loss of *n*-C_6H_{13} group leads to formation of base peak at *m/z* 235. Secondary decomposition releases C_6H_{12} due to *β*-hydrogen elimination from the ions $CH_3Sn(C_6H_{13})_2]^+$ and $(CH_3)_2SnC_6H_{13}]^+$ to give a low intensity peak for $CH_3SnC_6H_{13}(H)]^+$ at *m/z* 221 and a high intensity peak for $(CH_3)_2SnH]^+$ at *m/z* 151, respectively. Whereas, tertiary decomposition mostly occurs through elimination of CH_4 from $CH_3SnC_6H_{13}(H)]^+$ (221) and $(CH_3)_2SnH]^+$ (151) to give fragments



Scheme 3: Fragmentation Pattern for Compounds III and IV.



Scheme 4: Fragmentation Pattern for Compounds III and IV When R $=CH_3$ and $R' = n\text{-}C_6H_{13}$.

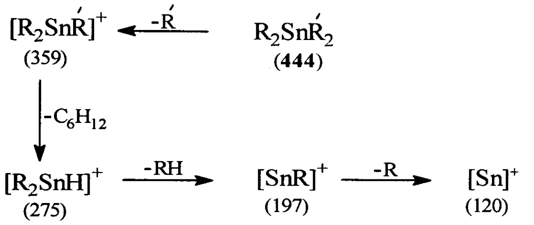
$SnC_6H_{13}]^+$ at *m/z* 205 and $CH_3Sn]^+$ at *m/z* 135, respectively. These fragments further decompose into $SnH]^+$ fragment at *m/z* 121 again *via* β-hydrogen elimination mechanism on releasing C_6H_{12} and CH_2 groups, respectively.

On the other hand in compound **IV** primary fragmentation may occur by loss of R (CH_3 or C_6H_{12}) to give peaks at *m/z* 235 and 166, respectively. Secondary decomposition may proceed *via* release of C_6H_{12} from $(CH_3)_2SnC_6H_{13}]^+$ (235) to give base peak at *m/z* 151 or may lose $n\text{-}C_6H_{13}$ group to form low intensity peak at *m/z* 150. Similarly, it may occur through release of CH_4 or CH_3 group from $(CH_3)_3SnH]^+$ (166) to give fragment at *m/z* 150 and base peak at *m/z* 151, respectively. The tertiary fragmentation involves loss of CH_4 from base peak fragment or releasing of CH_3 group from fragment $(CH_3)_2Sn]^+$ (150) and gives same peak at *m/z* 135. The final step involves loss of CH_2 group to give low intensity peak at *m/z* 121 for $SnH]^+$ fragment. In both compounds low intensity peak for ligand ($n\text{-}C_6H_{13}$) is observed at *m/z* 85. The progressive elimination of CH_2 gives small peaks at *m/z* 71, 57, 43 *etc.* while ligand peak for CH_3 group is not observed. Some common ions observed are $R_2SnR']^+$, $R_2SnH]^+$, $RSn]^+$, $SnH]^+$ and $CH_3(CH_2)_4CH_2]^+$.

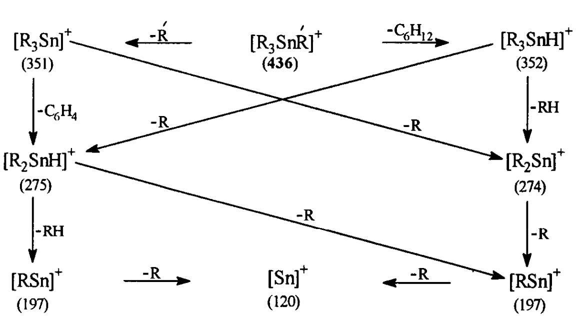
Diphenyldi-n-hexyltin(IV), V and Triphenyl-n-hexyltin(IV), VI

The fragmentation patterns in compound **V** and **VI** are comparatively simple (Scheme 5 and 6). Molecular ion peak of low intensity is observed only in triphenyl-*n*-hexyltin(IV) derivative (comp. **VI**).

In compound **V** primary fragmentation proceeds *via* loss of $n\text{-}C_6H_{13}$ to give a base peak at *m/z* 359 for $(C_6H_5)_2SnC_6H_{13}]^+$ ion. Secondary decomposition involves release of C_6H_{12} due to β-hydrogen elimination from the previous ion and gives a peak of an intermediate intensity for $(C_6H_5)_2SnH]^+$ fragment at *m/z* 275. The loss of benzene (C_6H_6) molecule from the ion $(C_6H_5)SnH]^+$ (275) gives a low intensity peak at *m/z* 197 which further decomposes into $Sn]^+$ ion by elimination of C_6H_5 group and appears as small peak at *m/z* 120 as shown in Scheme 5.



Scheme 5: Fragmentation Pattern for Compounds V and VI.

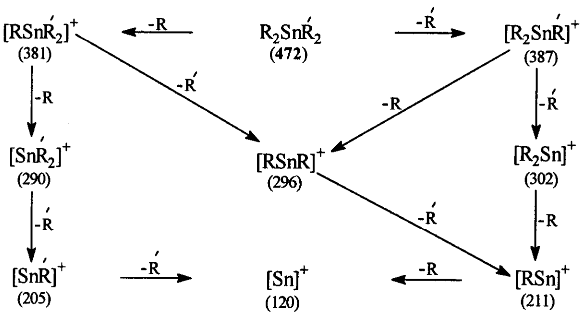


Scheme 6: Fragmentation Pattern for Compounds V and VI When $R = C_6H_5$ and $R' = n\text{-}C_6H_{13}$.

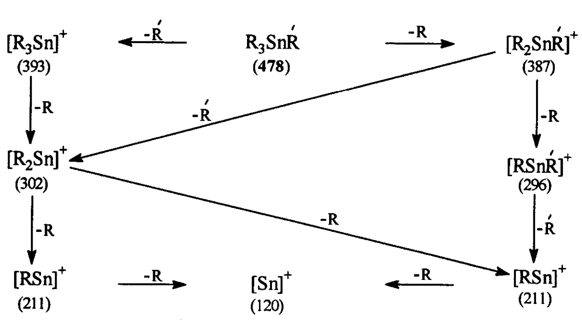
It is evident from the Scheme 6 that major route of the primary fragmentation in compound **VI** involves loss of *n*-C_6H_{13} group to give base peak at *m/z* 351 for $(C_6H_5)_3Sn\rceil^+$ ion. It may also proceed *via* β-hydrogen transfer mechanism and appears as an intermediate peak for $(C_6H_5)_3SnH\rceil^+$ at *m/z* 352. The loss of C_6H_4 from the base peak fragment gives $(C_6H_5)_2SnH\rceil^+$ ion at *m/z* 275 and elimination of benzene (C_6H_6) molecule from $(C_6H_5)_3SnH\rceil^+$ (352) ends into a fragment $(C_6H_6)_2Sn\rceil^+$ at *m/z* 274. Both these fragments on loss of benzene (C_6H_6) molecule and phenyl (C_6H_5) group, respectively, lead to formation of $C_6H_5Sn\rceil^+$ ion at *m/z* 197. It further decomposes into low intensity peak of $Sn\rceil^+$ at *m/z* 120. Peaks corresponding to ligands, *n*-C_6H_{13} and C_6H_5, appear in both compounds which may further decompose into fragments of low *m/z* values. The common fragments observed in these compounds are $R_2SnH\rceil^+$, $RSn\rceil^+$, $Sn\rceil^+$, $CH_3(CH_2)_4CH_2\rceil^+$, $CH_3(CH_2)_3CH_2\rceil^+$, $CH_3(CH_2)_2CH_2\rceil^+$ and $CH_3CH_2.CH_2\rceil^+$. The other common behavior observed is that the base peak is obtained by loss of the R′ (*n*-C_6H_{13}) group from the parent ions.

Dibenzyldi-n-hexyltin(IV), VII and Tribenzyl-n-hexyltin(IV), VIII

The fragmentation behaviours of compound **VII** and **VIII** are found to be comparatively different than other compounds in the series. For example in compound **VII** *n*-C_6H_{13} ion at *m/z* 85, appears as a base peak. Similarly, in compound **VIII** the base peak is due to $C_6H_5.CH_2\rceil^+$ ion at *m/z* 91 (Schemes 7 and 8). None of the other compounds in the series exhibit this behaviour. Furthermore molecular ion peaks are also not observed in these compounds. However, as shown in Scheme 7 and 8, other fragmentation pattern of these compounds is almost similar to their analogous. Common ions observed, include $R_2SnR'\rceil^+$, $R_2Sn\rceil^+$, $RSn\rceil^+$, $Sn\rceil^+$, $CH_3(CH_2)_4CH_2\rceil^+$, $CH_3(CH_2)_3CH_2\rceil^+$, $CH_3(CH_2)_2CH_2\rceil^+$, $CH_3CH_2CH_2\rceil^+$ and $C_6H_5.CH_2\rceil^+$ (Tables-1 and 2).



Scheme 7: Fragmentation Pattern for Compounds VII and VIII.



Scheme 8: Fragmentation Pattern for Compounds VII and VIII When R = $C_6H_5CH_2$ and R′ = *n*-C_6H_{13}.

Experimental

Synthesis and Instrumentation

All the compounds were synthesized as reported earlier [23]. The mass spectral data were recorded on a MAT-8500 Finnigan (Germany) mass spectrometer. The *m/z* values were evaluated assuming H = 1, C = 12 and Sn = 120.

Conclusion

We conclude from the above discussion that most of the tetraorganotin (IV) compounds, only with few exceptions, containing long chain alkyl groups follow the same fragmentation pattern. It suggests that primary decomposition follows the elimination of R or R′ and rarely R″ (C_6H_{12}). This leads to formation of $RSnR'_2\rceil^+$, $R_2SnR'\rceil^+$ and $R_3SnH\rceil^+$, respectively, depending on the nature of compound. The onward fragmentation often favors β-hydrogen transfer mechanism which is in consistence to the literature [25, 26]. In most of the cases base peak is observed after elimination of R′ (*n*-C_6H_{13}) group. Some times after elimination of R″ (C_6H_{12}) and rarely after elimination of R (*n*-C_4H_9) (comp. **II**). However, in compound **VII** and **VIII** ligands form base peak showing different behavior from their other counterparts (Tables-1 and 2).

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