Mass Spectrometric Studies of Tributyltin(IV) Carboxylates of Biologically Active Ligands

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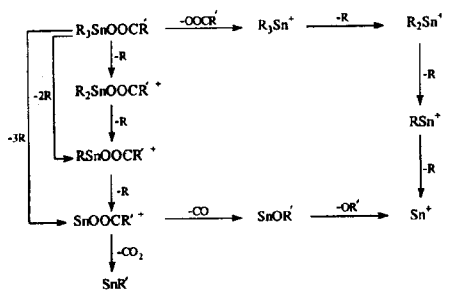
Summary: Electron impact mass spectra of six different tributytin(IV) derivatives of biologically active ligands are described and analysed for their fragmentation pathway. The destribution of butyl or carboxylic groups attached directly to tin atom were easily determined from their mass spectral cracking pattern and presented in various schemes.

Introduction

Beside other spectroscopic techniques such as infrared and multinuclear NMR (^{1}H, ^{13}C, ^{119}Sn) employed for structural characterization of organotin(IV) derivatives, mass spectrometry has been frequently used not only for the isotopic mass determination but can be quite helpful in structure elucidation and possible fragmentation pathway [1,2]. Reports are available on the fragmentation of organotin(IV) compounds by different ionization techniques [3-5]. Previously we reported the chemistry of organotin(IV) carboxylates with different aspects [6] as well as mass spectrometry [7]. In this paper we wish to report and compare the fragmentation pattern of six different tributyltin(IV) carboxylates of biologically active ligands by 70 ev electron impact technique. The fragmentation schemes are proposed on the bases of m/z value of the various fragments.

Results and Discussion

The general fragmentation pattern for tributyltin complexes is given in Scheme 1.



Scheme 1. General Fragmentation Pattern.

A molecular ion peak of very low intensity [10] was observed for all complexes. In all triorganotin derivatives, the primary fragmentation is due to the loss of –OOCR′ group followed by the successive loss of R groups ending as Sn^{+} (*m/z* = 120).

The secondary fragmentation is the consequent of loss of either three R groups by different routes and then CO_2. However, the latter is more frequent and more probable pathway. The most common fragments with their *m/z* ratio and relative abundance are given in Schemes 2-7.

In compound **1**, the molecular ion (M^{+}) peak was observed at *m/z* (533). It immediately loses a butyl radical to give *m/z* (476) and again by losing another butyl radical, it should give peak at m/z (419), which is not observed in the spectrum.

The other path of fragmentation was determined by the peak at *m/z* (362), which is due to the loss of three butyl radicals from molecular ion. The peak at *m/z* (318) is due to the subsequent loss of CO_2. Further fragments of compound are $CHCOOSn^{+}$ (177), Bu_2Sn^{+} (234), $BuSn^{+}$ (177), $C_4H_9^{+}$ (57) and $C_2H_5^{+}$ (29). The fragmentation pattern of the compound 1 is given in Scheme 2.

In compound **2**, the molecular ion peak is observed with low intensity. Bu_3SnL immediately loses a butyl radical to give *m/z* 528. The fragments at *m/z* 484 and 414 are due to losses of CO_2 and two butyl molecules, respectively. The other fragments observed are HSn^{+}/Sn^{+} (121/120), Bu_3Sn^{+} (291), Bu_2Sn^{+} (234), $BuSn^{+}$ (177), $C_6H_3^{+}$ (75), $C_4H_9^{+}$ (57)

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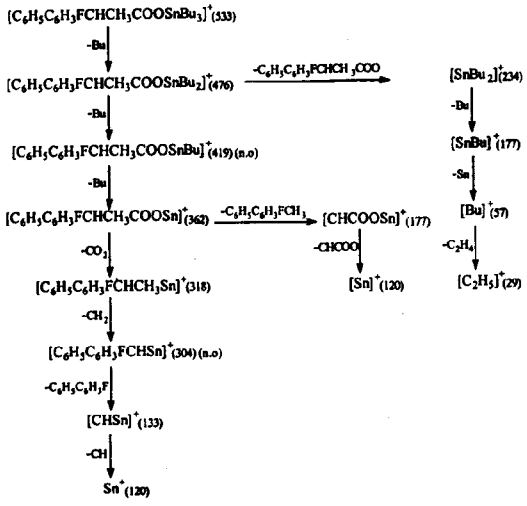
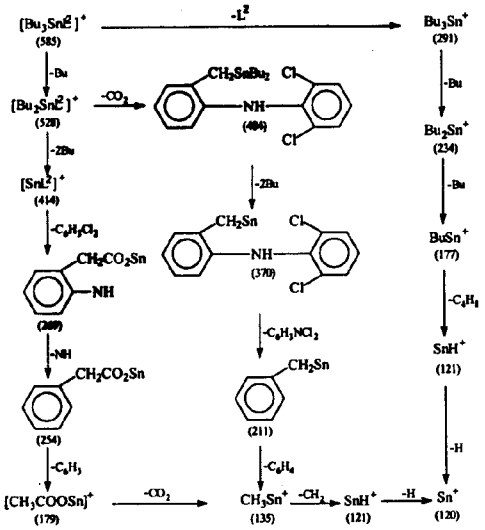


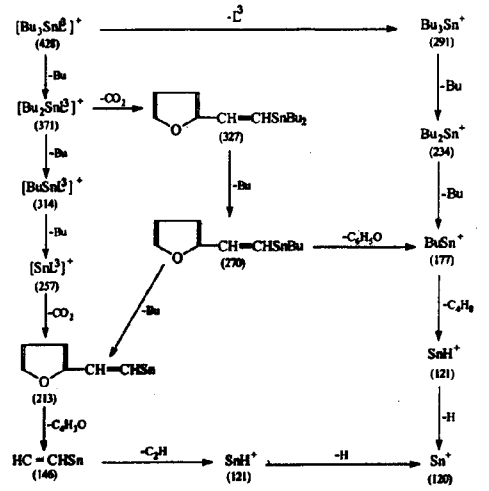
Scheme 2. Fragmentation Pattern of Compound **1**.



Scheme 3. Fragmentation Pattern of Compound **2**.

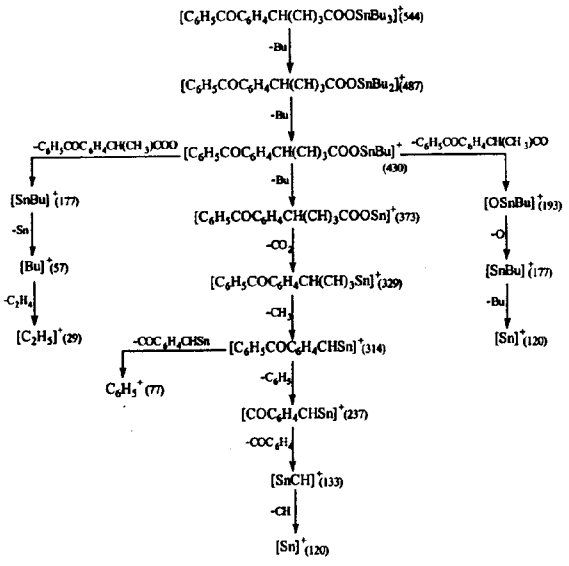
and $C_2H_5^+$ (29). The fragmentation pattern of the compound **2** is given in Scheme 3.

In compound **3**, the M^+ is observed with low intensity. Bu_3SnL immediately loses butyl radical to give *m/z* 371. The fragments at *m/z* 327 and 314 are due to loss of CO_2 and butyl molecules. Further fragments SnH^+/Sn^+ (121/120), Bu_3Sn^+ (291), Bu_2Sn^+ (234), $BuSn^+$ (177), ^+SnL (257), $HC{\equiv}CHSn^+$ (146), $C_4H_9^+$ (57) and $C_2H_5^+$ (29) were obtained. The fragmentation pattern of the compound **3** is given in Scheme 4.



Scheme 4. Fragmentation Pattern of Compound **3**.

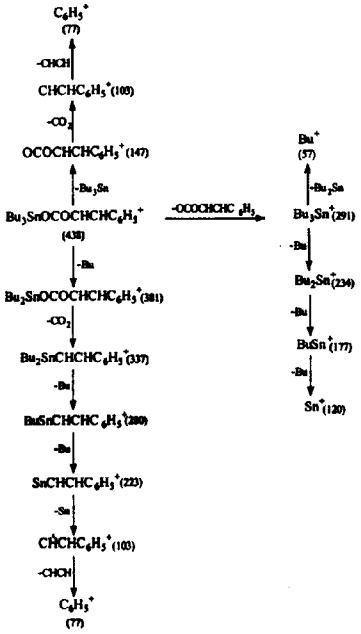
In compound **4**, the M^+ is observed at *m/z* (544). The peaks at *m/z* 487, 430 and 373 are due to the simultaneous loss of three C_4H_9 radicals. The other fragments 314, 237 and 133 are due to $C_6H_5COC_6H_4CHSn^+$, $COC_6H_4CHSn^+$ and $SnCH^+$, respectively. Further fragmentation gives $SnBu^+$ *m/z* (177), $OSnBu^+$ *m/z* (193), $C_6H_5^+$ *m/z* (77), $C_4H_9^+$ *m/z* (57) and $C_2H_5^+$ *m/z* (29) (see Scheme 5).



Scheme 5. Fragmentation Pattern of Compound **4**.

In compound **5**, the M^+ peak of very low intensity is observed. It immediately loses a butyl group to give base peak at *m/z* (381). The fragments at *m/z* (337) and (280) are due to loss of CO_2 and Bu group, respectively. The other fragments observed are Bu_3Sn^+ *m/z* (291), Bu_2Sn^+ *m/z* (234), $SnCHCHC_6H_5^+$ *m/z* (223), $BuSn^+$ *m/z* (177), $OCOCHCHC_6H_5^+$ *m/z* (147), Sn^+ *m/z* (120), $CHCHC_6H_5^+$ *m/z* (103), $C_6H_5^+$ *m/z* (77) and $C_4H_9^+$ *m/z* (57) (see Scheme 6).

In compound **6**, molecular ion M^+ peak is not observed. The fragment at *m/z* (439) is the base peak (100%) due to loss of Bu group. The other fragments observed are $Bu_2SnCH(CH_3)C_6H_5CH_2CH(CH_3)_2^+$ *m/z* (395), Bu_3Sn^+ *m/z* (291), Bu_2Sn^+ *m/z* (234), $HOCOCH(CH_3)C_6H_5CH_2CH(CH_3)_2^+$ *m/z* (206), $BuSn^+$ *m/z* (177), $CH(CH_3)C_6H_5CH_2CH(CH_2)_2^+$ *m/z* (206), $CH(CH_3)C_6H_5CH_2CH(CH_3)_2^+$ *m/z* (161), Sn^+ *m/z* (120), $C_6H_5CH_2^+$ m/z (91), C_6H_5 *m/z* (77) and $C_4H_9^+$ *m/z* (57). The fragmentation pattern for compound **6** is given in Scheme 7. Representative mass spectra are given in Figures 1and 2.



Scheme 6. Fragmentation Pattern of Compound **5**.

Experimental

Instrumentation

Mass spectra were recorded on MAT 8500 Finnigan (Germany).

Chemicals and Solvents

$(Bu_3Sn)_2O$ was obtained from Fluka AG Chemicals (Switzerland). Furylacrylic acid and

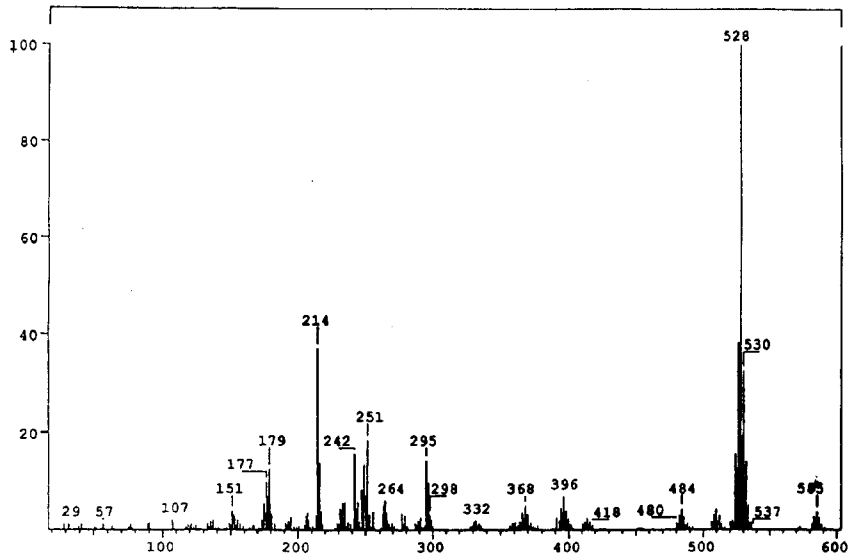


Fig. 1: Mass Spectrum of Compound **2**.

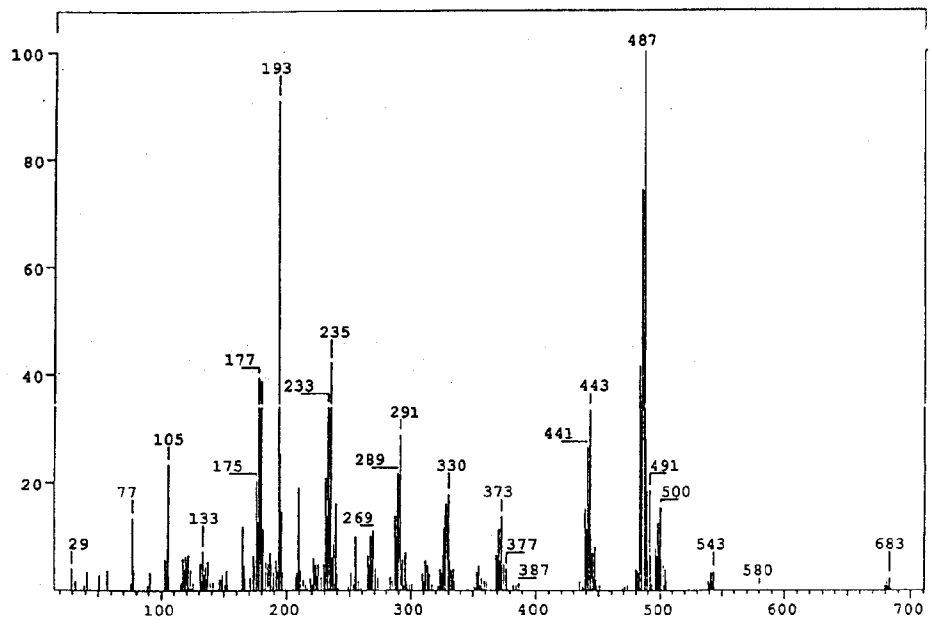
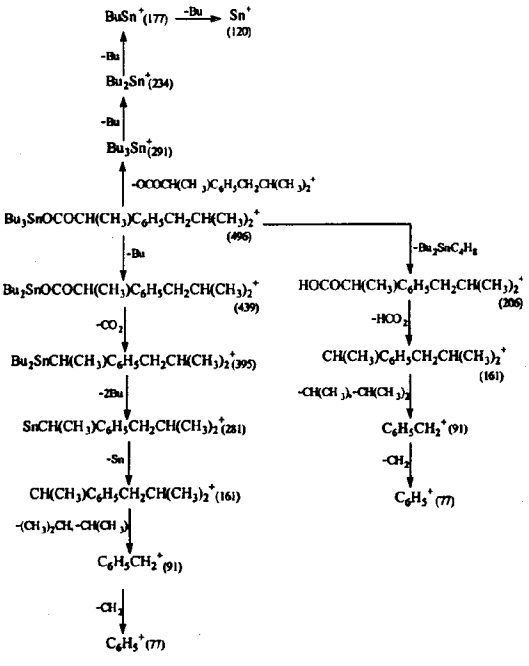


Fig. 2: Mass Spectrum of Compound **4**.



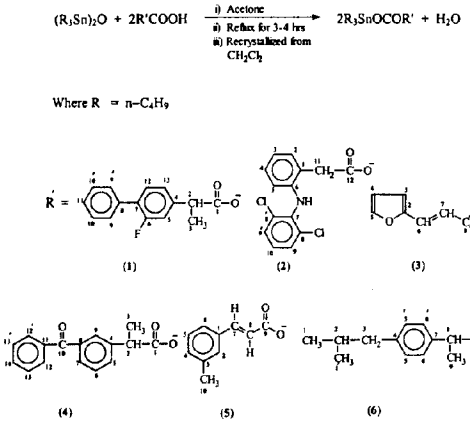
Scheme 7. Fragmentation Pattern of Compound **6**.

cinnamic acid were obtained from Aldrich Chemicals (USA). Diclofenac sodium and ketoprofen were kindly supplied by Wilson Pharmaceuticals, Islamabad. Ibuprofen was donated by Ferozesons Laboratories Ltd., Nowshera, Pakistan, while flurbiprofen was kindly provided by Upjohn Pakistan (Pvt) Ltd., Islamabad. All these chemicals were of high purity and used without further purification.

Acetone, dichloromethane and n-hexane were obtained from E-Merck Chemicals (Germany) and dried before use by reported methods [8].

General Procedure for Synthesis

As reported earlier [9], the bis(tributyltin) oxide 0.005 mole was added dropwise with constant stirring to 0.01 mole of organic acid in acetone (100 ml) contained in 250 ml two necked round bottom flask equipped with a water condenser and magnetic stirring bar,. The reaction mixture was refluxed for 3 to 4 hours. After cooling, acetone was removed through rotary apparatus under reduced pressure. All the complexes were recrystallized from CH_2Cl_2. The general chemical reaction is given below:



References

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