Maclafferty Rearrangement in Germyl Derivatives of Organo-tin Carboxylates

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Summary: Bimetallic compounds of general formula $[(R^1)_3GeCHR^2CHR^3COO]_2Sn[R^4]_2$ and $[R^1GeCHR^2CHR^3COO]Sn[CH_2C(CH_3)_3]_3$ have been synthesized by the reported methods and were studied by mass spectrometric analysis to explore their fragmentation pattern and formation of complexes as well. The spectral data indicates that these complexes undergo Maclafferty rearrangement during the fragmentation process. Another interesting feature observed was the formation of five membered germalactones, which may otherwise be formed by the classical synthetic routes. In diorganotin derivatives two fragmentation routes are observed. In route one, the loss of ligand takes place first and then loss of alkyl (R) group is observed. In second route, the loss of alkyl(R) group is followed by the loss of ligand. In *germatranyl* derivatives the base peak is always due to *germatrane* moiety reflecting its higher stability. Triorganotin derivatives of carboxylates containing germanium follow the same general pattern suggesting the primary decomposition of R group, followed by the removal of second R group and a loss of either carbon dioxide from ligand or of complete ligand. In most of the cases base peak is observed in triorganotin after the elimination of R group. The percentage abundance of major components was also compared. The fragment ions were in good agreement with the expected structure of the compounds.

Introduction

Tin is the only element that has ten naturally occurring isotopes. In the mass spectrum, these isotopes give rise to the characteristic peaks pattern (Fig. 1). Germanium also have characteristics isotopic distribution pattern. Its natural isotopic abundance are ^{70}Ge(20.5%), ^{72}Ge(27.4%), ^{73}Ge(7.8%), ^{74}Ge(36.5%), ^{76}Ge(7.8%).

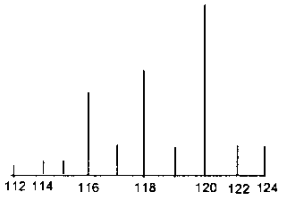

Fig. 1: Stable isotopes of tin.

Mass spectrometry has been growing as a tool in structural elucidation and an interpretation of organotin carboxylates [1, 2]. Bond dissociation energies for these compounds are relatively low, therefore, in organotin compounds, particularly large sized parent ions are not observed and the molecules suffer considerable fragmentation in the mass spectrometer. Smaller organotin molecules show molecular ion peaks as well as characteristics series of fragmentation ions [3].

The first mass spectrometric studies of orgnotin compounds reported in 1966 [4, 5] whereas, few reports are available on different aspects of mass spectrometry of organotin compounds [6-16]. Rather limited use has been made of mass spectrometry (MS) in the study of organotin compounds; though MS hyphenated gas-liquid chromatography (MS-GLC) is now being used for the identification of organotins, particularly in environmental studies. Most of the work has involved electron ionization (EI), though there are a few reports for other techniques such as chemical ionization (CI), fast atom bombardment (FAB), field adsorption, surface ionization, and electrospray also published [17-23].

Very little intensity of the molecular ion $R_4Sn^{\cdot+}$ is usually detected from R_4Sn at 70 eV. Fragmentation occurs to give R_3Sn^+ and $R^{\cdot}$, and indeed most of the ion current is carried by metal ions. When mixed groups present, alkyl is lost more readily than aryl, but, when alkyl with larger groups

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than methyl lost, the ion R_3Sn^+ can then eliminate olefin R(-H), to given R_2SnH^+ and this is the major ion in the spectrum of *n*-Pr_4Sn and *n*-Bu_2SnVin_2. R_2SnH^+ can eliminate another alkene R(-H), and $RSnH_2^+$ is the principal ion from R_4Sn. Groups R such as hydrogen, phenyl, or vinyl which cannot eliminate an alkene, instead lose the dimer R-R. The behavior of the tetra-1-, -2, and -3-butenylstannanes is similar. Allyl and benzyl compounds are reported to show no molecular ion under EI conditions, but do under CI in ammonia at 95.3 eV [24-31].

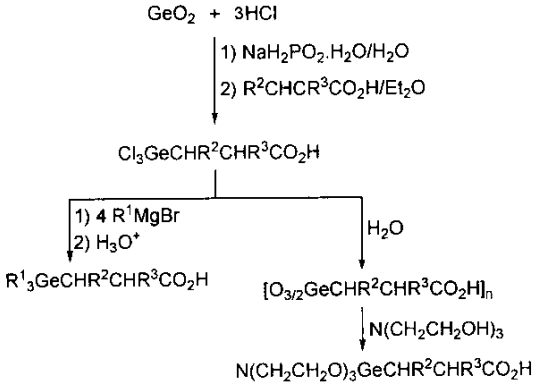
There has been much interest in organotin(IV) compounds due to its potential candidature as anti-tumor agent and biological applications [32]. Organogermanium compounds have attracted attention due to their physiological activities such as anticancer, antivirus and suppression of advanced glycation end product (AGE) [33]. Keeping in view the importance of organotin and organogermanium compounds we have reported the synthesis and characterization of organotin carboxylates containing germanium and their biological importance [34-38]. In present paper we are reporting mass spectral analysis of more than forty compounds. Detailed fragmentation of only five compounds is included that are the representative compound of each class. However, comparison of most important fragmentation is given in Tables-1 and 2.

Instrumentation

The mass spectral measurements of the compound were made on MAT 8500 mass spectrophotometer. The m/z values are computed by taking H = 1, C = 12 O = 16, Si = 28, F = 19, Ge = 74, Sn = 120 and N = 14.

Synthesis

The method used for the synthesis of the ligand containing germanium moiety is given in scheme 1 and synthesis of organotin carboxylates containing germanium is reported earlier [34-38].



Scheme 1: Synthesis of germanium containing ligand.

Results and Discussion

The investigated compounds were synthesized by reported methods [34-38] and are shown in Scheme 1 while nature of different R groups is given in Table-3.The electron impact mass

Table-1: Percentage of Main Fragments of Various Organotin Carboxylates containing germatranyl Moiety.

Common peaks	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
$N(CH_2CH_2O)GeCHRCH_2COO^+$	38	20	20	8	15	45	10	21	10	24	20	20	10	25	-	60	21	15	25	27	5	10
$CHRCH_2COO$	-	34	60	90	40	7	17	90	38	18	35	20	60	40	7	14	20	90	-	6	20	10
$Ge(CH_2CH_2O)N^+$	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
$CH_2CH_2O)_2CH_2Ge^+$	11	11	20	-	25	25	30	10	35	35	20	10	25	30	15	25	15	25	10	16	-	15
$CH_2CH_2O)_2CH_2\ CH_2Ge^+$	25	23	20	20	15	25	55	50	-	-	55	20	15	90	20	15	15	-	-	10	5	-
R_3Sn^+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	10	10	10
R_2Sn^+	10	7	18	10	10	16	34	80	24	25	5	15	15	30	34	15	25	15	15	10	20	15
RSn^+	14	8	10	-	50	23	23	90	20	25	10	8	10	60	23	10	20	10	-	6	10	10
SnH^+	8	18	6	16	70	13	13	50	40	20	15	6	70	20	15	12	10	70	12	15	10	28
Sn^+	12	12	12	19	35	12	12	15	20	20	15	5	35	7	12	12	12	35	13	14	16	13

Table-2: Percentage of Main Fragments of Various Organotin Carboxylates containing alkyl / aryl germyl moiety.

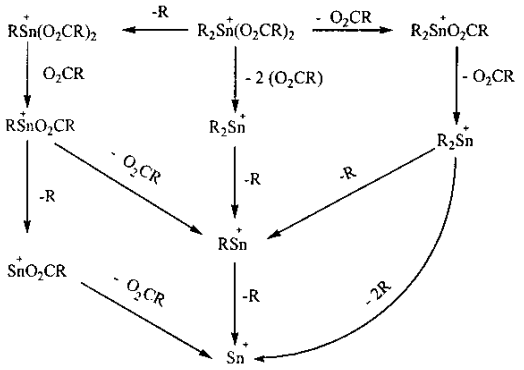
Common peaks	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44
R_3Ge	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
R_2Ge	5	78	12	50	72	60	25	40	15	35	20	5	20	7	35	35	15	5	15	-	-	-
RG	11	8	38	25	-	63	12	45	20	40	5	60	20	45	22	22	22	2	12	-	-	-
R_2Sn^+	5	14	-	15	-	14	15	20	15	40	40	20	20	5	10	10	10	50	2	15	7	7
RSn^+	-	11	-	10	-	7	10	8	12	4	30	20	20	10	35	35	35	2	2	23	8	8
SnH^+	6	31	12	6	6	10	7	7	5	4	10	10	12	5	15	15	15	10	10	-	10	10
Sn^+	12	12	12	12	20	12	7	12	15	5	12	8	12	18	20	20	20	8	8	12	10	10

Table-3: Description of groups in the synthesized compounds with general formula $[R_1GeCHR_2CHR_3COO]n\ Sn[R_4]m$.

Comp. No.	R_1	R_2	R_3	R_4
1	$(CH_2CH_2O)_3N$	C_6H_5	H	$CH_2Si(CH_3)_3$
2	$(CH_2CH_2O)_3N$	m-$CH_3OC_6H_4$	H	$CH_2Si(CH_3)_3$
3	$(CH_2CH_2O)_3N$	C_6H_5	H	$CH_2Si(CH_3)_2$ CH_2CH_3
4	$(CH_2CH_2O)_3N$	m-$CH_3OC_6H_4$	H	$CH_2Si(CH_3)_2$ CH_2CH_3
5	$(CH_2CH_2O)_3N$	p-ClC_6H_4	H	CH_3
6	$(CH_2CH_2O)_3N$	C_6H_5	H	CH_3
7	$(CH_2CH_2O)_3N$	p-ClC_6H_4	H	C_6H_5
8	$(CH_2CH_2O)_3N$	C_6H_5	H	C_6H_5
9	$(CH_2CH_2O)_3N$	CH_3	H	C_6H_5
10	$(CH_2CH_2O)_3N$	p-$CH_3OC_6H_4$	H	C_6H_5
11	$(CH_2CH_2O)_3N$	H	CH_3	C_6H_5
12	$(CH_2CH_2O)_3N$	p-$CH_3C_6H_4$	H	C_6H_5
13	$(CH_2CH_2O)_3N$	p-FC_6H_4	H	C_6H_5
14	$(CH_2CH_2O)_3N$	o-FC_6H_4	H	CH_3
15	$(CH_2CH_2O)_3N$	p-FC_6H_4	H	C_6H_5
16	$(CH_2CH_2O)_3N$	p-FC_6H_4	H	CH_3
17	$(CH_2CH_2O)_3N$	p-FC_6H_4	H	C_4H_9
19	$(CH_2CH_2O)_3N$	m-$CH_3OC_6H_4$	H	$(CH_3)_3CCH_2$
20	$(CH_2CH_2O)_3N$	C_6H_5	H	$(CH_3)_3CCH_2$
21	$(CH_2CH_2O)_3N$	o-FC_6H	H	$(CH_3)_3CCH_2$
22	$(CH_2CH_2O)_3N$	p-FC_6H_4	H	$(CH_3)_3CCH_2$
23	CH_3	m-$CH_3OC_6H_4$	H	$CH_2Si(CH_3)_3$
24	CH_3	C_6H_5	H	$CH_2Si(CH_3)_3$
25	C_2H_5	C_6H_5	H	$CH_2Si(CH_3)_2$ CH_2CH_3
26	C_2H_5	m-$CH_3OC_6H_4$	H	$CH_2Si(CH_3)_3$
27	C_2H_5	CH_3	H	$CH_2Si(CH_3)_2$ CH_2CH_3
28	C_2H_5	CH_3	H	$CH_2Si(CH_3)_3$
29	C_6H_5	C_6H_5	H	CH_3
30	C_6H_5	H	H	CH_3
31	C_6H_5	H	CH_3	CH_3
32	C_6H_5	CH_3	H	CH_3
33	p-$CH_3C_6H_4$	C_6H_5	H	C_6H_5
34	p-$CH_3C_6H_4$	p-$CH_3OC_6H_4$	H	CH_3
35	C_6H_5	CH_3	H	CH_3
36	C_6H_5	C_6H_5	H	C_6H_5
37	C_6H_5	H	H	C_6H_5
38	C_6H_5	CH_3	H	C_6H_5
39	p-$CH_3C_6H_4$	C_6H_5	H	C_6H_5
40	p-$CH_3C_6H_4$	p-$CH_3OC_6H_4$	H	C_6H_5
41	C_6H_5	CH_3	H	C_6H_5
42	C_6H_5	p-FC_6H_4	H	C_4H_9
43	C_6H_5	p-FC_6H_4	H	C_6H_5
44	C_6H_5	p-FC_6H_4	H	CH_3
45	C_6H_5	p-FC_6H_4	H	$(CH_3)_3CCH_2$-

For diorganotin compounds the value of n , m = 2
For triorganotin compounds n = 1 and m = 3
In germatranyl derivative R_1 is $=N(CH_2CH_2O-)_3$ and in all other compounds $R_1 = 3$,
All compounds are diorgantin dicarboxylates except 19-22 & 44 which are triorganotin carboxylates

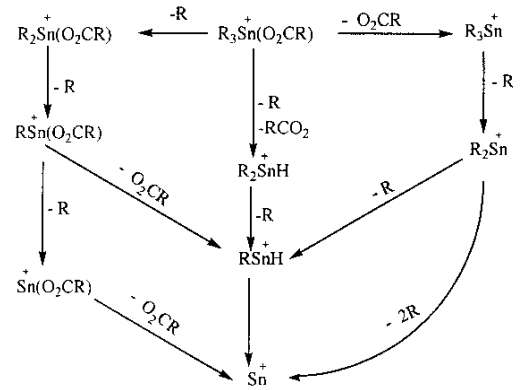
fragmentation of compounds and the general fragment patterns are given in Schemes 2 to 8. Molecular ion peak is observed only in compounds **2**, **6**, **13**, **15**, **19**, and **22**. Mostly the molecular ion peak is not observed in organotin derivatives. In compounds 1-4 organotin moiety containing silicon has the general formula $[RSi(CH_3)_2CH_2]_2Sn$ where R is either CH_3 or C_2H_5. The mass fragmentation of this moiety follows the same fragmentation pattern as observed in simple diorganotin derivatives.



Scheme 2: Plausible fragmentation pattern observed in diorganotin dicarboxylates

In dimethyltin, dibutyltin and diphenyltin derivatives fragmentation proceeds first with the loss of ligand and then successive loss of corresponding methyl, butyl, and phenyl group takes place. The possible mode of fragmentation is depicted in scheme 2.

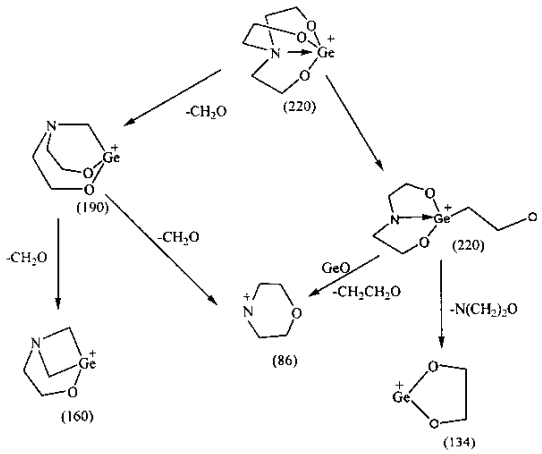
In triorganotin carboxylates, **19-22** and **44** where R group is neopentyl, cleavage of R group took place with the successive loss of second R group followed by loss of either carbon dioxide or ligand. Some time loss of ligand took place first followed by successive loss of R groups. The general fragmentation is shown in scheme 3.



Scheme 3: Plausible fragmentation pattern observed in triorganotin carboxylates.

In the mass spectra of germatrane compounds peak of highest intensity at m/z 220 a.m.u. corresponds to the germatranyl ion resulting from the cleavage of germanium-carbon bond in the parent ion. This behavior is analogous to that

observed for 1-allylgermatrane, 1-fluorenyl-germatrane and is assumed to be reflection of relative higher bond strength of Ge-O ring bonds as compared to that of Ge-C exocyclic bond. A cluster of peaks at m/z 130 a.m.u. has been attributed to the ion $[GeN(CH_2)_3]^+$. The general fragmentation of germatranyl derivatives follows the pattern given in Scheme 4. From the data, it is observed that the mass spectral breakdown of germatranes takes place by two main routes, the first of which is associated to three successive losses of m/z 30 a.m.u., formaldehyde molecules from the molecular ion. The second course of the fragmentation is associated with the germatranyl cation, which repeatedly eliminates OCH_2CH_2 (m/z 44 a.m.u.) to give Ge^+. The fragment ions are in good agreement with the expected structure of the compounds, also elucidated by other spectroscopic techniques.

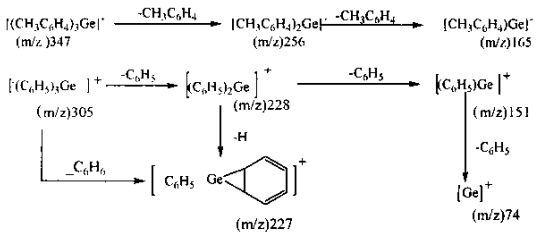


Scheme 4: Plausible fragmentation pattern of germatranyl moiety.

Compounds **23-28** contain silicon moiety attached to tin atom. The general formula of this silicon containing group is $[R(CH_3)_2SiCH_2]_2Sn$ where R is either methyl or ethyl group attached to silicon. The fragmentation follows same general route as observed in simple alkyl or aryl organotin derivatives. In compounds **1-3** and **23-28**, first cleavage took place through Sn-C bond as compared to Si-C bond indicating a greater stability of Si-C bond over Sn-C bond. This moiety then decomposes through the cleavage of Si-C bond with the loss of either CH_4 or CH_2=CH_2.

Diorganotin dicarboxylates containing alkyl/ aryl moiety are also subjected to electron impact mass spectrometry. The main fragments are listed in Table-3 and general fragmentation pattern is shown in Scheme 2. Molecular ion peaks are observed only for compounds **24**, **28**, **30**, and **44** of very low intensity. The fragmentation pattern of R_3Sn^+ and R_3Ge^+ can be compared. Trialkyltin and trialkayl-germanium moieties follow the same fragmentation route. The successive loss of R groups takes place in both cases. In a small number of compounds R_3Sn^+ appears as a base peak while R_3Ge^+ appears in most of the cases as a base peak, reflecting the stability of R_3Ge^+ over R_3Sn^+. Organotin compounds have a unique feature in mass spectrometric analysis which is not observed with other elements *i.e.* the existence of a cluster of peaks due to large no of naturally occurring stable isotopes of tin. Germanium has also isotopic effect but less pronounced as compared to tin. Cluster of peaks are observed in studied compounds due to the presence of tin (Sn) and germanium (Ge).

In mass spectral fragmentation of alkyl or aryl substituted germanium R_3Ge (where R is CH_3, C_2H_5, C_6H_5 and *p*-$CH_3C_6H_4$) the peak of highest intensity is found at 119, 161, 305 and 347 a.m.u., respectively. In alkyl or aryl substituted germanium R_3Ge the successive loss of alkyl or aryl groups takes place as shown in scheme 5.



Scheme 5: Fragmentation of aryl substituted germanium.

A peak at 227 a.m.u. was found in phenyl derivative, which is more likely due to $[C_6H_5GeC_6H_4]^+$. In recent years there has been a renewed interest in the synthesis of structurally simple germalactones [39].

This ring system widely present in secondary metabolites show interesting physiological activities [40]. Even though the lactone system is widely distributed in nature, very few reports are available on metallolactones. Mehboob *et al* have

reported the crystal structure of germa-γ-lactone Fig. 2 [41]. The EI-MS spectra indicate that Maclafferty rearrangement may take place during fragmentation. Scheme 6 illustrates this interesting behavior. Initially the molecular ion breaks into a germyl containing carboxylate ion in a normal fashion followed by Macklefferty rearrangement to form the germalactone. The decomposition of ligand containing germanium takes place first from organotin carboxylates. The germanium containing moiety having general formula [RGeCHRCH$_2$COO] shows Maclafferty rearrangement to form germalactone as shown in scheme 6 This germalactone eliminates an alkene molecule to give [Ge-CO$_2$]$^+$ which undergoes further decomposition yielding Ge$^+$ ion.

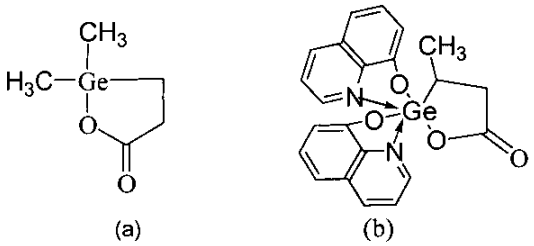
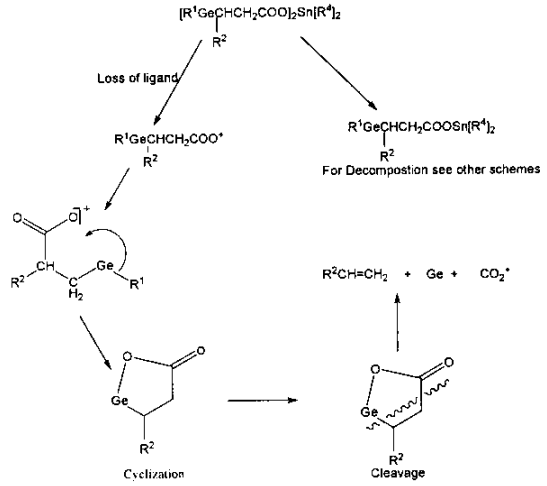


Fig. 2: Representative Germalactones.



Scheme 6: Maclafferty rearrangement in germyl derivatives of organotin.

Bis(trimethylsilymethylene) tin(IV) bis-(3-methoxy-phenyl-3-germatranyl) Proponoate (Compound 2)

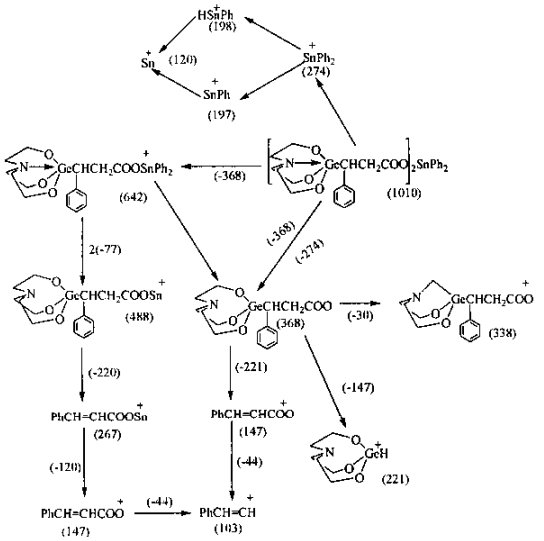
[((CH$_2$CH$_2$O)$_3$NGeCH(C$_6$H$_4$OCH$_3$)CH$_2$COO)$_2$Sn(CH$_2$ Si(CH$_3$)$_3$)$_2$]$^+$ 1090 (5),
[((CH$_2$CH$_2$O)$_3$NGeCH(C$_6$H$_4$OCH$_3$)CH$_2$COO)Sn(CH$_2$ Si(CH$_3$)$_3$)$_2$]$^+$ 692 (5),
[((CH$_2$CH$_2$O)$_3$NGeCH(C$_6$H$_4$OCH$_3$)CH$_2$COO)Sn(CH$_2$ Si(CH$_3$)$_3$)]$^+$ 605 (7),
[((CH$_2$CH$_2$O)$_3$NGeCH(C$_6$H$_4$OCH$_3$)CH$_2$COO)Sn]$^+$ 518 (32),
[(CH$_2$CH$_2$O)$_3$NGeCH(C$_6$H$_4$OCH$_3$)CH$_2$ COO)]$^+$ 398 (25), [Sn(CH$_2$Si(CH$_3$)$_3$)$_2$]$^+$ 294 (7),
[(CH$_2$CH$_2$O)$_3$NGe]$^+$ 220 (100), [Sn(CH$_2$Si(CH$_3$)$_3$)]$^+$ 207 (8),
[(CH$_2$CH$_2$O)$_2$NGe(CH$_2$)]$^+$ 190 (11), [CH(C$_6$H$_4$ OCH$_3$)CH$_2$COO)]$^+$ 178 (34),
[Sn(CH$_2$Si(H$_3$)]$^+$ 165 (38),
[((CH$_2$CH$_2$O) NGe(CH$_2$)$_2$]$^+$ 160 (23),
[(CH$_2$CH$_2$OH)$_3$N]$^+$ 149 (20),
[(CH$_2$CH$_2$O)$_3$N]$^+$ 146 (19), [(C$_6$H$_4$ OCH$_3$)CHCH$_2$)]$^+$ 134 (16), [((CH$_2$)$_3$NGe]$^+$ 130 (7),
[SnH]$^+$ 121 (8), [Sn]$^+$ 120 (12), [N(CH$_2$CH$_2$)$_2$O]$^+$ 86 (34) .

Dimethyltin(IV) bis-(3-phenyl-3-germatranyl) Propo-noate (Compound 6)

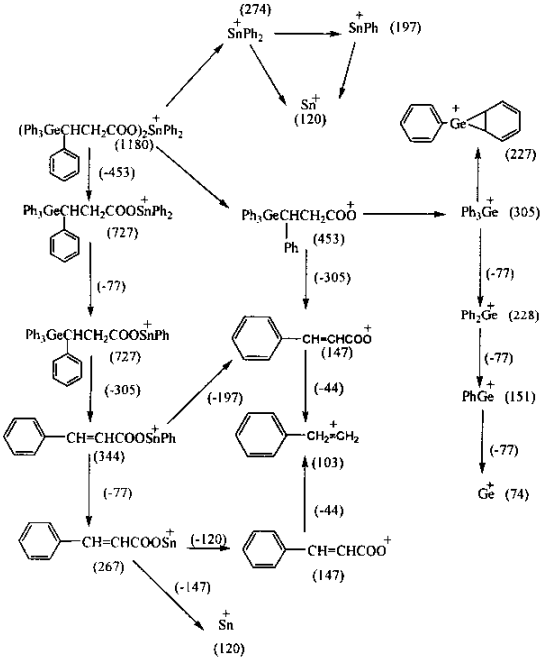
[((CH$_2$CH$_2$O)$_3$NGeCH(C$_6$H$_5$)CH$_2$COO)$_2$Sn(CH$_3$)$_2$]$^+$8 86 (5),
[((CH$_2$CH$_2$O)$_3$NGeCH(C$_6$H$_5$)CH$_2$COO)$_2$Sn(CH$_3$)]$^+$87 1 (6),
[((CH$_2$CH$_2$O)$_3$NGeCH(C$_6$H$_5$)CH$_2$COO)$_2$Sn]$^+$856 (8),
[((CH$_2$CH$_2$O)$_3$NGeCH(C$_6$H$_5$)CH$_2$COO)Sn(CH$_3$)$_2$]$^+$51 8 (32),
[((CH$_2$CH$_2$O)$_3$NGeCH(C$_6$H$_5$)CH$_2$COO)Sn(CH$_3$)]$^+$503 (20),
[((CH$_2$CH$_2$O)$_3$NGeCH(C$_6$H$_5$)CH$_2$COO)Sn]$^+$488 (34),
[((CH$_2$CH$_2$O)$_3$NGeCH(C$_6$H$_5$)CH$_2$COO]$^+$ 368 (45),
[(CH$_2$CH$_2$O)$_3$NGe]$^+$ 220 (100)
[((CH$_2$CH$_2$O)$_2$NGe(CH$_2$)]$^+$ 190 (25),
[((CH$_2$CH$_2$O) NGe(CH$_2$)$_2$]$^+$ 160 (25) [Sn(CH$_3$)$_2$]$^+$ 150 (16),
[CH(C$_6$H$_5$)CH$_2$COO]$^+$ 148 (7), [CH(C$_6$H$_5$)CHCOO]$^+$ 147 (5), [(CH$_2$CH$_2$O)$_3$N]$^+$ 146 (30), [Sn(CH$_3$)]$^+$ 135 (23), [(CH$_2$)$_3$NGeH]$^+$ 131 (60), [HSn]$^+$ 121 (13), [Sn]$^+$ 120 (12),[N(CH$_2$CH$_2$)$_2$O]$^+$ 86 (45) .

Tris(neopentyl)tin(IV) 3-F-phenyl-3-germatranyl) Proponoate (Compound 22)

[((CH$_2$CH$_2$O)$_3$NGeCH(C$_6$H$_4$F)CH$_2$COO)Sn(CH$_3$)$_3$CC H$_2$)$_3$]$^+$ 719 (n.o)
[((CH$_2$CH$_2$O)$_3$NGeCH(C$_6$H$_4$F)CH$_2$COO)Sn(CH$_3$)$_3$CC H$_2$)$_2$]$^+$ 649 (60)
[((CH$_2$CH$_2$O)$_3$NGeCH(C$_6$H$_4$F)CH$_2$COO)Sn(CH$_3$)$_3$CC H$_2$)]$^+$ 577(10)
[((CH$_2$CH$_2$O)$_3$NGeCH(C$_6$H$_4$F)CH$_2$COO)Sn]$^+$ 506 (8)



Scheme 7: Plausible fragmentation pattern observed in diorganotin dicarboxylates.



Scheme 8: Plausible fragmentation pattern observed in diorganotin dicarboxylates.

$[(CH_2CH_2O)_3NGeCH(C_6H_4F)CH_2)Sn]^+$ 459(15) $[((CH_2CH_2O)_3NGeCH(C_6H_4F)CH_2COO)]^+$ 386 (10) $[Sn(CH_3)_3CCH_2)_3]^+$ 333 (15)$[Sn(CH_3)_3CCH_2)_2]^+$ 262 (10), $[(CH_2CH_2O)_3NGe]^+$ 220 (50) $[Sn(CH_3)_3CCH_2)]^+$191 (10) , $[((CH_2CH_2O)_2NGe(CH_2)]^+$ 190 (15), $[(CH_2CH_2O)NGe(CH_2)_2]^+$ 160 (5), $[CH(C_6H_4F)CH_2COO)]^+$ 165 (10) $[(CH_2CH_2OH)_3]$ 149,(50)$[HSn]^+$ 121 (28), $[Sn]^+$ 120 (13), $[N(CH_2CH_2)_2O]^+$ 86 (5), [GeOH] 91 (5)$[(CH_3)_3CCH_2)]^+$ 71 (100) $[(CH_3)_3C)]^+$ 57 (60) .

Bis(trimethylsilymethylene) tin(IV) bis-(3-methoxyphenyl-3-tris(methyl)germyl) Proponoate (Compound 23)

$[((CH_3)_3GeCH(C_6H_4OCH_3)CH_2COO)_2Sn(CH_2Si(CH_3)_3)_2]^+$ 888 (n.o), $[((CH_3)_3GeCH(C_6H_4OCH_3)CH_2COO)_2Sn(CH_2Si(CH_3)_3)]^+$ 801(5), $[((CH_3)_3GeCH(C_6H_4$ $CH_3O)CH_2COO)CH(C_6H_4OCH_3)CH_2COO)Sn]^+$ 595 (3), $[((CH_3)_3GeCH(C_6H_4OCH_3)CH_2COO)Sn(CH_2Si(CH_3)_3)_2]^+$ 591 (60), $[((CH_3)_3GeCH(C_6H_4OCH_3)CH_2COO)Sn(CH_2Si(CH_3)_3)]^+$ 504 (15), $[(CH(C_6H_4OCH_3)CH_2COO)Sn(CH_2Si(CH_3)_3)_2]^+$ 471 (12), $[(CH_3)_3GeCH(C_6H_4OCH_3)CH_2COO]$ 297 (23), $[Sn(CH_2Si(CH_3)_3)_2]^+$ 294 (20), $[HSn(CH_2Si(CH_3)_3)]^+$ 208 (20) $[(CH(C_6H_4OCH_3)CH_2COO]^+$ 177 (4), $[(CH(C_6H_4OCH_3)CH_2]$ 134 (73), $[HSn]^+$ 121 (6), $[Sn]^+$ 120 (12), $[(CH_3)_3Ge]^+$119 (100), $[(CH_3)_2Ge]^+$104 (5), $[(CH_3)Ge]^+$89 (11), $[Ge]^+$ 74 (5), $[CH_2Si(CH_3)_3)_2]^+$ 72 (18), $[Si(CH_3)_3)]^+$ 58 (10)

Diphenyl tin(IV) bis(3-phenyl-3-(methyl-phenylgermyl) Proponoate (Compound 33)

$[((CH_3C_6H_4)_3GeCH(C_6H_5)CH_2COO)_2Sn(C_6H_5)_2]^+$ 1264 (n.o), $[((CH_3C_6H_4)_3GeCH(C_6H_5)CH_2COO)_2Sn(C_6H_5)_2]^+$ 1110 (8), $[((CH_3C_6H_4)_3GeCH(C_6H_5)CH_2COO)(CH(C_6H_5)CH_2$ $COO)Sn(C_6H_5)_2]^+$ 840(80), $[((CH_3C_6H_4)_3GeCH(C_6H_5)CH_2COO)Sn(C_6H_5)_2]^+$ 769 (50), $[((CH_3C_6H_4)_3GeCH(C_6H_5)CH_2COO)(CH(C_6H_5)CH_2$ $COO)Sn(C_6H_5)_2]^+$ 763 (20), $[(CH_3C_6H_4)_3GeCH(C_6H_5)CH_2COO)Sn]^+$ 615 (40), $[(C_6H_5)_3GeCH(C_6H_5)CH_2COO)]^+$ 495 (8), $[(CH_3C_6H_4)_3Ge]^+$ 347 (100), $[(CH_3C_6H_4)_3Ge]^+$ 256 (5), $[(CH_3C_6H_4)GeC_6H_4)]^+$ 255(30),$[Sn(C_6H_5)_2]^+$ 274 (50),

$[(CH(C_6H_5)CH_2COO)Sn]^+$ 267 (2),$[Sn(C_6H_5)]^+$ 197 (2), (15),
$[(CH_3C_6H_4Ge]^+$165 (60), $[(CH(C_6H_5)CH_2COO)]^+$ 147 (5),
$[HSn]^+$ 121 (15), $[Sn]^+$ 120 (20)
$[(CH(C_6H_5)CH_2)]^+$ 103 (5), $[CH_3C_6H_4]^+$ 91 (15)

Conclusion

It is concluded that triorganotin carboxylates containing germanium follow the same general pattern as observed for simple organotin derivatives. As depicted in scheme 4 which suggests the primary decomposition follows the elimination of R group. After the elimination of R group cleavage of ligand takes place and sometime loss of carbon dioxide take place and as a result $[SnR]^+$ is formed in tiorganotin compounds. In most cases base peak is observed after the elimination of R group. Diorganotin generally follows two fragmentation routes; first loss of ligand takes place and then loss of R group. In second route first loss of R group which follow then either second R group or loss of second ligand as shown in Scheme 2. In germatranyl derivatives the base peak is due to germatranyl moiety whereas in alkylgermanium derivatives same behavior is observed for the existence of base peak. Macklafferty rearrangement takes place in germanium containing moiety with the formation of germalactone. The complete decomposition detail is included for representative compound of each class.

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