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Synthesis and Mass Spectra of Butenyltin Compounds

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   Symmetrical tetra-n-butenyltins and tri-n-butenyltin bromides with double bonds at C-1, C-2, and C-3 were first synthesized. Then low-resolution electron-impact mass spectra of these compounds were obtained. The fragmentation patterns of the compounds are similar, but the ratios of tin-containing fragment ions are unique. The position of the double bonds could not be determined by distinctive fragmentations of the butenyl sidechains.

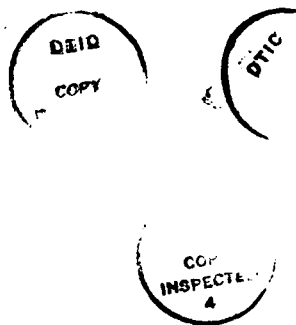| 20. DISTRIBUTION/AVAILABILITY OF ABSTRACT			21. ABSTRACT SECURITY CLASSIFICATION	
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INTRODUCTION

The Navy has become increasingly concerned with the potential effect on the environment of any of its activities or operations. One instance of this concern has focused on the Navy's use of tributyltin compounds as antifoulants on ships' hulls. Such compounds, though effective, appear to be harmful to the environment and may find their way into the food chain.

NOSC undertook a study to evaluate the feasibility of using organotin compounds with altered structures that will degrade more readily to a less toxic form while retaining sufficient toxicity to maintain effective antifouling properties.[1]

In the course of this study, NOSC chemists made some significant observations on correlations between the chemical structure and behavior of ions under electron impact. This report is intended to document those observations.

Tetraalkyltins exhibit characteristic mass spectra resulting from the successive loss of alkyl groups from the tin atom.[2-5] The parent ion is either weak or non-existent. There is low abundance of ions from fragmentation of the alkylchain. The favored ion is trisubstituted tin. Monosubstituted tin ions are relatively abundant; disubstituted tin ions are in low abundance and are probably not even present because an unfavorable tin oxidation state would result. Tetraallyltin and tetravinyltin spectra are similar except that neutral diene elimination is favored.[6,7] Trialkyltin halides show similar mass spectra fragmentation patterns where successive loss of the alkyl groups is favored over loss of the halide ion.[8]

Symmetrical tetra-n-butenyltin and tri-n-butenyltin compounds with double bonds at C-1, C-2, and C-3 were prepared. Their low-resolution electron impact mass spectra were obtained to explore the effect of double bond location on the resulting mass spectra.

EXPERIMENTAL

CHEMICALS

Tetraallyltin, tetravinyltin, 1-bromo-1-butene, 4-bromo-1-butene, and 1-chloro-2-butene were obtained from Pfaltz & Bauer (Waterbury, CT). Resublimed magnesium chips, tetrabutyltin and tributyltin bromide were obtained from Alfa Products (Danvers, MA). All were used without further purification.

PREPARATION OF TETRA-N-ALKENYLTIN COMPOUNDS

Tetra-n-alkenyltin compounds were prepared by Grignard synthesis.[9-13] For the synthesis of tetra-1-butenyltin and tetra-3-butenyltin, a Grignard reagent was prepared by the dropwise addition of approximately 10 g 1-bromo-1-butene or 4-bromo-1-butene in 10 ml anhydrous tetrahydrofuran to an excess of magnesium chips, which were just covered with tetrahydrofuran and kept under dry argon. After the alkenylhalide was added, the mixture was maintained at reflux for 4 hours. For the preparation of tetra-2-butenyltin, the Grignard reagent was formed from 1-chloro-2-butene. After the reaction was initiated, the reagent was immediately cooled to

-10°C and stirred at that temperature for 9 hours during and after the addition of 1-chloro-2-butene

To prepare the tetraalkenyltin compound, it was necessary, first, to decant the Grignard reagent from the excess magnesium chips, then cool it to 0°C. Approximately 2 g anhydrous SnCl₄ in 10 ml hexane was added dropwise to the stirred solution. The mixture was refluxed for 4 hours and then left at room temperature overnight.

The reaction mixture was cooled to 0°C and hydrolyzed with 3% HCl. The separated organic layer was shaken with 5% aqueous KF to precipitate organotin chlorides or bromides as insoluble fluorides. The solvent and low boiling side products were then removed under vacuum at room temperature from the separated organic layer, and the residue was washed through a 22X1-cm Florisil column with hexane. The solvent was again removed under vacuum. A typical yield of the tetrabutenyltins was ~80%; their purity was >98%.

PREPARATION OF TRI-N-ALKENYLTIN BROMIDES

Approximately 1 g tetraalkenyltin was suspended in 10 ml methanol. A stoichiometric amount of bromine in methanol was added dropwise in dim light to the stirred tetrabutenyltin mixture.[2,14] Monobromination of the tetraalkenyltin to form tri-1-butenyltin bromide, tri-2-butenyltin bromide, and tri-3-butenyltin bromide was achieved by conducting the reaction at 0°C, –50°C, and 20°C, respectively. Upon completion of the reaction, the solvent and low boiling side products were removed under vacuum at room temperature. The crude product was washed through a Florisil column, first with hexane to recover unreacted tetraalkenyltin and then with 1:4 (v/v) ethyl acetate/hexane to selectively elute the trialkenyltin bromide. Solvent was then removed under vacuum. Yields were 94% for tri-3-butenyltin bromide and 50% for tri-1-butenyltin bromide. Tri-2-butenyltin bromide was too reactive to undergo purification. The final purity of isolated compounds was >98%.

INSTRUMENTATION

Retention times and mass spectra of synthesized and purchased compounds were obtained with a Hewlett-Packard Model 5890A Gas Chromatograph directly connected to a Hewlett-Packard Model 5970 Mass Selective Detector (GC/MS). Data collection and reduction were performed with a Hewlett-Packard 9000-300 Computer using Model 59970C ChemStation software. Samples were run using splitless injection onto a 12.5 m by 0.2 mm-I.D. HP-1 fused-silica capillary column with a 0.33-μm coating thickness. Helium carrier gas was used at a head pressure of 40 kPa. The oven was programmed, after an initial 2-minute hold at 50°C, to 230°C at 30°C/min. Injector, transfer line, and detector were at 250°C. Masses were scanned between 50 and 450 amu. Electron energy is fixed at 70 eV for this instrument.

IR spectra were obtained using a Digilab FTS-60 Fourier Transform IR Spectrometer interfaced with a Hewlett-Packard Model 5890A Gas Chromatograph at the chromatographic conditions detailed above.

RESULTS AND DISCUSSION

A GC/MS was used to monitor the progress of the reactions and purity of the products. The tetrabutenyltins and the tributenyltin bromides were differentiated by gas chromatographic retention times, IR spectrometry, and mass spectrometry. Where cis-trans isomers were present in the starting butenylhalides, a mixture of isomeric butenyltins was formed. Although these isomers could be separated by gas chromatography, they could not be chemically separated and purified. Mass spectra of stereoisomers were identical.

Position and retention of the double bonds were verified by characteristic $C = C$ infrared vibration bands. These occurred at 1597.1 and 1600 cm^{-1} for tetra-1-butenyltin and tri-1-butenyltin bromide, respectively; at 1647 cm^{-1} for tetra-2-butenyltin and at 1639.5 cm^{-1} for tetra-3-butenyltin and tri-3-butenyltin bromide.[9,15]

Qualitatively, the mass spectra of the tetrabutenyltins resemble the mass spectrum of tetrabutyltin in their fragmentation patterns. The mass spectra of tetra-1-butenyltin, tetra-2-butenyltin, and tetra-3-butenyltin are shown in Fig. 1a, 1b, and 1c, respectively. In general, these spectra are characterized by analogous clusters of tin-containing fragments with two less mass units (H atoms) per attached carbon chain than the tetrabutyltin. The clusters are formed by the ten stable tin isotopes, their associated alkyl or alkenyl groups, and one or more abstracted hydrogen atoms.

The relative intensities of the major fragment ions, normalized to the largest peak occurring between m/z (mass/charge) 100 and 350 (referred to as the base peak for our purposes), for tetrabutyltin, the tetrabutenyltins, tetraallyltin, and tetravinyltin are shown in Table 1. These data for both experimental compounds and purchased reference materials were obtained in the laboratory. The observed base peaks are $RSnH_2^+$ for tetrabutyltin and RSn^+ for both tetra-2-butenyltin and tetraallyltin. R_3Sn^+ is the base peak for tetra-3-butenyltin and tetra-1-butenyltin. In tetravinyltin, the base peak is Sn^+, but RSn^+ and R_3Sn^+ are nearly as large. Similarity in fragment ion abundances is greatest between tetraallyltin and tetra-2-butenyltin.

The observed fragment ions arise from the successive elimination of R (the alkyl or alkenyl neutral fragment), R minus H (where the H remains with the tin-containing ion), R plus H, or R minus R (where two alkenyls form a diene leaving group). These are simultaneous and competing decomposition processes. Elimination of R appears to be the first step for all the compounds. The successive loss of R minus H or R plus H then seems to be the favored mechanism for most of the compounds. Tetraallyltin and tetra-2-butenyltin are exceptions. The low intensity of the fragment that contains two carbon chains in the mass spectra of these two compounds indicates the preferential elimination of R minus R to form RSn^+ from R_3Sn^+.

The fragmentation patterns of tributyltin bromide and tributenyltin bromides are dominated by SnBr-containing ions and resemble each other to the same extent as the R_4Sn compounds. Mass spectra of tri-1-butenyltin bromide, tri-2-butenyltin bromide and tri-3-butenyltin bromide are shown in Fig. 2a, 2b, and 2c, respectively. Because of the added isotope contribution from bromine, it is more difficult to determine the identities of the fragment losses, but some observations can be made. Intensities of the major fragment ions are summarized in Table 2. The base peak is R_2SnBr^+ for all but tri-2-butenyltin bromide, for which it is $SnBr^+$. Abundance of the
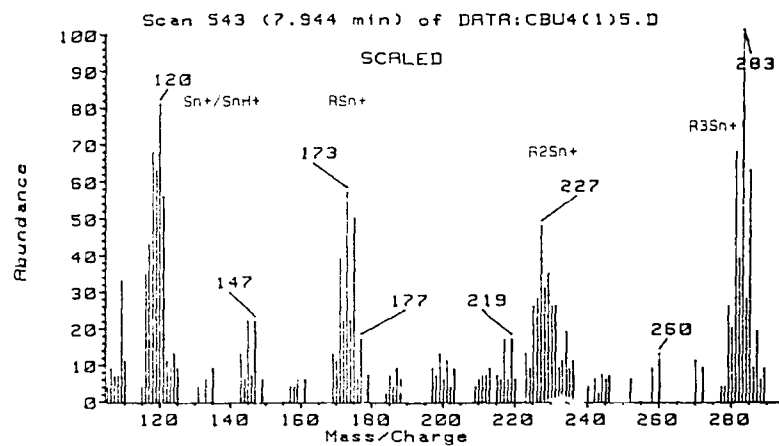
fragment $RSnBr^+$ or $RHSnBr^+$ is low for all the compounds containing double bonds; this suggests that R minus R fragment loss from the R_2SnBr^+ ion is a dominant mode of decomposition.

An examination of only the Sn^+ cluster, summarized in Table 3, shows detailed differences among the R_4Sn compounds. Column 1 shows the ion fragments from m/z 112 to 127 found in organotin compounds. The natural isotope abundances for the ten stable isotopes of tin are shown in column 2. The observed ion abundances between m/z 112 and 127 for tetravinyltin, tetraallyltin, tetrabutyltin, and tetrabutenyltins with the double bond in the 1, 2, and 3 positions are shown in columns 3 through 8, respectively. Similarities in ion abundances can be seen between tetravinyltin and tetra-1-butenyltin, with the double bond at C-1, and between tetraallyltin and tetra-2-butenyltin, which have the double bond at C-2. Tetra-3-butenyltin, with the double bond displaced farthest from the central tin atom, shows greatest similarity to tetrabutyltin. SnH^+ and SnH_3^+ ions alter the observed stable tin isotope abundances and are responsible for the appearance of ions at m/z where stable tin isotopes do not exist. SnH_2^+ is not formed because an unfavorable oxidation state would result.
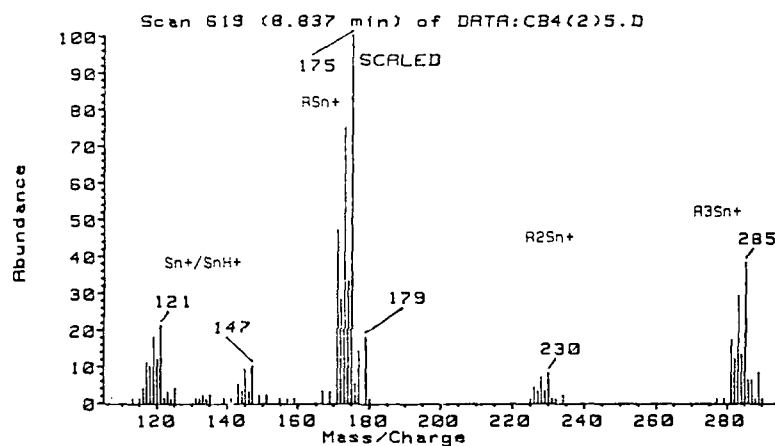
The marked differences in observed ion abundance for the $Sn^+/SnH^+/SnH_3^+$ cluster with double bond position do not occur if one of the carbon chains is replaced with bromine to form R_3SnBr. As seen in Table 4, the observed ion intensities between m/z 112 and 127 for tributyltin bromide and the three tributenyltin bromides are quite similar except for SnH_3^+ at m/z 127, which occurred only in the fully saturated compound.

The contribution from Sn^+, SnH^+, and SnH_3^+ to m/z 112 to 127 was determined algebraically for each compound. These data are summarized in Table 5. The greatest probability of the occurrence of SnH_3^+, which arises from successive R minus H loss from the tin, is in compounds with no double bonds. Increasing SnH_3^+ abundance is associated with increasing metal–carbon bond strength.[e] The experimental data would support this view since SnH_3^+ abundance appears in the following sequence: tetrabutyltin > tetra-1-butenyltin, tetra-3-butenyltin > tetra-2-butenyltin. R_4Sn compounds display greater SnH_3^+ than corresponding R_3SnBr compounds.

Double bond migration is a common occurrence under electron impact. Because of this, the double bond position in the parent compound cannot be directly determined by the presence or absence of distinctive ion fragments resulting from the directed fragmentation of the carbon chains. However, the location of double bonds in tetrabutenyltins and tributenyltin bromides influences the fragmentation patterns obtained under electron impact ionization. Unique fragment ion ratios, resulting from differences in dominant fragmentation mechanisms, clearly distinguish between the compounds containing double bonds.

Scan 543 (7.944 min) of DATA:CBU4(1)5.D

(a) Tetra-1-butenyltin.

Scan 619 (8.837 min) of DATA:CB4(2)5.D

(b) Tetra-2-butenyltin.

Scan 564 (8.230 min) of DATA:CB4(3)1.D
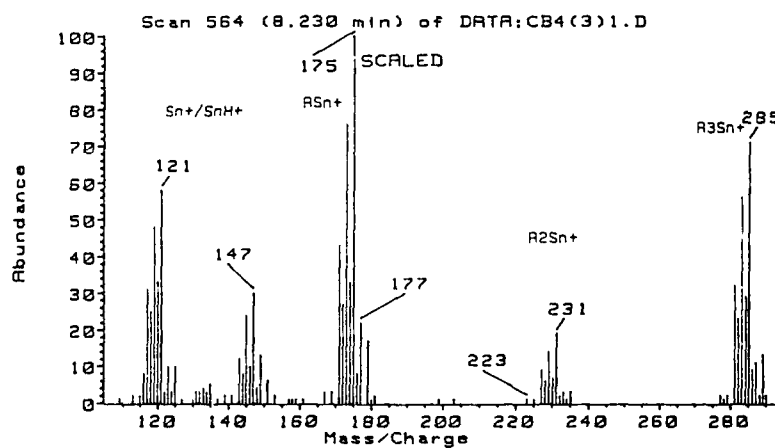
(c) Tetra-3-butenyltin.

Figure 1. Mass spectra of tetrabutenyltins.

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Scan 541 (7.936 min) of DATA:CB3(1)1.D

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(a) Tri-1-butenyltin bromide.

Scan 579 (8.401 min) of DATA:CB3(2)B.D

(b) Tri-2-butenyltin bromide.

Scan 432 (7.471 min) of DATA:TB3(3)A.D

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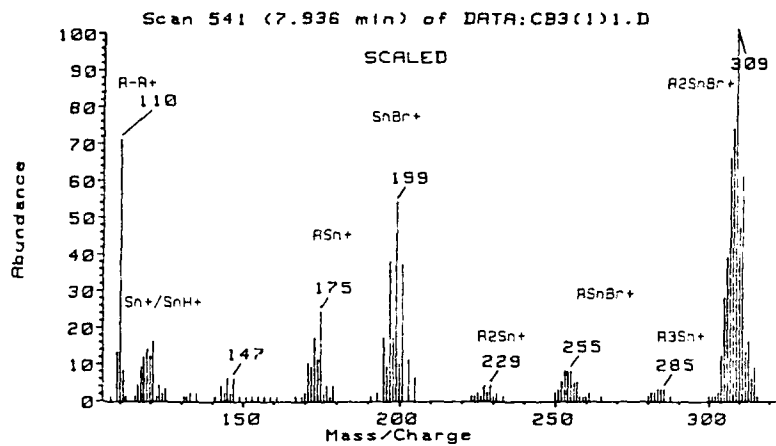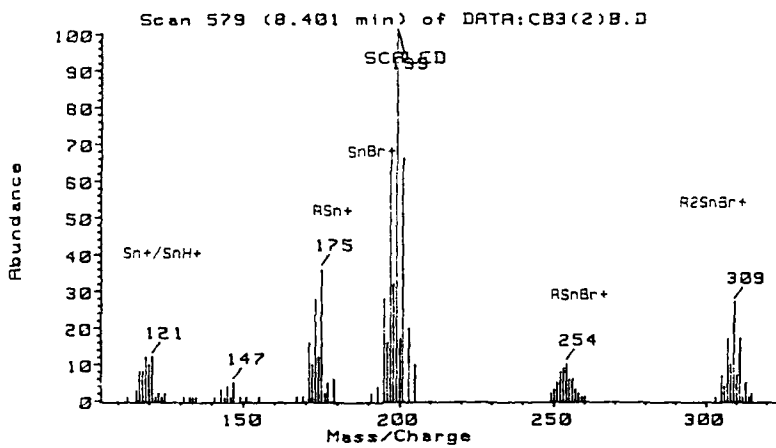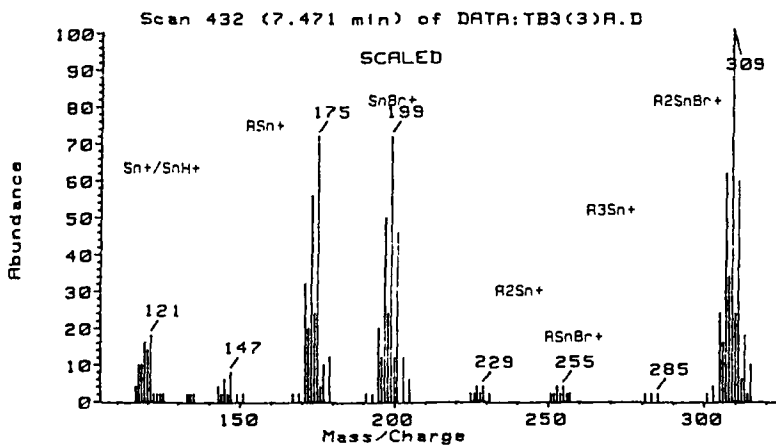
(c) Tri-3-butenyltin bromide.

Figure 2. Mass spectra of tributenyltin bromides.

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Table 1. Fragment ion intensities of tetraorganotin compounds (R_4Sn).

R Group	SnH_i^+		$RSnH_i^+$		$R_2SnH_i^+$		R_3Sn^+	
	m/z	Int.	m/z	Int.	m/z	Int.	m/z	Int.
Butyl	121	67	179	100	235	66	291	49
1-Butenyl	120	59	175	44	231	41	285	100
2-Butenyl	121	22	175	100	230	7	285	35
3-Butenyl	121	38	175	81	231	20	285	100
Allyl	120	21	161	100	202	9	243	22
Vinyl	120	100	147	82	175	55	201	75

i = 0-3

Table 2. Fragment ion intensities of triorganotin bromides (R_3SnBr).

R Group	SnH_i^+		$RSnH_i^+$		$SnBr^+$		$RSnBrH_i^+$		$R_2SnBrH_i^+$	
	m/z	Int.	m/z	Int.	m/z	Int.	m/z	Int.	m/z	Int.
Butyl	121	21	177	21	199	49	257	45	313	100
1-Butenyl	121	29	175	39	199	98	255	11	309	100
2-Butenyl	121	12	175	36	199	100	254	10	309	28
3-Butenyl	121	19	175	63	199	52	255	4	309	100

i = 0–3

Table 3. Fragment ion intensities (%) for tetraorganotin compounds (R_4Sn).

m/z	Natural Abundance (Sn)	R					
		Vinyl	Allyl	Butyl	1-Butenyl	2-Butenyl	3-Butenyl
112	1.0	0.8	0.6	0.1	0.6	0.3	0.2
113	0	0.3	0.6	0.6	0.4	0.7	0.8
114	0.7	0.6	0.3	0.2	0.4	0.2	0.1
115	0.4	0	0	0.7	0	0.7	0.7
116	14.7	10.6	6.7	3.1	8.4	4.0	3.4
117	7.7	9.9	11.6	10.5	10.6	13.1	12.8
118	24.3	19.4	15.1	8.9	17.0	12.2	10.8
119	8.6	13.7	16.7	18.8	15.4	20.1	20.4
120	32.4	25.2	19.9	12.9	21.6	14.5	14.2
121	0	8.9	17.1	24.2	13.8	23.4	25.0
122	4.6	3.3	2.5	2.6	3.0	1.1	1.4
123	0	1.7	2.6	10.1	2.4	3.8	4.1
124	5.6	4.2	2.9	1.2	3.6	1.5	1.1
125	0	1.6	3.1	4.6	2.4	4.5	4.8
126	0	0	0.1	0	0	0	0.1
127	0	0	0.3	1.3	0.2	0	0.2

Table 4. Ion intensities (%) for triorganotin bromides (R_3SnBr).

m/z	R			
	Butyl	1-Butenyl	2-Butenyl	3-Butenyl
112	0.3	0.4	0.4	0
113	0.6	0.6	1.0	0.6
114	0.4	0	0.4	0.3
115	0.7	0	0.8	1.1
116	3.8	5.1	4.7	4.7
117	12.2	12.2	12.0	13.2
118	11.1	12.9	13.7	12.2
119	20.9	19.2	18.8	19.8
120	14.3	17.0	16.2	14.6
121	23.8	20.1	20.9	23.5
122	2.0	1.5	1.7	1.3
123	4.5	4.6	3.5	2.9
124	1.6	2.1	2.5	2.0
125	3.4	4.3	3.8	3.7
126	0	0	0	0
127	0.3	0	0	0

Table 5. Contributions to m/z intensities.

Compound	% as Sn^+	% as SnH^+	% as SnH_3^+
Tetrabutyltin	20	60	20
Tetra-1-butenyltin	62	35	3
Tetra-2-butenyltin	28	72	0
Tetra-3-butenyltin	18	79	3
Tetraallyltin	46	54	0
Tetravinyltin	72	28	0
Tributyltin bromide	23	71	4
Tri-1-butenyltin bromide	38	62	0
Tri-2-butenyltin bromide	45	55	0
Tri-3-butenyltin bromide	36	64	0

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