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ORGANOMETALLIC COMPOUNDS

XXXVII*. MASS SPECTRA OF MIXED TETRAALKYLTINS AND OF TRIMETHYLTIN HALIDES

M. GIELEN and G. MAYENCE

Université Libre de Bruxelles, Faculté des Sciences, Collectif de Chimie Organique Physique, Avenue F. D. Roosevelt 50,B-1050 Bruxelles (Belgium)

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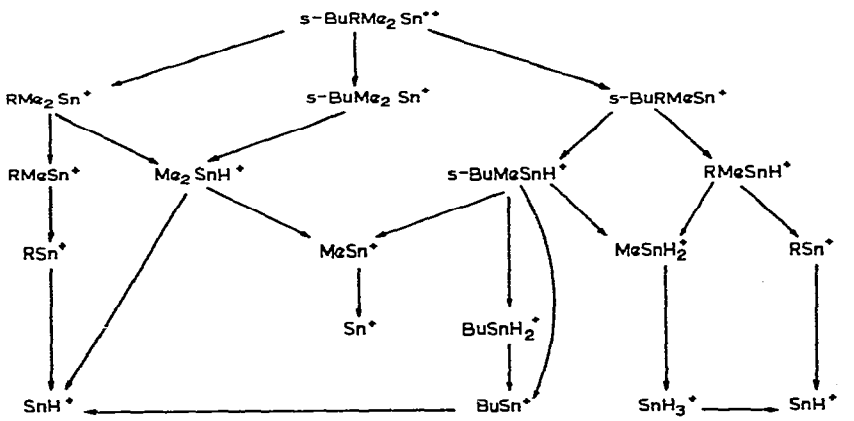
SUMMARY

The mass spectra obtained for a series of compounds of alkyldimethyl-sec-butyltin, alkyldimethyl(α-methylbenzyl)tin, alkyltriisobutyltin and trimethyltin halides confirm the fragmentation rules described earlier.

Diastereotopic nonequivalence has been described for molecules of the type $R'Me_2SnCHY(CH_3)$ with $Y = C_2H_5$, C_6H_5 and with various R' groups[2]. The purpose of this paper is to describe the mass spectra of these compounds, and to compare the obtained results with the conclusions of previous studies[3].

Table 1 gives the observed fragmentions for a series of alkyl- and phenyldimethyl-sec-butyltins. Table 2 presents the mass spectra of various dibutyldimethyltins. The results may be summarized in the following possible fragmentation pattern:



(*continued on p.* 284)

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* For part XXXVI see ref. 1.

TABLE 1

70 eV MASS SPECTRA OF A SERIES OF RMe_2-s-BuSn COMPOUNDS

(a), (b), (c): In a given column, (a) is indistinguishable from (a), (b) from (b), (c) from (c).
There are also tin-containing fragment-ions:
(d) at *m/e* 165 (intensity 1.0) (g) at *m/e* 185 (intensity 2.1): *m/e* 145 (SnC_2H^+) (intensity 2)
(e) at *m/e* 165 (intensity 1.6) (h) at *m/e* 165 ($MeSn^+$) (2.3); *m/e* 197 ($PhSn^+$) (0.3); *m/e* 226 [$Me(PhCH_2)Sn^+$] (0.2)
(f) at *m/e* 189 (intensity 9.4) (i) at *m/e* 165 (2.7); *m/e* 197 (5.8); *m/e* 213 ($PhMeSnH^+$) (3.1); *m/e* 227 ($PhMe_2Sn^+$) (23.2); *m/e* 303 (0.2)

Fragment	*R = Et*	*Pr*	*i-Pr*	*2-Pentyl*	*3-Pentyl*	*tert-Pentyl*	*Cyclo-pentyl*	*Cyclo-hexyl*	*Ph (g)*	*Benzyl (h)*	*Neophyl (i)*
Sn^+	3.4	4.6	3.4	3.1	4.1	3.3	3.8	3.9	11.6	5.8	2.1
SnH^+	5.1	7.7	7.7	9.9	6.2	4.8	4.5	6.6	2.3	3.3	2.8
SnH_3^+	0.4	0.2	0.3	0.3	0.2			0.3			
$MeSn^+$	11.7	19.8	16.7	1.1	3.3	14.8	12.7	16.4	10.7	0.4	9.2
$MeSnH_2^+$	3.7	4.9	5.0	18.4	18.1	2.2	3.6	3.4		17.1	0.1
Me_2Sn^+	1.2	0.4	0.7	0.8	1.2	0.9	2.2	1.0	1.5	1.7	0.8
Me_2SnH^+	32.2(a)	40.2	38.2	45.4	43.9	43.2	40.5	40.2	2.5	33.0	6.7
$BuSn^+$	2.5	0.7	0.5	0.5	0.5	0.4	0.3	0.4		0.4	0.2
$BuSnH_2^+$	21.3(b)	2.5(a)	2.5(a)			0.1					
$MeBuSnH^+$		14.0(b)	18.5(b)	2.2(b)	2.1(a)	1.9(a)	2.8	2.3	0.8	0.3	0.2
Me_2BuSn^+	6.7(c)	2.7	3.1	7.5(b)	7.6(b)	19.9	8.1	4.4		15.6	1.6
RSn^+	1.5	1.2	1.1			0.3	1.9	0.4	17.6	4.8	1.0
$RSnH_2^+$	32.2(a)	0.3	0.3	2.2(a)	2.1(a)	1.9(a)	0.3	1.2			
$MeRSnH^+$	7.1	2.5(a)	2.5(a)	7.5(b)	7.6(b)		1.5	9.3	7.3	0.8	1.2
Me_2RSn^+	21.3(b)	14.0(b)	18.5(b)	10.4	9.5	4.7	14.5		39.7	11.6	35.6
$BuRSnH^+$	6.7(c)					0.04		1.0		0.1	
$MeBuRSn^+$	1.7	1.1(c)	1.2(c)	1.0	0.9	1.5	0.9	0.4	1.0	0.8	2.9
Me_2BuRSn^+	0.9	0.3	0.5	0.2	0.1	0.7	0.8		0.1	1.1	0.1

TABLE 2

70 eV MASS SPECTRA OF A SERIES OF RMe_2-s-BuSn COMPOUNDS

Fragment	*R=n-Bu*	*R=i-Bu*	*R=t-Bu*
Sn^+	4.6	2.0	4.8
SnH^+	7.0	14.7	3.2
SnH_3^+	0.3	0.2	—
$MeSn^+$	15.6	18	15.3
$MeSnH_2^+$	5.1	4.2	2.6
Me_2Sn^+	0.4	30.8	1.8
Me_2SnH^+	40.9	40.3	46.7
$BuSn^+$	1.1	1.0	0.6
$MeBuSnH^+$	3.9	3.6	2.9
Me_2BuSn^+	20	14.1	20.8
Bu_2MeSn^+	1.0	0.7	1.3
$Bu_2Me_2Sn^+$	0.1	0.3	0.3

TABLE 3

70 eV MASS SPECTRA OF A SERIES OF $RMe_2[Ph(CH_3)CH]Sn$ COMPOUNDS

There are also tin-containing fragment-ions:
(g) at *m/e* 213 (intensity 0.9) and *m/e* 185 (intensity 1.9)
(h) at *m/e* 277 (intensity 0.2)
(i) at *m/e* 185 (intensity 3.0)
(j) at *m/e* 260 (intensity 0.2) and *m/e* 185 (intensity 1.1)

Fragment[a]	*R=Et*	*Pr* (*g*)	*i-Pr* (*h*)	*i-Bu*	*s-Bu* (*i*)	*t-Bu*	*i-Pentyl*	*Ph*	*Neophyl*
Sn^+	4.9	4.0	4.7	3.8	2.5	1.8	3.0	7.2	
SnH^+	6.6	5.3	6.1	5.8	5.5	3.5	5.3	2.3	
$MeSn^+$	12.6	12.4	12.9	13.3	12.7	9.9	14.2	6.1	11.7
$MeSnH_2^+$	0.7	1.7	0.6	0.7	1.0	0.3	0.8		
Me_2Sn^+								3.4	1.2
Me_2SnH^+	29.7	44	33.6	51.3	44	26.9	52		1.7
Me_3Sn^+				1.0	1.3	4.6	0.5		4.6
$PhSn^+$	1.9			1.4	1.5	1.7	1.3	14.8(a)	8.1
$PhenSn^+$	1.1	1.0	1.6	1.0	1.7	2.1	0.2		30.7
$PhenSnH_2^+$		0.2			0.7	0.2			
$MePhenSn^+$			0.2		0.3	0.3		1.3	
$MePhenSnH^+$	0.1	0.1	0.2	0.4	0.2	0.3	0.3	3.2	
$Me_2PhenSn^+$	1.7(a)	1.2	4.3		2.0	19.4	1.6	5.0	0.8
RSn^+	0.9	1.0	0.9	0.4	0.3		0.4	14.8(a)	1.7
$RSnH_2^+$		0.8	0.1						
$RMeSnH^+$	6.7	1.0	1.3	0.7	1.3	0.7	0.5	1.5	0.8
RMe_2Sn^+	29.4	21.5	30	18.2	18.6	20.9	18.8	52.8	37.5
$RPhenSn^+$								0.2	
$RPhenSnH^+$	1.7(a)								
$RPhenMeSn^+$	1.5	0.9	1.2	0.5	0.8	2.2	0.7	0.8	1.4
$RPhenMe_2Sn^+$	2.2	2.2	2.2	1.2	1.5	3.7	0.7	1.3	

[a] Phen = $Ph(CH_3)CH$.

TABLE 4

70 eV MASS SPECTRA OF ALKYLTRIISOBUTYLTINS

Fragment	*R=Me*	*R=Pr*[a]	*R=i-Pr*[b]
Sn^+	2.3	3.3	3.5
SnH^+	5.9	9.5	9.7
SnH_3^+	0.2	2.0	1.7
$MeSn^+$	10.4	0.3	5.7
$MeSnH_2^+$	13.4	0.4	
$EtSn^+$	0.4	0.5	0.7
$EtSnH_2^+$	8.8	1.3	
$PrSn^+$	0.2	1.5	1.6
$PrSnH_2^+$	1.0	6.4	9.8
$BuSn^+$	2.4	3.8	3.7
$BuSnH_2^+$	1.9	18.8	18.6
$BuMeSnH^+$	32	1.2	0.7
$BuEtSnH^+$	4.5	2.3	1.4
$BuPrSnH^+$	4.0	12.0	12.0
Bu_2SnH^+	1.4	21.8	17.7
Bu_2SnMe^+	14.1	0.4	0.4
Bu_2SnEt^+	0.1	0.8	0.6
Bu_2SnPr^+		4.5	3.7
Bu_3Sn^+	0.4	9.2	8.3
$Bu_3SnMe^{\cdot+}$	0.07		0.2
$Bu_3SnPr^{\cdot+}$			

[a] There is also a tin-containing fragment-ion corresponding to $BuPrSn^+$ (0.2). [b] There is also a tin-containing fragment-ion corresponding to $BuMeSn^+$ (0.4).

TABLE 5

70 eV MASS SPECTRA OF TRIMETHYLTIN HALIDES Me_3SnX

Fragment	*X=F*	*X=Cl*	*X=Br*	*X=I*
$Me_3SnX^{\cdot+}$	1.9	0.5	3.5	4.9
Me_2SnX^+	41.4	40.7	47.3	19.7
$MeSnX^+$	5.2	6.6	9.4	6.0
SnX^+	14.5	12.2	6.0	12.3
Me_3Sn^+	17.8	18.6	10.9	31.6
Me_2SnH^-	0.06	0.5	0.5	0.2
Me_2Sn^-	2.5	5.9	5.1	2.6
$MeSn^-$	9.8	8.7	9.5	14.8
CH_2Sn^+	1.9	2.5	1.8	3.6
SnH^+	1.3	1.5	1.7	2.1
Sn^+	5.7	5.7	5.8	7.7

Mass spectra at lower potentials (see *e.g.* fig. 1 to 6) confirm the sequence for the ease of cleavage of a carbon–tin bond of the molecular ion previously described[3], *viz.*

$$Ph(CH_3)CH \sim PhCH_2 > \text{s-Bu} \gtrsim \text{2-Pent} \gtrsim \text{Cyclopent} \gtrsim \text{Cyclohex} > \text{i-Bu} \gtrsim \text{Pr} \sim \text{Bu} > \text{Me}$$

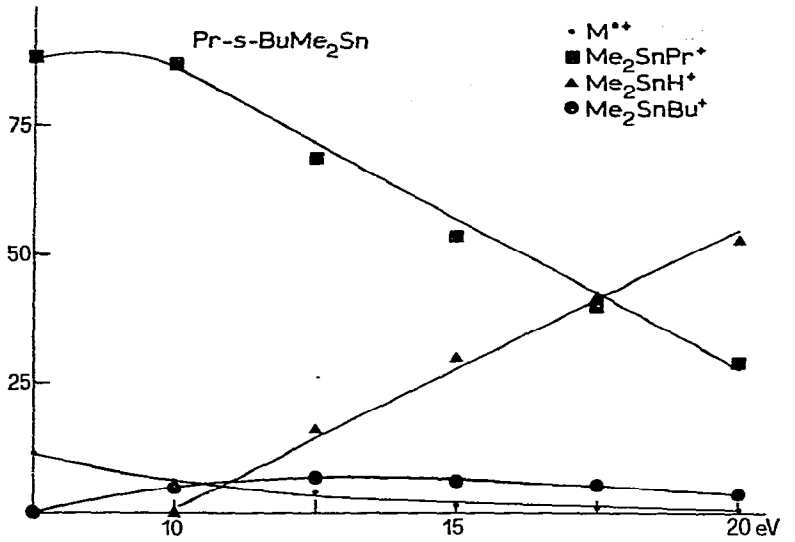

Fig. 1.

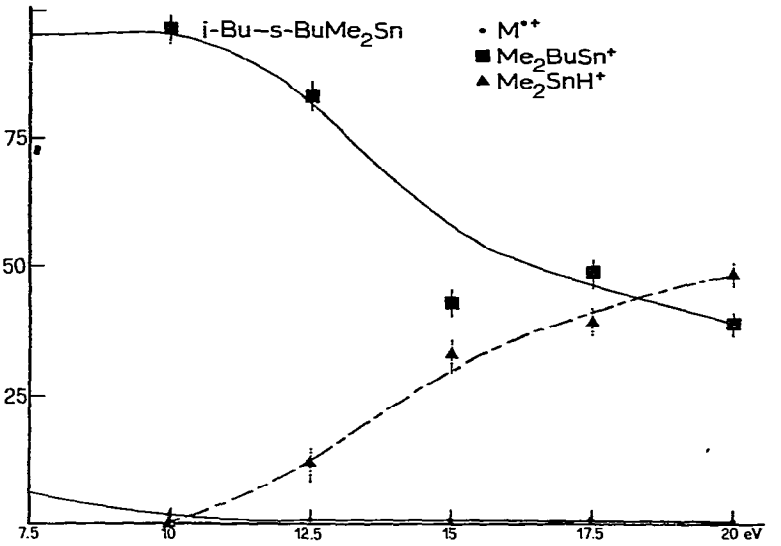

Fig. 2.

Table 3 shows the mono-isotopic spectra of alkyl- and phenyldimethyl-(α-methylbenzyl)tins. The same type of fragmentation pattern describes the fate of the molecular ion. The mass spectra of alkyltriisobutyltins are presented in Table 4, and show rather unexpected fragments corresponding to cleavage of carbon–carbon bonds (up to 19% of the sum of the intensities of all fragments for i-Bu_3SnMe). All the expected fragments are present.

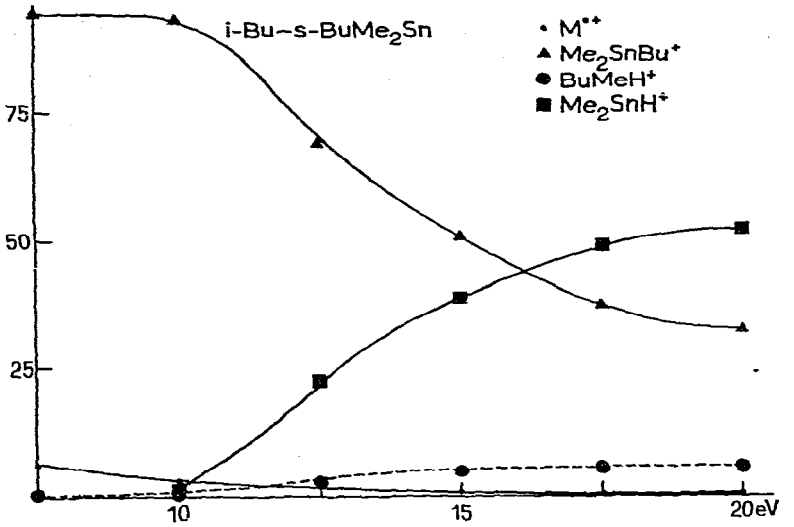

Fig. 3.

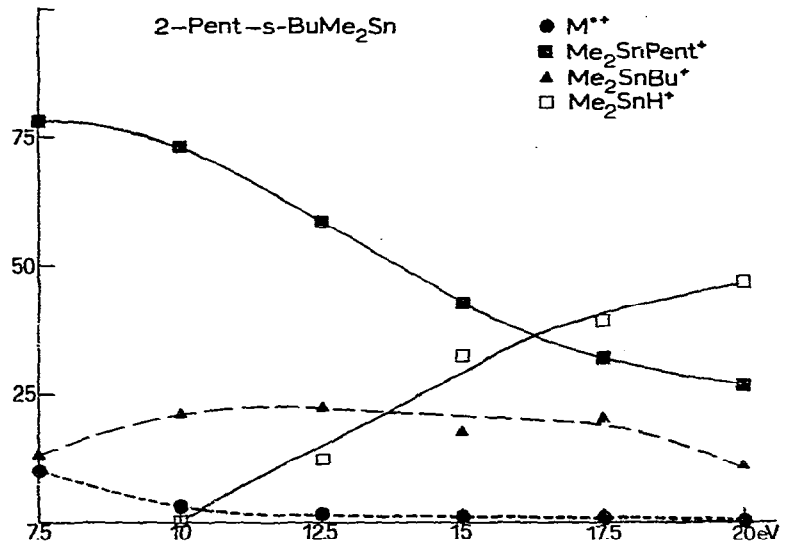

Fig. 4.

The 70 eV mass spectra of trimethyltin halides, which have been synthesized for a γ-spectroscopy investigation[4], are summarized in Table 5. All the expected[2] fragments are present.

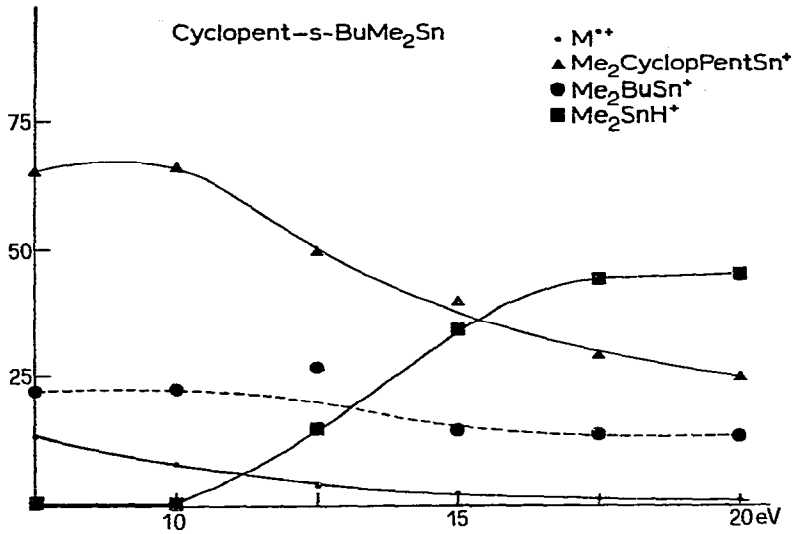

Fig. 5.

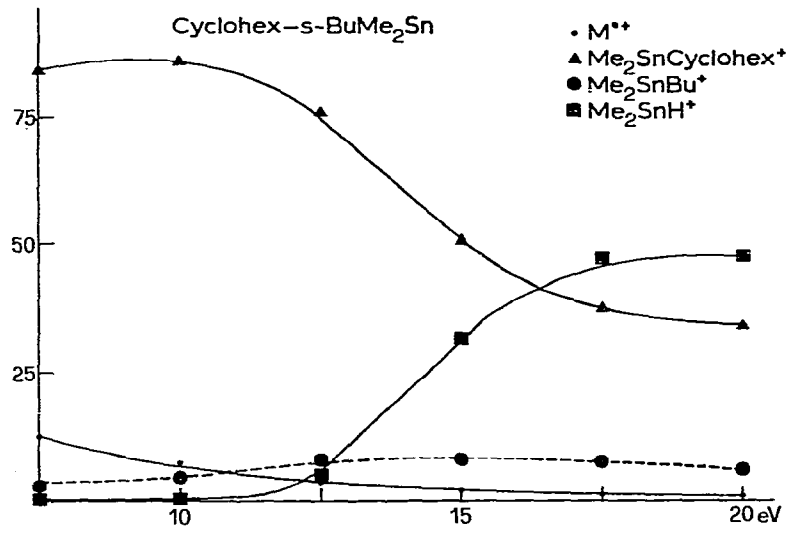

Fig. 6.

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