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MASS SPECTROMETRY OF ORGANIC COMPOUNDS

VIII—REMOTE GROUP INTERACTIONS IN HYDROXYORGANOTINS*

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Abstract—Hydroxyorganotins of the general formula $R_3Sn(CH_2)_nOH$ undergo rearrangement on electron-impact to yield ions in which oxygen has become directly bonded to the tin atom. The scope of this rearrangement is discussed, and it is shown that steric and structural factors play a significant but not decisive effect in its occurrence.

THE FRAGMENTATION of organic and organometallic molecules on electron-impact is only of use for structural elucidation if the processes giving rise to fragmentation are predictable. Rearrangement processes are particularly likely to prove troublesome in the interpretation of mass spectra, although certain well defined rearrangements such as the McLafferty rearrangement[1] have become useful precisely because their occurrence is predictable. In recent years it has become abundantly clear that molecules with an ionized trimethylsilyl group (or, more frequently, an ionized dimethylsiliconium residue derived from the former by the loss of a methyl radical) can undergo some dramatic rearrangements involving interaction of the silicon atom with a remote functional group having an unshared electron pair. Rearrangements are observed, for example, in the trimethylsilyl (TMS) derivatives of aliphatic diols,[2] of alicyclic diols and polyols, including carbohydrates,[3] of carboxylic acids and esters,[4] of halo acids and halo alcohols[5] and various phosphates.[6] In all of these examples the silicon atom is bonded to an oxygen atom, but rearrangement is also observed when the silicon atom is bonded initially to carbon,[7] and it is observed that a 'silyl McLafferty rearrangement' occurs as a significant fragmentation pathway in molecules where the silicon atom is situated on a carbon atom γ to a carbonyl group.[7b]

One of the most interesting aspects of the rearrangement reactions described in the cited references[8] is that they occur, for the most part, essentially independently of the separation between the interacting functionalities. Even when two functional groups are separated by a long carbon chain, interaction is frequently significant, the track record for remote group interaction currently being held by an α,ω-bis(trimethylsilyl)ether with 46 methylene groups separating the functional groups.[2b] These interactions have been proposed to occur essentially as gas phase internal ion–molecule reactions,[2b] and are presumably facilitated by a tendency for gaseous ions to 'solvate' themselves internally by coiling or winding.[9] In confirmation of this view, it has been shown that the trimethylsilyl cation and related ions do react via an ion–molecule reaction with various heteroatom containing molecules.[10]

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* Abstracted from the PhD Thesis of H. P. T., State University of New York at Albany, 1972. For Part VII, see Ref. 22.

In contrast to the well documented rearrangements of silyl groups in the mass spectrometer, information on the rearrangements of other Group IVB elements is meager. It has been shown that the diphenylgermyl as well as the diphenylsilyl group undergoes rearrangement from ester oxygen to phenyl,[11] and the trimethyltin group can undergo a 'stannyl McLafferty rearrangement',[12] but other examples of the skeletal rearrangements of Group IVA elements other than silicon are rare.* It has been shown, however, that both alkyl germanium and alkyl tin ions can undergo ion–molecule reactions with suitable heteroatom substrates.[10]

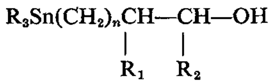
In view of the need for a better understanding of the factors governing the probable skeletal rearrangement of organotin ions, a study was made of structural and steric effects on the rearrangement of a number of hydroxyorganotins. The results of this investigation form the subject of this paper.

RESULTS AND DISCUSSION

The stannyl alcohols which were examined in this study are listed in Table 1, and the monoisotopic mass spectrum of 1-trimethyltin-hexan-6-ol (4) is shown in Fig. 1. Because of the large number of tin isotopes, it is convenient to represent the relative abundance of a fragment containing a tin atom as the sum of the abundances of all the isotopic ions, positioned at the mass corresponding to the ion containing the Sn^{120} isotope. This procedure is particularly useful when two ions containing tin atoms occur at mass separations of less than twelve mass units, since otherwise the ions from one isotopic cluster will be superimposed on ions from the second cluster, and interpretation may become difficult.† In all the subsequent discussion, reference will be made to such monoisotopic spectra, corrected to the Sn^{120} isotope.

In the absence of any interaction between the trialkyltin group and the hydroxyl group, it would be anticipated that the mass spectra would reflect fragments characteristic of one or both functional groups. The characteristic mass spectra of alkyltin

Table 1. Stannyl alcohols studied



$R_3Sn(CH_2)_n\underset{R_1}{CH}-\underset{R_2}{CH}-OH$

Compound	n	R	R_1	R_2
(I)	1	CH_3	H	H
(II)	2	CH_3	H	H
(III)	3	CH_3	H	H
(IV)	4	CH_3	H	H
(V)	1	CH_3	H	CH_3
(VI)	1	CH_3	CH_3	CH_3
(VII)	1	$n\text{-}C_4H_9$	H	H
(VIII)	1	$n\text{-}C_4H_9$	H	CH_3
(IX)	1	$n\text{-}C_4H_9$	CH_3	H

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* Lengyel and Aaronson[13] have noted an interaction between the oxygen atom and the tin atom in 10,10-dialkylphenoxastannins, but the two interacting groups can hardly be described as remote in this example.

† Correction of the observed spectra to monoisotopic spectra was performed by a computer program written by one of us (H. P. T.).

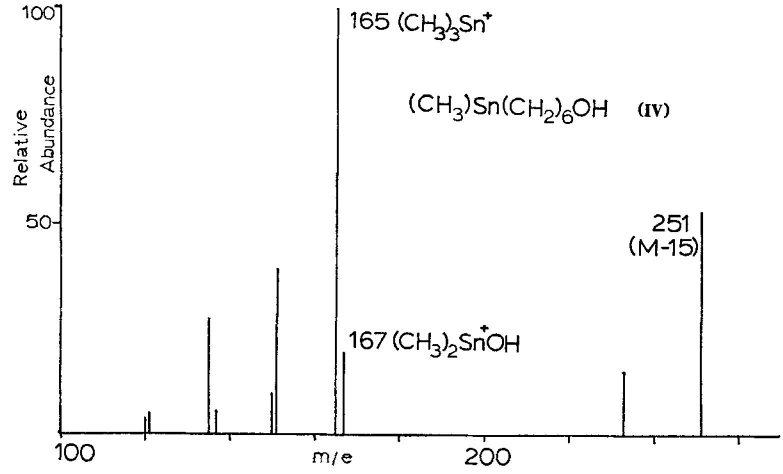


FIG. 1. Mass spectrum of 1-trimethyltin-hexan-6-ol.

compounds have been previously investigated and have been shown to consist largely of ions formed by cleavage of the tin–alkyl bond, both with and without hydrogen rearrangement, to produce predominantly tridentate and monodentate tin cations.[14] Since the ionization potential of tin is about 3 eV less than that for the hydroxyl group,[15] fragmentation of an organotin alcohol would be expected to yield predominantly tin-containing ions. Such is found to be the case for compounds I to IX, and very little fragmentation could be attributed directly to the hydroxyl group. Significant peaks were observed, however, for ions which must have been formed by interaction of the hydroxyl group and the tin atom, and these and other fragmentations will be discussed in the following sections.

Straight-chain trimethylstannyl alcohols. Effect of chain length on rearrangement

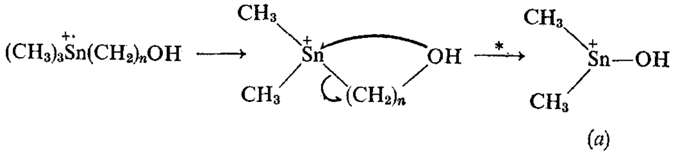
The principal ions detected in the mass spectra of the straight chain alcohols I to IV are listed in Table 2. An inspection of this table reveals that many of the ions detected are most reasonably formulated as products of simple cleavage reactions and rearrangements similar to those previously proposed for alkyl stannanes.[14] Ions in this category include $[M - CH_3]^+$ and $[(CH_3)_3Sn]^+$, formed respectively by loss of a methyl group and loss of the alkanol chain from the molecular ion. Other ions formed by well described processes include $[(CH_3)_2SnH]^+$, $[(CH_3)_2Sn]^+$ and $[CH_3Sn]^+$.

In addition to these expected ions, however, the spectra showed the presence of two ions *a* and *b* at *m/e* 167 and *m/e* 137, respectively. Exact mass measurements confirmed that these ions had compositions corresponding to the structures $[(CH_3)_2SnOH]^+$ and $[SnOH]^+$ and hence they must necessarily have been formed by a skeletal rearrangement process. In spectra run on compounds which had been equilibrated with D_2O in the inlet system, the peaks at *m/e* 167 and 137 were shifted to *m/e* 168 and 138 essentially completely, indicating transfer of one intact hydroxyl group in the rearrangement. In the case of ion *a*, metastable peaks were detected in the spectrum of each compound to indicate its formation directly from the $[M - CH_3]^+$ ion. The mechanism of Scheme 1 is proposed to account for these observations.

TABLE 2. PRINCIPAL IONS IN THE MASS SPECTRA OF ALCOHOLS I TO IV
$(CH_3)_3Sn(CH_2)_nOH$

Ion	(I) ($n = 3$)	(II) ($n = 4$)	(III) ($n = 5$)	(IV) ($n = 6$)
$[M]^{+\cdot}$	224 (0)	238 (0)	252 (0)	266 (0)
$[M - CH_3]^+$	209 (85)	223 (80)	237 (50)	251 (55)
$[M - CH_3 - H_2O]^+$(*c*)	191 (1)	205 (2)	219 (5)	233 (17)
$[(CH_3)_2SnCH_2CH_2OH]^+$(*d*)	195 (0)	195 (20)	195 (8)	195 (2)
$[(CH_3)_2SnCH_2CH{=}CH_2]^+$(*e*)	191 (1)	191 (0)	191 (18)	191 (1)
$[(CH_3)_2SnOH]^+$(*a*)	167 (85)	167 (50)	167 (33)	167 (20)
$[(CH_3)_3Sn]^+$	165 (100)	165 (100)	165 (100)	165 (100)
$[(CH_3)_2SnH]^+$	151 (10)	151 (20)	151 (30)	151 (40)
$[(CH_3)_2Sn]^{+\cdot}$	150 (20)	150 (15)	150 (10)	150 (10)
$[SnOH]^+$(*b*)	137 (12)	137 (8)	137 (7)	137 (5)
$[CH_3Sn]^+$	135 (45)	135 (32)	135 (30)	135 (25)
$[(CH_3)_2Sn]^+OH/[(CH_3)_3Sn]^+$	0·85	0·50	0·33	0·20

Ion *b* may be formed by an analogous process from the $^+[Sn(CH_2)_nOH]$ ion, or by loss of two methyl groups from ion *a*. No metastable peaks were detected to support either pathway.



SCHEME 1

Inspection of Table 2 indicates that the extent of the skeletal rearrangement shown in Scheme 1 (measured, for example, by the intensity of the peak corresponding to $[(CH_3)_2SnOH]^+$ relative to that corresponding to $[(CH_3)_3Sn]^+$) decreases steadily with increasing separation of the functional groups. This behavior is not unreasonable, especially in the light of the decrease in the relative abundance of the rearrangement ion at *m*/*e* 147 from polymethylene glycol bistrimethylsilyl ethers with increasing chain length. In the case of the alcohols I to IV the decrease in relative abundance of the rearrangement ion is more marked than in the above example, however; this probably indicates a relatively weaker interaction between the functional groups.

Various other peaks in the spectra of compounds I to IV may owe their origins to a remote group interaction, but the evidence is less clear cut. Although no peak is detected for the $[M - H_2O]^+$ ion characteristic[16] of aliphatic alcohols, an ion *c* corresponding to loss of water from the $[M - CH_3]^+$ ion was observed in the spectrum of each compound. The formation of this ion by loss of 18 mass units from the $[M - CH_3]^+$ ion was confirmed for compounds II to IV by the observation of the appropriate metastable peaks. The relative abundance of ion *c* increases significantly as the chain length of the alcohols is increased from three to six carbon atoms. One possible explanation of this observation is that the process leading to loss of water can compete more effectively in the longer chain molecules where the alternate rearrangements to give ions *a* and *b* are relatively less favorable. It is of course not necessary for change to be 'localized' on the hydroxyl group for elimination of water to occur: in a somewhat analogous situation, loss of methanol from methyl-4-phenylbutyrate was shown to occur even at ionizing voltages below the ionization potential of the carbonyl group.[17]

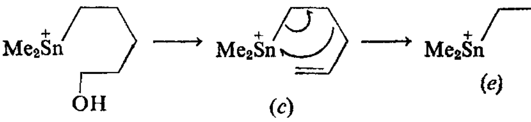
Two other ions in the spectra of compounds I to IV were only of significant intensity in the case of certain compounds. These are the ions *d*,

$$[(CH_3)_2SnCH_2CH_2OH]^+,$$

and *e*,

$$[(CH_3)_2SnCH_2CH{=}CH_2]^+.$$

Although the composition of these ions must correspond to the formulae given, the actual structures remain uncertain and those suggested are merely the ones that seem most probable. If these structures are correct, then *d* must be formed from II by loss of ethylene from the $[M - CH_3]^+$ ion, while *e* must be produced formally by loss of C_2H_6O (possibly ethylene and water) from III. Skeletal rearrangement of alkyltin ions involving losses of C_2H_4 has been observed before; for example, the ion $[CH_3Sn]^+$ in the spectrum of tetrapropyltin must arise by such a pathway.[18] The formation of ion *e* is without precedent, however. A weak metastable peak (at *m/e* 166·5) suggests that this ion is formed from the dehydrated ion (*c*); if this is indeed the case, then in the case of compound III at least a simple loss of ethylene from ion *c* is taking place, and Scheme 2 represents one possible pathway for the rearrangement.



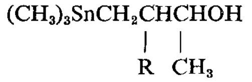
SCHEME 2

Branched chain trimethylstannyl alcohols. Effect of chain branching on the rearrangement

The principal ions detected in the mass spectra of the branched chain alcohols V and VI are listed in Table 3. A comparison of the relative intensities of the rearrangement ion $[(CH_3)_2\overset{+}{Sn}OH]$ in the spectra of compounds I, V and VI indicates that this rearrangement becomes progressively less important as branching on the alkyl chain increases. This effect could be explained in part by the increasing size of the branched chain molecules, giving more degrees of freedom over which the energy of the decomposing ion could be randomized, and also as a simple steric interaction. On this view the non-bonded interactions of the methyl and methylene hydrogen atoms would decrease the tendency of the methylene chain to coil back in a conformation suitable for rearrangement to occur. It is likely that both factors play a part in determining the extent of rearrangement; it is noteworthy that their joint effect is more than enough to outweigh the fact that the species expelled (presumably a diradical) would be more stable for compounds V and VI than for compound I.

Two peaks at *m/e* 194 and 179 were observed in the spectra of compounds V and VI which were not present in significant intensity in the spectra of compounds I to IV. Weak metastable peaks were detected indicating that *m/e* 179 is formed by loss of a methyl group from the ion at *m/e* 194, but in the absence of specific labeling

TABLE 3. PRINCIPAL IONS IN THE MASS SPECTRA OF ALCOHOLS V TO VI



$$\underset{}{(CH_3)_3SnCH_2}\underset{R}{CH}\underset{CH_3}{CH}OH$$

(V) R = H

(VI) R = CH$_3$

Ion	(V)	(VI)
$[M]^{+\cdot}$	238 (0)	252 (0)
$[M - CH_3]^+$	223 (25)	237 (17)
$[M - CH_2OH]^+$	207 (10)	221 (0)
$[M - CH_3 - H_2O]^+$	205 (3)	219 (16)
$[C_4H_{10}SnO]^+$	194 (40)	194 (16)
$[C_3H_7SnO]^+$	179 (42)	179 (18)
$\overset{+}{[}(CH_3)_2SnOH]$	167 (50)	167 (15)
$[(CH_3)_3Sn]^+$	165 (100)	165 (100)
$[(CH_3)_2SnH]^+$	151 (18)	151 (12)
$[(CH_3)_2Sn]^{+\cdot}$	150 (30)	150 (24)
$[SnOH]^+$	137 (10)	137 (6)
$[CH_3Sn]^+$	135 (80)	135 (48)

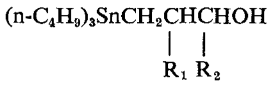
data it is not possible to be any more definitive about the origins and/or structures of these two ions. The remaining ions in the spectra of compounds V and VI are analogous to the corresponding ions in the spectra of compounds I to IV.

Tri-n-*butylstannyl alcohols*

The principal ions in the mass spectra of the tri-n-butylstannyl alcohols VII to IX are collected in Table 4. It is evident from inspection of the table that these compounds lose a butyl group relatively much more readily than the alcohols I to VI lose a methyl group. This is reasonable, since loss of large radicals is usually more favorable than the loss of small radicals in mass spectrometry;[19] the loss of the larger radical is presumably the result of more effective radical stabilization in the larger alkyl fragment.

The extent of skeletal rearrangement to form the ion $[(C_4H_9)_2SnOH]^+$ (*f*) appears to be slightly less in the tributylstannanes than for their trimethyl analogs. This may be due in part to steric interactions between the relatively bulky butyl groups and the

TABLE 4. PRINCIPAL IONS IN THE MASS SPECTRA OF ALCOHOLS VII TO IX



$$(n\text{-}C_4H_9)_3SnCH_2\underset{R_1}{CH}\underset{R_2}{CH}OH$$

(VII) R$_1$ = R$_2$ = H

(VIII) R$_1$ = H, R$_2$ = CH$_3$

(IX) R$_1$ = CH$_3$, R$_2$ = H

Ion	(VII)	(VIII)	(IX)
$[M]^{+\cdot}$	350 (0)	364 (0)	364 (0)
$[M - C_4H_9]^+$	293 (100)	307 (100)	307 (100)
$[(C_4H_9)_3Sn]^+$	291 (20)	291 (10)	291 (5)
$[(C_4H_9)_2SnOH]^+$(*f*)	251 (20)	251 (80)	251 (17)
$[(C_4H_9)_2SnH]^+$	235 (60)	235 (15)	235 (5)
$[(C_4H_9)_2Sn]^{+\cdot}$	234 (10)	234 (25)	234 (2)
$[H_2SnCH_2CH(R_1)CH(R_2)OH]^+$	181 (10)	195 (14)	195 (5)
$[SnCH_2CH(R_1)CH(R_2)OH]^+$	179 (70)	193 (8)	193 (5)
$[C_4H_9Sn]^+$	177 (100)	177 (58)	177 (24)
$[SnOH]^+$	137 (35)	137 (40)	137 (19)

propanol chain, but electronic factors probably play a part also. It is significant, for example, that the greatest amount of rearrangement occurs for the alcohol VIII, whose rearrangement would generate a secondary radical at one site. Because of this probable fine balance between steric and electronic effects, it is not possible to draw any firm conclusions about structural effects on the extent of rearrangement in these particular compounds.

The remaining peaks in the spectra of compounds VII to IX are unexceptional, being formed by processes analogous to those previously described for compounds I to VI and for other tetraalkylstannanes.[14]

In conclusion, it is clear that skeletal rearrangement of various stannyl alcohols to yield ions in which the hydroxyl group is bonded to the tin atom is an important process in all the cases investigated. The reaction probably involves attack of the lone pair electrons of the oxygen atom on a vacant orbital of the trivalent tin cation, and it occurs (albeit with a diminished relative abundance of the product ion) even in cases requiring an 8-membered transition state. Studies are currently in progress to define the scope of this reaction in related systems.[20]

EXPERIMENTAL

The synthesis of the alcohols I to IV has been previously reported[21] and compounds V to IX were prepared by Mr. Ross Andersen by a similar procedure. A typical preparation is given below; all compounds prepared by this method gave analytical data and spectroscopic properties in accord with the assigned structures.

1-*Trimethyltin-propan*-3-*ol* (I). Trimethyltin hydride (16·5 g, 0·1 mol) and allyl alcohol (6·8 g, 0·12 mol) were sealed in a pyrex tube under a nitrogen atmosphere and irradiated for 10 h by a low pressure mercury vapor lamp. 1-trimethyltin-propan-3-ol was obtained by distillation of the reaction mixture, b.p. 52°C/0·5 mm. (64% yield).

All compounds were purified immediately preceding mass spectrometric examination by preparative gas-liquid chromatography on a 6′ × ¼″ stainless steel column packed with 10% Carbowax 20 M on Chromosorb P, with a temperature program from 180° to 250°C. Mass spectra were obtained on an AEI MS-902 mass spectrometer, with sample introduction through an all-glass heated inlet system. The spectra of the trimethyltin alcohols were determined with the inlet at 250°C and the source at 170°C; the tri-n-butyltin alcohols were introduced at 150°C, with the source at 100°C, to avoid a dehydration which appeared to be facile with these compounds. Exact mass measurements were obtained at a resolving power of one in 10,000, using heptacosafluorotin-n-butylamine as a reference compound.

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