Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

SKELETAL REARRANGEMENTS OF SOME ACYCLIC KETOORGANOTINS ON ELECTRON IMPACT

H. G. KUIVILA, K.-H. TSAI AND D. G. I. KINGSTON
Department of Chemistry, State University of New York at Albany, Albany, N.Y. 12203 (U.S.A.)

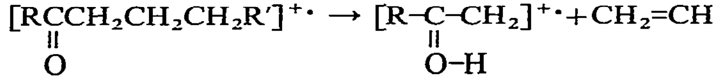
(Received November 26th, 1969)

SUMMARY

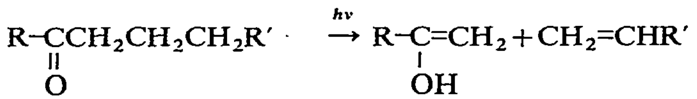
The mass spectra of ketoorganotins of general structure $RCO(CH_2)_nSn(CH_3)_3$ where $R=CH_3$ or Ph and $n=2$ or 3, are discussed. Ionisation occurs very largely at the tin atom, resulting in almost complete suppression of the McLafferty rearrangement. In addition to the generation of a fragmentation pattern analogous to that of other organotins[1-7] some novel skeletal rearrangements are observed, including an apparent transfer of the $Sn(CH_3)_3$ moiety to the carbonyl group via a six-membered transition-state, and the transfer of phenyl from carbonyl to tin.

INTRODUCTION

Interest in mass spectrometry has been greatly stimulated by the observation of parallels between mass spectrometric, photochemical, and thermal reactions. In particular, the parallel between the McLafferty rearrangement [eqn. (1)] and the

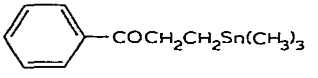


$$[R\underset{\underset{O}{\|}}{C}CH_2CH_2CH_2R']^{+\cdot} \rightarrow [R-\underset{\underset{O-H}{\|}}{C}-CH_2]^{+\cdot}+CH_2{=}CHR' \qquad (1)$$

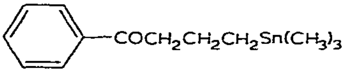


$$R-\underset{\underset{O}{\|}}{C}CH_2CH_2CH_2R' \xrightarrow{h\nu} R-\underset{\underset{OH}{|}}{C}{=}CH_2+CH_2{=}CHR' \qquad (2)$$

Norrish Type II fragmentation of ketones [eqn. (2)] has been investigated in some detail, and has been shown to hold for such details of the rearrangements as isotope effects and the preference for the abstraction of a tertiary hydrogen over a primary or secondary one[8]. With this background of close parallels between the two reactions it was of interest to determine what effect the trimethyltin group would have on both the photochemical and mass spectrometric reaction, and it was thus decided to investigate the mass spectra of the acyclic ketoorganotins (I)–(IV). The photochemistry of these compounds has been investigated, and the major primary chemical process has been found to be cleavage of a tin–carbon bond to give the trimethyltin radical and a ketoalkyl radical[9].



(I)



(II)

$CH_3COCH_2CH_2Sn(CH_3)_3$

(III)

$CH_3COCH_2CH_2CH_2Sn(CH_3)_3$

(IV)

RESULTS AND DISCUSSION

The principal ions in the mass spectra of compounds (I)–(IV) are indicated in the Table 1. The compositions of key fragment ions were determined by exact mass measurements (Table 2). In all other cases the ion compositions were readily deduced from the unit mass and the fact that the characteristic tin isotopes revealed the presence of this element in the majority of the ions.

Inspection of Table 1 indicates that the McLafferty rearrangement ions in which charge is retained on the enolic fragment [*m/e* 120 in (II) and *m/e* 58 in (IV)] or on the olefinic fragment are of negligible intensity. This system contrasts strongly with the case of butyrophenone, where the rearrangement ion is the most abundant ion in the spectrum. However, it was not unexpected in view of earlier findings that the McLafferty rearrangement can be suppressed by preferential ionisation at a site other than the carbonyl group[10,11]. In the present case the difference of 1.0 eV between the ionisation potential of the carbonyl group and that of the alkyltin group[12] would ensure effective localisation of the charge on the alkyltin group, and accounts for the low intensity of peaks due to the McLafferty rearrangement. It thus appears that the parallel between the Norrish Type II reaction and the McLafferty rearrangement will be a close one only when the primary excitation in both cases occurs at the carbonyl group. Thus the carbonyl group should be the group with the lowest ionisation potential in the molecule, or should be part of a conjugated system of low ionisation potential, for the McLafferty rearrangement to be a significant fragmentation pathway.

The fragmentation of compounds (I)–(IV) is thus dominated by tin-containing ions, and most of these are analogous to those previously observed in the spectra of other alkyltins[1-7]. All the compounds, for example, yield ions corresponding to $(M-CH_3)^+$, $(M-C_2H_6)^+$, and $(M-C_3H_9)^+$, and the intensities of the mono and trisubstituted tin ions are in general larger than those of the disubstituted and tetrasubstituted ions[1,5-7]. Similarly the formation of ions of the composition $[Sn(CH_3)_n]^+$, $[HSn(CH_3)_2]^+$, and $[H_2Sn(CH_3)]^+$ is unremarkable, except that the mass spectrometric fragmentation is much less specific than the photochemical reaction, where most of the products can be explained in terms of an initial specific cleavage of the alkyl–trimethyltin bond[9]. There are, however, two major ion series which have not been previously reported in this area, and which are of considerable mechanistic interest.

The spectra of compounds (II) and (IV) show substantial peaks at *m/e* $(M-28)$ and $(M-43)$. Exact mass measurements confirmed that these ions have compositions corresponding to the loss of C_2H_4 and C_3H_7 respectively from the molecular ion. That the loss of C_3H_7 is presumably a two-stage loss of a methyl group and ethylene, is indicated by metastable ions in the spectrum of (II) at *m/e* 243.7 ($297 \rightarrow 269$, m^* 243.9),

TABLE 1

RELATIVE INTENSITY OF THE PRINCIPAL IONS IN THE MASS SPECTRA OF COMPOUNDS (I)–(IV), $RCO(CH_2)_nSnMe_3$

	Relative intensity[a,b]			
	(I)(R = Ph, n = 2)	(II)(R = Ph, n = 3)	(III)(R = Me, n = 2)	(IV)(R = Me, n = 3)
$RCO(CH_2)_nSnMe_3^{+\cdot}$	< 1	1	< 0.1	< 0.1
$(M-H)^+$	32	9	< 1	1
$RCO(CH_2)_nSnMe_2^+$	160	58	250	65
$RCOCH_2SnMe_3^{+\cdot}$	Abs.	15	Abs.	33
$RCO(CH_2)_nSnMe^{+\cdot}$	2	< 2	2	< 1
$RCOCH_2SnMe_2^+$	Abs.	95	Abs.	70
$RCO(CH_2)_nSn^+$	25	< 2	45	< 2
$RCOCH_2Sn^+$	Abs.	8	Abs.	14
$RSnMe_2^+$	54	68	[c]	[c]
RSn^+	21	18	[d]	[d]
$SnMe_3^+$	100	100	100	100
$HSnMe_2^+$	14	4	25	5
$SnMe_2^{+\cdot}$	16	18	15	12
H_2SnMe^+	7	6	11	3
$SnMe^+$	51	41	67	45
SnH^+	5	3	9	7
$Sn^{+\cdot}$	19	12	21	11
$RCO(CH_2)_n^+$	3	3	< 1	< 1
$RCO(CH_2)_{n-2}CH{=}CH_2^{+\cdot}$	17	3	< 1	< 1
$RC(OH){=}CH_2^{+\cdot}$	Abs.	3	Abs.	< 1
RCO^+	58	33	12	10
R^+	50	33		

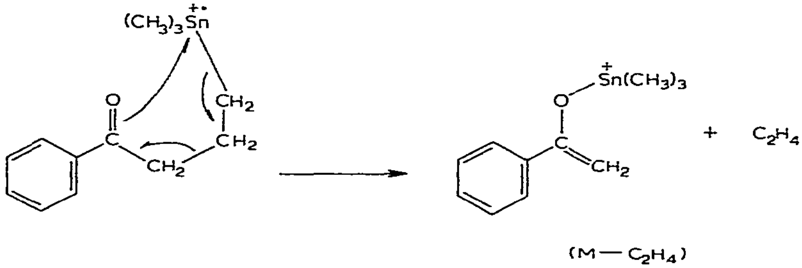
[a] $SnMe_3^+$ = 100. [b] Total ion current due to all isotopes of tin given for tin-containing ions. [c] Indistinguishable from $SnMe_3^+$. [d] Indistinguishable from $MeSn^+$.

TABLE 2

EXACT MASS MEASUREMENTS ON SOME IONS IN THE SPECTRA OF (I) AND (II)

Compound	Ion	Calculated mass	Measured mass	Δ(ppm)
$C_6H_5CO(CH_2)_2SnMe_3$	$C_6H_5{}^{120}SnMe_2$	226.9882	226.9875	3
	$C_6H_5{}^{118}SnMe_2$	224.9879	224.9873	3
$C_6H_5CO(CH_2)_3SnMe_3$	$C_6H_5CO(CH_2)_3{}^{120}SnMe_2$	297.0301	297.0288	5
	$C_6H_5COCH_2{}^{120}SnMe_3$	284.0222	284.0200	8
	$C_6H_5COCH_2{}^{120}SnMe_2$	268.9988	268.9975	6
	$C_6H_5COCH_2{}^{120}Sn$	238.9531	238.9505	10
	$C_6H_5{}^{120}SnMe_2$	226.9882	226.9895	6
	$C_6H_5{}^{118}SnMe_2$	224.9879	224.9858	9
	$C_6H_5{}^{120}Sn$	196.9413	196.9401	6
	${}^{120}SnMe_2$	149.9468	149.9476	6
	$C_6H_5C(OH){=}CH_2$	120.0575	120.0577	2
	${}^{120}Sn$	119.9021	119.9030	7
	C_6H_5CO	105.0340	105.0338	2

and *m/e* 254.8 (284→269, *m** 245.5), corresponding to $(M-CH_3) \rightarrow (M-C_3H_7)$ and $(M-C_2H_4) \rightarrow (M-C_3H_7)$, respectively. Both ions $(M-C_2H_4)$ and $(M-C_3H_7)$ thus have their origin in a common rearrangement which proceeds with the expulsion of a molecule of ethylene. It is highly significant that no peaks corresponding to loss of ethylene alone or any combination with other fragments are observed in the spectra of compounds (I) and (III), which have the trimethyltin group bonded to the carbon atom β to the carbonyl group. The most reasonable mechanism of formation of these ions involves a cyclic six-membered transition-state in which the tin atom migrates instead of a hydrogen atom [eqn. (3)]. Such a mechanism explains the non-occurrence of this rearrangement in compounds (I) and (III): in these cases a five-membered cyclic transition-state would be required.



(3)

The depiction of the charge as localised on the tin atom should not be taken as excluding an alternative formulation where a neutral tin atom migrates to an ionised carbonyl group, but for the reasons already discussed we feel that by far the majority of the $(M-C_2H_4)^{+\cdot}$ ions do have the charge localised on the tin atom. Rearrangement of organotins in this fashion has not been observed previously, although rearrangement of the trimethylsilyl group from ether oxygen to carbonyl oxygen[13,14] and also the diphenylsilyl and diphenylgermyl groups from ester oxygen to phenyl[15] have been reported. It would be of interest to investigate further this parallel between the hydrogen atom and the alkyl derivatives of Group IV elements other than carbon to determine, for example, the scope of the rearrangement reactions undergone by the latter. Meanwhile, the observations that some organometallic groups undergo migration to a carbonyl group, while alkyl groups do not[16], can be rationalised on the basis that the migrating atoms such as tin and silicon have low-lying *d*-orbitals available for bonding in the transition-state. A second factor, namely the greater strength of the metal–oxygen bond as compared to the metal–carbon bond (for example, Sn–O is quoted as 132 kcal/mole, and Sn–C as 68 kcal/mole[17]), may also be an important factor in the case discussed in this paper, but it is unlikely to be the sole factor responsible in view of the above-mentioned rearrangements of diphenylsilyl and diphenylgermyl groups.

The second ion series of interest is that giving rise to the ions $[C_6H_5Sn(CH_3)_2]^+$ and $[C_6H_5Sn]^+$ in the spectra of compounds (I) and (II); in the absence of isotopic labeling similar ions could not be distinguished from the unrearranged alkyl tin ions in the spectra of compounds (III) and (IV). Such ions must of necessity be produced by a skeletal rearrangement, but unlike the six-centered rearrangement just discussed this rearrangement appears not to be specific for a particular ring size, since the rearrangement ions are nearly as intense in the spectrum of (I) as in that of (II). This rearrangement is only significant in the case of the mono- and trisubstituted tin ions, again in agreement with the hypothesis[1,5–7] of preferred $\mathrm{Sn^{IV}}$ and $\mathrm{Sn^{II}}$ valence states in the tin-containing fragments.

It should be emphasized that the rearrangement peaks in both these series are among the most intense ions in the spectra of compounds (I)–(IV). Skeletal rearrangements of organotin compounds have been observed previously[1], but the rearrangement ions were of very low intensity. The observation of intense skeletal rearrangement ions in organotins means that mass spectrometry must be used with caution as a tool for structure elucidation in this area, and clearly an investigation into the scope of such rearrangements is called for.

In conclusion, the fragmentation pattern of the organotins (I)–(IV) can be summarized as in Fig. 1, although in the absence of metastable data for all the transitions suggested some of them must remain probable rather than confirmed transitions.

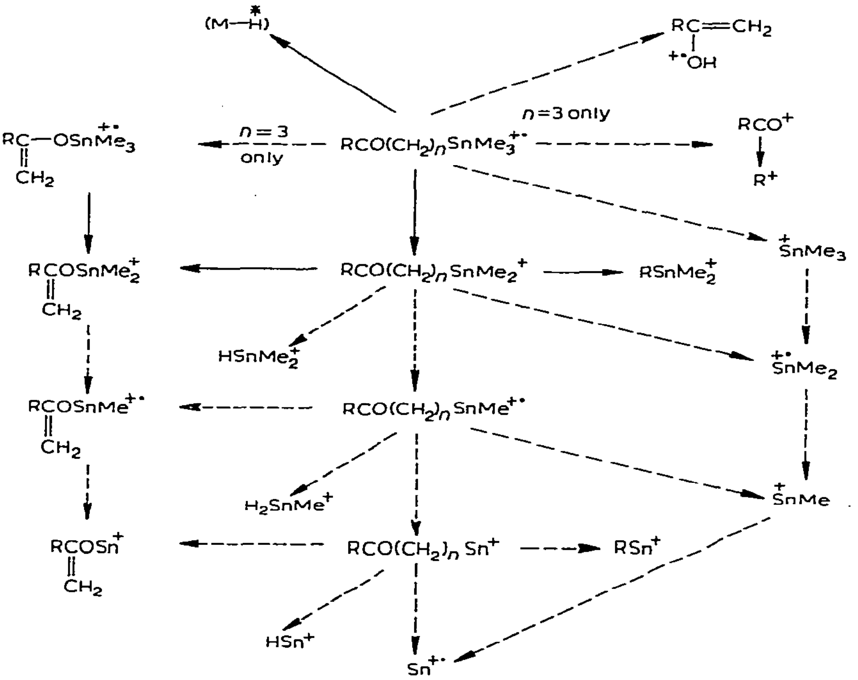


Fig. 1. Decomposition diagram for organotins RCO(CH$_2$)$_n$SnMe$_3$. Solid arrows indicate metastable-confirmed transitions.

EXPERIMENTAL

All of the ketoorganotins had elemental analyses as well as IR and PMR spectra in agreement with assigned structures. Details of preparation and properties will be submitted for publication.

Mass spectra were determined with an AEI MS-902 mass spectrometer operating at 70 eV and 8 kV. Samples were introduced via an all-glass heated inlet system at 150°, with an ion chamber temperature of 180°. Exact mass measurements were made at a resolving power of 12,000, using heptacosafluorotri-n-butylamine as a reference compound.

ACKNOWLEDGEMENTS

Purchase of the MS-902 mass spectrometer was made possible by a grant from the National Science Foudation Chemical Instrumentation Program. Thanks are also due to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

REFERENCES

1 D. B. Chambers, F. Glockling and M. Weston, *J. Chem. Soc. A*, (1967) 1759.
2 A. L. Yergey and F. W. Lampe, *J. Amer. Chem. Soc.*, 87 (1967) 4204.
3 J. L. Occolowitz, *Tetrahedron Lett.*, (1966) 5291.
4 J. J. Ridder and G. Dijkstra, *Recl. Trav. Chim. Pays-Bas*, 86 (1967) 737.
5 M. Gielen and J. Nasielski, *Bull. Soc. Chim. Belg.*, 77 (1968) 5.
6 S. Boue, M. Gielen and J. Nasielski, *Bull. Soc. Chim. Belg.*, 77 (1968) 43.
7 M. Gielen and G. Mayence, *J. Organometal. Chem.*, 12 (1968) 363.
8 H. Budzikiewicz, C. Djerassi and D. H. Williams, *Mass Spectrometry of Organic Compounds*, Holden–Day, San Francisco, 1967, pp. 155–162.
9 H. G. Kuivila and K.-H. Tsai, unpublished results.
10 T. Wachs and F. W. McLafferty, *J. Amer. Chem. Soc.*, 89 (1967) 5044.
11 D. G. I. Kingston and H. P. Tannenbaum, *Chem. Commun.*, (1968) 444.
12 R. W. Kiser, *Introduction to Mass Spectrometry and its Applications*, Prentice–Hall, Englewood Cliffs, N.J., 1965.
13 W. J. Richter and A. L. Burlingame, *Chem. Commun.*, (1968) 1158.
14 G. Eglington, D. H. Hunneman and A. McCormick, *Org. Mass. Spectrom.*, 1 (1968) 593.
15 A. G. Brook, A. G. Harrison and P. F. Jones, *Can. J. Chem.*, 46 (1968) 2862.
16 R. R. Arndt and C. Djerassi, *Chem. Commun.*, (1965) 578.
17 T. L. Cottrell, *The Strengths of Chemical Bonds*, Butterworth, London, 1958.