# Electron Impact Fragmentation of Isomeric Trimethylstannylnorbornenes and Some Related Compounds

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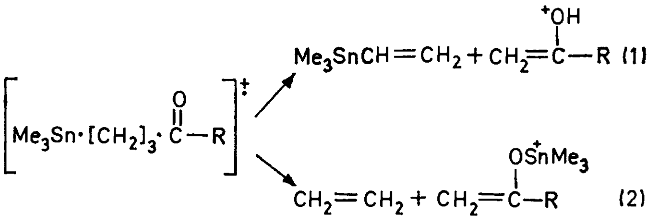
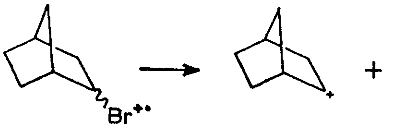
The mass spectra at two or more ionizing voltages of the following compounds have been studied: norborn-2-enes with a trimethylstannyl substituent in the *endo*-5-, *exo*-5-, *syn*-7-, *anti*-7-, and 2-positions, 7-trimethylstannylnorborna-2,5-diene, 3-trimethylstannylnortricyclene, and *syn*- and *anti*-7-trimethylsilylnorborn-2-ene. A number of novel characteristics attributable to the bicyclic system and/or the double bonds have been observed. In contrast to organotin compounds previously studied, *anti*-7-trimethylstannylnorborn-2-ene shows a very large peak due to a hydrocarbon cation, $C_7H_9^+$. This peak is very small, both in the spectrum of the *syn*- epimer and in those of the silyl analogues, and may be due to anchimeric assistance by the double bond in the loss of $Me_2Sn$ from the ion $Me_2SnC_7H_9^+$. The corresponding peak due to $C_7H_7^+$ appears in moderate degree in the spectrum of 7-trimethylstannylnorborna-2,5-diene. Some evidence has also been obtained for intramolecular interactions between double bonds and positively charged tin atoms in organotin cations.

RECENT mass spectrometric studies on organic molecules containing both electropositive and electronegative substituents have revealed electron impact fragmentation characteristics which can be considered to result from interaction between the cationic site and a neighbouring group.[1] It has been shown that, in compounds in which a keto-group and a trimethylstannyl group are suitably disposed, the normally anticipated McLafferty rearrangement [equation (1)] is supplanted by one in which the trimethyltin group migrates to oxygen [equation (2)].[2] This result is presumably a consequence of localization of the electron deficiency on the tin atom, rather than on the carbonyl group.[3] Similar results have been observed for analogous organosilicon compounds.[1b]



In this report, these studies are extended to unsaturated organotin compounds in order to determine how the double bond affects the fragmentation patterns. The compounds studied have the trimethylstannyl group attached to the bicyclo[2,2,1]carbocylic skeleton; because of the rigidity of this system, the relative positions, at least in the ground state, of most of the atoms in the molecules are accurately specified.

Some compounds containing electronegative substituents on this ring system have been subjected to electron impact fragmentation. For example, it has been shown that stereochemistry can play an important role in the fragmentation of 2-bromonorbornanes. The ratio of the intensity of the peak due to the $C_7H_{11}^+$ ion to that due to the molecular ion [equation (3)] is about ten times larger for the *exo*-isomer than for the *endo*-compound.[4] This effect is in the same direction as the relative rates of solvolysis of the two isomeric bromides,[5] and might be attributable to σ-participation in a transition state leading to a nonclassical ion. Similar investigations with the corresponding acetates produced results which were complicated by molecular ion isomerisation and competing fragmentation processes.[6] Parallel studies on norborn-2-en-5-yl chlorides revealed ready retro-Diels–Alder processes leading to spectra dominated by the resulting $C_5$ fragments, and to essentially identical spectra from the *exo*- and *endo*-chlorides;[7] a recent study on *exo*- and *endo*-5-bromonorbornenes, however, has produced evidence for anchimeric assistance in the expulsion of a bromine atom.[8]



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## RESULTS AND DISCUSSION

The following bicyclic organotin compounds were included in this investigation: *exo*-5-trimethylstannylnorborn-2-ene (I), *endo*-5-trimethylstannylnorborn-2-ene (II), 2-trimethylstannylnorborn-2-ene (IV), *syn*-7-trimethylstannylnorborn-2-ene (V), *anti*-7-trimethylstannylnorborn-2-ene (VI), and 7-trimethylstannylnorborna-2,5-diene (VII). The preparation and characterisation

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[1] See, for example (*a*) W. P. Weber, R. A. Felix, and A. K. Willard, *J. Amer. Chem. Soc.*, 1969, **91**, 6544; (*b*) 1970, **92**, 1420.

[2] H. G. Kuivila, K.-H. Tsai, and D. G. I. Kingston, *J. Organometallic Chem.*, 1970, **23**, 129.

[3] The ionization potential of tetramethyltin is 8·25 eV, and that of pentan-2-one is 9·25 eV; R. W. Kiser, ' Introduction to Mass Spectrometry and its Applications,' Prentice Hall, Englewood Cliffs, 1965, pp. 308 ff.

[4] D. C. DeJongh and S. R. Schrader, *J. Amer. Chem. Soc.*, 1966, **88**, 3881; D. C. DeJongh, S. R. Schrader, R. G. Isakson, N. A. LeBel, and J. H. Beynon, *Org. Mass. Spectrometry*, 1969, **2**, 919.

[5] J. D. Roberts, W. Bennett, and R. Armstrong, *J. Amer. Chem. Soc.*, 1950, **72**, 3329.

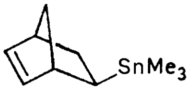
[6] A. F. Thomas and B. Willhalm, *Helv. Chim. Acta*, 1967, **50**, 826.

[7] W. C. Steele, B. H. Jennings, G. L. Botyos, and G. O. Dudek, *J. Org. Chem.*, 1965, **30**, 2886.

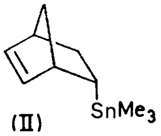
[8] K. B. Tomer, J. Turk, and R. H. Shapiro, *Org. Mass. Spectrometry*, 1972, **6**, 235.

of these and of 3-trimethylstannylnortricyclene (III) are described in another communication.[9]

Mass spectra were recorded with an A.E.I. MS902 instrument, using an 8 kV accelerating potential and selected ionizing voltages. The indicated temperature of the ionization chamber was 150°, as was that of the glass and Teflon inlet system. The compounds used were purified by preparative g.l.c. involving temperatures up to 210° with no detectable decomposition. Thus, fragmentations observed are presumed to result primarily from electron impact, although the possibility of a small amount of pyrolysis due to the hot filament cannot be rigorously excluded.



(I)



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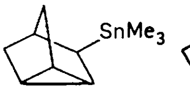

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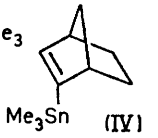

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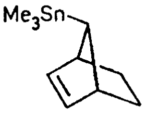

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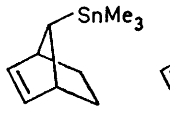

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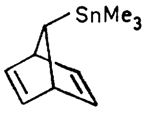


(VII)

Table 1

Mass spectra of trimethylstannylnorbornene isomers at 70 eV. Percent total ion content ($\Sigma_{33}$)

| | | Compound | | | | | |
|---|---|---|---|---|---|---|---|
| *m/e* | Assignment | (I) | (II) | (III) | (IV) | (V) | (VI) |
| 258 | $Me_3SnC_7H_9^+$ | 1·3 | 0·5 | 4·0 | 0·9 | Abs. | 2·6 |
| 243 | $Me_2SnC_7H_9^+$ | 8·6 | 8·0 | 16·0 | 21·9 | 3·0 | 16·0 |
| 230 | $Me_3SnC_5H_5^+$ | Abs. | Abs. | Abs. | Abs. | 5·9 | 1·0 |
| 215 | $Me_2SnC_5H_5^+$ | 0·2 | 0·2 | Abs. | 20·3 | 7·4 | 3·5 |
| 185 | $SnC_5H_5^+$ | 0·4 | 0·6 | 0·5 | 14·0 | 17·5 | 2·6 |
| 177 | $Me_2SnCH{=}CH_2^+$ | 15·8 | 15·8 | 16·0 | 0·3 | Abs. | 0·4 |
| 165 | $Me_3Sn^+$ | 23·7 | 16·5 | 27·4 | 4·3 | 35·8 | 12·1 |
| 151 | $Me_2SnH^+$ | 3·5 | 3·9 | 3·9 | 0·7 | 0·3 | 0·6 |
| 150 | $Me_2Sn^+$ | 2·3 | 2·1 | 2·2 | 2·6 | 4·9 | 2·0 |
| 147 | $SnCH{=}CH_2^+$ | 2·2 | 2·7 | 0·9 | <0·1 | 0·5 | 0·2 |
| 145 | $SnC{\equiv}CH^+$ | Abs. | Abs. | Abs. | 1·7 | 0·5 | 0·3 |
| 135 | $MeSn^+$ | 7·5 | 7·8 | 6·7 | 9·0 | 6·8 | 5·0 |
| 121 | $SnH^+$ | 1·7 | 1·9 | 1·4 | 3·4 | 1·7 | 0·9 |
| 120 | $Sn^+$ | 2·1 | 2·9 | 1·5 | 4·6 | 4·9 | 1·9 |
| 94 | $C_7H_{10}^+(93 + 1)$ | 0·2 | <0·1 | 0·5 | 0·1 | <0·1 | 2·5 |
| 93 | $C_7H_9^+$ | 1·8 | 1·4 | 6·0 | 0·5 | 1·0 | 30·5 |
| 91 | $C_7H_7^+$ | 2·8 | 3·4 | 3·7 | 1·1 | 1·2 | 6·7 |
| 79 | $C_6H_7^+$ | 0·3 | 0·3 | 0·5 | 1·0 | 0·8 | 0·2 |
| 77 | $C_6H_5^+$ | 2·8 | 2·6 | 3·7 | 1·2 | 1·4 | 5·7 |
| 66 | $C_5H_6^+$ | 2·4 | 2·5 | 0·8 | 0·3 | 0·9 | 0·3 |
| 65 | $C_5H_5^+$ | 2·1 | 2·4 | 1·2 | 0·9 | 1·2 | 1·4 |
| 41 | $C_3H_5^+$ | 1·1 | 1·4 | 1·3 | 1·1 | 0·9 | 1·0 |
| 39 | $C_3H_3^+$ | 2·6 | 3·2 | 1·3 | 2·6 | 1·3 | 1·0 |

Abs. = Absent.

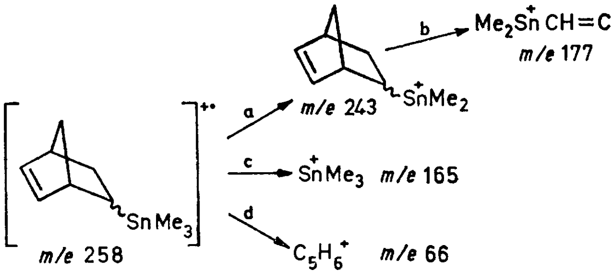
The principal fragmentations at 70 eV ionizing voltage of the isomers (I)—(VI) are given in Table 1. Intensities are recorded as the percentage of total ion content ($\Sigma_{33}$). The mass numbers of the tin-containing fragments refer to the isotopomer containing $^{120}Sn$ corrected for the other nine tin isotopes. General features of these spectra include low abundance or absence of molecular ions, low abundance of species containing trivalent ($R_2Sn^+$) and monovalent ($Sn^+$) tin, and high abundance of species containing tetravalent ($R_3Sn^+$) and divalent ($RSn^+$) tin. In previous reports on organotin compounds, only tin-containing ions were discussed, presumably because they were found to carry most of the ion current. For example, Chambers *et al.* report less than 5% ion current carried by hydrocarbon ions in a study of several organotin compounds.[10] Data in Table 1 show somewhat larger proportions of hydrocarbon ions, ranging from *ca.* 10% for compound (V) up to *ca.* 50% for compound (VI). These are discussed in connection with the other characteristics of the spectra of the individual compounds.

exo- *and* endo-*5-Trimethylstannylnorborn-2-enes* (I) *and* (II).—Examination of the data in Table 1 reveals very similar fragmentation patterns at 70 eV for these two epimers. The spectra at 14 eV (Table 2) show that the fundamental fragmentations are (i) a retro-Diels–Alder process in which the positive charge is borne by the organotin fragment [equation (4b)] or by the hydrocarbon fragment [equation (4d)] and (ii) loss of methyl radical [equation (4a)] or a $\cdot C_7H_9$ radical [equation (4c)] from the molecular ion. There was no significant loss of $Me_3Sn\cdot$ radical to produce a $C_7H_9^+$ cation, which would be equivalent to a process important in the corresponding bromo-compounds.[8] In organotin compounds the

Table 2

Mass spectra of *exo*-5- and *endo*-5-trimethylstannylnorbornenes at 14 eV. Percent total ion content ($\Sigma_{33}$)

| | | Compound | |
|---|---|---|---|
| *m/e* | Assignment | (I) | (II) |
| 258 | $Me_3SnC_7H_9^+$ | 7·8 | 9·6 |
| 243 | $Me_2SnC_7H_9^+$ | 46·8 | 51·0 |
| 177 | $Me_2SnCH{=}CH_2^+$ | 5·9 | 11·5 |
| 165 | $Me_3Sn^+$ | 33·4 | 16·6 |
| 66 | $C_5H_6^+$ | 6·1 | 10·6 |



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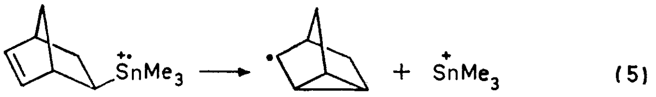
[9] H. G. Kuivila, J. D. Kennedy, R. Tien, and F. Pelczar, in preparation; but see also (*a*) H. G. Kuivila, *Accounts Chem. Research*, 1968, **1**, 299; (*b*) H. G. Kuivila, J. D. Kennedy, R. Y. Tien, I. J. Tyminski, F. L. Pelczar, and O. R. Khan, *J. Org. Chem.*, 1971, **36**, 2083; (*c*) C. H. W. Jones, R. G. Jones, P. Partington, and R. M. G. Roberts, *J. Organometallic Chem.*, 1971, **32**, 201; (*d*) H. G. Kuivila, J. L. Considine, and J. D. Kennedy, *J. Amer. Chem. Soc.*, 1972, **94**, in the press.

[10] D. B. Chambers, F. Glockling, and M. Weston, *J. Chem. Soc.* (*A*), 1967, 1759.

first priority is the formation of the more stable tetravalent tin species ($R_3Sn^+$) from the formally pentavalent species ($R_4Sn^+$), a process not available for the bromides.

It seems likely that the principal initial fragmentation is the loss of methyl radical from the trimethylstannyl group in the molecular ion. The absence of a fragment at *m/e* 192 ($Me_3SnCH{=}CH_2^+$) suggests that the retro-Diels–Alder process to give $Me_2SnCH{=}CH_2^+$ (*m/e* 177) occurs from the $Me_2SnC_7H_9^+$ ion (*m/e* 243) rather than from the molecular ion with a subsequent loss of methyl radical. The incidence of the fragment at *m/e* 66 ($C_5H_6^+$), on the other hand, does not increase with increasing ionizing voltage. Therefore, it seems likely that the retro-Diels–Alder dissociation to give this ion does occur from the molecular ion, and may well be the result of initial ionization at the double bond rather than the tin atom; it may be significant in this respect that 3-trimethylstannylnortricyclene (III), which has no double bond, shows a decreased intensity of the $C_5H_6^+$ ion, even though it shows a comparable extent of retro-Diels–Alder-type behaviour.

The *endo*-5-isomer gives a higher proportion of retro-Diels–Alder decomposition at 14 eV than does the *exo*-5-compound. This might be a consequence, according to the principle of microscopic reversibility, of the reduced activation energies in *endo- versus exo*-transition states in Diels–Alder processes involving cyclopentadiene. The *exo*-5-isomer, on the other hand, gives a higher proportion of $Me_3Sn^+$ than its epimer. It is thought unlikely that this is due to anchimeric assistance in the formation of a nortricyclyl radical (or a non-classical radical) as shown in equation (5), since there appears to be no evidence for such behaviour in free radical reactions of norbornenes.[11] The result may well reflect competition from the retro-Diels–Alder process, or from processes involving ring-ion formation with the double bond, both of which would be favoured with the *endo*-compound.



(5)

The increased fragmentation at the higher ionization voltage (Table 1) occurs at the expense of the fragments at *m/e* 258 ($Me_3SnC_7H_9^+$), 243 ($Me_2SnC_7H_9^+$), 177 ($Me_2SnCH{=}CH_2^+$), 165 ($Me_3Sn^+$), and 66 ($C_5H_6^+$) and also leads to an increase in the proportion of hydrocarbon ions. The norbornenyl ion ($C_7H_9^+$, *m/e* 93) appears, along with its initial decomposition product ($C_7H_7^+$, *m/e* 91), with about the same intensity from each isomer. These spectra were notable for the scarcity of metastable peaks; the only one observable was that for the transition 93 ⟶ 91 in the 70 eV spectra of both of these two isomers.

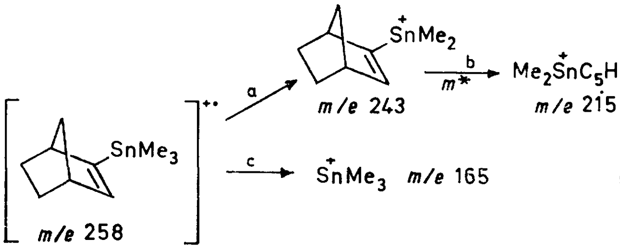
3-*Trimethylstannylnortricyclene* (III).—Although the molecular ion appears to be somewhat more stable, the fragmentation patterns for this compound (Table 1) are essentially similar to those observed for compounds (I) and (II). In particular, it easily undergoes the retro-Diels–Alder process, which however in this case formally requires the cleavage of three carbon–carbon bonds and a hydrogen shift. In contrast, it is interesting to note that compound (III) remains unchanged in conditions under which compounds (I) and (II) undergo a complete thermal retro-Diels–Alder process to give vinyltrimethyltin and cyclopentadiene.[12] On the other hand, if the trimethyltin substituents on compounds (I)—(III) are replaced by chlorine, then the electron impact fragmentation patterns are different. *endo*-5- and *exo*-5-Chloronorborn-2-enes exhibit substantially identical patterns in which the major peak is due to $C_5H_6^+$ from the retro-Diels–Alder process, whereas this peak is *ca.* one fifth as intense in the spectrum of 3-chloronortricyclene.[7] Similar differences are apparent in the mass spectra of norbornene and nortricyclene, of which a comprehensive treatment has recently been published.[13]

2-*Trimethylstannylnorborn-2-ene* (IV).—Data for this compound are given for 70 eV (Table 1) and 14 eV (Table 3) ionizing potentials. At 14 eV the principle fragmentation involves loss of methyl radical [equation (6)] to give $Me_2SnC_7H_9^+$ at *m/e* 243 to the extent of 87% of the total ion flux. Loss of the norbornenyl radical, $\cdot C_7H_9$, to give $Me_3Sn^+$ at *m/e* 165 occurs to a minor extent (1·7%). This contrasts to the other isomers discussed above which yield substantial peaks at *m/e* 165. This result is presumably a consequence of the greater strength of the $sp^2$–$sp^3$ vinyl–tin bond compared

TABLE 3

Mass spectra of 2-, *syn*-7-, and *anti*-7-trimethylstannylnorbornenes at 14 eV. Percent total ion content ($\Sigma_{33}$)

| | | Compound | | | |
|---|---|---|---|---|---|
| | | | (V) | | |
| *m/e* | Assignment | (IV) | (10 eV) | 14 eV | (VI) |
| 258 | $Me_3SnC_7H_9^+$ | 3·6 | Abs. | Abs. | 16·0 |
| 243 | $Me_2SnC_7H_9^+$ | 87·0 | Abs. | 14·7 | 39·4 |
| 230 | $Me_3SnC_5H_5^+$ | Abs. | 74·6 | 26·0 | 11·8 |
| 215 | $Me_2SnC_5H_5^+$ | 6·2 | Abs. | 9·6 | 3·2 |
| 185 | $SnC_5H_5^+$ | Abs. | Abs. | 2·1 | Abs. |
| 165 | $Me_3Sn^+$ | 1·7 | 25·4 | 38·6 | 8·7 |
| 93 | $C_7H_9^+$ | 0·2 | Abs. | Abs. | 24·1 |
| 66 | $C_5H_6^+$ | 0·5 | Abs. | 3·0 | 0·4 |



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[11] C. R. Warner, R. J. Strunk, and H. G. Kuivila, *J. Org. Chem.*, 1966, **31**, 3381.

[12] J. D. Kennedy and H. G. Kuivila, unpublished observations.

[13] J. L. Holmes and D. McGillivray, *Org. Mass. Spectrometry*, 1971, **5**, 1349.

to that of the $sp^3$–$sp^3$ carbon–tin bond. A similarly greater apparent stability of the vinyl–tin bond has been deduced from the mass spectrum of dibutyldivinyltin.[14] Indeed, Yergey and Lampe report that the bond dissociation energy of the vinyl–tin bond is about 10 kcal mol$^{-1}$ higher than that of the ethyl–tin bond.[15]

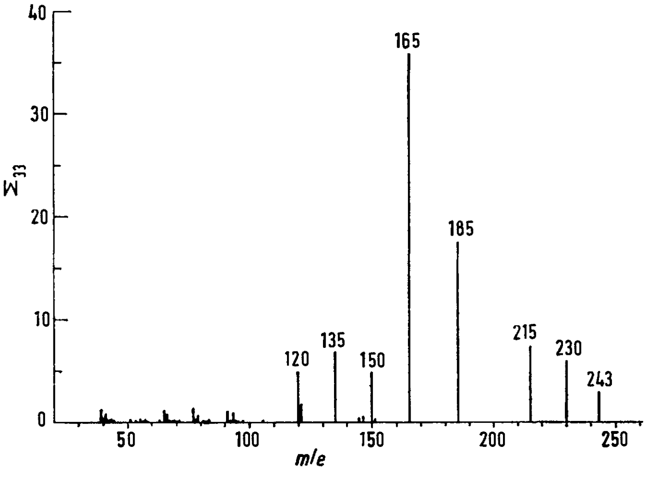

FIGURE 1 Mass spectrum of *syn*-7-trimethylstannylnorborn-2-ene (V) at 70 eV

At higher ionizing voltages the ions $Me_2SnC_5H_5^+$ (*m/e* 215) and $SnC_5H_5^+$ (*m/e* 185), which result from a retro-Diels–Alder process, become increasingly abundant. The absence of the ion $Me_3SnC_5H_5^+$ (*m/e* 230) suggests, together with a metastable, that *m/e* 215 is formed from the $(M - CH_3)^+$ ion [process (6)].

Thus, as with compounds (I)—(III), the methyl radical is probably lost from the molecular ion prior to the occurence of the retro-Diels–Alder process. The additional fragments observed in the 70 eV spectrum are unexceptional, although the contribution from hydrocarbon ions is lowest among the $C_7$ compounds examined in this report.

syn-7-*Trimethylstannylnorborn-2-ene* (V).—Data for this compound given in Tables 1 and 3, and in the bar-graph of Figure 1, reflect fragmentation processes analogous to those observed for the isomers discussed above, but with two important exceptions. First, the retro-Diels–Alder process, to give tin-substituted cyclopentadienyl ions, is very ready indeed; and, secondly, no molecular ion is evident even at the very low ionizing voltage of 10 eV (Table 3). The ion at *m/e* 230 ($Me_3SnC_5H_5^{+\cdot}$) is a significant one, and is the major one (74·6%) at 10 eV. This indicates that the retro-Diels–Alder fragmentation is so ready that it occurs in preference to the loss of methyl radical from the molecular ion, in contrast to the compounds discussed above. The same process occurs much less readily with the *anti*-7-epimer (VI) (see below); this parallels the relative ease with which the epimers undergo the thermal retro-Diels–Alder reaction, *i.e.* compound (V) faster than (VI).[12] It is noteworthy that $Me_3SnC_5H_5^{+\cdot}$ (if this is indeed the structure) is an odd-electron tin species like the molecular ion, which would be expected to appear in low abundance. Clearly the retro-Diels–Alder process has very low activation parameters, and in this instance much lower than for methyl–tin bond cleavage. Reasons may perhaps be sought in the known relative ease of formation of tin-substituted cyclopentadienyl compounds, together with their unique metallotropic fluxionality.[16] In the *syn*-7-isomer (V) the organostannyl group is ideally situated with respect to the incipient cyclopentadienyl ring, and so the dissociation may gain impetus from a metallotropic participation by the tin atom. Such an interpretation is however necessarily speculative, since at present insufficient data are available concerning general transition state requirements for the formation of *syn*-7- *versus anti*-7-substituted products in Diels–Alder processes involving substituted cyclopentadienes (for a recent investigation, see ref. 17).

anti-7-*Trimethylstannylnorborn-2-ene* (VI).—Data in Tables 1 and 3 show that the retro-Diels–Alder reaction occurs in a smaller degree for this isomer than for its *syn*-7-epimer (V), but to a degree comparable to that observed with the other isomers (I)—(IV). A comparison of the bar-graphs of the 70 eV spectra for compound (V) (Figure 1) and for (VI) (Figure 2) show differences such as are rarely seen in epimers. These are manifested in the remarkably high abundance of hydrocarbon ions of *m/e* 93, 91, and 77 in the spectrum of the *anti*-7-compound (VI). No other organotin compound examined to date has shown such behaviour. The ion at *m/e* 93, corresponding to $C_7H_9^+$, accounts for 24 (at 14 eV) to 30·5% (at 70 eV) of the total ion flux. It is formed at the expense of retro-Diels–Alder fragments and $Me_3Sn^+$.

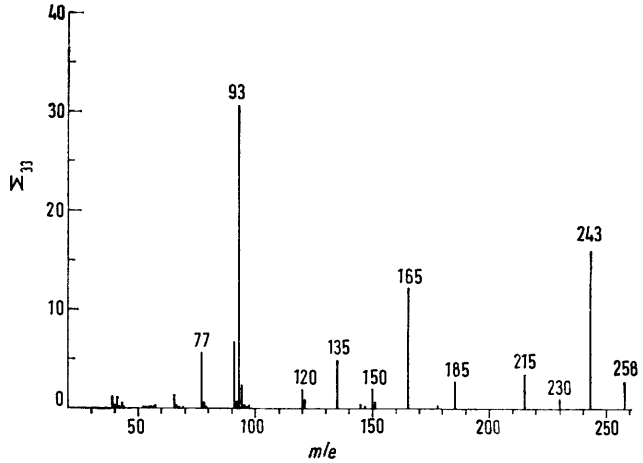

FIGURE 2 Mass spectrum of *anti*-7-trimethylstannylnorborn-2-ene (VI) at 70 eV

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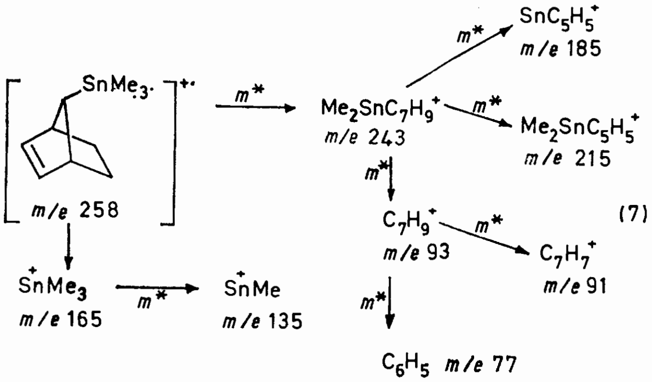
[14] J. L. Occolowitz, *Tetrahedron Letters*, 1966, 5291.

[15] A. L. Yergey and F. W. Lampe, *J. Amer. Chem. Soc.*, 1965, **87**, 4204.

[16] See, for example, A. V. Kisin, V. A. Korenevsky, N. M. Sergeyev, and Y. V. Ustynyuk, *J. Organometallic Chem.*, 1972, **34**, 93, and references therein.

[17] K. Williamson, Y.-F. L. Hsu, R. Lacko, and C. H. Youn, *J. Amer. Chem. Soc.*, 1969, **91**, 5099.

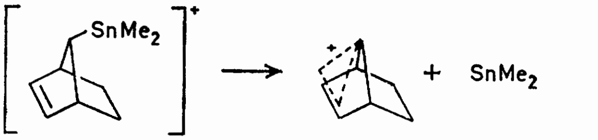
In contrast to compounds (I)—(V), metastables are observable for several processes [see process (7)]. The



(7)

pattern of these transitions merits some comment. The transition 258 ⟶ 243 supports the supposition that a principal initial fragmentation from the molecular ion leads to the loss of a methyl radical. Further fragmentation of the $Me_2SnC_7H_9^+$ ion can involve, first, formation of the $C_7H_9^+$ ion and the relatively stable $Me_2Sn$, secondly, the retro-Diels–Alder process, or, thirdly, the loss of two methyl radicals, which is a common fate of $Me_2SnR^+$ ions. Noteworthy in the spectra of this compound and the other isomers is the low incidence of an ion of *m*/*e* 79 ($C_6H_7^+$) which would result from the loss of the $Me_3SnCH_2{\cdot}$ radical from the molecular ion. This would correspond to a process which is important in the mass spectra of $C_7H_{10}$ isomers[18,19] (loss of ·Me) and norbornyl halides[4] (loss of $\cdot CH_2Cl$) (*cf.* ref. 13).

The exceptionally ready loss of the $C_7H_9^+$ ion might be attributed to steric factors or anchimeric assistance. Examination of models of the *syn*-7- and *anti*-7-isomers reveals that there may be very slight non-bonded interactions between the methyl hydrogens of the *anti*-7-trimethylstannyl group and the *exo*-5- and *exo*-6-hydrogens of the ring, whereas no such interaction is evident in the *syn*-7-epimer. However, the effect would appear to be too slight to account for the remarkable difference in behaviour of the two compounds. The alternative possibility would involve the participation of the double bond in a nucleophilic displacement of the $Me_2Sn\colon$ group and formation of the non-classical ion shown in equation (8). There is evidence that in the ground state of norbornenes and norbornadienes there is interaction between the π-orbital of the double bond and the backside of the orbital through which C-7 is bonded to the *anti*-7-substituent. For example, a coupling constant of *ca.* 0·9 Hz between the vinyl protons and the *anti*-7-proton is observed in norbornenes and norbornadienes;[20] the value is 6·3 Hz between the vinyl protons and $^{119}Sn$ in compound (VI).[9] This interaction would be maximised in the non-classical ion formed according to equation (8). It is also consistent with the extremely high reactivity of norborn-2-en-*anti*-7-yl toluene-*p*-sulphonate in acetolysis: this reacts $10^{11}$ times faster than does norborn-7-yl toluene-*p*-sulphonate, ten times faster than norborn-2-en-*exo*-5-yl toluene-*p*-sulphonate, and $10^5$ times faster than norborn-2-en-*endo*-5-yl toluene-*p*-sulphonate.[21] Thus mass spectrometry of organotins might have use as a probe for π-participation in the formation of non-classical carbonium ions in the gas phase. However, the geometrical requirements are highly specific, for there is no evidence for similar differences in the mass spectra of the *exo*-5- and *endo*-5-epimers (I) and (II), whose corresponding toluene-*p*-sulphonates differ in rates of acetolysis by $10^4$. This type of comparison must further be tempered by recognition of the fact that, on one hand, we are dealing in the mass spectra with highly energetic free species and, on the other hand, with thermally equilibrated but solvated species.



(8)

It was of interest to ascertain whether the trimethylsilyl analogues[9] of compounds (V) and (VI) would exhibit similar behaviour. The principal fragmentations observed at 14 and 70 eV ionizing potential are summarised in Table 4. Although qualitative similarities are evident, quantitative differences between the two epimers are substantial. These are due mainly to

TABLE 4

Mass spectra of *syn*-7- and *anti*-7-trimethylsilylnorborn-2-enes. Percent total ion content ($\Sigma_{33}$)

| | | Compound | | | |
|---|---|---|---|---|---|
| | | *syn*-7- | | *anti*-7- | |
| *m*/*e* | Assignment | 14 eV | 70 eV | 14 eV | 70 eV |
| 166 | $Me_3SiC_7H_9^+$ | 0·2 | 0·2 | 18·3 | 5·8 |
| 151 | $Me_2SiC_7H_9^+$ | 7·4 | 4·3 | 1·9 | 1·0 |
| 149 | $Me_2SiC_7H_7^+$ | 0·5 | 0·6 | 0·5 | 0·7 |
| 138 | $Me_3SiC_5H_5^+$ | 47·2 | 20·7 | 17·7 | 7·0 |
| 123 | $Me_2SiC_5H_5^+$ | 2·4 | 3·1 | 3·1 | 5·1 |
| 93 | $C_7H_9^+$ | Abs. | 0·5 | <0·1 | 0·9 |
| 92 | $SiC_5H_4^+$ | 0·2 | 0·6 | 7·9 | 4·2 |
| 85 | $Me_2SiCH{=}CH_2^+$ | 2·5 | 4·0 | 0·2 | 0·9 |
| 73 | $Me_3Si^+$ | 38·4 | 41·4 | 49·5 | 41·6 |
| 59 | $Me_2SiH^+$ | <0·1 | 3·7 | 0·2 | 3·3 |
| 45 | $MeSiH_2^+$ | Abs. | 4·0 | Abs. | 3·0 |
| 43 | $MeSi^+$ | Abs. | 3·1 | Abs. | 2·3 |
| | 151 ⟶ 149 | 147 | | | |
| | 166 ⟶ 151 | | | 137·5 | |
| | 166 ⟶ 138 | 114·8 | | 114·8 | |
| *m** | 138 ⟶ 123 | 109·7 | | 109·7 | |
| | 151 ⟶ 123 | 100·2 | | 100·2 | |
| | 166 ⟶ 92 | | | 51 | |
| | 138 ⟶ 73 | 38·7 | | 38·6 | |
| | 166 ⟶ 73 | | | 32·2 | |
| | 59 ⟶ 43 | | | | |
| | 73 ⟶ 45 | 27·7 | | 27·7 | |

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[18] C. Lifschitz and S. H. Bauer, *J. Phys. Chem.*, 1963, **67**, 1629.

[19] A. G. Harrison, P. Haynes, S. McLean, and F. Meyer, *J. Amer. Chem. Soc.*, 1965, **87**, 5099.

[20] E. I. Snyder and B. Franzus, *J. Amer. Chem. Soc.*, 1964, **86**, 1166.

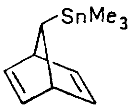
[21] S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Amer. Chem. Soc.*, 1955, **77**, 4183.

the low incidence of the molecular ion and the high incidence of retro-Diels–Alder dissociation in the *syn*-7-trimethylsilyl compound, a direct parallel with the behaviour of the organotin analogue (V). The molecular ion of the *anti*-7-trimethylsilyl compound is particularly stable, and four metastable transitions involving its fragmentation are observed. The major differences between these organosilicon compounds and the organotin analogues are the absence of significant fragmentation with the loss of $Me_2Si$, which can be attributed to the relatively low stability of divalent silicon species compared to divalent tin species, and the very small intensity of the $C_7H_9^+$ ion at *m*/*e* 93 in the spectra of the *anti*-7-trimethylsilyl compound.

These observations can be explained on the assumption that the positive charge is normally carried by the metal atom in organosilicon and organotin compounds. Carbon cations are observed in significant degree only when they are particularly stable, when the concomitantly formed heteroatom fragment is particularly stable (*e.g.* $R_2Sn$), and when the geometry of the precursor fragment satisfies rather rigid requirements. These requirements appear to be much more critical than for the anchimerically-assisted expulsion of bromine atoms from comparable systems,[8] and may therefore also be dependent on the relative ionization potentials of the double bond and the leaving group.

To test these ideas, we chose to extend our studies on organotin compounds to four additional unsaturated derivatives, 7-trimethylstannylnorborna-2,5-diene (VII), 1-trimethylstannylbut-3-ene (VIII), 1-trimethylstannyl-*trans*-but-2-ene (IX), and 1-trimethylstannyl-*cis*-but-2-ene (X). The preparation and characterisation of trimethylstannylnorbornadiene [9] and the trimethylstannylbutenes [22] are described elsewhere.

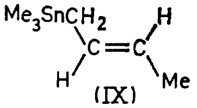
*7-Trimethylstannylnorborna-2,5-diene* (VII).—Data for this compound are summarised in Table 5. Only three metastable transitions [equation (9)] were observed.



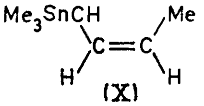
(VII)

$SnMe_3{\cdot}[CH_2]_2{\cdot}CH{=}CH_2$

(VIII)



(IX)



(X)

Only a small amount of retro-Diels–Alder fragmentation is evident, consistent with the behaviour of trimethylstannyl-norbornenes and -norbornadienes in thermal decomposition, the latter being more stable.[12] The $C_7H_7^+$ ion is formed as expected, but to a degree smaller than would be anticipated on the basis of the intensity of the $C_7H_9^+$ ion formed from compound (VI). (7-Chloronorbornadiene solvolyses in aqueous acetone *ca.* $10^3$ faster than *anti*-7-chloronorbornene.[23]) This might be attributed to stabilisation of the precursor of $C_7H_7^+$ by an interaction such as that shown in Figure 3 for the $Me_2SnC_7H_7^+$ ion, which is the most abundant species in the 14 eV spectrum. Ground-state organotin compounds of the appropriate structure have been examined for this type of interaction.[9b,c] The low abundance of the corresponding species in the 14 eV spectrum of compound (V) would be due to the facility with which it undergoes the retro-Diels–Alder process. The fragment ion with *m*/*e* 91 ($C_7H_7^+$), formed in the fragmentation of compound (VII), follows the expected decomposition course (91 ⟶ 65 ⟶ 39).

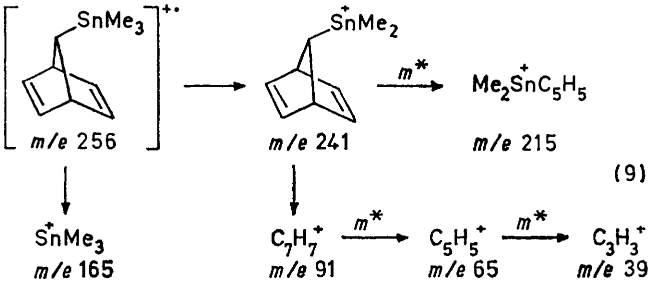


TABLE 5

Mass spectra of 7-trimethylstannylnorborna-2,5-diene (VII). Percent total ion content ($\Sigma_{33}$)

| *m*/*e* | Assignment | 14 eV | 70 eV |
|---|---|---|---|
| 256 | $Me_3SnC_7H_7^+$ | 4·8 | 0·2 |
| 241 | $Me_2SnC_7H_7^+$ | 74·1 | 8·9 |
| 215 | $Me_2SnC_5H_5^+$ | 1·3 | 2·8 |
| 185 | $SnC_5H_5^+$ | Abs. | 4·3 |
| 165 | $Me_3Sn^+$ | 11·4 | 11·3 |
| 151 | $Me_2SnH^+$ | 0·2 | 1·3 |
| 150 | $Me_2Sn^+$ | <0·1 | 3·2 |
| 135 | $MeSn^+$ | Abs. | 9·1 |
| 121 | $SnH^+$ | Abs. | 2·1 |
| 120 | $Sn^+$ | Abs. | 4·8 |
| 91 | $C_7H_7^+$ | 4·5 | 13·7 |
| 65 | $C_5H_5^+$ | <0·1 | 6·3 |
| 39 | $C_3H_3^+$ | Abs. | 7·2 |

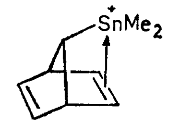


FIGURE 3

*Trimethylstannylbutenes* (VIII)—(X).—The spectra of 1-trimethylstannyl-*trans*-but-2-ene (IX) and 1-trimethylstannyl-*cis*-but-2-ene (X), summarised in Table 6, are substantially identical, but quite different from those of the terminal butene isomer (VIII). All three 70 eV spectra exhibit the characteristics of alkyltrimethyltin

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[22] J. A. Verdone, Ph.D. Dissertation, University of New Hampshire, 1963; N. S. Scarpa, Ph.D. Dissertation, State University of New York at Albany, 1969.

[23] S. Winstein and C. Ordronneau, *J. Amer. Chem. Soc.*, 1960, **82**, 2084.

Table 6

Mass spectra of 1-trimethylstannylbut-3-ene (VIII), 1-trimethylstannyl-*trans*- and -*cis*-but-2-enes (IX) and (X). Percent total ion content ($\Sigma_{33}$)

| | | Compound | | | |
|---|---|---|---|---|---|
| | | (VIII) | | (IX) | (X) |
| *m/e* | Assignment | 70 eV | 12 eV | 70 eV | 70 eV |
| 220 | $Me_3SnC_4H_7^+$ | Abs. | | 2·6 | 2·9 |
| 205 | $Me_2SnC_4H_7^+$ | 17·5 | 84 | 3·1 | 3·2 |
| 165 | $Me_3Sn^+$ | 19·4 | 15 | 51·5 | 50·5 |
| 151 | $Me_2SnH^+$ | 15·7 | | 10·2 | 9·9 |
| 150 | $Me_2Sn^+$ | 3·7 | | 7·9 | 7·7 |
| 135 | $MeSn^+$ | 8·4 | | 15·9 | 14·7 |
| 121 | $SnH^+$ | 2·6 | | 3·9 | 3·9 |
| 120 | $Sn^+$ | 2·0 | | 3·5 | 3·4 |
| 55 | $C_4H_7^+$ | 0·7 | | 3·3 | 3·0 |
| 54 | $C_4H_6^+$ | 0·5 | Trace | 0·2 | 0·2 |
| 53 | $C_4H_5^+$ | 0·4 | | 0·4 | 0·5 |
| 41 | $C_3H_5^+$ | 0·8 | | 0·6 | 0·6 |
| 39 | $C_3H_3^+$ | 1·1 | | 1·0 | 0·9 |

compounds,[24] low molecular ion intensity, stepwise loss of hydrocarbon groups from tin, a predominance of $Sn^{II}$ and $Sn^{IV}$ species and, in particular, the retention of the bulk of the positive charge on tin-containing fragments. The abundance of $SnH^+$ and $R_2SnH^+$ ions is much larger than that observed for the bicyclic compounds.

As reflected in the intensities of the $Me_3Sn^+$ ion (*m/e* 165), the but-2-enyl radical is formed much more readily than is the but-3-enyl radical, because of the delocalisation of the unpaired electron.

In contrast to the usual behaviour of alkyltrimethyltin compounds,[24] the but-3-enyl compound (VIII) undergoes loss of a methyl radical as the principal fragmentation at 12 eV. The absence of a molecular ion suggests a very ready process, and leads to the idea that $Me_2SnC_4H_7^+$ may be stabilised by 5-membered ring-ion formation.

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[2/733 *Received*, 28*th March*, 1972]

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[24] S. Boué, M. Gielen, and J. Nasielski, *Bull. Soc. chim. belges*, 1968, **77**, 43.