# Mass-spectral Rearrangement of Stannonium Ions: Migration of Oxygen from Carbon to Tin and Elimination of $C_6H_4$ in Some Phenoxastannins†

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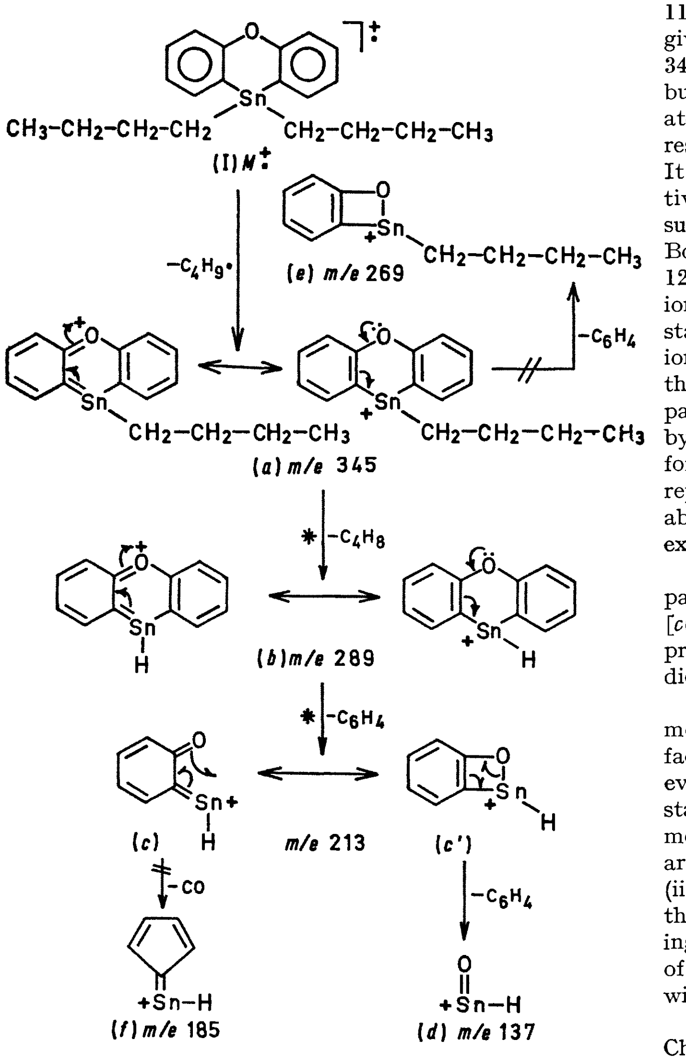
*Summary* The mass spectra of some 10,10-dialkyl phenoxastannins reveal a novel elimination–rearrangement reaction involving expulsion of a $C_6H_4$ fragment and Sn–O bond formation.

EVEN-ELECTRON fragment ions in the mass spectrometer frequently undergo elimination of a neutral fragment to form a new even-electron ion of lower mass number.[1] The neutral fragment expelled is usually a small organic or inorganic molecule of high stability, such as $C_2H_2$, $C_2H_4$, $CH_2O$, $CH_2CO$, CO, $CO_2$, HCN, HNCO, $H_2O$, *etc.*, and its stability often supplies an important part of the driving force for fragmentations of this type.



We now report a novel electron-impact induced reaction involving the migration of oxygen from carbon to tin and elimination of the $C_6H_4$ (benzyne?) fragment, observed in the mass spectra of some 10,10-dialkyl-substituted phenoxastannins. There is no previous published report on the mass spectra of these compounds.†

The major primary step in the electron-impact induced fragmentation of 10,10-di-n-butylphenoxastannin[2] (I; m.p. 118—119°) at 50—70 ev‡ is the ejection of a $C_4H_9$ radical to give the resonance-stabilized even-electron ion (*a*), *m/e* 345,§ $C_{16}H_{17}OSn$,¶ which in turn loses the elements of butene with concomitant rearrangement of a hydrogen atom from the alkyl ligand to the metal, leading to the resonance-stabilized even-electron ion (*b*), *m/e* 289, $C_{12}H_9OSn$. It is noteworthy that the energy requirement of the alternative elimination of $C_6H_4$, that would lead to ion (*e*), is sufficiently high to suppress the latter process completely. Both ions (*a*) and (*b*) are major species in the spectra *even* at 12 ev. One of the pathways of the further fragmentation of ion (*b*) involves elimination of $C_6H_4$ to afford the resonance-stabilized ion [*c*(*c′*),] *m/e* 213, $C_6H_5OSn$. The formation of ion [*c* (*c′*)] requires fission of several bonds and the loss of the resonance energy of the aromatic ring in the neutral particle: its presence strongly suggests anchimeric assistance by the neighbouring oxygen function resulting in O–Sn bond formation.** That ion *m/e* 213 is probably more accurately represented as (*c′*) rather than (*c*), can be surmised from the absence of ion (*f*): the quinoid structure (*c*) would be expected to eliminate CO.

Ion [*c* (*c′*)] subsequently eliminates a second $C_6H_4$ particle yielding ion (*d*), *m/e* 137, HSnO. Both ions [*c*(*c′*)] and (*d*) are absent in 12 ev scans. Entirely analogous processes have been observed in the mass spectrum of 10,10-diethylphenoxastannin.

The occurrence of this remarkable elimination–rearrangement reaction may be attributed to a combination of several factors: (i) the pronounced tendency of tin to form *further* even-electron ions[5] in which the tin is in the $Sn^{IV}$ oxidation state; (ii) the favourable arrangement of atoms for a four-membered transition state such that the ring can regain aromaticity by bond formation between tin and oxygen; (iii) the stability of the ionic product (HSnO) which contains the strong Sn=O double bond. A number of other interesting rearrangements were also revealed by the mass spectra of 10,10-disubstituted phenoxastannins. Details of these will be published shortly elsewhere.

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† A brief report on some aspects of the mass spectra of phenoxastannins was given by I. Lengyel, M. J. Aaronson, and J. P. Dillon at the 17th Annual Conference on Mass Spectrometry and Allied Topics, May 15—23, 1969, Dallas, Texas; *cf.* Abstracts of Papers, p. 403.

‡ Conventional ("low resolution") mass spectra were recorded on both a CEC 21-103C and a Hitachi RMU-6D instrument, with introduction of the sample *via* a direct probe.

§ All masses are given for the ${}^{120}Sn$ isotope.

¶ The elemental compositions of all ions in the spectrum were determined from high resolution spectra ("element maps"[3]) recorded on a CEC 21-110B doubly focusing instrument in conjunction with an IBM 1800 computer system.

** While one example of the electron-impact induced rearrangement of a methoxyl group from carbon to silicone has just been published (ref. 4) no bond formation between oxygen and tin has previously been reported.

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[3] K. Biemann, P. Bommer, and D. M. Desiderio, *Tetrahedron Letters*, 1964, 1725.
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[5] D. B. Chambers, F. Glockling, and J. R. C. Light, *Quart. Rev.*, 1968, **22**, 317.