Role of σ–π Conjugation in the Gas Phase: Electrophilic Cleavage Reactions of Benzyltin Compounds by Isobutane Chemical Ionization Mass Spectrometry

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Reaction of the *tert*-butyl cation, $(CH_3)_3C^+$, generated in a chemical ionization mass spectrometer (isobutane CIMS), with various benzyltin compounds provided the $[M + 57]^+$ ion, which we postulate to be the intermediate benzenonium ion. This intermediate ion is vertically stabilized by the carbon–tin σ-bond electrons of the $-CH_2SnR_3$ group (σ–π *conjugation) and fragments to give p-tert-butyltoluene and eventually the p-tert-*butylbenzyl cation, as well as the corresponding R_3Sn^+ cation. The intermediate benzenonium ion can also lose a proton to give a *p-tert*-butylbenzyltin compound, which itself undergoes further electrophilic cleavage reactions. Substitution at the para position with a *tert*-butyl group prevents *tert*-butyl cation attack, which implies para substitution as the predominate site for reaction. Interestingly, this latter reaction provides the $[M + 1]^+$ ion instead and gains insights into the steric factors of this gas-phase electrophilic reaction. Competitive cleavage of alkyl, benzyl, and phenyl groups will also be discussed along with the role of σ–π conjugation in these gas-phase electrophilic cleavage reactions.

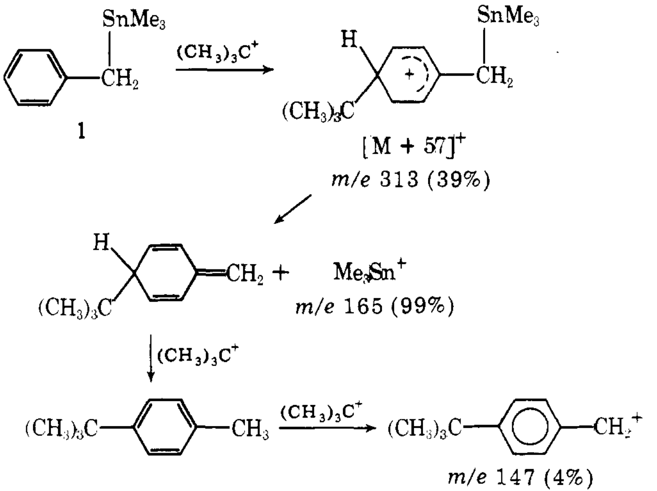
The concept of σ–π conjugation as a viable mechanism to explain the various properties of carbon–metal compounds has been amply documented in recent years.[2a–c] Pertinently, the use of benzyltin compounds as models for σ–π conjugation, utilizing such spectroscopic methods as nuclear magnetic resonance,[3a,b] ultraviolet,[2c] visible,[2c] and UV photoelectron spectroscopy,[4] has been paramount in revealing this interaction of carbon–metal σ electrons with the π orbitals of the benzene ring.

We have been involved in using chemical ionization mass spectrometry (CIMS) as a means of studying gas-phase protonolysis reactions of organotin compounds.[5a–c] Furthermore, we wanted to be able to identify intermediates in these reactions in order to clarify electronic effects without the influence of solvents. In this regard, we recently were able to study the 1,3-deoxystannylation reaction in the gas phase and demonstrated the formation of a carbonium ion intermediate with a series of γ-phenyl-γ-hydroxypropyltrimethyltin derivatives.[5b] An extension of this latter CIMS study, with the hope of observing intermediates in gas-phase electrophilic cleavage reactions, was initiated with a series of benzyltin compounds.

In this paper, we present evidence that the *tert*-butyl cation (isobutane CIMS) undergoes electrophilic attack at the para position of a benzene ring to provide the intermediate benzenonium ion. This intermediate ion, which is vertically stabilized by carbon–tin σ electrons of the $-CH_2SnR_3$ group, predominantly fragments to *p-tert*-butyltoluene and eventually forms the *p-tert*-butylbenzyl ion as well as the organotin cation, among other gas-phase reactions.

Results and Discussion

The isobutane CIMS spectra of all the benzyltin compounds, **1–9**, studied are tabulated in Table I. Compound 1 can be used to illustrate the electrophilic reaction of the *tert*-butyl cation in the gas phase (eq 1). This result strongly suggests that the $[M + 57]^+$ ion (39%) must be formed by electrophilic attack on the benzene ring by the *tert*-butyl cation. Supporting this assumption is the formation of the *p-tert*-butylbenzyl cation, *m/e* 147 (4%), which we presume results from the formation of *p-tert*-butyltoluene, **10,** followed by further reaction of **10** with *tert*-butyl cation, via hydride abstraction.[6] We substantiated this by independently studying the isobutane CIMS of *p-tert*-butyltoluene and found that the $[M - 1]^+$ ion, *m/e* 147, was readily formed in a concentration dependent ion–molecule reaction, i.e., at lower concentrations (solid probe) the $[M - 1]^+$ ion was predominant (eq 2, Table I).



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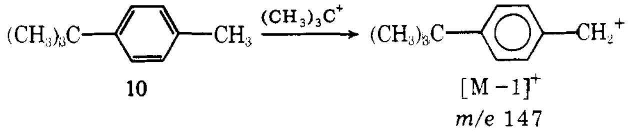

(2)

Further supportive evidence for electrophilic attack of the *tert*-butyl cation on a benzene ring was forthcoming with several ortho- and para-substituted benzyltrimethyltin compounds, **2–4.** Compound **2** provided the $[M + 57]^+$ ion (100%) as well as a $[M + 1]^+$ ion, *m/e* 271 (28%). Furthermore, the *p-tert*-butyl-*o*-methylbenzyl cation, *m/e* 161, was formed in 49% relative abundance along with the trimethyltin cation, *m/e* 165 (99%). Compound **3,** a para-substituted (fluoro) benzyltin compound, also gave the $[M + 57]^+$ ion (14%) as well as the trimethyltin cation (*m/e* 165, 100%).

Interestingly, the *p-tert*-butyl substituted benzyltin compound, **4,** provided only the $[M + 1]^+$ ion and no $[M + 57]^+$ ion (eq 3). Thus, when steric factors prevent *tert*-butyl cation

(3)

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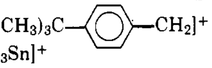
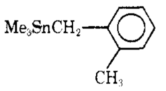
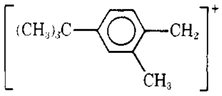
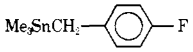
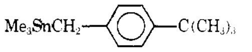
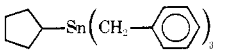
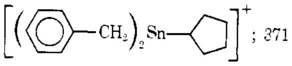
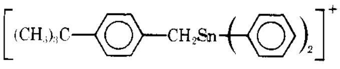
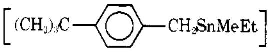
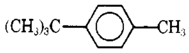
Table I. CIMS Spectra Data for Compounds 1-10

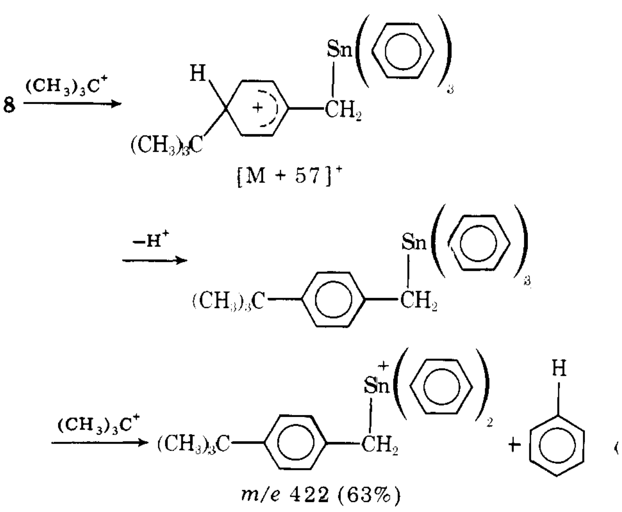
				m/e (rel intensity)[a]				
compd	structure	registry no.	parent[a] (*m/e*)	$[M + 1]^+$	$[M + 57]^+$	$[Me_3Sn]^+$		other ions
1	Me_3SnCH_2Ph	4314-94-7	256		313 (39)	165 (99)	147 (4)	
2		19962-44-8	270	271 (28)	327 (100)	165 (99)		 ; 161 (49)
3		706-26-3	274		331 (14)	165 (100)		
4		54030-97-6	312	313 (26)		165 (75)	147 (14)	
5	$MeSn(CH_2Ph)_3$	17841-74-6	408		465 (21)		147 (33)[c]	$[(PhCH_2)_2SnMe]^+$; 317 (36)
6		68024-62-4	462				147 (33)[c]	 ; 371 (22)
7	$PhSn(CH_2Ph)_3$	10074-33-6	471				147 (33)[c]	
8	Ph_3SnCH_2Ph	2847-58-7	442				147 (37)	 ; 422 (63) $[Ph_3Sn]^+$; 351 (40) $[PhCH_2SnPh_2]^+$; 365 (33)[d]
9	$PhSn(Me)(Et)CH_2Ph$	68024-63-5	332	333 (9)	389 (22)		147 (75)	 ; 311 (100) $[PhCH_2Sn(Et)Ph]^+$; 317 (9) $[PhCH_2Sn(Me)Ph]^+$; 303 (10) $[PhCH_2Sn(Me)Et]^+$; 255 (12) $[PhSn(Me)Et]^+$; 241 (9)
10		98-51-1	148	149 (50)[b]			147 (100)[b]	

[a] Based on ^{120}Sn isotope (total ion current normalized to 100%). [b] Concentration dependent, i.e., low concentration favored $[M - 1]^+$ ion. [c] Normalized for three benzyl groups. [d] Normalized for three phenyl groups.

attack at the para position, the *tert*-butyl cation acts as a Brønsted acid donating a proton to the benzene ring. This experiment enhances the presumption that the *tert*-butyl cation prefers attack at the para position (eq 1), thereby maximizing $\sigma-\pi$ interactions of the CH_2-SnR_3 group with the benzenonium ion.

Several tribenzyltin compounds, **5-7**, also were studied and indeed showed the *m/e* 147 ion to be predominantly formed. This further supports loss of the organotin cation as a major fragmentation pathway.

In this regard, we had indications that other reactions occurred from the intermediate benzenonium ion and they emanated with compounds **8** and **9**. Compound **8** provided the $[M + 57 - 77]^+$ ion (*m/e* 422, 63%), which we presume results from the *tert*-butyl cation attack followed by loss of a proton. This would give a neutral *p-tert*-butylbenzyltin compound, which would react further providing electrophilic cleavage of the phenyl group (eq 4).



(4)

The importance of this pathway and an indication of competition between alkyl, benzyl, and phenyl groups in this gas-phase cleavage reaction was clarified with compound **9**. The base ion (*m/e* 311, 100%) was formed by a reaction as described in eq 4, while the *p-tert*-butylbenzyl cation (*m/e* 147, 75%) was also formed as shown in eq 1. Evidently, the benzyl group is the predominant site for electrophilic attack (the $[M + 57]^+$ and $[M + 1]^+$ ions, 22 and 9%, respectively, are also evident).

The mechanism for cleavage of the benzyl and phenyl groups is different than that for the alkyl groups (in this case methyl and ethyl). In the former case, the intermediate benzenonium ion is formed and loss of the triorganotin cation follows, while in the latter case tin-carbon bond cleavage occurs directly. It is obvious that the former mechanism is more important and helps explain the increased reactivity of these groups under electrophilic cleavage conditions in the gas phase[5c] as well as in solution.[7]

A direct comparison between the four groups in **9** in these gas-phase cleavage reactions may not be entirely possible. For example the M − phenyl ion (*m/e* 255, 12%), M − benzyl ion (*m/e* 241, 9%), *p-tert*-butylbenzyl ion (*m/e* 147, 75%), M − ethyl ion (*m/e* 303, 10%), and M − methyl ion (*m/e* 317, 9%) can be compared, assuming the percentage of the *p-tert*-butylbenzyl ion is added to that of the M − benzyl ion, giving a cleavage ratio for benzyl:phenyl:ethyl:methyl of 9:1.3:1.1:1. However, if we add the M + 57 − 77 ion percentage to that for the M − phenyl ion the ratio becomes 9.3:12.4:1.1:1. These results create difficulties in comparing the benzyl and phenyl groups, but do qualitatively indicate their increased reactivity in the gas phase over alkyl groups.

Clearly, the stabilization afforded by $\sigma-\pi$ conjugation, via the $-CH_2SnR_3$ group, must be invoked to explain the formation of the $[M + 57]^+$ and $[M + 1]^+$ ions, since we have not previously observed these ions with the numerous nonfunctionally substituted organotin compounds we have studied.[5a-c,8]

Thus, vertical stabilization, in the gas phase, of the benzenonium ion by carbon–tin σ electrons can be readily observed by CIMS techniques and establishes this interaction as being of prime importance in electrophilic aromatic cleavage reactions of benzyltin compounds. To our knowledge this is the first example of carbon–metal σ–π conjugation being documented in the gas phase, as related to electrophilic reactions with aromatic compounds, and the results reported herein support previous spectroscopic techniques[2–4] as well as solvolysis studies[9] concerning the significance of this effect.

Experimental Section

The CIMS were obtained on a Finnigan 1015D instrument (isobutane at 0.5 torr) coupled to a System Industries Model 150 computer. The compounds, **1–10**, were introduced using the direct inlet technique and volatilized by slowly heating the probe (~100 °C). Compounds **1–4** and **8** were prepared according to literature ref 3a, 10, 11, 11, and 12, respectively, and were of analytical purity.

Compounds **5**, **6**, and **7** were prepared similarly from tribenzyltin chloride and the corresponding methyl, cyclopentyl, and phenyl Grignard reagents in diethyl ether and were purified by column chromatography (SiO_2 or Al_2O_3) using benzene as the eluent. Compound **5** (mp 47–49 °C) had a ^1H NMR spectrum (270 MHz, CCl_4, Me_4Si) with signals at 0.15 (CH_3Sn), 2.55 (CH_2Sn), and 6.80 and 7.46 ppm (aromatic) in the correct ratios; compound **6** (mp 66–69 °C; MeOH) had signals (60 MHz) at 1.1–1.8 (ring CH_2's), 2.20 (CH_2Sn), and 6.63 and 7.23 ppm (aromatic); compound **7** (thick oil) had signals (60 MHz) at 2.34 (CH_2Sn) and 6.63 and 7.20 ppm (aromatic). Compound **9** was prepared by the following procedure: diphenylethylmethyltin was reacted with hydrochloric acid in methanol to give phenylethylmethyltin chloride. Reaction of this compound with benzylmagnesium chloride gave **9** (bp 116–117 °C, 0.2 mm) in 77% yield. Compound **9** had signals at 0.18 (CH_3), 1.0 (CH_2CH_3), 1.15 (CH_2CH_3), and 7.0–7.38 ppm (aromatic). All new compounds (**5**, **6**, **7**, **9**) gave satisfactory C, H, and Sn analyses (±0.3%).

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Registry No.—Tribenzyltin chloride, 3151-41-5; diphenylethylmethyltin, 17842-01-2; phenylethylmethyltin chloride, 68024-64-6; benzylmagnesium chloride, 6921-34-2.

References and Notes

(1) (a) University of California; (b) Vrije Universiteit; (c) Aangesteld Navorser of the N.F.W.O.

(2) (a) T. G. Traylor, W.Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Brown, *J. Am. Chem. Soc.*, **93**, 5715 (1971); (b) C. G. Pitt, *J. Organomet. Chem.*, **61**, 49 (1973); (c) T. G.Traylor, H. J. Berwin, J. Jerkunica, and M. L. Hall, *Pure Appl. Chem.*, **30**, 599 (1972).

(3) (a) W. Adcock, B. D. Gupta, W. Kitching, D. Doddrell, and M. Geckle, *J. Am. Chem. Soc.*, **96**, 7360 (1974); (b) W. Adcock, B. D.Gupta, W. Kitching, and D. Doddrell, *J. Organomet. Chem.*, **102**, 297 (1975).

(4) A. Hosomi and T. G. Traylor, *J. Am. Chem. Soc.*, **97**, 3682 (1975).

(5) (a) R. H. Fish, R. L. Holmstead, and J. E. Casida, *Tetrahedron Lett.*, 1303 (1974); (b) R. H. Fish, R. L. Holmstead, and H. G. Kuivila, *J. Organomet. Chem.*, **137**, 175 (1977); (c) R. H. Fish and B. M. Broline, *ibid.*, **159**, 255 (1978).

(6) F. H. Field, *Acc. Chem. Res.*, **1**, 42 (1968).

(7) M. Gielen and J. Nasielski, "Organotin Compounds", A. K. Sawyer, Ed., Vol. 3, Marcel Dekker, New York, N.Y., 1972, p 625 and references therein.

(8) In a recently submitted paper on the gas-phase electrophilic cleavage reactions of organotin compounds, the mechanism we proposed was challenged because our spectra lacked $[M + 1]^+$ ions. Additionally, the reviewers suggested that our results could be explained by electron-transfer reactions rather than by electrophilic reactions. It is obvious that electron-transfer reactions with the *tert*-butyl cation are not significant with the benzyltin compounds, since most of the compounds reported gave an observed $[M + 1]^+$ or $[M + 57]^+$ ion. This supports the assumption that the ionization potential of the *tert*-butyl cation is lower than the organotin compounds precluding electron transfer reactions [see ref 5b].

(9) G. D. Hartmer and T. G. Traylor, *J. Am. Chem. Soc.*, **97**, 6147 (1975).

(10) E. H. Bartlett, C. Eaborn, and D. R. M. Walton, *J. Organomet. Chem.*, **46**, 267 (1972).

(11) R. Alexander, M. T. Attar-Bashi, C. Eaborn, and D. R. M. Walton, *Tetrahedron*, **30**, 899 (1974).

(12) Y. Sato, Y. Ban, and H. Shirai, *J. Org. Chem.*, **38**, 4313 (1973).

Regio- and Stereospecific Acyl–Metal Insertion from $Fe(CO)_5$-Mediated Photolysis of (+)-α-Thujene[†]

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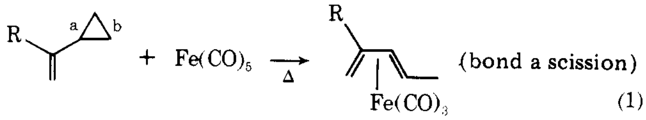
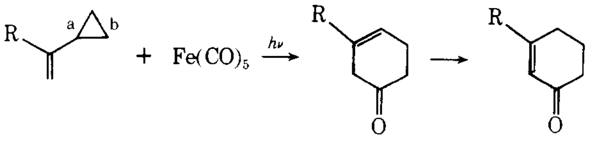
(+)-α-Thujene has been brought into reaction under photolytic conditions with $Fe(CO)_5$ and under thermal conditions with $Fe_3(CO)_{12}$. It was possible to isolate from both the thermal and the photochemical reaction an adduct resulting from ring opening and acyl-$Fe(CO)_3$ insertion to yield a complex accommodating both σ- and π-allyl components. The observed stereospecific and regiospecific rearrangement–insertion reaction is envisioned to arise from an orthogonal electrophilic attack of an $Fe(CO)_4$ species on the α-thujene from the side opposite to the cyclopropane ring. The photochemical reaction of (−)-umbellulone yielded an intractable heat-sensitive σ,π-allyl complex which readily ejects the metal to form (±)-umbellulone. Factors governing the course of this reaction are discussed.

Our previous studies of the reactions between iron carbonyl and systems in which cyclopropyl groups are conjugated with C–C π-electron units led to characterization of four distinctly different modes of rearrangement. The first one was the thermolysis of cyclopropylethylenes in presence of $Fe(CO)_5$ to form 1,3-dienes resulting from ring opening and a hydrogen shift (eq 1).[1] The second was the photochemical reaction, yielding cyclohexenones arising from rearrangement coupled with carbonyl insertion (eq 2).[2] We showed that the latter reaction is general for a number of cyclopropylethylenes and that it is quite sensitive to effects of substitution.[3]



(1)



(2)

[†] Dedicated to Professor E. Havinga on the occasion of his 70th birthday.

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