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GAS PHASE 1,3-DEOXYSTANNYLATION REACTIONS OF γ-SUBSTITUTED ORGANOTIN ALCOHOLS UTILIZING CHEMICAL IONIZATION MASS SPECTROMETRY *

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Summary

The gas phase 1,3-deoxystannylation reactions of γ-substituted organotin alcohols have been studied by methane and isobutane chemical ionization mass spectrometry. It was found that γ-hydroxybutyltributyltin and γ-hydroxybutyldibutyltin chloride undergo the 1,3-deoxystannylation reaction to a greater extent than the corresponding 1,4-deoxystannylation using the δ-substituted analogues of the above named compounds. This result substantiates the unusual reactivity of γ-substituted organotin alcohols under gas phase protonolysis conditions.

The electronic factors affecting the stabilization of the transition state were ascertained with γ-phenyl-γ-hydroxypropyltrimethyltin derivatives, in which the γ-phenyl group was substituted with groups such as H, *p*-OMe, *p*-Me, *p*-Cl, *p*-F, *m*-OMe, *m*-Me, *m*-Cl and *m*-CF_3. We observed a reasonably linear Hammett relationship when plotting the log $[P-17]_X^+/[P-17]_H^+$ vs. σ^+ with rho (ρ) equal to -1.0.

Thus electron-donating groups stabilize the $[P-17]^+$ ion and carbon—tin sigma (σ) electrons can either, by a neighbouring group effect, attack the nucleofugic center, or the carbonium ion can attack the carbon—tin σ electrons to form the trimethyltin cation and a cyclopropane derivative. Consequently, we propose that a two-step mechanism for the 1,3-deoxystannylation reaction is operating in the gas-phase with this type of compound. The factors contributing to this gas phase reaction will be discussed.

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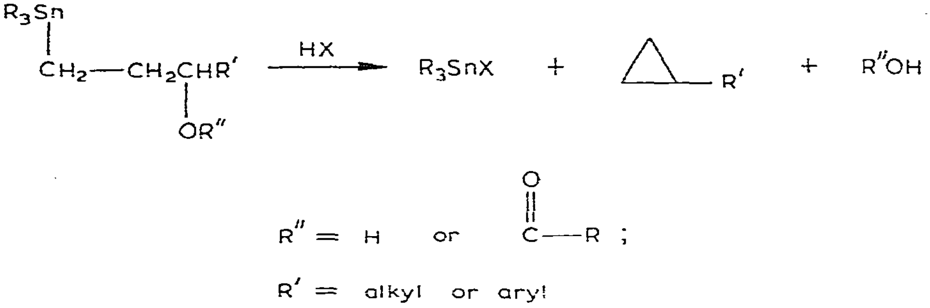
Introduction

The unusual reactivity of γ-substituted organotin alcohols and their derivatives under acidic conditions have recently been elucidated by Kuivila [2a,b] and Davis [3a—c] and their coworkers. The overall reaction (eq. 1) involves a 1,3-deoxystannylation with formation of a triorganotin derivative and cyclopropanes.



(1)

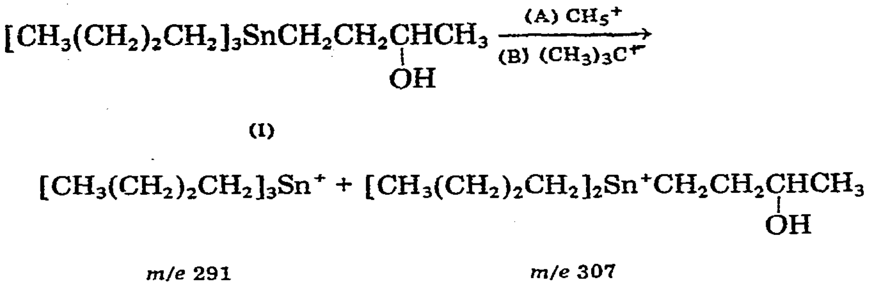
The solution studies [2,3] have not clarified whether this is a concerted or stepwise reaction. They have shown that there can be a large rate enhancement due to either percaudal homoconjugation [3b,c] or neighbouring group participation [2a,b] of the carbon—tin sigma (σ) bond. Furthermore, it was also shown that a double inversion [3c] mechanism is preferred in a rigid system, while significant carbonium ion character in the transition state was evident in the solvolysis of γ-aryl substituted-γ-hydroxyorganotin derivatives [2b].

We have initiated a program to study the gas phase protonolysis reactions of organotin compounds [1,4] utilizing chemical ionization mass spectrometry. It was thought that a survey of γ-hydroxyorganotin compounds, under gas phase protonolysis conditions, could provide some information concerning the electronic factors affecting the 1,3-deoxystannylation reaction as well as provide further knowledge with regard to the overall mechanism. In this paper we present the full account [1] of our study of the 1,3-deoxystannylation occurring in the gas phase.

Results and discussion

Our discovery of the gas phase 1,3-deoxystannylation reaction utilizing methane chemical ionization mass spectrometry was initially made with γ-hydroxybutyltributyltin (I) and γ-hydroxybutyldibutyltin chloride (II).

By comparing the loss of the γ-hydroxybutyl group to the unsubstituted butyl group,in I and II (γ-BuOH/Bu), to their corresponding δ-hydroxy isomers, III and IV (δ BuOH/Bu), we were able to ascertain an increased loss of the γ-hydroxybutyl group (γ-BuOH/Bu) under gas phase protonolysis conditions (eqns. 1—4 and Table 1). For example, compound I has a γ-BuOH/Bu ratio of 1.4 compared to 0.95 for the corresponding δ-BuOH/Bu ratio (III, methane). Thus generation of the tributyltin cation is 1.5 times greater for I than for III. This result is also consistent with compound II, which produces 2.5 times more of the dibutylchlorotin cation than the δ compound IV (methane).



$$[CH_3(CH_2)_2CH_2]_3SnCH_2CH_2\underset{\displaystyle OH}{CH}CH_3 \xrightarrow[(B)\ (CH_3)_3C^+]{(A)\ CH_5^+}$$

(I)

$$[CH_3(CH_2)_2CH_2]_3Sn^+ + [CH_3(CH_2)_2CH_2]_2Sn^+CH_2CH_2\underset{\displaystyle OH}{CH}CH_3 \qquad (1)$$

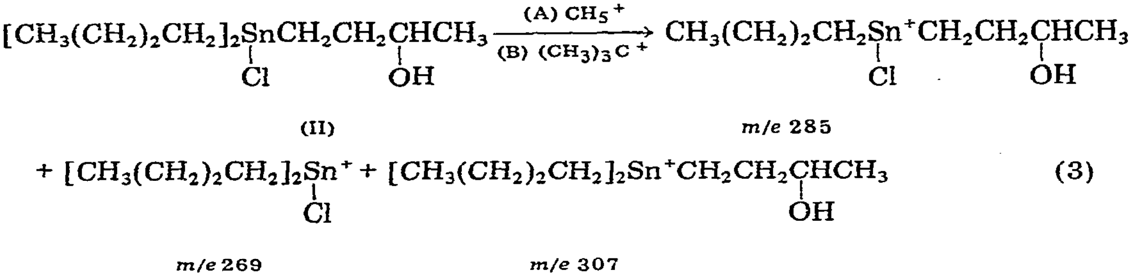
m/e 291 *m/e* 307

$$[CH_3(CH_2)_2CH_2]_3SnCH_2CH_2CH_2CH_2OH \xrightarrow[(B)\ (CH_3)_3C^+]{(A)\ CH_5^+} \qquad (2)$$

(III)

$$[CH_3(CH_2)_2CH_2]_3Sn^+ + [CH_3(CH_2)_2CH_2]_2Sn^+CH_2CH_2CH_2CH_2OH$$

m/e 291 *m/e* 307

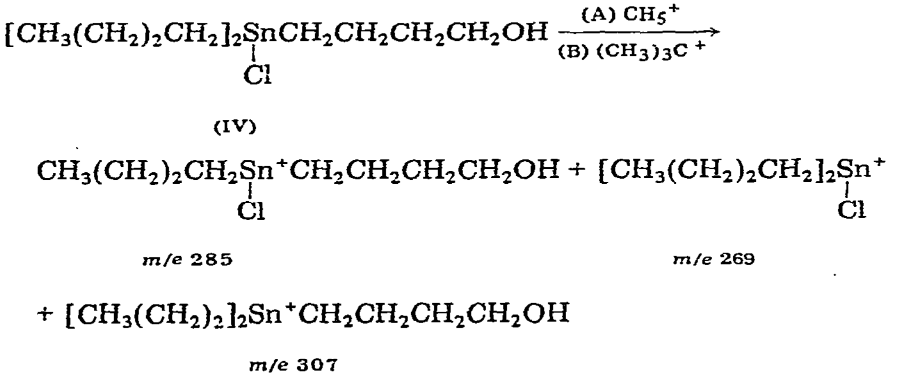


$$[CH_3(CH_2)_2CH_2]_2\underset{\displaystyle Cl}{Sn}CH_2CH_2\underset{\displaystyle OH}{CH}CH_3 \xrightarrow[(B)\ (CH_3)_3C^+]{(A)\ CH_5^+} CH_3(CH_2)_2CH_2\underset{\displaystyle Cl}{Sn^+}CH_2CH_2\underset{\displaystyle OH}{CH}CH_3$$

(II) *m/e* 285

$$+ [CH_3(CH_2)_2CH_2]_2\underset{\displaystyle Cl}{Sn^+} + [CH_3(CH_2)_2CH_2]_2Sn^+CH_2CH_2\underset{\displaystyle OH}{CH}CH_3 \qquad (3)$$

m/e 269 *m/e* 307



$$[CH_3(CH_2)_2CH_2]_2\underset{\displaystyle Cl}{Sn}CH_2CH_2CH_2CH_2OH \xrightarrow[(B)\ (CH_3)_3C^+]{(A)\ CH_5^+}$$

(IV)

$$CH_3(CH_2)_2CH_2\underset{\displaystyle Cl}{Sn^+}CH_2CH_2CH_2CH_2OH + [CH_3(CH_2)_2CH_2]_2\underset{\displaystyle Cl}{Sn^+} \qquad (4)$$

m/e 285 *m/e* 269

$$+ [CH_3(CH_2)_2]_2Sn^+CH_2CH_2CH_2CH_2OH$$

m/e 307

As seen in Table 1 there was also an increased selectivity in formation of the tributyltin or dibutylchlorotin cation with the γ-compounds I and II in going from methane as the reagent gas [CH_5^+] to isobutane [$(CH_3)_3C^+$]. For example, the γ-BuOH/Bu ratio for I goes to 2.0 (isobutane) and dramatically the δ-BuOH/Bu ratio for III goes to ~0.06 (isobutane). This represents an increase in the γ-BuOH/Bu/δ-BuOH/Bu ratio to 33 from 1.5 (methane). This is due to a lowering of the exothermicity of the proton transfer reaction causing the reaction of

TABLE 1

METHANE AND ISOBUTANE CIMS OF COMPOUNDS I—IV

Compound	M — BuOH (%) [a]		M — Bu (%) [b]		M — Cl (%)		(γ or δ BuOH/Bu)	
	CH_4 (A)	C_4H_9 (B)	CH_4 (A)	C_4H_9 (B)	CH_4 (A)	C_4H_9 (B)	CH_4	C_4H_9
I	47	63	33	33			1.4(γ)	2.0
III	32	2	33	33			0.95(δ)	~0.06
II	28	100	8	16	100	27	3.5(γ)	6.2
IV	26	100	19	23	100	70	1.4(δ)	4.3

[a] Relative abundance (total ion current normalized to 100%) based on ^{120}Sn isotope. These were the only major or minor (>5%) ions formed with these compounds. [b] Normalized for two or three butyl groups.

lowest activation energy to proceed at a greater rate. Obviously the γ-hydroxybutyl derivatives I and II are more selective in providing the tributyltin or dibutylchlorotin cation than are their δ-analogs. These latter results are consistent with a gas phase protonolysis reaction on the γ-hydroxyl function followed by loss of the organotin cation, water and the cyclopropane derivative (eq. 1).

Interestingly, by changing the leaving group from an alcohol (H_2O), I and III, to an acetate (HOAc), V (γ) and VI (δ), a greater difference in reactivity between compounds I and V and III and VI was observed (Table 2). This would be consistent with a better leaving group (HOAc) providing more carbonium ion character to the transition state and allowing γ-substituted carbon—tin σ electrons to interact to a greater extent at the incipient carbonium ion site than in the case of the alcohols.

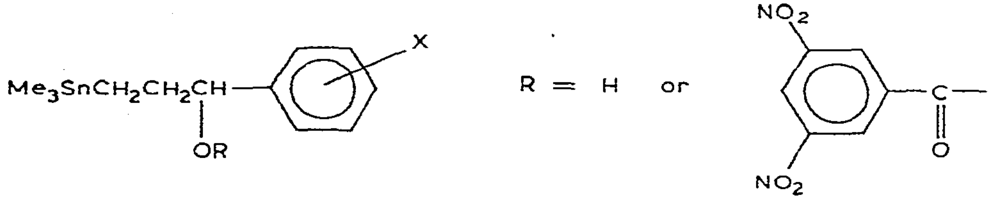
While a study of compounds I, II and V provided information about the overall reaction, it did not reveal much about the concertedness of the gas phase 1,3-deoxystannylation reaction. Recent solution kinetic studies [2b] of this reaction with benzoates of substituted γ-aryl-γ-hydroxypropyltrimethyltin compounds VII—XV showed considerable carbonium ion character being generated in the transition state via a linear Hammett plot (log k vs. σ^+; $\rho = -3.63$) with the electron-donating groups demonstrating an enhanced rate of solvolysis and electron-withdrawing retarding the rate. We thought an analogous study of these compounds VII—XV (R = H) in the gas phase would be informative. We found that the reagent gas isobutane gave us the selectivity we expected,

TABLE 2

METHANE AND ISOBUTANE CIMS OF COMPOUNDS V AND VI

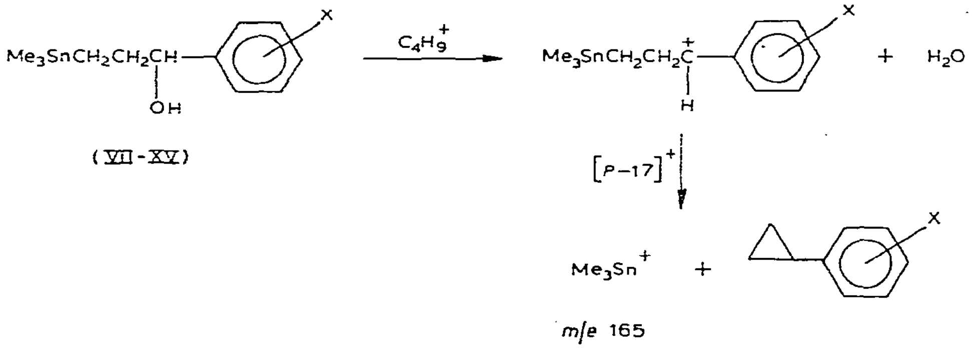
Compound	M — BuOAc (%) [a]		M — Bu (%) [b]		γ or δ BuOAc/Bu	
	CH_4 (A)	C_4H_9 (B)	CH_4 (A)	C_4H_9 (B)	CH_4	C_4H_9
V	71	100	33	15	2.2 (γ)	6.6
VI	44	25	33	33	1.3 (δ)	0.76

[a] Relative abundance (total ion current normalized to 100%) based on ^{120}Sn isotrope. [b] Normalized for three butyl groups.



VII, X = *m*-Cl ; VIII, *m*-CF_3 ; IX, *p*-OMe ; X, H ; XI, *m*-Me ;
XII, *p*-F ; XIII, *m*-OMe ; XIV, *p*-Me ; XV, *p*-Cl

i.e., *p*-OMe gave the greatest relative intensity of the quasi $[P + 1]^+$ ion minus H_2O, $[P - 17]^+$, while VII (*m*-Cl), VIII (*m*-CF_3), XII (*p*-F) and XV (*p*-Cl) gave the smallest intensity for this ion (eq. 5, Table 3).



(5)

The extent of formation of the intermediate carbonium ion in the gas phase with VII—XV should be linearly related to the substituent on the phenyl group. By plotting the log $[P - 17]_X^+/[P - 17]_H^+$ versus σ^+, a fairly linear relationship

TABLE 3

ISOBUTANE CIMS OF COMPOUNDS VII—XV (R = H)

Compound	X	$[P - 17]^{+}$ [a] (*m/e*)	$[Me_3Sn]^+$ (*m/e* 165)	$\log \frac{[P-17]_X^+}{[P-17]_H^+}$	σ^+
VII	*m*-Cl	5.7 (317) [b]	100	—0.43	0.40
VIII	*m*-CF_3	4.9 (351) [c]	100	—0.49	0.43
IX	*p*-OMe	69.5 (313) [d]	100	+0.66	—0.78
X	H	15.3 (283) [e]	100	0	0
XI	*m*-Me	28.5 (297) [f]	100	+0.27	—0.07
XII	*p*-F	3.7 (301) [g]	100	—0.62	—0.07
XIII	*m*-OMe	45.5 (314) [h]	79	+0.47	0.05
XIV	*p*-Me	22.1 (297) [i]	100	+0.16	—0.31
XV	*p*-Cl	2.1 (317) [j]	55	—0.81	0.11

[a] Percent relative abundance (total ion current normalized to 100%) based on ^{120}Sn isotope. [b] Other ions (% relative abundance) *m/e* 183 * (23.7) (* denotes tin containing ions). [c] *m/e* 183 * (23.6). [d] *m/e* 183 * (15.3), 147 (59), 148 (45.8), 149 (32), 121 (23.7), 137 (22). [e] *m/e* 183 * (17.7), 117 (20), 118 (11.3). [f] *m/e* 183 * (17.5), 131 (23.8), 132 (16.7). [g] *m/e* 183 * (19.2), 135 (5), 136 (9.6), 109 (16). [h] *m/e* 183 * (16.9), 121 (36.4). [i] *m/e* 183 * (12.3), 131 (38), 132 (24). [j] *m/e* 183 * (10.5), 151 (100), 152 (13), 153 (46.0), 125 (10).

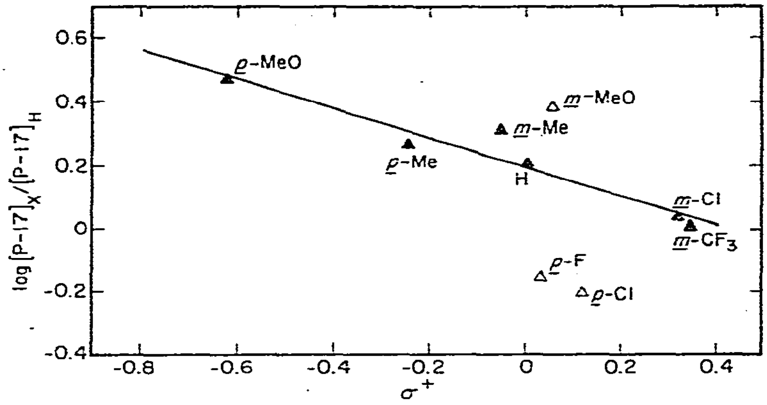


Fig. 1. Hammett plot of log $[P - 17]_X^+/[P - 17]_H^+$ vs. σ^+.

was obtained (Fig. 1), however, compounds XII, XIII and XV, i.e., X = *p*-F, *m*-OMe and *p*-Cl fall off the line *. The exact cause of these latter deviations remains to be established. The rho (ρ) value was calculated to be —1.0 from the slope with a correlation coefficient of 0.96. The gas phase reaction leading to the $[P - 17]^+$ ion is enhanced by electron-donating groups and retarded by electron-withdrawing groups, and provides the first direct evidence for an intermediate carbonium ion in the 1,3-deoxystannylation reaction. The trimethyltin ion, the base ion in compounds VII—XII and XIV is postulated to form when carbon—tin σ electrons either attack the nucleofugic center or alternatively the carbonium ion undergoes an electrophilic attack on the carbon—tin σ electrons with formation of substituted phenylcyclopropanes (eq. 5). Pertinently, these are the only tin containing ions of any significance that we have observed with compounds VII—XV.

CIMS versus EIMS

In this CIMS study with methane as the reagent gas we are generating the CH_5^+ ion as well as the $C_2H_5^+$ ion [1]. The CH_5^+ ion is an extremely efficient Brønsted acid, while the $C_2H_5^+$ ion can undergo electron transfer reactions with organometallic compounds [5a,b] ($RM + C_2H_5^+ \rightarrow RM^{+} + C_2H_5^{\cdot}$) **. Thus, it was important to ascertain that we were examining electrophilic reactions and not electron transfer reactions. We studied the electron impact mass spectra (EIMS) of compounds I—IV and they gave results (Fig. 2, Spectrum B, and Fig. 3, Spectrum D) which were totally different from the CIMS (Fig. 2, Spectrum A, and Fig. 3, Spectrum C) results. More importantly, the EIMS of compound I has been studied by Kingston et al. [6] and shows a rearrangement of the follow-

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* These points were not included in the least-squares regression analysis [▲], but are shown in Fig. 1 [△]. We thank Dr. Peter Rausch for the computer plot and the least-squares regression analysis.

** The ionization potential of $[C_2H_5]^+$ is slightly lower (8—9 eV) than the organotin compounds (9—10 eV) making electron transfer an endothermic process.

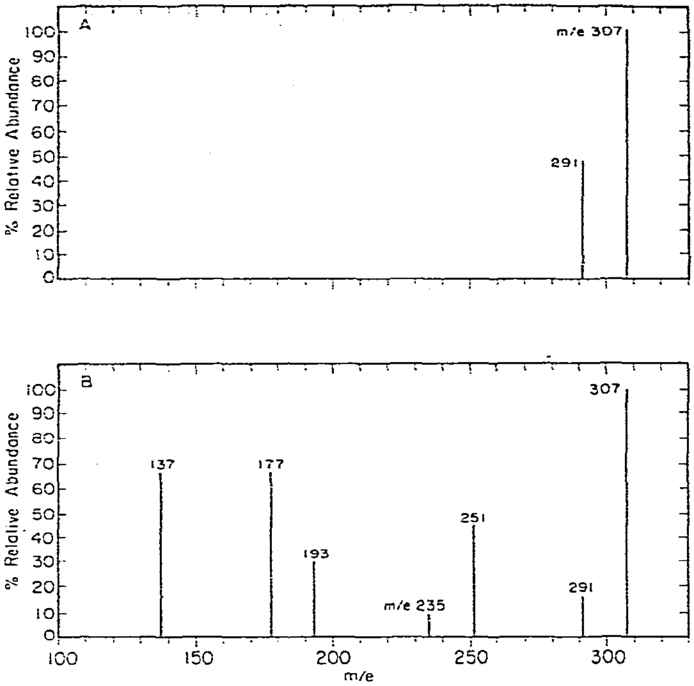


Fig. 2. A, Methane CIMS of I. B, EIMS of I.

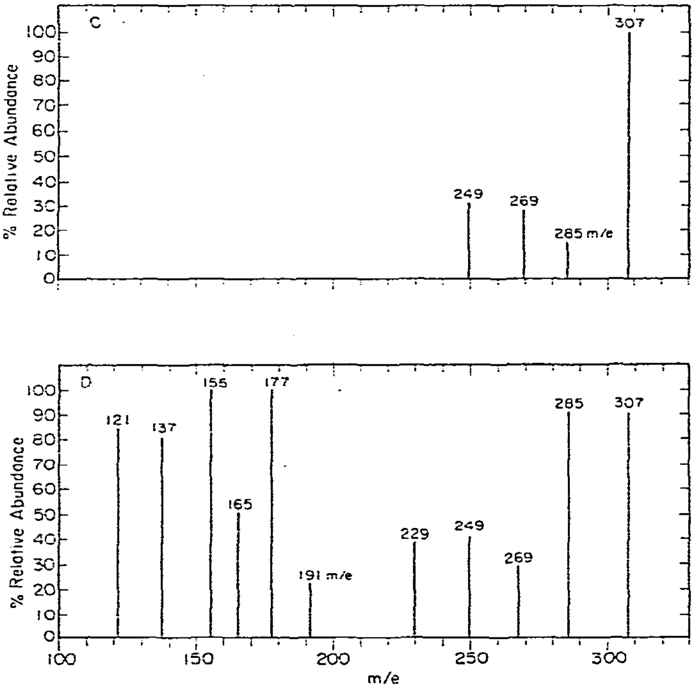
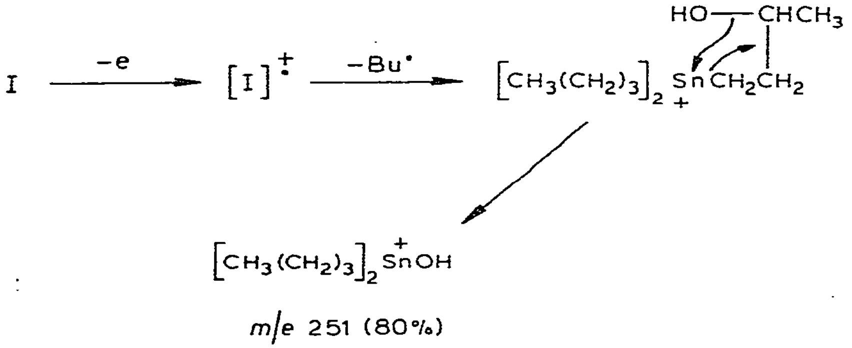


Fig. 3. C, Methane CIMS of II. D, EIMS of II.

ing type to be predominant in the γ-hydroxybutyltributyltin compound I (eq. 6).



(6)

Significantly this rearrangement with compounds I and II was not of major consequence under methane CIMS conditions (I, 5%; II, 2%), while the extent of the formation of the tributyltin ion, *m/e* 291, was reversed in EIMS versus CIMS. In the former case with I the *m/e* 291 ion was formed in a relative abundance of 10%, while under methane and isobutane CIMS it was 47% and 63% respectively. This latter result would indicate that the tributyltin ion was being formed under gas phase protonolysis conditions for the 1,3-deoxystannylation reaction to occur and not from any initial electron transfer process. However, the most conclusive evidence for this reaction comes from the formation of the $[P-17]^+$ ion with compounds VII—XV using isobutane as the reagent gas. Pertinently, there is no evidence that such ions are formed in the EIMS of compounds I—IV or VII—XV. We therefore conclude that the major reaction occurring with compounds VII—XV is proton transfer and that electron transfer reactions with $C_4H_9^+$ (isobutane) are not thermodynamically competing processes *.

Mechanism of 1,3-deoxystannylation in the gas phase

It is apparent that from our results we cannot conclude whether compounds I, II or V undergo a concerted or stepwise mechanism for the 1,3-deoxystannylation reaction under gas phase protonolysis conditions. However, it seems reasonable to postulate a two-step mechanism for the 1,3-deoxystannylation with the series of γ-hydroxyorganotin compounds VII—XV [2b]. Apparently the substituted phenyl group can impart moderate stabilization to the benzyl carbonium ion as indicated by results both in solution [2b] and the gas phase. It is also worthwhile to note that the ρ value for the gas phase reaction is −1.0 compared to −3.63 for the solution study. The lower ρ value in the gas phase may be due to the formation of a highly energetic conjugate acid, $R\overset{+}{O}H_2$, which requires little assitance for stabilization when R^+ is formed by delocalization of the positive charge into the benzene ring. Alternatively, the interaction of the carbon—tin σ electrons with the carbonium ion center, which would be

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* The ionization potential of $C_4H_9^+$ (~7—8 ev) is lower than the organotin compounds (9—10 ev) making electron transfer an endothermic process (see Ref. 7) but proton transfer an exothermic process.

more pronounced in the gas phase, could also be invoked to explain the lower ρ value in the gas phase.

We conclude from this study that the substituent at the γ-carbon of these γ-hydroxyorganotin compounds (i.e. substituted phenyl or alkyl groups) controls the concertedness of the reaction. The carbon—tin σ electrons contribute more or less to the stabilization of the incipient carbonium ion center depending upon the ability of the γ-carbon substitutent to itself stabilize the carbonium ion.

These and other aspects of the 1,3-deoxystannylation reaction await further clarification, however, this approach of comparing the solution results with the gas phase results should prove to be a powerful tool for separating electronic and solvent effects in future mechanistic studies.

Experimental

Materials and instrumentation

The MS were recorded with a Finnigan 1015D instrument (CIMS, methane at 1 Torr and isobutane at 0.5 Torr and EIMS, 70 eV; ratio of reagent ions to sample ions $> 10:1$) coupled to a System Industries Model 150 computer. The ion source temperature was ~100°C for all samples studied. Compounds I—VI were prepared according to literature procedures and were of analytical purity. The procedure entails addition of the appropriate organotin hydride to the unsaturated alcohols I and III [6] and II and IV [8], while V and VI were prepared by acetylation of the alcohols, I and III, with acetic anhydride/pyridine. Compounds VII—XV were prepared as described by Kuivila et al., and will be reported in a future publication [2b].

Acknowledgements

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