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ELECTROPHILIC DISPLACEMENT REACTIONS

XVIII*. PROTONOLYSIS OF ALLYLTINS. SUBSTITUENT, SOLVENT ISOTOPE AND TEMPERATURE EFFECTS ON RATE

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Summary

The kinetics of the protonolysis in methanol containing 4% water of nine acyclic allyltins and four cyclic allyltins have been measured and activation parameters computed from the temperature dependence on rate. Structural variations represented include changes in the substituents on the tin atom, substitution on the allyl group, and ring size. Primary solvent kinetic isotope effects have also been determined for a selected group of substrates. These reveal that the proton transfer occurs in the rate determining step of the reaction. The effects of the structural variations on rate are discussed in terms of the activation parameters.

Introduction

The mechanisms of the reactions of allylic organometallics with electrophiles are not fully understood, and yet have received only moderate attention. One generalization which has evolved from the investigations made to date is that the reactions proceed predominantly, if not exclusively, by the S'_E mechanism, eqn. 1, in which M is a metal atom of an organometallic group, and E is an electrophile [1,3-7].

$$M—CH_2CH{=}CHCHR + E^+ \rightarrow M^+ + CH_2{=}CHCHRE \qquad (1)$$

We have reported that the major product of the protonolysis 2-butenyltrimethyl-

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* For part XVII see ref. 1.

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TABLE 1

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR PROTONOLYSIS OF ALLYLTINS IN METHANOL—4% WATER

No.	Substrate	k_2 (mol^{-1} sec^{-1})				$\Delta H^{\neq}$	$\Delta S^{\neq}$
		0°C	25°C	35°C	45°C	(kcal · mol^{-1})	(cal mol^{-1} deg.$^{-1}$)
I	Allyltrimethyltin	0.0465	0.475	0.866	2.01	13.7	—14.0
II	Allyltriethyltin	0.0362	0.603	1.12		16.2	—5.2
III	Allyltriisopropyltin	0.0118	0.218	0.473		17.3	—3.5
IV	Allyltricyclohexyltin	0.0103	0.341	0.675	1.33	18.5	1.4
V	Allyltriphenyltin	0.000252	0.00441	0.00760	0.0273	16.9	—12.6
VI	*cis*-Crotyltrimethyltin	0.00266	0.0508	0.0995	0.199	16.2	—10.1
VII	*trans*-Crotyltrimethyltin	0.00117	0.0274	0.0644		18.8	—2.6
VIII	Crotyltriphenyltin	0.0000185	0.000320	0.000830		19.2	—10.1
IX	β-Methallyltrimethyltin	2.78	24.8			13.5	—6.9
X	Cyclopent-2-enyltrimethyltin		0.111	0.266	0.634	15.7	—10.2
XI	Cyclohex-2-enyltrimethyltin		0.0263	0.0725	0.184	17.2	—8.0
XII	Cyclohept-2-enyltrimethyltin		0.465	0.880	1.65	11.3	—22.1
XIII	Cyclooct-2-enyltrimethyltin		0.115	0.231	0.435	11.9	—22.9

tin in wet methanol is 1-butene. However, small amounts of *cis*- and *trans*-2-butenes are also formed, and the amounts depend upon the reaction conditions. We suggested that the 2-butenes were also formed by an S'_E reaction of the lyonium ion with small amounts of 1-buten-3-yltrimethyltin in equilibrium with its allylic isomer [1]. It was shown that only one deuterium atom is incorporated in the butene formed when the reaction was conducted in methanol-d_1, indicating a rate determining proton transfer. In the present paper we report on solvent kinetic isotope effects which substantiate this conclusion; on activation parameters and on the effects of variations in the nature of the allylic function and of the substituents on the tin atom on the rate of protonolysis [8].

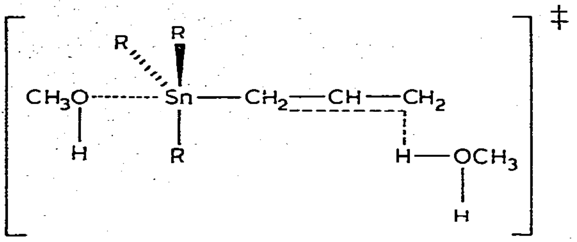
The organotins used in this work were prepared by standard methods detailed in the Experimental, and their elemental analyses and spectral properties provided verification of their identity and purity. Kinetics were studied spectrophotometrically in methanol containing 4 ml of water per 100 ml of solvent by exploiting the intense absorption of the substrates at 225 nm. The acid used was hydrogen chloride, and the reaction was verified as being first order in acid and in substrate under both second order and pseudo first order (excess acid) conditions.

Results and discussion

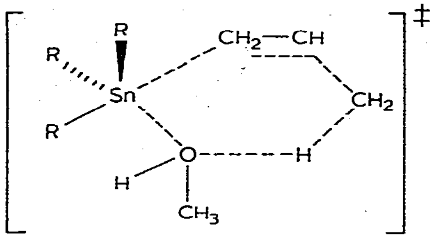
Kinetic results for nine acyclic and four cyclic allyltins are gathered in Table 1. Structural variations represented include substitution on the tin atom and on the allyl group; geometrical isomerism; and ring size. Results obtained at two or more temperatures were used to compute the activation enthalpies and entropies shown in the last two columns. In Table 2 are listed the rate constants for protonolysis in deuterated solvent and the primary kinetic hydrogen isotope effects for a selected group of substrates. The values are uniformly greater than unity, and are greater for the acyclic substrates than for the cyclic ones. These observations confirm the conclusion drawn earlier on the basis of deuterium incorporation in the product [1] that proton transfer occurs in the rate determining step of the reaction. Transition states which could lead to these results are the open S_E2' type, A, and the closed, or cyclic, S_E1 type, B [3]. These will be used as bases for the discussion which follows. It should be noted that the major loci of positive charge in either A or B are the proton being transferred, the β-carbon of the allylic system, and the departing tin atom. This will be true qualitatively whether the transition state is transformed into products directly or into a carbonium ion, C, which rapidly loses the organotin cation to form product. This follows because the cation can be highly stabilized by σ—π-hyperconjugation: D [9].

Effects of substituents on tin

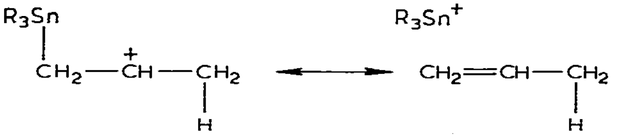
The stability of the transition state should be affected by the electronic character of the substituents on tin because the carbon—tin bond is either being broken or polarized in the transition state. In the first four entries of Table 1 the substituents are changed from methyl to ethyl, isopropyl, and cyclohexyl. The effect on rate is virtually negligible, being a modest monotonic decrease at 0°C, and an alternation at 35°C. This is seen to be due to nearly



(A)



(B)



(C) (D)

compensating effects in the enthalpies and entropies of activation, both of which increase as one goes down the series. If solvation at the tin atom is important in the transition state, the results become reasonable: increasing the electron releasing capacity of the groups on the tin atom will diminish the Lewis acidity of the tin and makes solvation less effective as a stabilizing factor in the transition state. Increasing the bulk of the substituents will have a parallel effect. The result will be an increase in entropy in the transition state which is compensated for by an increase in the enthalpy of activation. Evidence that the large tin atom does not completely damp inductive electron transmission is provided by the observations that the pK_a's of trimethyl-, triethyl-, and tributyltin hydrides are 23.5, 24.7 and 25.0 respectively (in dimethoxyethane); and that for triphenyltin hydride is estimated to be about 16 [10]. When the tricyclohexyltin group is replaced by the triphenyltin group of similar size, but more electron withdrawing, both the entropy and enthalpy of activation decreases, but the major factor in causing the forty to seventy-fold decrease in rate is the entropy, which decreases by fourteen units.

It should be pointed out that the compensation effect discussed in the

TABLE 2

SOLVENT DEUTERIUM ISOTOPE EFFECTS ON PROTONOLYSIS OF ALLYLTINS IN METHANOL—4% WATER

Substrate	k_D [a] (mol^{-1} sec^{-1})	k_H/k_D
Allyltrimethyltin	0.147	3.27
Allyltriphenyltin	0.00132	3.34
Allyltricyclohexyltin	0.0668	5.11
Cyclopent-2-enyltrimethyltin	0.0507	2.18
Cyclohept-2-enyltrimethyltin	0.179	2.62
Cyclooct-2-enyltrimethyltin	0.0481	2.40

[a] In 96-98% Methanol-d_1—4% D_2O, DCl, 25°C.

previous paragraph is not linear in the sense that changes in $\Delta H^{\neq}$ are uniformly compensated by changes in $\Delta S^{\neq}$. In such a case a plot of $\Delta H^{\neq}$ vs. $\Delta S^{\neq}$ would be linear with a slope with units of temperature, the isokinetic temperature of an isokinetic plot [11]. Compounds I-IV do in fact fall on such a plot yielding an isokinetic temperature of 313°C. However, compound V falls far off the line. The data can be subjected to the more rigorous test of a true isokinetic relationship in which log k/T is plotted vs. $1/T$ for each compound. All of the lines should cross a single temperature [12]. Such plots for compounds I-IV fail this test.

Effects of methyl substitution on the allyl group

Replacement of hydrogen on the β- and λ-carbons of the allyl group have opposite effects on the rate of protonolysis. β-Methylallyltrimethyltin reacts fifty times as fast as allyltrimethyltin. This effect is attributable to the ability of the methyl group to contribute to the stabilization of the developing positive charge in the transition state through hyperconjugation. The major thermodynamic manifestation of this effect is an increase in entropy of activation by about seven entropy units, with the enthalpy of activation remaining about the same. The entropy effect may be due to the increased dispersal of charge caused by the presence of the methyl group, thus diminishing the role of solvation in stabilizing the transition state.

When the methyl group is introduced into the λ-position in place of methyl the rate decreases by a factor of nine for the *cis*-isomer, and by a factor of seventeen for the *trans*-isomer. These effects appear to be due primarily to increases in the enthalpy of activation. The methyl group on the λ-carbon perturbs the π-electron density thus requiring a greater change in electron distribution when attack by the proton occurs. A qualitatively similar, but smaller, effect of methyl substitution for hydrogen on rate of proton attack was observed by Purlee, Taft and DeFazio. Isobutylene was observed to undergo hydration in aqueous nitric acid about 1.3 times as fast as trimethylethylene [13]; this was the result of a 1.1 kcal increase in enthalpy and a 2.6 unit increase in entropy of activation.

Effects of ring size in cyclic allyltins

If the immediate product formed via the rate determining transition state is the carbonium ion C then the primary change which occurs is the conversion of the carbon at which the proton is attacking from sp^2 hybridization to sp^3 hybridization. On the other hand, if the transition state collapses directly to product, and if it occurs about midway along the reaction coordinate, then the central carbon of the allylic triad will retain its sp^2 hybridization, and each of the two terminal carbons will be intermediate between sp^2 and sp^3. This will require substantial conformational restraints in the ring, which would be most pronounced in smaller rings. The results in Table 1 for four cyclic allyltins show the reactivity order $C_7 > C_5 > C_8 > C_6$. The activation parameters fall into two pairs: C_5 and C_6 have high enthalpies and lower entropies, whereas C_7 and C_8 have low enthalpies and higher entropies. Thus a certain degree of compensation between these two parameters is evident. These results may best be accommodated by assuming transition states similar to A or B as the most stable.

Then in the C_5 and C_6 compounds stabilization by σ—π hyperconjugation by the C—Sn bond is minimal because the requisite conformation will be of high energy. Thus, the enthalpy of activation will be high, as will the entropy because little positive charge is developing on the tin with resultant minimal solvation. On the other hand, the C_7 and C_8 rings can adopt the appropriate conformations more readily, with a greater resultant contribution from solvation and a smaller enthalpy requirement for achieving the transition state. Some fraction of the entropy decrease would result from freezing of the molecules into the favorable transition state conformations.

Primary kinetic isotope effects

The solvent hydrogen isotope effects, k_H/k_D, on rate shown in Table 2 increase with increased enthalpy of activation, although cyclopent-2-enyltrimethyltin is an exception. The largest value is observed for cyclohexyltrimethyltin, which also has the largest activation enthalpy; the acyclic pair, allyltrimethyltin and allyltriphenyltin, have intermediate values, and the lowest values are displayed by the C_7 and C_8 cycloalkenyl analogs. The high value of the enthalpy of activation for cyclohexyltrimethyltin suggests a later transition state than in the other examples, and the higher kinetic isotope effect implies that the proton is more nearly midway in the process of transfer from oxygen of the lyonium ion to the carbon of the allyl group. A corollary is that the lower isotope effects represent earlier transition states in accord with their lower ΔH^{+} values.

Experimental

Materials

The solvent for the kinetic studies was prepared by diluting 4.00 ml of distilled water to 100 ml with Fisher Certified Reagent grade methanol contain-

TABLE 3

SYNTHETIC AND ANALYTICAL DATA FOR ALLYLTINS

Compound No. [a]	Synthetic Method	% Yield	Analysis found (calcd.)	
			C	H
I	[a]	75		
II	1	76	44.11 (43.90)	7.94 (7.72)
III	1	82	50.22 (50.00)	9.13 (9.03)
IV	1	41	61.49 (61.76)	9.20 (9.31)
V	[b]		Sn, 30.48	(Sn, 30.35)
VI + VII	1	81	38.23 (38.41)	7.50 (7.37)
VIII	[c]			
IX	1	81	38.62 (38.41)	7.34 (7.37)
X	[d]		41.85 (41.61)	7.14 (6.94)
XI	2	22	44.60 (44.26)	7.46 (7.37)
XII	2	26	46.59 (46.51)	7.80 (7.75)
XIII	2	46	49.34 (48.53)	8.40 (8.09)

[a] See ref. 1. [b] Gift of M & T Chemicals Inc. [c] Gift of D.F. Whittemore. [d] Prepared by addition of trimethyltin hydride to cyclopentadiene [2].

TABLE 4

SPECTROSCOPIC DATA FOR ALLYLTINS AND REACTION PRODUCTS IN METHANOL—4% WATER

Compound [a] No.	λ_{max} (nm)	ϵ	λ [b] (nm)	$\epsilon_{reactants}$	$\epsilon_{products}$
I			225	7,120	0
II	209	13,200	225	8,400	0
III	209	13,960	225	9,650	2,055
IV	210	15,540	225	12,660	4,870
V			225	8,300	500
VI	215		225	5,710	0
VII	215		225	6,830	0
VIII			235	9,460	500
IX			225	7,730	0
X	217	9,820	225	8,710	0
XI	210	8,950	225	6,120	0
XII	222	11,000	225	10,800	0
XIII	213	9,200	225	8,064	0

[a] See Table 1 for identifications. [b] Wavelength used in analytical determinations.

ing 0.01-0.05% water. Methanol-d_1 was prepared according to the method of Streitwieser et al. [14] by the dimethyl sulfate catalyzed reaction of deuterium oxide (99.8%) with dimethyl carbonate. Deuterium chloride was obtained by the reaction of deuterium oxide with benzoyl chloride [15]. The halides used in the preparation of the allyltins were commercially available chlorides, or, in the case of compounds XI-XIII, 3-bromocycloalkenes prepared by reaction of the cycloalkenes with *N*-bromosuccinimide [16].

Method 1 for the preparation of the allyltins involved the preparation of the Grignard reagent from the allyl chloride using a three-fold excess of magnesium in ethyl ether, followed by reaction of the filtered reagent solution with the appropriate organotin chloride [17]. Method 2 was that of Kraus and Greer [18] in which trimethyltin sodium was prepared in liquid ammonia, and then allowed to react with the allylic halide. Data on yields and elemental analyses are gathered in Table 3.

Kinetics

The kinetic procedure was that described previously [1] using the spectral data for the allyltins shown in Table 4. The absorbance at 225 nm was taken as a direct measure of the concentration of the reactant excepting those cases (III-V, VIII) which gave products absorbing in the same region. Correction for product absorbance was made in calculating concentrations in these cases. The reactions followed kinetics first order in lyonium ion and in substrate in each case. All of the kinetic data presented in Tables 1 and 2 represent the averages of at least two experiments in which the rate constants agreed within ±5%.

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