Electrophilic Displacement Reactions. XVII. The Course and Kinetics of the Protonolysis of Allyltins[1]

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Abstract: The protonolysis of crotyltrimethyltins in methanol results in the formation of 1-butene as the major product, along with a mixture of *cis*- and *trans*-2-butenes with the former predominating. The detailed distribution of the isomers depends on reaction parameters including acidity of the protonating agent, solvent polarity, and concentration of reactants. These results can be explained if it is assumed that crotyltrimethyltins are in equilibrium with a small amount of α-methylallyltrimethyltin and that the protonolysis occurs only by an SE′ mechanism. The variations in the rate of equilibration and the rates of protonolysis of these isomers depend upon the reaction parameters and determine the product distribution. When methanol-*O-d* is used as solvent, the 1-butene formed bears a single deuterium in the 3-position, indicating that the mechanism involves a rate-determining proton transfer. The reaction rate is found to be first order in lyonium ion and in allyltin. With allyltrimethyltin as substrate in methanol containing small amounts of water, it is observed that the methyloxonium ion is a better proton donor by a factor of at least 66 than the hydronium ion, leading to a Bronsted α of about 0.85, suggesting a high degree of proton transfer in the transition state. In solvent containing moderate concentrations of chloride, the observed rate constant decreases with increased initial acid concentration. This is interpreted as being due to chloride ion bridging two lyonium ions to form a species which is less effective as a proton donor than the lyonium ions.

Organometallic compounds containing an allyl group attached to the metal atom are particularly susceptible to electrophilic cleavage. The allyl group has been shown to be cleaved in preference to vinyl or phenyl when attached to silicon,[3,4] germanium,[5] tin,[6] lead,[7,8] or mercury.[9,10] Sommer, Tyler, and Whitmore[3] have proposed a two-step mechanism, involving the addition of a proton to the terminal position of the allyl group, followed by departure of silicon in a second step, to account for the ease of cleavage of allylsilanes with acids (eq 1 and 2). Gielen and Nasielski[11a] have suggested an SE2′ mechanism

$$R_3SiCH_2CH{=}CH_2 + HA \rightleftarrows R_3SiCH_2\overset{+}{C}HCH_3 + A^- \quad (1)$$

$$R_3SiCH_2\overset{+}{C}HCH_3 + A^- \longrightarrow R_3SiA + CH_2{=}CHCH_3 \quad (2)$$

for the cleavage of tetraallyltin by iodine, primarily because this compound cleaves $\sim 10^8$ faster than tetra-*n*-propyltin. They represented the cleavage by the scheme seen in eq 3.

$$R_3SnCH_2CH{=}CH_2 + I{-}I \longrightarrow R_3Sn^+ + CH_2{=}CHCH_2I + I^- \quad (3)$$

A similar conclusion was reached by Roberts on the basis of product studies.[11b]

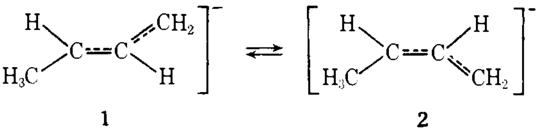
Sleezer, Winstein, and Young[9] and Kreevoy and coworkers[10] have reported clearcut evidence for an SE′ description for the cleavage of allylmercurials with acid. An SE′ mechanism has been advanced for the acid cleavage of allyltins[12] and allenyltins,[13] and SO_2 insertion into allytins[14] and allenyltins.[14]

We have been examining the protonolysis of allyltins and report in this paper on some aspects of synthesis, on kinetics, with emphasis on solvent and salt effects, and on the effects of reaction parameters on the course of the reaction with crotyltrimethyltins.

Results

Synthesis. The reaction of allylmagnesium chloride with trimethyltin chloride provided good yields of allyltrimethyltin.[15] Similarly, the Grignard reagent from crotyl chloride or 3-chlorobutene led to a mixture of approximately equal amounts of *cis*- and *trans*-2-butenyltrimethyltins when the reactions were conducted and worked up under normal conditions using diethyl ether as a solvent. However, under controlled reaction and work-up conditions up to 38% of the isomeric 1-buten-3-yltrimethyltin could be obtained. This isomer displayed two significant chemical properties. First, when separated by glpc and stored in the refrigerator it underwent very slow isomerization to crotyl isomers. When mixed with trimethyltin chloride before injection into the chromatograph, complete isomerization had occurred in the effluent. Also, when dissolved in methanol, isomerization occurred within a few minutes as shown by glpc. Secondly, the isomerization gave a mixture containing about 75% of *cis*-2-butenyltrimethyltin and 25% of the trans isomer in each case. When allowed to stand longer in methanol solution further isomerization occurred resulting in a 54% trans–46% cis mixture, indicating clearly that 1-buten-3-yltrimethyltin isomerizes by a kinetically controlled process preferentially to *cis*-2-butenyltrimethyltin, although the thermodynamic stability of this isomer is lower than that of the trans isomer. Observations which generally confirm these have been made by Matarasso-Tchiroukhine and Cadiot.[16a] They report formation of a 70/30 cis/trans mixture of 2-butenyltrimethyltins from 1-buten-3-yltrimethyltin. They also indicate that the reaction is facilitated by donor solvents.

These observations can be understood in terms of the concept proposed by Bank, *et al.*, that a "cis allylic anion is thermodynamically more stable than the trans form," *i.e.*, the equilibrium of eq 4 lies to the right.[17] A corollary of this idea is that in an allylic isomerization depicted in eq 5, which proceeds by a polar mechanism, the cisoid transition state **4** would benefit from similar stabilization. Indication of a polar mechanism is provided by the observations that methanol and donor solvents enhance the reaction rate. Structure **4** could also be considered to be an intermediate.



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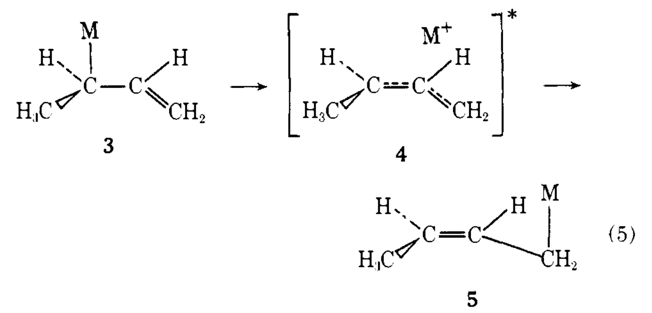

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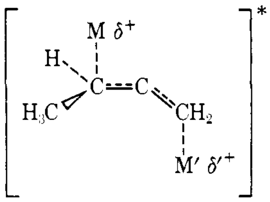
If it is, however, it must be a tight ion pair which collapses to **3** or **5** faster than it reacts with methanol, for no butene formation accompanies the isomerization. The role of trimethyltin chloride in the isomerization may be due to an SE′ reaction with a preferred transition state **6** (M = M′ = Me_3Sn) analogous to one suggested by Felkin in the reaction of the 1,3-dimethylallyl Grignard reagent with carbonyl compounds,[18] which yield cis products preferentially. Similar considerations can be applied to account for the predominance of *cis*-2-butene over the trans isomer in the protonolysis of 1-butenylmagnesium, -zinc, and -cadmium.[19] A striking characteristic of the results with bis(1-butenyl)magnesium is a pronounced increase in the proportion of 2-butenes, accompanied by an increased cis/trans ratio, with increased donor ability of the solvent.[19] Similar effects of solvent and of proton donor had been reported earlier.[20] Moreover, those reactions with aldehydes or ketones which lead to the formation of 1-buten-3-yl products usually give a predominance of the cis isomer.[18,20,21]



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An alternative synthetic method which we used exploited the reaction of trimethyltinsodium with the chlorobutenes in liquid ammonia.[22] When 3-chlorobutene was used a high yield of 1-buten-3-yltrimethyltin with a cis/trans ratio of 3/1 was obtained as product. When 1-chloro-3-butene (of undetermined geometrical isomer composition) was used, a high-yield of 2-butenyltrimethyltins was again obtained, but the cis/trans ratio was about 1/2. These results are easily rationalized in terms of a simple SN2 reaction between each chloride and the trimethyltinsodium. The 1-buten-3-yltrimethyltin rapidly isomerizes in the good coordinating solvent, ammonia, to the predominantly *cis*-2-butenyl product, whereas the crotyltrimethyltin isomer mixture formed directly from 1-chloro-2-butene reflects the isomeric composition of the initial chloride mixture more closely.

The assignments of configurations for the 1-buten-3-yltrimethyltins,[12] which have been accepted or confirmed by others,[16] were based primarily on analogies in the double bond stretching frequencies and the out-of-plane carbon-hydrogen bending frequencies with those the isomeric 2-pentenes. The pmr spectra were complex, and not amenable to first-order analysis.

Course of Reaction. In initial experiments it was observed that allyltri-*n*-butyltin reacted with hydrogen chloride in dioxane to form propene and trimethyltin chloride, both characterized by their infrared spectra, as the only reaction products. Further studies were conducted using trimethyltin derivatives because of their apparent greater stability and greater solubility in methanol, which was chosen as the solvent for kinetic studies.

Table I. Products of Protonolysis of *cis*- and *trans*-2-Butenyltrimethyltins by HCl in Methanol

Isomer(s)	%	M	HCl (M)	% 1-butene	% *cis*-2-butene	% *trans*-2-butene
Trans	64	0.0014	0.0015	87	12	1
Cis	36					
Trans	78	0.23	0.28	98	~1	Trace
Cis	22					
Trans	13	0.0012	0.0015	86	13	1
Cis	87					
Trans	100	0.08	0.25	94	5	Trace
Cis	100	0.15	0.25	95	5	Trace

The site of lyonium ion attack was established by examining the products of protonolysis of *cis*- and *trans*-2-butenyltrimethyltins. The product butenes could be separated by glpc on a column of dimethylsulfolane on firebrick. Results obtained using hydrogen chloride in methanol are gathered in Table I. These reveal that the major olefinic product is 1-butene, that its proportion is greatest when the initial concentrations of the reactants is highest, that the product distribution is essentially independent of the geometry of the starting crotyltin, and that *cis*-2-butene is formed in far greater proportion than *trans*-2-butene.

Reactions were also carried out using deuterium chloride in methanol-*O*-*d* (97% *d*) as solvent. The 1-butene was collected and the pmr spectrum examined. Of particular importance was the signal due to the methyl protons which was a doublet upon which was superimposed the triplet of normal 1-butene of low intensity. This clearly showed that only one deuterium atom was introduced into the molecule. This observation was further confirmed by mass spectral analysis of the product. The relative intensities of the *m/e* 57 and 58 were 100 and 6.2, respectively, for the reaction product and those of *m/e* 56 and 57 were 100 and 9.4 for authentic 1-butene,[23] facts which are attributed to the relatively poor resolution of the instrument used. Nonetheless, the data support the conclusion that the deuterolysis product contains only a single deuterium.

It was of interest to ascertain whether the proportions of isomeric butenes would be materially affected by changes in the reaction parameters. Table II shows the effects of some variations. Comparison of the first and fourth entries shows that temperature has no significant effect. The third entry shows that the presence of 1-buten-3-yltrimethyltin in the reaction mixture does not change the product composition. This is consistent with its rapid isomerization to 2-butenyltins mentioned above.

The addition of trimethyltin chloride increases the proportion of 2-butenes to a modest degree. Finally, changes to the less polar solvents, acetonitrile, dimethyl sulfoxide, dioxane, and benzene, cause distinct decreases in the amount of 2-butenes formed.

When acetic acid was used as the proton donor and/or solvent the proportion of 2-butenes increased to magnitudes ranging from 24 to 38% of the total hydrocarbon formed, as shown in Table III. Accompanying this increase in total 2-butenes was a significant decrease in the cis/trans ratio. The major effect apparently results from the change to acetic acid as the proton donor.

Data presented in Table IV reveal results obtained with other acids. Perchloric acid yields more 2-butenes in methanol than in the more strongly acidic solvent acetic acid. When approximately equal amounts of 2-butenyltrimethyltin and trichloroacetic acid were allowed to react in pentane, the amount of 2-butenes (6.5%) were intermediate. When propionic acid was used as solvent, 16.5% was found.

Table II. Cleavage of 2-Butenyltrimethyltin with Hydrogen Chloride[a]

			Butene distribution, %		
Crotyltin[b] (M)	HCl (M)	Solvent	1-	*cis*-2-	*trans*-2-
0.320[c]	0.326	4% H_2O-CH_3OH	97.0	3.0	Trace
0.400[d]	0.460		96.0	4.0	Trace
0.200[e]	0.200		96.5	3.5	
0.200	0.200[f]		92.5	7.5	Trace
0.250	0.250	CH_3CN	99.9	Trace	
0.270	0.270	Dioxane	100.0		
0.300	0.300	DMSO	99.0	1.0	
0.280	0.300	Benzene	99.7	0.3	

[a] Ambient temperature (~27°). [b] 66% *cis*-crotyl- and 34% *trans*-crotyltrimethyltin except as noted. [c] 91% *trans*- and 9% *cis*-crotyltrimethyltin. [d] 15% α-Methylallyl-, 58% *cis*-crotyl-, and 27% *trans*-crotyltrimethyltin. [e] At −5°. [f] At 0.40 M in Me_3SnCl.

Table III. Cleavage of 2-Butenyltrimethyltins with Acetic Acid

				Butene distribution, %		
Crotyltin (mmol)	Acid (mmol)	Solvent (ml)	Addends (mmol)	1-	*cis*-2-	*trans*-2-
2.7	HOAc (80)			72.7	22.7	4.6
2.7	HOAc (6)			73.4	22.5	4.1
2.7	HOAc (80)		H_2O (6)	70.4	24.6	5.0
3.0	DOAc (80)			72.6	20.8	6.5
4.8	DOAc (80)			78.9	16.9	4.1
3.2	HOAc (3.2)	CH_3OH (2.5)		66.4	29.2	4.3
3.2	HOAc (3.2)	CH_3OH (10)		57.7	37.5	4.8
2.7	HOAc (4.0)	CH_3OH (5)	Acetic anhydride (3.0)[a]	72.6	25.3	3.0

[a] Methanol solution containing HOAc and Ac_2O was refluxed for several hours before addition of methylallyltin to remove any water from solvent and HOAc.

Table IV. Cleavage of 2-Butenyltrimethyltins by Other Acids[a]

			Butene distribution, %		
Crotyltin (mmol)	Acid (mmol)	Solvent (ml)	1-	*cis*-2-	*trans*-2-
4.23	70% $HClO_4$ (3.0)	4% H_2O–MeOH (10)	91.4	7.6	0.9
2.9	70% $HClO_4$ (3.0)	HOAc (5)	99	1	Trace
2.9	CCl_3CO_2H (3.0)	n-C_5H_{12} (10)	96	4	Trace
3.0	CCl_3CO_2H (3.0)	n-C_5H_{12} (15)[b]	93.4	6.6	Trace
2.8	CCl_3CO_2H (3.0)	n-C_5H_{12} (50)	93.5	6.5	
2.7	$C_2H_5CO_2H$ (70)		81.0	16.3	2.8
3.2	p-$H_2NC_6H_4CO_2H$ (3.2)	CH_3OH (10)	61.8	33.4	4.8
3.2	p-$H_2NC_6H_4CO_2H$ (3.2)	CH_3OH (5)	70.7	26.0	3.3
3.2	p-$H_2NC_6H_4CO_2H$ (3.2)	CH_3OH (5)	79.1	17.6	3.3

[a] Ambient temperature (~27°). [b] At 0°.

Finally, *p*-aminobenzoic acid yielded this olefin in rather large proportion which reached 33% in the more dilute solution (0.3 M).

These results suggest that formation of 2-butenes is favored by the use of weak acids, polar solvents, and dilute solutions. The exception to the dilution effect is acetic acid which gives the same product composition whether it is present in a 2-fold or 30-fold excess over the crotyltin.

Kinetic Order and Solvent Effect on Rate. The kinetics of the protonolysis were followed by ultraviolet spectroscopy. Allyltrimethyltin has an intense absorption at 225 nm, whereas the products are transparent at this wavelength. The reaction was shown to be first order in stoichiometric hydrogen chloride concentration and in allyltin under pseudo-first-order conditions (acid in excess) giving linear plots over at least four half-lives. Linear integrated second-order rate plots were also obtained when the reactants were initially present in comparable concentrations (10^{-3} to 10^{-4} M) and the ratios varied over a 30-fold range. Variations in the rate constants in ostensibly identical experiments were eliminated when the glassware was cleaned with acid and thoroughly rinsed with water and then with the solvent to be used in the kinetic experiment. Further variations in rate constants observed when different batches of "anhydrous" methanol were used as solvent were shown to be due to differences in the (small) amounts of water present. When water was added to the methanol, rates decreased markedly, as shown by the data of Table V. In the solvent mixtures, and at the concentrations of acid used, the acid is completely dissociated.[24] The presence of water decreased the solubility of trimethylallyltin so that concentrations higher than 2.25 M could not be used conveniently. The addition of water depresses the acidity of the medium profoundly, a fact which was originally observed by Goldschmidt,[25] and has been treated quantitatively by emf,[26] indicator,[27] and conductivity[28] measurements and by kinetic determinations

Table V. Effect of Water Concentration on Rate of Protonolysis of Allyltrimethyltin in Methanol at 25°

H_2O, M	n[a]	k_2, M^{-1} sec^{-1}
0.005	9	5.88
0.03	4	5.06
0.12	1	3.82
0.25	2	2.85
0.47	2	1.70
0.92	1	0.873
1.14	2	0.790
2.25	11	0.475

[a] n = number of kinetic runs.

on esterification,[29] solvolysis of acetic anhydride,[30] and solvolysis of ethylene oxide.[31] These measurements have produced values for K of eq 6 ranging from 111 to 137.

$$MeOH_2^+ + H_2O \overset{K}{\rightleftharpoons} MeOH + H_3O^+ \qquad (6)$$

Each of the reactions used in the kinetic determinations of K involves a rapid protonation followed by rate-determining reaction with solvent. The deuterium incorporation experiments described above indicate a rate-determining proton transfer for the protonolysis, so the rate law should be given by eq 7

$$dx/dt = [S]\{k_h[H_3O^+] + k_m[MeOH_2^+]\} = k_2[HA][S] \qquad (7)$$

in which k_h and k_m are the specific rate constants for proton transfer from hydronium ion and methyloxonium ion, respectively, and S is allyltrimethyltin. From the definition of the equilibrium constant, eq 8, and the identity of the quantity in braces of eq 7 with k_2, the experimentally determined rate constant, one can derive expression 9, in which

$$K = \frac{[MeOH][H_3O^+]}{[MeOH_2^+][H_2O]} \qquad (8)$$

$$k_2 = \frac{k_m - k_h}{1 + KR} + k_h \qquad (9)$$

$R = [H_2O]/[MeOH]$. Thus, a plot of $1/(1 + KR)$ *vs.* k_2 should provide a line with slope $(k_m - k_h)$ and intercept k_h. Least-squares analyses with changes in the value of K in units of 10 from 140 to 110 gave correlation coefficients of 0.997 to 0.998 and standard deviations from 0.16 to 0.12. Values of the slope $(k_m - k_h)$ varied only slightly from 6.00 to 6.07. The only reasonable k's were obtained with K = 140 when $r = 0.997$, $s = 0.148$, $k_h = 0.089$, $k_m = 5.99$ M^{-1} sec^{-1}, Figure 1. These rate constants reveal that the methyloxonium ion is a better protonating agent than the hydronium ion by a factor of at least 66 in this reaction in methanol. Furthermore, a value for the Brönsted α can be estimated as $(\log k_m - \log k_h)/\log K = 0.85$.[32] This can be taken as a minimum value, for small values of K would also give smaller values of k_h, which would result in larger values for α. If one attributes the usual significance to the value of α, one is led to the conclusion that the proton transfer has proceeded to a high degree in the transition state of the protonolysis of allyltrimethyltin.

When perchloric acid was used as the proton source the rates (0.489 ± 0.021 M^{-1} sec.$^{-1}$) in solvent containing 2.25 M water were the same as those observed with hydrogen chloride (0.475 ± 0.015 M^{-1} sec^{-1}) in this solvent. Hence the counterion is not involved in the transition state.

The effect of added sodium perchlorate on the rate of the reaction is shown in Table VI. As the salt concentration is increased from 0 to 0.200 M, the rate constant increases by 86%, indicating an increase in polarity on going from reactants to transition state. A secondary salt effect is not the cause of this rate increase for hydrogen chloride is completely dissociated in 4% methanol at the concentrations used in these experiments.[24]

Table VI. The Effect of $NaClO_4$ on the Rate of Protonolysis

10^4·$[Me_3SnAl]_0$, M	$10^4[HCl]_0$, M	$[NaClO_4]$, M	k_2, M^{-1} sec^{-1}
1.023	8.123	0.0125	0.560
1.023	8.123	0.0250	0.567
1.023	16.25	0.0250	0.555
0.948	4.062	0.0250	0.583
1.895	4.062	0.0250	0.577
1.176	4.828	0.0500	0.587
1.023	8.123	0.0500	0.593
1.023	16.25	0.0500	0.580
1.176	4.828	0.1000	0.698
1.176	4.828	0.2000	0.882

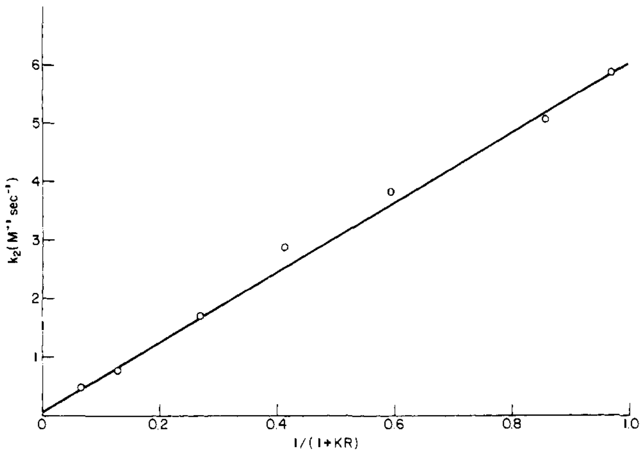


Figure 1. Plot of k_2 *vs.* $1/(1 + KR)$ with K = 130 used in estimating k_h and k_m: points experimental, line from least-squares computation, 4.05% water in methanol, 25°.

Addition of sodium chloride also causes an increase in the rate constant which amounts to about 50% when 0.0500 M salt is added, as shown in Table VII. Here are given results for two different initial concentrations of hydrogen chloride. At the lower of these concentrations the rates are *uniformly higher* than at the higher concentration. The results of a more detailed examination of the effect of initial hydrogen chloride concentration at constant sodium chloride concentration are shown in Table VIII. An inverse relationship between rate constant over an eightfold change in hydrogen chloride concentration is revealed and is depicted graphically in Figure 2. The arbitrarily drawn line is assigned no quantitative significance.

Discussion

The observations of kinetics first order in lyonium ion and in allyltin, of the formation of 1-butene as the major reaction product, and the formation of 3-deuterio-1-butene in methanol-*O-d* from 2-butenyltrimethyltin argue that the major course of reaction is by an SE2′ mechanism in which the proton transfer occurs in the rate determining step. These results, and those of others,[9-11,14,16,18-21] suggest that this type of mechanism is, in most cases at least, energeti-

Table VII. Effect of Chloride Ion Concentration on Protonolysis Rate

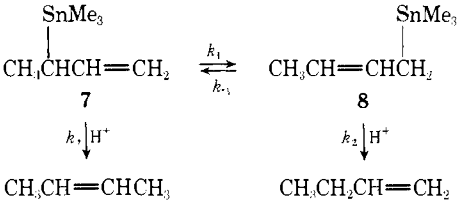
$10^4[HCl]_0$, M	$10^4[Me_3SnAl]_0$, M	[NaCl], M	k_2, M^{-1} sec^{-1}
8.123	1.041	0.0006	0.557
8.123	1.041	0.0031	0.617
8.123	1.041	0.0063	0.663
8.123	1.041	0.0125	0.710
8.123	1.041	0.0250	0.787
8.123	1.041	0.0500	0.858
16.29	1.010	0.0000	0.473
16.29	1.010	0.0006	0.459
16.29	1.010	0.0013	0.489
16.29	1.101	0.0031	0.489
16.29	0.981	0.0063	0.523
16.29	0.981	0.0125	0.572
16.29	0.981	0.0250	0.615
16.29	0.981	0.0500	0.655

Table VIII. Rates of Protonolysis in the Presence of 0.0250 M NaCl

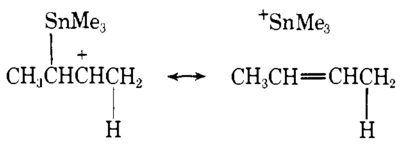
$10^4[\mathrm{HCl}]$, M	$10^4\cdot[\mathrm{Me_3SnAl}]$, M	k_2, M^{-1} sec^{-1}	Average k_2, M^{-1} sec^{-1}	$10^{-4}\cdot(1/[\mathrm{HCl}])$
2.398	0.997	1.25	1.25	0.417
2.414	1.176	1.15	1.15	0.415
4.796	0.997	0.887	0.887	0.209
4.822	1.298	1.15	1.19	0.208
4.822	1.298	1.23		
7.194	0.997	0.724	0.724	0.139
8.123	1.041	0.787	0.787	0.139
9.592	1.077	0.688		
9.592	1.077	0.722	0.708	0.104
9.592	0.997	0.713		
9.644	1.263	0.807	0.807	0.096
14.38	0.997	0.627	0.627	0.0695
16.29	0.981	0.615	0.615	0.0615
19.18	0.997	0.602	0.602	0.0521

cally more favorable than the SE2 mechanisms in electrophilic displacements in allylic systems. It remains to be established whether this is true for all allylic systems except those into which special inhibitory restraints are built.

If the SE′ mechanism is general, then the 2-butenes formed in our protonolysis experiments must arise from 1-buten-3-yltrimethyltin, and predominantly by way of a cisoid transition state like **6** in which M′ is the lyonium ion and M is the trimethyltin group. A further requirement is that the equilibrium between the isomeric methylallyltins in eq 10 be rapidly established, under some conditions, although it lies far to the right. Then, if $k_3[\mathbf{7}]$ is sufficiently large relative to $k_2[\mathbf{8}]$, the 2-butenes will be formed in measurable amounts. This requires that $k_3 \gg k_2$, and it is reasonable because allyltrimethyltin, upon which electrophilic attack occurs at a terminal methylene carbon, reacts 10 (for cis) to 20 (for trans) times faster than does 2-butenyltrimethyltin,[12] in which the attack occurs at a carbon of an internal double bond. Furthermore, 2-methylallyltrimethyltin reacts about 50 times as fast as allyltrimethyltin,[12] indicating development of substantial positive charge on the β-carbon. This charge can be stabilized by hyperconjugation with the attached methyl group in the transition state. In 1-buten-3-yltrimethyltin the stabilization of this charge can result from σ-π conjugation with the carbon-tin bonding electrons **9** ↔ **10**.[33] The inductive effect of the α-methyl group should increase the electron availability from the C-Sn bond relative to that provided by the analogous structure in the 2-butenyltrimethyltin transition state. Now the effect of a nonpolar solvent (pentane) would be to slow down the rate of equilibration of the methylallyltins so that $k_{-1} < k_2[\mathrm{H^+}]$. Use of a strongly acidic system such as perchloric



$$\begin{array}{ccc} \mathrm{CH_3\overset{SnMe_3}{\overset{|}{C}}HCH{=}CH_2} & \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} & \mathrm{CH_3CH{=}CH\overset{SnMe_3}{\overset{|}{C}}H_2} \\ \mathbf{7} & & \mathbf{8} \\ \downarrow{\scriptstyle k_3,\,H^+} & & \downarrow{\scriptstyle k_2,\,H^+} \\ \mathrm{CH_3CH{=}CHCH_3} & & \mathrm{CH_3CH_2CH{=}CH_2} \end{array} \qquad (10)$$



$$\underset{\mathbf{9}}{\mathrm{CH_3\overset{SnMe_3}{\overset{|}{C}}H\overset{+}{C}H\underset{\underset{H}{|}}{C}H_2}} \longleftrightarrow \underset{\mathbf{10}}{\mathrm{CH_3CH{=}CH\overset{^+SnMe_3}{\underset{\underset{H}{|}}{C}H_2}}}$$

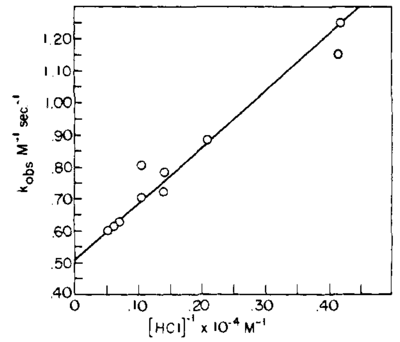
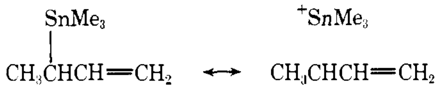


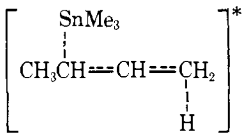
Figure 2. Effect of initial HCl concentration on second-order rate constant: 4.05% water in methanol, 0.025 M NaCl, 25°.

acid–acetic acid would have the same net effect by increasing the magnitude of $k_2[\mathrm{H^+}]$ more than k_{-1}. 1-Butene is the major product in each case. Similarly, at high concentrations in methanol, 1-butene also predominates, but at low concentrations 2-butenes become more evident because the isomerization is a first-order reaction, whereas the protonolysis is second order. Addition of trimethyltin chloride increases the rate of isomerization with the same net result. Acetic acid as solvent and p-aminobenzoic acid in methanol give the same result because k_2 and k_3 for these acids are smaller than for hydronium or methyloxonium ions, while trichloroacetic acid is intermediate in protonating ability and gives intermediate amounts of 2-butenes.

The presence of a positive charge in the transition state for protonolysis requires that its preferred cisoid conformation existed in its ground state precursor, **11**. Presumably the relative population of this conformation depends on the degree of negative charge in the allylic moiety of the resonance hybrid **11** ↔ **12**. Thus, the more electropositive the metal atom, the more highly populated the cisoid conformation, and the faster the rate of reaction with an electrophile, and **13** may approximate the transition state. Conversely, the more nearly covalent the carbon-metal bond, the more the transition state would resemble **9**, the more likely that **9** would be an intermediate, and the smaller the cis/trans ratio.



$$\underset{\mathbf{11}}{\mathrm{CH_3\overset{SnMe_3}{\overset{|}{C}}HCH{=}CH_2}} \longleftrightarrow \underset{\mathbf{12}}{\mathrm{CH_3\overset{^+SnMe_3}{\overset{}{C}}HCH{=}CH_2}}$$



$$\left[\mathrm{CH_3\overset{SnMe_3}{\overset{\vdots}{C}}H{\cdots}CH{\cdots}\underset{\underset{H}{\vdots}}{C}H_2}\right]^{*}$$

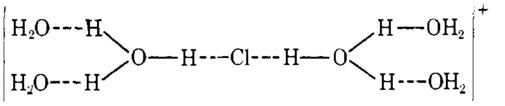
13

This analysis appears to embrace all of the data presented here and should be applicable to other allylic systems. Although it may prove to be incomplete or deficient, it does provide a rationale that can be tested by further experimental work.

The observation of a positive primary kinetic salt effect upon which is superimposed an opposing effect of initial hydrogen chloride concentration when sodium chloride is present is unusual. The latter cannot be due to a chloride common ion effect, for its concentration is considerably larger than the initial acid concentration, and is not materially affected by its presence. Hence, it must be due to a lyonium common ion effect. A reasonable explanation appears to be that the lyonium ion is converted into a less reactive species by association with more than one chloride ion. Equation 11 (sol = solvent) represents such a possibility in macroscopic terms.

$$2HCl_{sol} \rightleftharpoons H_2Cl^+_{sol} + Cl^-_{sol} \tag{11}$$

The concentration of H_2Cl^+ depends upon the square of the concentration of stoichiometric hydrogen chloride, whereas the concentration of lyonium ion depends upon the first power. Structures such as **14** can be written to represent H_2Cl^+ approximately at the molecular level. Here a chloride ion bridges two hydronium ions by assuming the role normally played by water molecules in $H_9O_4^+$.



14

Experimental Section

General Procedure. The allyl and butenyl chlorides were commercial samples and were used as obtained. Trimethyltin chloride was a gift from M & T Chemicals Inc. Other reagents were reagent grade materials.

Infrared spectra were taken with a Beckman IR 10 instrument, ultraviolet spectra with a Beckman DU, and pmr spectra with a Varian A 60A instrument. Elemental analyses were performed by Galbraith Laboratories.

Trimethylallyltin was prepared by the method of Jones, *et al.*,[15] in yields of 65–75%: bp 93–97° (0.65 Torr); pmr τ (no. of protons, multiplicity) 9.93 (9, s), 8.29 (2, d), 5.34, 5.29 (2, m), 4.11 (1, m); ir (cm^{-1}) 1630 (s), 890 (s), 929 (m), 982 (s), 1020 (m).

Butenyltrimethyltins. A. *Via* 2-Butenylmagnesium Chloride. In a typical experiment the Grignard reagent was prepared, using initiation by 1 g of ethylene dibromide, from 0.4 mol of 3-chlorobutene and 1 g-atom of magnesium in 200 ml of ether under nitrogen. After filtration through glass wool and heating to reflux, 0.3 mol of trimethyltin chloride in 100 ml of ether was added over 3 hr. The reaction mixture was cooled to 0° and hydrolyzed with 200 ml of 25% aqueous ammonium chloride. The ether layer was separated, dried over anhydrous magnesium sulfate, and concentrated and the product was distilled, bp 56–59° (30 Torr). The ratios of *cis*- to *trans*-2-butenyltrimethyltins ranged from 1/1 to 3/2, and 1-buten-3-yltrimethyltin proportions varied from 21 ± 4% in reactions carried out at 35° to 35 ± 3% in reactions at 0°. Product distribution could be determined by glpc on a ¼ in. × 20 ft column of silicone gum rubber SE-30 (20%) on Chromosorb-W (40–60 mesh).

Anal. Calcd for $C_7H_{16}Sn$ (isomer mixture): C, 38.41; H, 7.37. Found: C, 38.23; H, 7.50.

1-Buten-3-yltrimethyltin: ir (cm^{-1}) 3085, 1625 (s), 1190 (m), 770. *cis*-2-Butenyltrimethyltin: ir (cm^{-1}) 1650 (s), 720 (m), 895 (w), 959 (w), 990 (s); pmr τ (no. of protons, multiplicity) 9.94 (9, 1), 8.30 (2, m), 4.25–5.12 (2, m), 8.45 (3, m); uv λ_{max} 215 nm (ϵ n.d.; ϵ_{225nm} 5710). *trans*-2-Butenyltrimethyltin: ir (cm^{-1}) 1655 (s), 884 (w), 900 (m), 957 (s), 1030 (m); pmr τ 9.94 (9, 1), 8.32 (2, 4), 4.66 (1, m), 4.76 (1, m), 8.36 (3, 2); uv λ_{max} 215 nm (ϵ n.d.), ϵ_{225nm} 6830).

B. *Via* Trimethyltinsodium and Chlorobutenes. Trimethyltinsodium was synthesized by an adaptation of the method of Kraus and Greer.[22] To a vigorously stirred suspension of 30 g (0.15 mol) of trimethyltin chloride in 100 ml of liquid ammonia was added small slices of sodium metal until the deep blue color characteristic of sodium dissolved in ammonia persisted for about 10 min. A small quantity of trimethyltin chloride, sufficient to change the color of the mixture from deep blue to the dark yellow color characteristic of trimethyltinsodium in ammonia was then carefully added.

A solution of 15.8 g (0.17 mol) of 3-chlorobutene with 15 ml of diethyl ether was then added to the mixture, which discharged the yellow color immediately. Diethyl ether was added, the ammonia allowed to evaporate, and the mixture filtered. The solid was washed with ether and the washings were added to filtrate, which was then stripped of solvent and fractionated, bp 151–152.5°, 78%.

Isomerization of 1-Buten-3-yltrimethyltin. A neat mixture of isomers containing 35% of 1-buten-3-yl, 25% *trans*-, and 40% *cis*-2-butenyl was stored in a refrigerator under argon and monitored by glpc. The 1-buten-3-yltrimethyltin decreased at the rate of about 1% per day and after 2 weeks the composition of the mixture was 65% *cis*- and 34% *trans*-2-butenyltrimethyltin. If this same initial isomer mixture was mixed with either trimethyltin chloride or methanol and then injected into the glc, the 1-buten-3-yl peak no longer was present and the *cis-/trans*-2-butenyl ratio was 2/1.

Acetic Acid-*O-d*. Acetic anhydride, 40 g (0.41 mol), and deuterium oxide, 8 g (0.41 mol), were refluxed for 1 hr, when the mixture had become homogeneous. Distillation gave 36 g (82%) of deuterioacetic acid, bp 117–119°. Ir showed no -OH band at 3050 cm^{-1} but did show an -OD band at 2325 cm^{-1}.

Methanol-*d*. The methanol-*O-d* used in these studies was prepared from methyl carbonate and deuterium oxide (99.8% D) following the procedure of Streitwieser and coworkers.[34] The deuterium content analyzed by infrared analysis was 96–98%.

Deuterium Chloride. Deuterium chloride was conveniently prepared by the method of Brown and Groot.[35] Deuterium oxide, 0.5 mol, was added dropwise to 1.5 mol of freshly distilled benzoyl chloride and the mixture was heated to reflux until DCl was no longer generated. The DCl was trapped by passing the gas into methanol-*O-d*.

Protonolysis Products. An appropriate amount of either the pure crotyltrimethyltins or a mixture was placed in a 50-ml three-necked round-bottom flask equipped with a pressure equalizing addition funnel and gas inlet and outlet tubes. The inlet tube was connected to a nitrogen tank and prepurified N_2 was passed through the system during the subsequent reaction. The outlet tube was connected in series with a calcium chloride drying tube, a trap immersed in liquid nitrogen, and a mercury seal. An appropriate amount of either HCl in methanol or DCl in methanol-*O-d* was added dropwise through the addition funnel and the reaction mixture was stirred magnetically. After the reaction was complete, the displaced butenes which had been carried along in the nitrogen stream, and frozen out in the trap, were withdrawn in a gas syringe and analyzed by glpc using a 15 ft column of 28% dimethylsulfolane on C-22 Firebrick, 40–60 mesh. The butenes were identified by comparing their retention times with the retention times of authentic samples. Product composition was determined from peak areas.

Nmr analysis of the butenes from cleavage with DCl was obtained by distilling the collected olefin mixture into an nmr tube containing carbon tetrachloride and determining the spectrum on a Varian A-60 nmr spectrometer using TMS as internal standard.

Mass spectral analysis was obtained by distilling the collected butenes from DCl cleavage into a gas collection cell and insertion of the cell into the inlet of a CIC-620 mass spectrometer.

Kinetic Procedure. A direct spectrophotometric kinetic procedure was utilized. In a specially constructed reaction flask was placed 5 ml of a stock solution of HCl in methanol and 10 ml of 8% water–methanol solution. Five milliliters of allyltrimethyltin stock solution was then pipetted into a concentric cylinder within the flask, and the flask was stoppered. The reaction flask was brought to temperature in a constant temperature bath and the reaction started by inverting the flask. An aliquot was quickly transferred to a cuvette which was placed in the Beckman DU spectrophotometer cell compartment which was thermostated at 25° and controlled to ±0.1°. Absorbance readings were taken at suitable intervals. When salts were used as addends, the salt was dissolved in the water–methanol solvent before a run was started. Rate constants were calculated in the standard manner. The glassware used cleaned by soaking overnight with concentrated nitric acid and rinsing at least eight times with distilled water and three times with methanol.

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Anodic α-Cleavage of Ketones

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Abstract: Ketones with branching at the α position were potentiostatically oxidized at platinum gauze. The anolyte was acetonitrile–lithium perchlorate and the reference electrode Ag|0.1 *M* $AgNO_3$. α-Cleavage was observed to be the main route of these oxidations. 2,2-Dimethyl-3-butanone, 2,2-dimethyl-3-hexanone, acetyladamantane, 2-methyl-3-butanone, and 2,5-dimethyl-3-pentanone of the general formula RCOR′ gave α-cleavage products of the type $RNHCOCH_3$ and R′COOH. 2,2-Dimethylpropanal and 2,2,4,4-tetramethyl-3-pentanone gave acetylpivaloylimide in addition to acid and amide products. It was found that small amounts of water are necessary for the obtention of high amide ($RNHCOCH_3$) yields. A mechanism involving generation of carbonium ions from α-cleavage of a ketone cation radical is proposed, and analogies with photochemistry and mass spectrometry are drawn.

The simplest mechanistic paradigm for most anodic organic reactions involves initial electron transfer from substrate to the electrode followed by reactions of the resultant cation radical. This paradigm suggests that there should be analogies between mass spectrometry and anodic chemistry, because both processes are controlled by formation and reaction of cation radicals. Verification of this analogism would provide some unusual solution phase chemistry with synthetic ramifications, and this has been a goal of our recent research.

Although there is a surprisingly general correlation between gas-phase ionization potentials and electrochemical oxidation potentials,[2] there are presently few meaningful analogies between anodic and mass spectral chemistry. A primary reason for this dissimilarity appears to be that bimolecular reactions are favored in solution. Thus, cation radicals in solution typically give dimeric products or products resulting from attack by nucleophiles.[3] These processes are extremely unlikely in a dilute gas. Recent explorations in this laboratory using direct anodic oxidation in acetonitrile solvent have, however, revealed fragmentation reactions which mimic mass spectral chemistry.[4,5] In this paper, we report several examples of α-cleavage of carbonyl compounds. This is a very common reaction in the mass spectrometer.[6] It is also common in ketone photochemistry (Norrish Type I process).[7] In the following paper, results from ketones without α-branching are presented.[8] The oxidation products in these cases are ketoamides produced by hydrogen abstraction. The abstraction appears to be intramolecular so that these reactions are also reminiscent of mass spectral and photochemical processes.

Experimental Section

Equipment. A Perkin-Elmer 457 ir spectrometer, Varian A-60A and T-60 nmr spectrometers, and an AEI MS-12 mass spectrometer were used for structure determination. Gas–liquid chromatographic (glc) analyses were performed on a Bendix 2300 or an F&M 720 gas chromatograph equipped with thermal conductivity detectors. The potentiostats employed were a Wenking Model 70 HV 1/90 or a Princeton Applied Research Model 373. Coulometry during preparative electrolysis was performed with a counter constructed from an Acromag integrator–totalizer. An Exact Model 126-VCF function generator was used to pulse the anode potential during preparative oxidations. Cyclic voltammograms (cv) were run on a Princeton Applied Research Model 170 instrument.

Materials. Acetonitrile (Eastman 0.01% water or Fisher 0.03% water) was freshly purified by distillation from phosphorus pentoxide under nitrogen and stored over 4A molecular sieves. Purification involving an initial distillation from permanganate, followed

Miller et al. / Anodic α-Cleavage of Ketones