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SUBSTITUENT EFFECTS IN THE SE2' PROTONOLYSIS OF ALLYLTINS[1,2]

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Organometallic compounds containing an allyl group attached to the metal atom are particularly susceptible to cleavage by electrophilic reagents. 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

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[2] Taken from the doctoral dissertation of Joseph A. Verdone, November, 1963.

[3] L. H. Sommer, L. J. Tyler and F. C. Whitmore, J. Am. Chem. Soc., 70, 2872 (1948).

[4] D. Grafstein, ibid, 77, 6650 (1955).

[5] A. D. Petrov and V. F. Mironov, Angew. Chemie, 73, 59 (1961).

[6] S. D. Rosenberg, E. Debreczeni and E. L. Weinberg, J. Am. Chem. Soc., 81, 972 (1959).

[7] P. Austin, ibid, 53, 3514 (1931).

[8] H. Gilman, E. B. Towne and H. L. Jones, ibid, 55, 4689 (1933).

mercury[9]. Sommer, Tyler and Whitmore[3] proposed a two-step mechanism involving the addition of a proton to the terminal carbon of the allylic group followed by departure of silicon in a second step to account for the ease of cleavage of allylsilanes by acid. Gielen and Nasielski[10] suggested the SE2' mechanism for the cleavage of tetraallyltin with iodine primarily on the basis of the fact that this compound is cleaved about eight powers of ten more rapidly than tetra-n-propyltin. More recently Sleezer, Winstein and Young[9] provided clearcut evidence for an SE' mechanism in the cleavage of allylmercurials by acid with the observation that crotyl- and cinnamylmercuric derivatives gave 1-butene and allylbenzene, respectively, as nearly exclusive products. We wish to report evidence for an SE2' mechanism in the cleavage of allytin compounds by hydrogen chloride in methanol, along with observations on the effect of structure on rate.

The kinetics of the cleavage of allyltin compounds can be studied by following the diminution in absorption in the 225-235 mu region. The reaction of trimethylallyltin (10^{-4} to 10^{-3}M) with hydrogen chloride (10^{-4} to 10^{-2}M) to form trimethyltin chloride and propene in methanol containing 4 volume percent water is first order in each reactant. Perchloric acid gives the same specific rate constant as hydrogen chloride.

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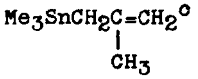
[9] P. D. Sleezer, S. Winstein and W. G. Young, ibid., 85, 1890 (1963).

[10] M. Gielen and J. Nasielski, Bull. Soc. Chim. Belg., 71, 32 (1962).

Rates of cleavage of six allyltin derivatives are given in Table 1. Substitution by methyl in the γ-position of the allyl group in trimethylallyltin decreases the rate: the allyl compound reacts nearly ten times as fast as the *cis*-crotyl and more than seventeen times as fast as the *trans*-crotyl derivative. Substitution by methyl in the β-position increases the rate by a factor greater than fifty. Replacement of the trimethyltin group by triphenyltin decreases reactivity by a hundred-fold. This result may be compared with a factor of 87 by which tri-n-butyltin hydride undergoes protonolysis faster than triphenyltin hydride in methanol.[11]

Table I

Specific Rate Constants for the Cleavage of Allyltins with Hydrogen Chloride in Methanol Containing 4 Volume Percent Water at 25.00°.

Allyltin	k_2(1./mol. sec.)[a]
 $Me_3SnCH_2C(CH_3)=CH_2$[c]	24.8
$Me_3SnCH_2CH=CH_2$	0.475[b]
cis-$Me_3SnCH_2CH=CHCH_3$	0.0508
trans-$Me_3SnCH_2CH=CHCH_3$	0.0274
$(C_6H_5)_3SnCH_2CH=CH_2$	0.00441
$(C_6H_5)_3SnCH_2CH=CHCH_3$[c,d]	0.000320

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[11] H. G. Kuivila and P. L. Levins, *J. Am. Chem. Soc.*, **85**, (1963).

[a] Mean values of at least three experiments with agreement within ± 4%.

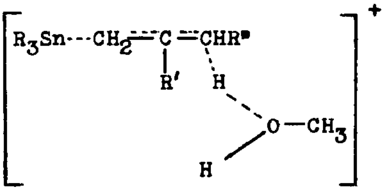
[b] With perchloric acid instead of hydrogen chloride k_2 =0.489 l./mol. sec.

[c] We thank Mr. Donald O. Whittemore, National Science Foundation Research Participation Fellow, for providing this compound.

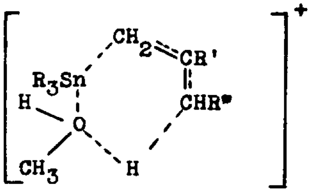
[d] Isomeric composition undetermined.

Cleavage of mixtures of the isomers of trimethylcrotyltin (0.24 M) with trans/cis ratios of 3.5 and 0.33 with hydrogen chloride (0.28 M) in the methanolic solvent provided 80-90% of olefinic product as determined by bromine titration. In each case the product contained 98% 1-butene, a trace of product having the same retention time as trans-2-butene, and 1-2% of product having the same retention time as cis-2-butene on a 15-foot column of 28% dimethylsulfolane on 40-60 mesh firebrick.

The results presented suggest a transition state which contains a lyonium ion and a substrate molecule as a minimum, and in which some positive charge has developed on the central carbon of the allylic triad. Therefore, proton transfer has begun, and the tin-carbon bond is broken to a substantial degree. Either of the structures shown below would be consistent with the experimental facts.



1



2

The trimethylcrotyltin isomers were prepared and characterized as follows. Trimethyltinsodium reacted with 3-chloro-1-butene in liquid ammonia to produce, in 80% yield, a mixture of <u>cis</u>- and <u>trans</u>-trimethylcrotyltin in a ratio of about 3 to 1. Under similar conditions a mixture (undetermined composition) of <u>cis</u>- and <u>trans</u>-crotyl chloride provided in 70% yield a mixture of the <u>cis</u>- and <u>trans</u>-trimethylcrotyltins in a ratio of about 1 to 2.5. The isomers were separated by gas chromatography on a column of 17% General Electric XF 1150 silicone nitrile on 40-60 mesh Chromosorb P Structures[12] were confirmed by measurement of peak areas in the n.m.r. spectra. The <u>cis</u>-isomer had infrared bands at 1658(s), 720(m), 895(w), 959(w), and 990(s) cm^{-1}; the <u>trans</u>-isomer had bands at 1670(m), 900(m) and 957(s) cm^{-1}.

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[12] Calculated and observed analyses of all new compounds reported herein agreed within the usually acceptable limits.