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A MECHANISTIC STUDY OF THE ACID- AND BASE-CATALYSED CLEAVAGES OF β-TRIMETHYLSTANNYLSTYRENES *

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Summary

The cleavages of *cis*- and *trans*-PhCH=CHSnMe$_3$ in 1/10 AcOD-MeOD have been shown to give *cis*- and *trans*-PhCH=CHD, respectively. The rates of cleavage of some XC$_6$H$_4$CH=CHSnMe$_3$ compounds in 1/10 AcOH-MeOH at 50°C have been measured; there is no significant difference between the rates for *cis*- and *trans*-PhCH=CHSnMe$_3$, and the relative rates of cleavage as X is varied are (X = H), 1.0; *p*-OMe, 7.0; *p*-Me, 2.3; *m*-Cl, 0.34; *m*-Br, 0.36. There is an excellent correlation with σ^+ constants, with a ρ value of 1.1. The results are interpreted in terms of rate-determining proton transfer to the β-carbon atoms, and it is suggested that acid cleavages of vinyl—HgX bonds involve analogous mechanisms. PhSnMe$_3$ is cleaved 20 times as slowly as PhCH=CHSnMe$_3$ in the 1/10 AcOH/MeOH.

The rates of cleavage of XC$_6$H$_4$CH=CHSnMe$_3$ compounds by a mixture of MeOH (3 vol.) and 2 *M* aqueous NaOH (2 vol.) have been measured; *trans*-PhCH=CHSnMe$_3$ is cleaved about 1.3 times as rapidly as its *cis*-isomer, and about 12 times as rapidly as a mixture of *cis*- and *trans*-PhCH=CHSnEt$_3$. The relative rates for the various XC$_6$H$_4$CH=CHSnMe$_3$ compounds (mainly *trans*-isomers) are (X =) H, 1.0; *p*-OMe, 0.99; *p*-Me, 0.92; *m*-Cl, 1.67; *m*-Br, 1.65. Cleavage of *trans*-PhCH=CHSnMe$_3$ by NaOD/D$_2$O/MeOD gives exclusively *trans*-PhCH=CHD. For cleavages in methanolic NaOMe the values of the rate isotope effects, (the ratio k_{MeOH}/k_{MeOD}) are 2.3—2.6, and those of the product isotope effects, PIE (the product ratio RH/RD on cleavage of RSnMe$_3$ by NaOMe in 1 : 1 MeOH/MeOD) are 4.5—5.0.

The results are interpreted in terms of proton transfer from the solvent to the leaving carbon atom in the rate determining step as the Sn—C bond breaks as a result of the attack of the base anion at tin in a prior or synchronous process. PhCH=CHSnMe$_3$ is cleaved by the aqueous alcoholic base about 5 times as rapidly as PhSnMe$_3$.

* Dedicated to Professor G.A. Razuvaev on his 85th birthday.

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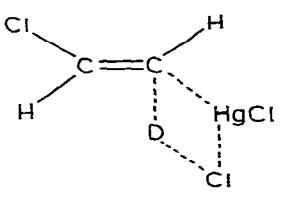
Cleavage of *trans*-PhCH=CHSnMe$_3$ by PhCOCl in presence of AlCl$_3$ in CH$_2$Cl$_2$ gives *trans*-PhCH=CHCOPh, and cleavage of a 90/10 mixture of *trans*- and *cis*-PhCH=CHSnMe$_3$ by bromine in CCl$_4$ gives a corresponding mixture of *trans*- and *cis*-PhCH=CHBr.

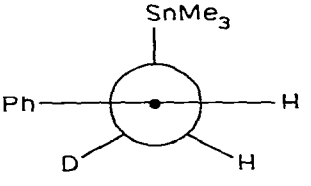
Introduction

There have in the past been kinetically-based mechanistic studies of the acid- and base-catalysed solvolytic cleavage of aryl—MMe$_3$ (M = Si, Ge, Sn, Pb) [1—7], benzyl—MMe$_3$ (M = Si, Ge, Sn) [8,9], alkynyl—MMe$_3$ (M = Si, Ge) [10], and allyl—MMe$_3$ (M = Si, Sn) [11,13] bonds * but not of vinyl—MMe$_3$ bonds, and the study described below was undertaken to remedy this omission.

Kinetic studies have been carried out previously, however, on the cleavages of ClCH=CHHgCl by hydrogen chloride in methanol and aqueous dioxan [14] **, and the stereospecificity of the reaction (for example *trans*-ClCH=CHHgCl with DCl gives *trans*-ClCH=CDH) led Beletskaya and Reutov to propose a four-centre mechanism (I), since the intermediacy of the carbonium ion ClCH$^+$-CH$_2$HgCl would, they argued, lead to loss of configurational identity by rotation about the C—C bond of the ion [16]. Kreevoy and Kretchmar also rejected the intermediacy of the carbonium ion CH$_2$CHHgI in the cleavage of CH$_2$=CHHgI by perchloric or sulphuric acid in water containing a little methanol, on the grounds that this would be inconsistent with the fact that the cleavage was much faster than the hydration of ethylene in such media [17], the very large stabilization of a carbon ion by a β-HgX substituent [19] not having been appreciated at that time. More recently, Koenig and Weber observed that the cleavage of *cis*- and *trans*-CH=CHSiMe$_3$ by HCl in CH$_3$CN is also stereospecifically *cis* [18], but showed that this stereospecificity is consistent with rate determining formation of a carbonium ion when account is taken of the stereochemical requirements of the hyperconjugative (σ-π) electron release from the Me$_3$Si—C bond [19] (possibly with some contribution from bridging by the Me$_3$Si group [20]) which markedly stabilizes the carbonium ion [18].



(I)



(II)

* The references given in this sentence are meant to be illustrative, not comprehensive.

** The reaction in Me$_2$SO was also studied, and considered to involve rate-determining ionization of the ClCH=CH$_2$—HgCl bond [14]. For an account of other cleavages of vinyl—HgX bonds by electrophiles see ref. 15.

Results and discussion

Acid cleavage

Compounds of the type *cis*- and *trans*-$XC_6H_4CH{=}CHSnMe_3$ were chosen for the study, and their rates of cleavage by 1/10 v/v AcOH/MeOH were measured spectrophotometrically, with the results shown in Table 1. The products in all cases were the corresponding styrenes, $XC_6H_4CH{=}CH_2$. The compounds *cis*- and *trans*-*p*-$MeC_6H_4CH{=}CHSnMe_3$ on cleavage with AcOD-MeOD, stereospecifically gave *cis*- and *trans*-*p*-$MeC_6H_4CH{=}CHD$, respectively.

The main features of the results in Table 1 are as follows:

(a) For the compounds with X = *p*-OMe, *p*-Me, or H, there is no significant difference between the rates of reaction of the *cis* and *trans* isomers, and the (notably low) activation energies which can be derived for *cis*- (7.3 k cal mol^{-1}) and *trans*-$PhCH{=}CHSnMe_3$ (7.5 k cal/mol^{-1}) are effectively identical. For X = *m*-Cl and *m*-Br the *cis*-*trans* mixtures (very predominantly *trans*) were used.

(b) There is an excellent linear correlation between values of log k_{rel} (at 50°C) and σ^+, with a slope of −1.1 (corr. coeff. 0.999), every point being on the line within the experimental error.

The results are wholly consistent with a mechanism (analogous to that proposed by Koenig and Weber for cleavage of $PhCH{=}CHSiMe_3$ by HCl in CH_3CN [13]), shown in Scheme 1, involving rate determining formation of the carbonium ion, the configuration of which is held by the stereochemical

TABLE 1

RATES OF CLEAVAGE OF $RSnMe_3$ COMPOUNDS IN 1/10 v/v AcOH—MeOH

R	Isomer	λ [a] (nm)	Temp. (°C)	$10^5 k$ [b] (s^{-1})	k_{rel} [c] (at 50°C)
p-$MeOC_6H_4CH{=}CH$	*cis* [d]	268	31.5	137	
	trans	268	31.5	127	
			40.0	245	
			50.0	520	7.0
p-$MeC_6H_4CH{=}CH$	*cis* [e]	297	31.5	42	
			40.0	78	
	trans	297	31.5	42	
			40.0	77	
			50.0	170	2.3
$C_6H_5CH{=}CH$ [f]	*cis* [e]	293	31.5	21	
			40.0	36	
			50.0	77	
$C_6H_5CH{=}CH$	*trans*	293	31.5	19	
			40.0	37	
			50.0	73	1.0
m-$ClC_6H_4CH{=}CH$	[g]	301	40.0	12.3	
			50.0	25	0.34
m-$BrC_6H_4CH{=}CH$	*trans* [h]	300	40.0	12.8	
			50.0	26	0.36
Ph		258	50.0	3.8	0.05
p-$MeOC_6H_4$		281	40.0	45	
			50.0	100	1.4

[a] Wave-length used to monitor reaction. [b] Observed first-order rate constant. [c] Rate relative to *trans*-$PhCH{=}CHSnMe_3$ at 50°C. [d] Contained 4% *trans*. [e] Contained 10% *trans*. [f] $PhCH{=}CHSnEt_3$ (44/56 *cis*/*trans* mixture) gave 10^5k = 77 s^{-1} at 50.0°C. [g] A 23/77 *cis*/*trans* mixture. [h] Contained 10% *cis*.

requirements of the hyperconjugative stabilization of the carbonium ion (and possibly some bridging) by the Me_3Sn group; the preferred conformation of the ion from *cis*-PhH=CHSnMe_3 and AcOD is that shown in II.

SCHEME 1

$$XC_6H_4CH{=}CHSnMe_3 + H^+ \overset{\text{slow}}{\rightleftharpoons} XC_6H_4\overset{+}{C}HCH_2SnMe_3$$

$$XC_6H_4\overset{+}{C}HCH_2SnMe_3 + MeOH \xrightarrow{\text{fast}} XC_6H_4CH{=}CH_2 + Me_3Sn\overset{+}{O}MeH$$

(The acid is written as H^+ to leave open the question of whether $Me\overset{+}{O}H_2$ or AcOH, or both, supply the proton.) The similarity in the reactivities of the *cis*- and *trans*-isomers can be understood in terms of persistence into the transition state (which is probably not far removed from the initial state) of most of any small differences which exists between the isomers themselves.

The value of ρ and the need to use σ^+ constants demonstrate that carbonium ion character is developed at the α-carbon atom in the transition state, thus ruling out a four-centre process analogous to I. The conjunction of a fairly low ρ value with an excellent correlation with σ^+ (rather than with $[\sigma + r(\sigma^+ - \sigma)]$ with a value of r substantially below 1, as observed for acid cleavage of ArSn-$(C_6H_{11})_3$ compounds [21]) can be attributed to the marked degree of stabilization of the forming carbonium ion by the hyperconjugative electron release from the Me_3Sn—C bond. The fact that the presence of the second α-Ph group in $Ph_2CH{=}CHSnMe_3$ causes only a 1.6-fold increase in the rate of cleavage is consistent with this explanation and with the ρ value. It is relevant to note that in hydration of the styrenes $XC_6H_4CH{=}CH_2$ by aqueous perchloric acid, which is also thought to involve rate-determining attachment of a proton to give the carbonium ion $XC_6H_4\overset{+}{C}HCH_3$, also gives a correlation with σ^+ values but with the markedly larger ρ value of −3.42 [22].

The similarity of the rates of cleavage of PhCH=CHSnMe_3 and PhCH=CHSn-Et_3 is also consistent with the proposed mechanism, since nucleophilic attack on the tin, which would be somewhat sterically inhibited by the larger Et groups, occurs after the rate-determining step. The result indicates that the hyperconjugative release from the C—$SnMe_3$ is very similar to that from C—$SnEt_3$ bond.

In order to provide a comparison of the relative ease of cleavage of PhCH=CH—$SnMe_3$ and aryl—$SnMe_3$ bonds the rates of cleavage of $PhSnMe_3$ and *p*-Me-$OC_6H_4SnMe_3$ in the AcOH-MeOH medium at 50°C were measured, and the results (Table 1) show that (*cis* or *trans*) PhCH=CHSnMe_3 is cleaved about 20 times as readily as $PhSnMe_3$. A *p*-OMe substituent causes a markedly greater acceleration in the aryl—$SnMe_3$ than in the β-styryl—$SnMe_3$ cleavage (the factors being 26 and 7, respectively), with the result that *trans*-*p*-$MeOC_6H_4CH{=}$CHSnMe_3 is cleaved only 5 times as readily as *p*-$MeOC_6H_4SnMe_3$.

The rate of cleavage of *trans*-PhCH=CHSnMe_3 was also measured in a mixture of MeOH (10 vol.) and aqueous 0.100 *M* $HClO_4$ (1.0 vol.) and a first order rate constant of 120×10^{-5} s^{-1} at 31.5°C was derived. Under the same conditions $CH_2{=}CHCH{=}CHSnMe_3$ gave a rate constant of 64×10^{-5} s^{-1}, and it seems that the α-Ph group stabilizes the intermediate carbonium ion (relative to the

substrate) slightly more effectively than does an α-vinyl group.

There is no reason to doubt that the acid cleavages of vinyl—HgX bonds also proceed by mechanism analogous to that in Scheme 1, the high rate and the stereospecificity both being attributable to hyperconjugative electron release from the β-C—HgX bond. We suspect that even in cleavages of vinyl—HgX bonds by halogens the configuration is held by this hyperconjugation rather than by the halogen-bridging usually assumed (see, e.g. ref. 28).

Cleavage by other electrophiles

Treatment of *trans*-PhCH=CHSnMe$_3$ with PhCOCl and AlCl$_3$ in CH$_2$Cl$_2$ gave *trans*-PhCH=CHCOPh in 60% yield after purification.

$$\textit{trans}\text{-PhCH=CHSnMe}_3 + \text{PhCOCl} \xrightarrow{\text{AlCl}_3} \textit{trans}\text{-PhCH=CHCOPh}$$

Treatment of a 90/10 mixture of *trans*- and *cis*-PhCH=CHSnMe$_3$ with bromine in CCl$_4$ gave a 96% yield of an 86/14 mixture of *trans*- and *cis*-PhCH=CHBr; the apparent slight deviation from stereospecificity was within the experimental error.

$$\textit{trans}\text{-PhCH=CHSnMe}_3 + \text{Br}_2 \rightarrow \textit{trans}\text{-PhCH=CHBr}$$

Stereospecific cleavage of PhCH=CHSiPh$_3$ by Br$_2$ has been shown to involve *cis*-addition of Br$_2$ followed by *trans*-elimination of Ph$_3$SiBr [23], but this does not rule out the possibility that the cleavage of the tin compound PhCH=CH-SnMe$_3$ proceeds by attack of Br$^-$ on the intermediate PhCHCHBrSnMe$_3$, in a process analogous to that in Scheme 1.

Base cleavage

The rates of cleavage of some XC$_6$H$_4$CH=CHSnMe$_3$ compounds by a mixture of MeOH (3 vol.) and aqueous 2 *M* NaOH (2 vol.) at 50°C were measured spectrophotometrically; the results are shown in Table 2, which also includes data for cleavage of PhCH=CHSnEt$_3$ and *m*-FC$_6$H$_4$SnMe$_3$. The main features of the results are as follows:

TABLE 2

RATES OF CLEAVAGE OF XC$_6$H$_4$CH=CHSnMe$_3$ AND SOME OTHER TIN COMPOUNDS IN A MIXTURE OF MeOH (3 vol) AND AQUEOUS 2.0 *M* SODIUM HYDROXIDE (2 vol) AT 50.0°C

Compound	Isomer	λ [a] (nm)	$10^5 k$ [b] (s^{-1})	k_{rel} [c]
m-ClC$_6$H$_4$CH=CHSnMe$_3$	*d*	301	62.5	1.67
m-BrC$_6$H$_4$CH=CHSnMe$_3$	*trans* [e]	300	62	1.65
PhCH=CHSnMe$_3$	*trans*	293	37.5	1.0
PhCH=CHSnMe$_3$	*cis* [f]	293	29	0.77
p-MeOC$_6$H$_4$CH=CHSnMe$_3$	*trans*	268	37	0.99
p-MeC$_6$H$_4$CH=CHSnMe$_3$	*trans*	297	34.5	0.92
PhCH=CHSnEt$_3$	*g*	293	3.2	0.085
m-FC$_6$H$_4$SnMe$_3$		270	42	1.1

[a] Wave-lengths used to monitor the reaction. [b] Observed first-order rate constant. [c] Rate relative to that of *trans*-PhCH=CHSnMe$_3$. [d] A 77/23 *trans*/*cis* mixture. [e] Contained 10% of *cis*-isomer. [f] Contained 10% of *trans*-isomer. [g] A 56/44 *trans*/*cis* mixture.

TABLE 3

SOLVENT ISOTOPE EFFECTS IN THE CLEAVAGE OF *trans*-$XC_6H_4CH{=}CHSnMe_3$ COMPOUNDS BY 3.46 *M* NaOMe IN METHANOL AT 50°C

X	$10^5 k_{MeOH}$ [a] (s^{-1})	$10^5 k_{MeOD}$ [b] (s^{-1})	RIE [c]	PIE [d]	RIE/PIE
p-Me	31.3	12.2	2.57	5.0	0.51
H	34.3	15.0	2.29	4.6	0.50
p-OMe				4.8	
m-Cl	59.8	25.8	2.31	4.5	0.51

[a] Observed first-order rate constant in 3.46 *M* NaOMe—MeOH. [b] Observed first-order rate constant in 3.46 *M* NaOMe—MeOD. [c] Ratio k_{MeOH}/k_{MeOD}. [d] Product isotope effect derived from cleavage in 1/2 MeOH—MeOD; estimated uncertainty ca. ±0.4. (Slightly lower values were derived from cleavages in 1/1 MeOH - MeOD - see Experimental section.)

(a) There is a small but significant difference between the rates of cleavage of *cis*- and *trans*-$PhCH{=}CHSnMe_3$, the latter being 1.3 times the more reactive.

(b) Since the samples of *m*-Cl and *m*-Br compounds used were *cis/trans* mixtures, the rate constants are not quite those which would be obtained if the pure *trans*-isomers were used, but this minor inaccuracy is unimportant for the discussion below. The prominent features of the effects of the substituents are the absence of any effect of the *p*-MeO group and the smallness of the deactivating effect of the *p*-Me group, especially in comparison with the sizeable activation by the *m*-Cl and *m*-Br substituents, which correspond to an approximate ρ value of 0.6.

(c) The triethyl compound $PhCH{=}CHSnEt_3$ (a *cis/trans* mixture was used) is ca. 12 times less reactive than *trans*-$PhCH{=}CHSnMe_3$.

(d) The compound *m*-$FC_6H_4SnMe_3$ is cleaved 1.1 times as readily as *trans*-$PhCH{=}CHSnMe_3$; since *m*-$FC_6H_4SnMe_3$ is cleaved in the medium 5.5 times as readily as $PhSnMe_3$ [5], *trans*-$PhCH{=}CHSnMe_3$ is cleaved 5 times as readily as $PhSnMe_3$.

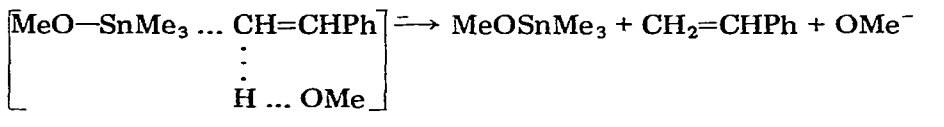
To establish the mechanism, the rate isotope effect, RIE (the ratio k_{MeOH}/k_{MeOD} of the rate constant in MeOH-MeONa to that in MeOD-MeONa), and the product isotope effect, PIE (the product ratio RH/RD obtained on cleavage of $RMMe_3$ by NaOMe in 1 : 1 MeOH/MeOD) were measured for some $XC_6H_4CH{=}CHSnMe_3$ compounds, and the results are shown in Table 3. The observation of large PIE and RIE values, and of RIE/PIE ratios in the region of 0.5 indicates that the mechanism of the cleavage in MeOH-MeONa is the same as that for the great majority of $RSnMe_3$ compounds studied, with the rate-determining step involving proton transfer from the solvent to the carbon atom of the C—Sn bond as it breaks as a result of the attack of the MeO^- ion at the tin atom [4,8]. As usual [4,8] we cannot distinguish between the type A mechanism (Scheme 2), in which formation of a pentacoordinate species preceeds the rate-determining bond-breaking and the type A_S (synchronous) mechanism in which the bond-breaking is concerted with the attack of the nucleophile, but we can conclude from the values of the RIE/PIE ratios that the MeO—Sn bond is either fully or almost fully formed in the rate-determining transition state [4,8], and for the present purposes the difference between the two transition states is un-

SCHEME 2

Type A.

$$MeO^- + Me_3SnCH{=}CHPh \rightleftharpoons [MeOSnMe_3CH{=}CHPh]^-$$

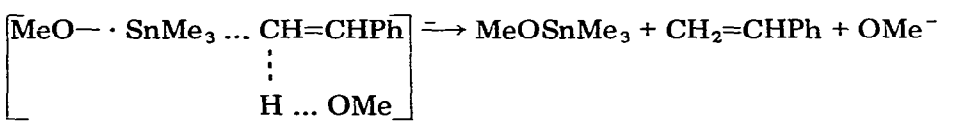
$$[MeOSnMe_3CH{=}CHPh]^- + MeOH \rightarrow$$



transition state

Type A_S

$$MeO^- + Me_3SnCH{=}CHPh + MeOH \rightarrow$$

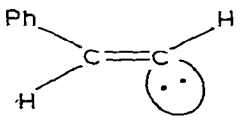


transition state

important. From the magnitude of the PIE values we roughly estimate that the proton transfer is one-quarter complete in the transition state, and since overall negative charge is developed at the β-carbon the breaking of the C—Sn bond must be rather more advanced, perhaps roughtly half complete. In the discussion below we assume that a similar mechanism operates with aqueous methanolic base.

Retention of configuration would be expected for this mechanism, and the effects of the substituents X are readily understood if it is assumed that, as in the base cleavages of other R—$SnMe_3$ bonds [4,8,24], the proton transfer lags behind the C—Sn bond breaking, so that some carbanionic character is developed in the transition state at the leaving carbon atom, and the *meta*-halogeno substituents thus activate. Even if the carbanion III were being formed in the rate-determining step a large activation by these substituents would not be expected, since the negative charge is relatively remote from the aromatic ring and the lone pair cannot, of course, be delocalized through the π-system. If the carbanion III were actually formed, then we might expect the pattern of substituent effects to be similar to that in the substituted-phenyl anions (V) though with all the effects markedly smaller, and calculations indicate that the destabilizing effects of the *p*-Me and *p*-OMe groups in V should be similar, and very small in comparison with the stabilizing effect of the *m*-Cl group [3]. The effects of substituents X in cleavage of $XC_6H_4SiMe_3$ compounds by hydroxide in 1/9 v/v H_2O/Me_2SO at 40°C, which is thought to involve rate-determining separation of the anion V, are consistent with this, the *m*-Cl substituent activating by a factor of 400 and the *p*-Me and *p*-OMe groups deactivating by factors of 3.7 and 4.1, respectively [7]. Furthermore, in the cleavage of the $XC_6H_4CH{=}CHSnMe_3$ compounds the electrophilic attack represented by the proton transfer to the β-carbon atom will be retarded by *m*-Cl and *m*-Br and assisted by *p*-Me and *p*-OMe, especially by the latter, so that the effects are all

damped down, and overall the *p*-OMe group has no significant effect. It is noteworthy that in the cleavage of $XC_6H_4SnMe_3$ compounds in the medium used for the present study, the *p*-OMe group actually activates by a small factor (1.64) (with the *p*-Me group deactivating slightly, by a factor of 1.2) while the *m*-Cl group activates by a factor of 8.1 [5]. (The latter figure corresponds to a ρ factor of 2.4, while use of data for a range of *m*-X derivatives gives a value of 2.2.)



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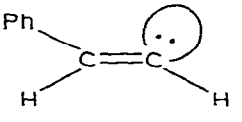

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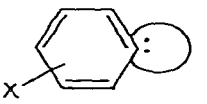

(V)

The small but significant difference between the rates of cleavage of *cis*- and *trans*-$PhCH{=}CHSnMe_3$ can be associated with the existence of a substantial amount of carbanionic character at the β-carbon atom in the transition state, since it would not be surprising to find the movement of π-charge away from this atom into the aromatic ring, to compensate for the large σ-charge, to be more effective in the *trans*-structure (III) than in the *cis*-structure (IV). (Any difference between the energies of the reactants would tend to operate in the opposite direction, since for steric reasons *cis*- would be expected to be slightly less stable than *trans*-$PhCH{=}CHSnMe_3$.)

The 12-fold lowering of the reactivity on going from $PhCH{=}CHSnMe_3$ to $PhCH{=}CHSnEt_3$ can be attributed to steric hindrance in a transition state which not only involves 5 groups around the Sn atom but also a solvent molecule (with other associated, hydrogen-bonded molecules) near the adjacent leaving carbon atom. Lowering of reactivity by factors of 21—33 was noted for cleavage of some $arylSnR_3$ species in MeOH-MeONa on going from R = Me to R = Et [4].

The fairly similar reactivities of $PhCH{=}CHSnMe_3$ and $PhSnMe_3$ in base cleavage are of interest. Clearly, if our mechanistic proposals are correct, both the stability of the carbanion R^- and the ease of electrophilic attack on the leaving carbon of the R group determine the ease of cleavage of $R{-}SnMe_3$ bonds of the type concerned. We have seen that $PhCH{=}CHSnMe_3$ is cleaved by acid some 20 times as readily as $PhSnMe_3$, and so the fairly similar factor of 5 in the base cleavage implies that there is not much difference between the ease of separation of the carbanions in the two cases, and so between the acidities of $PhCH{=}CH_2$ and PhH, with the styrene possibly slightly more acidic than benzene.

Finally we note that the α-styryltrimethylstannane, $H_2C{=}C(Ph)SnMe_3$ did not undergo any detectable cleavage in the medium used for the β-isomers even when the concentration of the aqueous sodium hydroxide was increased to 4.0 *M*. The large difference in reactivity between the α- and β-isomers can be understood in terms of the mechanism proposed. In the first place the proton transfer to the α-carbon could not in this case be assisted by the presence of the Ph group (which would not be conjugated with the positive centre in the notionally formed carbonium ion $H_2CCH(Ph)SnMe_3$). Second, and probably more importantly, carbanionic character is less likely to form at the α- than at the β-carbon; again the lone pair cannot be delocalized, but furthermore in this

case the π-system can adjust to remove π-electron density away from the centre of high σ-charge only at the expense of the conjugation between the double bond and the aromatic ring. If our reasoning is correct, the implication is that the α-hydrogen of styrene is less acidic than the β-hydrogens.

Syntheses of styryl-tin compounds

The styryltrimethylstannanes were mostly made by treatment of the appropriate styryl halide in THF with Me_3SnLi, but some were made by treatment of the styrylmagnesium bromide with Me_3SnCl. Noteworthy features were as follows:

(a) The reaction of Me_3SnLi with PhCH=CHBr occurred with almost complete retention of configuration, while that with PhCH=CHI occurred with virtually complete inversion. It is likely that the reaction of the iodide involves a direct nucleophilic substitution at the vinyl carbon centre, while that of the bromide involves an initial exchange to give PhCH=CHLi and Me_3SnBr. Similar stereochemical crossovers have been noted previously [29].

(b) The styrylmagnesium bromides were usually made in Et_2O and treated with Me_3SnBr in THF, and there was predominant retention of configuration (Table 4). However when the Grignard reagent from *cis*-β-bromostyrene was made in THF and treated with Me_3SnBr in the same solvent the product was virtually pure *trans*-PhCH=CHSnMe_3.

Experimental

Preparations of styryl-tin compounds

(A) From Grignard reagents

(i) In a typical procedure (cf. ref. 25), a mixture of *cis* (10%) and *trans* (90%) β-bromostyrene (33.9 g, 0.185 mol) in tetrahydrofuran (THF) (50 cm^3) was added dropwise under nitrogen during 1 h to magnesium turnings (22 g, 0.91 g-atom) in ether (175 cm^3) and THF (25 cm^3) containing a little 1,2-dibromoethane. The mixture was refluxed for 20 h then cooled, and Me_3SnBr (34.1 g, 0.14 mol) in THF (50 cm^3) was added dropwise. The mixture was refluxed for 3 h then cooled and treated with saturated aqueous NH_4Cl. The ethereal layer was dried (Na_2SO_4), the solvent removed, and the residue subjected to a low-efficiency fractional distillation to give PhCH=CHSnMe_3 (70%; see Table 4) and GLC analysis showed that this was a 93/7 *trans/cis* mixture. Careful fractionation through a spinning band column gave the pure (>99%) *trans*-isomer, b.p. 93°C/2 mm Hg, n_D^{25} 1.5657, λ_{max} (MeOH) 293 nm (ϵ = 1960), and the predominantly *cis*-isomer (containing 10% of the *trans*-isomer), b.p. 63°C/0.25 mm Hg, n_D^{25} 1.5525, λ_{max} (MeOH) 293 nm (ϵ = 720).

The separate *trans*- and *cis*-isomers were obtained analogously in the case of *p*-MeC_6H_4CH=CHSnMe_3 [*trans* (>95%), b.p. 89°C/0.35 mmHg, n_D^{25} 1.5646, λ_{max} (MeOH) 297 nm (ϵ = 2495); *cis* (>95%), b.p. 80°C/0.2 mmHg, n_D^{25} 1.5529, λ_{max} (MeOH) 297 nm (ϵ = 770)] and *p*-$MeOC_6H_4CH$=CHSnMe_3 [*trans* (>95%) m.p. 34—35°C, λ_{max} (MeOH) 268 nm (ϵ = 24 380); *cis* (>95%), b.p. 104°C/0.6 mmHg, n_D^{25} 1.5634, λ_{max} (MeOH) 267 nm (ϵ = 16 940)]. The yields of the initial isomer mixtures were 64 and 60%, respectively.

TABLE 4

PREPARATIONS FROM HALIDES VIA GRIGNARD REAGENTS OR Me_3SnLi

Halide, with *trans/cis* ratio	Product, with *trans/cis* ratio	Yield (%)	b.p. (°C)/mmHg	n_D (°C)
(a) Via Grignard reagents				
PhCH=CHBr; 90/10	PhCH=CHSnMe$_3$; 93/7	70	84–88/1.5 [a]	1.5655 (20)
PhCH=CHBr; 98/2	PhCH=CHSnMe$_3$; 100/0	64	63/0.25	1.5638 (25)
p-MeC$_6$H$_4$CH=CHBr; 86/14	*p*-MeC$_6$H$_4$CH=CHSnMe$_3$; 83/13	60	78/0.2	1.5635 (20)
p-MeOC$_6$H$_4$CH=CHBr; 55/45	*p*-MeOC$_6$H$_4$CH=CHSnMe$_3$; 41/59	65	110–118/0.9	1.5701 (20)
(b) Via Me_3SnLi				
PhCH=CHCl; 0/100	PhCH=CHSnMe$_3$; 70/30	52	92–96/2	1.5661 (25)
PhCH=CHBr; 90/10	PhCH=CHSnMe$_3$; 95/5	65	92–98/2	1.5663 (25)
PhCH=CHBr; 0/100	PhCH=CHSnMe$_3$; 7/93	45	92–96/2	1.5621 (20)
PhCH=CHI; 10/90	PhCH=CHSnMe$_3$; 95/5	38	84–86/1	1.5664 (25)
m-ClC$_6$H$_4$CH=CHBr; 0/100	*m*-ClC$_6$H$_4$CH=CHSnMe$_3$; 77/23	37	85–90/0.3	1.5652 (20)
Ph$_2$C=CHBr;	Ph$_2$C=CHSnMe$_3$	32	114–118/0.4	1.5993 (25)
Ph(Br)C=CH$_2$	Ph(Me$_3$Sn)C=CH$_2$	75	60–62/0.4 [b]	1.5534 (24)
Ph(Cl)C=CH$_2$	Ph(Me$_3$Sn)C=CH$_2$	37	64/0.4	1.5560 (22)
MeCH=CHBr; 0/100	MeCH=CHSnMe$_3$; 0/100	50	64/70 [c]	1.4744 (20)
CH$_2$=CHCH=CHBr	CH$_2$=CHCH=CHSnMe$_3$	60	73/46	1.5060 (20)
CH$_2$=CHC(Br)=CH$_2$	CH$_2$=CHC(SnMe$_3$)=CH$_2$	64	64–66/40	1.5275 (20)

[a] For a previous preparation see ref. 25. [b] For a previous preparation see ref. 26. [c] For a previous preparation see ref. 27.

When the preparation of $PhCH{=}CHSnMe_3$ was carried out from *cis*-$PhCH{=}CHBr$ with THF alone as solvent, the first, low efficiency, fractionation gave only *trans*-$PhCH{=}CHSnMe_3$ (>98%), which was obtained in 64% yield.

Analyses are given in Table 5.

(ii) A similar procedure starting from $Ph_2C{=}CHBr$, with THF alone as solvent, gave $Ph_2CH{=}CHSnMe_3$ (77%) b.p. 116—118°C/0.2 mmHg, n_D^{25} 1.5999. (For additional data see Tables 4 and 5.)

(iii) By a similar procedure, with THF alone as solvent, $Ph(Br)C{=}CH_2$ gave $Ph(Me_3Sn)C{=}CH_2$ (77%), b.p. 60—62°C/0.4 mmHg, n_D^{25} 1.5534 (lit. [26], b.p. 110°C/2 mmHg, n_D^{20} 1.5570).

(B) From Me_3SnLi

In a typical procedure β-bromostyrene (10.5 g, 0.06 mol) (1 90/10 *trans/cis* mixture) in THF (20 cm^3) was added dropwise at 0°C under N_2 to a solution of Me_3SnLi made from Me_3SnBr (15 g, 0.06 mol) and lithium (1.0 g, 0.14 mol) in THF (40 cm^3). The mixture was kept in a bath at 70°C for 2 h, then stirred overnight at room temperature. Treatment with saturated aqueous NH_4Cl followed by separation, washing, and drying (Na_2SO_4), of the organic layer and fractionation of the residue gave (i) a mixture (1.1 g) of Me_3SnBr and Me_3Sn-$SnMe_3$, (ii) unchanged $PhCH{=}CHBr$ (3.2 g), and (iii) $PhCH{=}CHSnMe_3$ (7 g, 65%), b.p. 93—97°C/2 mmHg, n_D^{21} 1.5655. GLC analysis showed this to be a 95/5 mixture of *trans*- and *cis*-isomers.

Similar procedures were carried out with a variety of other β-styryl halides and also with $Ph(Br)C{=}CH_2$, $Ph(Cl)C{=}CH$, $MeCH{=}CHBr$, $CH_2{=}CHCH{=}CHBr$, and $CH_2{=}CHCH(Br){=}CH_2$; the results are shown in Table 4, with analytical data in Table 5.

(C) Preparation of m-$BrC_6H_4CH{=}CHSnMe_3$

Trimethylstannane (8.4 g, 0.050 mol) was added to m-$BrC_6H_4C{\equiv}CH$ (9.8 g, 0.050 mol) under N_2 and the mixture was kept at 80°C for 7 days. Distillation gave m-$BrC_6H_4CH{=}CHSnMe_3$ (2.3 g, 24%), b.p. 98°C/0.05 mmHg, n_D^{25} 1.5846 (along with 4.8 g of unchanged m-$BrC_6H_4C{\equiv}CH$). Analysis by GLC indicated that two isomers were present in 90/10 ratio, and by comparison with the

TABLE 5

ANALYSES OF $XC_6H_4CH{=}CHSnMe_3$ AND OTHER VINYLTIN COMPOUNDS

Compound	Calc. (%)		Found (%)	
	C	H	C	H
$PhCH{=}CHSnMe_3$	49.4	6.0	49.7	6.0
m-$ClC_6H_4CH{=}CHSnMe_3$	43.8	5.0	44.2	5.0
m-$BrC_6H_4CH{=}CHSnMe_3$	38.1	4.3	37.6	4.3
p-$MeC_6H_4CH{=}CHSnMe_3$	51.2	6.4	51.3	6.2
p-$MeOC_6H_4CH{=}CHSnMe_3$	48.5	6.1	48.3	6.3
$Ph_2C{=}CHSnMe_3$	59.5	5.8	59.4	5.8
$Ph(Me_3Sn)C{=}CH_2$	49.4	6.0	49.4	5.9
$CH_2{=}CHCH{=}CHSnMe_3$	38.7	6.45	38.6	6.4
$CH_2{=}CHC(SnMe_3){=}CH_2$	38.7	6.45	38.3	6.3

properties of the isomers of other $XC_6H_4CH{=}CHSnMe_3$ compounds it was assumed that the less abundant isomer, which came off the column first, was the *cis*. In this case pure samples of the separate isomers could not be obtained by preparative GLC.

NMR spectra

The ^1H NMR spectra (in CCl_4) of the $XC_6H_4CH{=}CHSnMe_3$ compounds (including the integrations) were all consistent with the assumed formulae. The Me_3Sn protons in each case appeared as a singlet at τ 9.7—10.0 ppm; for the *trans* (or very predominantly *trans*) isomers the CH=CH protons gave singlets at τ 3.25—3.40, while for the *cis*-isomers they gave two doublets (J = 12—14 Hz), at τ 2.5—2.75 and 4.1—4.2, respectively. For $Ph_2C{=}CHSnMe_3$ the Me_3Sn protons gave a singlet at τ 10.05, and the CH=CH protons a doublet at τ 3.4 (J = 6 Hz), and for $Ph(Me_3Sn)C{=}CH_2$ the Me_3Sn protons gave a singlet at τ 9.37 and the $C{=}CH_2$ protons a doublet at τ 4.25 (J = 2 Hz).

Identification of isomers, and determination of cis/trans ratios

The proportion of *cis*- and *trans*-isomers in a mixture was usually determined by GLC. Mass spectrometry linked to GLC used to confirm that the two peaks did arise from isomers.

The assignments of configuration to the separate isomers were made on the basis of the IR, UV and ^1H NMR spectra. In the IR spectrum there were the expected differences between some of the vinylic C—H frequencies [25]: *trans*-CH=CH, 3040—3010m, 990—960s; *cis*-CH=CH, 3040—3010m, 1310—1395s-w; 640—690 cm^{-1} s-m. In the UV spectrum the *cis*-isomers show lower extinction coefficients.

Stereochemistries of the cleavages

(a) A solution of (>95%) *cis*-*p*-$MeC_6H_4CH{=}CHSnMe_3$ in MeOH (10 cm^3) and AcOH (1 cm^3) was kept at 31.5° C for 15 min. (ca. one half-life) then added to an excess of aqueous $NaHCO_3$. The organic material was extracted with ether and GLC analysis showed that *p*-$MeC_6H_4CH{=}CH_2$ was produced and that no isomerization of the *p*-$MeC_6H_4CH{=}CHSnMe_3$ had occurred.

(b) A solution of *trans*-$PhCH{=}CHSnMe_3$ in MeOH (10 cm^3) and AcOD (1 cm^3) was kept at 31.5° C for 8 h. After work-up as in (a) but with extraction into CCl_4 the product was shown by its ^1H NMR spectrum [18] to be *trans*-PhCH=CHD containing no detectable amount of the *cis*-isomer. Similarly the product from *cis*-$PhCH{=}CHSnMe_3$ containing 10% of the *trans*-isomer gave *cis*-PhCH=CHD containing 8—12% of the *trans*-isomer.

(c) A solution of *trans*-$PhCH{=}CHSnMe_3$ (2 g) in a mixture of MeOD (6 cm^3) and 2.0 *M* NaOH in D_2O (4 cm^3) was kept at 50° C for 5 h. The cold mixture was then neutralized with hydrochloric acid, and extracted with ether. The extract was dried (Na_2SO_4) and fractionated to give *trans*-β-deuteriostyrene (0.67 g, 86%), b.p. 74—76° C/75 mmHg, n_D^{25} 1.5299; ^1H NMR spectroscopy showed it to be *trans*-PhCH=CHD containing no detectable amount of the *cis*-isomer.

Rate measurements

(a) For most of the acid cleavages, 1.00 cm^3 of pure AcOH was added to

10.0 cm^3 of a solution of the organostannane in MeOH pre-warmed to the reaction temperature, and a sample of the well-shaken mixture was transferred to a stoppered 1 cm absorption cell, which was then placed in the thermostated cell-compartment of a Unicam SP 1700 UV spectrophotometer. After a few minutes, recording of the absorption (relative to MeOH) at the chosen wave-length (Table 1) was begun, and it was continued for at least 2 half-lives. Good first-order kinetics were observed, and first-order constants were derived in the usual way. Examination of the UV spectrum of the solution after 10 half-lives showed it to be identical to that of a solution of the expected product.

(b) For *trans*-$PhCH{=}CHSnMe_3$, the rate of cleavage was also measured in a mixture made up by adding 1.00 cm^3 of 0.100 *M* aqueous $HClO_4$ to 10.0 cm^3 of a methanolic solution of the organostannane, with other procedures as in (a). A wave-length of 392 nm was used, and the first-order rate constant was 120×10^{-5} s^{-1} at 31.5°C. Under the same conditions (with λ = 233 nm) $CH_2{=}CHCH{=}CHSnMe_3$ gave a rate constant of 64×10^{-5} s^{-1}.

(c) For most of the base cleavages, 4.0 cm^3 of aqueous 2.00 *M* NaOH was mixed with 6.0 cm^3 of a solution of the organostannane in MeOH. The subsequent procedure was as in (a), and the wave-lengths used are listed in Table 2.

(d) For cleavages in MeOH or MeOD containing MeONa, sodium was dissolved in MeOD to give a solution which was found to be 3.46 *M*. A solution of NaOMe of identical concentration in MeOH was then prepared by careful dilution of a slightly more concentrated solution. A small sample (<0.1 cm^3) of a concentrated solution of the organostannane in MeOH or MeOD was injected by syringe into 10 cm^3 of the MeONa-MeOH or MeONa-MeOD to give a solution of appropriate UV absorption, and the subsequent procedure was as in (a). The results are listed in Table 3.

Product isotope effects (cf. ref. 4)

(a) A solution of the $XC_6H_4CH{=}CHSnMe_3$ compound (0.6 mmol) in a 1.3 *M* solution (4.0 cm^3) of MeONa in 1 : 2 MeOH/MeOD was sealed in an ampoule which was then kept at 50°C for 72 h. The mixture was added to water (6 cm^3) at 0°C and the organic material extracted with n-heptane (2×5 cm^3). The extract was washed with water (3×2 cm^3) and dried (Na_2SO_4), and the H/D ratio in the styrene product was determined by use of an Applied Research Laboratories MPD 850 Analyzer linked to a Pye Model 64 gas chromatograph. The derived PIE values are listed in Table 3.

(b) A similar procedure was used with 1.9 *M* NaOMe in 1 : 1 MeOH/MeOD. The approximate PIE values obtained were as follows: (X =) H, 4.2; *p*-Me, 4.5; *p*-OMe, 4.9; *m*-Cl, 4.2. Because of the lower deuterium contents of the product mixtures, these values are likely to be less accurate than those obtained from the 1/2 MeOH/MeOD media, but within the rather wide limits of the experimental error the two sets of values are in agreement.

Cleavage of $PhCH{=}CHSnMe_3$ by PhCOCl and by Br_2

(a) A solution of PhCOCl (2 g, 0.015 mol) in CH_2Cl_2 (20 cm^3) was added under nitrogen to a suspension of powdered $AlCl_3$ (2.5 g, 0.018 mol) in CH_2Cl_2 (35 cm^3), and the mixture was stirred at room temperature for 20 min then filtered quickly under nitrogen through glass wool. The filtered solution was

added dropwise to *trans*-PhCH=CHSnMe$_3$ (4.0 g, 0.015 mol) in CH_2Cl_2 (35 cm^3), under nitrogen. The mixture was kept at room temperature for 6 h, then treated with dilute hydrochloric acid. The organic layer was separated, washed, and dried (Na_2SO_4), and the ether removed. The residue was chromatographed on silica gel with light petroleum as eluant to give *trans*-PhCH=CHCOPh (1.85 g, 60%), m.p. 55°C (lit. [30], m.p. 55—57°C) (Found: C, 86.2; H, 5.8. Calcd. $C_{15}H_{12}O$: C, 86.5; 5.8%). The ^{1}H NMR spectrum and mass spectrum (parent ion at *m/e* 208) were as expected.

(b) A solution of bromine (1.6 g, 0.010 mol) in CCl_4 (15 cm^3) was added dropwise at 0°C with exclusion of light to a solution of PhCH=CHSnMe$_3$ (a 91/9 *trans/cis* mixture) (2.6 g, 0.010 mol) in CCl_4 (20 cm^3). The bromine colour disappeared immediately. The solvent was removed and the residue was fractionated to give Me_3SnBr (2.3 g), b.p. 75°C/40 mmHg, and PhCH=CHBr (1.77 g, 96%), b.p. 78—80°C/5 mmHg, n_D^{20} 1.6012 (lit. [31], b.p. 44—54/0.2—0.8 mmHg, n_D^{25} 1.6037) (Found: C, 52.7; H, 3.8. Calcd. for C_8H_7Br: C, 52.8; H, 3.8%). GLC showed it to be a 86/14 *trans/cis* mixture. The ^{1}H NMR and mass spectrum (parent ion at *m/e* 182) were as expected.

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