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CLEAVAGE OF ALLYLIC TIN COMPOUNDS BY IODINE

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SUMMARY

A kinetic study has been made of the cleavage of allylic derivatives of tin of the type $Ph_3SnCH_2CH{=}CHR$ (R = H, Me, Ph) by iodine in a variety of solvents and in the presence of NaI. The rate-determining step is thought to involve unimolecular decomposition of the π-complex $Ph_3SnCH_2CH{=}CHR \cdot I_2$.

In weakly polar media, the 3-methylallyl(=2-butenyl)tin compound yields 1-methylallyl iodide in quantitative yield whereas in highly polar media such as DMSO, appreciable amounts of 3-methylallyl iodide are formed. For the 3-phenylallyl series only 3-phenylallyl iodide is obtained. The reaction is suggested to have an S'_E type mechanism in weakly polar solvents with the incursion of an S_E2 mechanism in more polar media. The conversion of 1-methylallyl into 3-methylallyl iodide has been briefly studied.

INTRODUCTION

Reactions of organometallic compounds with halogens have received much attention in the last two decades, and have provided an insight into the mechanism and stereochemical course of electrophilic aliphatic and aromatic substitution reactions.

In organotin chemistry, the iodine cleavage of aromatic, olefinic and aliphatic derivatives has been examined in detail. Iododestannylation of aryltrialkylstannanes has been studied by Eaborn *et al.*[1] and by Nasielski *et al.*[2-6] who attempted to correlate reactivity with substituent effects by using linear free energy relationships for a variety of aromatic derivatives of tin. Gielen and Nasielski[7] have shown that predominant retention of configuration accompanies the iodination of vinylic tin compounds. Both homolytic and heterolytic processes have been studied for reactions involving aliphatic compounds.

For heterolytic processes, it has been possible to characterise three principal mechanisms in simple bimolecular processes, namely S_E2, $S_F(S_Ei)$, S_E2C. These mechanisms have been distinguished by an examination of steric, polar, and solvent effects[8,9]. The cleavage of allylic organometal compounds by various electrophiles has recently been investigated for elements silicon[10], germanium[10], tin[11,12], and mercury[13]. The only quantitative study of iododestannylation of allylic compounds dealt briefly with the cleavage of tetraallyltin in solvent acetone[14]. Bimolecular allylic S_E mechanisms can be classified according to the position of electrophilic attack along the allylic chain. Attack at metal bearing carbon atom 1 is defined as an S_E2 or S_Ei mechanism, depending on whether the transition state is considered to be "open" or cyclic, whilst attack on carbon atom 3 yields a rearranged product, giving rise to the nomenclature S'_E2 or S'_Ei. The purpose of this work is to determine which mechanism dominates under various reaction conditions.

RESULTS AND DISCUSSION

The iododestannylations were performed in acetic acid, acetone, acetonitrile, methanol, ethanol, and dimethyl sulphoxide using triphenylallyl, 3-methylallyl and 3-phenylallyl derivatives of tin. In most cases, the reaction with iodine was too rapid for convenient measurement, and usually a large excess of iodide ion was used to reducing the "free" iodine concentration, in accordance with the equilibrium (1).

$$I_2 + I^- \overset{K_1}{\rightleftharpoons} I_3^- \tag{1}$$

The rate of reaction was measured spectrophotometrically by following the rate of disappearance of I_3^- in the spectral region 360–370 mμ, where products were found to have a minimal absorption.

The general form of the rate equation for bimolecular iodinations in the presence of I^- can be written as follows[14]

$$v = k_2 \cdot [M] \cdot [I_2] + k_1 \cdot [M] \cdot [I_2] \cdot [I^-] + k_3 \cdot [M] \cdot [I_3^-] \tag{2}$$

The first term results from a simple S_E2 or S_F transition state (a), the second term indicates nucleophilic assistance by I^- prior to the rate determining step (S_E2C) (b), and the third term represents the contribution from attack by I_3^-, again either S_E2 or S_F(c). From (1) and (2) the observed second order rate constant k_{obs} is given by

$$k_{obs} = k_2/K_1 \cdot [I^-] + k_1/K_1 + k_3 \tag{3}$$

A plot of k_{obs} versus $[I^-]^{-1}$ will not, in general, pass through the origin.(The ionic strength of the solution must, of course, be maintained constant). Knowing K_1, it is then possible to calculate the true second order rate constant k_2 for the process; it is not, however, possible to separate out the last two terms of expression (3).

If the reaction with I_3^- is very slow compared with that of I_2, and nucleophilic assistance by I^- is absent, then direct proportionality between k_{obs} and $[I^-]^{-1}$ results. Variation of $[I^-]$ therefore constitutes a useful test for the incursion of mechanistic types (b) and (c). This technique, allied with nuclear magnetic resonance data on $[R_3SnBr \cdot X]^-$ complexes, has been used successfully by Gielen and Nasielski[15] to evaluate the contribution made by each component of the general rate equation.

In the work outlined here, the experimentally observed rate of reaction was satisfactorily described by the equation[14]

$$v = k_{obs} \cdot [Sn] \cdot [I_3^-] \tag{4}$$

(where [Sn] refers to the concentration of the organotin compound) for all solvents used, and was found to be valid for greater than 80% reaction (Table 1).

TABLE 1

VALUES OF k_{obs} FOR THE CLEAVAGE OF TRIPHENYLALLYLTIN BY IODINE

In 0.01 M NaI in ethanol at 43.3° [a].

T (sec)	D_t	D_0-D_t	D_t-D_∞	$\frac{D_0-D_t}{D_t-D_\infty}$	k_{obs}
0	0.259				
60	0.208	0.051	0.198	0.258	430
90	0.187	0.072	0.177	0.407	453
120	0.172	0.087	0.162	0.538	448
150	0.161	0.098	0.151	0.648	433
180	0.147	0.112	0.137	0.819	454
210	0.138	0.121	0.128	0.945	450
240	0.130	0.129	0.120	1.08	450
270	0.121	0.138	0.111	1.24	459
300	0.115	0.144	0.105	1.37	456
360	0.104	0.155	0.094	1.65	458
420	0.094	0.165	0.084	1.96	466
480	0.085	0.174	0.075	2.32	483
540	0.080	0.179	0.070	2.56	474
600	0.073	0.186	0.063	2.95	491
∞	0.010			ave	457

[a] $[Ph_3SnCH_2CH{=}CH_2] = [I_2] = 1.00 \times 10^{-5}$ M; $\lambda = 360$ mμ.

Quantitative yields of Ph_3SnI and $CH_2{=}CHCH_2I$ were obtained for the cleavage of $Ph_3SnCH_2CH{=}CH_2$ by I_2 in solvents acetone, ethanol and DMSO, showing the stoichiometry of the reaction to be

$$Ph_3SnCH_2CH{=}CH_2 + I_2 \rightarrow Ph_3SnI + ICH_2CH{=}CH_2 \qquad (5)$$

Moreover, the reaction did not appear to be homolytic in nature since:

(*i*). no induction period was observed;
(*ii*). no hexaphenyldistannane or 1,5-hexadiene were formed;
(*iii*). the rates of reaction were unaffected by rigorous degassing of reaction solutions.

All the reactions studied were found to be first order with respect to both substrate and electrophile, even for the cleavage of $Ph_3SnCH_2CH{=}CHPh$ in solvent DMSO, where an S_E1 (S'_E1) mechanism could have been anticipated from the stability of the incipient carbanion (Table 2).

TABLE 2

OBSERVED SECOND ORDER RATE CONSTANTS k_{obs} FOR THE CLEAVAGE OF TRIPHENYL(3-PHENYLALLYL)TIN BY IODINE

In 0.01 M sodium iodide in DMSO at 30.0°.

$10^5[Ph_3SnCH_2CH{=}CHPh]$	$10^5[I_2]$	k_{obs} ($l \cdot mole^{-1} \cdot sec^{-1}$)
2.00	2.00	30.0
4.00	2.00	28.6
8.00	2.00	28.7
2.00	4.00	31.6

According to eqn. (3), k_{obs} should be inversely proportional to K_1. The value of K_1 is thus of great importance in the evaluation of the true constant k_2, and also in the calculation of thermodynamic activation parameters. The overall process which is being observed can be formulated as

$$I_2+I^- \overset{K_1}{\rightleftharpoons} I_3^- \qquad (1)$$

$$I_2+Ph_3SnCH_2CH{=}CHR \xrightarrow{k_2} \text{Products} \qquad (6)$$

The observed free energy of activation $\Delta G^{\neq}_{obs}$ will be compounded from the standard free energy change for process (1), ΔG_0, and the free energy of activation of process (6), $\Delta G^{\neq}$. Using a similar nomenclature, the enthalpies and entropies of these processes may be related as follows

$$\Delta H^{\neq}=\Delta H^{\neq}_{obs}+\Delta H_0 \qquad (7)$$

$$\Delta S^{\neq}=\Delta S^{\neq}_{obs}+\Delta S_0 \qquad (8)$$

Account must therefore be taken of the triodide equilibrium parameters ΔH_0, ΔS_0 in the computation of the true activation parameters.

Effect of change of solvent on K_1 and k_2

Parker *et al.*[16] have made a detailed study of equilibrium (1) and have concluded that K_1 is larger for dipolar aprotic than for protic solvents due to the greater solvation of the more polarisable I_3^- ion compared with the I^- ion. The degree of solvation of these species is important when distinguishing between S_E2, S_Ei and S_E2C mechanisms. Although solvation of I_2 by a dipolar aprotic solvent would reduce its electrophilicity, the effect is usually counterbalanced by nucleophilic assistance due to solvation of the metal atom, thus giving rise to an S_E2 transition state. In such a situation, I^- would be even more solvated, reducing its nucleophilicity and inhibiting an S_F mechanism. Hydrogen bonding equally inhibits an S_F mechanism. Therefore, in protic and dipolar aprotic solvents the reaction should proceed via an open transition state.

Values of k_{obs} appear in Table 3. In the more polar solvents methanol, ethanol and DMSO, k_{obs} was directly proportional to $[I^-]^{-1}$ as shown in Table 4. The rate equation obeyed in these media is that of a simple bimolecular attack by I_2:

$$v=k_2\cdot[Sn]\cdot[I_2] \quad \text{where} \quad k_2=K_1\cdot[I^-]\cdot k_{obs}$$

By using known values of K_1 for these solvents, k_2 can be evaluated. (see Table 3). It seems, therefore, that in polar media the solvent provides the nucleophilic assistance. The addition of small controlled amounts (0.54 M) of polar solvent to solvent acetone results in an increase in reactivity in the order

$$Me_2CO < MeCN < EtOH < H_2O < DMSO$$

This sequence parallels the reactivity in the pure solvents. The effect must be one of specific solvation (affecting both K_1 and k_2), since the bulk dielectric constant will not be greatly altered by the addition of such small quantities of the second solvent. One practical result of these findings is that solvents must be rigorously dried prior to use.

TABLE 3

VALUES OF SECOND ORDER RATE CONSTANTS k_2 FOR THE IODINATION OF $Ph_3SnCH_2CH{=}CHR$ IN VARIOUS SOLVENTS AT 25°

Solvent	R	k_{obs}	$10^{-6}K_1$	$10^2[I^-]$	$10^{-5}k_2$ $(l\cdot mole^{-1}\cdot sec^{-1})$
$(CH_3)_2CO$[a]	H	0.101	200[b]	1.00	2.02
	CH_3	0.026		1.00	0.52
CH_3CN	H	9.3	6.3[c]	1.00	4.2[d]
	C_6H_5	0.078		1.00	0.024[d]
CH_3OH	H	480	0.0199[c]	10.0	9.5
	CH_3	174		10.0	3.46
	C_6H_5	21.9		10.0	0.436
$(CH_3)_2SO$	H	180	7.9[c]	1.00	142
	CH_3	145		1.00	114
	C_6H_5	22.9		1.00	18.1

[a] k_{obs} obtained from Arrhenius plot. [b] Ref. 17. [c] Ref. 16. [d] Calculated from eqn. 3.

TABLE 4

EFFECT OF CHANGE OF $[I^-]$ ON k_{obs} FOR THE CLEAVAGE OF TRIPHENYLALLYLTIN BY I_2 IN ETHANOL
At 30.0°; μ constant at 0.01 by added $NaClO_4$.

$10^2[I^-]$	k_{obs}	$k_{obs}\cdot[I^-]$	$10^2[I^-]$	k_{obs}	$k_{obs}\cdot[I^-]$
1.00	335	3.35	0.50	688	3.44
0.80	440	3.52	0.40	815	3.26
0.70	445	3.12	0.20	1640	3.28
0.60	569	3.41			

For weaker solvating solvents such as acetonitrile, eqn. (3) was found to hold. Table 5 shows that the term k_1/K_1+k_3 has a finite value suggesting that either nucleophilic assistance by I^- or attack by I_3^- is important. In view of the findings of Gielen and Nasielski[15], the former would seem more probable.

TABLE 5

VALUES OF THE TRUE SECOND ORDER RATE CONSTANT k_2 FOR THE CLEAVAGE OF $Ph_3SnCH_2CH{=}CHR$ BY IODINE
In acetonitrile at 24.9° as calculated from eqn. (3).

R	Added salt	$k_1\cdot K+k_3$	$10^4k_2/K$	10^3k_2 $(l\cdot mole^{-1}\cdot sec^{-1})$
H		1.9	660	420
Ph		0.029	3.8	2.4
Ph	$LiClO_4$	0.033	4.8	3.0

Effect of added salt

In most of the reactions studied, no appreciable primary salt effect was observed, although the cleavage of triphenyl(3-methylallyl)tin in the absence of I^-

showed quite a strong positive salt effect. However, in the absence of data on the effect of added electrolytes on substrate and electrophile activities, it is difficult to draw any firm conclusions from these results.

Effect of 3-substituents

Table 6 shows the ratios of the observed second order rate constants k_H/k_R for the 3-methylallyl and 3-phenylallyl derivatives. The ratio is always highest for

TABLE 6

RATIOS OF OBSERVED SECOND ORDER RATE CONSTANTS $k(H)/k(Me)$ AND $k(H)/k(Ph)$

Solvent	$[I^-]$	$k(H)/k(Me)^a$	$k(H)/k(Ph)^a$
HOAc	0.01	4.1	
$(CH_3)_2CO$	0.00	4.5	
$(CH_3)_2CO$	0.01	3.6	
CH_3CN	0.01	3.1	124
C_2H_5OH	0.01	2.5	
CH_3OH	0.10	2.4	20.5
$(CH_3)_2SO$	0.01	1.3	7.8

[a] Mean of values obtained at four different temperatures.

(*i*). R = phenyl;

(*ii*). solvents of relatively low polarity and weak solvating power.

When R = Me, the ratio drops from a value of about 3 for solvent acetonitrile to just over unity for solvent DMSO. This suggests that an S'_E mechanism is important in weakly nucleophilic solvents, since electrophilic attack at C_3 would be much more sensitive to steric factors than a comparable attack at C_1. This effect is even more marked for the case of the 3-phenylallyl derivatives, where the ratio falls from a value of about 120 in solvent acetonitrile to 7.8 for solvent DMSO. In this instance, both polar and steric effects act in concert, since the olefinic π electrons are partially delocalised over the adjacent benzene ring.

The activation parameters appearing in Table 7 show that all the reactions studied are characterised by large negative observed activation entropies and small observed activation enthalpies. Gielen and Nasielski[14] have investigated the effect of temperature on K_1 in solvent methanol and have found a value of -8.0 kcal·mole^{-1} for ΔH_0 for equilibrium (1). Table 7 shows that $\Delta H^{\neq}_{obs}$ for the cleavage of allyl; (3-methylallyl) and (3-phenylallyl)tin derivatives by iodine in methanol are all less than ΔH_0, giving rise to apparent negative activation enthalpies ($\Delta H^{\neq}$). ΔS_0 has a value of -70 e.u. as calculated from Gielen and Nasielski's data, which gives rise to a value of $\Delta S^{\neq}$ of approximately -100 e.u. These values are clearly anomalous.

The problem is resolved by a detailed examination of the products of reaction. In weakly solvating media such as acetone and acetonitrile, cleavage of the (3-methylallyl)tin compound yielded 1-methylallyl iodide in almost quantitative yield. Although no direct evidence for π complex formation was obtained, it is likely that such a complex is formed in an equilibrium step prior to the rate determining step.

$$I_2 + I^- \overset{K_1}{\rightleftharpoons} I_3^- \qquad (1)$$

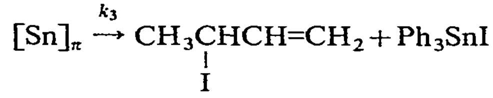
TABLE 7

OBSERVED THERMODYNAMIC ACTIVATION PARAMETERS FOR THE CLEAVAGE OF $Ph_3SnCH_2CH{=}CHR$ BY IODINE IN VARIOUS SOLVENTS[a]

Solvent	R	E_a (kcal·mole^{-1})	$\Delta H^{\ddagger}_{obs}$ (kcal·mole^{-1})	$\Delta S^{\ddagger}_{obs}$[b] (e.u.)
Acetone	H	2.38	1.78±0.89	−42.9±2.9
	CH_3	5.16	4.56±2.01	−36.9±6.5
0.01 *M* NaI/acetone	H	8.84	8.24±0.56	−35.5±1.8
	CH_3	9.13	8.53±0.13	−37.2±0.4
0.01 *M* NaI/MeCN	H	5.67	5.07±0.30	−37.1±1.0
	CH_3	6.26	5.66±0.09	−37.4±0.3
	Ph	6.67	6.07±0.25	−43.2±0.8
0.1 *M* NaI/MeOH	H	4.74	4.15±0.44	−32.4±1.4
	CH_3	7.16	6.57±0.54	−26.2±1.8
	Ph	6.04	5.44±0.38	−34.2±1.2
0.01 *M* NaI/DMSO	H	6.54	5.93±0.42	−28.3±1.4
	CH_3	6.00	5.40±0.50	−31.0±1.9
	Ph	6.61	6.01±0.62	−32.1±2.0

[a] Observed activation parameters for cleavage of tetraallyltin[14] by iodine in 0.5 *M* NaI/acetone had the values $\Delta H^{\ddagger}_{obs} = 6.0$ kcal·mole^{-1}, $\Delta S^{\ddagger}_{obs} = -34$ e.u. [b] Calculated at 25°C.

$$I_2 + [Sn] \overset{K_2}{\rightleftharpoons} [Sn]_\pi \tag{9}$$



$$[Sn]_\pi \xrightarrow{k_3} CH_3\underset{\displaystyle I}{\underset{|}{C}}HCH{=}CH_2 + Ph_3SnI \tag{10}$$

where $[Sn] = Ph_3SnCH_2CH{=}CHCH_3$; $[Sn]_\pi = \pi$ complex.

If (1) and (9) are rapidly established equilibria, then

$$v = \frac{K_2}{K_1} \cdot \frac{k_3 \cdot [Sn] \cdot [I_3^-]}{[I^-]} \tag{11}$$

and

$$k_{obs} = \frac{K_2}{K_1} \cdot \frac{k_3}{[I^-]} \tag{12}$$

In terms of free energy

$$-\Delta G^{\neq}_{obs} = -\Delta G_0(2) + \Delta G_0(1) - \Delta G^{\neq} \tag{13}$$

where $\Delta G_0(1)$, $\Delta G_0(2)$ are the standard free energies of steps (1) and (9) respectively. Eqn. (13) leads in turn to (14) and (15)

$$\Delta H^{\neq} = \Delta H^{\neq}_{obs} - \Delta H_0(2) + \Delta H_0(1) \tag{14}$$

$$\Delta S^{\neq} = \Delta S^{\neq}_{obs} - \Delta S_0(2) + \Delta S_0(1) \tag{15}$$

For reactions in the absence of iodide ion, very small values of $\Delta H^{\neq}_{obs}$ $[= \Delta H^{\neq} + \Delta H_0(2)]$ were found, indicating that $\Delta H^{\neq} \approx -\Delta H_0(2)$. On changing to more strongly polar media, significant quantities of 3-methylallyl iodide are formed (MeOH 10%, DMSO 30%). This reflects a change in the position of attack of iodine from carbon 3 to carbon 1. The effect of 3-methyl and 3-phenyl substituents will be minimal for attack at carbon 1. This does, in part, explain the reduction in k_H/k_R on increasing the solvent polarity, since tin–carbon bond fission is likely to be more advanced in the transition state, reducing, in effect the activation energy difference between the $S_E'2$ and S_E2 mechanisms. The corresponding trend in k_H/k_R is much more pronounced in the case of the (3-phenylallyl)tin compound. Unfortunately, 1-phenylallyl iodide rearranges extremely rapidly and the yield from the primary fission of the tin–carbon bond could not be obtained. It is likely, however, that less of the 1-isomer is formed than in the corresponding cleavage of the (3-methylallyl)tin compound because more Sn–C bond stretching in the transition state is anticipated for the 3-phenylallyl compound, and, electrophilic attack at C_3 will be less probable because of delocalisation of the π electrons.

k_H/k_{Me} for solvent ethanol has a value of 2.5 whereas that for the corresponding cleavage by HgI_2 is at least 100 times larger[11]. It seems that, unlike the mercury substitution, little homoallylic interaction occurs in the case of iodination. Ingold *et al.* have postulated a Sn–C–I bond angle of 76° for iodination of aliphatic tin compounds. Molecular models of possible transition states, show that overlap of the allylic π electrons and empty tin orbitals cannot occur unless the above angle is $>90°$. The size of this angle will be largely determined by the size of the incoming electrophile and outgoing R_3Sn group. Presumably in the case of HgI_2 the increased steric bulk requires a larger angle and hence homoallylic assistance can become important. The most significant difference between HgI_2 and I_2 as reagents is that the latter can act both as an electrophile and a nucleophile since it possesses highly polarisable lone pairs of electrons. In strongly polar media it is difficult, *a priori* to assess the relative contribution to nucleophilic assistance of the solvent molecules and lone pairs on iodine.

In summary, reactions in solvents Me_2CO and MeCN probably proceed via an iodide assisted $S_E'2$ mechanism whereas in solvents MeOH and DMSO, no iodide assistance is found and incursion of an S_E2 mechanism becomes important.

EXPERIMENTAL

Preparation and purification of starting materials

Triphenylallyltin (m.p. 75°) was prepared in 70% yield from triphenyltin chloride and allylmagnesium bromide in dry ether. Using a similar method, triphenyl(3-methylallyl)tin (m.p. 44–45°) was formed in 60% yield, but was found to contain about 30% of the *cis* isomer which was removed only with difficulty. Pure triphenyl(*trans*-3-methylallyl)tin (m.p. 59°) was obtained from triphenyltinsodium and pure *trans*-3-methylallyl chloride in liquid ammonia/petroleum ether (40–60°) mixture in 55% yield[12]. Triphenyl(*trans*-3-phenylallyl)tin (m.p. 74°) was formed in 55% yield from triphenyltin bromide and (*trans*-3-phenylallyl)magnesium chloride in dry ether, using a tenfold excess of magnesium.

All three derivatives were recrystallised from methanol prior to use, the 3-phenylallyl compound being noticeably less soluble than the other two.

Resublimed Analar iodine was used throughout. A Teflon spatula was used when weighing out iodine to avoid contamination with transition metal ions formed when nickel spatulae are employed.

All salts used were of reagent grade and dried at 110° for 12 h prior to use. Solvents were purified by conventional methods and stored over 4A molecular sieve.

Kinetic technique

All runs were conducted in thermostatted silica cells at concentration ranges 5×10^{-5}–5×10^{-4} M and absorbances measured in the wavelength range 360–370 mμ using a Unicam SP 500 Series 2 spectrophotometer. In this spectral region only I_3^- (or I_2) had appreciable absorbances.

For runs in glacial acetic acid, solutions of I_2 in excess sodium iodide were prepared by simply allowing a 5×10^{-3} M solution of sodium iodide to stand for 30 min, whereupon oxidation of I^- occurred with the liberation of iodine. Under these conditions, runs were conducted under pseudo-first order conditions using a huge excess of tin compound. Pseudo-first order conditions were also used for convenience in the few instances where the reaction could be studied in the absence of I^-, having firstly verified the bimolecular nature of the reaction.

Some runs were conducted under anaerobic conditions by rigorously degassing samples at $-78°$, under 0.5 mm Hg prior to mixing, using a Y tube with side arm and tap, and equipped with a ground glass cone which fitted directly into the neck of the reaction cell. Stray light was excluded by using a specially constructed heavy metal hood which fitted accurately over the cell housing of the spectrophotometer. Observed rate constants were evaluated from the appropriate integrated rate equation using the relationship for X, the amount of reaction.

$$X = \left(\frac{D_0 - D_t}{D_0 - D_\infty}\right)\cdot b \tag{16}$$

where D_0, D_t, D_∞ are the absorbances of the reaction solution at times $t=0$, $t=t$ and $t=\infty$ respectively and b is the initial concentration of iodine used. All substrates showed a negligible adsorbance at the wavelengths employed.

Thermodynamic parameters were obtained by computer using the Arrhenius equation and a least squares programme.

Product analyses

Reaction products were characterised using gas–liquid chromatography (GLC), NMR and UV spectroscopy.

GLC analyses. The iodides were analysed using an Aerograph 200 instrument. The methylallyl iodides were separable on a 5 foot column packed with 10% NPGS on Chromosorb W, (column temp. 60°, injection temp. 100° detector temp. 118°, sensitivity 2×1). 3 μl samples of the reaction mixtures were injected directly at various reaction times and the volatile components detected by a flame ionisation device. Calibrant solutions of 3-methylallyl iodide (II) were made up by treating a solution of pure *trans*-3-methylallyl chloride with an excess of sodium iodide and allowing to stand for 30 min. Under these conditions (II) had a retention time of 4.5 min. A preliminary investigation of the cleavage of $Ph_3SnCH_2CH{=}CHCH_3$ by I_2 in solvent methanol revealed the presence of two products, one of which had a retention time identical with that of (II) and the other (I) a retention time of 2.25 min. No iodobenzene was found in any of the reaction mixtures. It was found that on standing, (II) increased in concentration at the expense of (I) and the interconversion was accelerated by the addition of sodium iodide. These results indicate that (I) is in fact 1-methylallyl iodide which is converted to (II) by means of an $S_N'2$ mechanism.

$$\underset{\text{(I)}}{CH_3CH(I)CH{=}CH_2} \xrightarrow{Ph_3SnI \text{ or } I^-} \underset{\text{(II)}}{CH_3CH{=}CHCH_2I} \qquad (17)$$

More quantitative measurements showed that in solvents CCl_4, $(CH_3)_2CO$, CH_3CN, (I) was formed first almost exclusively, but was converted to (II) on standing. Using standard solutions of reagents, it was possible to evaluate the yields of (I) and (II). For solvents methanol and DMSO, however, appreciable quantities of (II) (10% and 30%, respectively) were formed prior to rearrangement (17).

The phenylallyl iodides were analysed using a non-polar column (10% Apiezon L on Chromosorb P, column temp. 80°, injection temp. 75°, flow-rate 25%). Calibrant solutions of 3-phenylallyl iodide were prepared as for the methylallyl analogue, but were found to be rather unstable in all solvents used. Injections of reaction solutions had to be made as soon as possible after mixing. 3-Phenylallyl iodide was synthesised by the method of Kaiser *et al.*[18], but was found to decompose rapidly on standing in air to a dark red polymeric solid.

Some iodobenzene was formed in reactions of $Ph_3SnCH_2CH{=}CHPh$ with iodine in solvents acetone (15% PhI) and acetonitrile (15% PhI), indicating that cleavage of the phenyl–tin bond was competitive. No iodobenzene was formed in solvents methanol and DMSO. In all reaction mixtures studied, 1-phenylallyl iodide could not be detected.

NMR analysis. 0.2 *M* solutions of substrate and iodine were made up in CCl_4, $(CD_3)_2CO$, CH_3CN and $(CD_3)_2SO$. Equal volumes of the reagent solutions were mixed and PMR spectra of the mixtures run at various time intervals.

3-Methylallyl iodide (II) was characterised by a three proton doublet at τ 8.37 (CH_3), a two proton multiplet at τ 6.02 (CH_2) and a two proton multiplet at τ 4.25 (CH=CH). In DMSO-d_6 the spectra of reaction mixtures showed the presence of II and another species which had proton resonances at τ 8.10 (doublet), τ 4.9 (multiplet) and τ 3.7 (multiplet). 2-Iodobutane shows a three proton doublet at τ 8.08 due to grouping $CH_3CH(I)$–.

The spectrum of the second species corresponds to that predicted for 1-methylallyl iodide (I). It is therefore possible to distinguish between (I) and (II) by their methyl resonances, and by integrating this portion of the spectrum the relative amounts of each isomer can be obtained to within about 10%. On standing overnight the spectrum broadened due to some decomposition of the iodides. At these concentrations (I) is converted to (II) quite rapidly as the GLC results show. Thus the amount of (II) present in this case is not the original concentration of (II) formed by cleavage of the tin compound. The results confirm the GLC findings. In acetone-d_6 however, (I) is converted to (II) only slowly and the amount of (I) found present ($\approx$ 100%) is a true reflection of the initial tin–carbon bond fission. In solvent DMSO-(I) is converted quantitatively to (II) on standing (Table 8). As in the case of GLC analysis, only 3-phenylallyl iodide was found in reaction mixtures of Ph_3SnCH_2-$CH{=}CHPh$ and I_2, even in non polar solvents such as CCl_4. It was characterised by a two proton doublet at τ 5.81 (CH_2), a two proton multiplet at τ 3.37 (CH=CH) and a five proton multiplet at τ 2.65 (C_6H_5), though the latter was obscured by proton

TABLE 8

PRODUCT ANALYSES FOR THE REACTION OF $Ph_3SnCH_2CH{=}CHCH_3$ AND I_2 IN VARIOUS SOLVENTS USING THE NMR METHOD[a]

Solvent	Time (min)	1-isomer (%)	3-isomer (%)
CCl_4	5	60	40
	100	30	70
	9000	0	100
Acetone-*d*$_6$	5	85	0
	60	≈100	≈0
DMSO-*d*$_6$	5	40	60
	60	≈0	≈100

[a] Concentration of both reactants 0.2 *M*.

signals from Ph_3SnI in actual reaction mixtures. Solutions of 3-phenylallyl iodide and reaction mixtures allowed to stand overnight have similar spectra but differ from that of freshly prepared 3-phenylallyl iodide, having complex multiplets at τ 5.78, 5.3, 3.2 and 2.65.

U V spectroscopic analysis. NMR methods could not be employed for the cleavage of triphenyl(3-phenylallyl)tin in solvent methanol owing to low solubility. Use can be made of the large difference in extinction coefficients between the 1- and 3-phenylallyl iodide in the 250–270 mμ region, the 3-isomer having an extended conjugation. By using solutions of Ph_3SnI and $PhCH{=}CHCH_2I$ as calibrants, estimates of yields of the latter can be made to within 10%. After 2 min reaction time 70% 3-phenylallyl iodide was formed (reaction concentrations 2.5×10^{-5} *M*).

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