Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

SULFUR DIOXIDE INSERTION INTO CARBON–TIN BONDS
II. REARRANGEMENTS ACCOMPANYING INSERTION

CLIFFORD W. FONG AND WILLIAM KITCHING
Department of Chemistry, University of Queensland, St. Lucia, Brisbane, (Australia)

(Received October 6th, 1969)

SUMMARY

A number of allylic, allenylic and 2-propynylic (R′) derivatives of tin of the type R_3SnR' have been synthesized, and shown to undergo ready insertion of sulfur dioxide into the Sn–R′ bond. Rearrangement accompanies insertion so that the products have the alternate allylic, 2-propynylic and allenylic structures respectively. Di-insertion occurs only when groups attached to tin are quite susceptible to electrophilic cleavage. NMR data for the compounds are reported.

INTRODUCTION

In Part I[1] of this series, devoted to exploration of details of sulfur dioxide insertion into carbon–tin bonds, we outlined the scope of the reaction and presented the evidence relating to the structures of the insertion products. Recently, we also discussed important aspects of insertions into carbon–lead bonds[2], and emphasised the similarities with carbon–tin systems[1,3]. In the present paper, we describe a number of allylic, and 2-propynylic–allenylic rearrangements accompanying sulfur dioxide insertion into carbon–tin bonds, and show how such rearrangements are blended harmoniously into the mechanistic framework for an electrophilic cleavage description of the insertion process.

EXPERIMENTAL

With the exception of 2-butenyltrimethyltin, all compounds were synthesized by methods similar to the general Grignard procedure outlined previously.

The Grignard reagent formed from 2-propynyl bromide and magnesium was prepared in ether and the required R_3SnCl added slowly as the solid.

1,2-Propadienyltrimethyltin[4]

Colourless liquid with pungent odour; b.p. 59–61° (47 mm) [lit.[4] 135° (755 mm)]; yield 35%. IR (neat): ν(C=C=C) 1925 cm^{-1}. (Found: C, 35.70; H, 5.71. $C_6H_{12}Sn$ calcd.: C, 35.52; H, 5.92%.)

---

* For Part I see ref. 1.

2-*Propynyltriphenyltin*[4]

White crystals recrystallized from n-hexane; m.p. 61–62°; yield 60%. IR (nujol mull): ν(H–C≡) 3315 cm^{-1}, ν(C≡C) 2110 cm^{-1}. (Found: C, 64.56; H, 4.75. $C_{21}H_{18}Sn$ calcd.: C, 64.83; H, 4.63%.)

The compound contained a small amount of the allenyl isomer [ν(C=C=C) 1930 cm^{-1}).

2-Propynyltriphenyltin was slowly isomerized to 1,2-propadienyltriphenyltin in a $CDCl_3/CD_3COOD$ mixture. IR (nujol mull): ν(C=C=C) 1930 cm^{-1}.

Acid cleavage proceeded at a much slower rate than the isomerization process.

Di-1,2-*propadienyldimethyltin*[5]

Colourless liquid with offensive odour; b.p. 90–91° (21 mm) [lit.[5] 62° (5 mm]); yield 23%. IR (neat): ν(C=C=C) 1925 cm^{-1}.

The compound previously reported was the 2-propynylic isomer.

Methylisopropylcyclopentyl-2-propynyltin and methylisopropylcyclopentyl-1,2-*propadienyltin*

These compounds were prepared as an isomeric mixture (1/6 respectively) from the 2-propynyl Grignard reagent and methylisopropylcyclopentyltin chloride[6].

Colourless liquid with pungent odour; distilled at 120–121° (10 mm); yield 38%. IR (neat): ν(C=C=C) 1920 cm^{-1}, ν(H–C≡) 3305 cm^{-1}, ν(C≡C) 2110 cm^{-1}. (Found: C, 49.98; H, 7.77. $C_{12}H_{22}Sn$ calcd.: C, 50.57; H, 7.72%.)

Mass spectrum [*m/e*, abundance (%), assignment]: 286, 1.0, $M^{+\bullet}$; 271, 0.7, $M^{+\bullet}-CH_3$; 247, 33.3, $M^{+\bullet}-C_3H_3$; 243, 48.3, $M^{+\bullet}-C_3H_7$; 217, 15.2, $M^{+\bullet}-C_5H_9$; 135, 100.0, $[Sn{-}CH_3]^+$.

(3-*Methyl*-1,2-*butadienyl*)*trimethyltin*

This compound was prepared from 3-bromo-3-methylbutyne[7] by formation of the Grignard reagent in ether followed by addition of trimethyltin chloride.

Colourless liquid distilling at 80–84° (70 mm); yield 42%. IR (neat): ν(C=C=C) 1940 cm^{-1}. (Found: C, 41.60; H, 6.66. $C_8H_{16}Sn$ calcd.: C, 41.37; H, 6.89%.)

2-*Butenyltrimethyltin*

This compound was synthesized by the addition of metallic sodium to a solution of trimethyltin chloride in liquid ammonia, followed by addition of 2-butenyl bromide in the manner previously reported[8].

Colourless liquid, b.p. 150–154° [lit.[8] 151° (*trans* isomer), 152.5° (*cis* isomer)]; no separation of isomers was attempted, but ratio of *cis*/*trans* isomers was *ca*. 1/1 (PMR); yield 75%.

2-*Butenyltriphenyltin*

This compound was synthesized by the *in situ* generation of the Grignard reagent from 2-butenyl bromide and magnesium in THF in the presence of triphenyltin chloride.

Colourless crystals, m.p. 51–52° (lit.[8] 51–52°); yield 80%. The compound was a *ca*. 1/1 mixture of *cis* and *trans* isomers (PMR). (Found: C, 65.72; H, 5.25. $C_{22}H_{22}Sn$ calcd.: C, 65.22; H, 5.48%.)

Cinnamyltrimethyltin

This compound was prepared by the *in situ* generation of the cinnamyl Grignard reagent in the presence of trimethyltin chloride in ether.

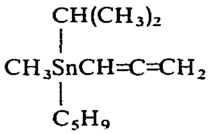
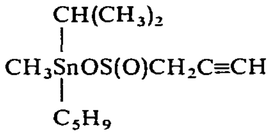
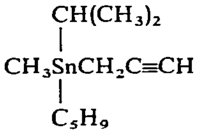
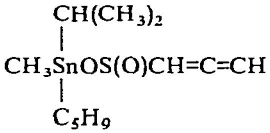
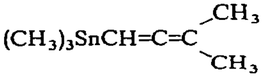
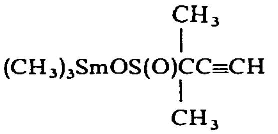
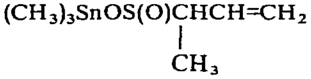
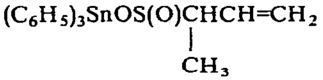
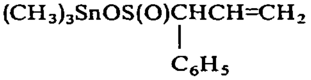
Colourless liquid, b.p. 126° (7 mm); yield 21%. IR (neat): ν(C=C) 1635 cm^{-1}, γ(CH) 955 cm^{-1}. (Found: C, 51.55; H, 6.30. $C_{12}H_{18}Sn$ calcd.: C, 51.55; H, 6.41%.)

Cinnamyltriphenyltin

This compound was prepared by the *in situ* Grignard method.

Colourless crystals, m.p. 69–69.5° (lit.[9] 69.5°); yield 40%. IR (nujol mull): ν(C=C) 1635 cm^{-1}, γ(CH) 955 cm^{-1}.

TABLE 1[a]

Organotin compound	Insertion compound	Calcd. (%)		Found (%)		M.p. (°C)
		C	H	C	H	
$(CH_3)_3SnCH=C=CH_2$	$(CH_3)_3SnOS(O)CH_2C\equiv CH$	26.99	4.49	26.39	4.66	83–84°
$(C_6H_5)_3SnCH=C=CH_2$	$(C_6H_5)_3SnOS(O)CH_2C\equiv C{-}H$	55.62	3.97	55.65	4.01	110–111°
$(C_6H_5)_3SnCH_2C\equiv CH$	$(C_6H_5)_3SnOS(O)CH=C=CH$	55.62	3.97	55.65	4.01	110–111°
$(CH_3)_2Sn(CH=C=CH_2)_2$	$(CH_3)_2Sn[OS(O)CH_2C\equiv CH]_2$	27.06	3.38	26.63	3.58	85–86°
 $CH_3\underset{C_5H_9}{\overset{CH(CH_3)_2}{Sn}}CH=C=CH_2$	 $CH_3\underset{C_5H_9}{\overset{CH(CH_3)_2}{Sn}}OS(O)CH_2C\equiv CH$	41.29	6.30	41.67	6.39	Oil
 $CH_3\underset{C_5H_9}{\overset{CH(CH_3)_2}{Sn}}CH_2C\equiv CH$	 $CH_3\underset{C_5H_9}{\overset{CH(CH_3)_2}{Sn}}OS(O)CH=C=CH$	41.29	6.30	41.67	6.39	Oil
 $(CH_3)_3SnCH=C{<}^{CH_3}_{CH_3}$	 $(CH_3)_3SmOS(O)\underset{CH_3}{\overset{CH_3}{C}}C\equiv CH$	32.43	5.40	31.53	5.57	Oil
$(CH_3)_3SnCH_2CH=CHCH_3$	 $(CH_3)_3SnOS(O)\underset{CH_3}{CH}CH=CH_2$	29.71	5.65	30.23	5.85	Oil
$(C_6H_5)_3SnCH_2CH=CHCH_3$	 $(C_6H_5)_3SnOS(O)\underset{CH_3}{CH}CH=CH_2$	56.17	4.68	56.45	4.61	132–133°
$(CH_3)_3SnCH_2CH=CHC_6H_5$	 $(CH_3)_3SnOS(O)\underset{C_6H_5}{CH}CH=CH_2$	41.79	5.22	42.01	5.39	Oil
$(C_6H_5)_3SnCH_2CH=CHC_6H_5$	$(C_6H_5)_3SnOS(O)CH_2CH=CHC_6H_5$	61.05	4.52	61.44	4.40	111–112°

[a] Several types of rearrangement are apparent from examination of this Table and the structures of the compounds involved are based on proton NMR and in some cases, IR spectra. The different types of rearrangement studied are now outlined in detail.

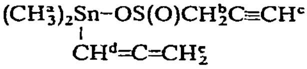
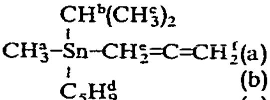
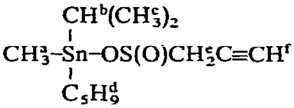
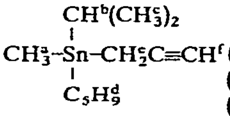
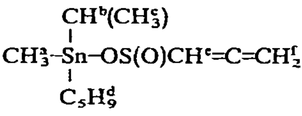
RESULTS AND DISCUSSION

The starting compounds and the insertion products (with analyses and where appropriate melting points for the latter) are located in Table 1. IR spectra, chiefly in the S–O stretching and Sn–C stretching regions, were examined in detail in Part I.

Allylic rearrangements

To test for allylic rearrangement the systems indicated below were explored *i.e.* 2-butenyl and cinnamyl ($R_3Sn\text{–}CH_2\text{–}CH{=}CH\text{–}R^1$, where R and $R^1 = CH_3$, C_6H_5).

TABLE 2[a]

Organotin compound		Insertion compound	
$(CH_3^a)_3SnCH^b{=}C{=}CH_2^c$	(a) 9.80, 1, $J^1 = 56.5$ (b) 4.49, 3, $J = 7.5$, $J^1 = 12$ (c) 5.80, 2, $J = 7.5$, $J^1 = 40$	$(CH_3^a)_3SnOS(O)CH_2^bC{\equiv}CH^c$	(a) 9.38, 1, $J^1 = 70$ (b) 6.88, 2, $J = 3$, $J^1 = 0$ (c) 7.69, 3, $J = 3$, $J^1 = 0$
$(C_6H_5^a)_3SnCH^b{=}C{=}CH_2^c$	(a) 2.55, complex (b) 4.64, 3, $J = 7.5$, $J^1 = 12$ (c) 5.72, 2, $J = 7.5$, $J^1 = 44$	$(C_6H_5^a)_3SnOS(O)CH_2^bC{\equiv}CH^{c,b}$	(a) (b) 7.58, 2, $J = 3$, $J^1 = 0$ (c) 7.88, 3, $J = 3$, $J^1 = 0$
$(C_6H_5^a)_3SnCH_2^bC{\equiv}CH^c$	(a) 2.55, complex (b) 7.88, 2, $J = 3$, $J^1 = 63$ (c) 8.17, 3, $J = 3$, $J^1 = 24$	$(C_6H_5^a)_3SnOS(O)CH^b{=}C{=}CH_2^c$	(a) 2.34, complex (b) 4.43, 3, $J = 6.5$, $J^1 = 0$ (c) 5.18, 2, $J = 6.5$, $J^1 = 0$
$(CH_3^a)_2Sn(CH^b{=}C{=}CH_2^c)_2$	(a) 9.68, 1, $J^1 = 59$ (b) 4.93, 3, $J = 7.5$, $J^1 = 12$ (c) 5.78, 2, $J = 7.5$, $J^1 = 44$	 $(CH_3^a)_2\underset{CH^d{=}C{=}CH_2^e}{Sn}\text{–}OS(O)CH_2^bC{\equiv}CH^c$	(a) 9.39, 1, $J^1 = 75$ (b) 6.92, 2, $J = 3$, $J^1 = 0$ (c) 7.74, 3, $J = 3$, $J^1 = 0$ (d) 4.69, 3, $J = 7.0$ (e) 5.60, 2, $J = 7.0$, $J^1 = 58$
		$(CH_3^a)_2Sn[O(SO)CH_2^bC{\equiv}CH^c]_2$	(a) 9.09, 1, $J^1 = 75$ (b) 6.92, 2, $J = 3$, $J^1 = 0$ (c) 7.74, 3, $J = 3$, $J^1 = 0$
 $CH_3^a\text{–}\underset{C_5H_9^d}{\overset{CH^b(CH_3^c)_2}{Sn}}\text{–}CH_2^e{=}C{=}CH_2^f$	(a) 9.95, 1, $J^1 = 49$ (b) ? (c) 8.76, 2, $J = 4.5$ (d) 8.48, complex (e) 5.08, 3, $J = 7$, $J^1 = 14$ (f) 5.92, 2, $J = 7$, $J^1 = 35$	 $CH_3^a\text{–}\underset{C_5H_9^d}{\overset{CH^b(CH_3^c)_2}{Sn}}\text{–}OS(O)CH_2^eC{\equiv}CH^f$	(a) 9.55, 1, $J^1 = 56$ (b) ? (c) 8.68, 2, $J = 6$ (d) 8.43, complex (e) 7.75, 3, $J = 3$, $J^1 = 0$ (f) 6.91, 2, $J = 3$, $J^1 = 0$
 $CH_3^a\text{–}\underset{C_5H_9^d}{\overset{CH^b(CH_3^c)_2}{Sn}}\text{–}CH_2^eC{\equiv}CH^f$	(a) 9.95, 1, $J^1 = 49$ (b) ? (c) 8.76, 2, $J = 4.5$ (d) 8.48, complex (e, f) ?	 $CH_3^a\text{–}\underset{C_5H_9^d}{\overset{CH^b(CH_3^c)}{Sn}}\text{–}OS(O)CH^e{=}C{=}CH_2^f$	(a) 9.55, 1, $J^1 = 56$ (b) ? (c) 8.68, 2, $J = 6$ (d) 8.43, complex (e) 4.20, 3, $J = 6.5$, $J^1 = 0$ (f) 4.93, 2, $J = 6.5$, $J^1 = 0$
$(CH_3^a)_3SnCH^b{=}C{=}C(CH_3^c)_2$	(a) 9.89, 1, $J^1 = 56$ (b) 5.06, 7, $J = 3.5$, $J^1 = 34.5$ (c) 8.42, 2, $J = 3.5$, $J^1 = 24$	$(CH_3^a)_3SnOS(O)C(CH_3^b)_2C{\equiv}CH^c$	(a) 9.38, 1, $J^1 = 70$ (b) 8.80, 1, $J^1 = 0$ (c) 7.66, 1, $J^1 = 0$

(*Continued p.* 111)

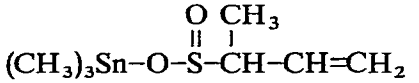
TABLE 2 (*continued*)

Organotin compound		Insertion compound	
$(CH_3^a)_3SnCH_2^bCH^c{=}CH^dCH_3^e$ (1/1 *cis/trans*)	(a) 9.96, 1, $J^1=52$ 9.97, 1, $J^1=52$ (b, e) 8.31, complex (c, d) 4.58, complex	$(CH_3^a)_3SnOS(O)\underset{\underset{CH_3^c}{\vert}}{CH^b}CH^d{=}CH_2^e$	(a) 9.44, 1, $J^1=70$ (b) 7.21, 5, $J=7$, $J^1=0$ (c) 8.82, 2, $J=7$, $J^1=0$ (d, e) 4.50, complex
$(C_6H_5^a)_3SnCH_2^bCH^c{=}CH^d{-}CH_3^e$ (1/1, *cis/trans*)	(a) 2.80, complex (b) 7.63, 2, $J=9$, $J^1=72$ (c,d) 4.50, complex (e) 8.44, 2, $J=6$, $J^1=13$ 8.55, 2, $J=7$, $J^1=11$	$(C_6H_5^a)_3SnOS(O)\underset{\underset{CH_3^c}{\vert}}{CH^b}{-}CH^d{=}CH_2^{e,c}$	(a) 2.80, complex (b) 7.47, 5, $J=7$, $J^1=0$ (c) 9.04, 2, $J=7$, $J^1=0$ (d) 4.45, complex (e) 5.13, complex
$(CH_3^a)_3SnCH_2^bCH^c{=}CH^d{-}C_6H_5^e$	(a) 9.88, 1, $J^1=53.5$ (b) 8.07, 2, $J=7.5$, $J^1=68$ (c, d) 3.68, complex (e) 2.77, 1	$(CH_3^a)_3SnOS(O)\underset{\underset{C_6H_5^e}{\vert}}{CH^b}{-}CH^c{=}CH_2^d$	(a) 9.47, 1, $J^1=70$ (b) 6.18, 2, $J=8.5$, $J^1=0$ (c) 3.80, complex (d) 4.66, complex (e) 2.75, 1
		$(CH_3^a)_3SnOS(O)CH_2^bCH^c{=}CH^d{-}C_6H_5^e$	(a) 9.47, 1, $J^1=70$ (b) 6.77, 2, $J=7$, $J^1=0$ (c, d) 3.67, complex (e) 2.70, 1
$(C_6H_5^a)_3SnCH_2^bCH^c{=}CH^d{-}C_6H_5^e$	(a) 2.60, complex (b) 7.38, 2, $J=7$, $J^1=74$ (c, d) 3.58, complex (e) 2.80, 1	$(C_6H_5^a)_3SnOS(O)\underset{\underset{C_6H_5^e}{\vert}}{CH^b}{-}CH^c{=}CH_2^d$	(a) 2.80, complex (b) 6.92, 2, $J=8.5$, $J^1=0$ (c) 4.45, complex (d) 5.22, complex (e) *ca.* 2.80
		$(C_6H_5^a)_3SnOS(O)CH_2^bCH^c{=}CH^d{-}C_6H_5^e$	(a) 2.80, complex (b) 8.13, 2, $J=5$, $J^1=0$ (c, d) 3.58, complex (e) *ca.* 2.80

---

[a] Protons are indicated by superscripts and are tabulated in the order: τ value, multiplicity, J (proton–proton coupling, Hz), J^1 (^{119}Sn–proton coupling, Hz). All spectra were measured in $CDCl_3$ solution from internal TMS standard. [b] Measured in pyridine solution. [c] Measured in DMSO-d_6 solution.

2-Butenyltrimethyltin was obtained as an approximately 50/50 mixture of the *cis* and *trans* isomers (PMR) and details of the spectra are located in Table 2. A $CDCl_3$ solution of this isomeric mixture reacts very rapidly with gaseous SO_2 and an oil (Table 1) analysing for a monoinsertion product can be obtained. That the product is the rearranged 1-methylallyl isomer is immediately evident from the PMR spectrum. (Monomeric structures have been written for convenience).



$$(CH_3)_3Sn{-}O{-}\overset{\overset{O}{\|}}{S}{-}\overset{\overset{CH_3}{|}}{CH}{-}CH{=}CH_2$$

Thus the presence of three vinyl protons, a $-C-CH_3$ doublet, and a "quintet" resonance for $\rangle CH-$ (due to equal coupling to $-CH_3$ and $-CH{=}$) are in accord with the above structure. (In the starting 2-butenyl compound, there are two vinyl protons).

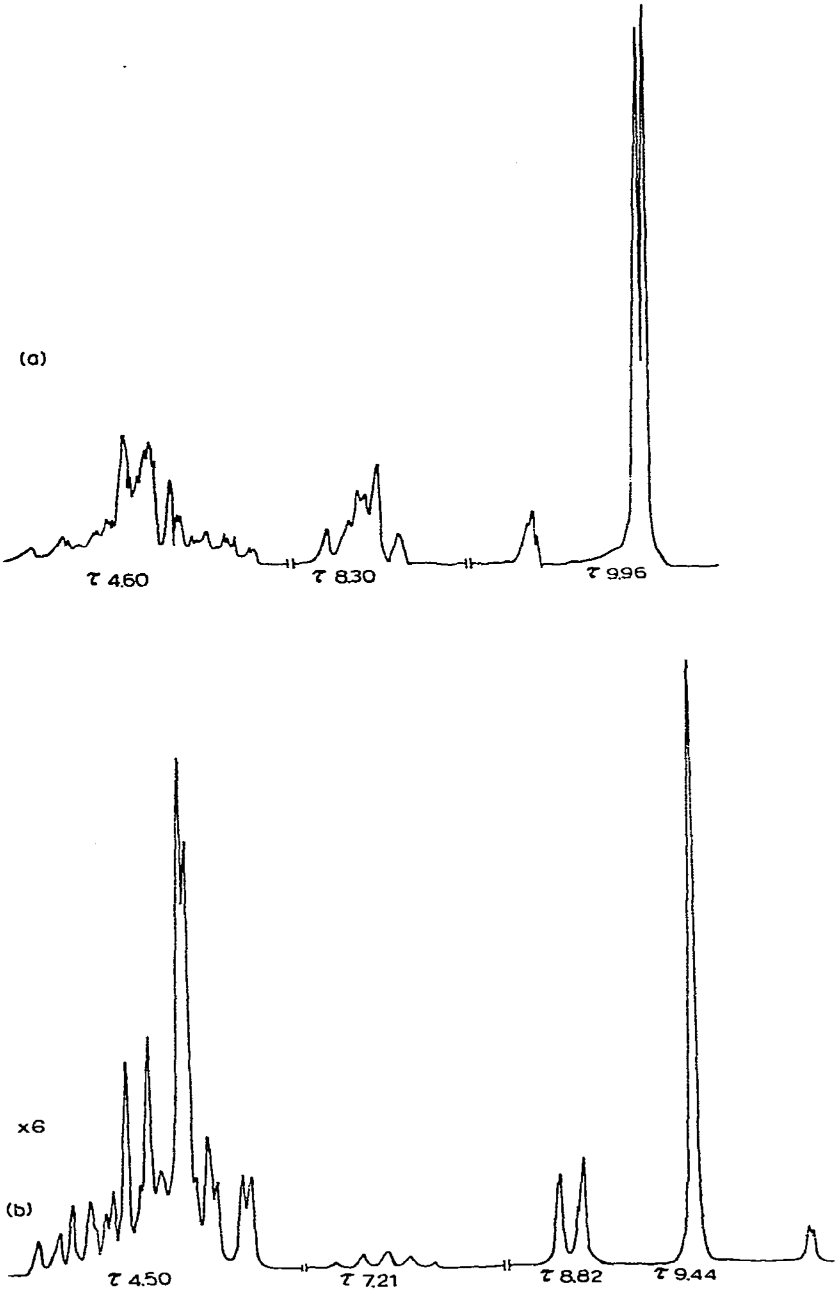


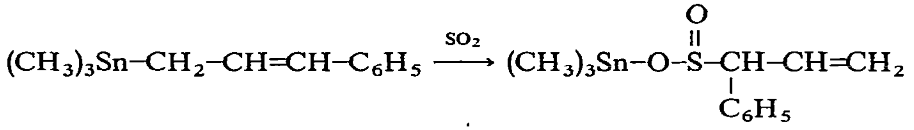
Fig. 1. (a). 60 MHz spectrum of $CH_3-CH=CH-CH_2-Sn(CH_3)_3$ ($CDCl_3$, TMS); *ca.* 50/50 mixture of *cis* and *trans* isomers. Resonances have τ values shown. Only the lower field $(CH_3)_3Sn$ satellite is shown, and the vinyl region is at increased gain. (b). Spectrum of $(CH_3)_3Sn-O-S(O)-CH(CH_3)-CH=CH_2$ ($CDCl_3$, TMS). Resonances have τ values indicated and the vinyl region is at increased gain. The $-CH-$ resonance appears as a quintet due to roughly equal coupling ($^1H-^1H$) from CH_3-C and $C-CH=$. Satellites occur only about the $(CH_3)_3Sn$ resonance.

The complete PMR data is located in Table 2, and chemical shifts and ^1H–^1H couplings are of the anticipated magnitudes.

Products of kinetic control only are pertinent to mechanism, and the possibility exists (admittedly quite remote) that this product may be in fact the unrearranged insertion product, which isomerises relatively rapidly to the 1-methylallyl structure. Although such behaviour is contrary definitely to thermodynamic considerations for 1- and 2-olefin systems, direct evidence against such a scheme has been obtained by monitoring the reaction by PMR (Fig. 1). No signals appropriate for the insertion product with the 2-butenyl structure were observed at any stage, and the spectral features were a super-position of those for the starting 2-butenyltin compound and the 1-methylallyl insertion product.

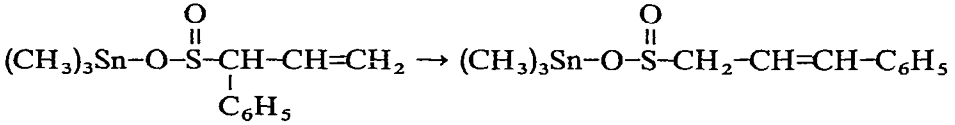
Similar behaviour was observed for triphenyl-2-butenyltin, and of course no ^{119}Sn–^1H coupling is observable about the allyl proton resonances (Table 2).

The cinnamyl systems ($R = CH_3$, C_6H_5 and $R^1 = C_6H_5$) are of considerable interest, since in these cases it is possible to observe allylic isomerisation of the products. Cinnamyltrimethyltin reacts very readily with SO_2 and the PMR spectrum confirms the structure below for the insertion product (kinetic control).



$$(CH_3)_3Sn{-}CH_2{-}CH{=}CH{-}C_6H_5 \xrightarrow{SO_2} (CH_3)_3Sn{-}O{-}\overset{\overset{O}{\|}}{S}{-}\underset{\underset{C_6H_5}{|}}{CH}{-}CH{=}CH_2$$

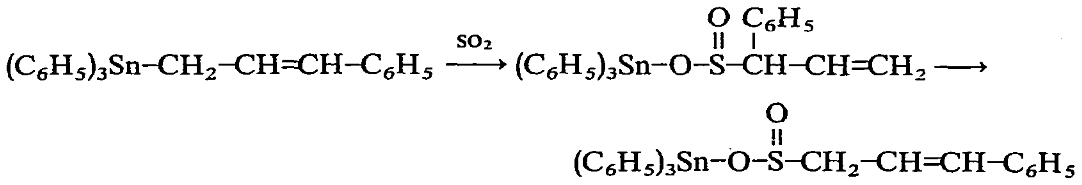
Aside from aromatic and $(CH_3)_3Sn$ resonances, the spectrum shows three vinyl protons and a higher field doublet for –CH– as required. (See Table 2 for details). With the passage of time, it is clear that the following product rearrangement is occurring (by as yet an unknown pathway)



$$(CH_3)_3Sn{-}O{-}\overset{\overset{O}{\|}}{S}{-}\underset{\underset{C_6H_5}{|}}{CH}{-}CH{=}CH_2 \rightarrow (CH_3)_3Sn{-}O{-}\overset{\overset{O}{\|}}{S}{-}CH_2{-}CH{=}CH{-}C_6H_5$$

since new signals at τ 6.77 ppm (doublet $J = 7$ Hz) ($-CH_2$) and in the vinyl region appear, with intensities appropriate for the primary cinnamyl insertion product (Table 2). This observation confirms allylic rearrangement as a mechanistic consequence of insertion. Basic considerations account for this product isomerisation being more facile for cinnamyl than for 2-butenyl, since resumption of phenyl conjugation must constitute a better motive than CH_3 (hyper) conjugation, apart from any steric considerations (Fig. 2).

Rearrangement also accompanies insertion into cinnamyltriphenyltin, but here some persistence is required to observe the (secondary allylic) kinetic control product.



$$(C_6H_5)_3Sn{-}CH_2{-}CH{=}CH{-}C_6H_5 \xrightarrow{SO_2} (C_6H_5)_3Sn{-}O{-}\overset{\overset{O}{\|}}{S}{-}\overset{\overset{C_6H_5}{|}}{CH}{-}CH{=}CH_2 \longrightarrow (C_6H_5)_3Sn{-}O{-}\overset{\overset{O}{\|}}{S}{-}CH_2{-}CH{=}CH{-}C_6H_5$$

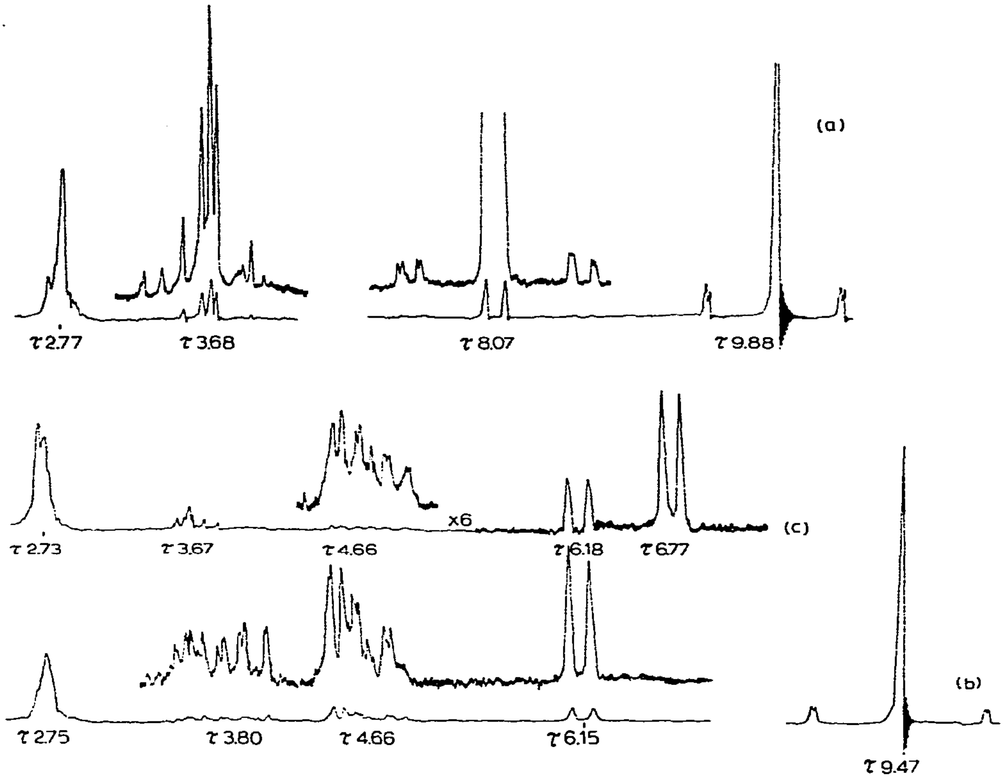


Fig. 2. (a). 60 MHz spectrum of cinnamyltrimethyltin, showing ^{119}Sn satellites about the CH_3–Sn and CH_2–Sn resonances. (b). Spectrum of the rearranged insertion product having the 1-phenylallyl structure. (c). Spectrum of the insertion product, showing its isomerisation from the 1-phenylallyl to the primary cinnamyl structure. The resonance at τ 6.18 assigned to S(O)–CH–C of $(CH_3)_3Sn$–OS(O)–$CH(C_6H_5)$–$CH{=}CH_2$ diminishes in intensity as the signal ascribable to S(O)–CH_2–C of $(CH_3)_3Sn$–O–S(O)–CH_2–$CH{=}CH$–C_6H_5 emerges. Appropriate changes are also occurring in the vinyl region of the spectrum.

These observations on cinnamyl systems* are of importance in relation to reports by Wojcicki[10], who observed that rearrangement accompanied SO_2 insertion into certain 2-butenyl–transition metal systems, but concluded rearrangement did not occur with the corresponding cinnamyl systems. We consider that very facile rearrangement of the kinetic controlled 1-phenylallyl insertion product to the (primary) cinnamyl structure is a superior explanation, being in line with our data, and with elementary mechanistic considerations.

Allenylic–2-propynylic rearrangements

1,2-Propadienyltrimethyltin (Fig. 3), essentially free of its acetylenic isomer (2-propynyltrimethyltin) reacts rapidly with gaseous SO_2 to yield a product having the PMR spectrum in Fig. 3. No satellites are present about the two proton doublet at τ 6.88 ppm nor the one-proton triplet at τ 7.69 ppm. These resonances positions

---

* Wojcicki and Downs[14] have studied a number of isomeric cinnamylsulfinate mixtures, and they interpret some data in terms of two different and simultaneous insertion pathways, only one yielding rearrangement. See also ref. 13.

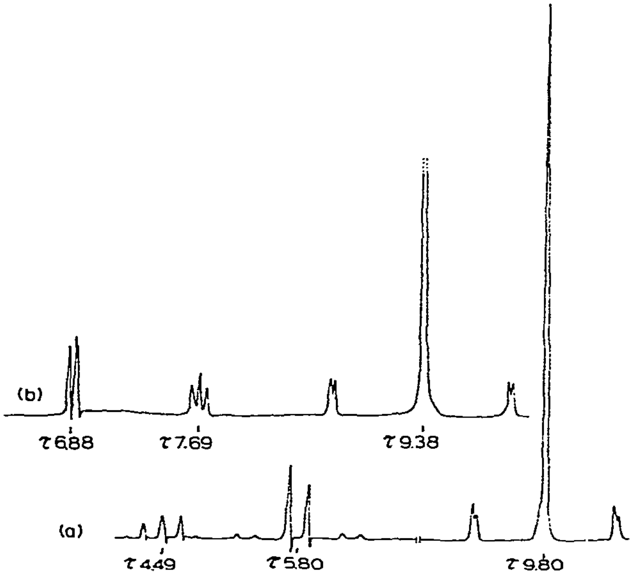
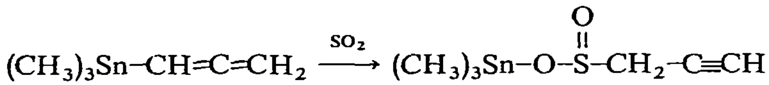


Fig. 3. (a). 60 MHz spectrum of $(CH_3)_3Sn{-}CH{=}C{=}CH_2$ ($CDCl_3$, TMS). Resonances have the τ values indicated. ^{119}Sn and ^{117}Sn satellites are visible about the main resonances. (b). 60 MHz spectrum of $(CH_3)_3Sn{-}O{-}S(O){-}CH_2{-}C{\equiv}CH$ ($CDCl_3$, TMS). Resonances have τ values shown, and satellites occur only about the $(CH_3)_3Sn$ resonances.

and multiplicities are wholly in accord with the acetylenic structure below (see Table 2 for details):



$$(CH_3)_3Sn{-}CH{=}C{=}CH_2 \xrightarrow{SO_2} (CH_3)_3Sn{-}O{-}\overset{\overset{O}{\|}}{S}{-}CH_2{-}C{\equiv}CH$$

In addition, no allene absorption [ν(C=C=C)] was present in the IR spectrum of the

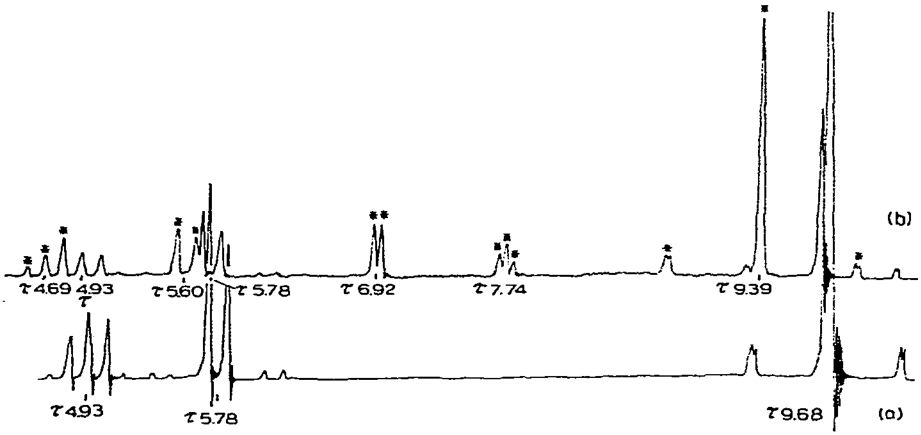
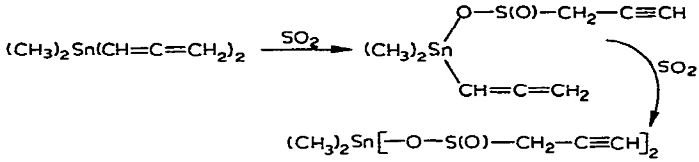


Fig. 4. (a). 60 MHz spectrum of $(CH_3)_2Sn(CH{=}C{=}CH_2)_2$. (b). Spectrum after *ca.* 60% reaction leading to $(CH_3)_2Sn(CH{=}C{=}CH_2){-}O{-}S(O){-}CH_2{-}C{\equiv}CH$, signals due to which are asterisked. There is a small downfield shift of the $CH_3{-}Sn$ resonance of the starting compound in (b) compared with (a).

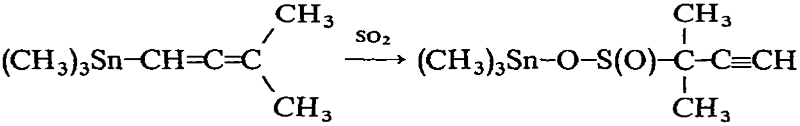
product but the chracteristically strong band for $\nu(\equiv C{-}H)$ at 3275 cm^{-1} was evident. Monitoring the reaction by PMR was possible, and no intermediate signals assignable to $(CH_3)_3Sn{-}O{-}S(O){-}CH{=}C{=}CH_2$ were visible, and rearrangement again seems a result of the insertion mechanism.

Di-1,2-propadienyldimethyltin is of interest since it is possible to observe (via PMR) the stepwise insertion of SO_2 (Fig. 4). At early reaction times, signals appear ascribable to the monoinsertion product, but further insertion occurs to yield the diinsertion product actually isolated and fully characterised.



Rearrangement accompanies both acts of insertion, and $\nu(\equiv C{-}H)$ appears at 3270 cm^{-1} in the final product. Crude rate comparisons indicated the second act (after allowing for the statistical factor) to proceed more slowly than the first, in line with our mechanistic ideas. No product isomerisation (*i.e.* 2-propynyl→allenyl) was noticed.

(3-Methyl-1,2-butadienyl)trimethyltin was synthesized and its 60 MHz PMR spectrum is reproduced in Fig. 5 and is of considerable interest. In addition to a long range $^1H{-}^1H$ coupling ($J \sim 3.5$ Hz) between CH_3 and CH (formally traversing five bonds) and giving a septuplet pattern for CH), long range ^{119}Sn coupling to the CH_3 groups is also evident ($J^1 = 24$ Hz) quite comparable with that for the methine proton ($J^1 \sim 34.5$ Hz) although the latter involves only two bonds. The unique electronic system in allenes apparently accounts for these strong coupling mechanisms. The product of insertion is clearly the rearranged acetylene, (Fig. 5) since a six proton singlet (two equivalent CH_3) (τ 8.80 ppm) and a one proton singlet ($\equiv$CH) (τ 7.66 ppm) are observed ($^1H{-}^1H$ coupling is reduced in acetylenes). IR spectra [$\nu(\equiv C{-}H)$ 3280 cm^{-1}] are in agreement.



$$(CH_3)_3Sn{-}CH{=}C{=}C\begin{matrix}{}^{\diagup CH_3}\\{}_{\diagdown CH_3}\end{matrix} \xrightarrow{SO_2} (CH_3)_3Sn{-}O{-}S(O){-}\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}{-}C{\equiv}CH$$

Reaction of triphenyltin chloride with the Grignard reagent from 2-propynyl bromide yields, after work-up, quite predominantly the 2-propynyl isomer, but some 1,2-propadienyl isomer persists, based on IR data [$\nu(C{=}C{=}C)$ 1930 cm^{-1}], but scarcely observable in the routine PMR spectrum. Reaction of this compound with SO_2 in $CDCl_3$ is conveniently followed by PMR and the spectrum shows the following to be occurring [$\nu(C{=}C{=}C)$ 1935 cm^{-1} for the product]:

$$(C_6H_5)_3Sn{-}CH_2{-}C{\equiv}CH \xrightarrow{SO_2} (C_6H_5)_3Sn{-}O{-}S(O){-}CH{=}C{=}CH_2$$

The isomer $(C_6H_5)_3Sn{-}CH{=}C{=}CH_2$ became available by our observation

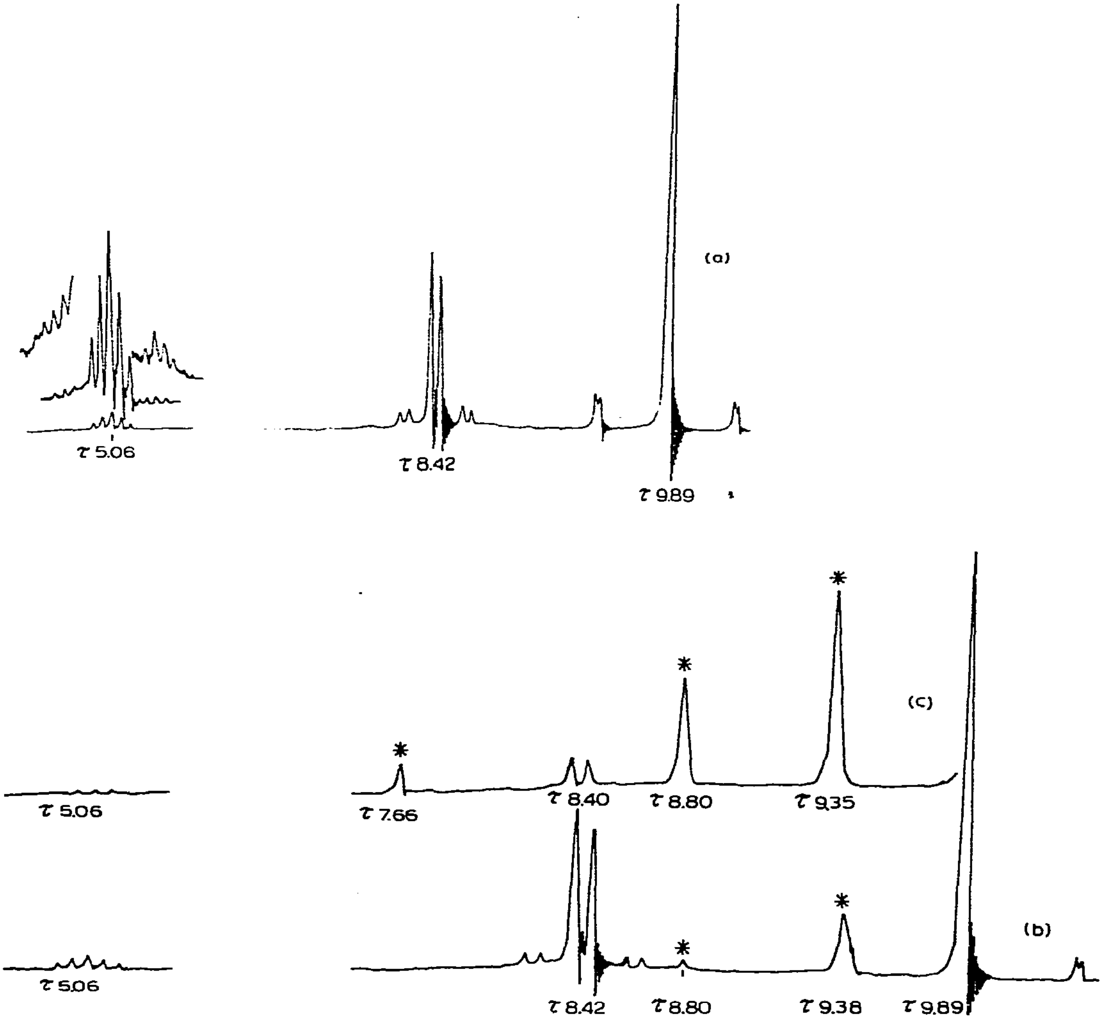


Fig. 5. (a). Spectrum of (3-methyl-1,2-butadienyl)trimethyltin, showing resonance values and Sn–H coupling. (b). Spectrum after partial reaction showing emerging signals for the rearranged acetylene insertion product. (c). Spectrum at virtual completion of the reaction. Products are asterisked in both (b) and (c).

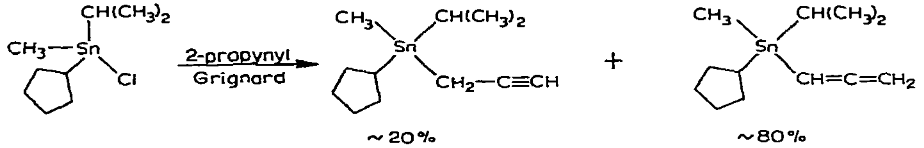
(in connection with other work), that isomerisation in a $CDCl_3/CD_3COOD$ mixture occurred faster than acid cleavage. Details of the PMR data are in Table 2, *i.e.*:

$$(C_6H_5)_3Sn\text{–}CH_2\text{–}C{\equiv}CH \rightarrow (C_6H_5)_3Sn\text{–}CH{=}C{=}CH_2$$

Direct reaction of the $CDCl_3/CD_3COOD$ solution of the above allene with SO_2 was observed to yield the acetylenic insertion product, characterised completely [$\nu(\equiv C\text{–}H)$ 3275 cm^{-1}].

$$(C_6H_5)_3Sn\text{–}CH{=}C{=}CH_2 \xrightarrow{SO_2} (C_6H_5)_3Sn\text{–}O\text{–}S(O)\text{–}CH_2\text{–}C{\equiv}CH$$

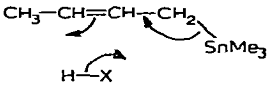
In connection with our interest in the magnetic effects of asymmetric (tetrahedral) metal centers on adjacent methylene protons, we had cause to react cyclopentylmethylisopropyltin chloride with 2-propynyl Grignard reagent, yielding the isomeric mixture below (PMR and IR spectra).



The mass spectrum of this mixture showed a molecular ion (*m/e* 286), with peaks corresponding to $(M^{+\cdot}-15)$, $(M^{+\cdot}-43)$, $(M^{+\cdot}-39)$ and $(M^{+\cdot}-69)$ *i.e.* the attached organic groups. Reaction with SO_2 was facile and insertion occurred into the allenyl and acetylenic C–Sn bonds (loss of satellites) yielding the acetylenic and allenylic insertion products respectively (Table 2 for details). IR spectra in the C=C=C (1923 cm^{-1}) and ≡C–H (3300 cm^{-1}) regions were confirmatory.

The above examples (eleven in all) demonstrate clearly that SO_2 insertion into allylic, allenylic and acetylenic tin systems is accompanied by rearrangement of these groups to the alternative allylic, acetylenic and allenylic structures respectively.

Authentic electrophilic cleavage[11] of suitable allylic groups from tin is definitely accompanied by allylic rearrangement, since in the 2-butenyl case, the less thermodynamically stable butene isomer (1-butene) is produced, and the mechanism S_Ei^1 appears appropriate. (No fine details are implied by this and subsequent portraits).



In the allene case however, the situation for protic cleavage does not appear to be straightforward, since Kuivila[12] has reported that allene and acetylene products are formed in comparable amounts.* The fact is however, that

$$(CH_3)_3Sn{-}CR{=}C{=}CHR' \xrightarrow{HX} (CH_3)_3SnX + CHR{=}C{=}CHR' + RC{\equiv}C{-}CH_2R'$$

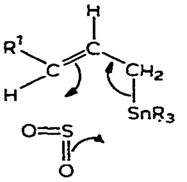
a rearrangement cleavage mechanism (S'_E) competes quite well with its more ordinary counterpart (S_E).

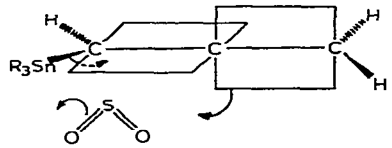
The rearrangement outlined in this report are in accord with expectations for S'_Ei descriptions of the processes. The greatly enhanced rates for insertion into allylic, allenylic carbon–tin systems are in line with results for electrophilic cleavage in such organometal systems generally, and mechanisms of the following types are probably applicable. The reason(s) for the essentially complete absence of an S_E component of the insertion into allene–tin systems is not clear.

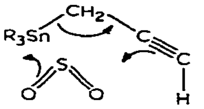
The actual order in SO_2 in the kinetic expression may be higher than one due

---

* Observations in this laboratory indicate that post-kinetic equilibration of the isomers may be troublesome under some conditions.







to donor–acceptor interactions with metal or unsaturated centers.

In subsequent reports we shall outline the steriochemical and kinetic dependences of these insertion processes.

ACKNOWLEDGEMENTS

We are grateful to Professors D. Seyferth, H. G. Kuivila and M. Gielen for information relating to synthesis of some organotin compounds, and to Dr. D. Doddrell for some NMR spectra. This research was supported in part by grants (Grant Number – A.R.G.C.-23) from the Australian Research Grants Committee. We acknowledge informative discussions with Dr. G. Deacon on aspects of some IR spectra.

REFERENCES

1 C. W. Fong and W. Kitching, *J. Organometal. Chem.*, 22 (1970) 95.
2 C. W. Fong and W. Kitching, *J. Organometal. Chem.*, in press.
3 W. Kitching, C. W. Fong and A. J. Smith, *J. Amer. Chem. Soc.*, 91 (1969) 767.
4 M. Le Quan and P. Cadiot, *Bull. Soc. Chim. Fr.*, (1965) 45.
5 A. M. Sladkov and L. K. Luneva, *Zh. Obshch. Khim.*, 36 (1966) 533.
6 S. Boué, M. Gielen and J. Nasielski, *Tetrahedron Lett.*, (1968) 1047.
7 T. L. Jacobs and W. L. Petty, *J. Org. Chem.*, 28 (1963) 1360.
8 J. A. Verdone, Ph.D. Thesis, University of New Hampshire (1963).
9 R. M. G. Roberts and F. El Kaissi, *J. Organometal. Chem.*, 12 (1968) 79.
10 F. A. Hartman and A. Wojcicki, *Inorg. Chim. Acta*, 2 (1968) 289; R. L. Downs, *Dissertation Abstracts*, 29 (1969) 1593-B.
11 H. G. Kuivila and J. A. Verdone, *Tetrahedron Lett.*, (1964) 119.
12 H. G. Kuivila and J. C. Cochran, *J. Amer. Chem. Soc.*, 89 (1967) 7152.
13 C. W. Fong and W. Kitching, *Organometal. Chem. Rev.*, in press.
14 R. L. Downs, Ph.D. Thesis, Ohio State University.