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Addition of stannyl phosphines to alkynes and allenes

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Abstract

Diphenyl(trimethylstannyl)phosphine adds to alkynes (both terminal and non-terminal) and allenes under free radical conditions. The former reaction occurs regiospecifically with preferential formation of *E*-isomers, the latter regioselectively. Product identification was based on NMR spectroscopic data. With one exception, addition to alkenes was not observed.

Introduction

Trialkylstannylphosphines of the type $R_3SnPR'_2$ have been known for 30 years [1], and a number of methods for their preparation have been reported [2–7]. Their chemistry has, however, remained almost totally unstudied. Some years ago, Schumann presented preliminary reports of reactions involving addition to alkenes and alkynes [18], but no structural proof was given for the proposed product structures. Recently, Stille [9] reported the use of Me_3SnPPh_2 in palladium-catalysed substitution reactions with aryl bromides to give unsymmetrical triarylphosphines. Our interest in additions of organotin compounds to alkynes and allenes prompted us to look more closely into reactions of the type studied by Schumann, and we present our detailed results below. A preliminary communication has appeared [10].

Results and discussion

(a) Reactions with alkenes

Schumann [8] obtained an adduct between Ph_3SnPPh_2 and styrene in 67% yield. In contrast, Me_3SnPPh_2 causes styrene to polymerise under our reaction conditions. No reaction is observed with cycloheptene, the stannyl phosphine undergoing decomposition to give Me_6Sn_2 and Ph_4P_2. The same behaviour is observed when trimethylvinylgermane is treated with Me_3SnPPh_2; however, trimethylvinyltin undergoes rapid regioselective addition to give β-[bis(trimethylstannyl)ethyl]diphenylphosphine in 80% yield.

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$$\mathrm{Me_3SnPPh_2 + Me_3SnCH{=}CH_2 \longrightarrow (Me_3Sn)_2CHCH_2PPh_2}$$

While Ph_3SnPPh_2 is reported to add to the double bond of allyl chloride [8], the latter reacts with Me_3SnPPh_2 under the influence of UV light to give trimethyltin chloride and allyldiphenyltin; the reaction with allyl bromide is exothermic at room temperature and gives analogous products.

$$\mathrm{Me_3SnPPh_2 + CH_2{=}CH{-}CH_2X \longrightarrow Me_3SnX + CH_2{=}CH{-}CH_2PPh_2}$$

$$\mathrm{(X = Cl, Br)}$$

(b) Addition to terminal alkynes

Ph_3SnPPh_2 was reported to add to phenylacetylene with the formation of two regioisomeric products which could not be separated [8]; the reaction was accelerated by addition of AIBN, and was therefore assumed to be a free radical chain process. Et_3GePEt_2, in contrast, affords all four possible isomeric adducts [11].

$$\mathrm{Ph_3SnPPh_2 + PhC{\equiv}CH \longrightarrow Ph_3SnCPh{=}CHPPh_2 + Ph_3SnCH{=}C(Ph)PPh_2}$$

$$\mathrm{Et_3GePEt_2 + PhC{\equiv}CH \longrightarrow}$$

$$Z/E\text{-}\mathrm{PhC(PEt_2){=}CHGeEt_3} + Z/E\text{-}\mathrm{PhC(GeEt_3){=}CHPEt_2}$$

$$(65\%) \qquad\qquad (28\%)$$

We observed that this alkyne reacts with Me_3SnPPh_2 under photolytic conditions to give two stereoisomers in a ratio of 10/1, the *E*-isomer predominating:

$$\mathrm{Me_3SnPPh_2 + PhC{\equiv}CH \longrightarrow} Z/E\text{-}\mathrm{Me_3SnCH{=}C(Ph)PPh_2}$$

A number of other 1-alkynes react in a similar manner (Table 1), almost no by-products being observed: the major product is the *E*-isomer, and studies with butyl- and phenyl-acetylene show that this is the kinetic product. It undergoes isomerisation to the *Z*-isomer in the presence of Me_3SnPPh_2 when heated at 80 °C. Attempts to carry out the reaction at this temperature in the presence of AIBN resulted in establishment of the following equilibrium:

$$\mathrm{Me_3SnPPh_2 + PhC{\equiv}CH \longrightarrow Me_3SnC{\equiv}CPh + Ph_2PH}$$

A complex series of reactions follow [12], so that the required adduct is formed in only small amounts.

Table 1

Yields, isomer ratios and boiling points of adducts from Me_3SnPPh_2 and terminal alkynes $RC{\equiv}CH$

R	Yield [a]	Z/E	B.p. (°C/mmHg)
Ph	59	10/90 [b]	125–128/0.001
$MeOCH_2CH_2$	30	40/60	145–148/0.05
Et_2NCH_2	59	20/80	155–167/0.001
Bu	82	38/62 [c]	137–139/0.005
$PhCH_2$	16	50/50	181–184/0.005

[a] Under irradiation conditions. [b] After 2 days (100% reactants consumed). After 12 days $Z/E = 42/58$. [c] After 5 min 12% reactants consumed, Z/E 14/86, after 2 h 78% consumed, $Z/E = 37/63$, after 9 h 95% consumed, $Z/E = 38/62$.

Only in the case of trimethylstannylethyne is a 1/1 mixture of two regioisomers observed:

$$\mathrm{Me_3SnPPh_2 + Me_3SnC{\equiv}CH} \longrightarrow$$

$$\underset{\textbf{(A)}}{\mathrm{(Me_3Sn)_2C{=}CHPPh_2}} + \underset{\textbf{(B)}}{E\text{-}\mathrm{Me_3SnCH{=}C(PPh_2)SnMe_3}}$$

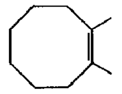
The former is also obtained (as the sole product) from the hydrostannation of $\mathrm{Me_3SnC{=}CPPh_2}$. Its formation in the above reaction is not due to photolytic isomerisation of the latter: on photolysis of the product mixture **A** remains unchanged and **B** decomposes to give a series of unidentified products. The results presented above indicate that the addition of $\mathrm{Me_3SnPPh_2}$ to 1-alkynes does not occur via a cyclic 4-membered transition state (as for hydroboration) but via a free radical chain mechanism involving primary addition of a trimethylstannyl radical (which should be reversible [13]), followed by abstraction of $\mathrm{PPh_2}$ from a molecule of $\mathrm{Me_3SnPPh_2}$. If a phosphoryl radical were the primary attacking species, the opposite regiochemistry would be expected.

(c) Additions to non-terminal alkynes

These were carried out under three sets of conditions: photolytic at room temperature, thermal (80 °C) with AIBN, and thermal in the absence of AIBN and light. The results are presented in Table 2. Cyclooctyne reacts on photolysis to give a single product, which must for geometric reasons be the *Z*-isomer (because of the thermal instability of this alkyne, other conditions were not employed). Diphenylacetylene and the dimethyl ether of but-2-yne-1,4-diol both give a *Z/E* mixture in which the *E*-isomer predominates: the yields are much lower under purely thermal conditions, although the *E/Z* ratio is apparently independent of the conditions. 1-Phenylbutyne is attacked under photolytic conditions in a regiospecific manner:

Table 2

Yields, isomer ratios and boiling points of adducts from $\mathrm{Me_3SnPPh_2}$ and non-terminal alkynes $\mathrm{RC{\equiv}CR}$.

R	R′	Yield $(h\nu)$ [a]	Z/E	Yield (Δ/AIBN) [b]	Z/E	Yield (Δ) [c]	Z/E	B.p. (°C/mmHg)
		42	100/0	[d]		[d]		181/0.005
Ph	Ph [f]	75	0/100	95(78)	0/100	28	0/100	155/0.001
Ph	Et	95(75)	2/98 [g]	[d]		[d]		148–50/0.001
$\mathrm{MeOCH_2}$	$\mathrm{CH_2OMe}$ [f]	61	13/87	47(39)	7/93	15	10/90	147–49/0.001
Ph	CN [j]	[d]		[d]		[d]		m.p. 157
Ph	$\mathrm{CONMe_2}$	88	0/100 [h]	90(6 [h])	42/58	84	42/58	185–95/0.001
Bu	$\mathrm{CONMe_2}$	80	[e]	97(93)	87/13	98	87/13	m.p. 79–82
$\mathrm{Me_2NCH_2}$	$\mathrm{CONMe_2}$	66	25/75	97(81)	27/73	[d]		m.p. 105–107

[a] Yields calculated from NMR spectra (isolated yields in brackets). [b] 80 °C, AIBN added. [c] 80 °C, in the dark, AIBN absent. [d] Not carried out. [e] 4 isomers (see text). [f] Reaction time in each case 16 h. [g] *Z/E* ratio at 100% consumption as follows: 6 h 2/95, 18 h 19/81, 30 d 49/51. [h] Reaction time, consumption and *Z/E* ratio as follows: 0.5 h, 43%, 0/100; 1.5 h, 65%, 6/94; 3 h, 81%, 17/83; 8h, 100%, 40/60. [i] Decomposed on attempted distillation. [j] Exothermic reaction (at 0 °C), $Z/E = 36/64$.

the *E*-isomer is the primary product, but undergoes partial isomerisation to the *Z*-isomer on further irradiation.

1-Cyano-2-phenylethyne reacts exothermically at 0 °C in a regiospecific manner to give an *E/Z* mixture (1/2) in what must be a polar reaction.

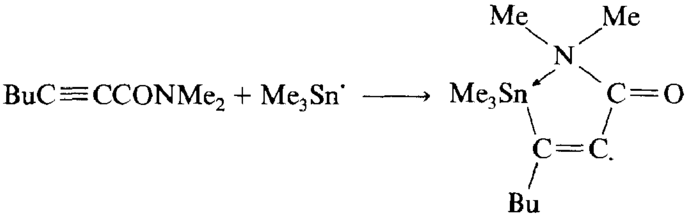
$$\mathrm{PhC{\equiv}CCN + Me_3SnPPh_2 \longrightarrow Me_3SnC(CN){=}C(Ph)PPh_2}$$

Two amides $\mathrm{RC{\equiv}CCONMe_2}$ (R = Ph, Bu) were also used: in these cases yields were equally good under all conditions employed. With one exception, only *Z/E* mixtures of one regioisomer were observed; however, photolytic reaction in the case where R = Bu gave a mixture of all four possible isomers:

$$\mathrm{BuC{\equiv}CCONMe_2 + Me_3SnPPh_2 \longrightarrow}$$
$$\mathrm{Me_3SnC(CONMe_2){=}C(Bu)PPh_2 + Me_3SnC(Bu){=}C(CONMe_2)PPh_2}$$

71%; *Z/E* 77/23 29%; *Z/E* 4/96

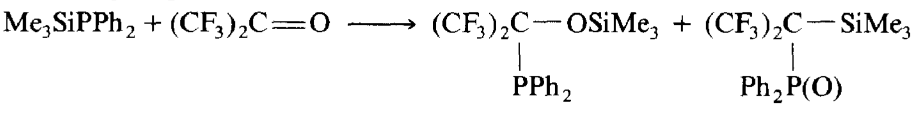
This experiment is thus unusual in two respects: firstly the predominance of the *Z* stereoisomer in the major regioisomer (for R = Ph the primary product is the *E*-isomer in the photolytic experiment, the mixture obtained in the thermal experiments probably corresponding to the situation at thermal equilibrium), and secondly the presence of a second major reaction path. The latter could involve attack of the stannyl radical on the carbon atom bearing the butyl group to give an intermediate radical stabilised by intramolecular coordination: this would account for the virtually completely stereospecific formation of the *E*-isomer:



Unusual behaviour was also shown by 1,3-diphenylpropyne-3-one, which afforded a 1-stannyl-3-diphenylphosphinoxyallene:

$$\mathrm{Me_3SnPPh_2 + PhC{\equiv}C{-}COPh \longrightarrow Me_3Sn(Ph)C{=}C{=}C(Ph)P(O)Ph_2}$$

This reaction has a certain similarity to that reported by Abel [14], who on treating hexafluoroacetone with $\mathrm{Me_3SiPPh_2}$ obtained a mixture of a silyl ether and the isomeric phosphine oxide:

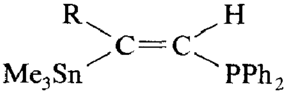


$$\mathrm{Me_3SiPPh_2 + (CF_3)_2C{=}O \longrightarrow \underset{\displaystyle PPh_2}{(CF_3)_2C{-}OSiMe_3} + \underset{\displaystyle Ph_2P(O)}{(CF_3)_2C{-}SiMe_3}}$$

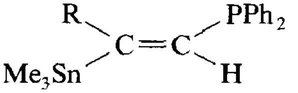
In our case the reaction could involve a similar 1,2-addition followed by two rearrangement steps (stannyl ether → phosphine oxide and propargyltin → allenyltin).

(d) Identification of adducts between Me_3SnPPh_2 and alkynes

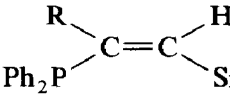
In the case of 1-alkynes four adducts are theoretically possible:



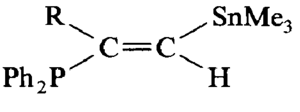
(I)



(II)



(III)



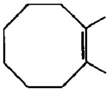
(IV)

I can be eliminated at once, since it would require a value of $J(\mathrm{Sn,H_{vin}})$ above 120 Hz, whereas the actual value is near 80 Hz. The observed isomerisation of the primary product to a secondary product makes it almost certain, however, that we obtained either a mixture of I and II or a mixture of III and IV. Elimination of I as a possible product leads us to propose that III and IV are formed: this hypothesis is consistent with the invariance of $J(\mathrm{Sn,H_{vin}})$ on isomerisation.

The vinyl proton also couples with phosphorus, the coupling in one isomer being ca. 11–15 Hz and in the second ca. 60 Hz; in the first isomer $J(\mathrm{H_{vin},C_R})$ is larger (ca. 11 Hz) than in the second (ca. 7 Hz); and in the first $^3J(\mathrm{Sn,P})$ is smaller (38–61

Table 3

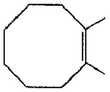
Tin-119 and phosphorus-31 chemical shifts and tin-phosphorus coupling constants for compounds of the type $\mathrm{RC(PPh_2){=}C(R')SnMe_3}$ (δ-values in ppm w.r.t. internal $\mathrm{Me_4Sn}$ or external 85% $\mathrm{H_3PO_4}$ respectively, J in Hz, average value from Sn and P spectra).

R	R′	E/Z	$\delta(^{119}\mathrm{Sn})$	$\delta(^{31}\mathrm{P})$	$^3J(\mathrm{SnC{=}CP})$
H	H[a]	*E*	−38.7	−3.9	130.3
H	H[a]	*Z*	−54.7	−10.8	85.2
Ph	H	*E*	−52.1	9.4	38.2
Ph	H	*Z*	−65.0	8.5	84.5
Bu	H	*E*	−60.3	4.3	56.9
Bu	H	*Z*	−65.6	7.4	99.6
$\mathrm{PhCH_2}$	H	*E*	−57.1	4.7	48.4
$\mathrm{PhCH_2}$	H	*Z*	−61.5	5.9	101.7
$\mathrm{Et_2NCH_2}$	H	*E*	−65.6	5.0	52.9
$\mathrm{Et_2NCH_2}$	H	*Z*	−61.9	2.0	103.7
$\mathrm{MeOCH_2CH_2}$	H	*E*	−58.6	5.3	61.0
$\mathrm{MeOCH_2CH_2}$	H	*Z*	−65.8	6.9	99.6
		*Z*	−59.9	12.2	63.8
Ph	Ph	*E*	−39.7	−3.6	68.5
Ph	Et	*E*	−46.7	−8.0	69.3
Ph	Et	*Z*	−57.9	14.6	46.6
$\mathrm{MeOCH_2}$	$\mathrm{MeOCH_2}$	*E*	−51.5	−14.1	74.5
$\mathrm{MeOCH_2}$	$\mathrm{MeOCH_2}$	*Z*	−52.4	8.3	78.1
Ph	CN	*E*	−12.5	10.5	27.8
Ph	CN	*Z*	−28.1	13.1	27.8
Ph	$\mathrm{CONMe_2}$	*E*	−33.5	4.5	115.8
Ph	$\mathrm{CONMe_2}$	*Z*	−45.5	13.3	54.8
Bu	$\mathrm{CONMe_2}$	*E*	−39.1	−0.6	132.4
Bu	$\mathrm{CONMe_2}$	*Z*	−49.6	9.8	66.8
$\mathrm{CONMe_2}$	Bu	*E*	−40.8	−19.0	52.6
$\mathrm{CONMe_2}$	Bu	*Z*	−62.3	28.0	50.5
$\mathrm{Me_2NCH_2}$	$\mathrm{CONMe_2}$	*E*	−46.7	1.4	53.1
$\mathrm{Me_2NCH_2}$	$\mathrm{CONMe_2}$	*Z*	−68.5	10.0	67.3

[a] Obtained by hydrostannation of $\mathrm{Ph_2PC{\equiv}CH}$ with $\mathrm{Me_3SnH}$

Table 4

Selected phosphorus-carbon coupling constants for compounds of the type $RC^2(PPh_2)=C^1(R')SnMe_3$

R	R′	E/Z	$^1J(PC^2)$	$^2J(PC^1)$	$^4J(PC=CSnC)$	$^2J(PC_R)$
H	H [a]	E	25.1	8.9	[b]	
H	H [a]	Z	3.0	63.2	7.6	
Ph	H	E	26.0	2.9	<1	22.8
Ph	H	Z	[b]	77.6	8.2	[a]
Bu	H	E	25.4	1.5	<1	26.7
Bu	H	Z	8.9	76.3	8.9	<1
$PhCH_2$	H	E	25.4	1.3	<1	27.9
$PhCH_2$	H	Z	10.1	73.8	8.9	<1
Et_2NCH_2	H	E	22.8	1.3	<1	26.7
Et_2NCH_2	H	Z	8.9	71.3	8.9	<1
$MeO(CH_2)_2$	H	E	25.4	1.5	<1	26.7
$MeO(CH_2)_2$	H	Z	[c]	75.0	8.9	<1
		Z	1.2	78.8	13.9	[b]
Ph	Ph	E	30.5	25.4	<1	<1
Ph	Et	E	29.2	21.6	<1	<1
Ph	Et	Z	6.3	80.1	12.7	<1
$MeOCH_2$	$MeOCH_2$	E	27.9	13.9	<1	<
$MeOCH_2$	$MeOCH_2$	Z	6.3	72.4	17.7	<1
Ph	CN	E	39.4	14.1	<1	<1
Ph	CN	Z	16.5	69.6	10.1	2.5
Ph	$CONMe_2$	E	33.0	27.9	<1	<1
Ph	$CONMe_2$	Z	12.7	80.1	11.4	<1
Bu	$CONMe_2$	E	30.5	23.4	<1	<1
Bu	$CONMe_2$	Z	7.6	78.8	11.4	<1
$CONMe_2$	Bu	E	30.5	15.2	<1	<1
$CONME_2$	Bu	Z	[b]	[b]	11.4	<1
Me_2NCH_2	$CONMe_2$	E	25.4	27.9	<1	<1
Me_2NCH_2	$CONMe_2$	Z	7.6	77.5	12.7	<1

[a] Obtained by hydrostannation of $Ph_2PC{\equiv}CH$ with Me_3SnH. [b] Not observed. [c] Hidden.

Hz) than in the second (84–104 Hz; the complete data are given in Tables 3–5). The first isomer must be IV in which Sn and P are *trans*, since $^3J_{trans}(H_{vin},C_R)$ will be larger than $^3J_{cis}(H_{vin},C_R)$; thus $^3J_{trans}(Sn,P)$ is smaller than $^3J_{cis}(Sn,P)$.

Table 5

Three-bond carbon-proton and proton-phosphorus coupling constants for compounds of the type $RC(PPh_2)=CHSnMe_3$ (in Hz)

R	E/Z	$^3J(HC=C-C_R)$ [a]	$^3J(HC=C-CP)$
Bu	E	[a]	14.0
Bu	Z	[a]	62.9
$PhCH_2$	E	11.4	12.6
$PhCH_2$	Z	6.9	61.8
$MeOCH_2CH_2$	E	10.8	13.9
$MeOCH_2CH_2$	Z	6.3	61.7

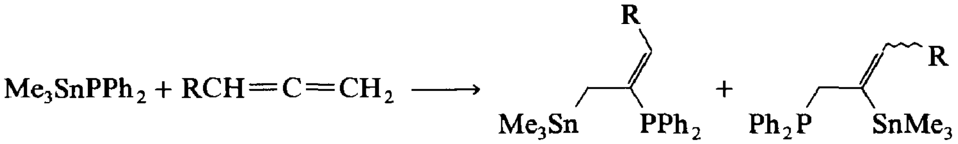
[a] Values obtained from decoupling experiments. [b] Not measured.

On the basis of these assignments, further empirical correlations become available which can be used for the products of addition to non-terminal alkynes where no vinylic proton is present: $^1J(\mathrm{P{-}C_{vin}})$: *Z*-isomer 9–10 Hz, *E*-isomer 23–26 Hz; $^2J(\mathrm{P,C_{vin}})$: *Z*-isomer 71–78 Hz, *E*-isomer 1–3 Hz; $^4J(\mathrm{PC{=}CSnC})$: *Z*-isomer 8–9 Hz, *E*-isomer < 1 Hz; $^2J(\mathrm{P,C_R})$: *Z*-isomer < 1 Hz, *E*-isomer 23–28 Hz.

In the terminal alkynes, $^2J(\mathrm{P,CR})$ is not visible in either isomer, but the other three correlations can be applied, the ranges being as follows: $^1J(\mathrm{P{-}C_{vin}})$: *Z*-isomer 1–16 Hz, *E*-isomer 25–40 Hz; $^2J(\mathrm{P,C_{vin}})$: *Z*-isomer 70–80 Hz, *E*-isomer 9–28 Hz; $^4J(\mathrm{PC{=}CSnC})$: *Z*-isomer 10–18 Hz, *E*-isomer < 1 Hz.

(e) Addition to allenes

Under photolytic conditions, $\mathrm{Me_3SnPPh_2}$ adds to allene and several monosubstituted allenes (Table 6) to give a mixture consisting mainly of two regioisomeric products; that in which the phosphine is attached to the central carbon atom predominates:



(A) **(B)**

NMR examination (Table 7) shows that the major product (**A**) is present only in the *E*-form; because of the low abundance of (**B**), its exact geometry could not be determined. In the case of allene itself, hexamethylditin is formed as well as by-products which are formally those of addition to allene of $\mathrm{Ph_4P_2}$ and $\mathrm{Me_6Sn_2}$. We were able, however, to show that the latter are however not formed in free-radical additions of these species but by subsequent reaction of $\mathrm{Me_3SnPPh_2}$ with **A** and/or **B**. $\mathrm{Me_6Sn_2}$ and bis(diphenylphosphino)propene are also formed as by-products in the reactions with methyl- and butyl-allene. Phenylallene does not react under photolytic conditions, presumably because it is the phenyl group that undergoes excitation. The ditin/cyanoallene adduct decomposes on attempted distillation, while the other adducts can be distilled without decomposition.

Neither 1,1- nor 1,3-dimethylallene undergo addition reactions with $\mathrm{Me_3SnPPh_2}$.

Table 6

Yields and boiling points of adducts formed from $\mathrm{Me_3SnPPh_2}$ and the allenes $\mathrm{RCH{=}C{=}CH_2}$

R	Reaction Conditions	Isolated yield (%)	Ratio **A**/**B** [a]	B.p. (°C/mmHg)
H	*hν*/8 h	78	94/6	165–70/0.15
Me	*hν*/16 h	68	78/28	147–49/0.001
Bu	*hν*/16 h	58	88/12	150–53/0.001
Ph	80 °C/4 h [b]	83	99/1	178–80/0.001
CN	0 °C/0.5 h [c]	71 [d]	99/1	[e]

[a] For isomer definition see text. [b] 20% reaction after UV-irradiation for 3 days. [c] exothermic reaction. [d] NMR yield. [e] Decomposes on attempted distillation at 0.001 mmHg.

Table 7

Selected NMR data for adducts between Me_3SnPPh_2 and allenes $RCH{=}C{=}CH_2$

R	Isomer	$\delta(^{119}Sn)$	$\delta(^{31}P)$	$^3J(Sn,P)$	$^3J(HC{=}CC)$
H	**A**	−3.0	−1.4	10.1	10.1(t), 6.3(c)
H	**B**	−34.0	−19.6	22.3	[a]
Me	**A**	−1.7	4.3	4.0	[a]
Me	**B**	−30.6	−18.2	23.0	[a]
Bu	**A**	−2.5	5.0	4.4	10.1
Bu	**B**	−30.5	−17.7	22.3	[a]
Ph	**A**	−0.9	6.8	7.6	10.1
CN	**A**	20.7	0.8	11.8	9.5

[a] Not observed.

Experimental

All experimental manipulations involving organotin compounds were carried out under argon. Me_3SnPPh_2 was prepared by a published procedure [2]. New compounds were characterised by elemental analysis and by multinuclear NMR spectroscopy (^1H, ^{13}C, ^{31}P, ^{119}Sn); here we report only those data which are required to characterise the substances, in particular the ^{31}P and ^{119}Sn data. Spectra were recorded with a Bruker AM-300 spectrometer operating at 300 MHz for ^1H and 59.60 MHz for ^{29}Si (standard: internal TMS), 111.93 MHz (for ^{119}Sn (standard: internal Me_4Sn) and 121.50 MHz for ^{31}P (standard: external 85% H_3PO_4).

The following general procedures were used for reactions of Me_3SnPPh_2:

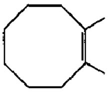
(a) Reactions under photolytic conditions. A mixture of Me_3SnPPh_2 (11 mmol, 3.84 g) and an equimolar amount of the alkyne or allene in a quartz tube was irradiated for 2–4 days at room temperature (or in the case of the alkynes at 0 ° C in an ice-water bath to check the temperature-dependence of the E/Z ratio) using a TQ 150 high pressure mercury lamp (Heraeus, Hanau). The reactions were monitored by ^1H NMR spectroscopy. When addition was complete the products were vacuum-distilled in a semi-micro apparatus. In the case of allene itself, the procedure was as follows: Me_3SnPPh_2 (20 mmol, 6.98 g) was placed in a quartz tube and irradiated for 8 h; during this time, gaseous allene was bubbled slowly through the liquid. Alkenes were irradiated on a smaller scale (ca. 1 g Me_3SnPPh_2, in each case with an equimolar amount of the alkene) in NMR tubes, again for 2–4 d. Product yields were obtained from the integrated ^1H NMR spectra.

The following alkenes were used: styrene (polymerisation and decomposition of Me_3SnPPh_2), 3,3-dimethyl-1-butene, cycloheptene, vinyltrimethylgermane, (decomposition of Me_3SnPPh_2), Z/E-$Me_3SnCH{=}CHSnMe_3$ (decomposition of Me_3SnPPh_2 and complete isomerisation to the E-isomer), vinyltrimethylstannane. In the latter case addition was complete after 6 h, giving $(Me_3Sn)_2CH{-}CH_2PPh_2$. NMR: $\delta(^{119}Sn)$ 22.1, $\delta(^{31}P)$ 11.8 ppm, $^3J(Sn,P)$ 146 Hz; $\delta(CH_3Sn)$ −8.0, $\delta(CHSn)$ 2.0, $\delta(CH_2)$ 30.2; $\delta(CH_3Sn)$ 0.20, $\delta(CH)$ 0.68, $\delta(CH_2)$ 2.58 ppm, $^3J(H,H)$ 8.8, $^3J(P,H)$ 11.4, $^3J(Sn,H)$ 75.0 Hz.

(b) Reactions under thermal conditions. These were carried out at 80 ° C using the same quantities of starting materials in a 2-necked flask fitted with a reflux condenser. As noted in the Discussion, reactions were carried out both with and without the addition of catalytic amounts of AIBN.

Table 8

Elemental analysis data for adducts between Me_3SnPPh_2 and alkynes $RC{\equiv}CR'$

R	R′	Molecular Formula	Analysis(Found(calcd.)(%))	
			C	H
Ph	H	$C_{23}H_{25}PSn$	60.5 (61.2)	5.4 (5.6)
$MeOCH_2CH_2$	H	$C_{20}H_{27}OPSn$	55.1 (55.5)	6.2 (6.3)
Et_2NCH_2	H	$C_{22}H_{32}NPSn$	56.9 (57.4)	7.3 (7.0)
Bu	H	$C_{21}H_{29}PSn$	59.2 (58.5)	5.7 (5.9)
$PhCH_2$	H	$C_{24}H_{27}PSn$	60.9 (61.9)	5.7 (5.9)
		$C_{25}H_{31}PSn$	61.7 (62.4)	6.2 (6.5)
Ph	Ph	$C_{29}H_{29}PSn$	66.2 (66.1)	5.6 (5.6)
Ph	Et	$C_{25}H_{29}PSn$	62.0 (62.6)	6.3 (6.1)
$MeOCH_2$	CH_2OMe	$C_{21}H_{29}O_2PSn$	54.1 (54.5)	6.2 (6.3)
Ph	CN	$C_{24}H_{24}NPSn$	60.6 (60.5)	4.9 (5.0)
Ph	$CONMe_2$	$C_{26}H_{30}NOPSn$	58.5 (59.8)	5.3 (5.8)
Bu	$CONMe_2$	$C_{26}H_{34}NOPSn$	57.9 (57.4)	7.4 (6.8)
Me_2NCH_2	$CONMe_2$	$C_{23}H_{33}N_2OPSn$	55.2 (54.9)	6.8 (6.6)

Yields, boiling points and isomer ratios for the adducts obtained are given in Tables 1,2 and 6, elemental analysis values in Tables 8 and 9 and selected NMR data in Tables 3–5 and 7.

Table 9

Elemental analysis data for adducts between Me_3SnPPh_2 and allenes $RCH{=}C{=}CH_2$

P	Molecular formula	Analysis (Found (calcd.) (%))	
		C	H
H	$C_{18}H_{23}PSn$	55.0 (55.6)	5.7 (6.0)
Me	$C_{19}H_{25}PSn$	56.4 (56.6)	6.1 (6.3)
Bu	$C_{22}H_{31}PSn$	58.7 (59.5)	7.1 (6.8)
Ph	$C_{24}H_{27}PSn$	60.9 (61.9)	6.0 (5.8)

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