α-METALLATED VINYL CARBANIONOIDS

I. FORMATION OF α-STANNYLVINYL ANIONOIDS FROM 1,1-BIS(TRIMETHYLSTANNYL)ALKENES *

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Summary

Hydrostannation of 1-stannyl-1-alkynes leads to the formation of 1,1- and 1,2-distannyl-1-alkenes. The former can undergo lithiation (by alkyllithium in THF) with varying degrees of stereospecificity. 1,1-Dilithio-1-alkenes cannot be prepared by double lithiation. The strongly basic α-stannyl vinyllithiums react with carbon electrophiles, but in some cases cause enolisation or dehydrohalogenation of the substrate. They can be readily converted into the corresponding vinyl Grignard reagents or vinylcopper derivatives.

Introduction

We recently reported in a Preliminary communication [1] that the hydrostannation of 1-stannyl-1-alkynes leads to the formation of 1,1-distannyl-1-alkenes, 1,2-distannyl-1-alkenes being formed as side products, and that the former can be lithiated to give α-stannyl vinyl carbanionoids. We now report in more detail on these reactions, on the stereochemistry of the lithiation reaction, and on routes to other carbanionoids.

Results and discussion

Hydrostannation of 1-trimethylstannyl-1-alkynes

The results of these studies are summarised in Table 1. Two products are formed

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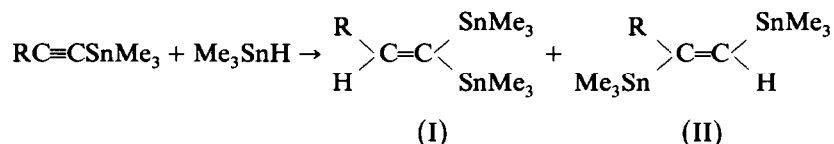* Taken from the doctoral thesis of A. Amamria, Dortmund, 1982.

TABLE 1

DATA ON PRODUCTS OF HYDROSTANNATION OF 1-TRIMETHYLSTANNYL-1-ALKYNES
$RC\equiv CSnMe_3$ with Me_3SnH

R	Yield [b] (%)	B.p. [c] (°C/mmHg)	Ratio I/II [d]	Analytical data (Calcd. (found) (%))	
				C	H
CH_3	55	97/14	97/3	29.40 (28.51)	6.00 (5.58)
n-Bu	71	68/0.08	94/6	35.17 (35.74)	6.84 (7.17)
t-Bu [a]	34	59/0.01	98/2	35.17 (34.18)	6.84 (7.37)
Ph	81	86/0.005	95/5	39.13 (38.98)	5.60 (5.27)
$PhCH_2$	94	95/0.001	91/9	40.60 (40.11)	5.91 (5.72)
$MeOCH_2\cdot$	58	60/0.02	59/41 [e]	30.20 (30.18)	6.08 (6.24)
$PhOCH_2$	57	102/0.03	61/39 [e]	39.18 (38.98)	5.66 (5.82)
PhO	64	90/0.001	95/5	37.72 (36.73)	5.39 (4.66)

[a] Product obtained by UV irradiation of reactants: thermal reaction leads to isomerisation of initial product. [b] After distillation. [c] Refers to mixture. [d] See text. [e] The same ratio was obtained for the bis(triethylstannyl)alkenes.

in this reaction:

$$RC\equiv CSnMe_3 + Me_3SnH \rightarrow \quad {R \atop H}\!\!>\!\!C\!\!=\!\!C\!\!<\!\!{SnMe_3 \atop SnMe_3} \quad + \quad {R \atop Me_3Sn}\!\!>\!\!C\!\!=\!\!C\!\!<\!\!{SnMe_3 \atop H}$$

$$\text{(I)} \qquad\qquad\qquad \text{(II)}$$

These have been characterised in detail by NMR spectroscopy; while the full results of this study will be published elsewhere, the relevant spectral data are given in Tables 2 and 3. The assignment of II as the (E)-isomer follows in particular from the ^{119}Sn spectra: it is known that in (E)-1,2-bis(trimethylstannyl)ethylene the value of $^3J(^{119}Sn-^{119}Sn)$ is 1013 Hz [2], and the measured values of $^3J(Sn-Sn)$ in the present study (see Table 2) confirm the structure of II.

When R = H, only isomer II is formed [3]; when R = SiMe$_3$, GeMe$_3$ or SnMe$_3$ no hydrostannation product is formed, though addition of a stannyl radical to the alkyne does apparently occur, as shown by the following experiment: treatment of $Me_3SnC\equiv CSnMe_3$ with Bu_3SnH under hydrostannation conditions leads to rapid formation of Me_3SnH and $Me_3SnC\equiv CSnBu_3$.

The formation of relatively large amounts of II when R = R'OCH$_2$ may well be due to complexation of either the tin hydride or the stannyl radical by oxygen [4]. This suggestion is supported by the fact that $PhOC\equiv CSnMe_3$, which would lead to a different geometry on complexation, again gives only one isomer of type I. This compound shows extremely low values of $^3J(SnH)$ and $^3J(Sn-Sn)$ (see Table 2), but its structure follows clearly from the ^{13}C NMR spectrum.

TABLE 2

SELECTED COUPLING CONSTANT DATA FOR 1,1-BIS(TRIMETHYLSTANNYL)-1-ALKENES $RCH=C(SnMe_3)_2$ (in Hz); Accuracy of measurement: $J(SnH)$ and $J(SnC)\pm 2$ Hz, $J(SnSn)\pm 5$ Hz. "Sn" refers in all cases to ^{119}Sn

R	$^3J_{cis}(SnH)$	$^3J_{trans}(SnH)$	$^3J_{cis}(SnC)$	$^3J_{trans}(SnC)$	$^2J(SnSn)$	$^3J(SnSn)$ [b]
H [a]	124	208	–	–	608	[c]
CH_3	113	199	79	106	671	834
n-Bu	114	201	73	98	693	[c]
t-Bu	131	227	41	96	683	[c]
Ph	112	194	55	100	580	[c]
$PhCH_2$	108	196	76	103	643	880
$MeOCH_2$	119	200	64	105	603	906
$PhOCH_2$	98	192	73	109	540	836
PhO	50	124	–	–	277	[c]

[a] For formation see text. [b] In (E)-1,2-bis(trimethylstannyl)-1-alkenes $RC(SnMe_3)=CHSnMe_3$. [c] Not observed.
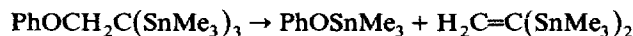
Hydrostannation of 1,1-distannyl-1-alkenes

With the exception of R = t-Bu, all the distannylalkenes obtained undergo a second hydrostannation to give the corresponding 1,1,1-tristannylalkanes:

$$RCH=C(SnMe_3)_2 + Me_3SnH \rightarrow RCH_2C(SnMe_3)_3$$

The structure of these follows in particular from the ^{119}Sn NMR spectra, which show a single signal with a chemical shift of ca. +30 ppm and a geminal tin–tin coupling constant of ca. 220 Hz; data on these compounds are given in Table 4.

While the tristannylalkanes are generally thermally stable, the compound with R = PhO decomposes on distillation in vacuo or on heating to 140–160°C with the formation of trimethyltin phenoxide and 1,1-bis(trimethylstannyl)ethylene, the latter being clearly characterised by NMR spectroscopy.
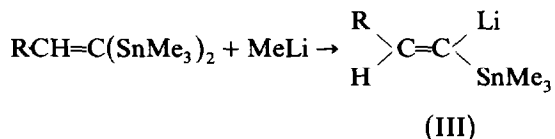
$$PhOCH_2C(SnMe_3)_3 \rightarrow PhOSnMe_3 + H_2C=C(SnMe_3)_2$$

Lithiation of 1,1-distannyl-1-alkenes

The work of Seyferth and Vaughan [5] led us to expect that these compounds would be readily lithiated by alkyllithiums, as proved to be the case. We found that it is important to have the same alkyl group on tin and lithium, since otherwise alkyl-exchange equilibria lead to the formation of mixtures of compounds; such equilibrium processes occur particularly readily in THF, the solvent used by us. Thus treatment of I with 2 eq BuLi leads to the formation of MeLi as the organolithium reagent in excess, while under our reaction conditions Me_4Sn undergoes exchange with butyllithium, leading to the formation of methyllithium and compounds of the type Me_nSnBu_{4-n}.

The lithiation reaction would be of particular interest if it were to occur stereospecifically. While trapping reactions (see below) indicated this to be the case, NMR spectroscopy was expected to give information on the species present in solution. The results were particularly clear for R = Ph and t-Bu; while for both I showed two values of $^3J(SnH)$ of ca. 120 (*cis*) and 200 (*trans*) Hz for the vinylic

proton, after lithiation with methyllithium the single vinyl proton signal * at 8.3 and 7.3 ppm, respectively, showed $^3J(\text{SnH})$ ca. 275 Hz, while the coupling between tin and the methyl protons decreased to ca. 40 Hz. This ^3J value must be compared to that of 224 Hz for $^3J_{cis}(\text{SnH})$ in (E)-Bu$_3$SnCH=CHLi; since in stannyl alkenes $^3J(\text{SnH})$ is ca. 10% higher for trimethyl- than for tributyl-tin species a value of ca. 245 Hz would be expected for (E)-Me$_3$SnCH=CHLi. Thus the species formed clearly have the E-structure (III).

$$\text{RCH=C(SnMe}_3)_2 + \text{MeLi} \rightarrow \quad \begin{array}{c} \text{R} \\ \\ \text{H} \end{array}\!\!\!\!\!>\!\!\text{C=C}\!\!<\!\!\!\!\!\begin{array}{c} \text{Li} \\ \\ \text{SnMe}_3 \end{array}$$

(III)

$(R = Ph, t\text{-}Bu)$

For other groups R, proton NMR spectra * indicated the formation of III and the corresponding (Z)-isomer in approximately equal amounts; this was confirmed by treating the vinyllithium reagents with methyl iodide, when for example with R = Ph the (E)-isomer of RCH=C(Me)SnMe$_3$ was formed almost exclusively, while for R = Bu a 1/1 mixture of (E)- and (Z)-isomers was formed.

While this work was in progress, a report on the formation of the corresponding α-silylvinyllithiums (R = n-Bu, t-Bu, cyclohexyl) appeared [6], in which was shown indirectly that the (E)- and (Z)-isomers exist in an equilibrium in which the (E)-isomer predominates.

The α-stannylated vinyllithiums are thermally unstable, decomposing fairly rapidly at room temperature with formation of Me$_3$SnLi. This would indicate their potential use as precursors for unsaturated carbenes of the type RCH=C|, but experiments so far carried out do not confirm this, perhaps not surprisingly in view of the work of Cunico and Han [7]. The thermal stability of III is increased if salt-free solutions are used in its preparation.

Possibility of formation of 1,1-dilithioalkenes

The lithiation of 1,1-distannylalkenes offers a potential route to 1,1-dilithioalkenes. However, in view of the lack of success suffered by Seyferth [8] in his attempted preparation of 1,2-dilithioethylene from 1,2-distannylethylene it seemed unlikely, that the 1,1-dilithioalkenes would in fact be formed. ^{1}H NMR studies confirmed this: when 2 eq methyllithium were added to a compound of type I, one equivalent remained unconsumed.

Attempts to modify Seyferth's system (Bu$_3$SnCH=CHSnBu$_3$ + BuLi) by replacing n-butyl residues by phenyl or cyclohexyl groups were also unsuccessful, so that it did not appear worthwhile to try to modify our system in a similar manner.

It is however possible (see below) to carry out syntheses which give the same result as if a 1,1-dilithioalkene were present.

Synthetic potential of 1-lithio-1-trimethylstannylalkenes

At this stage we can only give a preliminary report on this topic, since we are at

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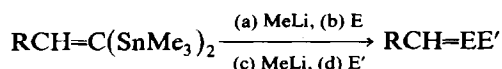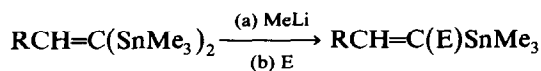* These measurements were carried out at room temperature.

TABLE 3

SELECTED CHEMICAL SHIFT DATA FOR 1,1-BIS(TRIMETHYLSTANNYL)-1-ALKENES $RCH=C(SnMe_3)_2$

(in ppm; Standard: for ^{13}C internal TMS, for ^{119}Sn internal Me_4Sn)

R	$\delta(Me_3Sn)$[b]	$\delta(C_a)$	$\delta(C_b)$	$\delta(Sn_a)$	$\delta(Sn_b)$
H[a]	−9.6/−9.6	157.2	142.2	−19.3	−19.3
CH_3	−7.4/−8.7	144.3	151.6	−45.0(−69.7)	−15.7(−45.5)
n-Bu	−7.1/−8.5	142.6	158.0	−45.6(−70.7)	−15.8(−47.6)
t-Bu	−4.5/−7.3	136.8	168.7	−46.8(−69.2)	−1.1(−47.0)
Ph	−6.7/−8.2	150.8	155.6	−38.0(−65.9)	−9.6(−38.3)
$PhCH_2$	−7.1/−8.5	144.8	155.5	−44.0(−68.4)	−14.2(−43.3)
$MeOCH_2$	−6.7/−8.5	141.1	152.2	−43.9(−68.6)	−9.9(−46.1)
$PhOCH_2$	−7.0/−8.1	141.1	151.1	−40.5(−65.4)	−9.4(−43.4)
PhO	−7.5/−8.4	152.7	113.4	−28.3	−7.2

[a] For formation see text. [b] First shift refers to methyl bound to Sn_a. Nomenclature:

$$\begin{array}{c} R \qquad\quad Sn_aMe_3 \\ \diagdown C_b{=}C_a\diagup \\ H \qquad\quad Sn_bMe_3 \end{array}$$

Values in parentheses refer to $Me_3Sn_aCH{=}CR(Sn_bMe_3)$.

present exploring the synthetic potential of these reagents. Two basic reaction types are of interest:

$$RCH{=}C(SnMe_3)_2 \xrightarrow[\text{(b) E}]{\text{(a) MeLi}} RCH{=}C(E)SnMe_3$$

$$RCH{=}C(SnMe_3)_2 \xrightarrow[\text{(c) MeLi, (d) E}']{\text{(a) MeLi, (b) E}} RCH{=}EE'$$
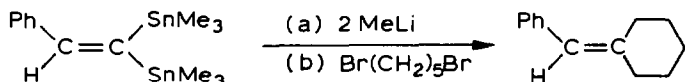
E is a carbon electrophile. On preparative grounds we have taken the compound with R = Ph as our model system. We can summarise our conclusions by saying that while in a limited number of cases the synthetic goal can be attained, the high basicity of the lithium reagent often causes problems, as was anticipated. Thus while reactions with methyl iodide or dimethyl sulphate proceed in good yields, a number of other alkyl halides of various types undergo elimination of hydrogen halide as a side or even major reaction. Examples are allyl bromide, trimethyl(bromomethyl)tin and t-butyl bromide. Similarly, while formaldehyde and benzophenone give the expected allylic alcohols, enolisable compounds such as acetone or acetophenone do not react in the required manner. α, β-Unsaturated carbonyl compounds give 1,2- or 1,4-addition depending on the substrate: thus $PhCH{=}CHCHO$ gives 1,2- but $PhCH{=}CHCOPh$ gives 1,4-addition [9].

A second problem which can occur is that of stereospecificity. Thus while the reaction of III (R = Ph) with methyl iodide or dimethyl sulphate leads to the formation of ca. 95% (GLC) of the (E)- and only 5% of the (Z)-product, the reaction with trimethylchloro- or -iodosilane gives only the (presumably thermodynamically more stable) (Z)-product. This indicates that even for R = Ph a small amount of (Z)-III is present in solution.

One somewhat more successful reaction could prove to be synthetically useful: treatment of III with two equivalents of methyllithium and one equivalent of 1,5-dibromopentane (reversed addition conditions) gave a 40% (isolated) yield of the

substituted methylenecyclohexane:

$$\begin{array}{c}Ph\\H\end{array}C=C\begin{array}{c}SnMe_3\\SnMe_3\end{array} \xrightarrow[\text{(b) } Br(CH_2)_5Br]{\text{(a) } 2\,MeLi} \begin{array}{c}Ph\\H\end{array}C=C\big\langle\bigcirc$$

While this reaction is unlikely to provide a viable alternative to the Wittig or Peterson syntheses, it might be useful in special cases, e.g. in the formation of exocyclic olefins with a heteroatom in the ring as shown below:

$$\begin{array}{c}R\\H\end{array}C=C\begin{array}{c}(CH_2)_n\\(CH_2)_m\end{array}\!\!\!\searrow X$$
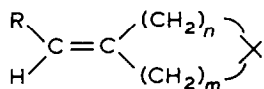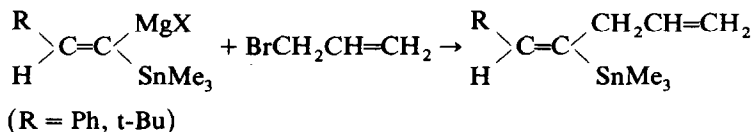
Alternative carbanionoids: replacement of lithium by magnesium and copper

It seemed likely that the magnesium reagent IV might react more uniformly with

$$\begin{array}{c}R\\H\end{array}C=C\begin{array}{c}MgX\\SnMe_3\end{array}$$
$$(IV)$$
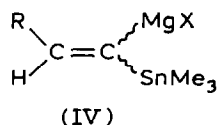
electrophiles. While I itself does not react with magnesium bromide even on prolonged heating, III reacts readily to give (when R = Ph or t-Bu) (E)-IV: this could be shown directly by means of proton NMR spectroscopy, the values of $^3J(SnH)$ of 212 (R = Ph) and 228 Hz (R = t-Bu) clearly corresponding to a *cis*-coupling. The α-stannyl Grignard reagents react with allyl bromide to give the pentadienyl and heptadienyltin compounds, whose stereochemistry was determined by proton NMR spectroscopy:

$$\begin{array}{c}R\\H\end{array}C=C\begin{array}{c}MgX\\SnMe_3\end{array} + BrCH_2CH=CH_2 \rightarrow \begin{array}{c}R\\H\end{array}C=C\begin{array}{c}CH_2CH=CH_2\\SnMe_3\end{array}$$

(R = Ph, t-Bu)

Preparation of 2-methyl-1-phenyl-1-butene via Grignard reagents using methyl iodide and ethyl bromide gave 24% of a mixture containing 96% of the (E)-isomer:

$$\begin{array}{c}Ph\\H\end{array}C=C\begin{array}{c}SnMe_3\\SnMe_3\end{array} \xrightarrow[\text{(d) MeLi, (e) MgBr}_2\text{, (f) EtBr}]{\text{(a) MeLi, (b) MgBr}_2\text{, (c) MeI}} \begin{array}{c}Ph\\H\end{array}C=C\begin{array}{c}Me\\Et\end{array} + 4\%(Z)\text{-isomer}$$
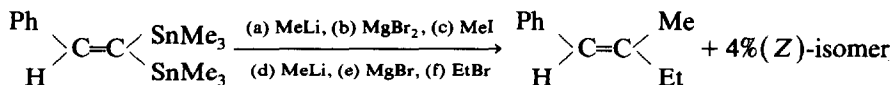
Similarly, treatment of III, (R = t-Bu) with copper(I) chloride at $-78°C$ leads to the formation of a single organocopper species (presumably RCu · LiCl) with $^3J(SnH)$ 155 Hz: treatment of this species with deuteromethanol gives the expected deuterated stannyl alkene t-BuCH=CDSnMe_3. The identical species is obtained on deuterolysis of III, and is clearly identified as the (E)-isomer by the values of $^3J(HD)$ and $^3J(SnH)$.

Experimental

Starting materials were either commercial products or were prepared according to literature procedures. All manipulations involving organotin compounds were car-

ried out in an argon atmosphere.

^{1}H NMR spectra were recorded using a Varian EM-360 spectrometer, ^{13}C and ^{119}Sn NMR spectra on a Bruker HFX-90 spectrometer.

Hydrostannation of 1-trimethylstannyl-1-alkynes

The general procedure was as follows: equimolar amounts of alkyne and trimethyltin hydride were heated to 70°C in the presence of catalytic amounts of azobisisobutyronitrile as catalyst. The reactions, which could readily be followed by IR or ^{1}H NMR spectroscopy, were complete after 3–4 h. In the case where R = t-Bu, the reaction mixture (with AIBN) was irradiated using a UV-source (mercury high pressure lamp TQ 150) for 11 h. Products were distilled under reduced pressure.

Identification of the isomers was carried out primarily on the basis of ^{1}H NMR data (see Table 2); corroboration was provided by ^{13}C and ^{119}Sn NMR data. IR spectra showed ν(C=C) between 1550 (R = t-Bu) and 1600 cm^{-1} (R = Ph, PhOCH$_2$).

Hydrostannation of 1,1-bis(trimethylstannyl)-1-alkenes

The hydrostannation of compounds RCH=C(SnMe$_3$)$_2$ was carried out as described above; compounds with R = Ph, PhO, MeOCH$_2$ and PhOCH$_2$ (the latter two as mixtures with the 1,2-distannylalkenes) reacted under thermal conditions, those with R = Me, n-Bu and PhCH$_2$ only under photolytic conditions.

The tristannylalkanes with R = n-Bu, PhCH$_2$, CH$_3$OCH$_2$ and PhOCH$_2$ were obtained as oils and distilled without decomposition under reduced pressure. The compound with R = PhO decomposed on distillation as described above, while those with R = Me and Ph were solids. These were freed from volatiles by heating at 60°C and 10^{-3} mmHg. Physical properties are recorded in Table 4.

Lithiation of 1,1-bis(trimethylstannyl)-1-alkenes

The following procedure is typical: PhCH=C(SnMe$_3$)$_2$ (8.1 g, 19.1 mmol) was diluted with 5 ml THF and cooled to −78°C. A solution of methyllithium in THF (20.5 ml containing 19.1 mmol MeLi) was added slowly with stirring, the solution turning yellow immediately. After stirring for 1 h, the mixture was subjected to NMR analysis at room temperature; the starting materials were completely consumed. Apart from signals due to tetramethyltin, the following were observed: δ(ppm) −0.03 (s, Me$_3$Sn; ^{2}J(SnH) 38 Hz), 6.8–7.5 (m, Ph), 8.31 (s, =CH; ^{3}J(SnH) 280 Hz).

For R = t-Bu the vinylic proton absorbed at 7.3 ppm and showed ^{3}J(SnH) 273 Hz, while for the methyltin protons ^{2}J(SnH) 40 Hz.

Reactions of (1-trimethylstannyl-2-phenyl)vinyllithium

These were carried out by adding the electrophile to the organolithium reagent, prepared as described above, at −78°C. The following reactions led to the formation of the required products.

(i) With dimethyl sulphate (scale 9.5 mmol). After the addition to the vinyllithium, the reaction mixture was warmed to room temperature, stirred for 1 h and heated for 15 min under reflux. Volatile components were removed at the oil pump and subjected to distillation, first under atmospheric pressure to remove THF and Me$_4$Sn and finally under reduced pressure. (*E*)-2-phenyl-2-(trimethylstannyl)-1-propene (40% yield) was obtained as a colourless oil, b.p. 74–79°C/0.03 mmHg. GLC

TABLE 4

YIELDS, PHYSICAL, ANALYTICAL AND SELECTED NMR SPECTROSCOPIC DATA FOR COMPOUNDS RCH$_2$C(SnMe$_3$)$_3$

R	Yield [a] (%)	B.p. (°C/mmHg) [M.p.(°C)]	Analytical data (Calcd. (found) (%))		δ(SnMe$_3$) (ppm)	^2J(SnSn) (Hz)	^3J(SnH) (Hz)
			C	H			
CH$_3$	75	[203–207]	27.06 (27.21)	6.10 (6.15)	34.1	230	80
n-Bu	67	110/0.07	31.35 (31.03)	6.62 (6.21)	35.0	229	[b]
Ph	80	[73]	34.34 (33.60)	5.72 (5.12)	34.7	229	73
PhCH$_2$	80	[ca. 5]	35.52 (35.75)	5.92 (6.26)	35.6	230	73
MeOCH$_2$	41	92/0.001	27.75 (28.08)	6.05 (6.04)	36.2	235	74
PhOCH$_2$	52	142/0.002	34.61 (34.60)	5.77 (5.77)	37.8	235	72
PhO	[c]	[c]			30.9	220	66

[a] After distillation. [b] Not recorded. [c] Decomposes on distillation.

analysis indicated the presence of ca. 5% of the (Z)-isomer.

Anal. Found: C, 50.94; H, 6.22. C$_{12}$H$_{18}$Sn calcd.: C, 51.30; H, 6.46%.

^{1}H NMR (neat): δ 0.20 (s, 9H, ^2J(SnH) 54 Hz, SnMe$_3$); 2.11 (d, 2 Hz, 3H, ^3J(SnH) 52 Hz, CH$_3$); 6.70 (q, 2 Hz, 1H, ^3J(SnH) 80 Hz, CH=); 6.8–7.3 (m, 5H, Ph)

(ii) With deuteromethanol, CH$_3$OD (scale 15.6 mmol). Procedure: as above. (E)-(2-deutero-2-(trimethylstannyl)vinylbenzene (31%) was obtained as a colourless oil, b.p. 73°C/0.01 mmHg.

^{1}H NMR (neat): δ 0.20 (s, 9H, ^2J(SnH) 56 Hz, SnMe$_3$); 6.81 (t, 2.5 Hz, ^3J(SnH) 72 Hz, CH=); 7.2 (m, 5H, Ph).

(iii) With trimethylsilyl chloride and iodide (scale: 25 mmol). Procedure: after addition of Me$_3$SiX to the vinyllithium, the reaction mixture was kept 1 h at −78°C, allowed to warm to room temperature and heated 1 h under reflux. After removal of volatiles at the water pump the residue was subjected to a fractional distillation. After a forerun of 2-trimethylstannylstyrene, (Z)-(2-trimethylsilyl-2-trimethylstannyl)vinylbenzene was obtained as a colourless oil, b.p. 64°C/0.01 mmHg. Yield: from Me$_3$SiCl 23%, from Me$_3$SiI 45%.

^{1}H NMR: δ 0.0 (s, 9H, ^2J(SnH) 54 Hz, Me$_3$Sn); 0.2 (s, 9H, SiMe$_3$); 7.2 (m, 5H, Ph); 7.8(s, 1H, ^3J(SnH) 187 Hz, CH=)

Anal. Found: C, 49.11; H, 6.92. C$_{12}$H$_{18}$Sn calcd.: C, 49.58; H, 7.13%.

(iv) With benzophenone (scale: 14 mmol). Procedure: after addition of a solution of benzophenone in THF to the vinyllithium, the reaction mixture was kept 1 h at −78°C and slowly hydrolysed by the addition of water. It was then allowed to warm to room temperature and the organic layer was separated. The aqueous layer was extracted with ether and the combined organic phases dried over MgSO$_4$. After distilling off the volatile components a white solid remained which was recrystallised from hexane. The solid, (E)-1,1,3-triphenyl-2-trimethylstannylallyl alcohol, melted at 87–90°C.

^{1}H NMR (in CCl$_4$): δ 0.0 (s, 9H, ^2J(SnH) 53 Hz, SnMe$_3$); 2.7 (s, 1H, OH); 6.6 (m, 5H, Ph); 6.8 (s, 1H, ^3J(SnH) 91 Hz, CH=); 7.1 (m, 10H, 2 Ph).

Anal. Found: C, 63.72; H, 5.44. C$_{12}$H$_{18}$Sn calcd.: C, 64.15; H, 5.79%.

Reactions leading to trialkyl olefins

(i) Formation of 2-methyl-1-phenyl-1-propene. A solution of methyllithium in THF (30.2 mmol in 35 ml) was added slowly to a solution of PhCH=C(SnMe$_3$)$_2$ (6.5 g, 15.1 mmol) in THF (5 ml) at −78°C; the solution became dark brown in colour. After 1.5 h at −78°C dimethyl sulphate (3.8 g, 30.2 mmol) was added. The yellow solution was allowed to warm to room temperature and heated for 1 h under reflux. Volatile components were distilled off and the residue distilled at the water pump. B.p. 76°C/14 mmHg (lit. [10] 76–77°C/14 mmHg).

(ii) Formation of 2-methyl-1-phenyl-1-butene. A solution of methyllithium in THF (21 mmol in 25 ml) was added to a solution of PhCH=C(SnMe$_3$)$_2$ (9.0 g, 21 mmol) at −78°C, the reaction mixture turning dark brown. After stirring for 1 h at this temperature, methyl iodide (3.0 g, 21 mmol) was added, the solution turning yellow. After 1 h at room temperature the reaction mixture was cooled to −73°C and the procedure repeated with addition of 21 mmol each of methyllithium solution and of ethyl iodide. Finally the reaction mixture was heated 1 h under reflux, cooled to room temperature and shaken with water (10 ml). The organic phase was separated, dried over MgSO$_4$ and subjected to distillation, first at normal pressure to remove volatiles and then at the water pump. The product (0.8 g, 27%) showed a b.p. of 65–70°C/14 mmHg (Lit. [11] 86°C/12 mmHg). The yield of isolated product was 0.8 g (27%). GLC analysis (on a 4 m Emulphor column) indicated a composition of 90% (*E*)- and 10% (*Z*)-isomers. This was confirmed by ^{1}H and ^{13}C NMR spectroscopy.

(iii) Formation of benzylidenecyclohexane. A solution of 16.8 mmol methyllithium in THF was added to PhCH=C(SnMe$_3$)$_2$ (7.2 g, 16.8 mmol) in 5 ml THF at −78°C. The dark brown solution was stirred for 1 h at this temperature and transferred to a precooled dropping funnel, from which it was added to a solution of 1,5-dibromo-pentane (3.8 g, 16.5 mmol) in 3 ml THF, also at −78°C. The reaction mixture was stirred at −78°C for 1 h, during which time it became yellow in colour. It was then again cooled to −78°C and a solution of 16.8 mmol methyllithium in THF added: the red-brown mixture was kept for 2 h at this temperature, allowed to warm to room temperature and heated for 1 h under reflux. All volatile components were removed at the oil pump and then distilled. Benzylidenecyclohexane was obtained in 40% yield (1.14 g) and identified by IR, ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry as well as by elemental analysis.

Replacement of lithium by magnesium

Two molar equivalents (3.24 g, 17.6 mmol) of magnesium bromide were added in portions to a solution of 8.8 mmol (*E*)-PhCH=CLiSnMe$_3$ in THF at −78°C. The initially yellow solution became colourless and was stirred for 1 h at this temperature before being subjected to ^{1}H NMR spectroscopy at room temperature.

It exhibited signals at δ 0.07 (s, 9H, ^2J(SnH) 46 Hz, SnMe$_3$); 7.26 (m, 5H, Ph); 7.97 (s, ^3J(SnH) 212 Hz, CH=).

The corresponding t-butyl derivative showed the following values: −0.03 (s, 9H, ^2J(SnH) 44 Hz, SnMe$_3$); 1.07 (s, 9H, t-Bu); 6.97 (s, 1H, ^3J(SnH) 228 Hz, CH=).

Reaction of PhCH=C(SnMe₃)MgBr with allyl bromide

Allyl bromide (2.1 g, 17.4 mmol) was added to a solution of the Grignard reagent in THF (17.4 mmol) at $-78°C$. The reaction mixture was kept at this temperature for 2 h before being allowed to warm to room temperature. All low-boiling volatile components were removed at the water pump and the residue distilled at the oil pump. (E)-1-Phenyl-2-trimethylstannyl-1,4-pentadiene was obtained as a colourless oil, b.p. $61°C/0.01$ mmHg, the yield being 2.7 g (50%).

Anal. Found: C, 54.08; H, 5.89. Calcd.: C, 54.77; H, 6.52%.

^{1}H NMR (CCl$_4$): δ 0.2 (s, 9H, ^2J(SnH) 54 Hz, SnMe$_3$); 3.3 (dd, 6 Hz, 2 Hz, 2H, ^3J(SnH) 62 Hz, CH$_2$); 4.9 (m, 1H), 5.2 (m, 1H), 5.7 (m, 1H): all CH=CH$_2$; 6.7 (t, 2 Hz, 1H, ^3J(SnH) 80 Hz, C*H*=); 7.2 (m, 5H, Ph).

Mass spectra and ^{13}C NMR data also agreed with the proposed structure.

The Grignard reagent with R = t-Bu also reacted with allyl bromide to give the corresponding stannyl heptadiene in good yield. ^3J(SnH) for the vinyl proton was in this case 88 Hz.

Replacement of lithium by copper

Treatment of a solution of t-BuCH=C(Li)SnMe$_3$ in THF at $-78°C$ with freshly prepared copper(I) chloride in slight excess gave a solution the ^{1}H NMR spectrum of which at room temperature showed only one vinyl proton resonance with ^3J(SnH) 155 Hz; deuterolysis of this solution with MeOD caused this resonance to be replaced by a triplet with ^3J(HD) 2.5 Hz and ^3J(SnH) 77 Hz. The coupling constant values are identical with those observed for the compound obtained on direct deuterolysis of the organolithium species.

Acknowledgements

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