

α -METALLATED VINYL CARBANIONOIDS

II *. PREPARATION AND STABILITY OF VINYL LITHIUMS CONTAINING TRIORGANOSTANNYL GROUPS ON THE α -CARBON ATOM

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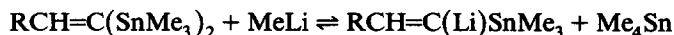
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Summary

The influence of intramolecular coordination and solvent effects on the formation and stability of α -stannylvinyl lithium reagents $RR'C=C(Li)SnMe_3$ ($R' = H$, alkyl, aryl) has been investigated; intramolecular coordination via a 5-membered ring is particularly effective. Mechanisms for the isomerisation and thermal decomposition of $RR'C=C(Li)SnMe_3$ are discussed, and multinuclear NMR data (^{119}Sn , ^{13}C and 1H) for these species are presented.

Introduction

We were previously able to show that treatment of 1,1-bis(trimethylstannyl)-1-alkenes with methyllithium leads to the formation of α -stannyl vinyl anionoids [1]:



These thermally labile vinyl lithiums exist almost exclusively in the *E*-form when $R = Ph$ or *t*-Bu, but otherwise as an *E/Z* mixture. We later showed, as the work of Zweifel [2] had led us to expect, that the corresponding α -silylvinyl lithiums were thermally more stable; reactions of α -silyl- and α -stannylvinyl lithiums with aldehydes and ketones were reported [3].

Our discovery that distannylalkenes of the type $RR'C=C(SnMe_3)_2$ are available starting from geminal dibromoalkenes and trimethylstannyl lithium [4] caused us to look at the α -stannylvinyl lithiums in more detail: the results of these investigations are described in the present paper.

* For part I see ref. 1.

Results and discussion

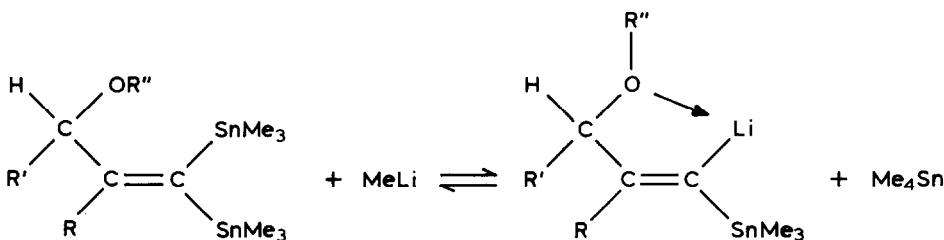
1. Preparation and stability of α -stannylvinylolithiums

The reaction in which compounds $\text{RCH}=\text{C}(\text{Li})\text{SnMe}_3$ is formed is an equilibrium reaction: because of the lability of such compounds, we have been unable to remove tetramethyltin from the equilibrium mixture and thus obtain the pure compounds $\text{RCH}=\text{C}(\text{Li})\text{SnMe}_3$. The presence of tetramethyltin provides a problem when $\text{RCH}=\text{C}(\text{Li})\text{SnMe}_3$ is to be reacted with relatively unreactive electrophiles, as these may react preferentially with methylolithium present in the equilibrium mixture. A further problem is the formation of mixtures of *E*- and *Z*-isomers of $\text{RCH}=\text{C}(\text{Li})\text{SnMe}_3$, which may in principle react at different rates with electrophiles.

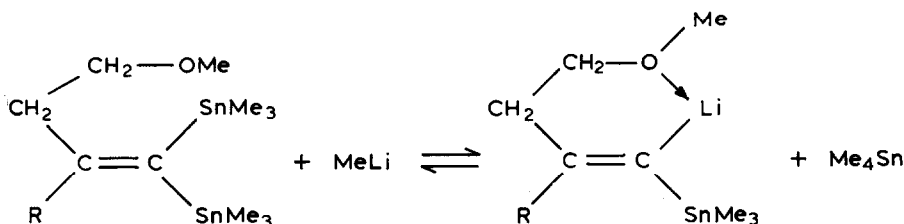
We have thus carried out relatively detailed studies on the effect of intramolecular stabilisation and solvent on the reaction leading to the formation of α -stannylvinyl anionoids.

(a) *Intramolecular effects.* Preliminary studies [1] showed that the transmetallation in THF occurs quantitatively when $\text{R} = \text{Ph}$ or $t\text{-Bu}$ to give only (*E*)- $\text{RCH}=\text{C}(\text{Li})\text{SnMe}_3$; with other groups R the products $\text{RCH}=\text{C}(\text{Li})\text{SnMe}_3$ could not be detected NMR-spectroscopically. By treating the product with D_2O we could show that in these latter cases little or no transmetallation in fact occurs [5]. Introduction of a donor atom into the group R ($\text{R} = \text{Me}_2\text{NCH}_2$, MeOCH_2 , $\text{MeOCH}_2\text{CH}_2$, $\text{MeOCH}(\text{CH}_3)$) in order to induce intramolecular solvation of $\text{RCH}=\text{C}(\text{Li})\text{SnMe}_3$ does not increase the degree of transmetallation measurably, but when $\text{R} = \text{MeOCMe}_2$ the *E*-anion can be detected chemically as well as spectroscopically; the (1-methoxy)-1-cyclohexyl residue has the same effect.

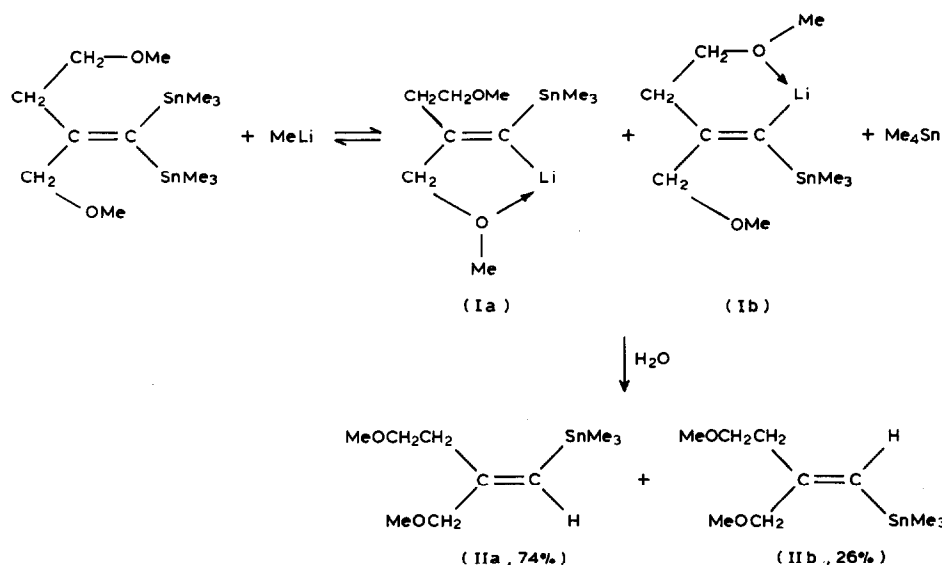
Distannyl alkenes $\text{RR}'\text{C}=\text{C}(\text{SnMe}_3)_2$ are much more readily converted to their lithium derivatives $\text{RR}'\text{C}=\text{C}(\text{Li})\text{SnMe}_3$; the degree to which $\text{RR}'\text{C}=\text{C}(\text{Li})\text{SnMe}_3$ was formed in THF (as shown by proton NMR at room temperature) was as follows: $\text{R}, \text{R}' = \text{Me}, \text{Me}$, 75%; Me, Et , 72%; $c\text{-C}_4\text{H}_8$, 53%; $c\text{-C}_5\text{H}_{10}$, 75%. The presence of a phenyl group ($\text{R}, \text{R}' = \text{Ph}, \text{Me}$; Ph, Ph ; Ph, CF_3) induces quantitative formation of $\text{RR}'\text{C}=\text{C}(\text{Li})\text{SnMe}_3$ as shown by NMR and/or deuterolysis. In several cases we were able to observe intramolecular coordination in the carbanionoid:



However, this type of coordination is also possible when a six-membered ring is involved:



When both possibilities are available, the five-membered ring coordination is preferred:



In solution, only species Ia is observed; the relative proportions of IIa and IIb were determined by proton NMR spectroscopy.

(b) *Solvent influences.* Since we have not been able to obtain anionoids $\text{RCH}=\text{C}(\text{Li})\text{SnMe}_3$ or $\text{RR}'\text{C}=\text{C}(\text{Li})\text{SnMe}_3$ in a pure state, we have no information on their degree of aggregation. However, the use of solvents with differing donor abilities or of chelating solvents should provide information not only on the degree of transmetallation but also (via NMR spectroscopy) on their influence on the structure of the anionoid.

In diethyl ether, $\text{Me}_2\text{C}=\text{C}(\text{SnMe}_3)_2$ undergoes transmetallation to the extent of only ca. 5%, while in dimethoxyethane (DME) the reaction is ca. 98% complete. The importance of intramolecular stabilisation is shown by the fact that $\text{EtOCMe}_2\text{CH}=\text{C}(\text{SnMe}_3)_2$ is at least 98% converted to the vinyl lithium even in diethyl ether. Our expectation that tetramethylethylenediamine (TMEDA) would be more effective than DME was not confirmed: in this solvent, only ca. 70% of the anionoid is formed from $\text{Me}_2\text{C}=\text{C}(\text{SnMe}_3)_2$.

DME favours the transmetallation of compounds $\text{RCH}=\text{C}(\text{SnMe}_3)_2$: with $\text{R} = \text{H}$ or $n\text{-Bu}$, $\text{RCH}=\text{C}(\text{Li})\text{SnMe}_3$ is formed quantitatively; in the latter case the E/Z ratio (NMR) is 36/64. In TMEDA the reaction is not quantitative, but (obviously for steric reasons) only (Z)- $\text{RCH}=\text{C}(\text{SnMe}_3)_2$ is observed.

The degree of transmetallation observed in the various systems studied is summarised in Table 1.

2. Isomerisation of α -stannylvinylolithiums

Distannylalkenes $\text{RCH}=\text{C}(\text{SnMe}_3)_2$ or (when unsymmetrical) $\text{RR}'\text{C}=\text{C}(\text{SnMe}_3)_2$ can in principle give a mixture of (Z)- and (E)-vinylolithiums. In cases where there is neither strong intramolecular solvation nor a strong chelating solvent, intercon-

TABLE 1

DEGREE OF TRANSMETALLATION OF DISTANNYLALKENES $RR'C=C(SnMe_3)_2$

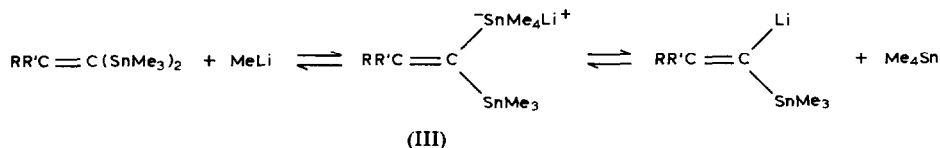
R	R'	Solvent	Vinyl lithium (%)	E/Z ratio
H	H	TMEDA	98	
Me	H	THF	67	80/20 ^a
Me	H	TMEDA	80	0/100 ^b
n-Bu	H	THF	67	64/36 ^a
n-Bu	H	DME	> 95	33/67 ^b
n-Bu	H	TMEDA	77	0/100 ^b
c-Hex	H	THF	67	56/44 ^a
c-Hex	H	TMEDA	69	0/100 ^b
t-Bu	H	THF	> 95	> 95/ < 5 ^{a,b}
Ph	H	THF	> 95	> 95/ < 5 ^{a,b}
EtOCMe ₂	H	Et ₂ O	> 95	> 95/ < 5 ^{a,b}
MeO(C ₆ H ₁₀)	H	THF	> 95	92/8 ^a
Me	Me	THF	75	
Me	Me	DME	90	
Me	Me	TMEDA	48	
	c-C ₄ H ₈	THF	53	
	c-C ₅ H ₁₀	THF	75	
Ph	Me	THF	> 95	33/67 ^{a,c}
Ph	Ph	THF	> 95	
Ph	CF ₃	THF	> 95	> 95/ < 5 ^a
EtOCH ₂	Me	THF	> 95	78/22 ^a
MeOCH ₂	MeOCH ₂	THF	> 95	
MeOCH(Me)	Me	THF	> 95	82/18 ^a
MeOCH ₂ CH ₂	Me	THF	> 95	83/17 ^a
MeOCH ₂ CH ₂	MeOCH ₂	THF	> 95	69/31 ^a

^a According to hydrolysis or deuterolysis at -78°C . ^b According to proton NMR at room temperature.^c At room temperature 68/32.

version of the *E*- and *Z*-isomers (either via the starting material or via a true intramolecular isomerisation) must be discussed.

Isomerisations of this type have previously been observed for α -silylvinylolithiums [2,6]: in this case it seems clear that a genuine intramolecular isomerisation is involved.

In the case of the α -stannylvinylolithiums, it at first glance seems likely that any isomerisation observed will occur via the starting material, since they are formed in an equilibrium reaction which is fast even at -78°C . This equilibrium probably involves the formation of ate complexes [7], though these have not been observed spectroscopically:

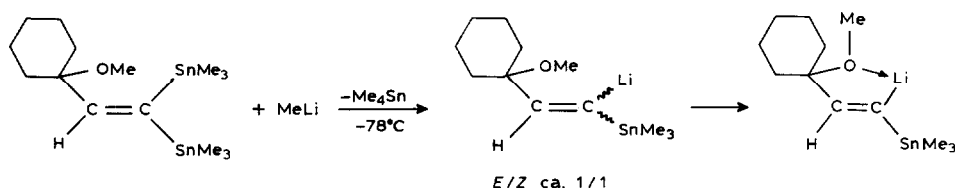


If III is formed, it seems conceivable that a methyl group transfer between the two organostannyl groups in the ate complex may occur, so that isomerization could involve the ate complexes III as well as or rather than the distannyl alkenes. In two

cases we followed the *E/Z* isomerisation by means of ^{119}Sn NMR spectroscopy. Treatment of $\text{PhMeC}=\text{C}(\text{SnMe}_3)_2$ with methyl lithium in THF at -78°C gave an organotin species with $\delta(\text{Sn}) - 87$ ppm (tin chemical shifts are discussed in section 4 below). Deuterolysis at this stage gave a 1/2 mixture of (*Z*)- and (*E*)- $\text{PhMeC}=\text{C}(\text{SnMe}_3)\text{D}$. On warming the sample in the NMR tube, a second tin signal was observed at -90 ± 1 ppm (temperature-dependent); deuterolysis at 25°C gave a 2/1 mixture of (*Z*)- and (*E*)- $\text{PhMeC}=\text{C}(\text{SnMe}_3)\text{D}$.

Similarly, treatment of $\text{PhCH}=\text{C}(\text{SnBu}_3)_2$ with BuLi in THF at -78°C gave species with $\delta(\text{Sn}) - 77$ and -45 ppm (ca. 10/1); on deuterolysis the *Z/E* product ratio was 93/7. At 0°C the high-field signal was no longer present, the low-field signal occurring at -50 ppm. Deuterolysis at this stage gave a product mixture containing *Z* and *E* isomers in the ratio 3/7.

The following result indicates that the *E*-isomers observed when intramolecular chelation is possible are the thermodynamic rather than the kinetic product: addition of MeLi at -78°C in THF to $\text{MeO}(\text{C}_6\text{H}_{10})\text{CH}=\text{C}(\text{SnMe}_3)_2$ followed by immediate deuterolysis gives an *E/Z* product ratio of 59/41, while after only a few minutes only the *E*-organolithium reagent is present:



3. Spectroscopic characterisation of α -stannyvinylolithiums

In cases where the distannyalkene has a proton on the β - sp^2 carbon, characterisation of the vinylolithium by means of the chemical shift of this proton and by

TABLE 2

VINYL PROTON CHEMICAL SHIFTS (in ppm vs. TMS) AND TIN-PROTON COUPLING CONSTANTS (in Hz) FOR COMPOUNDS OF THE TYPE $\text{RCH}=\text{C}(\text{Li})\text{SnMe}_3$

R	Solvent	$\delta(=\text{CH})$	$^3J_{\text{cis}}(\text{Sn}, \text{H})$	$^3J_{\text{trans}}(\text{Sn}, \text{H})$
H	DME	7.10, 7.24 ^b	292	436
H	TMEDA	7.26, 7.31 ^b	297	448
Me	TMEDA	7.33	^c	436
n-Bu	THF	7.11	255	438
n-Bu	DME	7.17, 7.32	258	434
n-Bu	TMEDA	7.17	^c	442
c-Hex	TMEDA	6.92	^c	432
t-Bu	THF	7.31	273	^c
Me_2NCH_2	TMEDA	7.35	260	^c
EtOCMe_2	Et_2O	7.26	249	^c
EtOCMe_2	THF	7.30	264	^c
$\text{MeO}(\text{C}_6\text{H}_{10})$ ^a	THF	7.60	263	^b
Ph	THF	8.30	280	^c

$\delta(\text{SnCH}_3) - 0.1$ – 0.2 ppm, $^2J(\text{SnCH}_3)$ 38–40 Hz.

^a (1-Methoxy)-1-cyclohexyl. ^b $^2J(\text{H}, \text{H})$ 8 Hz. ^c Not observed.

TABLE 3

TIN-119 CHEMICAL SHIFTS (in ppm vs. internal Me_4Sn) FOR VINYLITHIUMS ^a OF THE TYPE $\text{RR}'\text{C}=\text{C}(\text{Li})\text{SnMe}_3$

R	R'	Solvent	$\delta(^{119}\text{Sn})$	
H	H	TMEDA	-64.8	
Me	H	TMEDA	^b	-87.9
n-Bu	H	THF	^b	-87.9
n-Bu	H	TMEDA	-54.2	-86.2
c-Hex	H	TMEDA	^b	-91.5
t-Bu	H	THF	-47.2	^b
Me_2NCH_2	H	TMEDA	-48.9	^b
$\text{MeO}(\text{C}_6\text{H}_{10})$ ^c	H	THF	-40.0	^b
Ph	H	THF	-40.7	^b
Me	Me	THF	-89.6	
Et	Me	THF	-86.5	-80.2
EtOCH_2	Me	THF	-75.1	^b
$\text{MeOCH}(\text{Me})$	Me	THF	-73.4	^b
Ph	Me	THF	-90.1	-86.7
Ph	CF_3	THF	-74.2	-69.8
Ph	Ph	THF	-83.6	
	c- C_4H_8	THF	-84.2	
	c- C_5H_{10}	THF	-88.0	
MeOCH_2	MeOCH_2	THF	-74.5	
$\text{MeOCH}_2\text{CH}_2$	MeOCH_2	THF	-74.3	-83.1

^a Vinylithium concentration: ca. 2 mol/l. ^b Not observed. ^c (1-Methoxy)-1-cyclohexyl.

TABLE 4

CARBON-13 NMR DATA FOR VINYLITHIUMS OF THE TYPE $\text{RCH}=\text{C}(\text{Li})\text{SnMe}_3$

($\delta(^{13}\text{C})$ in ppm vs. external $(\text{CD}_3)_2\text{C}=\text{O}$ = 207 ppm, $^1J(\text{Sn}, \text{C})$ (in brackets), in Hz. Vinylithium concentration ca. 2 mol/l, solvent THF.)

R	Z/E	$\delta(\text{SnMe}_3)$	$\delta(\text{C}(1))$	$\delta(\text{C}(2))$	$\delta(\text{C}(3))$	$\delta(\text{C}(4))$	$\delta(\text{C}(5))$	$\delta(\text{C}(6))$
H	-	-7.4 (202.5)	216.3	141.3				
Me	Z	-5.1	192.5	144.5	28.1			
n-Bu ^a	Z	-4.1 (188.7)	196.5	152.9 (89.9)	46.9 (196.9)	34.0 (12.5)	24.5	15.6
c-Hex	Z	-4.5 (184.5)	189.8	160.4 (91.6)	56.7 (184.1)	34.4 (13.9)	27.3	27.0
t-Bu	E	-8.3 (191.0)	^b	158.8	38.8	30.8		
Me_2NCH_2	E	-7.6 (202.5)	206.4	150.2	72.3 (208.1)	46.7		
$\text{EtO}(\text{CH}_3)_2\text{C}$	E	-8.7 (228.9)	193.7	162.3 (73.8)	82.5 (209.8)	27.1	58.9	16.4
$\text{MeO}(\text{c-C}_6\text{H}_{10})$	E	-8.4 (198.4)	200.3	155.4	82.6 (221.0)	36.0	27.0	24.4 ^d
Ph	E	-8.9 (180.8)	219.1	148.8 (71.2)	147.4 (265.8)	125.5	127.3	123.6

^a In TMEDA. ^b Not observed.

the $^3J(\text{Sn}-^1\text{H})$ coupling is simple and satisfactory. ^{119}Sn and ^{13}C NMR give additional information. Values of $^3J(\text{Sn}, \text{C})$ can be used as a basis for the assignment of the stereochemistry of compounds $\text{RR}'\text{C}=\text{C}(\text{Li})\text{SnMe}_3$, where proton NMR is no longer useful. The spectroscopic data obtained are to be found in Tables 2-5.

The values of $^3J(\text{Sn}, \text{H})$ (*trans* > *cis*, following the normal pattern) are extremely large (Table 2), reflecting the increase of electron density at the carbon bearing the lithium atom. This coupling is apparently not strongly solvent-dependent.

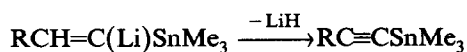
In compounds $\text{RCH}=\text{C}(\text{Li})\text{SnMe}_3$ the tin chemical shift (Table 3) is diagnostic of the geometry of the compound; replacement of the proton at the sp^2 carbon by an alkyl or aryl group leads to a δ -value similar to that of (*Z*)- $\text{RCH}=\text{C}(\text{Li})\text{SnMe}_3$, while the geometry of $\text{RR}'\text{C}=\text{C}(\text{Li})\text{SnMe}_3$ now has little effect on the tin chemical shift.

Several features of the ^{13}C data are worthy of note: firstly the low value of $^1J(\text{Sn}-\text{CH}_3)$, corresponding to the low value of $^2J(\text{Sn}-\text{CH}_3)$; secondly the extreme low-field shift (up to 70 ppm compared with the corresponding distannyl alkene) of the carbon atom bearing the lithium atom [8] (this signal is always broad, linewidth > 100 Hz, so that $^1J(\text{SnC})$ could not be determined); thirdly the extremely high value of $^2J(\text{SnC}=\text{C})$, which in stannyl alkenes is often near zero [9].

The geometry of the anionoid species is expected to be reflected by the values of $^3J(\text{Sn}, \text{C})$; however, Table 4 shows that these are not necessarily very different for the *E* and *Z* geometries. However, the pairs of values in Table 5 are sufficiently different to permit a reasonably unequivocal stereochemical assignment; they represent the only clearly diagnostic parameter for compounds $\text{RR}'\text{C}=\text{C}(\text{Li})\text{SnMe}_3$.

4. Decomposition of α -stannylvinylolithiums

The increase in the stability of the vinylolithiums on going from $\text{RCH}=\text{C}(\text{Li})\text{SnMe}_3$ to $\text{RR}'\text{C}=\text{C}(\text{Li})\text{SnMe}_3$ indicates that a β -elimination of lithium hydride may well be the primary decomposition pathway for $\text{RCH}=\text{C}(\text{Li})\text{SnMe}_3$ (as observed for other organolithiums [10,11]):



For $\text{R} = n\text{-Bu}$, however, the stannyl alkyne is not observed, but addition of Me_3SiCl to a decomposed sample of the vinylolithium yields the corresponding silyl alkyne $\text{RC}\equiv\text{CSiMe}_3$. Thus presumably transmetalation with MeLi present in equilibrium leads to the formation of $\text{RC}\equiv\text{CLi}$ and Me_4Sn (which is the sole organotin species observed apart from $\text{RCH}=(\text{SnMe}_3)_2$).

Variation of R appears to cause another elimination mechanism to come into play: thus for $\text{R} = \text{Ph}$ the primary elimination appears to be that of Me_3SnLi , which is observed by proton and ^{119}Sn NMR. Examination of the products of decomposition of $\text{Ph}_2\text{C}=\text{C}(\text{Li})\text{SnMe}_3$ showed the presence of 10% diphenylacetylene as well as Me_3SnLi ; this is consistent with an elimination of Me_3SnLi with either concomitant or subsequent phenyl migration.

It should be noted that decomposition reactions generally lead to the formation of polymeric organic products.

5. Reactions of α -stannylvinylolithiums

Trapping reactions of the vinylolithium reagents with several electrophiles have already been described [3] for the case of $\text{RCH}=\text{C}(\text{Li})\text{SnMe}_3$. Since preliminary

TABLE 5

CARBON-13 NMR DATA FOR COMPOUNDS OF THE TYPE $RR'C=C(Li)SnMe_3$ (Chemical shifts in ppm vs. external $(CD_3)_2C=O$ 207 ppm, $^1J(Sn, C)$ in brackets (in Hz). Vinyl lithium concentration ca. 2 mol/l, solvent THF.)

R	R'	E/Z	$\delta(SnMe_3)$	$\delta(C(1))$	$\delta(C(2))$	$\delta(C(3))$	$\delta(C(3'))$	$\delta(C(4))$	$\delta(C(4'))$	$\delta(C(5))$	$\delta(C(5'))$	$\delta(C(6))$
Me	Me	-	-6.0 (151.6)	^a	^a	^a	^a					
EtOCH ₂	Me	E	-6.3 (188.2)	188.2	142.7	81.0 (217.4)	28.4 (193.2)	66.4		15.2		
CH ₃ O(CH ₂)CH	Me	E	-6.5 (183.1)	189.7	147.8	86.9 (221.9)	29.34 (191.4)	19.7		55.4		
Ph	Me	E	-6.0 (158.2)	210.0	149.1	152.3 (198.4)	32.3 (198.4)	^b		^b		^b
Ph	Me	Z	-6.5 (173.4)	204.0	^a	154.4 (151.2)	32.4 (292.4)	^b		^b		^b
Ph	CF ₃	E	-7.5 (231.4)	^a	^a	147.1		129.5		127.9		125.4
Ph	Ph	-	-6.2 (197.1)	222.7	160.0	151.7 (227.2)	153.8 (147.5)	128.4 ^c	127.4 ^c	128.0 ^c	129.6 ^c	124.6
CH ₃ OCH ₂	CH ₃ OCH ₂	-	-6.3 (203.5)	200.0	143.5	82.7	81.1	58.1 ^c	55.4 ^c			
CH ₃ OCH ₂ CH ₂	CH ₃ OCH ₂	E	-6.4 (193.3)	192.3	143.9	75.4 (220.0)	47.8 (170.4)	57.7 ^c	68.3		57.4 ^c	

^a Not observed. ^b Not assigned. ^c Assignment uncertain.

investigations showed the reactivity of $RR'C=C(Li)SnMe_3$ to be similar, detailed studies of the reactions of these reagents with "organic" electrophiles were not carried out: however, those with "organometallic" electrophiles Me_3MCl ($M = Si, Ge, Pb$) were the subject of a more detailed study, the results of which will be presented in a separate communication [12].

Experimental

All manipulations involving organotin and organolithium reagents were carried out under argon. NMR spectra were recorded using Varian EM-360 (1H) and Bruker AM-300 (^{13}C , ^{119}Sn) spectrometers. Distannylalkenes were prepared as described previously [1,4]. α -Stannylvinylolithiums were prepared by dropwise addition of the distannylalkene in the required solvent to a solution of methylolithium in the same solvent at $-78^\circ C$. The molar ratio used was always 1/1; the scale of the experiments was normally 3–10 mmol, total solvent volume 3–8 ml. The progress of the reactions was monitored by proton NMR spectroscopy (at room temperature), and in addition (see Discussion and Table 1) by hydrolysis or deuterolysis. In the latter cases the organic phase was dried, the solvent removed and the hydrolysis/deuterolysis product subjected to NMR spectroscopy. In those cases where the experiments were carried out on a larger scale (10 mmol), the reaction products were distilled. The geometry of the hydrolysis/deuterolysis products was determined from $^3J(H, H)$, $^3J(H, D)$ and/or the value(s) of $^3J(Sn, C)$.

Boiling points and selected NMR data for these compounds are given in Table 6: all gave satisfactory elemental analysis data.

TABLE 6

BOILING POINTS AND SELECTED NMR DATA FOR PRODUCTS FROM DEUTEROLYSIS/HYDROLYSIS OF VINYLITHIUMS $RR'C=C(Li)SnMe_3$

R	R'	H/D	B.p. ($^\circ C/mmHg$)	E/Z	$\delta(=CH)$	$^3J(Sn, C)$	$\delta(^{119}Sn)$
EtOCMe ₂	H	H	^b	E	5.9, 6.1 ^c	67.4	-35.1
Me ₂ NCH ₂	H	D	65-75/12	E	5.9 ^d	73.7	-39.6
MeO(C ₆ H ₁₁) ^a	H	D	55/0.02	E	5.7 ^e	63.5	-36.2
				Z	6.6 ^f	^b	^b
Me	Me	H	42/12		5.4	42.5, 70.3	-58.8
Ph	Ph	H	126/0.02		6.8	29.6, 61.0	-48.0
Ph	Me	H	125/12	E	5.9	42.5, 65.0	-53.3
				Z	6.3	29.6, 64.7	-53.6
Ph	CF ₃	H	105/12	E	7.1	26.2, 73.0	-42.0
EtOCH ₂	Me	H	83-89/12	E	5.8	42.0, 68.7	-55.4
				Z	^b	^b	-62.2
MeOCH(Me)	Me	H	^b	E	6.4	42.5, 71.2	-55.8
				Z	^b	^b	-61.2
MeOCH ₂ CH ₂	Me	H	90/12	E	5.5	43.2, 64.9	-57.2
				Z	^b	^b	-63.0
MeOCH ₂	MeOCH ₂	H	100/12		6.2	28.9, 69.3	-58.0
MeOCH ₂ CH ₂	MeOCH ₂	H	^b	E	5.8	38.1, 67.4	-55.4
				Z	5.6	30.5, 64.8	-60.7

^a (1-Methoxy)-1-cyclohexyl. ^b Not determined. ^c $^3J(H, H)$ 19.5. ^d $^3J(H, D)$ 3, $^3J(H, Sn)$ 73. ^e $^3J(H, D)$ 3, $^3J(H, Sn)$ 81. ^f $^3J(H, D)$ <1, $^3J(H, Sn)$ 166 Hz.

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