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FORMATION OF α-SILYLVINYLLITHIUM REAGENTS: REACTIONS OF α-SILYL- AND α-STANNYL-VINYLLITHIUMS WITH ALDEHYDES AND KETONES *

TERENCE N. MITCHELL ** and WERNER REIMANN
Abteilung Chemie, Universität Dortmund, Postfach 500 500, 4600 Dortmund 50 (F.R.G.)

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Summary

The formation of α-trimethylsilylvinyllithium compounds from 1-trimethylsilyl-1-trimethylstannyl-1-alkenes have been studied and their stabilities investigated. α-Trimethylsilyl- and α-trimethylstannyl-vinyllithiums undergo 1,2-addition to aldehydes and non-enolisable ketones, to give silyl- or stannyl-substituted allylic alcohols; α,β-unsaturated ketones, however, undergo 1,4-addition to give homoallylic ketones.

Introduction

We recently reported [1] that 1,1-bis(trimethylstannyl)-1-alkenes readily undergo lithiodestannylation with methyllithium to give strongly basic α-stannylvinyllithiums:

$$RCH{=}C(SnMe_3)_2 + MeLi \rightleftharpoons Me_4Sn + \underset{(I)}{RCH{=}C(SnMe_3)Li} \qquad (1)$$

When R = Ph or t-Bu, only the (*E*)-isomer of I could be detected by means of NMR spectroscopy: reaction with methyl iodide gave only the corresponding (*E*)-monostannyl olefin. Reactions of I, R = Ph, with a number of electrophiles, including benzophenone, were described.

We now report on the reactions of I with a series of aldehydes and ketones and compare their reactivities with those of the corresponding α-trimethylsilylvinyllithiums $RCH{=}C(SiMe_3)Li$ (II), which have not previously been characterised spectroscopically, though Zweifel [2] has described some reactions involving their formation. Reactions of I and II with electrophiles yield organosilicon- and organo-

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* Taken from the Diplomarbeit of W. Reimann, Dortmund 1983.

** Correspondence author.

tin-substituted compounds which have considerable potential for use in organic synthesis, particularly if they can be prepared as pure stereoisomers.

Results and discussion

(a) Formation of precursors for II

Since hydrostannation of silylacetylenes $RC{\equiv}CSiMe_3$ occurs in a non-regiospecific manner (except for R = Ph, where the regioselectivity is appreciable) [3], we felt it necessary to examine the reaction of I with trimethylchlorosilane to see whether it is suitable for the regiospecific preparation of precursors for II:

$$\mathrm{I} + Me_3SiCl \rightarrow \underset{\substack{(\mathrm{III}) \\ \downarrow \mathrm{MeLi} \\ \mathrm{II}}}{RCH{=}C(SiMe_3)SnMe_3} \qquad (2)$$

Parallel to this study, the series of vinyllithiums of type I was also allowed to react at −78°C with two other electrophiles, MeOD and dimethyl sulphate, since quantitative assessments of the (E/Z) ratios in reactions of I were not available. The results of these trapping reactions according to eq. 3 are presented in Table 1.

$$\mathrm{I} + E{-}X \rightarrow LiX + (E/Z)\text{-}RCH{=}C(E)SnMe_3 \qquad (3)$$

It is clear that only (I) with R = Ph, reacts with a sufficient stereospecificity with a relatively unreactive electrophile such as Me_3SiCl to give a silylstannyl olefin suitable as a precursor for II, unless the latter in its turn undergoes ready and quantitative isomerisation to the (E) or (Z) form under the conditions of its formation. This point will be discussed below.

The deuterolysis experiments point to a further complication which must be taken into account: I is prepared from the distannyl olefin, and because of its limited thermal stability cannot be freed from tetramethyltin. Since eq. 1 is reversible, the electrophile can in principle react with the methyllithium rather than with I, in which case the distannyl olefin will be recovered.

(b) Formation and stability of II

The reaction of III, R = Ph, t-Bu, with methyllithium at −78°C in THF is quantitative: proton NMR spectroscopy at room temperature shows the presence of only one carbanionic species which is stable for 24 h. When R = Me, n-Bu or c-Hex (cyclohexyl) the situation is more complex.

As can be seen from Table 1, the starting material is in each case an (E/Z) mixture containing similar or equal amounts of both isomers. Addition of ca. 10 mol% of methyllithium at room temperature changes the (E/Z) ratio to ca. 90/10; a similar isomerisation has been described previously by Zweifel [2]:

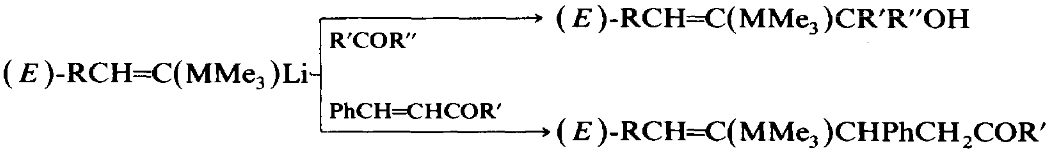
$$(E)\text{-}RCH{=}C(SiMe_3)I \xrightarrow[-78^\circ C]{BuLi} \underset{(\mathrm{II})}{(Z)\text{-}RCH{=}C(SiMe_3)Li} \xrightarrow{20^\circ C} \underset{(\mathrm{II})}{(E)\text{-}RCH{=}C(SiMe_3)Li}$$

Quenching of the anion mixture with water showed that at −78°C the (E/Z) ratio for II corresponded to that of the precursor, while irrespective of the stereochemistry of the latter the (E/Z) ratio at room temperature was 86/14 (±5%) (R = n-Bu, c-Hex, t-Bu). The reaction between III and methyllithium at −78°C in equimolar quantities leads to the formation of II: however, the reaction is not quantitative, (*Z*)-III remaining unchanged, as shown by NMR spectroscopy at room temperature. The product mixture in each case contains ca. 50% (*Z*)-III and 50% II, the latter (as will be shown below) in the (*E*)-form.

A decision as to whether II exists in the *E* or *Z* form cannot be made directly from the proton NMR spectrum, but only by quenching with an electrophile and identifying the species formed. This is done most readily using MeOD; deuterolysis at room temperature leads to the formation of (*E*)-RCH=CDSiMe$_3$, (*Z*)-III (for R=Me, c-Hex, n-Bu) remaining unchanged. Deuterolysis at −78°C gives only III for R = Me, c-Hex, n-Bu but for R = Ph (*E*)-PhCH=CDSiMe$_3$. Reaction with dimethyl sulphate gives for R = Ph and t-Bu $\geqslant$ 95% (*E*)-RCH=C(Me)SiMe$_3$; for R = Me, n-Bu and c-Hex the (*E*/*Z*) ratios are as given in Table 1.

(*c*) *Reactions of I and II with carbonyl compounds*

We treated vinyllithiums I and II with a series of aldehydes and ketones, including α,β-unsaturated compounds. While 1,2-addition occurs with all the aldehydes and aromatic ketones investigated, 1,4-addition takes place with α,β-unsaturated ketones:



$$(E)\text{-RCH=C(MMe}_3\text{)Li} \xrightarrow{\text{R'COR''}} (E)\text{-RCH=C(MMe}_3\text{)CR'R''OH}$$

$$(E)\text{-RCH=C(MMe}_3\text{)Li} \xrightarrow{\text{PhCH=CHCOR'}} (E)\text{-RCH=C(MMe}_3\text{)CHPhCH}_2\text{COR'}$$

Details are given in Table 2. R was in most cases Ph, but in three cases for comparison it was t-Bu; the yields were similar. Phenyl t-butyl ketone did not react, and enolisable ketones such as acetone or acetophenone gave only (*E*)-PHCH=CHMMe$_3$. The olefin stereochemistry was shown by proton NMR to be unchanged for the tin compounds: the values of ^3J(SnC=CH) were in each case ca. 70 Hz, typical for a *cis* coupling. Since the silyl carbanions also gave only one

TABLE 1

(*E*/*Z*) PRODUCT RATIO FOR REACTIONS OF VINYLLITHIUMS RCH=C(Li)MMe$_3$ (M = Sn, Si) WITH ELECTROPHILES AT −78°C (values for M = Si in parentheses)

R	Electrophile E–X		
	D–OMe	Me–OSO$_3$Me	Me$_3$Si–Cl
Me	80/20 [a] [b]	70/30 (40/60)	55/45 [c]
n-Bu	64/36 [a] [b]	65/35 (55/45)	55/45 [c]
c-Hex	56/44 [a] [b]	53/47 (66/34)	50/50 [c]
t-Bu	$\geqslant$95/$\leqslant$5 [c]	$\geqslant$95/$\leqslant$5 ($\geqslant$95/$\leqslant$5)	30/70 [c]
Ph	$\geqslant$95/$\leqslant$5 ($\geqslant$95/$\leqslant$5)	$\geqslant$95/$\leqslant$5 ($\geqslant$95/$\leqslant$5)	$\leqslant$5/$\geqslant$95 [c]

[a] Ca. 30% of the educt RCH=C(SnMe$_3$)$_2$ was reformed. [b] Only educt RCH=C(SiMe$_3$)SnMe$_3$ isolated. [c] Reaction not carried out.

TABLE 2

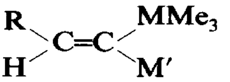
REACTIONS OF CARBONYL COMPOUNDS RCOR′ WITH VINYLLITHIUMS $R''CH{=}C(Li)MMe_3$ (M = Si,Sn)

R	R′	R″	M	Addition	M.p. (°C)	Yield (%)
H	H	Ph	Si	1,2	79	67
H	H	Ph	Sn	1,2	109	73
Me	H	Ph	Sn	1,2	[a]	81
Et	H	Ph	Sn	1,2	[a]	70
i-Pr	H	Ph	Sn	1,2	[a]	60
Ph	H	Ph	Sn	1,2	[a]	83
PhCH=CH	H	Ph	Si	1,2	62	68
PhCH=CH	H	Ph	Sn	1,2	[a]	65
MeCH=CH	H	Ph	Si	1,2	[a]	87
MeCH=CH	H	Ph	Sn	1,2	[a]	62
Ph	Ph	Ph	Si	1,2	73–75	91
Ph	Ph	Ph	Sn	1,2	88–90	75
Ph	Ph	t-Bu	Sn	1,2	119–122	70
Ph	o-$CH_3C_6H_4$	Ph	Sn	1,2	101–103	53
Ph	t-Bu	Ph	Sn	1,2		0
PhCH=CH	Ph	Ph	Si	1,4	85	86
PhCH=CH	Ph	Ph	Sn	1,4	[a]	72
PhCH=CH	Ph	t-Bu	Sn	1,4	63–65	85
PhCH=CH	t-Bu	Ph	Si	1,4	58–62	83
PhCH=CH	t-Bu	Ph	Sn	1,4	[a]	85
PhCH=CH	t-Bu	t-Bu	Sn	1,4	[a]	75

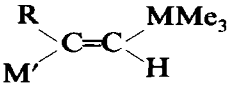
[a] Colourless viscous oil.

isomer, with an analogous proton chemical shift, this was also assumed to be the (*E*)-isomer.

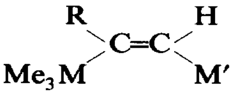
The reactions reported here provide a route to β-trimethylmetal-substituted allylic alcohols and to trimethylmetal-substituted homoallylic ketones. The organolithium species (*E*)-I and (*E*)-II complement other carbanionoids such as IV–VI which have been described previously:



(IV)



(V)



(VI)

Thus for example (*Z*)-IV (M = Si, M′ = MgBr, R = n-Bu) has been prepared by Sato et al. [4], its isomer (*E*)-IV (M = Si, M′ = Cu) by Obayashi et al. [5], V (M = Si, M′ = Li) by Boeckman and Bruza [6]. These authors have also reported the preparation of (*E*)-II (M = Si, R = Pr), while triphenylsilyl-substituted carbanionoids of type (*E*)-II were obtained by Brook and Duff [7] and by Westmijze et al. [8]. VI (M = Si, M′ = $CuSMe_2$, R = $(CH_2)_nX$ with $n = 1$–6, X = Cl, O) was reported by Piers and Chong [9].

Experimental

Starting materials were either commercial products or were prepared by published procedures. The following have not previously been reported: c-HexC≡$CSnMe_3$, b.p.

110°C/14 mmHg (88% yield, from c-HexC≡CH and Me_3SnNEt_2); c-HexCH=C($SnMe_3$)O_2, b.p. 52°C/0.005 mmHg (50% yield, from c-HexC≡CSnMe$_3$ and Me_3SnH). Satisfactory elemental analysis data were obtained for new compounds.

Reactions of I with electrophiles at −78°C

The procedure used was basically the same for the electrophiles MeOD, Me_2SO_4 and Me_3SiCl. A typical procedure for MeOD is given below.

To a solution (1 *M*) of methyllithium (0.12 g, 5.8 mmol) in THF at −78°C was slowly added a solution of 5.8 mmol of the distannylalkene in ca. 2 ml THF. The solution turned pale yellow (R = Me, n-Bu, c-Hex), pale green (t-Bu) or dark brown (R = Ph). After 2 h, 0.5 ml MeOD was added: the solution was decolorised immediately. The mixture was allowed to warm to room temperature and treated with 10 ml water. After the standard work-up, the solvent was removed and the residue distilled.

The products were identified and the isomer ratios determined by proton NMR spectroscopy using the olefinic proton and the value of its coupling constant to tin-119. Table 3 contains details of isolated product yields, boiling points and the relevant NMR data. The low product yields in the case of the reaction with MeOD are due to the isolation of ca. 30% distannylalkene and in general to losses during work-up and distillation; the reactions proceeded essentially quantitatively.

Formation of II from III

Vinyllithiums (II) were prepared by adding III to a solution of methyllithium in THF at −78°C. Product mixtures were characterised by proton NMR at room temperature. The NMR parameters for the vinyl proton of (*E*)-II are as follows: R = Me, 7.1 ppm, ^3J(HH) 5 Hz; R = n-Bu, 7.3 ppm, ^3J(HH) 6 Hz; R = c-Hex, 7.5 ppm, ^3J(HH) 6 Hz; R = t-Bu, 7.2 ppm; R = Ph, 8.2 ppm. The protons of the trimethylsilyl group absorb at −0.2 (Ph −0.1) ppm).

TABLE 3

DATA FOR PRODUCTS OF REACTIONS OF VINYLLITHIUMS RCH=C($SnMe_3$)Li WITH ELECTROPHILES

R	Electrophile	Yield (%)	B.p.(°C/mmHg)	δ (=CH) (ppm) [a]	$^3J(^{119}Sn–H)$ (Hz) [a]
Me	MeOD	15	140/760	5.9(6.5)	68(148)
Me	Me_2SO_4	30	46/14	5.7(6.0)	80(148)
Me	Me_3SiCl	43	80/14	6.6(6.8)	124(193)
n-Bu	MeOD	18	75/14	6.1(6.5)	78(150)
n-Bu	Me_2SO_4	48	105/14	5.6(6.1)	82(148)
n-Bu	Me_3SiCl	54	65/0.02	6.4(6.7)	125(194)
c-Hex	MeOD	20	100/14	5.9(6.3)	76(156)
c-Hex	Me_2SO_4	40	135/14	5.3(5.7)	83(152)
c-Hex	Me_3SiCl	42	80/0.02	6.2(6.4)	125(194)
t-Bu	Me_2SO_4	36	155/14	5.3	90
t-Bu	Me_3SiCl	40	50/0.01	6.5(6.9)	146(224)
Ph	MeOD	35	68/0.1	6.8	56
Ph	Me_2SO_4	40	79/0.03	6.7	80
Ph	Me_3SiCl	23	60/0.01	(7.9)	(182)

[a] NMR data for the (*Z*)-isomer in parentheses; solvent CCl_4.

Reactions of II with MeOD and Me_2SO_4

These were carried out as described above for I. Only II, with R = Ph, gave a product with MeOD; the yield was 39%, b.p. 90°C/14 mmHg. Proton NMR data: ($SiMe_3$) 0.1, (=CH) 6.9 ppm, ^3J(HD) 3 Hz. Table 4 gives details of the products of methylation with dimethyl sulphate. The stereochemistry of (*E*)-t-$BuCH{=}C(Me)SiMe_3$ was checked by treating it with concentrated HI; the product was identified by IR spectroscopy as (*Z*)-t-BuCH=CHMe: λ_{max} 1650, 1700 cm^{-1}.

(Continued on p. 171)

TABLE 4

DATA FOR PRODUCTS OF REACTIONS OF VINYLLITHIUMS $RCH{=}C(SiMe_3)Li$ WITH DIMETHYL SULPHATE [a]

R	Yield (%),	B.p. (°C/mmHg)	δ (=C*H*) (ppm)
Me	55	150/760	5.8(5.9)
n-Bu	53	65/14	5.7(5.9)
c-Hex	50	110/14	5.6(5.8)
t-Bu	30	[b]	5.6
Ph	71	110/14	6.8

[a] Reactants: 11.6 mmol $RCH{=}C(SiMe_3)SnMe_3$, 11.6 mmol MeLi in THF, 0.55 ml (5.9 mmol) Me_2SO_4. [b] Not determined. [c] Values for the (*Z*)-isomer in parentheses (in CCl_4).

TABLE 5

SELECTED PROTON NMR DATA FOR ALLYLIC ALCOHOLS (*Z*)-$RCH{=}C(MMe_3)CR'R''OH$ (M = Si, Sn) (in CCl_4)

R	R′	R″	δ(=C*H*) (ppm) [a]	^3J(SnH) (Hz)	δ (R′) (ppm) [a]
Ph	H	H	6.7(6.7)	80	4.4(4.4)
Ph	H	Me	6.6	84	5.0
Ph	H	Et	6.5	81	4.7
Ph	H	Pr	6.5	86	4.7
Ph	H	i-Pr	6.7	82	4.5
Ph	H	Ph	6.9	[b]	5.0
Ph	Ph	Ph	6.8	91	6.6–7.5
t-Bu	Ph	Ph	6.0	111	7.3
Ph	H	PhCH=CH	6.7(6.9)	[b]	5.4(5.4)
Ph	H	MeCH=CH	6.5(6.8)	80	5.3(5.2)

[a] Values for M = Si in parentheses. [b] Not determined because of line overlap.

TABLE 6

SELECTED PROTON NMR DATA [a] FOR HOMOALLYLIC KETONES (*E*)-$RCH{=}C(MMe_3)$-$CH_XR'CH_AH_BCOR''$ (M = Si, Sn) (in CCl_4; δ in ppm vs. TMS, *J* in Hz)

R	R′	R″	δ(=C*H*)	^3J(SnH)	δ(H_A)	δ(H_B)	δ(H_X)	^3J(AX)	^3J(BX)	^2J(AB)
Ph	Ph	Ph	6.7(6.9)	80	3.6(3.2)	3.0(2.7)	5.0(5.0)	8(8)	6(6)	15(16)
Ph	Ph	t-Bu	6.8(6.9)	80	3.4(3.5)	2.8(2.4)	5.1(4.8)	9(10)	5(4)	18(18)
t-Bu	Ph	Ph	5.5	85	3.6	2.8	5.1	11	6	17
t-Bu	Ph	t-Bu	5.6	87	3.4	2.6	5.1	10	4	18

[a] Values for M = Si in parentheses.

TABLE 7

SELECTED CARBON-13 NMR DATA[a] FOR ALLYLIC ALCOHOLS (E)-RCH=C(MMe$_3$)CR′R″OH (M = Si, Sn) (in CDCl$_3$; δ in ppm vs. TMS, J in Hz)

R	R′	R″	δ(SnMe$_3$)	δ(C(1))	δ(C(2))	δ(C(2′))	δ(C(3))
Ph	H	H	−8.3[−0.8] (351)	152.1[144.2] [b]	137.0[139.7] (30)	64.6[61.8] (18)	138.0[139.7] [b]
Ph	Me	H	−7.7 (346)	156.1 (462)	136.0 (32)	68.2 (18)	137.7 (72)
Ph	Et	H	−7.7 (356)	155.1 (462)	139.6 (34)	73.9 (18)	137.1 (73)
Ph	i-Pr	H	−7.5 (346)	153.7 (461)	138.9 (32)	77.3 (21)	138.2 (73)
Ph	Ph	H	−8.0 (347)	152.7 (455)	138.6 [c]	73.0 (18)	137.5 (69)
Ph	Ph	Ph	−7.0[1.2] (350)	158.5[152.1] (476)	138.4[139.8] (29)	83.9[83.9] (27)	137.4[138.4] (73)
Ph	Ph	o-Tol	−7.1 (348)	157.2 (474)	137.4 (32)	85.1 (30)	137.3 [b]
t-Bu	Ph	Ph	−6.5 (343)	151.3 (517)	150.2 (23)	83.7 (34)	36.1 (69)
Ph	PhCH=CH	H	−7.8[0.6] (348)	152.8[146.2] (466)	137.2[138.7] [c]	72.3[72.6] (16)	137.6[137.8] [c]
Ph	MeCH=CH	H	−7.7[0.6]	152.1[146.7]	137.5[139.0]	72.2[72.2]	136.6[137.5]

[a] Coupling constants $^nJ(^{13}C-^{119}Sn)$ in parentheses, chemical shifts for M = Si in square brackets. [b] Not determined. [c] Not measurable because of line overlapping.

Numbering of carbon atoms is as follows:

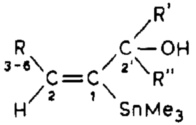


TABLE 8

SELECTED CARBON-13 NMR DATA FOR HOMOALLYLIC KETONES $RCH{=}C(MMe_3)CHR'CH_2COR''$ (M = Si, Sn) (δ in ppm vs. TMS, J in Hz)

R	R′	R″	δ(MMe₃)	δ(C(1))	δ(C(2))	δ(C(3))	δ(C(2′))	δ(C(3′))	δ(C(4′))
Ph	Ph	Ph	−7.9[0.5] (341)	152.1[147.0] (462)	138.3[139.8] [b]	137.8[138.4] [b]	42.9[41.0] (32)	42.9[42.6]	198.5[197.8]
Ph	Ph	t-Bu	−7.7[0.3] (338)	152.9[147.1] (473)	138.2[139.0] [b]	138.2[138.3] (69)	42.4[39.8] [b]	41.3[40.6]	211.7[212.0]
t-Bu	Ph	Ph	−7.4 (342)	148.0 (485)	149.3 (28)	35.2 (66)	41.8 (36)	43.4	197.5
t-Bu	Ph	t-Bu	−7.8 (332)	148.4 (497)	148.4 (30)	34.7 (68)	40.8 (37)	41.8	211.0

[a] Coupling constants $^nJ(^{13}C-^{119}Sn)$ in parentheses, chemical shift values for M = Si in square brackets. [b] Not determined because of line overlapping. Numbering of carbon atoms as follows:

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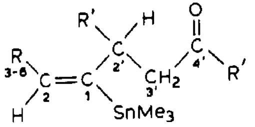

Since the protolysis reaction occurs with retention of configuration [10], the silyl alkene formed is the (*E*)-isomer.

Reactions of I and II with carbonyl compounds

I and II (generally 5.8 or 11.6 mmol) were prepared as solutions in THF at −78°C as described above and treated with an equimolar amount of the relevant carbonyl compound. The reactions were considered to be complete when the reaction mixture become colourless. After hydrolytic work-up, the solvent was removed to leave colourless crystalline compounds or viscous oils; the latter were not distilled, since a trial distillation led to decomposition. Solids were recrystallised from n-hexane. Details of yields and melting points are given in Table 2. Products were characterised by proton and carbon-13 NMR spectroscopy, and in addition in a number of cases by mass spectrometry. Selected NMR data are contained in Tables 5–8.

Acknowledgement

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