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Rearrangements of silyl- and stannyl-substituted diallyl ethers: competition between the allyl-vinyl ether rearrangement and the [2,3] Wittig sigmatropic rearrangement

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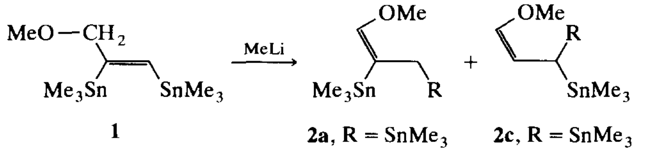
Abstract

Diallyl ethers containing two trimethylstannyl moieties or one triorganostannyl and one trimethylsilyl moiety attached to the olefinic carbon atoms of one allyl group can undergo either an allyl-vinyl ether rearrangement or a [2,3] Wittig sigmatropic rearrangement when treated with a strong non-nucleophilic base. While the use of lithium diisopropylamide favours the Wittig rearrangement, lithium diethylamide can shift the course of reaction towards the allyl–vinyl ether rearrangement.

Keywords: Silicon; Tin; Allyl–vinyl ether rearrangement; Wittig rearrangement

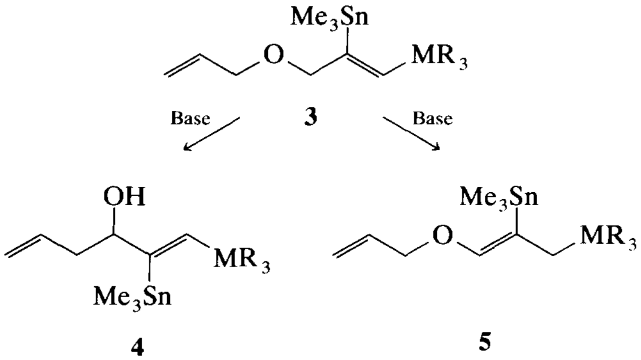
1. Introduction

In experiments directed towards the methyllithium-induced lithiodestannylation of the ether **1** obtained by palladium-catalysed addition of hexamethylditin to methyl propargyl ether we observed an unexpected reaction. Rather than undergoing lithiodestannylation the allyl methyl ether **1** was mainly converted to the methyl vinyl ether **2a**; as well as tetramethyltin (about 35%), three other byproducts were formed:



1 **2a**, R = SnMe$_3$ **2b**, R = H **2c**, R = SnMe$_3$ **2d**, R = H

Replacement of methyllithium by lithium diisopropylamide (LDA) led to the formation of **2a** as the sole product. While in the case of alkyl allyl ethers such as **1** there is no energetically comparable alternative to the observed allyl–vinyl ether rearrangement, the same is not true for diallyl ethers of the type **3** containing tin and/or silicon substituents. The latter can in principle undergo the well-known [2,3] Wittig sigmatropic rearrangement [1] to give **4** as well as the allyl–vinyl ether rearrangement [2] to give **5**:



3 **4** **5**

While diallyl ethers of the type shown above have not previously been shown to undergo the [2,3] Wittig reaction, one example of the rearrangement of a monosilyl diallyl ether has been described [3]; tin-containing ethers have so far only been used to generate the initial carbanion via tin–lithium exchange [4–7].

The present paper reports initial investigations carried out to determine the course of reaction preferred by diallyl ethers containing either one or two stannyl substituents or one silyl and one stannyl substituent.

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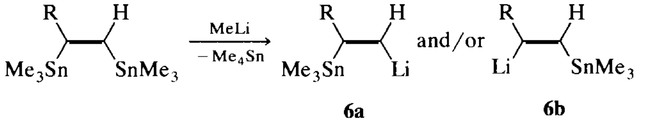
2. Results and discussion

2.1. The preliminary studies

The reaction between alkyllithiums and vinyltins to give vinyllithium reagents is a "classical" and synthetically often extremely useful synthetic procedure [8]. We therefore expected that the distannyl olefins obtained from palladium-catalysed addition reactions between hexamethylditin and 1-alkynes should also be subject to this type of reaction:



The situation is complicated in this case by the possibility of the formation of two regioisomeric organolithiums **6a** and **6b**, an additional complication is provided by the necessity of using *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) as solvent rather than ether or tetrahydrofuran (THF), which suffice in the case of monostannyl olefins. While in the case where R = Ph mesomeric stabilization by the phenyl group directs the lithiodestannylation towards the vinyllithium **6b**, the presence of substituents CR′R″OH leads after hydrolysis to the formation of products derived from both **6a** and **6b**. However, the presence of such substituents demands the use of at least two equivalents of methyllithium, and in addition it is necessary to remove the volatile tetramethyltin in vacuo in order to shift the transmetallation reaction to the right. We therefore transferred our attention to the distannyl olefin obtained from methyl propargyl ether. In spite of the presence of the ether functionality which could help in the complexation of the vinyllithium transmetallation product, no reaction occurred in THF. Replacement of THF by TMEDA led to a relatively complex reaction which could be controlled in such a manner that the major product was that of an allyl–vinyl ether rearrangement (**1** → **2**).

In spite of considerable attempts [9,10] we were unable to provide a complete mechanistic rationale for this process and therefore studied the action of various other bases. LDA was found to be an ideal base for carrying out the allyl-vinyl ether rearrangement even when used in only catalytic amounts.

This positive result led us to vary the nature of the second ether functionality. No reaction was observed in the case of the corresponding phenyl allyl ether [11] and we therefore decided to turn to diallyl ethers.

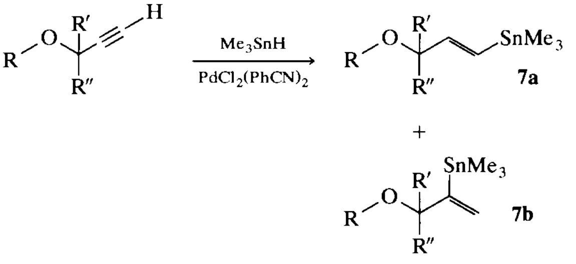
2.2. Preparation and reactions of monostannyl bisallyl ethers

Free-radical hydrostannylation of allyl propargyl ethers leads to mixtures of a total of six products [11].

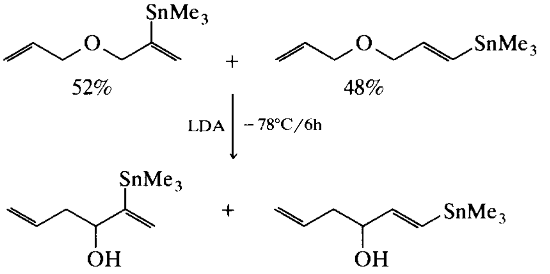
Table 1
Products of palladium-catalysed hydrostannylation of propargylic ethers $RCH_2OCR'R''C{\equiv}CH$

R	R′	R″	Yield (%)	Boiling point (°C (Torr))	**7a**:**7b** ratio
$H_2C{=}CH$	H	CH_3	75	47 (0.1)	48:52
E-$CH_3CH{=}CH$	H	H	65	60 (0.3)	45:55
$H_2C{=}CH$	H	CH_3	73	40 (0.04)	89:11
$H_2C{=}CH$	CH_3	CH_3	75	42 (0.01)	100:0
$PhCH_2$	H	H	80	83 (0.02)	37:63
$PhCH_2$	H	CH_3	82	90 (0.03)	80:20
$PhCH_2$	CH_3	CH_3	83	105 (0.09)	100:0

In contrast, the palladium-catalysed reaction as described by Zhang et al. [12] proceeds with good yields (65–83%); however, only in two cases was a clean reaction observed:



Details of the product distribution are given in Table 1. Our initial investigations were carried out with isomer mixtures using LDA as the base. The 1:1 mixture of E-1- and 2-trimethylstannyl-3-(2-propenyloxy)-1-propene was completely consumed after 6 h at room temperature (at −78°C, consumption was only 75% after 6 h); the products were the corresponding 1,5-hexadienols:



The use of *E*-2-butenyloxy rather than propenyloxy derivatives made it clear that the Wittig process is occurring; again the reaction could be carried out at room temperature without the occurrence of side reactions:

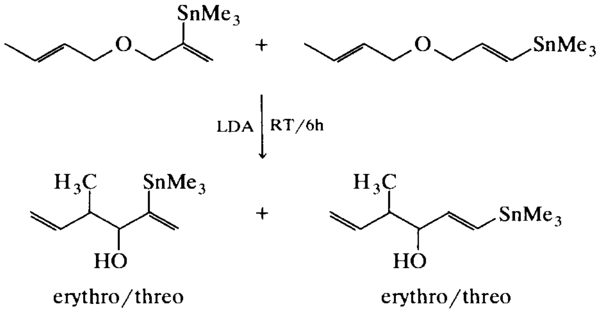


Table 2

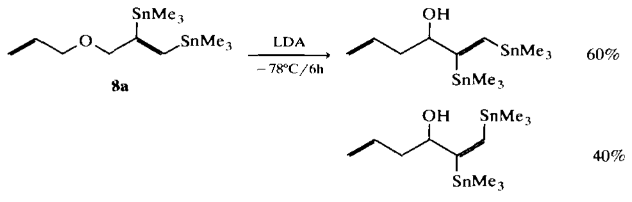
Products of palladium-catalysed addition of Me_3SnMMe_3 (M = Sn or Si) to propargylic ethers $RCH_2OCHR'C{\equiv}CH$

M	R	R′	Conditions		Yield (%)	Boiling point (°C (Torr))
			Temperature (°C)	Time (h)		
Sn	CH_2=CH	H	70	19	85	75 (0.001)
Sn	*E*-MeCH=CH	H	65	24	71	70 (0.001)
Sn	CH_2=CH	Me	80	14	10	78 (0.001)
Sn	$PhCH_2$	H	70	8	78	125 (0.001)
Sn	$PhCH_2$	Me	70	106	21	152 (0.001)
Si	CH_2=CH	H	80	39	69	57 (0.001)
Si	*E*-MeCH=CH	H	80	39	71	75 (0.025)

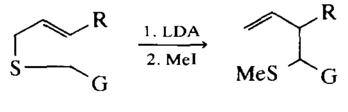
The three benzyl allyl ethers referred to in Table 1 were unreactive towards LDA. Thus at this stage it was clear that the [2,3] shift is a viable alternative to the allyl–vinyl ether shift under appropriate conditions, but that the monostannyl ethers are not preparatively useful. We thus turned our attention to the corresponding distannyl ethers.

2.3. Formation and reactions of distannyl ethers

The addition of hexamethylditin to allyl propargyl ethers affords (*Z*)-1,2-bis(trimethylstannyl)-3-alkoxy-1-propenes [13]. Table 2 gives details of the compounds **8** prepared in this manner. In the simplest case, that of the propenyloxy derivative, the reaction with LDA is 90% complete after 1 h and complete after 6 h at room temperature; the [2,3] Wittig rearrangement appears to have occurred, but is accompanied by a *Z*-to-*E* rearrangement at the tin-carrying double bond, so that two products are formed in the ratio of 60:40 (at −78°C the reaction is only 65% complete after 6 h but the *E*:*Z* ratio is 50:50):

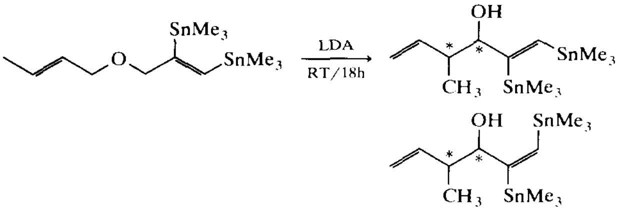


The corresponding butenyloxy compound reacts much more slowly; after 18 h at room temperature, only 58% of the starting material have been consumed, and heating at 45°C for 60 h has no noticeable effect on the progress of the reaction. This behaviour reflects the observation reported by Nakai and Mikami [1] that in the case of related thioethers the crotyl compound reacts more slowly than the allyl compound:

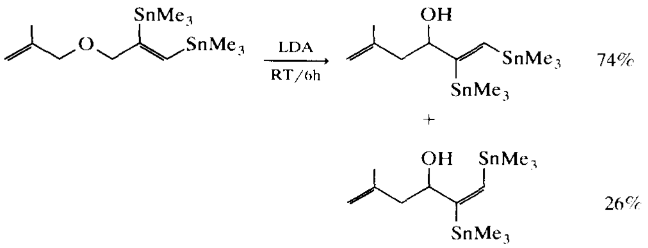


G = CO_2Et, CN

The [2,3] Wittig rearrangement is again accompanied by a *Z*/*E* isomerization, so that a total of four products in formed:



The introduction of a methyl group in the α position of the bisstannylpropenyl residue (**8c**) blocks the reaction with LDA completely, while the presence of a methyl group in the β position of the tin-free allyl group has no great effect (reaction complete after 6 h at room temperature (RT):

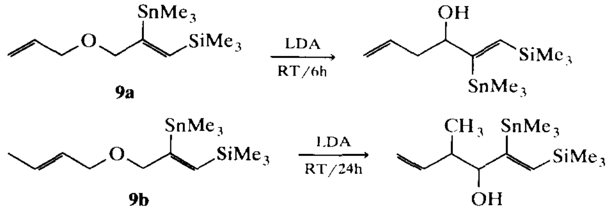


The behaviour of the benzyl ethers **8d** and **8e** is complex, leading to as yet unidentified products.

It appears that again the [2,3] Wittig reaction can be carried out without difficulty; however, the *Z*-to-*E* isomerization provides an extremely negative feature as far as preparative applications are concerned. While it seemed unlikely that replacement of one of the stannyl residues by a silyl residue would have any great effect, we decided to study the analogous silylstannyl ethers.

2.4. Formation and reactions of silylstannyl ethers

The palladium-catalysed reaction between Me_3Sn-$SiMe_3$ and allyl propargyl ethers also occurs readily [14]. We thus prepared the two silylstannylsubstituted ethers **9a** and **9b** corresponding to **8a** and **8b** above (for details see Table 2) and allowed them to react with LDA at room temperature. The reactions were complete after 6 and 24 h respectively and occurred in the expected manner:



The silylstannyl ethers are apparently more reactive than the distannyl ethers, since the crotyl compound is consumed quantitatively; there is no tendency towards *Z*/*E* isomerization of the silylstannylalkene unit.

Table 3
Selected NMR data [a] for diallyl ethers of the type $RCH{=}CHCH_2OC(3)R'_2C(2)(Sn(2)Me_3){=}CH(1)(Sn(1)Me_3)$

R	R′	$\delta(Sn(2))$ (ppm)) (^3J(Sn,Sn) (Hz))	$\delta(Sn(1))$ (ppm)	$\delta(C(1))$ (ppm) (^1J(Sn,C), ^2J(Sn,C) (Hz))	$\delta(C(2))$ (ppm) (^1J(Sn,C), ^2J(Sn,C) (Hz))	$\delta(C(3))$ (ppm) (^2J(Sn,C), ^3J(Sn,C) (Hz))	$\delta(C(1)H)$ (ppm) (^2J(Sn,H), ^3J(Sn,H) (Hz))	$\delta(C(3)H)$ (ppm) (^3J(Sn,H) (Hz))
H	H, H	−49.6 (362)	−60.0	144.5 (492, 66)	165.2 (488, 37)	82.1 (56, 107)	6.92 (82, 182)	4.20 40
E-Me	H, H	−49.7 (366)	−59.9	144.4 (496, 68)	165.3 (491, 36)	81.8 (587, 107)	6.91 (83, 192)	4.09 40
H	Me, H	−55.9 (378)	−60.3	142.7 (493, 66)	172.1 (ND [b], 32)	87.3 (51, 101)	6.77 (79, 194)	3.95 ND [b]
$PhCH_2$	H, H	−49.1 (362)	−59.6	144.8 (493, 64)	165.1 (488, 38)	82.3 (58, 107)	7.09 (84, 183)	4.23 39
$PhCH_2$	Me, Me	−58.5 (432)	−58.9	138.8 (506, 71)	177.2 (501, 33)	82.6 (41, 97)	6.85 (72, 209)	–

[a] For solutions in $CDCl_3$; δ vs. tetramethylsilane or Me_4Sn.

[b] ND, not determined.

Table 4
Selected ^{119}Sn, ^{29}Si and ^{13}C NMR data [a] for 1,5-hexadiene-3-ols formed in [2,3] Wittig rearrangement of diallyl ethers

Substituents (E/Z)	Δ(SnMe$_3$) (ppm) (^3J(Sn,Sn) (Hz))	δ(SiMe$_3$) (ppm) (^3J(Si,Sn) (Hz))	δ(C(1)) (ppm) (^nJ(Sn,C) (Hz))	δ(C(2)) (ppm) (^nJ(Sn,C) (Hz))	δ(C(3)) (ppm) (^nJ(Sn,C) (Hz))	δ(C(4)) (ppm)	δ(C(5)) (ppm)	δ(C(6)) (ppm)
2-SnMe$_3$	−35.5		122.9	159.1	77.3 (66.9)	42.4	134.3	117.2
1-SnMe$_3$(E)	−37.1		127.8	149.8 (443.8)	73.6 (34.3)	41.4	134.6	117.1
2-SnMe$_3$,4-Me	−36.2, −37.0		123.6, 124.8	158.4, 157.7 (443.8)	82.2, 81.1 (29.3, 35.6)	43.0, 44.0	140.3, 140.1	115.9
1-SnMe$_3$(E),4-Me	−36.7, −37.6		128.7, 129.3 (452.5, 459.3)	148.4, 147.1	77.9, 77.5	43.2, 43.4	140.3, 141.2	114.5
1,2-SnMe$_3$(Z)	−53.9, −58.1 (376)		141.4 (497.2, 67.4)	170.9 (490.8, 36.9)	81.4 (57.2, 99.2)	42.9	134.7	117.8
1,2-SnMe$_3$(E)	−47.4, −67.5 (852)		140.7 (443.8, 12.7)	170.2 (ND [b], 39.4)	78.8 (63.6, ND [b])	42.2	134.6	118.1
1,2-SnMe$_3$(Z),4-Me	−54.8, −58.8 (393)		140.5	165.6	82.1	42.7	129.8	116.8
	−56.1, −60.6 (376)		141.5	168.3	87.2	45.8	127.3	114.9
1,2-SnMe$_3$(E),4-Me	−47.1, −65.6 (850)		140.4	167.3	83.5	43.8	126.4	116.6
	−47.8, −68.5 (891)		141.5	168.9	84.2	44.5	127.0	114.3
1-SiMe$_3$,2-SnMe$_3$(Z)	−57.7	−9.8 (39.2)	140.7 (61.0)	168.3 (447.6)	81.2 (56.0)	41.9	134.2	117.5
1-SiMe$_3$,2-SnMe$_3$(Z),4-Me	−57.5	−9.7 (40.6)	141.5 (63.6)	167.1 (450.1)	87.1 (53.4)	43.5	140.2	114.1
	−59.9	−10.1 (40.6)	143.9 (63.6)	167.1 (450.1)	84.8 (53.4)	42.4	140.2	116.6

[a] For solutions in CDCl$_3$; δ vs. tetramethylsilane or Me$_4$Sn.

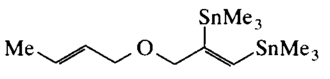
[b] ND, not determined.

It is therefore clear at this stage that the silylstannyl ethers show the greatest potential for synthetic work; however, the problem of the formation of two diastereomers must still be solved.

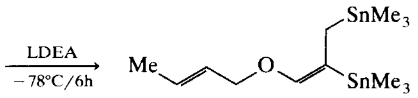
2.5. The effect of replacement of lithium diisopropylamide by lithium diethylamide

Since we observed that reactions can be sluggish or non-existent when LDA is used as the base we decided to explore the use of a less hindered but still non-nucleophilic base, lithium diethylamide (LDEA).

The *E*-crotyl distannyl ether **8b** was allowed to react with LDEA at −78°C for 6 h. Surprisingly there was no Wittig rearrangement but instead 60% conversion of the distannylallyl moiety to a distannylvinyl moiety:

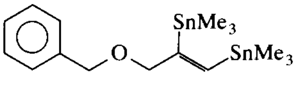


8b

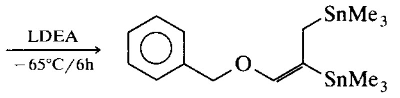


At −40°C the reaction is complete after 6 h, but a further temperature increase leads to the partial formation of the products of the [2,3] Wittig reaction; at RT this reaction dominates, only 11% of the product mixture coming from the allyl vinyl ether rearrangement.

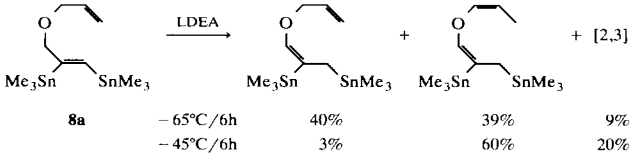
The corresponding benzyloxy ether **8d** undergoes complete conversion to the vinyl ether after 6 h at −65°C:



8d



The unsubstituted allyl distannylallyl ether **8a** behaves in a rather complex manner, since both allylic residues are able to undergo an allyl–vinyl ether rearrangement; in addition the [2,3] rearrangement occurs to a small extent. There is a considerable temperature dependence:



While at −65°C double and single allyl–vinyl shifts compete, the double shift predominates at −45°C; NMR spectra show that at −65°C after 45 min only the allyl–vinyl shift in the stannylated allyl residue has taken place (20% conversion), however, the product mixture obtained after 6 h at −65°C does not react further even after 24 h at RT.

It is apparent at this stage that the nature of the base plays an unexpectedly vital part in determining the course of the reaction and thus the nature of the products. Future investigations must therefore be concerned not only with the nature of the ether substrate but also with variations in the size of the base and in the reaction temperature. The way to useful synthetic applications appears open.

3. Experimental details

All manipulations involving organotin compounds were carried out under argon. NMR spectra were recorded for solutions in CDCl$_3$ using Bruker AM-300 or AC-200 spectrometers. All new organotin compounds have been characterized by multinuclear NMR spectroscopy; details are to be found in Tables 3–5.

3.1. Reaction of Z-1,2-bis(trimethylstannyl)-3-methoxy-1-propene with MeLi–H$_2$O

A solution of MeLi (10 mmol) in TMEDA was prepared by removing the solvent from a solution in ether and adding TMEDA to the dry methyllithium. The solution was cooled to −78°C and treated with the distannyl alkene (4.0 g, 10 mmol) in TMEDA (5 ml). The reaction mixture was allowed to warm to 0°C.

Table 5
Selected ^{119}Sn and ^{13}C NMR data [a] for allyl vinyl ethers RCH$_2$OC(1)H=C(2)(Sn(1)Me$_3$)C(3)H$_2$Sn(2)Me$_3$ formed from diallyl ethers

R	δ(Sn(1)) (ppm) (^3J(Sn,Sn) (Hz))	δ(Sn(2)) (ppm)	δ(C(1)) (ppm) (^nJ(Sn,C) (Hz))	δ(C(2)) (ppm) (^nJ(Sn,C) (Hz))	δ(C(3)) (ppm) (^nJ(Sn,C) (Hz))
H$_2$C=CH	−22.1	−8.5	144.4	113.1	13.9
	(146)		(48.4, 91.6)	(478.0, 56.0)	(312.8, 28.0)
E-MeCH=CH	−21.2	−6.4	142.1	115.6	14.0
	(120)		(49.6, 97.9)	(464.1, 53.4)	(302.6, 25.4)
PhCH$_2$	−22.2	−9.0	144.6	113.8	14.1
	(140)		(49.6, 94.0)	(483.2, 57.2)	(310.2, 28.0)

[a] For solutions in CDCl$_3$; δ vs. tetramethylsilane or Me$_4$Sn.

Me_4Sn, contaminated with some TMEDA, was removed under reduced pressure; the maximum amount obtained was 3.5 mmol (35%). Quenching of the reaction mixture with water (5 ml) at 0°C followed by a standard work-up gave a mixture of four products (gas–liquid chromatography); these were identified by multinuclear NMR as *E*-2,3-bis(trimethylstannyl)-1-methoxy-1-propene (**2a**) (56%), *Z*-3,3-bis(trimethylstannyl)-1-methoxy-1-propene (**2b**) (12%), *E*-2-trimethylstannyl-1-methoxy-1-propene (**2c**) (6%) and *Z*-3-trimethylstannyl-1-methoxy-1-propene (**2d**) (2%).

3.2. Reaction of Z-1,2-bis(trimethylstannyl)-3-methoxy-1-propene with MeLi–H_2O

A solution of BuLi (12 mmol) in *n*-hexane (8 ml) was diluted with THF (10 ml) and treated at room temperature with $^{i}Pr_2NH$ (1.2 g, 10 mmol). After stirring for 2 h, the distannyl alkene (4.0 g, 10 mmol) in TMEDA (6 ml) was added dropwise at RT, the reaction mixture turning brown. After 30 min, water (10 ml) was added. Standard work-up afforded diisopropylamine and *E*-2,3-bis(trimethylstannyl)-1-methoxy-1-propene (**2a**) as the sole organotin product.

3.3. Reactions involving lithium diisopropylamide or lithium diethylamine

All reactions in which LDA or LDEA were used as based were also carried out according to the following general procedure.

Diisopropylamine or diethylamine (3.6 mmol) was diluted with THF (10 ml) and treated at the reaction temperature required with a solution of butyllithium (3.6 mmol) in *n*-hexane. After stirring for 0.5 h, the organotin substrate (3.0 mmol) in THF (5 ml) was added, the colour of the reaction mixture darkening immediately. The reaction was stirred for 6 h (unless otherwise stated in the discussion) and then hydrolysed with 10 ml water. The reaction mixture lightened in colour immediately, it was extracted with ether (3 × 10 ml) and the combined organic phases were dried over $MgSO_4$. After filtration, the volatile materials were removed at the water pump and the residue analysed by multinuclear NMR spectroscopy.

Acknowledgements

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