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1,4-Silyl Migration from Oxygen to Carbon in Silyl Allyl Ethers: Kinetic and Thermodynamic Factors

Terence N. Mitchell* and Marc Schütze

Fachbereich Chemie, Universität Dortmund, Otto-Hahn-Straße, D-44221 Dortmund, Germany

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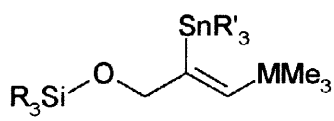
Abstract

The lithium amide-induced rearrangement reactions of silyl allyl ethers bearing two organometal(loid) residues on the vinylic carbon atoms have been studied as a function of various parameters: metal(loid) groups, base, silyl moiety, base concentration, reaction time and temperature. Kinetic and thermodynamic effects are discussed. It is often possible using the appropriate conditions to select either one of the two possible reaction processes (1,4-silyl migration and 1,3-hydrogen migration). © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: rearrangement; silyl allyl ethers; lithium amide; organometal(loid)

Introduction

While 1,4-migration of a silyl moiety from oxygen to carbon is not unknown, relatively few examples have been reported previously [1-5]. We have recently been concerned with [2,3]-Wittig [6] and related rearrangements [7] of diallyl ethers in which one of the allyl groups contains either two stannyl moieties or one silyl and one stannyl moiety at the two vinylic centres and have now included this work to include reactions in which a series of related allyl silyl ethers **1** and **2** (R_3 as defined below) react with lithium amides [8].



1, R' = Me, M = Sn
2, R' = Bu, M = Si

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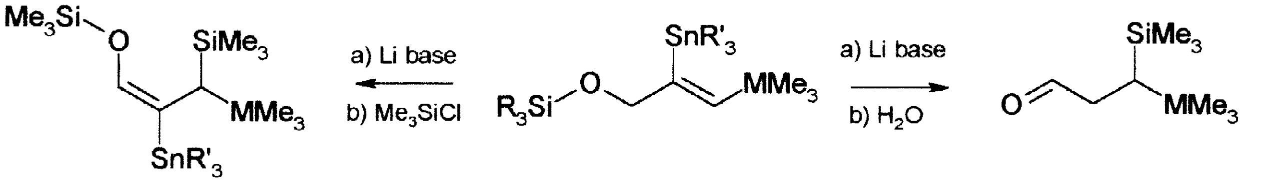
Results and Discussion

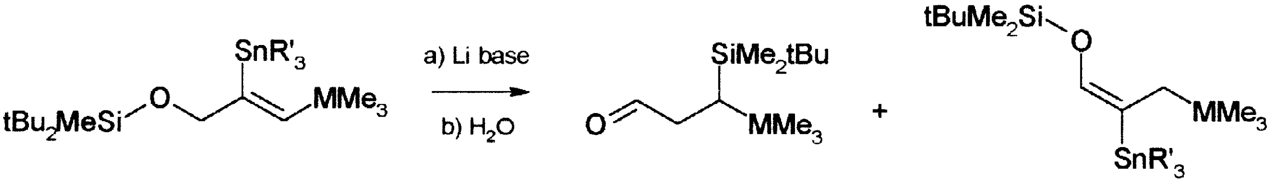
Deprotonation of **1** or **2** is expected to occur α to oxygen to afford a resonance-stabilised anion, so that in principle either 1,2- or 1,4-migration could be observed. A 1,4-migration would lead to formal replacement of hydrogen by an organometallic moiety to afford a new bimetallic centre. We initially treated **1a** and **2a** (R = Me) with either LDA or LTMP (lithium 2,2,6,6-tetramethylpiperidide) at room temperature; after quenching the reaction mixture with either Me_3SiCl, silyl enol ethers **3a** and **4a** were obtained in quantitative yield: thus only 1,4-migration took place.

If the intermediate enolate was not quenched in this manner but subjected to a standard aqueous workup the products were aldehydes **5a** and **6a**; thus hydrolytic workup is accompanied by loss of the relatively labile stannyl residue.



3a **1a** **5a**
4a **2a** **6a**

Since recent related work by Lautens [5] involved 1,4-migration of a t-butyldimethylsilyl group to a carbanionic centre generated by transmetallation of a tributylstannyl group with lithium, thus leading to indirect substitution of a stannyl by a silyl moiety, we next turned our attention to the silyl allyl ethers **1b** and **2b**. Here the behaviour pattern was quite different: using LDEA (lithium diethylamide) at room temperature (**1b**) or –30°C (**2b**) the only reaction observed was quantitative conversion of the allyl ether to the corresponding enol ethers **7b** and **8b**, i.e. a simple 1,3-hydrogen shift. However, with LDA at room temperature and after the usual workup 55:45 mixtures of the aldehydes **5b** or **6b** and the silyl enol ethers **7b** or **8b** were obtained. It thus appeared that as in the case of our earlier studies on diallyl ethers [6] two possible reaction pathways lie energetically very close together, the nature of the base determining the mode of reaction. Only the E-enol ether was observed in each case as shown by NMR spectroscopy, the three-bond coupling between the vinylic proton and the vinylic tin lying close to 35 Hz.



1b **5b** **7b**
2b **6b** **8b**

We thus felt it necessary to extend our work in order to shed more light on the importance of the various factors involved (base, silyl moiety, reaction time).

A combination of factors will affect the reactivity of the three bases used:

a) their basicity (pK_S: LDEA 31.7, LDA 34.4, LTMP 37.0 [9])
b) steric factors: we can assume that all three bases are dimeric under the reaction conditions chosen [10-13], but that the increasing size of the organic moieties leads to a clear decrease in reactivity on going from LDEA to LDA
c) „kinetic" factors: Ahlbrecht [9] has characterised LDEA as a „fast" base.
d) Because of the dimeric nature of the bases, lithiodeprotonation of the allyl ether may initially lead to a complex between the base itself and the free amine or (perhaps more likely) to an aggregate consisting of base, amine and lithiated allyl ether. Reprotonation can occur via the complex or within the aggregate. This was demonstrated earlier by Kwetkat [14], who allowed Z-1,2-bis(trimethylstannyl)-3-methoxy-1-propene (i.e. a methyl allyl ether) to react with LDA: after quenching the reaction mixture with D_2O he obtained deuterodiisopropylamine as the sole deuterium-containing product.

Base Dependence of the Rearrangement of Trimethylsilyl Ethers

Z-1,2-bis(trimethylstannyl)-3-trimethylsilyloxy-1-propene (**1a**) and Z-1-trimethylsilyl-2-tributylstannyl-3-trimethylsilyloxy-1-propene (**2a**) were allowed to react with the three lithium bases and subjected to a conventional aqueous workup. Reaction conditions and product ratios are listed in Table 1.

Table 1
Base dependence of the rearrangement of Z-1,2-bis(trimethylstannyl)-3-trimethylsilyloxy-1-propene (**1a**) and Z-1-trimethylsilyl-2-tributylstannyl-3-trimethylsilyloxy-1-propene (**2a**)

Compound	Base	Reaction Conditions (°C/h)	Consumption (%)	Aldehyde **5a/6a** (%)	Silyl Enol Ether **7a/8a** (%)
1a	LTMP	-78/6	92	100	0
1a	LTMP	RT/6	100	100	0
2a	LTMP	-78/6	100	85	15
2a	LTMP	RT/6	100	100	0
1a	LDA	-78/6	87	82	18
1a	LDA	RT/6	100	100	0
2a	LDA	-78/6	72	100	0
2a	LDA	RT/6	100	100	0
1a	LDEA	-78/6	5	0[a]	100[a]
1a	LDEA	RT/6	100	[b]	0
2a	LDEA	-78/6	93	60	40
2a	LDEA	RT/6	100	[b]	[b]

[a] relative amounts of product
[b] decomposition

In general the behaviour of **1a** and **2a** is very similar, as is that of LDA and LTMP (thus LTMP was not used in the investigations described below). With both these bases the silyl shift is clearly favoured, the hydrogen shift only competing well when LDEA is used. However, the latter base causes decomposition when used at room temperature (with **1a** the results are not reproducible), while at -78°C the consumption of **1a** is very low. Clearly the 1,4-migration of the trimethylsilyl residue is an extremely facile process.

Base Dependence of the Rearrangement of Other Trialkylsilyl Ethers

Z-1,2-bis(trimethylstannyl)-3-trialkylsilyloxy-1-propenes **(1a-1g)** and Z-1-trimethylsilyl-2-tributylstannyl-3-trialkylsilyloxy-1-propenes **(2a-2g)** were allowed to react with LDA and LDEA under standard conditions (6 h at room temperature). In most cases the silyl ethers were completely consumed at the end of this period. Details are given in Table 2. In the presence of LDEA there was generally no migration of the silyl moiety: exceptions are provided by **2b**, where about 20% of migration was observed, and **1g** and **2g.** In the latter cases migration was accompanied by O-desilylation.

Table 2
Base dependence of the rearrangement of Z-1,2-bis(trimethylstannyl)-3-trialkylsilyloxy-1-propenes (**1b-1g**) and Z-1-trimethylsilyl-2-tributylstannyl-3-trialkylsilyloxy-1-propenes (**2b-2g**)

Compound/ R_3Si	Base	Reaction Conditions (°C/h)	Consumption (%)	Aldehyde **3/5** (%)	Silyl Enol Ether **7/8** (%)
1b/^{i}Pr Me_2Si	LDA	RT/6	100	100	0
2b/^{i}Pr Me_2Si	LDA	RT/6	100	72	28
2b/^{i}Pr Me_2Si	LDEA	RT/6	100	21	79
1c/^{t}Bu Me_2Si	LDA	RT/6	100	57	43
1c/^{t}Bu Me_2Si	LDEA	RT/6	100	0	100
2c/^{t}Bu Me_2Si	LDA	RT/6	100	55	45
2c/^{t}Bu Me_2Si	LDEA	-30/6	100	0	100
1d/^{t}Hex Me_2Si	LDA	RT/6	100	30	70
1d/^{t}Hex Me_2Si	LDEA	RT/6	100	0	100
2d/^{t}Hex Me_2Si	LDA	RT/6	72	33[a]	67[a]
2d/^{t}Hex Me_2Si	LDEA	RT/6	100	0	100
1e/^{i}Pr$_2$MeSi	LDA	RT/6	66	22[a]	78[a]
1e/^{i}Pr$_2$MeSi	LDEA	RT/6	100	0	100
2e/Pr$_2$Me^{i}Si	LDA	RT/6	100	30	70
2e/^{i}Pr$_2$MeSi	LDEA	RT/6	100	0	100
1f/^{i}Pr$_3$Si	LDA	RT/6	92	17[a]	83[a]
1f/^{i}Pr$_3$Si	LDEA	RT/6	100	0	100
2f/^{i}Pr$_3$Si	LDA	RT/6	50	0[a]	100[a]
2f/ ^{i}Pr$_3$Si	LDEA	RT/6	100	0	100
1g/Ph$_2$MeSi	LDA	RT/6	82	48[b]	0
1g/ Ph$_2$MeSi	LDEA	RT/6	87	59[c]	0
2g/Ph$_2$MeSi	LDA	RT/6	91	61[d]	0
2g/Ph$_2$MeSi	LDA	RT/6	86	52[b]	0

[a] relative amounts of product
[b] 34% desilylation
[c] 28% desilylation
[d] 30% desilylation.

Even with LDA there was only one case (compound **1b**) in which silyl migration was the sole process observed: however, silyl migration was also only suppressed completely in the case of the very bulky triisopropyl group, and even here only for compound **2g** but not for **1g**. We also prepared compounds bearing the diphenyl*tert.*-butylsilyl moiety, but here neither silyl nor hydrogen migration occurred.

Thus at this stage the conclusion to be drawn is that silyl migration is only facile when a trimethylsilyl moiety is involved. Our qualitative results are in agreement with those of Rücker [2], who observed migration of a trimethylsilyl moiety in carbanions derived from γ-silyloxy-alkyl phenyl thioethers to be complete after 5 sec at -78°C, while the triisopropyl (TIPS) group required 5 min. after base addition.

The question arises as to the nature of the "1,4-silyl migration": this is generally described in the literature [2,15-16] as an intramolecular nucleophilic substitution at silicon, i.e. a reaction which proceeds via a transition state in which the silicon is pentavalent. On this basis the decreasing tendency towards migration can be understood as a simple steric effect at silicon, due to increasing steric congestion in the transition state.

The Effect of Base Concentration and Reaction Time

Since LDA, in contrast to LDEA, favours silyl migration when used in an equimolar ratio with the silyl ether, it appeared worthwhile to consider the effect of using an excess of the base and of increasing the reaction time dramatically. This study was confined to compounds in which the silyl moiety is relatively bulky, and in view of the similarity between the behaviour of compounds **1** and **2** only the former were considered. The results are contained in Table 3, and make it clear that silyl migration is indeed the thermodynamically favoured process. Even the bulky TIPS group undergoes silyl migration to the extent of 86% when 3 molar equivalents of the base are used and the reaction time increased to 5 days, while in **1c** silyl migration is almost quantitative under similar conditions.

Table 3
Dependence of the rearrangement of Z-1,2-bis(trimethylstannyl)-3-trimethylsilyloxy-1-propenes on base concentration and reaction time

Compound/ R_3Si	Base/Equiv.	Reaction Conditions (°C/time)	Consumption (%)	Aldehyde **3/5** (%)	Silyl Enol Ether **7/8** (%)
1c/$^tBuMe_2Si$	LDA/1.2	RT/3 d	100	64	36
1c/$^tBuMe_2Si$	LDA/3	RT/6 h	100	29	71
1c/$^tBuMe_2Si$	LDA/3	RT/3 d	100	97	3
1d/$^tHexMe_2Si$	LDA/3	RT/3 d	100	66	34
1e/$^iPr_2MeSi$	LDA/3	RT/5 d	100	86	14
1f/$^iPr_3Si$	LDA/3	RT/7 d	100	74	26

*O-Desilylation of Silyl Enol Ethers **3** and **4***

The introduction and removal of silyl protecting groups has been developed to a fine art [17], and we expected that it would be a simple manner to remove the silyl moieties in compounds **3** or **4** to give 2,3-bismetallated aldehydes; the use of aggressive desilylation reagents would of course have to be avoided in order not to cleave metal-carbon as well as metal-oxygen bonds.

Compound **4c** derived from LDEA-induced rearrangement of **1c** was used as a model for this brief study, and was subjected to treatment with the following reagents: a) tetrabutylammonium fluoride in THF (2 eq., 4h at room temperature or 4 eq., 8h at room temperature); b) 1.6 eq. potassium fluoride/18-crown-6 in THF, 12h at room temperature; c) 0.4 eq. pyridinium tosylate in ethanol, 2h at 55°C. In no case was desilylation observed. Recourse to HCl in ethanol led to cleavage of both Si-O and M-C bonds. Thus the use of standard reagents for silyl deprotection is apparently not possible for this particular type of silyl enol ether.

Experimental

All experiments were carried out in an argon atmosphere. Propargyl alcohol was converted to the required silyl propargyl ethers using the procedure described by Corey [18] (chlorosilane/imidazole/DMF); yields were between 40 and 78%. The bismetallated silyl allyl ethers **1** and **2** were prepared by addition of Me_6Sn_2 (**1**, using $Pd_2(dba)_3$ as catalyst) or $Bu_3SnSiMe_3$ (**2**, using $Pd(PPh_3)_4$ as catalyst) to the silyl propargyl ethers. New compounds were characterised by elemental analysis, multinuclear NMR spectroscopy and mass spectrometry.

General procedure for palladium-catalysed addition reactions

Equimolar amounts of the silyl propargyl ether and either hexamethylditin or tributylstannyltrimethylsilane (4-20 mmol) were mixed and treated in the absence of solvent with catalytic amounts (ca. 5 mol%) of the catalyst. Reactions involving hexamethylditin were exothermic and were complete within 1-2h. Larger-scale preparations would require cooling of the reaction mixture or dilution with an inert solvent. Reactions involving the stannylsilane were carried out at 80°C and generally required 16h. Products **1** and **2** were purified by distillation.

Z-1,2-bis(trimethylstannyl)-3-trimethylsiloxy-1-propene **1a**: scale 20 mmol, b.p. 81°C/0.012 mm Hg, yield 7.66g (84%). Anal. calcd. for $C_{12}H_{31}SiSn_2$, C 32.7, H 7.1; found, C 32.3, H 6.9.

Z-1,2-bis(trimethylstannyl)-3-t-butyldimethylsiloxy-1-propene **1b**: scale 20 mmol, b.p. 87°C/0.021 mm Hg, yield 7.82g (80%). Anal. calcd. for $C_{15}H_{37}SiSn_2$, C 37.3, H 7.7; found, C 36.9, H 7.6.

Z-1,2-bis(trimethylstannyl)-3-t-hexyldimethylsiloxy-1-propene **1c**: scale 5 mmol, b.p. 105°C/0.021 mm Hg, yield 2.07g (78%). Anal. calcd. for $C_{17}H_{41}SiSn_2$, C 40.0, H 8.1; found, C 40.1, H 8.0.

Z-1,2-bis(trimethylstannyl)-3-isopropyldimethylsiloxy-1-propene **1d**: scale 4.3 mmol, b.p. 115°C/0.02 mm Hg, yield 1.01g (83%). Anal. calcd. for $C_{14}H_{35}SiSn_2$, C 35.9, H 7.5; found, C 35.8, H 7.4.

Z-1,2-bis(trimethylstannyl)-3-diisopropylmethylsiloxy-1-propene **1e**: scale 4.1 mmol, b.p. 150°C/0.001 mm Hg, yield 1.84g (88%). Anal. calcd. for $C_{16}H_{39}SiSn_2$, C 38.7, H 7.9; found, C 38.5, H 7.9.

Z-1,2-bis(trimethylstannyl)-3-triisopropylsiloxy-1-propene **1f**: scale 4.9 mmol, b.p. 175°C/0.003 mm Hg, yield 2.15g (82%). Anal. calcd. for $C_{18}H_{43}SiSn_2$, C 41.2, H 8.3; found, C 41.1, H 8.1.

Z-1,2-bis(trimethylstannyl)-3-diphenylmethylmethylsiloxy-1-propene **1g**: scale 5 mmol, b.p. 170°C/0.008 mm Hg, yield 2.23g (77%). Anal. calcd. for $C_{22}H_{35}SiSn_2$, C 46.8, H 6.2; found, C 46.5, H 6.0.

Z-1,2-bis(trimethylstannyl)-3-t-butyldiphenysiloxy-1-propene **1h**: scale 4.3 mmol, b.p. 225°C/0.003 mm Hg, yield 2.14g (80%). Anal. calcd. for $C_{23}H_{45}SiSn_2$, C 47.1, H 7.7; found, C 47.0, H 7.4.

Z-1-trimethylsilyl-2-tributylstannyl-3-trimethylsiloxy-1-propene **2a**: scale 20 mmol. b.p. 105°C/0.019 mm Hg, yield 7.77g (79%). Anal. calcd. for $C_{21}H_{49}Si_2Sn$, C 52.9, H 10.4; found, C 52.6, H 10.2.

Z-1-trimethylsilyl-2-tributylstannyl-3-t-butyldimethylsiloxy-1-propene **2b**: scale 20 mmol, b.p. 110°C/0.015 mm Hg, yield 8.11g (76%). Anal. calcd. for $C_{24}H_{55}Si_2Sn$, C 55.6, H 10.7; found, C 55.5, H 10.6.

Z-1-trimethylsilyl-2-tributylstannyl-3-t-hexyldimethylsiloxy-1-propene **2c**: scale 5 mmol, b.p. 140°C/0.006 mm Hg, yield 2.03g (72%). Anal. calcd. for $C_{26}H_{59}Si_2Sn$, C 57.1, H 10.9; found, C 56.9, H 10.6.

Z-1-trimethylsilyl-2-tributylstannyl-3-isopropyldimethylsiloxy-1-propene **2d**: scale 4.8 mmol, b.p. 150°C/0.013 mm Hg, yield 1.98g (78%). Anal. calcd. for $C_{23}H_{53}Si_2Sn$, C 54.8, H 10.6; found, C 54.5, H 10.6.

Z-1-trimethylsilyl-2-tributylstannyl-3-diisopropylmethylsiloxy-1-propene **2e**: scale 5 mmol, b.p. 150°C/0.003 mm Hg, yield 1.66g (61%). Anal. calcd. for $C_{25}H_{57}Si_2Sn$, C 56.4, H 10.8; found, C 56.1, H 10.5.

Z-1-trimethylsilyl-2-tributylstannyl-3-triisopropylsiloxy-1-propene **2f**: scale 5 mmol, b.p. 195°C/0.08 mm Hg, yield 2.22g (77%). Anal. calcd. for $C_{27}H_{61}Si_2Sn$, C 57.8, H 11.0; found, C 57.6, H 10.9.

Z-1-trimethylsilyl-2-tributylstannyl-3-t-butyldiphenylsiloxy-1-propene **2h**: scale 3.2 mmol, b.p. 250°C/0.007 mm Hg, yield 1.43g (68%). Anal. calcd. for $C_{32}H_{63}Si_2Sn$, C 61.7, H 10.2; found, C 61.5, H 10.1.

NMR Data

All chemical shifts and coupling constants except for those involving the siloxy residues are very similar, so that only the data for **1a** and **2a** are given for reference (chemical shifts in ppm vs. Me_4Sn or TMS, coupling constants in Hz).

Z-1,2-bis(trimethylstannyl)-3-trimethylsiloxy-1-propene **1a**, $Me_3Si\text{-}O\text{-}C^3H^3_2\text{-}C^2(Sn^aMe_3)\text{=}C^1H^1Sn^bMe_3$: ^{119}Sn NMR: $\delta(Sn^a)$ –51.6, $\delta(Sn^b)$ –58.7, $^3J(^{119}Sn,^{119}Sn)$ 417.6. ^{29}Si NMR: $\delta(Si)$ 17.8. ^{13}C NMR: $\delta(C^1)$ 140.8, $^1J(^{119}Sn,C)$ 500.5, $^2J(^{119}Sn,C)$ 66.1; $\delta(C^2)$ 167.7, $^1J(^{119}Sn,C)$ 496.6, $^2J(^{119}Sn,C)$ 37.9; $\delta(C^3)$ 73.5, $^2J(^{119}Sn,C)$ 65.1, $^3J(^{119}Sn,C)$ 112.7; $\delta(SnMe_3)$ –7.3, $^1J(^{119}Sn,C)$ 337.3; -7.7, $^1J(^{119}Sn,C)$ 345.0; $\delta(SiMe_3)$ –0.4, $^1J(^{29}Si,C)$ 58.3. ^1H NMR: $\delta(H^1)$ 6.81, $^4J(H^1,H^3)$ 1.76, $^2J(^{119}Sn, H^1)$ 84.3, $^3J(^{119}Sn,H^1)$ 194.3,; $\delta(H_3)$ 4.21, $^3J(^{119}Sn,H^3)$ 35.9; $\delta(SnMe_3)$ 0.15, $^2J(^{119}Sn,H)$ 51.9; 0.16, $^2J(^{119}Sn,H)$ 51.8; $\delta(SiMe_3)$ 0.01.

Z-1-trimethylsilyl-2-tributylstannyl-3-trimethylsiloxy-1-propene **2a**, $Me_3Si\text{-}O\text{-}C^3H^3_2\text{-}C^2(SnBu_3)\text{=}C^1H^1SiMe_3$: ^{119}Sn NMR: $\delta(Sn)$ –59.9, $^3J(^{119}Sn,^{29}Si)$ 34.0. ^{29}Si NMR: $\delta(Si)$ –9.9, 17.8. ^{13}C NMR: $\delta(C^1)$ 139.4, $^2J(^{119}Sn,C)$

51.5; δ(C^2) 163.5, $^1J(^{119}Sn,C)$ 388.8; δ(C^3) 73.3, $^2J(^{119}Sn,C)$ 69.0; δ($SiMe_3$) 0.17, $^1J(^{29}Si,C)$ 70.0; –0.4, $^1J(^{29}Si,C)$ 58.3. ^{1}H NMR: δ(H^1) 6.59, $^4J(H^1,H^3)$ 1.70, $^3J(^{119}Sn,H^1)$ 172.9, $^2J(^{119}Sn, H^1)$ 84.3,; δ(H_3) 4.20, $^3J(^{119}Sn,H^3)$ 25.9 ; δ($SiMe_3$) 0.01.

Mass spectra (70 eV)

Molecular ions are not observed. As is usual for organotin compounds under these ionisation conditions, the ions of greatest m/e observed are those in which a methyl group (for **1**) or a butyl group (for **2**) has been split off.

General procedure for base-catalysed rearrangement reactions

Rearrangement reactions of the silyl ethers **1** and **2** with lithium bases were carried out according to the following standard procedure: butyl lithium (2 mmol of a 1.6 M solution in hexane) was added dropwise over 30 min to a solution of the free amine (2 mmol) in THF (5 mL). The silyl ether (1.7 mmol, dissolved in 5 mL THF) was added dropwise to the solution of the lithium base at the appropriate temperature and stirred for the stated time (generally 6 h, see Tables 1 and 2). The reaction mixture was treated with water (10 mL), the organic phase separated, the aqueous phase extracted 3 times with ether (10 mL), the combined organic phases dried over magnesium sulphate and the volatiles removed using a rotary evaporator. The products were subjected to GLC analysis and characterised by multinuclear NMR, GC-FTIR and GC-MS. Product ratios were determined by GLC and NMR.

Base concentrations were varied as described above (Table 3).

NMR Data of products derived from rearrangement reactions

As in the case of the starting materials, the nature of the groups R attached to silicon in the siloxy residues has very little effect on chemical shifts and coupling constants (except for those directly involved), so that only the data for **3a** and **4a, 5a** and **6a**, and **7a** and **8a** are given for reference (chemical shifts in ppm vs. Me_4Sn or TMS, coupling constants in Hz).

E-1-Trimethylsiloxy-2,3-bis(trimethylstannyl)-3-trimethylsilyl-1-propene **3a**, Me_3Si-O-C^1H^1=$C^2(Sn^{vin}Me_3)$-$C^3H(Sn^{all}Me_3)SiMe_3$: ^{119}Sn NMR: δ(Sn^{all}) 0.9, δ(Sn^{vin}) –19.0, $^3J(^{119}Sn,^{119}Sn)$ 340.4, $^3J(^{119}Sn^{vin},^{29}Si)$ 26.4. ^{29}Si NMR: δ(Si) 1.2 (C^3Si), 19.6 (OSi). ^{13}C NMR: δ(C^1) 137.6, $^2J(^{119}Sn,C)$ 53.5, $^3J(^{119}Sn,C)$ 115.7; δ(C^2) 117.2, $^1J(^{119}Sn,C)$ 496.6, $^2J(^{119}Sn,C)$ 57.3; δ(C^3) 19.5, $^1J(^{119}Sn,C)$ 243.0, $^2J(^{119}Sn,C)$ 47.6; ($Sn^{all}Me_3$) –7.0, $^1J(^{119}Sn,C)$ 301.9; ($Sn^{vin}Me_3$) –9.3, $^1J(^{119}Sn,C)$ 323.0; δ($SiMe_3$) –0.1, $^1J(^{29}Si,C)$ 43.7; δ($OSiMe_3$) 0.7. ^{1}H NMR: δ(H^1) 5.75 (s), $^3J(^{119}Sn,H^1)$ 37.1; δ(H_3) 0.35 (s), $^2J(^{119}Sn,H^3)$ 58.1; δ($Sn^{all}Me_3$) 0.03, $^2J(^{119}Sn,H)$ 51.1; δ($Sn^{vin}Me_3$) 0.05, $^2J(^{119}Sn,H)$ 53.0; δ($CSiMe_3$) -0.03; δ($OSiMe_3$) 0.14.

E-1-Trimethylsiloxy-2-tributylstannyl-3,3-bis(trimethylsilyl)-1-propene **4a**, Me_3Si-O-C^1H^1=$C^2(SnBu_3)$-$C^3H(SiMe_3)_2$: ^{119}Sn NMR: δ(Sn) –30.8, $^3J(^{119}Sn,^{29}Si)$ 19.1. ^{29}Si NMR: δ(Si) 0.6 (C^3Si), 21.9 (OSi). ^{13}C NMR: δ(C^1) 138.5, $^2J(^{119}Sn,C)$ 97.3; δ(C^2) 114.9, $^1J(^{119}Sn,C)$ 413.1; δ(C^3) 23.4, $^2J(^{119}Sn,C)$ 43.2; δ($SiMe_3$) 1.2, $^1J(^{29}Si,C)$ 50.5; δ($OSiMe_3$) –0.2, $^1J(^{29}Si,C)$ 58.3. ^{1}H NMR: δ(H^1) 5.81 (s), $^3J(^{119}Sn,H^1)$ 37.9; δ(H_3) 0.21 (s), $^2J(^{119}Sn,H^3)$ 26.4; δ($CSiMe_3$) -0.07; δ($OSiMe_3$) 0.19.

3-Trimethylsilyl-3-trimethylstannylpropanal **5a**, $Me_3SnC^3H(SiMe_3)C^2H_2C^1HO$: ^{119}Sn NMR: δ(Sn) 15.2, $^2J(^{119}Sn,^{29}Si)$ 15.5. ^{29}Si NMR: δ(Si) 4.7. ^{13}C NMR: δ(C^1) 200.5, $^3J(^{119}Sn,C)$ 28.3; δ(C^2) 42.8, $^2J(^{119}Sn,C)$ 24.3; δ(C^3) 3.8, $^1J(^{119}Sn,C)$ 269.2, $^1J(^{29}Sn,C)$ 49.6; δ($SiMe_3$) –0.7, $^1J(^{29}Si,C)$ 50.5; δ($SnMe_3$) –8.0, $^1J(^{119}Sn,C)$ 327.5. ^{1}H NMR: δ(H^1) 9.68, $^3J(H^1,H^{2a})$ 1.5, $^3J(H^1,H^{2b})$ 1.1, $^4J(^{119}Sn,H^1)$ 170.7; δ(H^{2a}) 2.66, $^3J(H^{2a},H^3)$ 5.6; δ(H^{2b}) 2.75, $^3J(H^{2b},H^3)$ 6.8; δ(H_3) 0.04; δ($SnMe_3$) 0.02, $^2J(^{119}Sn,H)$ 52.7; δ($SiMe_3$) -0.05.

Bis(trimethylsilyl)propanal **6a**, $(Me_3Si)_2C^3HC^2H_2C^1HO$: ^{29}Si NMR: δ(Si) 4.1. ^{13}C NMR: δ(C^1) 202.0; δ(C^2) 40.8; δ(C^3) 5.9, $^1J(^{29}Sn,C)$ 44.7; δ($SiMe_3$) –0.7, $^1J(^{29}Si,C)$ 50.7. ^{1}H NMR: δ(H^1) 9.66, $^3J(H^1,H^2)$ 1.5; δ(H^2) 2.45, $^3J(H^2,H^3)$ 6.0; δ(H_3) 0.44; δ($SiMe_3$) -0.06.

2,3-Bis(trimethylstannyl)-1-trimethylsiloxy-1-propene **7a**, $Me_3Si\text{-}O\text{-}C^1H{=}C^2(SnMe_3)\text{-}C^3H_2SnMe_3$: ^{119}Sn NMR: δ($Sn^{all}$) -7.9, δ($Sn^{vin}$) –23.8, $^3J(^{119}Sn,^{119}Sn)$ 120.2, ^{29}Si NMR: δ(Si) 19.1. ^{13}C NMR: δ(C^1) 138.0, $^2J(^{119}Sn,C)$ 50.9, $^3J(^{119}Sn,C)$ 101.7; δ(C^2) 116.9, $^1J(^{119}Sn,C)$ 486.8, $^2J(^{119}Sn,C)$ 56.0; δ(C^3) 18.9, $^1J(^{119}Sn,C)$ 315.4, $^2J(^{119}Sn,C)$ 49.1; ($Sn^{all}Me_3$) –9.2, $^1J(^{119}Sn,C)$ 316.6; ($Sn^{vin}Me_3$) –9.8, $^1J(^{119}Sn,C)$ 344.9; δ($SiMe_3$) –0.1, $^1J(^{29}Si,C)$ 51.3. ^{1}H NMR: δ(H^1) 5.72, $^4J(H^1,H^3)$ 1.0, $^3J(^{119}Sn,H^1)$ 33.7, $^4J(^{119}Sn,H^1)$ 26.6; δ(H_3) 1.90, $^2J(^{119}Sn,H^3)$ 70.3, $^3J(^{119}Sn,H^1)$ 72.3; δ($Sn^{all}Me_3$) 0.03, $^2J(^{119}Sn,H)$ 52.4; δ($Sn^{vin}Me_3$) 0.06, $^2J(^{119}Sn,H)$ 54.2; δ($SiMe_3$) -0.11.

3-Trimethylsilyl-2-tributylstannyl-1-trimethylsiloxy-1-propene **8a**, $Me_3Si\text{-}O\text{-}C^1H{=}C^2(SnBu_3)\text{-}C^3H_2SiMe_3$: ^{119}Sn NMR: δ(Sn) –34.2, $^3J(^{119}Sn,^{29}Si)$ 10.6, ^{29}Si NMR: δ(CSi) 10.6, δ(OSi) 19.1. ^{13}C NMR: δ(C^1) 139.3, $^2J(^{119}Sn,C)$ 85.5; δ(C^2) 114.1, $^1J(^{119}Sn,C)$ 418.9; δ(C^3) 19.4, $^2J(^{119}Sn,C)$ 25.3; δ($CSiMe_3$) –0.9, $^1J(^{29}Si,C)$ 50.8; δ($OSiMe_3$) –2.0. ^{1}H NMR: δ(H^1) 5.81, $^4J(H^1,H^3)$ 1.0, $^3J(^{119}Sn,H^1)$ 31.4; δ(H_3) 1.65, $^2J(^{119}Sn,H^3)$ 59.7; δ($CSiMe_3$) –0.11; δ($OSiMe_3$) 0.10.

IR Data

Silyl enol ethers **3**, **4**, **7** and **8** are characterised by a C=C vibration which varies between 1583 and 1593 cm^{-1}, aldehydes **5** and **6** by the carbonyl vibration which lies between 1711 and 1739 cm^{-1}.

MS (70 eV)

There is no clear pattern with respect to observation of molecular ions. In the majority of cases the ion of highest m/e observed results from the loss of a methyl group, even when no tin is present in the molecule concerned. However, molecular ions are observed for compounds **5b** (40%), 5c (14%), **5d** (7%), 5e (6%), **5f** (10%), **7e** (14%), **7f** (24%), **8c** (5%), **8e** (1%) and **8f** (7%); values in parentheses refer to the relative intensity.

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References

[1] Evans DA, Takacs JM, Hurst KM. J. Am. Chem. Soc. 1979; 101, 371.

[2] Rucker C. Tetrahedron Lett. 1984; 25, 4349.

[3] Bures EJ, Keay BA. Tetrahedron Lett. 1987; 28, 5965.

[4] Mora J., Costa A. Tetrahedron Lett. 1984; 25, 3493.

[5] Lautens M, Delanghe PHM, Goh JB, Zhang CH. J. Org. Chem. 1992; 57, 3270.

[6] Mitchell TN, Gießelmann F. J. Organometal. Chem. 1995; 492, 191; Mitchell TN, Gießelmann F. Synlett. 1995, 333.

[7] Mitchell, T. N.; Gießelmann, F. Synlett. 1996, 475.

[8] Preliminary communication: Mitchell TN, Schütze M, Gießelmann F. Synlett. 1997, 183.

[9] Ahlbrecht H, Schneider G. Tetrahedron. 1986; 42, 4729.

[10] Romesberg FE, Gilchrist JH, Harrison AT, Fuller DJ, Collum DB. J. Am. Chem. Soc. 1991; 113, 5751.

[11] Lipshutz BH, Wood MR, Lindsley CW. Tetrahedron Lett. 1995; *36*, 4385.

[12] Williard PG, Salvino JM. J. Org. Chem. 1993; 58, 1.

[13] Hall PL, Gilchrist JH, Harrison AT, Fuller DJ, Collum DB. J. Am. Chem. Soc. 1993; 113, 9575.

[14] Kwetkat K. Diplomarbeit, Univ. Dortmund 1991.

[15] Eisch JJ, Tsai M.-R. J. Organomet. Chem. 1982; 225, 5.

[16] Kim KD, Magriotis PA.Tetrahedron Lett., 1990; 31, 6137.

[17] Kocienski PJ. Protecting Groups. G. Thieme Verlag: Stuttgart, 1994.

[18] Corey EJ, Venkateswarlu A. J. Am. Chem. Soc., 1972, 94, 6190.