A New Route to α-Trialkylsilyl Aldehydes. The First Isolation of α-Trimethylsilyl Aldehydes

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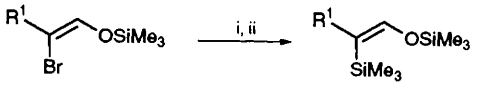
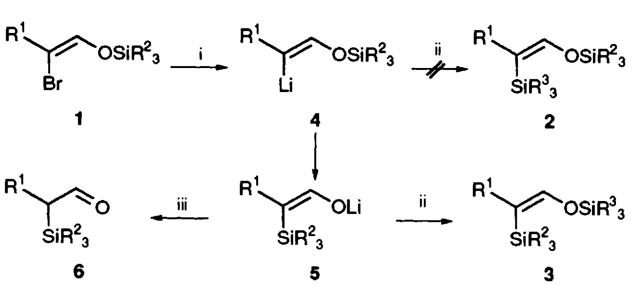
α-Trimethylsilyl and α-triethylsilyl aldehydes **6** were obtained from trimethylsilyl and triethylsilyl β-bromo enol ethers **1**, using a bromine–lithium exchange and a 1–3 migration of the trialkylsilyl group.

We have shown recently that the reaction of trimethylsilyl β-bromo enol ethers with *tert*-butyllithium followed by condensation with chlorotrimethylsilane leads to trimethylsilyl-β-trimethylsilyl enol ethers[1] (Scheme 1).

We now report that in trying to apply this procedure to the preparation of such compounds with mixed trialkylsilyl groups, we obtained enol ethers **3** instead of the expected isomeric enol ethers **2**.[2] This result can be explained by an isomerisation of vinylic anions **4** into enolates **5** or by an equilibration of the two species (Scheme 2). Thus we were also



Scheme 1 *Reagents and conditions*: i, Bu^tLi, THF, −70 °C, ii, $ClSiMe_3$



Scheme 2 *Reagents and conditions*: i, Bu^tLi, THF, −70 °C; ii, $XSiR^3_3$; iii, H_2O

Table 1 Silyl enol ethers **3**

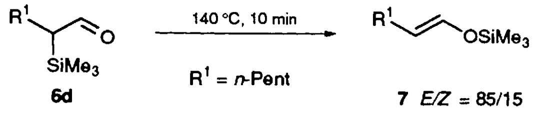
3	R^1	SiR^2_3	SiR^3_3	Yield[a] (%)	**3**	R^1	SiR^2_3	SiR^3_3	Yield[a] (%)
a	Me	$SiMe_3$	$SiEt_3$	43	e	Me	$SiMe_3$	$SiMe_2Bu^t$	46
b	Pr^i	$SiMe_3$	$SiEt_3$	40	f	Et	$SiMe_3$	$SiMe_2Bu^t$	41
c	Pent	$SiMe_3$	$SiEt_3$	48	g	Pr^i	$SiMe_3$	$SiMe_2Bu^t$	40
d	Pr^i	$SiEt_3$	$SiMe_3$	49					

[a] After chromatography on Florisil.

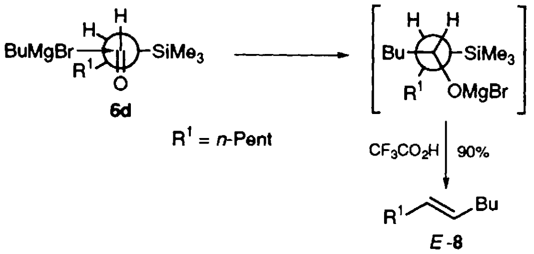
Table 2 α-Trialkylsilyl aldehydes **6**

6	R^1	SiR^2_3	Yield[a] (%)	**6**	R^1	SiR^2_3	Yield[a] (%)
a	Et	$SiMe_3$	50	d	Bu^t	$SiMe_3$	40
b	Pr^i	$SiMe_3$	60	e	Pr^i	$SiEt_3$	60
c	Pent	$SiMe_3$	55	f	Pent	$SiEt_3$	53

[a] Of distilled **6**.



Scheme 3



Scheme 4

incited to use this 1–3 migration of the silyl group from oxygen to carbon[3] for a new preparation of α-silyl aldehydes **6** and in particular of the hitherto elusive α-trimethylsilyl aldehydes. In fact only α-trialkylsilyl aldehydes with crowded silyl groups have been described. α-Trimethylsilyl aldehydes which are reputed to be very sensitive, losing silicon easily and isomerising to enol ethers, have to date never been isolated;[4–7] in some cases their formation has been verified by trapping *in situ* with Grignard reagents.[4b,5]

The silyl enol ethers **3**[2] were obtained from β-bromo enol ethers **1** (*Z*/*E* 67/33 to 95/5),[1] after treatment with *tert*-butyllithium, then reaction with chlorotriethylsilane (**3a–c**), chlorotrimethylsilane (**3d**) or *tert*-butyldimethyl triflate (**3e–g**) (Table 1).

The structural analyses of compounds **3** which is very difficult with classical ^1H and ^{13}C NMR spectroscopy, becomes unambiguous with ^{29}Si NMR spectroscopy by using an SPT (Selective Population Transfer) method[8]. The structures of **3b**, **d**, **e** were assigned by this procedure.† From their ^1H NMR spectroscopic data and from data of similar compounds,[8] we have noted that in C_6D_6 the methyl groups on a silicon atom linked to an oxygen atom exhibit resonance at 0.03 ppm while those on a silicon atom linked to a vinyl carbon atom exhibit resonance at 0.3 ppm. These observations helped us to establish the structure of the other compounds reported in Table 1.

α-Trimethylsilyl aldehydes **6** were obtained similarly from bromo enol ethers **1**, after reaction with *tert*-butyllithium and hydrolysis. They were isolated by distillation at room temperature under high vacuum (Table 2).‡ Their ^1H NMR and IR spectra indicate the absence of the corresponding desilylated aldehydes or enol ethers.

We briefly report two of their properties. After heating at 140 °C for 10 min, aldehyde **6d** was entirely isomerised into trimethylsilyl enol ether **7** with predominant (*E*)-configuration§ (Scheme 3).

It has been noted that the classical preparation of **7** from heptanal ($ClSiMe_3$, NEt_3, $ZnCl_2$ cat., Et_2O, reflux 3 h) led predominantly to the (*Z*)-isomer (*E*/*Z* = 33/67).

Finally, condensation of butylmagnesium bromide with aldehyde **6d** followed by treatment with trifluoroacetic acid led exclusively to alkene (*E*)-**8**. This result is explained by a condensation according to the model of Felkin–Anh[9] and a Peterson[10] elimination without isolation of the intermediate hydroxysilane. For identification, alkenes (*Z*)- and (*E*)-**8** were prepared by reduction of undec-5-yne with diisobutylalumi-

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† Compounds **3** were fully characterised by spectroscopic methods. The spectra data of **3d** are given as an example: ν (NaCl) cm^{-1} 1600; δ_H (C_6D_6; 400 MHz) 0.03 (9 H, s), 0.54 (6 H, q, *J* 8.1 Hz), 0.98 (9 H, t, *J* 8.0 Hz), 1.06 (6 H, d, *J* 6.9 Hz), 2.35 (1 H, m, *J* 6.9 and 1.0 Hz) and 6.79 (1 H, d, *J* 1.0 Hz); δ_{Si} (C_6D_6; 400 MHz) −7.0 (C-$SiEt_3$) and +19.3 (O-$SiMe_3$). The selective irradiation of the $SiMe_3$ groups (9 protons) with a pulse of 180° followed by magnetisation on the silicon led to a multiplicity of 10 ($n + 1$) for the signal at +19.3 ppm indicating that the trimethylsilyl group is fixed on the oxygen atom. (Bruker ARX 400 Fourier transform NMR Spectrometer equipped with a Bruker X32 Computer).

‡ To bromo enol ether **1** (4 mmol) in THF (10 cm^3), Bu^tLi (1.7 mol dm^{-3} in pentane, 10 mmol) was added, under argon. After 150 min at −70 °C, the mixture was warmed to 20 °C (10 min) and treated with saturated aqueous NH_4Cl (5 cm^3). After extraction with ether, drying ($MgSO_4$) and elimination of solvents (15 mmHg), the residue was distilled at room temp. under 0.02 mmHg. The aldehydes **6** were trapped in a vessel cooled at −70 °C. Compounds **6** were fully characterised by spectroscopic methods ν (NaCl) cm^{-1} 1688–1698; δ_H ($CDCl_3$; 200 MHz) **6a**: 9.50 (1 H, d, *J* 2 Hz); **6b**: 9.62 (1 H, d, *J* 4.4 Hz); **6c**: 9.50 (1 H, d, *J* 3.4 Hz); **6d**: 9.64 (1 H, d, *J* 3.6 Hz); **6e**: 9.60 (1 H, d, J 0.5 Hz); **6f**: 9.55 (1 H, d, *J* 3.2 Hz).

§ The isomerisation of 1-propyl-1-trimethylsilyl epoxide to (*Z*)-1-trimethylsilyloxypent-1-ene in ether in the presence of zinc bromide was reported to occur *via* α-trimethylsilylpentanal.[4a]

nium hydride and sodium in liquid ammonia, respectively (Scheme 4).¶

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¶ Compound **8** was analysed by CPG on a methylsilicon HP1 capillary column: Retention time (Z)-**8**: 23.03 min; (*E*)-**8**: 23.57 min.