Journal of Organometallic Chemistry, 464 (1994) C11–C13

JOM 24167PC

Preliminary Communication

A novel 1,3-migration of the trimethylsilyl group from oxygen to carbon

L. Duhamel, J. Gralak and B. Ngono

Unité Associée au CNRS 464, Faculté des Sciences et des Techniques de Rouen et IRCOF, 76821 Mont Saint Aignan Cedex (France)

(Received July 22, 1993)

Abstract

Condensation of 1-lithio-2-trimethylsiloxyethylene **1** with t-butyl(dimethyl)silyl triflate **2a** leads to silylated enol ethers **4a** or **4b** according to the experimental conditions. The formation of **4b** is due to a 1,3-migration of the trimethylsilyl group from oxygen to carbon of **1**. Condensation with chlorosilane **2b** lead exclusively to **4b**.

Key words: Trimethylsilyl

During our work on the properties of β-lithiotrimethylsilylenol ethers, we observed the trapping of 1-lithio-2-trimethylsiloxyethylene **1** with carbonyl compounds or with t-butyl(dimethyl)silyl triflate **2a** leading to the expected silylenol ethers **3** [1] or **4a** [2]. Compounds **3** and **4a** were transformed as expected into aldehydes **5** and **6**, respectively, when treated in mild aqueous acidic conditions [1,2] (Scheme 1).

We now show that the condensation of **1** with the chlorosilane **2b** does not lead to the corresponding triflate derivative **2a** but to a different product [3]. Under the same experimental conditions (preparation of **1** from (*Z*)-1-bromo-2-trimethylsiloxy ethylene by bromine-lithium exchange in ether, addition of **2b** in THF), no reaction was detected, but the condensation occurs in the presence of two equivalents of hexamethylphosphoramide (HMPA) leading to the enol ether (*Z*)-**4b**, an isomer of (*Z*)-**4a** (Scheme 1) [4,5]. To confirm the formulation, **4b** was prepared from 1-bromo-2-t-butyl(dimethylsiloxy)ethylene [6] (Scheme 2).

The ^{1}H and ^{13}C NMR spectra of **4a** and **4b** are slightly different as are also their retention times in CPG, but the simplest method for their differentiation is their behaviour towards aqueous acid: after 5 min with a 1M HCl solution, **4a** is entirely hydrolysed to aldehyde **6** [2] whereas **4b** is completely inert [3]. This chemical property allows a rapid determination of mixtures of the two isomers.

We re-examined the condensation of the triflate **2a** with lithioenol ether **1** and we showed that the results are very dependent on the experimental conditions, leading either to **4a** or to **4b** (Table 1, Scheme 3). In all experiments reported in Table 1, the triflate **2a** was added at −70°C in THF to **1** prepared in ether. Two experimental factors are important: the contact time of the two reagents between −70°C and 0°C and the quality of the triflate **2a**. Experiment 1 shows that no condensation occurs at −70°C. By using freshly distilled **2a**, and if the reaction is warmed as rapidly as possible from −70°C to 0°C (2 or 3 min) and then kept at this temperature for 20 min (condition A), only **4a** was obtained as previously reported (2) (experiment 2), whereas a slow warming (90 min to reach 0°C) (condition B) led to an equimolar mixture of **4a** and **4b** (experiment 3). Using commercial **2a** under condition B furnished **4b** alone (experiment 5).

In all the above experimental conditions, the chlorosilane **2b** always gave **4b** (Scheme 3).

The results can be interpreted by an isomerisation of the carbanion **1** to the enolate **7**, which is favoured by the raising of the temperature or by an equilibrium of the two species. In the first case, the rate of isomerisation should be lower than the rate of condensation at 0°C (experiments 2, 4) and faster at temperatures < 0°C (experiment 5). In the second case, the condensation should occur more rapidly with **1** than with **7** at 0°C, and it should be the converse at lower temperatures (Scheme 4).

Finally the ^{1}H NMR spectra of the anionic species at −70°C in Et_2O-d_{10} are consistent with the proposed structure **1**; the isomeric enolate **7** is not detected. However, an equilibrium of the two species cannot be ruled out [8].

1. Experimental section

1.1. 2-Trimethylsilyl-1-t-butyl(dimethylsiloxy)ethylene ***4b***

Lithium t-butyl (1.5 M in pentane, 3.1 ml, 4.6 mmol) freshly measured [7] was added during 10 min under argon to a solution of 1-bromo-2-(trimethyisiloxy)ethylene (0.5 g, 2.56 mmol) in anhydrous ether (12.8 ml) at −70°C. After 90 min at −70°C a solution of chloro(t-butyl)dimethyl silane **2b** (0.276 g, 2.05 mmol) or com-

---

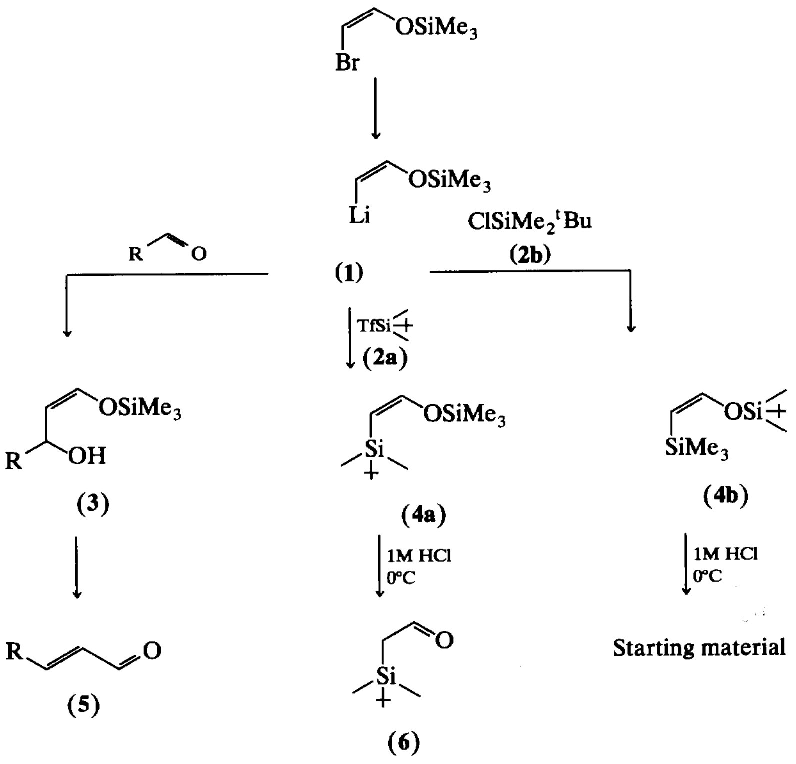
Correspondence to: Professor P. Duhamel.

0022-328X/94/$7.00
SSDI 0022-328X(93)24167-4

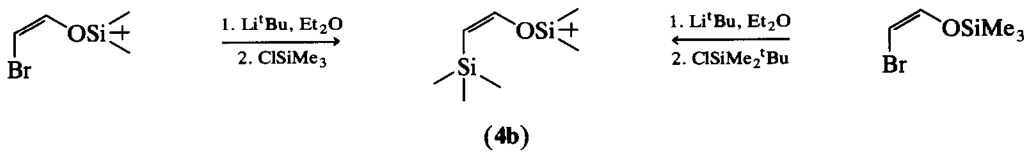
mercial t-butyl(dimethyl)silyl triflate **2a** (0.47 ml, 2.05 mmol), in THF (3 ml) was added during 6 min, and then HMPA (0.7 ml, 0.403 mmol) after 10 min. The reaction mixture was kept at −70°C during 1h, warmed to 0°C in 90 min, kept at 0°C during 20 min and finally treated with a saturated Na_2CO_3 solution (2.5 ml). After extraction with ether the organic layer was washed (H_2O), dried ($MgSO_4$), and concentrated. Crude yield: 88%. The residue was purified by chromatography (Florisil, petroleum ether, 30–50). Yield 53%.

IR (film) 1600, 1250 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.10 (s, 9H); 0.15 (s, 6H); 1.0 (s, 9H); 4.27 (d, 1H, $J = 7.9$); 6.77 (d, 1H, $J = 7.9$).

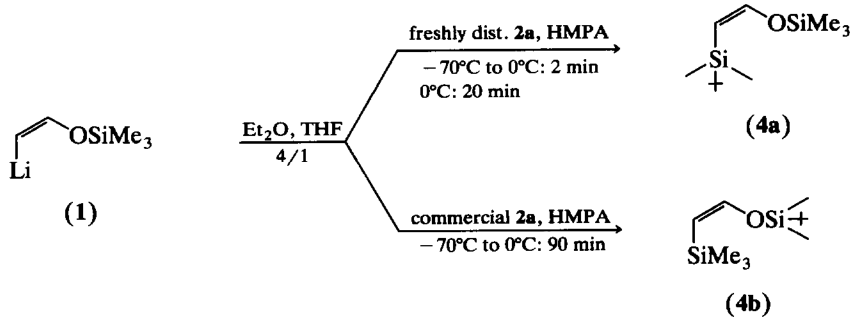
Anal.: $C_{11}H_{26}OSi_2$ calc.: C, 57.32; H, 11.36. Found: C, 57.1; H, 11.2%.



Scheme 1.



Scheme 2.



Scheme 3.

TABLE 1. Reaction of triflate **2a** with lithioenol ether **1**

Experiment	**2a**	Conditions [a]	**4a/4b** [b]	Crude yield
1	Commercial	[c]		0
2	Freshly distilled	A	100/0	88
3	Freshly distilled	B	50/50	90
4	Commercial	A	90/10	78
5	Commercial	B	0/100	78

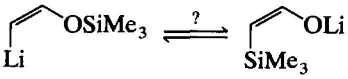
[a] *Conditions A*: **2a** in THF was added to **1** in Et_2O at −70°C, then the mixture was warmed to 0°C in approximately 2 min, kept at 0°C for 20 min and treated at 0°C with an aqueous saturated solution of Na_2CO_3. *Conditions B*: idem, except that the mixture was warmed to 0°C in 90 min.

[b] Determined by ^{1}H NMR by the ratio **6/4b**, after treatment with 1 M HCl.

[c] After addition of **2a**, and 10 min at −70°C, the mixture was treated at −70°C with a saturated Na_2CO_3 solution.

Freshly distilled **2a** and the preceding conditions except for the warming from −70 to 0°C (3 min instead of 90 min) led to (*Z*)-**4a** (2) (Table 1).

4b was also obtained using the preceding conditions (warming from −70 to 0°C; 90 min), from 1-bromo-2-t-butyl(dimethylsiloxy)ethylene and chlorotrimethylsilane. Yield: 57%.



1 **7**

Scheme 4.

References

1 L. Duhamel and F. Tombret, *J. Org. Chem., 46* (1981) 3741; L. Duhamel, F. Tombret and Y. Mollier, *J. Organomet. Chem., 280* (1985) 1.

2 L. Duhamel, J. Gralak and B. Ngono, *J. Organomet. Chem., 363* (1989) C$_4$.

3 B. Ngono, *Thèse*, Rouen, 1989.

4 For other 1,3-migrations of a trialkylsilyl group from oxygen to carbon, see G. Simchen and J. Pfletschinger, *Angew. Chem., Int. Ed. Engl., 15* (1976) 428; I. Kuwajima and R. Takeda, *Tetrahedron Lett., 21* (1981) 2381; E.J. Corey and C. Rucker, *Tetrahedron Lett., 24* (1984) 4345; P. Sampson and D.F. Wiemer, *J. Chem. Soc., Chem. Commun.*, (1985) 1746; P. Sampson, G.B. Hammond and D.F. Wiemer, *J. Org. Chem., 51* (1986) 4342; S. Raucher and D.C. Schindele, *Synth. Commun., 17* (1987) 637.

5 For some other migrations of a silyl group from oxygen to carbon, see 1,2-migration, R. West, R. Lowe, H.F. Stewart and A. Wright, *J. Am. Chem. Soc., 93* (1971) 282; J.B. Verlhac, H.A. Kwon and M. Pereyre, *J. Organomet. Chem., 437* (1992) C$_{13}$; G. Boche, A. Oppel, M. Marsch, K. Harms, F. Haller, J.C. Lohrenz, C. Thümmler and W. Koch, *Chem. Ber., 125* (1992) 2265; 1,4-migration, C. Rucker, *Tetrahedron Lett., 24* (1984) 4349; 1,5-migration, C.P. Casey, C.R. Jones and H. Tukada, *J. Org. Chem., 46* (1981) 2084.

6 M.C. Pirrung and J.R. Hwu, *Tetrahedron Lett., 24* (1983) 565.

7 L. Duhamel and J.C. Plaquevent, *J. Org. Chem., 44* (1979) 3404.

8 V. Baudrillard *et al.*, to be published.