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Carbanion or Enolate? A ^{1}H, ^{13}C, and ^{29}Si NMR Spectroscopic Analysis

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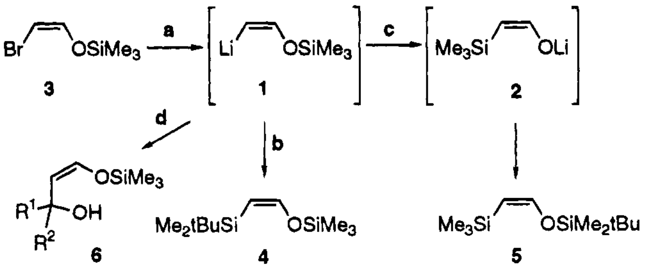
Several 1−3 migrations of a silyl group from oxygen to carbon have been reported in the literature for anionic species derived from silyl enol ethers in cyclic or acyclic series.[1,2] All these results have been indirectly deduced from the isolated products obtained after reaction with electrophilic reagents. Interestingly, all published migrations have been observed in THF. We wish to report here the first direct observation of such a 1−3 migration through the NMR analysis of the intermediate anionic species. Our results indicate the exclusive formation of carbanion **1** in diethyl ether (Et_2O), while this same compound evolves toward enolate **2** in THF.

Moreover, we have shown that the migration we are reporting does not occur in Et_2O. In this solvent, the original anion **1** is stable (at −75 °C) and remains as such for a long time (24 h), as already reported.[3] An equilibrium between the two anionic structures **1** and **2** can thus be ruled out.

It was recently reported that the bromine−lithium exchange reaction from (*Z*)-2-bromo-1-(trimethylsiloxy)ethylene (**3**) followed by condensation with *tert*-butyldimethyl triflate or chlorosilane leads, depending on the experimental conditions, either to the trimethylsilyl enol ether[4] **4** or to the isomeric *tert*-butyldimethylsilyl enol ether[5] **5** (Scheme 1).

Other results by our group dealing with new vinylogation methods indicated that the condensation of carbonyl compounds with the anionic species **1** (obtained after the bromine lithium exchange reaction on **3**) leads to isolable hydroxy enol ethers[3] **6** (Scheme 1). The formation of **4** and **6** is in agreement with an intermediate carbanionic structure **1**, whereas the isolation of **5** suggests an enolate species **2** obtained by 1−3 migration of the trimethylsilyl group from the oxygen atom to the carbon atom. The observation that **6** was obtained in Et_2O alone while **5** was produced in an Et_2O−THF mixture (THF/Et_2O = 25/75) prompted us to determine, by NMR spectroscopy, the structure of the anionic species obtained from **3** when the bromine lithium exchange reaction was done in pure Et_2O or THF.

Scheme 1[a]



[a] Key: (a) t-BuLi, Et_2O, −70 °C; (b) $TfOSiMe_2$-t-Bu, THF, HMPA, −70 to 0 °C, 2 min; (c) $TfOSiMe_2$-t-Bu or $ClSiMe_2$-t-Bu, THF, HMPA, −70 to 0 °C, 90 min; (d) (i) R^1R^2CO, Et_2O, −70 °C, (ii) dilute Na_2CO_3, −70 °C.

In Et_2O, the ^{1}H NMR spectrum[6] obtained 90 min after the end of the addition of the 2-bromo-1-(trimethylsiloxy)ethylene (**3**) to *tert*-butyllithium puts into evidence the presence of only one anionic species. The spectroscopy data (δ in ppm: ^{1}H = 7.4 (1H, H^1), 5.1 (1H, H^2); ^{13}C = 147.0 (C^1), 138.7 (C^2); ^{29}Si = 16.41 ($OSiMe_3$) and especially the ^{29}Si chemical shift are in favor of the exclusive formation of the carbanionic species **1** (Figure 1).[8]

When THF is used, the ^{1}H NMR spectrum of the reaction medium, also recorded after 90 min, shows that the carbanionic species **1** still is the main product, but together with another anionic species. The ^{1}H NMR spectrum changes with time (from 90 to 480 min) and indicates the transformation of the major species **1** into the other one. The complete transformation is achieved after 8 h (50% after 3 h). The spectroscopic data (δ in ppm: ^{1}H = 7.5 (1H, H^1), 3.1 (1H, H^2); ^{13}C = 168.0 (C^1), 86.0 (C^2); ^{29}Si = −14.60 ($SiMe_3$) clearly demonstrate the enolic structure **2** for the species in the medium (Figure 1).

The two species **1** and **2** show important differences in their chemical shifts [$\Delta(\delta_1 - \delta_2)$] especially for H^2 (2 ppm), C^2 (52.7 ppm), and the Si atom (31 ppm).

The 1D ^{29}Si and 2D $^{1}H/^{29}Si$ NMR spectra (Figure 1) have been obtained using the optimized techniques described previously.[8]

The obtention of the disilylated compound **5** (Scheme 1), corresponding to migration of the silyl group from oxygen to carbon, calls for a 2-fold explanation: (i) the slow temperature increase of conditions c, Scheme 1 (−70 to 0 °C in 90 min), allows the small amount of THF in the medium to trigger the transposition of **1** into **2**; (ii) **2** is much more reactive than **1** toward silylating agents. The transformation of **1** into **2** comes with some byproducts, all identified,[7] among which 1-(trimethylsiloxy)-2-trimethylsilyl ethylene **7** was detected.[9] Thus, we propose an intermolecular migration of the trimethylsilyl group,[10] at least partial, to explain the **1**→**2** isomerization. In THF, a solvent considered as more basic than Et_2O,

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(1) Simchen, G. ; Pfletschinger, J. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 428.

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(6) The complexity of the signals corresponding to H^1 and H^2 in the ^{1}H NMR spectra of **1** and **2** can be explained by the presence of many lithio aggregates.[7]

(7) Baudrillard, V. et al. Manuscript in preparation.

(8) Baudrillard, V.; Davoust, D.; Plé, G. *Magn. Reson. Chem.* **1994**, *32*, 40.

(9) Compound **7** (from 3% since 10 min to 8% after 90 min) has been identified by NMR spectroscopy after optimization of the experimental acquisition parameters[8] [δ in ppm: ^{1}H = 6.88 (1H, H^1), 4.31 (1H, H^2); ^{13}C = 151.9 (C^1), 103.1 (C^2); ^{29}Si = 20.6 ($OSiMe_3$), −10.9 ($SiMe_3$)].

(10) An intramolecular migration was proposed from 2-bromo-1-(trimethylsiloxy)benzene.[1]

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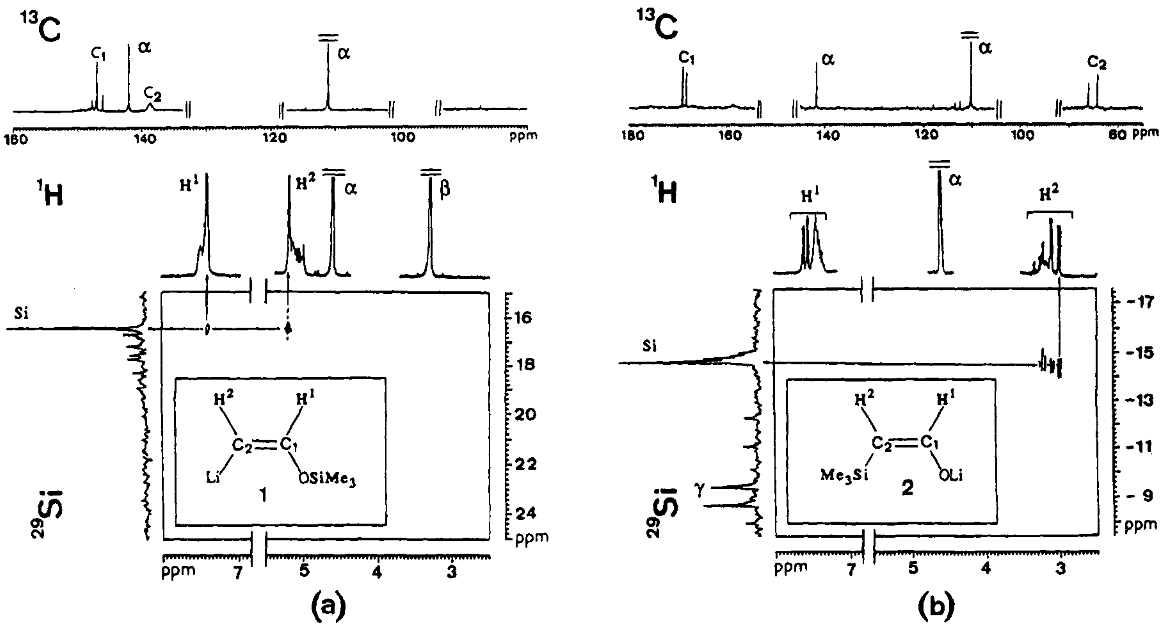


Figure 1. ^1H, ^{13}C, ^{29}Si 1D and $^1H/^{29}Si$ 2D NMR spectra of carbanion **1** in Et_2O-d_{10} after 90 min (a) and enolate **2** in THF-d_8 after 480 min (b). Key: (α) isobutene signals; (β) solvent signal (Et_2O); (γ) signals of various acetylenic derivatives formed by degradation of **1** in THF.[7]

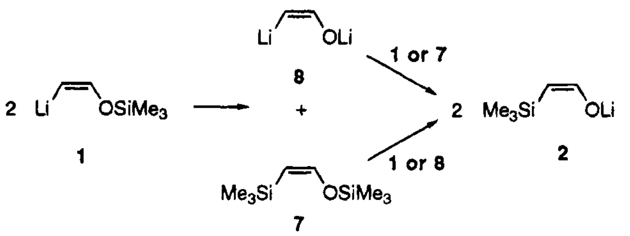
the carbanionic species **1** is more nucleophilic than in Et_2O and becomes able to cleave the O–Si bond of another molecule of **1**, leading to **7** and **8**. The formation of enolate **2** can then occur either by reaction of the dianion **8** with **1** or **7** or by reaction of the disilylated product **7** with **1** or **8** (Scheme 2).

Experimental Section

General. NMR spectra were obtained on a Bruker ARX 400 operating at 400 MHz for proton, 100.61 MHz for carbon, and 79.49 MHz for silicon. ^1H and ^{13}C shifts were referenced to the solvent lines (Figurel (a) Et_2O-d_{10}; (b) THF-d_8). ^{29}Si chemical shifts were referenced to TMS.

Halogen–Metal Exchange. The experiments were performed directly in the NMR tube. The brominated reagent **3** (0.13 mmol) in a cooled solution (−75 °C) of pure Et_2O-d_{10} or THF-d_8 (0.4 mL) was added under argon to a cooled solution of *tert*-butyllithium in pentane (0.13 mL, 1.8 M, 0.23 mmol).

Scheme 2



The ^1H, ^{13}C, ^{29}Si 1D NMR spectra and 2D heteronuclear $^1H/^{29}Si$ spectra were recorded 90 min after the end of the addition when Et_2O was used and after 480 min in the case of THF.

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