

Elimination–Rearrangement in β -Functionalised Silanes—the Direction of the Rearrangement and its Scope

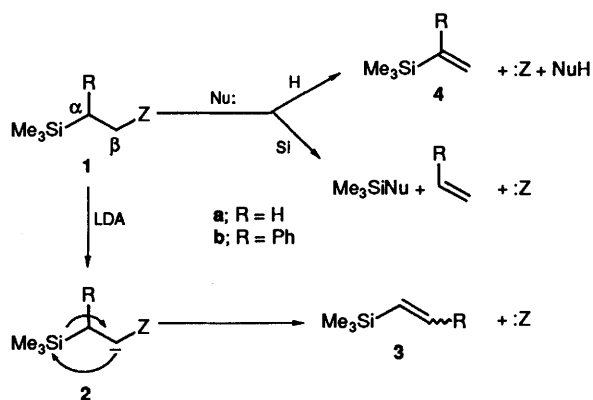
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A new eliminative rearrangement of β -silyl carbanions requires phenyl on carbon α - to silicon when the conjugate acid has a pK_a (DMSO) in the range 12–30; rearrangement involves silicon and not phenyl migration.

In an earlier communication,¹ we reported that when silanes **1** were treated with strongly basic but silicophilic nucleophiles such as *tert*-butoxide, competition between silicophilic and protophilic eliminations was observed (Scheme 1).



When, however, a strong but poorly silicophilic base, such as LDA, was used, the reaction took a third course, *via* **2** to give² the rearranged alkene **3**. The latter process was observed with $R = Ph$ and when Z was a carbanion-stabilising leaving group such as SPh , SO_2Ph or CN . The rearrangement occurs *via* the β -carbanion **2** for $Z = CN$ and SO_2Ph , but formation of **3** from **1** is concerted when $Z = SPh$.

These studies left three significant questions unanswered.

(i) Is the formation of **3a** from **1a** by rearrangement *via* **2** [$pK_a^{(DMSO)}$ of $EtSO_2Ph = 31.0^3$] or by protophilic elimination as for **1a** to **4a**?

(ii) In the formation of **3b** from **1b**, is rearrangement by migration of the trimethylsilyl group or of the phenyl group?

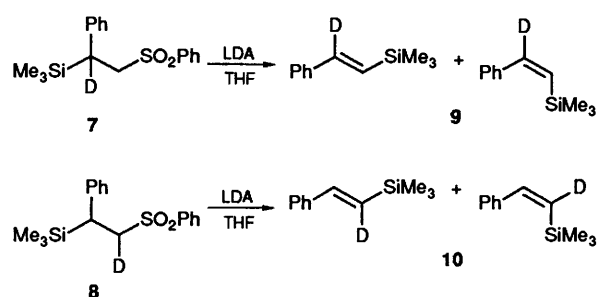
(iii) Are there limits to the observed rearrangement?

We now have answers to these questions as follows.

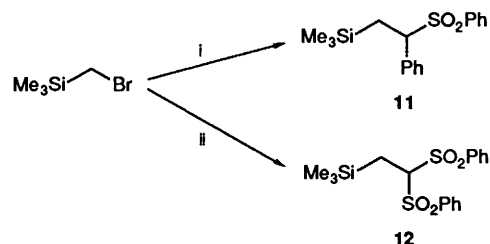
(i) Silane **1** ($R = D$; $Z = SO_2Ph$)¹ was treated with a three molar excess of LDA in THF. After reflux (3 h) and work-up, the solvent and volatiles including trimethyl(vinyl)silane were distilled off and treated at $-30^\circ C$ with an excess of toluene-4-sulfonyl chloride. The silyl sulfide **5**, but none of the isomer **6**, was detected by 1H NMR spectroscopy, demonstrating that the α -phenyl group is required for rearrangement.

(ii) Our earlier studies did not distinguish between phenyl

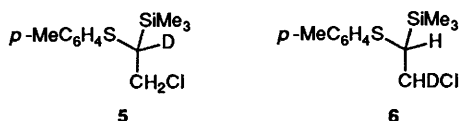
and trimethylsilyl migration. Treatment of **7**¹ and **8** [obtained by quenching the anion **2b** ($Z = SO_2Ph$) with D_2O] separately with LDA in THF gave *E/Z* mixtures of styrenes **9** and **10** respectively (Scheme 2). These results exclude phenyl migration.



(iii) As already mentioned, **1a** ($Z = SO_2Ph$) undergoes protophilic elimination rather than rearrangement; treatment of both **11** and **12** obtained as shown in Scheme 3, with LDA–THF under forcing conditions (reflux, 24 h) gave no products and they were recovered in high yields. These much more acidic substrates [$pK_a^{(DMSO)}$ $PhSO_2Ph$ 23.4⁴; $pK_a^{(DMSO)}$ $(PhSO_2)_2CH_2 = 12.2^3$] are presumably completely converted into their β -anions which are too weakly reactive to rearrange without an α -phenyl group present, but the protophilic pathway is thereby inhibited.



Reagents: i, $PhSO_2CH_2Ph$ –LDA–THF; ii, $(PhSO_2)_2CH_2$ – $EtONa$ – $EtOH$



Acknowledgements

We thank the University of Sheffield for support, CNR (Rome) for a fellowship (to Stefano Menichetti) and Dr. I. Fleming for useful discussions.

References

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Paper 2/01230H

Received 6th March 1992

Accepted 20th March 1992