A New Elimination–Rearrangement Involving Silicon Migration

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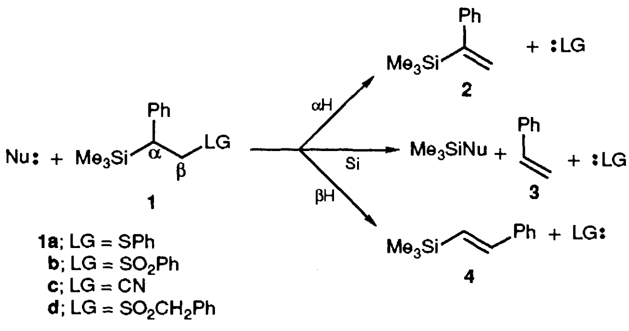
Lithium diisopropylamide (LDA), a strongly basic, poorly silicophilic nucleophile reacts with α-phenylsilanes bearing β-leaving groups to cause 1,2-silyl migration and loss of the leaving group.

In an earlier study,[1] we showed that nucleophiles cause 1,2-elimination in silanes **1** with a choice of silicophilic or α-protophilic pathways determined by the nucleophile, and the leaving group. For example, silane **1a** with *tert*-butoxide in *tert*-butyl alcohol gives **2** (68%, protophilic) and **3** (32%, silicophilic) (Scheme 1).

We have now investigated the reaction of silanes **1** with the strongly basic but poorly silicophilic reagent, lithium diisopropylamide (LDA) with the initial intention of discovering the effect of the reagent on the competition between the silicophilic and α-protophilic pathways. We find, however, that *neither* pathway is a major route; instead the principal product in each case is the *E*-alkenylsilane **4** with minor amounts of the vinyl silane **2** for silanes **1a** and **1d** (Table 1).



Scheme 1 Nu = nucleophile; LG = leaving group.

Formation of alkenylsilane **4**, appears to involve β-deprotonation and *intramolecular* attack on silicon (Scheme 2). Hydrogen deuterium exchange at Cβ is observed when partial reactions of **1b** and **1c** are quenched with D_2O and we think that, for **1b** and **1c**, formation of the carbanion **5** is rapid and complete. For these substrates, the approximate rates of reaction (Table 1) are unaffected by changing the silane : LDA ratio. This excludes a concerted conversion of **1** to **4**. Such

Table 1 Reaction of silanes **1** with LDA in tetrahydrofuran (THF)[a]

Silane	Silane: LDA ratio	$t_{\frac{1}{2}}$[b]/h	Conversion[c] (%)	4:2[c]	Yield[d] (%)
1a	1:4	10[f]	100	10:1	80
1b	1:4	1.5[e]	100	∞	79
1c	1:4	1.5[e]	100	∞	78
1d	1:4	1.5	90	4:1	65

[a] LDA 0.3 mol dm^{-3} at 63 °C. [b] Approximate. [c] By ^1H NMR spectroscopy. [d] Isolated by chromatography. [e] Same value with silane : LDA ratio = 1 : 10. [f] 5.5 h with substrate : LDA ratio of 1 : 10.

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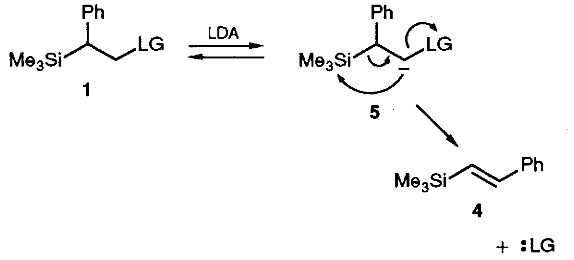
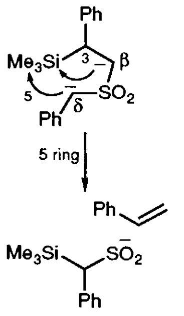


Scheme 2



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anionic 1,2-migration of silicon from carbon to carbon has been reported previously only for special cases.[2]

The leaving group clearly has two effects on the reaction. First, it determines the β-deprotonation equilibrium; secondly, it must affect the rate of rearrangement–elimination of the anion **5**. Silanes **1b** and **1c** have β-protons of comparable acidities[3] but the nucleofugalities of CN and SO_2Ph in 1,2-eliminations are enormously different.[4] We conclude, therefore, that the very similar overall reactivities of **1b** and **1c** suggest a transition structure for **5** → **4** that involves little cleavage of the Cβ–LG bond. For **1a** the β-C–H acidity is much lower[3] and the quenching of partial reactions does not lead to the recovery of deuteriated starting material. We conclude, in this case, that deprotonation is slow and that rearrangement–elimination is rapid.

While these observations raise many questions about the nature of the **5** → **4** reaction, which we shall address in future publications, we have briefly examined the effect of change in the ring size using silane **1d**. In this case, the δ-protons are undoubtedly more acidic than the β (or α) protons but as Table 1 shows, the yield of **4** is high and we find no evidence for ion **6** or styrene. A large 3 > 5 preference for intramolecular nucleophilic substitution by carbanions on carbon electrophiles is very familiar.[5‡]

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[‡] *Note added in proof*: We have shown by deuterium labelling at both Cα and Cβ that for **1b**, it is migration of the silyl group and not of the phenyl group that leads to **4**, together with 10–15% of the *Z*-isomer.