

# A new silicon-mediated elimination–rearrangement †

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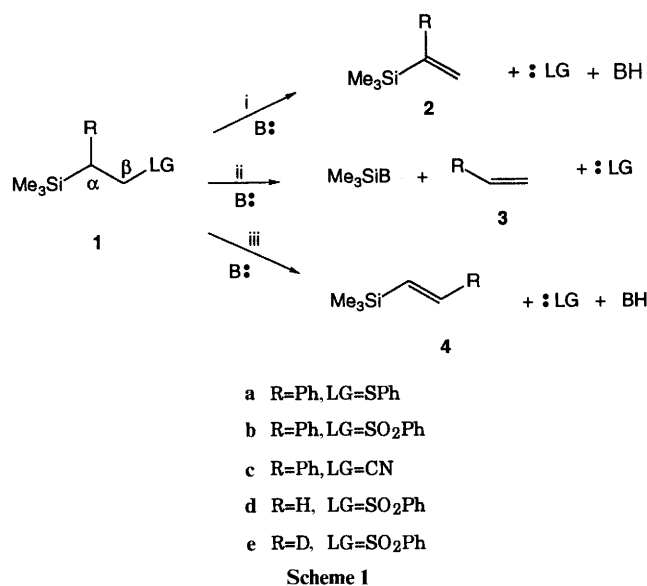
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Treatment of trimethylsilyl ethanes bearing  $\alpha$ -phenyl groups and  $\beta$ -phenylthio, phenylsulfonyl or cyano groups with LDA causes elimination–rearrangement mediated by the  $\beta$ -carbanionic species. Mechanistic conclusions are based on isotopic labelling experiments, the effects of substituents and approximate kinetics. These suggest that trimethylsilyl is the migrating group, that cleavage of the bond to the leaving group is little advanced in the transition structure and that placing of a substituent to encourage Si–C bond cleavage is mandatory.

Fleming has likened<sup>1</sup> the silicon atom of a silane to a proton, and against this background we extended our work on eliminations in carbon systems<sup>2</sup> to eliminations in silanes. We have shown<sup>3</sup> that reactions of silanes **1** with simple bases/nucleophiles follow (i) protophilic and (ii) silicophilic pathways (Scheme 1). Pathway (i), analogous to that in carbon



systems, gives the alkene **2** by deprotonation and (probable) concerted loss of a range of leaving groups. The rate of elimination showed a primary kinetic deuterium isotope effect for system **1a** greater than unity and this pathway was also followed for **1b**. The silicophilic pathway (ii), however, predominated for all leaving groups studied. This pathway was also dominant with the strongly silicophilic but poorly protophilic fluoride ion.<sup>4</sup>

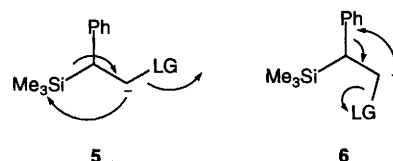
These observations prompted us to examine a very strongly basic and poorly nucleophilic (silicophilic) species, lithium diisopropylamide (LDA). Our objective was to find out whether the silicophilic *vs.* protophilic balance would alter in systems with LG = SPh, SO<sub>2</sub>Ph and CN.

When  $\alpha$ -phenylsilanes **1a–c** were treated with a 4 molar excess of LDA in THF (Table 1, entries 1–6) neither pathway (i) or (ii)

was significant; instead the major product in each case was the styryl silane **4**. Only in the case of **1a** was a minor proportion of the protophilic product **2** formed. These observations reveal a new rearrangement involving [1,2]carbon-to-carbon migration of either a silyl or phenyl group. An anionic carbon-to-carbon silicon migration has been reported previously<sup>5</sup> but occurs only in special cases. A number of questions about the mechanism of this process arise and these we address in order. Results are collected in Table 1.

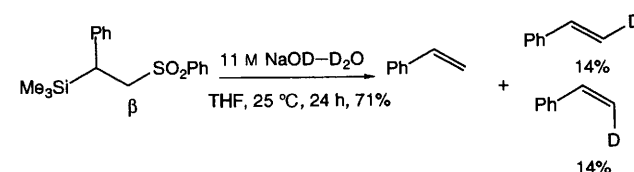
**Which is the deprotonation site and is the process concerted or stepwise?**

Our working hypothesis was that deprotonation at C <sub>$\beta$</sub>  occurs with subsequent intramolecular attack at silicon (structure **5**) or at the phenyl group (structure **6**). When partly-reacted reaction



mixtures of **1b** and of **1c** were quenched with D<sub>2</sub>O the <sup>1</sup>H NMR of the recovered starting materials showed that deprotonation had rapidly occurred at C <sub>$\beta$</sub>  only with no incorporation of D elsewhere. In the case of **1a** no incorporation of D was observed and clearly for this substrate, deprotonation is involved in the rate-determining step. For substrates **1b** and **1c** but not **1a**, the approximate half-lives are independent of the [substrate]:[LDA] ratio. The results are consistent with either of processes **5** and **6**; for **1a** deprotonation appears to be concerted with rearrangement.

In reactions with the silyl sulfone **1b**, 10% of styrene accompanied the rearrangement product, **4**, in reactions at 25 °C. Control experiments showed no reaction of PhSO<sub>2</sub>Li with the starting material; however, with sodium deuteroxide in D<sub>2</sub>O, the reaction occurred smoothly (Scheme 2). The products



Scheme 2

are consistent with silicophilic attack of the hydroxy ion on the starting material which becomes partially deuteriated with

† Parts of this work have been communicated in preliminary form: S. Menichetti, G. Griffiths and C. J. M. Stirling, *J. Chem. Soc., Chem. Commun.*, 1992, 54; S. Menichetti and C. J. M. Stirling, *J. Chem. Soc., Perkin Trans. 2*, 1992, 741.

**Table 1** Reaction of  $\beta$ -substituted silanes with LDA<sup>a</sup>

Entry	Substrate	T/°C	t <sub>3</sub> /h <sup>b</sup>	Ratio 4:2	Conversion <sup>c</sup>	Yield (%) (2 + 4) <sup>d</sup>
1	<b>1a</b>	25	—	— <sup>e</sup>	0	—
2	<b>1a</b>	67	11 <sup>a</sup> ; 5.5 <sup>f</sup>	10:1 <sup>e</sup>	100	80
3	<b>1b</b>	25	132	100:0	100	—
4	<b>1b</b>	67	1.5 <sup>g,h,i</sup>	100:0	100	79
5	<b>1c</b>	25	48	100:0	100	—
6	<b>1c</b>	67	1.5 <sup>g</sup>	100:0	100	63
7	<b>1e</b>	67	1	—	100	60 <sup>j,k</sup>
8	<b>15</b>	67	— <sup>l</sup>	—	—	—
9	<b>16</b>	67	— <sup>l</sup>	—	—	—
10	<b>17</b>	25	∞	—	0	—
11	<b>17</b>	67	15	4:1	90	65
12	<b>17</b>	67	40	Traces <sup>m</sup>	—	—

<sup>a</sup> 4 Equivalents in THF. <sup>b</sup> Approximate. <sup>c</sup> By <sup>1</sup>H NMR. <sup>d</sup> Isolated. <sup>e</sup> No incorporation of deuterium in part reactions on D<sub>2</sub>O quenching. <sup>f</sup> With 10 equiv. LDA. <sup>g</sup> With 4 or 10 equiv. of LDA. <sup>h</sup> If HCl is used in quenching, 10% of styrene is formed from **4b**. <sup>i</sup> The E/Z ratio was 85:15 and independent of [LDA]. <sup>j</sup> Product is vinyltrimethylsilane. <sup>k</sup> Trapped as adduct with 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SCl; see text. <sup>l</sup> No reaction detected after 24 h. <sup>m</sup> Main product is styrene.

concomitant formation of styrene. The alternative of silicophilic attack on the rearrangement product **4** (R = Ph) is not consistent with the labelling pattern.

#### What is the dependence of the reaction on the leaving group?

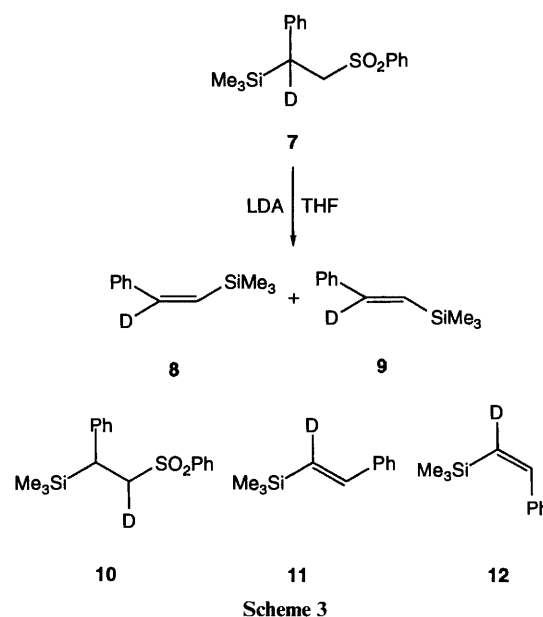
For the tentative intermediates/transition structures **5** and **6** two important effects of the leaving group can be envisaged; firstly, deprotonation is much greater with **1b** and **1c** than with **1a**. Matthews *et al.*<sup>6</sup> have measured pK<sub>a</sub>s (in DMSO) for PhSMc, PhSO<sub>2</sub>Me and MeCN at *ca.* 35, 29 and 31 respectively. Dissociation will therefore be complete for **1b** and **1c** in the presence of LDA. Consistently, as mentioned above, rates for these two substrates are independent of LDA concentration. Secondly, the departure of the leaving group must be involved in the RDS for substrates **1b** and **1c** as shown by the H/D exchange observations. Earlier work from our group has examined nucleofugalities of SPh, SO<sub>2</sub>Ph and CN in  $\beta$ -eliminations activated either by carbanion-stabilising groups or by  $\beta$ -silicon.<sup>2,3</sup> A striking pattern emerges from this earlier work; while SPh and SO<sub>2</sub>Ph have rather similar nucleofugalities, that of CN is very low. Cyanide is a rarely encountered leaving group except in carbonyl-forming eliminations.<sup>7</sup> Notwithstanding this difference, however, the reactivities of **1b** and **1c** are similar. This implies rather little separation of the leaving group in the transition structure of the elimination–rearrangement. In this connection, we plan to use ‘Hammett’ leaving groups to test the sensitivity of the system and hence draw further conclusions about the  $\beta$ -C–LG cleavage.

#### What is the direction of the rearrangement?

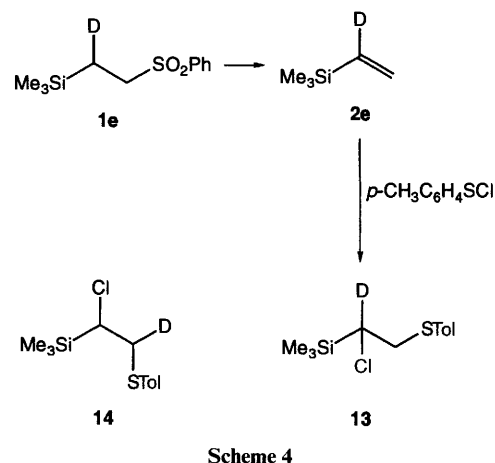
We established that it is the silicon atom and not the phenyl group that becomes attached to C <sub>$\beta$</sub> . Substrate **7** with deuterium at C <sub>$\alpha$</sub>  was prepared by photoaddition of PhSD to  $\alpha$ -styryltrimethylsilane, **2** (R = Ph) and subsequent oxidation. Treatment of **7** with LDA under the usual conditions gave a mixture of **8** and **9** while the sulfone **10**, obtained by quenching the sulfonyl-stabilised anion **5** with D<sub>2</sub>O, gave a mixture of the styrenes **11** and **12** as well as **4** (R = Ph) (Scheme 3). These results exclude migration of the phenyl group; when the label and the phenyl group are on the same atom they are not separated and when they are on adjacent atoms, they are not brought together.

#### What is the scope of the rearrangement?

The requirement for the  $\alpha$ -phenyl group was explored by subjecting the unsubstituted sulfone **1d** to the reaction conditions. The only product was vinyltrimethylsilane **2** (R = H). This product is that to be expected from either  $\alpha$ -protophilic elimination or  $\beta$ -protophilic rearrangement–elimination. These alternatives were again distinguished by isotopic



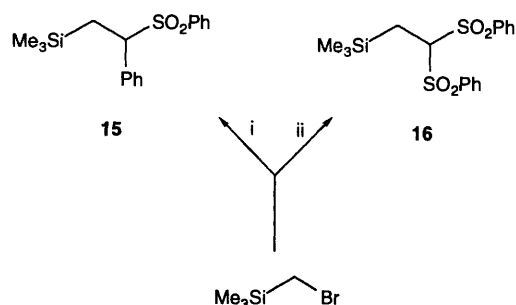
labelling. Sulfone **1e** (entry 7) was treated with a three-fold excess of LDA in THF and the volatiles were distilled off into a solution of toluene-*p*-sulfonyl chloride at –30 °C. Sulfide **13** but none of the isomer **14** was isolated showing that no rearrangement has occurred (Scheme 4).



Evidently the phenyl group is required for rearrangement. This is notwithstanding the fact that it must considerably accelerate the  $\alpha$ -protophilic pathway, as seen for  $\beta$ -elimination

in alkyl halides which a  $\beta$ -phenyl group can accelerate some 500-fold.<sup>8</sup> In the silicophilic rearrangement, the role of the phenyl group is, presumably, to weaken the Si-C bond, a phenomenon clearly seen in the ejection of carbon leaving groups in nucleophilic attack at silicon.<sup>9</sup>

With regard to the nature of the  $\beta$ -carbanion which initiates the rearrangement, we altered the basicity of this ion in structures **15** and **16** (Scheme 5). These substrates are much

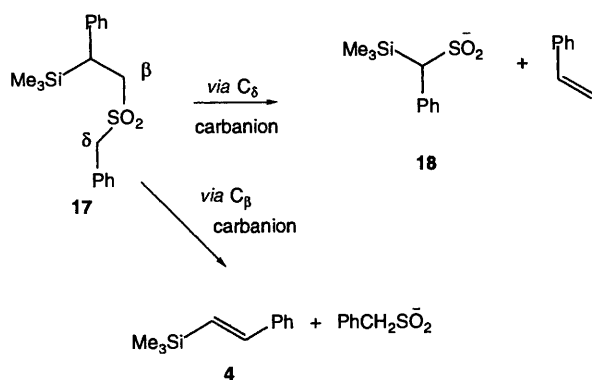


**Scheme 5** Reagents: i,  $\text{PhCH}_2\text{SO}_2\text{Ph}$ , LDA, THF; ii,  $\text{PhSO}_2\text{CH}_2\text{SO}_2\text{Ph}$ , EtONa, EtOH

more acidic than **1b**; **15** can be compared with  $\text{PhCH}_2\text{SO}_2\text{Ph}$ ,  $\text{p}K_a(\text{DMSO}) = 23.4$ <sup>10</sup> and **16** with  $(\text{PhSO}_2)_2\text{CH}_2$ ,  $\text{p}K_a(\text{DMSO}) = 12.2$ .<sup>11</sup> Even in forcing conditions (LDA in THF at reflux) neither sulfone reacted by any of the three possible pathways. The substrates would essentially be completely ionised under the reaction conditions, suppressing the protophilic pathway. The silicophilic pathway is not observed with the very weakly silicophilic and hindered amide ion and the stabilised  $\beta$ -carbanion is evidently too unreactive to engage in the rearrangement-elimination sequence.

#### What is the dependence of the elimination-rearrangement on the separation of silicon and distal carbanion?

We have not made a comprehensive study of this point but we have examined the behaviour of substrate **17** (Scheme 6).



**Scheme 6**

Treatment of **17** with an excess of LDA-THF under the standard conditions slowly gave (Table 1) a 4:1 mixture of the rearrangement product **4** and the protophilic elimination product **2**. These observations are consistent with rearrangement only *via* the  $\beta$ -carbanion (Scheme 6). This is slow, presumably because of the formation of the  $\beta,\delta$ -dicarbanion, and allows competition *via* the protophilic pathway mediated by deprotonation at  $C_\alpha$ . When **17** is briefly treated with an excess of LDA and then quenched with  $\text{D}_2\text{O}$ , it is recovered with deuterium at both  $\beta$  and  $\delta$  positions. When, however, only a slight excess (1.2 equiv.) of LDA is used, quenching with  $\text{D}_2\text{O}$  gives only  $\delta$ -deuteriated starting materials. When the mixture is kept at elevated temperatures over a long period, the main product is styrene with traces of protophilic product **2** and  $\beta$ -rearrangement product **4**. Styrene can result either from

intermolecular or intramolecular silicophilic attack by the  $\delta$ -carbanion. Clearly there is no favouring of a five ( $\delta$ ) versus three ( $\beta$ ) ring transition structure for rearrangement.<sup>12</sup>

## Conclusions

This new rearrangement requires a  $\beta$ -leaving group which is also carbanion-stabilising together with an appropriate  $\alpha$ -substituent, such as phenyl, to weaken the  $\alpha$ -carbon-silicon bond selectively. The transition structure appears to involve little carbon-leaving group bond fission and a three-ring transition structure is probably preferred over other ring sizes.

## Experimental

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$  at 250 and 75 MHz, using residual  $\text{CHCl}_3$  at  $\delta_{\text{H}}$  7.27 and the central line of  $\text{CDCl}_3$  at  $\delta_{\text{C}}$  77.00 as references;  $J$  values are given in Hz. IR spectra were recorded on a Perkin-Elmer 1725X infrared spectrometer. Melting points were obtained using a Kofler hot-stage apparatus and are uncorrected. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Trimethylsilyl chloride and diisopropylamine were distilled before use. All other commercial reagents were used as received without further purifications. Lithium diisopropylamide (LDA)<sup>13</sup> and toluene-*p*-sulfonyl chloride<sup>14</sup> were prepared following literature procedures. Light petroleum refers to the fraction bp 40–60 °C.

### $\alpha$ -Trimethylsilylstyrene **2**

$\alpha$ -Bromostyrene (13.40 g, 74.0 mmol) in dry THF (50  $\text{cm}^3$ ) was added dropwise during 1 h to a suspension of magnesium turnings (1.80 g, 75.0 mmol) in dry THF (50  $\text{cm}^3$ ). Trimethylsilyl chloride (8.60 g, 80.0 mmol) in dry THF (50  $\text{cm}^3$ ) was added and the mixture heated at reflux for 5 h with complete consumption of the magnesium. Quenching with saturated ammonium chloride and extraction with dichloromethane ( $3 \times 50 \text{ cm}^3$ ) gave crude material which was distilled *in vacuo* to give **2** (10.42 g, 79%) as a colourless oil, bp 90 °C/18 mmHg (lit.,<sup>15</sup> 73–77 °C/8 mmHg);  $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$  3042, 2945, 1595, 1245;  $\delta_{\text{H}}$  7.42–7.33 (m, 5 H), 5.91 (d,  $J$  2.4, 1 H), 5.68 (d,  $J$  2.4, 1 H), 0.28 (s, 9 H).

### 1-Phenylthio-2-phenyl-2-trimethylsilylethane **1a**

A mixture of thiophenol (2.40 g, 2.2 mmol),  $\alpha$ -trimethylsilylstyrene **2** and azoisobutyronitrile (AIBN) (50 mg, 0.3 mmol) was heated at 90 °C for 1 h, when additional AIBN (60 mg) was added and the mixture was again heated at 90 °C for 1 h. The crude product was purified by bulb-to-bulb distillation (bp 170 °C/0.5 mmHg) to give **1a** (4.90 g, 86%) as a pale yellow oil;  $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$  3060 and 3020, 2950, 1600, 1585, 1250;  $\delta_{\text{H}}$  7.30–7.02 (m, 10 H), 3.45–3.30 (m, AB part of an ABX system,  $J_{\text{AB}}$  12.5, 2 H), 2.40–2.30 (m, X part of an ABX system, 1 H), –0.01 (s, 9 H).

By the same procedure the following silyl sulfides were prepared and oxidised (below) to the corresponding sulfones without further purifications: 1-phenylthio-2-trimethylsilylethane from thiophenol and vinyltrimethyl silane; 1-phenylthio-2-trimethylsilyl[2- $^2\text{H}$ ]ethane from PhSD and vinyltrimethylsilane; 1-phenylthio-2-phenyl-2-trimethylsilyl[2- $^2\text{H}$ ]ethane from PhSD and **2**; 1-benzylthio-2-phenyl-2-trimethylsilyl[2- $^2\text{H}$ ]ethane from  $\text{PhCH}_2\text{SD}$  and **2**.

### General procedure for the preparation of sulfones **1b**, **1d**, **1e**, **7** and **17**

To a solution of the sulfide in methanol, ammonium molybdate heptahydrate  $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 7\text{H}_2\text{O}]$  (0.05 equivalents) and 30% aqueous hydrogen peroxide (6 equivalents) were added and the mixture was kept at 20 °C for 16 h. The mixture was diluted with brine and extracted with dichloromethane. The organic layer was washed successively with aqueous 10%

sodium hydrogen sulfite, and brine and dried ( $\text{Na}_2\text{SO}_4$ ). Evaporation gave the crude sulfone which was purified by chromatography on silica and/or recrystallisation.

**1-Phenylsulfonyl-2-phenyl-2-trimethylsilylethane 1b.** Mp 109–111 °C (ethanol) (65%). (Found: C, 63.97; H, 7.05; S, 9.89.  $\text{C}_{17}\text{H}_{22}\text{O}_2\text{SSi}$  requires C, 64.11; H, 6.96; S, 10.07%);  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3065 and 3030, 2980 and 2930, 1610 and 1595, 1320, 1260, 1150;  $\delta_{\text{H}}$  7.58–7.52 (m, 2 H), 7.44–7.35 (m, 1 H), 7.28–7.19 (m, 2 H), 7.02–6.88 (m, 3 H), 6.76–7.71 (m, 2 H), 3.74 (dd,  $J$  12.5 and 14.5, 1 H), 3.37 (dd,  $J$  2.0 and 14.5, 1 H), 2.68 (dd,  $J$  2.0 and 12.5, 1 H), –0.08 (s, 9 H).

**1-Phenylsulfonyl-2-trimethylsilylethane 1d.** Mp 49–51 °C (hexane) (81%). (Found: C, 54.79; H, 7.35; S, 13.48.  $\text{C}_{11}\text{H}_{18}\text{O}_2\text{SSi}$  requires C, 54.5; H, 7.48; S, 13.23%);  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3094 and 3062, 2954 and 2901, 1585; 1309, 1260, 1139;  $\delta_{\text{H}}$  7.90–7.85 (m, 2 H), 7.70–7.50 (m, 3 H), 3.02–2.92 (m, 2 H), 0.94–0.84 (m, 2 H), 0.94–0.84 (m, 2 H), –0.04 (s, 9 H).

**1-Phenylsulfonyl-2-trimethylsilyl[2- $^2\text{H}$ ]ethane 1e.** Mp 47–52 °C (hexane) (80%).  $^1\text{H}$  NMR showed 70% deuteration at position 2:  $\delta_{\text{H}}$  7.90–7.85 (m, 2 H), 7.70–7.50 (m, 3 H), 3.02–2.92 (m, 2 H), 0.94–0.84 (m, 0.6 H), –0.04 (s, 9 H).

**1-Benzylsulfonyl-2-phenyl-2-trimethylsilylethane 17.** Mp 124.5–126 °C (ethanol) (22.5%). (Found: C, 64.91; H, 7.23; S, 9.48.  $\text{C}_{18}\text{H}_{24}\text{O}_2\text{SSi}$  requires C, 65.06; H, 7.22; S, 9.63%);  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3075 and 3050, 2975 and 2930, 1610, 1310, 1260, 1135;  $\delta_{\text{H}}$  7.42–7.01 (m, 10 H), 3.61 (br s, AB system, 2 H), 3.50 (dd,  $J$  11.6 and 14.6, 1 H), 3.10 (dd,  $J$  1.4 and 14.6, 1 H), 2.79 (dd,  $J$  1.40 and 11.60, 1 H), –0.02 (s, 9 H).

**1-Phenylsulfonyl-2-phenyl-2-trimethylsilyl[2- $^2\text{H}$ ]ethane 7.** Mp 107–111 °C (ethanol) (61%).  $^1\text{H}$  NMR showed 60% deuteration at position 2:  $\delta_{\text{H}}$  7.58–7.52 (m, 2 H arom.), 7.44–7.35 (m, 1 H), 7.28–7.19 (m, 2 H), 7.02–6.88 (m, 3 H), 6.76–7.71 (m, 2 H), 3.74 (m, 1 H), 3.37 (m, 1 H), 2.68 (m, 0.4 H), –0.08 (s, 9 H).

#### 1-Cyano-2-phenyl-2-trimethylsilylethane 1c

To a mixture of trimethylsilyl chloride (10.80 g, 100 mmol) and magnesium turnings (800 mg, 33 mmol) in hexamethylphosphorus triamide (HMPT) (30  $\text{cm}^3$ ) kept at 40–50 °C, cinammotrile (4.30 g, 33 mmol) in HMPT (10  $\text{cm}^3$ ) was added dropwise during 1 h. The mixture was kept at 70 °C for 12 h, diluted with ether and quenched with ice. The organic phase was separated, washed with water until neutral, dried over anhydrous sodium sulfate and evaporated to give the crude product which was purified by bulb-to-bulb distillation (bp 170 °C/0.7 mmHg) to give 1-cyano-2-phenyl-1,2-bis(trimethylsilyl)ethane (6.5 g) [ $\nu_{\text{max}}(\text{C}\equiv\text{N}$  str) 2220  $\text{cm}^{-1}$ , lit.,<sup>16</sup> 2215  $\text{cm}^{-1}$ ] as a glassy solid which was directly used for the preparation of **1c** without further purification.

To a solution of 1-cyano-2-phenyl-1,2-bis(trimethylsilyl)ethane (4.0 g, 14.5 mmol) in acetic acid (10  $\text{cm}^3$ ), aluminium trichloride (260 mg, 2 mmol) was added and the mixture was heated at reflux for 24 h. The dark solution was diluted with water (40  $\text{cm}^3$ ) and extracted with dichloromethane (3  $\times$  40  $\text{cm}^3$ ). The organic phase was washed with aqueous saturated sodium hydrogen carbonate and with brine, dried ( $\text{Na}_2\text{SO}_4$ ) and evaporated to give crude material which was chromatographed on silica [ethyl acetate–light petroleum (1 : 20)] to give **1c** (2.4 g, 80%), mp 42–43 °C (lit.,<sup>16</sup> 46 °C) from hexane;  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3060 and 3020, 2950 and 2895, 2210, 1600, 1250;  $\delta_{\text{H}}$  7.30–7.01 (m, 5 H), 2.75 (m, 2 H), 2.42 (m, 1 H), 0.02 (s, 9 H).

#### 1-Phenyl-1-phenylsulfonyl-2-trimethylsilylethane 15

To lithium diisopropylamide (4 mmol) in dry THF (10  $\text{cm}^3$ ), benzyl phenyl sulfone (928 mg, 4 mmol) in THF (20  $\text{cm}^3$ ) was added and the mixture kept at 0 °C for 1 h. Bromomethyltrimethylsilyl silane (835 mg, 5 mmol) in THF (3  $\text{cm}^3$ ) was added and the mixture was heated at reflux for 15 h. Quenching with saturated aqueous ammonium chloride and dichloromethane extraction

(3  $\times$  30  $\text{cm}^3$ ) gave crude material which was recrystallised to give **15** (840 mg, 66%) as pale yellow crystals, mp 78.5–79.5 °C (from hexane) (Found: C, 64.22; H, 7.07; S, 9.89.  $\text{C}_{17}\text{H}_{22}\text{O}_2\text{SSi}$  requires C, 64.1; H, 6.91; S, 10.06%);  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3090, 3067 and 3030, 2958 and 2905, 1606, 1308, 1249, 1145,  $\delta_{\text{H}}$  7.55–7.02 (m, 10), 4.05 (m, 1 H), 1.65 (m,  $J_{\text{AB}}$  12.5, 2 H), 0.02 (s, 9 H).

#### 1,1-Bis(phenylsulfonyl)-2-trimethylsilylethane 16

To bis(phenylsulfonyl)methane (889 mg, mmol) in anhydrous ethanol (50  $\text{cm}^3$ ), sodium (70 mg, 3 mmol) was added. A white solid precipitated from the solution and after 1 h at 20 °C bromomethyltrimethylsilane (730 mg, 4.1 mmol) was added and the mixture was heated at reflux for 23 h. TLC showed the presence of starting material and additional bromoethyltrimethylsilyl silane (501 mg, 3 mmol) was added. The mixture was refluxed for 70 h, quenched with saturated ammonium chloride and extracted with dichloromethane to give a crude product which was chromatographed on silica [ethyl acetate–light petroleum (1 : 3)] to give **16** (286 mg, 25%), mp 99–101 °C (from ethanol) (Found: C, 53.25; H, 5.89; S, 17.01.  $\text{C}_{17}\text{H}_{22}\text{O}_4\text{S}_2\text{Si}$  requires C, 53.37; H, 5.80; S, 16.76%);  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3110, 3090 and 3060, 2950 and 2930, 1585, 1330, 1250, 1155;  $\delta_{\text{H}}$  7.95–7.90 (m, 4 H), 7.73–7.65 (m, 3 H), 7.61–7.52 (m, 4 H), 4.48 (t,  $J$  7.0, 1 H), 1.39 (d,  $J$  7.0, 2 H), 0.11 (s, 9 H).

#### Reaction of substrates 1a–e, 7 and 15–17 with LDA

To a solution of LDA, prepared as described by Brandsma,<sup>13</sup> the substrate in dry THF was added to give a 0.25–0.30 M solution. The mixture was heated at reflux and monitored by TLC and/or gas chromatography;  $^1\text{H}$  NMR integral ratios of small aliquots of the mixture were used for the quantitative measurements of the progress of the reaction. When consumption of the substrate was complete the reaction mixture was quenched with ice and extracted with dichloromethane. Trimethylsilylstyrenes **4** (and/or **2**) were isolated by column chromatography on silica with light petroleum as eluent.

The stabilities of the products to the reaction conditions were confirmed by treating styrenes **2** and **4** with LDA in THF under the reaction conditions, and with water under the working up conditions. Use of 2% HCl in quenching produced *ca.* 10% of styrene from **4b** ( $^1\text{H}$  NMR).

#### Labelling studies of the direction of the rearrangement

Silyl sulfone **1b** (1.1 g, 3.46 mmol) in THF (15  $\text{cm}^3$ ) at –60 °C under argon was treated with butyllithium in hexane (3.6 mmol). After 3 h at –60 °C and 16 h at 15 °C,  $\text{D}_2\text{O}$  (10 mmol) was added and after quenching ( $\text{NH}_4\text{Cl}-\text{H}_2\text{O}$ ), extraction and recrystallisation (ethanol) gave the  $\beta$ -monodeuterio compound **10** (57%) which was 100% monodeuteriated  $\alpha$  to the phenylsulfonyl group as a 44 : 56 mixture of diastereoisomers.

Treatment of the diastereoisomeric mixture, **10**, with LDA in THF at reflux for 4 h gave a mixture of the isomers **11** and **12** (82%) in an 87 : 13 ratio in which, by  $^1\text{H}$  NMR, 64% of the original deuterium had been retained corresponding to a primary deuterium isotope effect of *ca.* 2.

When the  $\alpha$ -deuterio substrate **7** was similarly treated, the isomers **8** and **9** (80%) in a 14 : 86 ratio were obtained. Compound **7** was 60%  $\alpha$ -deuteriated and the silyl styrenes obtained also contained 60% of deuterium  $\alpha$ - to the phenyl group.

In neither of the pair of experiments was there any evidence for phenyl migration.

#### Isotope labelling study of elimination vs. rearrangement

Silyl sulfone **1e** (729 mg, 3 mmol) in THF (5  $\text{cm}^3$ ) was treated with LDA (12 mmol) in THF (25  $\text{cm}^3$ ). The mixture was kept for 3 h at 67 °C when TLC showed the reaction to be complete. The mixture was quenched with water and extracted ( $\text{CH}_2\text{Cl}_2$ ). Distillation of the extracts gave a fraction with bp 36–67 °C

which was cooled to  $-30^{\circ}\text{C}$  and treated with toluene-*p*-sulfenyl chloride (474 mg, 3 mmol). The colourless solution was kept for 1 h at  $-30^{\circ}\text{C}$  and was then washed with saturated aqueous  $\text{NaHCO}_3$  and evaporated to give an oil. This crude product was chromatographed on silica [ethyl acetate–light petroleum (1:20)] to give silane **13** (412 mg, 60%) contaminated with a trace of di-*p*-tolyl disulfide;  $\delta_{\text{H}}$  7.45–7.30 (m, 2 H), 7.20–7.10 (m, 3 H), 3.75 (m, 2 H), 2.70 (m, 0.3 H), 2.32 (s, 3 H), 0.24 (s, 9 H), consistent with literature data.<sup>14</sup> The starting sulfone was 70% deuteriated ( $^1\text{H}$  NMR) at  $\text{C}_x$  and the label was retained completely at  $\text{C}_x$  in the trapping product.

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