

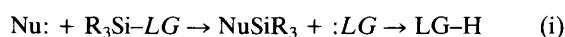
## Protophilic versus Silicophilic Reactions in $\beta$ -Substituted Silanes

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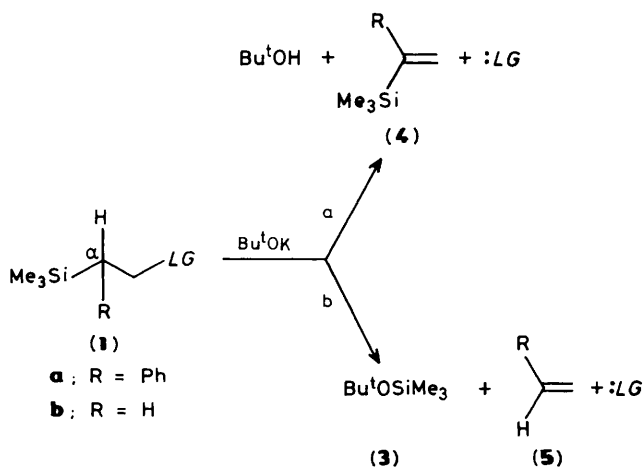
Reactivity in  $\beta$ -eliminations mediated by nucleophilic attack at silicon has been measured as a function of nucleophile, leaving group, and  $\alpha$ -substituent; in some instances competition between protophilic and silicophilic reactions is observed.

Nucleophilic attack at silicon with displacement of a carbanion species is a familiar process<sup>1</sup> [reaction (i)]. Fluoride and alkoxide ions are particularly effective silicophiles for such reactions because of the very high Si-F and Si-O bond strengths.



The range of leaving groups (LG) that can be expelled in such processes is wide, but quantitative work has been restricted hitherto to the extensive studies of Eaborn and his collaborators<sup>2</sup> on the displacement of carbon leaving groups. In these reactions, protonation of the leaving group follows its displacement.

We now report quantitative results on the coupling of desilylation of  $\beta$ -substituted silanes (1) with expulsion of a



$\beta$ -leaving group, against the background of earlier quantitative work on carbanionic eliminations.<sup>3</sup> In addition, we report the first evidence that  $\alpha$ -deprotonation and desilylation by basic nucleophiles can occur in parallel in the same substrate.

Results for the expulsion of a series of leaving groups contingent upon desilylation are in Table 1. Eliminations of acetoxy<sup>4</sup> and phenylsulphonyl<sup>5</sup> groups have been reported previously in connection with qualitative studies of the application of  $\beta$ -trimethylsilylethyl groups for functional group protection. It can be seen that there is broad correlation between the results for desilylation and the nucleofugality values for eliminations from  $\beta$ -substituted carbanions. The

Table 1. Desilylation-elimination reactions.

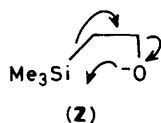
LG	$k_{\text{rel}}$ (DMF) <sup>a</sup>	$k_{\text{rel}}$ (THF) <sup>a</sup>	Rank <sup>b</sup>
OTs	v. fast <sup>i</sup>	v. fast <sup>i</sup>	>11 <sup>d</sup>
OAc	v. fast <sup>c</sup>	>100	>11 <sup>d</sup>
SO <sub>2</sub> Ph	$1 \times 10^{-3}$		8.7
SPh	$5 \times 10^{-4}$	$5 \times 10^{-4}$	8.7
OH	1 <sup>g</sup>	1 <sup>h</sup>	5 <sup>e</sup>
CN	$1.7 \times 10^{-5j}$		-5 <sup>f</sup>

<sup>a</sup> Values for 0.1M Bu<sup>t</sup>OK at 30°C; disappearance of substrate followed by g.l.c. <sup>b</sup> Nucleofugality derived from PhSO<sub>2</sub>[CH<sub>2</sub>]<sub>2</sub> LG relative rates, ref 3. <sup>c</sup> Reactions complete in less than 1 s at 20°C. <sup>d</sup> Maximum value of rank for stepwise process = 11. <sup>e</sup> Value for OMe. <sup>f</sup> Estimate. <sup>g</sup> Absolute value:  $2.2 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . <sup>h</sup> Absolute value:  $9.8 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . <sup>i</sup> Spontaneous formation of ethylene and trimethylsilyl tosylate above 0°C. <sup>j</sup> Cyanide ion appears and then disappears in a complex reaction.

**Table 2.** Protophilic-silicophilic competition in desilylation of  $\alpha$ -phenyl- $\beta$ -substituted silanes (**1a**).

LG	$k_{\text{obs}}$ (rel)	% Silicophilic	% Protophilic
SPh <sup>†c,d</sup>	1 <sup>a</sup>	32	68
SPh <sup>†c,d</sup>	0.55 <sup>b</sup>	57	43
SPh <sup>*c,d</sup>	$2 \times 10^4$	100	0
SO <sub>2</sub> Ph <sup>†c</sup>	34	90	10
OH <sup>†c,d</sup>	v. fast	100	0
CN <sup>†c,e</sup>	0.3	100	0
OAc <sup>†c,d</sup>	v. fast	100	0

† Reactions in THF. \* Reactions in DMF. <sup>a</sup>  $\alpha$ -H. <sup>b</sup>  $\alpha$ -D. <sup>c</sup> Reactions followed by appearance of styrene or  $\alpha$ -trimethylsilylstyrene. <sup>d</sup> Reactions followed by disappearance of substrate. <sup>e</sup> Reactions followed by appearance of CN.



outstanding anomaly, however, is for hydroxy as leaving group; this is very much more readily expelled than would be expected from its rank value, and in the  $\alpha$ -phenyl series (Table 2) a catalytic quantity of base suffices for complete reaction. We suggest that intramolecular attack of oxygen at silicon in the derived alkoxide ion (**2**) is responsible for the high reactivity, and the absence from the products of *t*-butyl trimethylsilyl ether, the complementary product of intermolecular reaction, is in agreement with this finding. This type of process is familiar in the Peterson olefination reaction,<sup>1</sup> and the high reactivity we encounter is entirely in accord with earlier qualitative investigation of  $\beta$ -hydroxy- and  $\beta$ -alkoxy-silanes.<sup>6</sup> It is notable that when the much less basic tetrabutylammonium fluoride is used as the desilylation reagent, desilylation is very slow.

We have also examined the reactivity of  $\alpha$ -phenyl substrates (Table 2). In this case, product analyses reveal that *t*-butoxide attacks *both* silicon *and*  $\alpha$ -hydrogen when the leaving group is

SPh or SO<sub>2</sub>Ph, but not when it is OH, OAc, or CN. The intramolecular oxyanion process undoubtedly accounts for the lack of protophilic reaction in the highly reactive hydroxy-silane and 10 mole % of *t*-butoxide suffices for complete reaction. In the case of SO<sub>2</sub>Ph, OAc, and CN as leaving groups the lesser (or non-existent) extent of protophilic attack may be due to the inductive effect of the  $\beta$ -substituent favouring silicophilic *versus* protophilic attack. We are currently examining the sensitivity of silicon to  $\beta$ -induction; deprotonation is known for a range of  $\beta$ -substituted carbon acids<sup>7</sup> and varies greatly with the nature of the carbanion involved. For SPh as substituent, the primary kinetic deuterium isotope effect has been determined for the  $\alpha$ -deuterio substrate obtained by radical-catalysed addition of PhSD to  $\alpha$ -trimethylsilylstyrene. The magnitude of this isotope effect (2.77) clearly shows that deprotonation is involved in the rate-determining transition state of the process and the presence of the heavy isotope diverts attack of the nucleophile to silicon. Interestingly, when the solvent is changed from tetrahydrofuran (THF) to dimethylformamide (DMF), the protophilic component of the reaction disappears. The effect of the change is, presumably, to deaggregate the base and raise its nucleophilicity/basicity ratio.

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