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1,2- versus 1,3-Silyl migration in the reaction of acylsilanes with silyl-substituted carbanions

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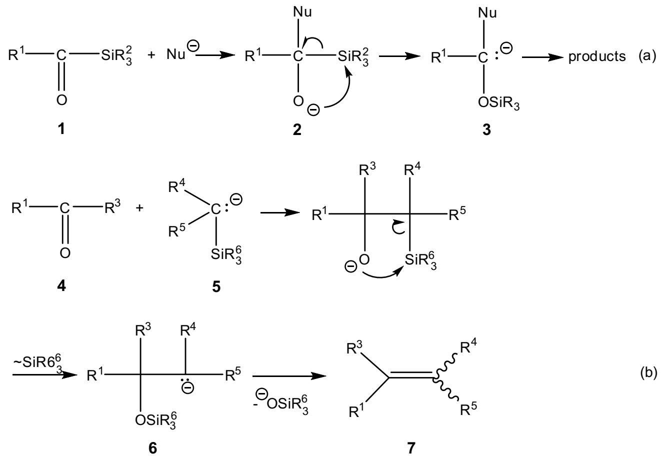
Abstract

The Peterson olefination of acylsilanes **1** by silylated carbanions **5**,**14** to give alkenes **13**,**17** via a 1,3-silyl shift is favored by the stabilization of the carbanion intermediate **16** through two sulfide units versus one as in **12**, while a combination of DMPS on **1** and TBS on **14** leads to 1,2-migration product **15**.

Keywords: Silyl shift; Acylsilane; Carbanion; Peterson olefination

1,2-C → O Silyl migrations have emerged as a powerful tool to generate a reactive carbanion intermediate **3** by nucleophilic attack on acylsilane **1** via the initial adduct **2** (Scheme 1, Eq. a).[1,2] Similarly, a 1,3-C → O silyl migration is the crucial step in the base-induced Peterson olefination of a carbonyl compound **4** to give alkene **7** (Scheme 1, Eq. b).[3,4] For the latter pathway, an alternative mechanism involves (2+2) cycloreversion at the stage of an intermediate 1,2-oxasiletanide to give the alkene product.[3,5] However, in the presence of electron-withdrawing substituents such as the sulfide units of the present study, the evidence suggests that the basic elimination pathway is not concerted, but includes an intermediate of type **6**.[3]

An aspect that has been widely neglected is the potential competition between a 1,2-silyl shift and a 1,3-silyl shift in the reaction of acylsilane **1** with a silicon-substituted carbanion **5** as nucleophile Nu (Scheme 2). The only available evidence is the slight preference for the 1,3 shift (Peterson olefination) in the reaction of **1-TMS** with lithiated silylthioanisole **5-TMS** to give vinylsilane **13-TMS** along with acetophenone apparently as the secondary product of α-silyl ketone **11** (Table 1, entry 1).[6] In our hands, this reaction is not clean; after extensive chromatography (SiO$_2$, ether/hexane) we did find silylketone **11**,[7] but also acetophenone as secondary product (combined yield, 27%); Peterson product **13-TMS** was obtained in the same yield.



Scheme 1.

A handle to influence the ratio of 1,2- versus 1,3-silyl shifts may be the use of different residues R^2, R^6 (Scheme 1) on the silicon resulting in different migratory aptitudes.

Abbreviations: TBS, SiMe$_2t$Bu; DMPS, SiMe$_2$Ph

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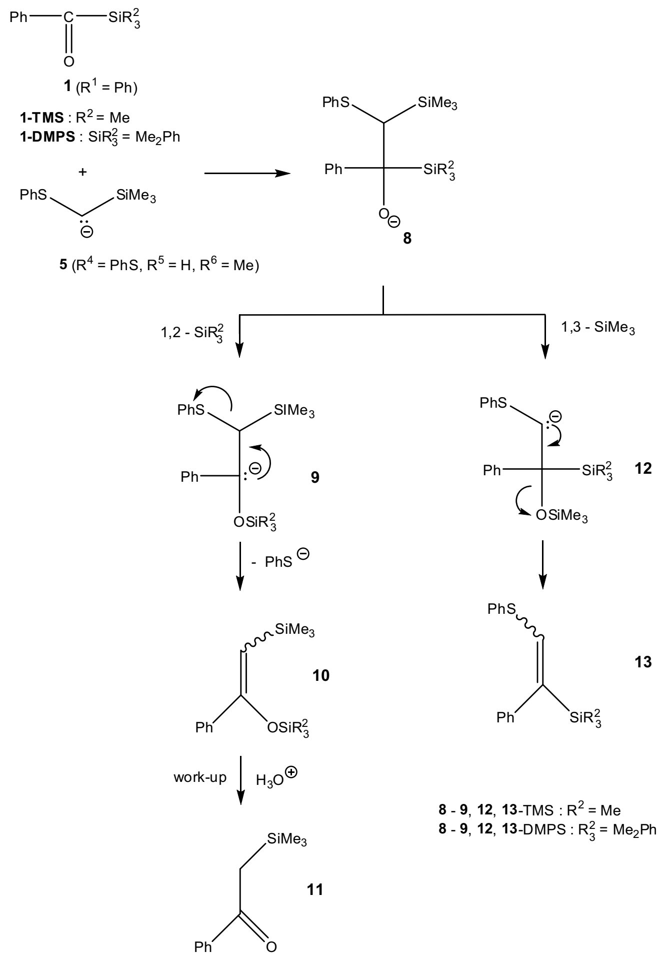


Scheme 2.

Actually, the study of the reaction of bis-silylated thioanisole (**5** with $R^4 = SPh$, $R^5 = SiR_3^7$) with oxiranes had revealed the following sequence of increased ease of migration:[8–10]

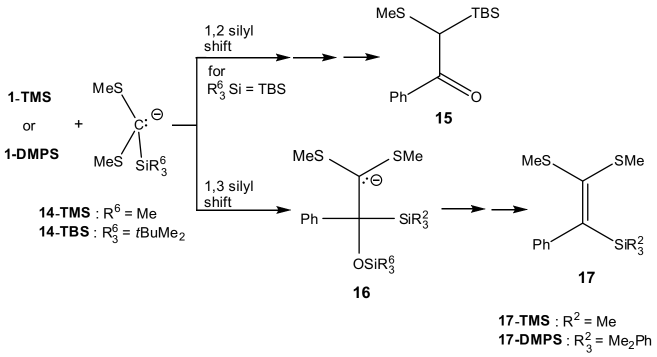
$$\mathrm{SiMe_2}t\mathrm{Bu(TBS)} \approx \mathrm{SiMePh_2} < \mathrm{SiMe_3} < \mathrm{SiMe_2Ph(DMPS)}$$

So, we assumed that a Ph group in the SiR_3^2 unit of the acylsilane **1-DMPS** should favor the 1,2 shift. In fact, the reaction of **1-DMPS** with carbanion **5-TMS** gives an increased yield of acetophenone, the desilylation product of the 1,2-silyl shift pathway (Scheme 2; Table 1, entry 2). At the same time, the yield of the Peterson product **13** goes down to ca. 13% (Table 1).

The ratio of 1,2- versus 1,3-silyl shift may also be influenced by the stability of the intermediate carbanion **12** as formed from **8** by 1,3-silyl migration. We have successfully employed lithiated silyl thioacetals like **14** in the reaction with functionalized oxiranes to give eventually cycloalkanes.[8,9] Using **14** should give, after the 1,3 shift, the stabilization of the negative charge by two sulfur substituents as in **16** versus one phenylthio group in **12**, but should be without appreciable effect on intermediate **9** of the 1,2-silyl migration route (Schemes 1–3). In fact, in a much cleaner reaction, acylsilane **1-TMS** and lithiated trimethylsilylthioacetal **14-TMS** give a high yield of alkene **17-TMS** while a ketone of type **15** or the corresponding desilylated species could not even be detected in trace amounts by GC–MS combination (Table 1, entry 3).[11]

Furthermore, we again checked the influence of the silyl residue on the 'regioselectivity' of silyl migration. Here, we assumed that a *t*Bu group in the SiR_3^6 unit should suppress the 1,3 shift. However, the increased bulk in carbanion **14-TBS** as compared to **14-TMS** widely slows down the addition to acylsilane **1-TMS** and allows only minor conversion. But it could be established by GS–MS analysis that products **15**, **17-TMS** are formed in equal amounts demonstrating that the 1,2 shift is encouraged relative to the use of carbanion **14-TMS** (Table 1, entry 4).

On the other hand, the attempt to enhance the contribution of the 1,2 shift by using acylsilane **1-DMPS** with the most easily migrating silyl group and carbanion **14-TMS**



Scheme 3.

Table 1
Competition experiments in the reaction of acylsilanes **1** with carbanions **5**, **14** (counterion Li)

Entry	Acylsilane	Carbanion	Reaction time [h] (temp)	Product **11**, **15**	Product **13**
1	**1-TMS**	**5-TMS**	0.3 (0 °C)	27%[a]	**13-TMS** (27%)
2	**1-DMPS**	**5-TMS**	0.3 (0 °C)	42%[b]	**13-DMPS** (13%)
3	**1-TMS**	**14-TBS**	12 (−78 °C), then 10 (20 °C)	—	**17-TMS** (84%)
4	**1-TMS**	**14-TBS**	12 (−78 °C), then 28 (20 °C)	**15** (trace)	**17-TMS** (trace)[c]
5	**1-DMPS**	**14-TMS**	12 (−78 °C), then 5 (20 °C)	—	**17-DMPS** (49%)
6	**1-DMPS**	**14-TBS**	12 (−78 °C), then 48 (20 °C)	**15** (42%)	—

[a] Product contaminated with acetophenone from silyl ketone **11**.

[b] Only acetophenone as desilylation product.

[c] GC–MS analysis showed equal amounts of **15** and **17-TMS**.

failed as shown by the formation of alkene **17-DMPS** as the only detectable product in a complex reaction mixture (Table 1, entry 5). Obviously, carbanion stabilization in intermediate **16** overrules the effect of silicon migratory aptitude.

In contrast, when additional hindrance to the 1,3 shift by using **14-TBS** is introduced, a total swing to the 1,2-silyl shift is observed (Table 1, entry 6). Obviously, in spite of the steric hindrance, small amounts of the primary addition product of type **8** give rapid DMPS migration pulling the reaction to the observed ketone product.

Thus, it could be demonstrated that the ambiguity between 1,2- and 1,3-silyl shift in the reaction of acylsilanes **1** with carbanions **5**,**14** can be further supported or totally suppressed by the adequate choice of the carbanion component and of the residues R^2, R^6 on the silicon.

Acknowledgments

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11. *Standard reaction conditions*: THF, generation of carbanion **5** (**14**) from the corresponding CH acid (1.0 equiv) with butyl lithium (1.1 equiv) at −78 °C (0.5 h) and 0–20 °C (0.5 h). Addition of acylsilane **1** (1 equiv) at −78 °C and stirring (see Table 1), finally allowing the mixture to reach room temperature (overnight). If the reaction was incomplete, stirring was continued (Table 1) and finally the reaction mixture was quenched with water. After the usual work-up, products **11**, **13**, **15**, **17** were isolated by flash chromatography (silica or Al_2O_3, eluent petroleum ether with 0–5% ethyl acetate).