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Comparing α-Carbanion-Stabilizing Ability of Substituents Using the Brook Rearrangement

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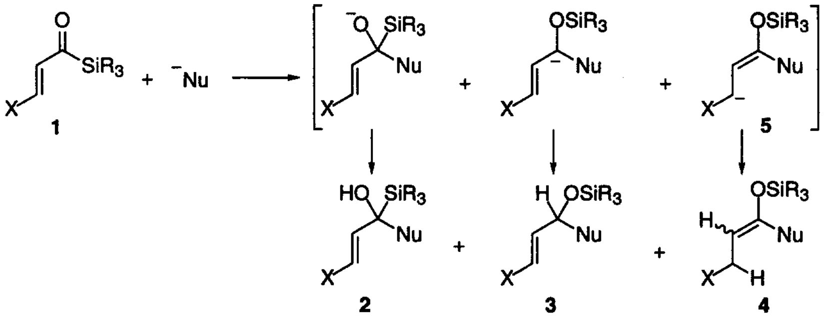
Abstract

The α-carbanion-stabilizing ability of the phenylthio and trimethylsilyl groups was compared based on the relative rate of the base-catalyzed Brook rearrangement of the β-substituted α-silylallylalcohol.

Keywords: Carbanions; Rearrangements; Silicon and Compounds; Substituent effects

In connection with our studies of the mechanism of the Brook rearrangement-mediated [3 + 2][1] and [3 + 4][2] annulations, we needed to determine the relative stability of α-heteroatom-substituted carbanions in solution, particularly α-trimethylsilyl and α-phenylthio carbanions. Although both silicon and sulfur atoms are well recognized to stabilize α-carbanions by negative hyperconjugation and/or (p-d)π bonding, the difference in the degree of the stabilization by both atoms, especially in solution, has been much less known.[3],[4] We envisaged that the relative stability of the α-heteroatom-substituted carbanions would be roughly evaluated on the basis of the ratio of 1,2-adduct **2** to Brook rearrangment product **3** and Brook rearrangement/allylic rearrangement (B-A) product **4** in the reaction of β-heteroatom-substituted acryloylsilane **1** with an appropriate nucleophile.



This stems from the fact that the Brook rearrangement,[5] a 1,2-anionic shift of the silyl group from the carbon atom to the oxygen atom, is facilitated by electron-withdrawing

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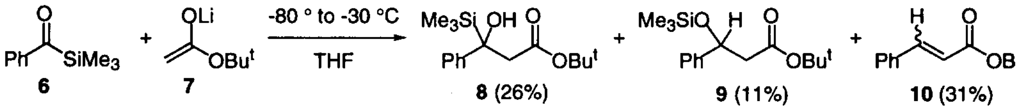
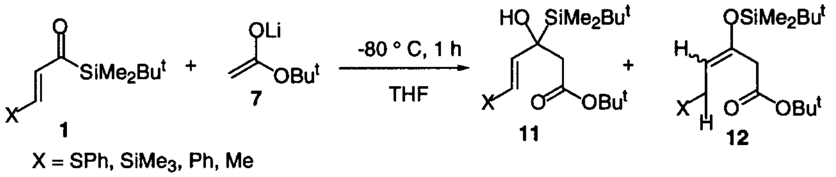
substituents. Thus, the ratio of **3** and **4** to **2** would increase as the α-carbanion-stabilizing ability of the substituent X in **5**, a B-A intermediate, is more increased.

As the nucleophile, we selected the lithium enolate of *t*-butyl acetate **7** based on the preliminary experiments using the reaction of benzoyltrimethylsilane **6**[6] with the enolate in which the 1,2-adduct **8**, Brook rearrangement product **9**, and silanol elimination product of the rearrangement product **10** were obtained in an appropriate ratio.[7]



The reaction was carried out using crotonoylsilane **1d**[8] and β-phenylacryloylsilane **1c**[8] in addition to β-trimethylsilyl and β-phenylthio derivatives **1a,b**[1],[9] in THF (0.02 M) at -80 °C for 1 h and then quenched with acetic acid (1 equiv) to give both the 1,2-addition product and the B-A product except for **1d** (Table 1). This observation that the reaction of the β-phenyl derivative **1c** affords both the 1,2-adduct and the B-A product in contrast to the reaction of the β-methyl derivatives with only the formation of the 1,2-adduct **11d** suggests that the system may be used for comparing α-carbanion stabilization of the substituents. The phenylthio derivative **1a** affords more of the rearrangement product **12** relative to the trimethylsilyl derivative **1b**, indicating that the phenylthio group stabilizes the α-carbanion more strongly than does the trimethylsilyl group. A troubling aspect of this system, however, was the lack of reproducibility; the ratio of **11** to **12** varied over a considerable range, particularly in the β-phenylthio derivative, presumably because even subtle changes in experimental conditions affect the ratio.

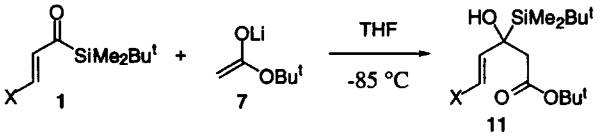
Table 1



	X	yield (%)	ratio (**11** : **12**)
1a	SPh	67-68	0 : 100-50 : 50
1b	$SiMe_3$	75-83	68 : 32-54 : 46
1c	Ph	63-72	81 : 19-89 : 11
1d	Me	90	100 : 0

Next we turned our attention to comparison of the relative rate of base-catalyzed rearrangement of the 1,2-adduct **11** to **12**. Besides **11a-c**, the β-sulfinyl, β-stannyl, β-chloro and β-bromo derivatives were prepared by quenching of the reaction of **1** with **7** at low temperature by addition of acetic acid (Table 2).

Table 2

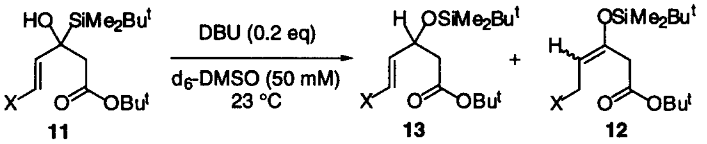


	X	time	yield (%)
11a	SPh	30 min	31
11b	$SiMe_3$	60 min	33
11c	Ph	40 min	56
11e	S(O)Ph	10 min	4^b
11f	$SnBu_3$	60 min	50
11g	Cl^a	30 min	44
11h	Br	30 min	52

[a] Z-isomer was used.
[b] Major product was the Brook rearrangement product.

Effective reaction conditions for the rearrangement were examined on **11a** and **11b** using several amine bases including diethylamine, diisopropylethylamine, pyridine, and DBU in $CDCl_3$ and d_6-DMSO on monitoring by ^1H NMR.[10] The reaction proceeded at a reasonable rate when using 0.2 equiv of DBU in d_6-DMSO (50 mM) at 23 °C. Under these conditions, the half-lives of the reactions for **11** were measured (Table 3). Unfortunately, for the tributylstannyl derivative **11d**, the half-life could not be measured because of its low solubility in d_6-DMSO under the conditions.

Table 3



		product	$t_{1/2}$ (min)
11a	SPh	**12**	3.2
11b	$SiMe_3$	**12**, **13** (*ca* 2:1)	27.5
11c	Ph	**12**	5.5
11e	S(O)Ph	**12**	<1.0
11g	Cl	**13**	**11** : **13** = 2.2 : 1 (25 h)
11h	Br	**13**	**11** : **13** = 4.5 : 1 (43 h)

These results show that the α-carbanion-stabilizing ability of the phenylthio group is considerably greater than that of the trimethylsilyl group, even than that for the phenyl group. Particularly noteworthy is the fact that, in the case of the trimethylsilyl derivative, the Brook rearrangement product **13** was formed in addition to the B-A product **12**, suggesting that α-carbanion stabilization by the trimethylsilyl group is not much greater than that by the siloxy group, although in the latter case, stabilization by the β-carbonyl group must be considered. In the case of phenyl sulfinyl derivative **11c**, the rearrangement occurred spontaneously. The reaction of β-halogen derivatives reached equilibration with the B-A product **13**, not unexpectedly, indicating that the stabilization by the halogen groups was quite small.

In summary, we have demonstrated that comparison of the rate of Brook rearrangement in β-substituted α-silylallylalcohol **11** has the potential of becoming a tool for the assessment of the α-carbanion-stabilizing ability of the β-substituent in solution.

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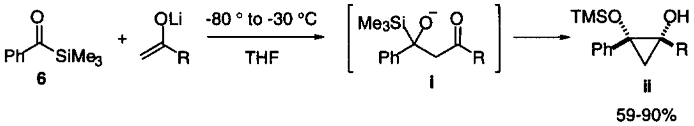

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