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A novel synthesis of silyl enol ethers from α-silylbenzylthiols and carboxylic acid derivatives via C–C bond formation; thermal rearrangement of *S*-α-silylbenzyl thioesters

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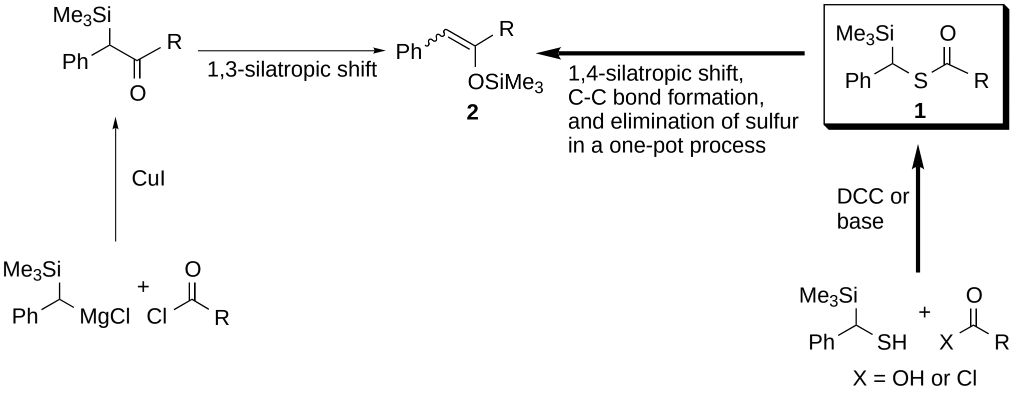
Abstract—A new procedure for the synthesis of silyl enol ethers from *S*-α-silylbenzyl thioesters without need for either bases or catalysts via C–C bond formation is described. Solutions of *S*-α-silylbenzyl thioesters were simply heated at 180°C for 24 h in a sealed tube to give silyl enol ethers in good yields with high stereoselectivity. Cyclization of the dipoles generated by thermal rearrangement of the silyl group and elimination of sulfur afforded silyl enol ethers. © 2001 Elsevier Science Ltd. All rights reserved.

It is well known that silyl enol ethers are very useful species for carbon–carbon bond formation via reactions such as the Mukaiyama aldol condensation and the Mannich reaction.[1] Because of this, the preparation and use of silyl enol ethers have been extensively studied over the past decades.[2] Silyl enol ethers are generally prepared by thermodynamic reactions of carbonyl compounds with silylating reagents in the presence of tertiary amines via enolates, or by kinetic reactions of metal enolates which are formed by treatment of carbonyl compounds with metal amides or alkoxides.[3] While these methods required the addition of basic reagents, alternative procedures for the preparation of silyl enol ethers under neutral conditions would involve the intramolecular rearrangement of silyl groups.[4] For example, the preparation of silyl enol ethers from β-keto silanes via the 1,3-thermal rearrangement of the silyl group represents a convenient route, but this method is not generally used because of problems encountered in the synthesis of β-keto silanes (Scheme 1).[5] From these points of view, we wish to report on a new method for the formation of silyl enol ethers from *S*-α-silylbenzyl thioesters via silicon migration. The method represents a new preparative method of silyl enol ethers under completely neutral conditions, with no need for any catalysts or additives, and involves a



Scheme 1.

Keywords: silyl enol ethers; thermal rearrangement; *S*-silylmethyl thioesters; C–C bond formation.

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thermal 1,4-shift of the silyl group onto the oxygen of the carbonyl function, followed by C–C bond formation. Since *S*-α-silylbenzyl thioesters **1**[6] are easily prepared by the condensation of α-silylbenzylthiols[7] and carboxylic acid derivatives, silyl enol ethers can be produced by this procedure from readily available starting materials with simple manipulation as shown in Scheme 1.

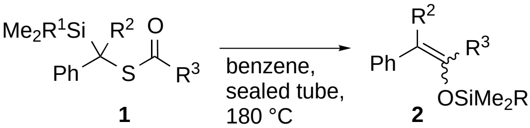
S-α-Trimethylsilylbenzyl thiobenzoate (**1a**, 0.05 mmol) in benzene (0.5 ml) was heated in a sealed tube at 180°C for 24 h to give 1,2-diphenyl-1-trimethylsiloxyethylene (**2a**) in 93% yield with high *Z*-selectivity. In a similar manner, silyl enol ethers **2b**–**h** could be efficiently prepared from thioesters **1b**–**h**, and the results are summarized in Table 1. The structures and *Z*–*E* ratios of the products were determined by ^{1}H NMR spectral analysis.[8]

In cases where aromatic thioesters were used as the starting materials (entries 1–3, 7, and 8), high yields as well as high *Z*-selectivity of the corresponding silyl enol ethers were observed. The reaction of **1c**, bearing an electron-donating group on the aromatic ring of the benzoyl function, was complete within a shorter reaction time than those of **1a**, **b** containing no substituents or electron-withdrawing groups.

It would be expected that the reaction of **1c** occurs at an accelerated rate due to an increase in the interaction between the silicon and the oxygen electron-donated from the 4-methoxyphenyl group in the rate-limiting rearrangement step. The *Z*-selectivity of the products from aromatic thioesters **1a**–**c**, **g**, and **h** is higher than that of the silyl enol ethers prepared by treatment of benzyl phenyl ketone with LDA and trimethylsilyl chloride at −78°C.[9] Furthermore, compared to the thermodynamic reaction of benzyl methyl ketone with triethylamine and trimethylsilyl chloride,[10] the *Z*-selectivity of the silyl enol ether **2d** prepared from aliphatic thioester **1d** was slightly improved. It is noteworthy that the reactions of α,β-unsaturated thioesters **1e**, **f** gave dienol silyl ethers **2e**, **f** along with small amounts of 4-substituted 5-phenyl-2-trimethylsiloxythiophenes (entries 5 and 6). When **1g**, having a dimethylphenylsilyl group, was employed, the reaction was accelerated in spite of its bulkiness, since the partial negative charge developing on the silicon atom in the transition state can be delocalized by the phenyl group on the silyl group (entry 7). In the case where α,α-bissilylated thioester **1h** was used, the reaction was complete within 1 h, and gave a single isomer of the corresponding enol ether **2h** (entry 8). The observed acceleration of the reaction of **1h** may be due partly to the stabilization of the positive charge on the sulfur atom during the rearrangement step by a β-effect of another silyl group and partly to the relaxation of steric repulsion between the two bulky silyl groups. On the other hand, the reaction of α-trimethylsilylbenzyl benzoate did not occur, even at 200°C, probably because the interaction between the silicon and the oxygen of the carbonyl group is weaker than that of the corresponding thioester due to the greater electronegativity of the oxygen of alkoxy group vis-à-vis that of sulfur.

We propose a mechanism for the present silyl enol ether forming reaction as shown in Scheme 2 based on the generation of 1,3-dipoles from *N*-(α-silylbenzyl)amides via 1,4-silatropy and their cycloaddition as outlined in our previous studies.[11] Initially, the thermal 1,4-shift of the silyl group onto the oxygen in thioesters **1** gives 1,3-dipolar intermediates **3** (thiocarbonyl ylides). Thiiranes **4** are formed by the intramolecular cyclization of dipoles **3**, followed by the elimination of sulfur from **4** to give the silyl enol ethers **2**. When α,β-unsaturated thioesters **1e**, **f** are employed in the reactions, α,β-unsaturated thiocarbonyl ylides **3e**, **f** undergo 1,3- and 1,5-cyclization to give silyl enol ethers **2** and thiophenes,

Table 1. Synthesis of silyl enol ethers **2** from *S*-α-silylbenzyl thioesters **1**



Entry	Thioester[a]	R^1	R^2	R^3	Time (h)	Yield (%)[b]	Ratio *Z*:*E*[b]
1	**1a**	Me	H	Ph	24	93	91:9
2	**1b**	Me	H	*p*-$NO_2C_6H_4$	24	92	91:9
3	**1c**	Me	H	*p*-$MeOC_6H_4$	8	91	91:9
4	**1d**	Me	H	Me	64	44[c]	75:25
5	**1e**	Me	H	(*E*)-PhCH=CH	12	76[d,e]	85:15
6	**1f**	Me	H	(*E*)-CH_3CH=CH	2	68[d]	78:22
7	**1g**	Ph	H	Ph	5	87	88:12
8	**1h**	Me	Me_3Si	Ph	1	91	SI[f]

[a] All reactions were carried out with 0.05 mmol of thioesters in sealed tubes.

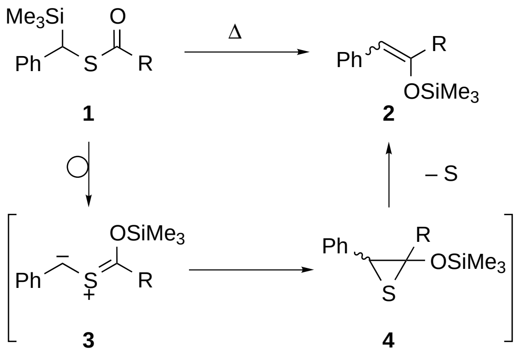
[b] Determined by ^{1}H NMR in the presence of mesitylene as an internal standard.[6]

[c] Starting material (45%) remained in the reaction mixture.

[d] 4-Substituted 5-phenyl-2-trimethylsiloxythiophene was detected.

[e] A mixture of *E*- and *Z*-isomers of **2e** and a small amount of 1,4-dipheyl-3-buten-2-one which was produced by the hydrolysis of **2e** were isolated by preparative TLC.

[f] Product **2h** was a single isomer, but the geometry was not determined.



Scheme 2.

respectively. The formation of thiophene derivatives in the reactions of **1e**, **f** provides us with additional persuasive evidence for thiocarbonyl ylides as intermediates in the reactions.

In summary, we report on the successful development of a simple new method for the preparation of silyl enol ethers from *S*-α-silylbenzyl thioesters via the thermal 1,4-silatropy and cyclization of dipoles. In this method, the starting materials, *S*-α-silylbenzyl thioesters, can be readily prepared by esterification of carboxylic acid derivatives with α-silylbenzylthiols, and the reactions proceed under completely neutral conditions. We are currently investigating the mechanism for this reaction in more detail, as well as dipolar cycloaddition utilizing in situ generated intermediates **3**.

Acknowledgements

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