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Preparation of Allylsilanes by the Olefination of Carbonyl Compounds Using β-Silylthioacetals

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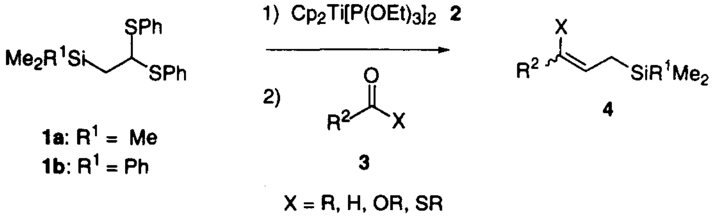
Abstract: Titanocene(II)-promoted olefination of various carbonyl compounds using 1,1-bis(phenylthio)-2-triorganosilylethanes gave allylsilanes in good yields. γ-Alkoxy and alkylthio group substituted allylsilanes were also obtained by using carboxylic esters and thiolesters, respectively.

Since allylsilanes are useful synthetic intermediates, a variety of methods for their preparation have been investigated.[1] Most of these are classified into the following categories; i) reaction of allylic acetate or halide with silyl-metal species or disilane,[2] ii) allylic Grignard reaction with halotriorganosilane,[3] iii) hydrosilylation of 1,3-diene,[4] iv) reduction or carboalumination of propargylsilane,[5] v) Wittig olefination of carbonyl compound using $Ph_3P{=}CHCH_2SiMe_3$,[6] vi) olefin cross-metathesis with allyltrialkylsilane,[7] and vii) [2+1] carbenoid insertion of vinylcarbene complex with trialkylsilane.[8] The latter two methods are characteristic of transition metal-carbene complexes.

Recently we have reported the preparation of titanium-carbene complexes by the reductive desulfurization of thioacetals or their analogues with the titanocene(II) species and their reaction with various organic molecules having a multiple bond, such as carbonyl compounds, alkenes, and alkynes.[9] We also reported the two types of preparation of allylsilanes using these Schrock type carbene complexes. The first method involves the reaction of carbene complexes with allyltrialkylsilanes through the olefin metathesis process, in which *Z*-isomers predominate.[10] The second procedure utilizes the reaction of vinylcarbene complexes prepared from β,γ-unsaturated thioacetals or 1,3-bis(phenylthio)alk-1-enes with triorganosilane, which affords γ-substituted allylsilanes with *E*-stereoselectivity.[11] In this communication, we wish to describe an alternative approach to allylsilanes using β-trialkylsilyl group substituted thioacetals **1** outlined in the following scheme.



The starting materials **1** were easily prepared by the reaction of lithium salt of bis(phenylthio)methane[12] with trialkyl(iodomethyl)silanes (THF / 0 °C ~ room temperature, **1a**: 80%, **1b**: 62%). The successive treatment of a small excess of **1a** with the low valent titanium $Cp_2Ti[P(OEt)_3]_2$ **2** and 1,5-diphenylpentan-3-one (**3a**) produced the allylsilane **4a** in 72% yield. As shown in Table 1, the similar reactions of various ketones with **1a** or **b** afforded the corresponding allylic silanes in good yields. However, the γ-monosubstituted allyl-

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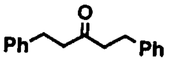
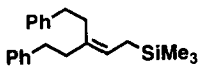
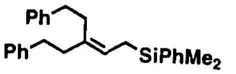
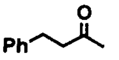
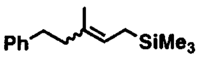
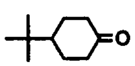
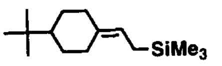
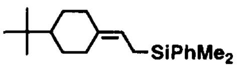
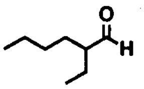
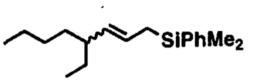
silane **4f** was produced only in a moderate yield when the aldehyde **3d** was treated with the carbene complex formed from **1b** (Entry 6).

A typical experimental procedure: To a flask charged with finely powdered molecular sieves 4A (180 mg), magnesium turnings (53 mg, 2.2 mmol), and Cp_2TiCl_2 (448 mg, 1.8 mmol) were added THF (4 ml) and $P(OEt)_3$ (0.62 ml, 3.6 mmol) with stirring at room temperature under argon. After 3 h, **1b** (228 mg, 0.6 mmol) in THF (1 ml) was added to the reaction mixture which was further stirred for 10 min. Then 4-*tert*-butylcyclohexanone (**3c**) (77 mg, 0.5 mmol) in THF (1.5 ml) was added dropwise over 15 min. After being stirred for 2 h, the reaction was quenched by the addition of 1M NaOH and the resulting insoluble materials were filtered off through Celite. The filtrate was extracted with ether and the extract was dried over Na_2SO_4. After removing the solvent, the residue was purified by using preparative TLC (hexane) to give 1-*tert*-butyl-4-[2-(dimethylphenylsilyl)ethylidene]cyclohexane (**4e**) (97 mg, 64%).

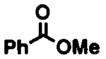
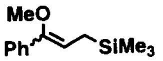
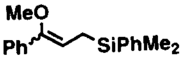
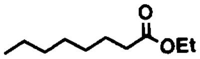
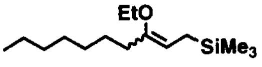
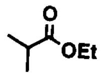
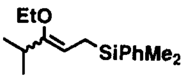
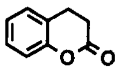
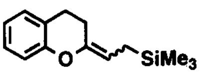
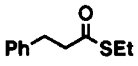
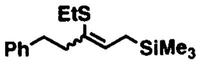
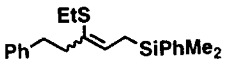
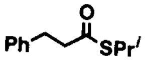
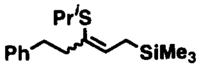
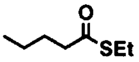
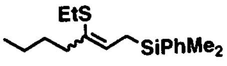
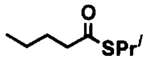
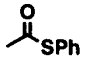
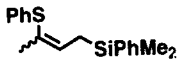
The advantage of this reaction over the conventional carbonyl olefination using silyl group substituted phosphorus ylide is that it is capable of being employed for the olefination of carboxylic acid derivatives. The reaction of methyl benzoate (**3e**) with **1a** under similar reaction conditions and the purification by column chromatography [Merck aluminum oxide 90 (Brockmann III)] produced the γ-methoxy allylsilane **4g** in 72% yield. With attention to the detailed reaction conditions employed, the yield of **4g** was improved to 81% (see, Entry 1 in Table 2). The major isomer of allylsilane thus obtained was found to be *Z* by NOE experiment. The reactions of carboxylic esters **3f** and **g** also afforded the olefination products stereoselectively though their configuration was not determined. On the other hand, the stereoselectivity was lost when 2-coumaranone (**3h**) was

Table 1. Preparation of Allylsilanes[a]

Entry	Carbonyl Compound 3		β-Silyl-thioacetal 1	Time (h)	Product 4		*E* : *Z*[b]	Yield (%)
1		3a	1a	2.5		4a	-	72
2	3a		1b	3.5		4b	-	66
3		3b	1a	2.5		4c	53 : 47[c]	66
4		3c	1a	3.0		4d	-	62
5	3c		1b	2.0		4e	-	64
6		3d	1b	3.0		4f	69 : 31	45

a) All reactions were performed following the procedure described in the text. b) Determined by NMR spectroscopy. c) The ratio of two stereoisomers.

Table 2. Preparation of γ-Heteroatom Substituted Allylsilanes[a]

Entry	Carbonyl Compound 3		β-Silylthioacetal 1	Product 4		*E* : *Z*[b]	Yield (%)
1[c]		3e	1a		4g	18 : 82[d]	81
2[c]	3e		1b		4h	14 : 86[d]	81
3		3f	1a		4i	78 : 22[e]	78
4[c]		3g	1b		4j	f	90
5		3h	1a		4k	44 : 56[d,g]	79
6		3i	1a		4l	39 : 61[d,g]	77
7	3i		1b		4m	38 : 62[d,h]	78
8[c]		3j	1a		4n	38 : 62[g,h]	86
9[c]		3k	1b		4o	36 : 64[d,g]	89
10		3l	1a		4p	41 : 59[d,g]	79
11		3m	1b		4q	25 : 75[d,g]	58[i]

a) All reactions were performed following the procedure described in the text, unless otherwise noted. b) Determined by NMR spectroscopy. c) Cp$_2$TiCl$_2$ (4.5 equiv), magnesium (5.4 equiv), and P(OEt)$_3$ (9 equiv) were used. d) The configuration was determined by NOE experiment. e) The ratio of two stereoisomers. f) Obtained as a single stereoisomer. The configuration was not determined. g) The two stereoisomers were separated each other by PTLC. The ratio was determined based on the isolated yields. h) The configuration was determined after being transformed to the sulfone. i) The NMR spectrum showed some unidentified signals.

employed (Entry 5). The transformation of thiolesters to γ-alkylthio substituted allylsilanes was also examined, and it was found that the olefination products were produced in good yields. The stereochemistry of these trisubstituted olefins was determined by NOE experiment and/or on the basis of chemical shift of vinyl proton after they were transformed into the corresponding sulfones by the treatment with Oxone®.[9d] Similarly to the olefination of carboxylic esters, the *Z* isomers predominated in all the reactions examined though the selectivity was moderate.

Although the various γ-heteroatom substituted allylstannanes have been prepared and employed as reagents for organic transformations,[13] only a few silicon congeners, such as γ-amino[14] and halo[15] allylsilanes, were prepared and used in the reactions with certain electrophiles. It should be noted that the present reaction provides a convenient synthetic route to allylsilanes including the heteroatom substituted ones. The application of these silanes is now under investigation.

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