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Preparation of alka-2,4-dienylsilanes and 3-cyclopropylprop-2-enylsilanes by the titanocene(II)-promoted reaction of 2,4-bis(phenylthio)but-3-enylsilanes

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Abstract

Preparation of allylsilanes by the $Cp_2Ti[P(OEt)_3]_2$ (**1**)-promoted reaction of 2,4-bis(phenylthio)but-3-enylsilanes **5** is described. The olefination of carbonyl compounds **6** using the silanes **5** and the low-valent titanium species **1** produced alka-2,4-dienylsilanes **2**. 3-Cyclopropylprop-2-enylsilanes **3** were obtained by the reaction of **5** with **1** in the presence of terminal olefins **9**.

Keywords: carbonyl olefination; cyclopropanation; organosulfur compounds; titanium and compounds.

Allylsilanes are useful reagents for organic synthesis and their characteristic reactions are employed for the construction of complex molecules.[1] Although a variety of methods for the preparation of allylsilanes have been developed, preparation and reactions of functionalized allylsilanes have not been fully studied yet. Recently, we reported three different methods for the synthesis of allylsilanes using titanium–carbene complexes formed by the reaction of thioacetals with $Cp_2Ti[P(OEt)_3]_2$ (**1**).[2] We further studied the preparation of various allylsilanes using our titanium–carbene chemistry, and here we wish to disclose convenient methods for the preparation of allylsilanes having a conjugated diene system or a cyclopropane moiety, **2** or **3**, by the reaction of vinylcarbene complexes **4** carrying a triorganosilyl group (Scheme 1).

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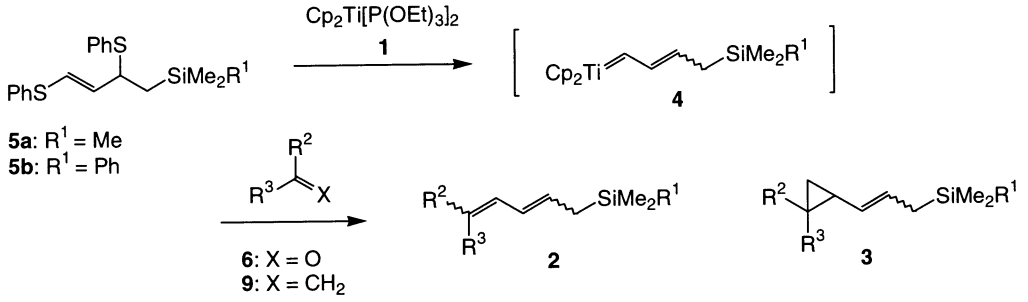
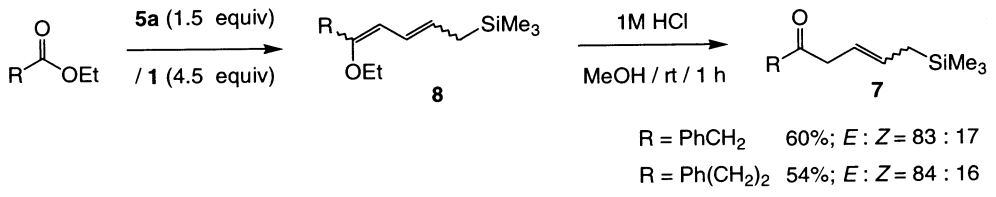


Scheme 1.

The starting materials, 2,4-bis(phenylthio)but-3-enylsilanes **5**, were easily synthesized by the alkylation of 1,3-bis(phenylthio)allyllithium with trialkylsilylmethyl iodide (1.1 equiv./−78°C/4 h) and easily isolated by recrystallization from hexane (**5a**: $R^1 = Me$; 75%, **5b**: $R^1 = Ph$; 71%). The allyllithium was prepared by the treatment of 2-methoxy-1,3-bis(phenylthio)propane with LDA (2.05 equiv./−78°C/2 h) similarly to the method reported by Corey et al.[3] First, the preparation of alka-2,4-dienylsilanes **2**, vinylogues of allyltrialkylsilanes, was studied. Although the olefination of aldehydes was found to be messy, the dienylsilanes **2** were obtained in moderate to good yields by the reaction of ketones **6** with **5** (Table 1). For example, after the silane **5a** (1.2 equiv.) was desulfurized with the titanocene(II) species **1** (3.6 equiv.) at room temperature for 20 min, the resulting vinylcarbene complex was further treated with 1,5-diphenylpentan-3-one **6a** to produce the dienylsilane **2a** in 58% yield (entry 1). An interesting application of this method is the synthesis of 5-oxoalk-2-enylsilanes **7**. After the olefination of esters under the usual reaction conditions, the resulting vinyl ethers **8** were selectively hydrolyzed with hydrochloric acid under argon to give **7**, which would be difficult to prepare by the conventional methods (Scheme 2).

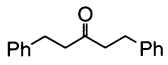
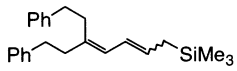
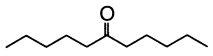
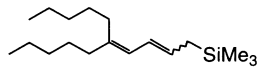
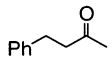
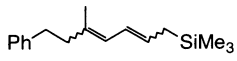
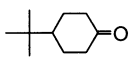
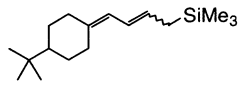
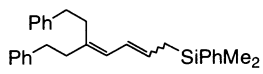
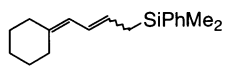
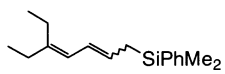
Preparation of (penta-2,4-dienyl)trimethylsilane by silation of the pentadienyl anion and its addition to carbonyl compounds has been investigated.[4] Its derivatives carrying a stereogenic center have been studied as reagents for the synthesis of optically active compounds.[5] A notable feature of the present method is that the pentadienylsilanes bearing different substituents at the 5-position are readily prepared from ketones.

Since the vinylcarbene complexes react with terminal olefins **9** to produce vinylcyclopropanes,[6] we expected that the γ-cyclopropylallylsilanes **3** would be formed by the reaction of the silanes **5** with **9**. As expected, the silanes **3** were produced in good yields by the treatment of **5** with the low-valent titanium reagent **1** (2 equiv.) in the presence of excess **9** at room temperature for 2 h. It was found that the stereoselectivity of the double bond was higher than that of the carbonyl olefination (Table 2).



Scheme 2.

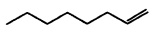
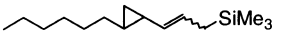
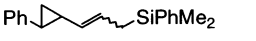
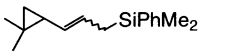
Table 1
Carbonyl olefination of ketones **6** using the silanes **5**-titanocene(II) **1**

Entry	Silane **5**	Ketone **6**	Product **2** (Yield / %)	$E : Z^a$
1	**5a**	 **6a**	 **2a** (58)	89 : 11
2	**5a**	 **6b**	 **2b** (66)	89 : 11
3	**5a**	 **6c**	 **2c** (57)	b
4	**5a**	 **6d**	 **2d** (53)	90 : 10
5	**5a**	 **6e**	 **2e** (51)	87 : 13
6	**5b**	**6a**	 **2f** (54)	89 : 11
7	**5b**	**6d**	 **2g** (48)	87 : 13
8	**5b**	 **6f**	 **2h** (57)	89 : 11

a) Determined by ^{1}H NMR. b) A mixture of the four stereoisomers (2*E*-isomers : 2*Z*-isomers = 86 : 14).

The following is a typical experimental procedure. Finely powdered molecular sieves 4 A (100 mg), magnesium turnings (29 mg, 1.2 mmol; purchased from Nacalai Tesque Inc., Kyoto, Japan) and Cp_2TiCl_2 (249 mg, 1 mmol) were placed in a flask and dried by heating with a heat gun under reduced pressure (2–3 mmHg). During this procedure, care is taken not to sublime Cp_2TiCl_2. After cooling, THF (3 ml), $P(OEt)_3$ (0.34 ml, 2 mmol), and styrene (**9a**) (0.12 ml, 1 mmol) were added successively with stirring at room temperature under argon. After 3 h, a THF

Table 2
Titanocene(II) **1**-promoted reaction of silanes **5** with terminal olefins **9**

Entry	Silane **5**	Olefin **9**	Product **3** (Yield / %)	$E:Z^a$
1	**5a**			98 : 2
		9a	**3a** (84)[b]	
2	**5a**			94 : 6
		9b	**3b** (80)[c]	
3	**5b**	**9a**		97 : 3
			3c (82)[d]	
4[e]	**5b**			94 : 6
		9c	**3d** (85)	
5	**5b**			94 : 6
		9d	**3e** (85)[f]	
6[g]	**5b**			97 : 3
		9e	**3f** (83)	

a) The ratio of *E*-isomer(s) and *Z*-isomer(s) determined by ^{1}H NMR. b) A mixture of the three stereoisomers (the ratio of isomers = 89 : 9 : 2). c) A mixture of the four stereoisomers (the ratio of isomers = 57 : 37 : 4 : 2). d) A mixture of the three stereoisomers (the ratio of isomers = 88 : 9 : 3). e) Ten equiv of **9c** were used. f) A mixture of the four stereoisomers (the ratio of isomers = 60 : 34 : 5 : 1). g) The reaction was carried out under an ethylene atmosphere.

(1.5 ml) solution of 1,3-bis(phenylthio)-4-(trimethylsilyl)but-1-ene (**5a**) (172 mg, 0.5 mmol) was added and the reaction mixture was stirred for 2 h. The reaction was quenched by addition of 1 M NaOH and the insoluble materials were filtered off through Celite. The filtrate was extracted with ether and the organic phase was dried over Na_2SO_4. After removal of the solvent, the residue was purified by PTLC (hexane) to yield 97 mg (84%) of 1-phenyl-2-[3-(trimethylsilyl)prop-1-enyl]cyclopropane (**3a**).

Although the preparation and reactions of cyclopropylcarbinylsilanes have been studied,[7] to the best of our knowledge, a synthetic route to its vinylogue has yet not appeared. It should be noted that the cyclopropanation of olefins using the silanes **5**-titanocene(II) system provides a convenient tool for the synthesis of such compounds. Further study on the reactions of the functionalized allylsilanes described above is currently under way.

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