



Diversity oriented synthesis of conjugate dienes and alkenylcyclopropanes utilizing silyl group-substituted titanium carbene complexes as bimetallic synthetic reagents



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ARTICLE INFO

Article history:

Received 16 May 2014

Received in revised form 11 June 2014

Accepted 12 June 2014

Available online 24 June 2014

Keywords:

Alkenylcyclopropanes

Alkenylsilanes

Cross-coupling

1,3-Dienes

Titanium carbene complexes

ABSTRACT

Diversity oriented synthesis of conjugate dienes and alkenylcyclopropanes by the sequential reactions using silyl group-substituted titanium carbene complexes was studied. Dienylsilanes were obtained by the olefination of carbonyl compounds with γ -silylvinylcarbene complexes. Cyclopropanation of 1-alkenes with the vinylcarbene complexes produced (*E*)-(β -silylvinyl)cyclopropanes with high stereoselectivity. The reaction of β -(trialkylsilyl)carbene complexes with zinc alkoxides of homopropargyl alcohols produced 6-silyl-3,5-hexadien-1-ols with high regio- and stereoselectivity. The (*E*)-alkenylsilanes thus obtained were transformed into a range of unsaturated compounds by the palladium-catalyzed or copper(I)-promoted cross-coupling with organic halides with retention of configuration.

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1. Introduction

Alkenylsilanes are useful building blocks in organic synthesis. In response to the growing interest in palladium-catalyzed cross-coupling of organosilicon compounds, alkenylsilanes have increasingly become an important class of organic materials.¹ A variety of approaches to the stereoselective preparation of alkenylsilanes have been developed.² Among them, silylation of alkenylmetals with halosilanes,³ reduction of alkenylsilanes,⁴ and transition-metal-catalyzed hydrosilylation⁵ of alkynes have commonly been used from practical point of view. However, these methods often require a multistep procedure for preparation of alkenylsilanes having unsaturated groups such as alkenyl (i.e., dienylsilanes) or cyclopropyl group (i.e., (β -cyclopropylvinyl)silanes).

We have studied the desulfurizative titanation of thioacetals and related organosulfur compounds with titanocene(II)-triethyl phosphite complex. The process is useful for the preparation of titanium carbene complexes, which are difficult to prepare by conventional methods.⁶ The reactions of organotitanium species thus prepared with carbonyl compounds, alkenes, and alkynes are useful for the construction of a variety of unsaturated systems.

Apart from the chemistry of organotitanium compounds, we have continuously studied the transmetalation of alkenyl- and arylsilanes to the corresponding copper(I) species by the copper(I) *tert*-butoxide promoted Brook-like silyl-migration.

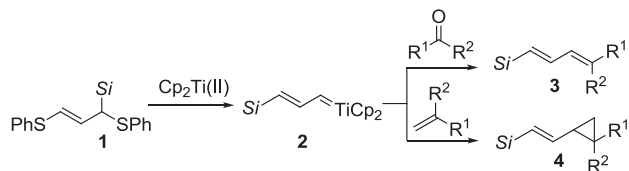
The reaction proceeds through the formation of cyclic silicates by intramolecular coordination of a copper(I) alkoxide group.^{7,8} The organocopper(I) species thus formed are reactive toward a variety of organic halides and cross-coupling products were obtained in stoichiometric and catalytic manners.

Recently we found that alkenylbenzylidimethylsilanes were readily transformed into alkenylcopper(I) compounds without requiring the intramolecular coordination when treated with copper(I) iodide-triethyl phosphite-tetrabutylammonium fluoride.⁹ This finding prompted us to investigate the construction of a variety of unsaturated systems by the combination of the titanium carbene chemistry and the palladium-catalyzed¹⁰ or copper(I)-promoted cross-coupling⁹ of alkenylsilanes. Based on our titanium carbene chemistry, we reasoned that the desulfurizative titanation of 1,3-bis(phenylthio)-1-propenes **1** bearing a silyl group could produce γ -silylvinylcarbene complexes **2** stereoselectively. The carbonyl olefination and cyclopropanation with these species provide new approaches to the dienylsilanes **3** and their homologs **4** (Scheme 1). In addition, we conceived that the dienylsilanes **5** should be formed by the titanocene(II)-promoted reaction of β -silyl thioacetals **6** with alkynes via formation of β -silylcarbene complexes **7**. Here, we would like to demonstrate the synthetic utility of

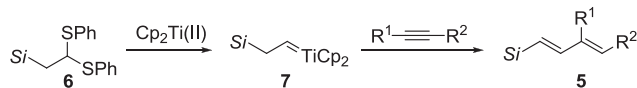
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the silyl group containing titanium carbene complexes **2** and **7** as bimetallic synthetic reagents for the preparation of highly substituted conjugated dienes **8**, **9**, and alkenylcyclopropanes **10**.

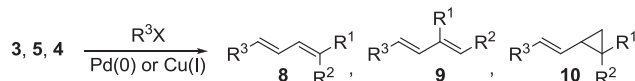
Carbonyl olefination and cyclopropanation using γ -silylvinylcarbene complexes **2**



Reaction of β -silylcarbene complexes **7** with alkynes



Pd(0) Catalyzed or Cu(I) promoted cross-coupling

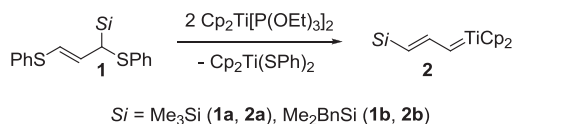


Scheme 1. Preparation of conjugate dienes and alkenylcyclopropanes utilizing silyl group-substituted titanium carbene complexes.

2. Results and discussion

2.1. Synthesis of 1-silyl-1,3-dienes **3**

We first examined the preparation of dienyilsilanes **3** by the reaction of γ -silylvinylcarbene complexes **2** with carbonyl compounds **11**. Previously we reported that the vinylcarbene complexes were generated from 1,3-bis(phenylthio)-1-alkenes by treatment with titanocene(II)-triethyl phosphite complex.¹¹ Therefore, it was expected that the unsaturated carbene complexes **2** would be readily prepared by the reductive titaniation of 1,3-bis(phenylthio)-3-(trialkylsilyl)-1-propenes **1** with the titanocene(II) reagent, and the dienyilsilanes **3** would be obtained by the reaction of **2** with **11** with loss of titanocene oxide from oxatitanacyclobutane intermediates **12** (**Scheme 2**).¹²



Scheme 2. Reaction of γ -silylvinylcarbene complexes **2** with carbonyl compounds **11**.

The treatment of bissulfide **1a** (1.2 equiv) with titanocene(II)-triethyl phosphite complex (3.6 equiv) at 25 °C for 10 min produced the carbene complex **2a**, and its reaction with 1,5-diphenyl-3-pentanone (**11a**) gave the *E*-dienylsilane **3a** in 61% yield with high stereoselectivity (**Table 1**, entry 1). In a similar fashion, various carbonyl compounds are transformed into dienyilsilanes **3**. The reaction of **2** with esters and thioesters are useful for the preparation of heteroatom-substituted dienyilsilanes, which are difficult to

prepare by conventional methods (entries 4–8). Although the formation of double bond by carbonyl olefination of the lactone **11f** showed poor stereoselectivity, the reaction of esters **11d** and **11e**, and thioesters **11g** and **11h** gave the *Z*-isomers as major products.

Table 1

Preparation of dienyilsilanes **3** by the titanocene(II)-promoted olefination of carbonyl compounds **11** with the bissulfides **1**

Entry	1	11	3 (Yield/%; ^a <i>dr</i> ^b)
1	1a	11a	Me ₃ Si- 3a (61; <i>E:Z</i> = 95:5)
2	1b	11b	Me ₂ BnSi- 3b (50; single isomer)
3	1b	11c	Me ₂ BnSi- 3c (41; <i>EE:EZ</i> = 58:42)
4	1b	11d	Me ₂ BnSi- 3d (71; <i>EE:EZ</i> = 22:78)
5	1b	11e	Me ₂ BnSi- 3e (58; <i>EE:EZ</i> = 21:79)
6	1b	11f	Me ₂ BnSi- 3f (63; 59:41 ^c)
7	1b	11g	Me ₂ BnSi- 3g (50; <i>EE:EZ</i> = 10:90)
8	1a	11h	Me ₃ Si- 3h (60; <i>EE:EZ</i> = 28:72)

^a Isolated yield based on the carbonyl compound **11** used.

^b The configuration of trisubstituted olefin was confirmed by NOE experiment and the stereochemistry of alkenylsilyl moiety was determined as *E* based on the *J* value (ca. 18 Hz) of vinyl protons.

^c The stereochemistry was not determined.

2.2. Synthesis of (2-silylethenyl)cyclopropanes **4**

As we have disclosed previously, alkenylcarbene complexes react with terminal alkenes to produce alkenylcyclopropanes,¹¹ which are useful intermediates for the synthesis of cyclopentenes through the thermal or transition-metal-catalyzed rearrangement.¹³ As we expected, the treatment of bissulfides **1b** bearing a benzyldimethylsilyl group with titanocene(II) reagent (3 equiv) in the presence of 1-alkenes **13** at 25 °C for 3 h produced (*E*)-(2-silylethenyl)cyclopropanes **4** via titanacyclobutane intermediates **14** in good yields (**Scheme 3**). In most cases, the reaction proceeded with complete *E* selectivity. Ethylene was a good substrate for the present cyclopropanation (**Table 2**, entry 1). The reactions of 1,1-disubstituted as well as mono-substituted ethylenes gave the alkenylcyclopropanes in good yields (entries 2–5). It is noteworthy that the 1,3-diene **13f** also reacted with **2b** to produce the 1,2-dialkenylcyclopropane **4f** as a single isomer (entry 6) because the

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