Synthesis of highly substituted allenylsilanes by alkylidenation of silylketenes

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Abstract

Background: Allenylsilanes are useful intermediates in organic synthesis. An attractive, convergent but little used approach for their synthesis is the alkylidenation of stable silylketenes. Reactions thus far have been limited to the use of unsubstituted silylketenes (or equivalents) with stabilised or semi-stabilised ylides only. The current study explores the reactions of substituted ketenes prepared through rhodium(II)-mediated rearrangement of silylated diazoketones.

Results: A range of novel 1,3-disubstituted and 1,3,3-trisubstituted allenylsilanes were prepared using stabilised and semi-stabilised ylides. Alkylidenation with non-stabilised phosphorus ylides was not viable, but the use of titanium-based methylenating reagents was successful, allowing access to 1-substituted allenylsilanes.

Conclusion: Many novel allenylsilanes may be accessed by alkylidenation of substituted silylketenes. Importantly, for the first time, simple methylenation of silylketenes has been achieved using titanium carbenoid-based reagents.

Keywords

allenylsilanes; rhodium(II) octanoate-mediated rearrangement; silylketenes; titanium carbenoids; ylide

Introduction

Allenylsilanes are versatile intermediates for organic synthesis [1,2]. They have two main modes of reactivity: firstly, as propargyl anion equivalents in thermal [3,4] or Lewis acid-mediated [5,6] addition to carbonyls, acetals and imines, and secondly as three-carbon partners in [3+2] annulation reactions. Thus, reaction with aldehydes [7], imines/iminiums [7,8], enones [9-11] and nitrosyl cations [12] leads to dihydrofurans, dihydropyrroles, cyclopentenes and isoxazoles respectively [13]. In most cases the silicon is retained in the final product and can be used as a handle for further synthetic elaboration.

Amongst the myriad methods to prepare allenylsilanes [1,14], an attractive disconnection is to consider a Wittig-type alkylidenation of a silylketene (Figure 1).
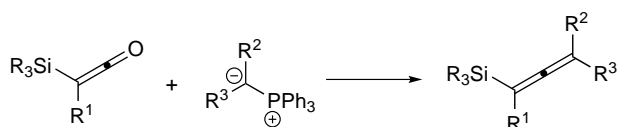
**Figure 1:** Alkylidenation approach to the synthesis of allenylsilanes.

[. . .]

Results and Discussion

Our investigations began with the preparation of substituted silylketenes **1** as substrates for the alkylidenation chemistry. This was carried out under our previously reported conditions for rhodium(II) octanoate-mediated rearrangement of silyl diazoketones **2**, which in turn were prepared by *C*-silylation of the parent diazoketones **3** with triethylsilyl triflate (Scheme 1). It should be noted that while the alkyl-substituted silylketenes are relatively stable and show little decomposition at room temperature over several days, the (hetero)aromatic-substituted silylketenes are much less robust and should be used quickly or stored in a freezer.

[. . .]

With the requisite silylketenes in hand, attention turned to their reaction with the carboethoxy-stabilised phosphoranes **4** and **5**. At the outset, it was by no means certain that these would re-
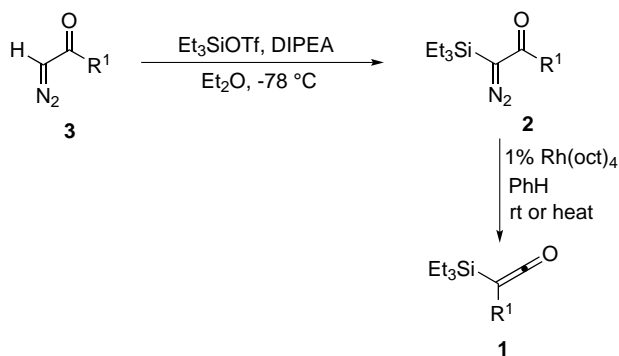
Scheme 1: Synthesis of substituted silylketenes **1**.

act efficiently with substituted silylketenes **1** since it is well documented that nucleophiles attack

silylketenes *anti* to the silicon, i.e. the phosphoranes would be approaching from the same side as

the R^1-substituent. Since in all previous examples this substituent has been a hydrogen atom, the

extension to bulkier substituents could not be taken for granted. In the event, however, we were

pleased to find that in nearly all cases the desired allenylsilanes were formed in moderate to excel-

lent yield (Scheme 2, Table 1, see Supporting Information File 1 for full experimental data).
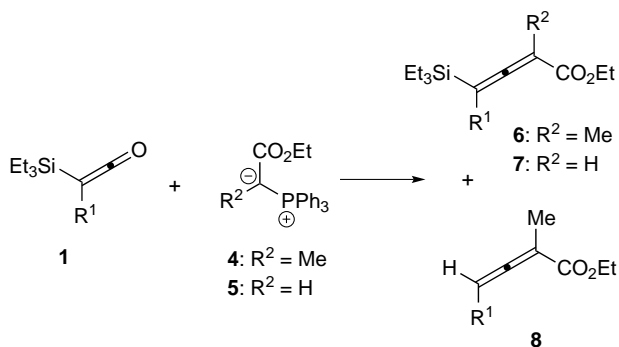
Scheme 2: Reaction of substituted silylketenes with ester-stabilised phosphoranes.

As expected, reactions with the more substituted ylide **4** were significantly slower than those with

the parent ylide **5** (compare reaction temperatures and times, entries 1, 3 and 5 versus entries 2, 4

and 6). [...]

Table 1: Reaction of substituted silylketenes with ester-stabilised phosphoranes.

Entry	Ketene	Ylide	Temp [°C]	t [h]	Solvent	Yield 6/7 (8)
1	**1a**	**4**	80	24	PhH	54 %
2	**1a**	**5**	rt	3	CH$_2$Cl$_2$	60 %
3	**1b**	**4**	110	24	toluene	45 %
4	**1b**	**5**	reflux	24	CH$_2$Cl$_2$	77 %
5	**1c**	**4**	80	24	PhH	60 %
6	**1c**	**5**	rt	6	CH$_2$Cl$_2$	81 %
7	**1d**	**4**	110	48	toluene	22 %^{a}
8	**1d**	**5**	80	48	toluene	78 %
9	**1e**	**4**	80	24	PhH	55 % (7 %)
10	**1f**	**4**	60	5	CH$_2$Cl$_2$	44 % (3 %)
11	**1h**	**4**	rt	6	CH$_2$Cl$_2$	0 % (57 %)
12	**1h**	**4**	50	1	CH$_2$Cl$_2$	7 % (23 %)
13	**1i**	**4**	rt	10	CH$_2$Cl$_2$	0 % (67 %)
14	**1i**	**5**	rt	2	CH$_2$Cl$_2$	98 %
15	**1j**	**4**	80	12	PhH	74 % (19 %)

^{a} 60 % of starting material recovered

Supporting Information

Supporting information features copies of ^{1}H NMR spectra of silylated diazoketones **2** and silylketenes **1**, plus ^{1}H and ^{13}C NMR spectra of allenylsilanes **6**, **7**, and **14–19**.

Supporting Information File 1:

File Name: S1.pdf

File Format: PDF

Title: Experimental part

Supporting Information File 2:

File Name: S2.pdf

File Format: PDF

Title: NMR spectra of compounds **1**, **2**, **6** and **7**

Supporting Information File 3:

File Name: S3.pdf

File Format: PDF

Title: NMR spectra of compounds **14–19**

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