

1 **Synthesis of highly substituted allenylsilanes by alkylidenation of** 2 **silylketenes**

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8 **Abstract**

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

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

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

21 **Keywords**

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

24 Introduction

25 Allenylsilanes are versatile intermediates for organic synthesis [1,2]. They have two main modes
26 of reactivity: firstly, as propargyl anion equivalents in thermal [3,4] or Lewis acid-mediated [5,6]
27 addition to carbonyls, acetals and imines, and secondly as three-carbon partners in [3+2] annula-
28 tion reactions. Thus, reaction with aldehydes [7], imines/iminiums [7,8], enones [9-11] and nitrosyl
29 cations [12] leads to dihydrofurans, dihydropyrroles, cyclopentenes and isoxazoles respectively
30 [13]. In most cases the silicon is retained in the final product and can be used as a handle for fur-
31 ther synthetic elaboration.

32 Amongst the myriad methods to prepare allenylsilanes [1,14], an attractive disconnection is to con-
33 sider a Wittig-type alkyldienation of a silylketene (Figure 1).

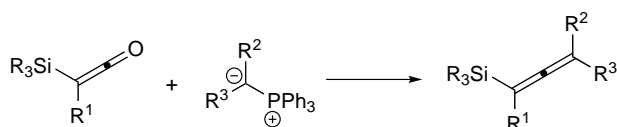


Figure 1: Alkyldienation approach to the synthesis of allenylsilanes.

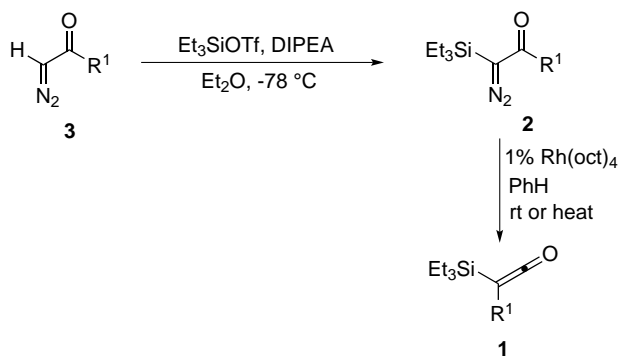
34 [...]

35 Results and Discussion

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

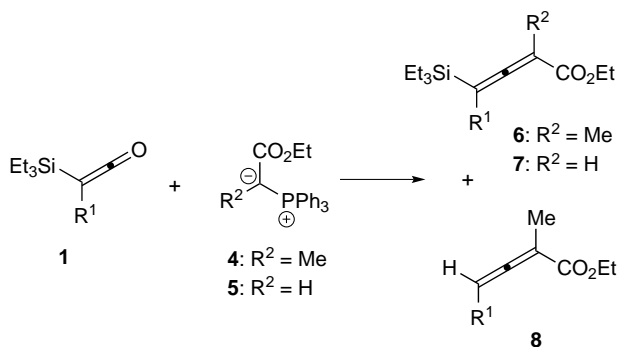
43 [...]

44 With the requisite silylketenes in hand, attention turned to their reaction with the carboethoxy-
45 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 R¹-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 excellent 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

55 Supporting Information

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

58 Supporting Information File 1:

59 File Name: S1.pdf

60 File Format: PDF

61 Title: Experimental part

62 Supporting Information File 2:

63 File Name: S2.pdf

64 File Format: PDF

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

66 Supporting Information File 3:

67 File Name: S3.pdf

68 File Format: PDF

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

70 **Acknowledgements**

71 We acknowledge EPSRC grant GR/L60135/01 (PCD) and generous unrestricted research funding
72 from Pfizer for financial support.

73 **References**

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⁹⁰ This article is published in full length in *Beilstein J. Org. Chem.* **2005**, *1*, No. 5.