A New Synthesis of Allylsilanes

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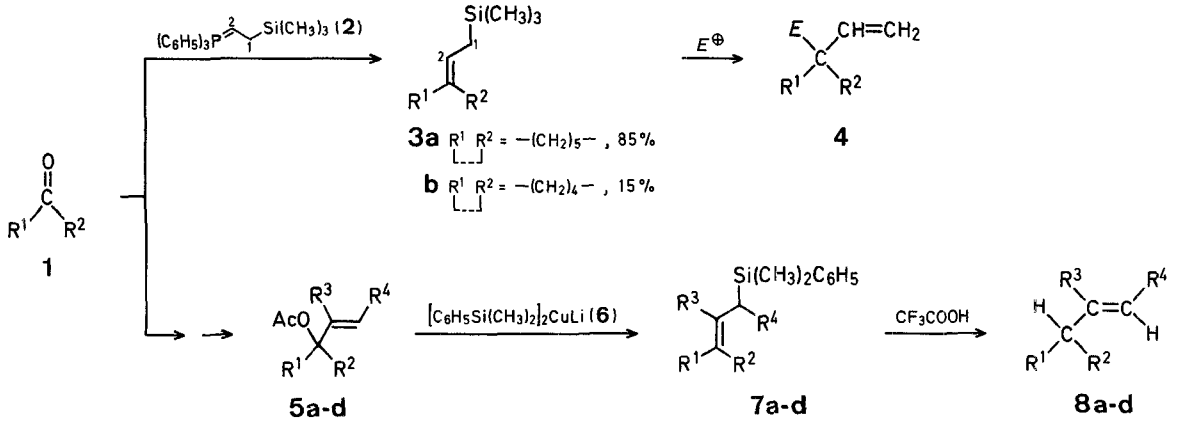
There is a need for general and regiospecific syntheses of allylsilanes, because they are usually well-behaved and regiospecific carbon nucleophiles[1]. One such synthesis uses the Wittig reaction **(1+2→3)** developed by Seyferth et al.[2,3] (see also Ref.[4]) and used by us[5] as part of a simple sequence for the geminal alkylation of ketones and aldehydes **(1→3→4)**. However, this approach to allylsilanes is limited. Although it works with aldehydes ($R^2 = H$) and with some ketones such as cyclohexanone [$R^1—R^2 = —(CH_2)_5—$] and acetophenone[6], it gives poor yields both with cyclopentanones[7,8] and when there is a substituent on C-2[2,3,4] of **2**. Furthermore, allylsilanes with a substituent on C-1 are not available by this route because there is no easy way to make the corresponding ylids.

We now report a new synthesis of allylsilanes, which promises to avoid all three of these limitations. The ketones **1** are first converted by standard procedures[9,10] to the allylic acetates **5**, and these are then treated with our silyl-cuprate reagent **6**[11,12]. The products obtained in good yields are the allylsilanes **7** (Table 1). As further confirmation of their structures, each of the allylsilanes **7** was reacted with acid to give the alkenes **8** cleanly via an allyl-shift (Table 2). Secondary allylic acetates do not give allylsilanes when treated with the silyl-cuprate reagent.



5,7,8	R^1	R^2	R^3	R^4
a	$-(CH_2)_5-$		H	H
b	$-(CH_2)_4-$		H	H
c	$-(CH_2)_4-$		CH_3	H
d	$-(CH_2)_4-$		H	CH_3

Allylsilanes 7; General Procedure:

The cuprate **6** is prepared by mixing phenyldimethylsilyllithium[11] (40 mmol) and copper(I) iodide (20 mmol) in tetrahydrofuran (140 ml) at 0 °C for 15 min. The allyl acetate **5**, prepared from ketone **1** according to Ref.[9,10], (15 mmol) in tetrahydrofuran (20 ml) is added under nitrogen and the mixture is kept at 0 °C for 1 h and at room temperature overnight. An aqueous work-up, extraction with pentane, column chromatography (silica gel/light petroleum ether) and distillation gives the allylsilanes **7** (Table 1).

Table 1. Allylsilanes **7** from Allyl Acetates **5**

Product	Yield [%]	b.p. [°C]/torr	Molecular formula[a]	^{1}H-N.M.R. (CCl_4) δ [ppm]
7a	93	86–88°/0.2	$C_{16}H_{24}Si$ (244.2)	0.46 (s, 6H); 1.4–2.5 (m, 12H); 5.17 (t, 1H, J=9 Hz); 7.2–7.7 (m, 5H_{arom})
7b	93	102–104°/0.5	$C_{15}H_{22}Si$ (230.2)	0.28 (s, 6H); 1.3–2.5 (m, 10H); 5.18 (t, 1H, J=9 Hz); 7.0–7.6 (m, 5H_{arom})
7c	87	75–77°/0.1	$C_{16}H_{24}Si$ (244.2)	0.60 (s, 6H); 1.4–2.7 (m, 19H, overlaid with 2s at 1.83 and 1.93); 7.2–7.7 (m, 5H_{arom})
7d	86	114–116°/2	$C_{16}H_{24}Si$ (244.2)	0.42 (s, 6H); 1.20 (d, 3H, J=7 Hz); 1.4–2.6 (m, 9H); 5.15 (d m, 1H, J=11 Hz); 7.1–7.7 (m, 5H_{arom})

[a] Satisfactory microanalyses obtained: C ±0.3, H ±0.1.

Table 2. Alkenes **8** by Protodesilylation of Allylsilanes **7**

Product[a]	Yield [%][b]	M.S. *m/e* for M^+ (*m/e* calculated)	^{1}H-N.M.R. (CCl_4) δ [ppm]
8a	95	—	1.2–2.4 (m, 11H); 4.90 (dd, 1H, J=10 Hz, 2 Hz); 4.95 (dd, 1H, J=17 Hz, 2 Hz); 5.82 (ddd, 1H, J=17 Hz, 10 Hz, 6 Hz)
8b	98	—	1.0–2.5 (m, 9H); 4.70 (br. d, 1H, J=10 Hz); 5.60 (ddd, 1H, J=17 Hz, 10 Hz, 2 Hz)
8c	92	110.1096 (110.1096)	1.80 (s, 3H); 1.4–2.5 (m, 12H); 4.6 (m, 2H)
8d	99	110.1103 (110.1096)	1.73 (d, 3H, J=5 Hz); 1.3–2.7 (m, 12H); 5.3 (m, 2H)

[a] All compounds are previously known. [b] Yield determined by ^{1}H-N.M.R. spectrometry.

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Alkenes 8 by Protodesilylation of Allylsilanes 7; General Procedure: The allylsilane (0.3 mmol) and trifluoroacetic acid (0.3 mmol) in carbon tetrachloride (1.5 ml) are kept at room temperature for 20 h, and examined by ^{1}H-N.M.R. spectrometry using 9,10-dihydroanthracene as an internal standard with which to assess the yield, since the products **8** are too volatile for the determination of accurate preparative yields. The product **8c** is unstable in the presence of excess acid and gives isopropylidenecyclopentane if care is not taken to minimise the amount of acid. The other products **8a, b,** and **d** are stable to the reaction conditions (Table 2).

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