Allylsilanes in Organic Synthesis: A Method for the Introduction of Two Carbon Substituents in Place of Carbonyl Oxygen

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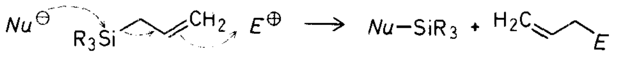
Allylsilanes are useful synthons for at least three reasons: (a) they are, as allylmetal compounds go, allylically stable[1]; (b) they are comparatively unreactive, and can be carried through many reactions unscathed[2]; and (c) they are, nevertheless able to react with appropriate electrophiles[3] in the sense (**1**). We should like to add two new alkylating agents which react with allylsilanes in this sense, and to point out that allylsilane chemistry provides a simple method of "geminal alkylation"[4].



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We find that the allylsilanes **3**, **10a**, and **10b** react with ethylene oxide in the presence of titanium(IV) chloride to give the alcohols **4**, **11a**, and **11b**, respectively. (Propylene oxide, however, gave mixtures of unidentified products, which probably come at least in part from rearrangement of the oxide taking place faster than its reaction with the allylsilane.) The same allylsilanes react with *t*-butyl chloride in the presence of titanium(IV) chloride to give the alkylation products **5a**, **12a**, and **12b**. Other reactive alkyl halides work as well, as shown by the similar reaction of **3** with *t*-amyl chloride, 1-methylcyclohexyl chloride, and α-methylbenzyl bromide to give **5b**, **5c**, and **5d**, respectively. (Benzyl chloride and isopropyl chloride, however, did not work.) In contrast, alkylation of allyllithium derivatives is not highly regioselective[6], and is not possible at all using tertiary alkyl halides. Allylsilanes are remarkably similar to silyl enol ethers[5]: in general electrophiles which work with the one work with the other comparably well.

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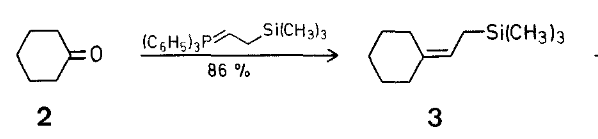
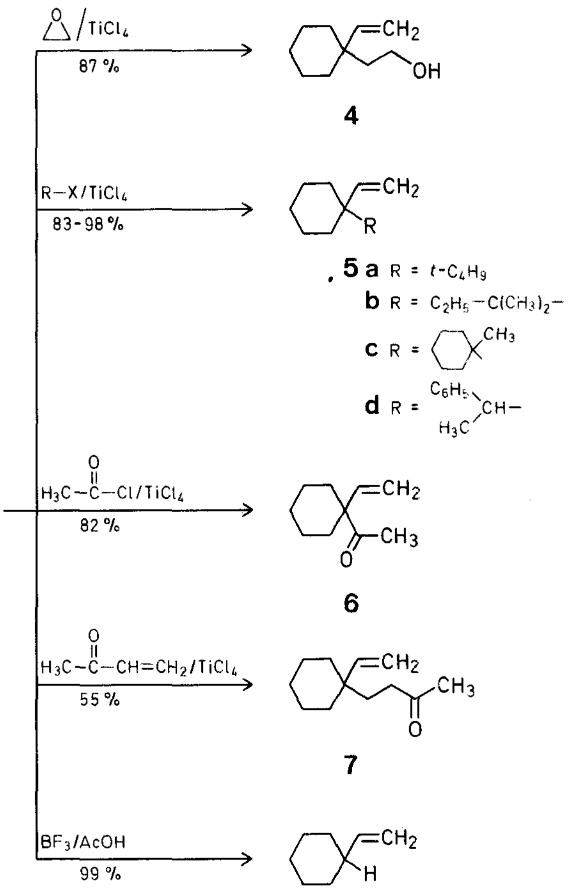
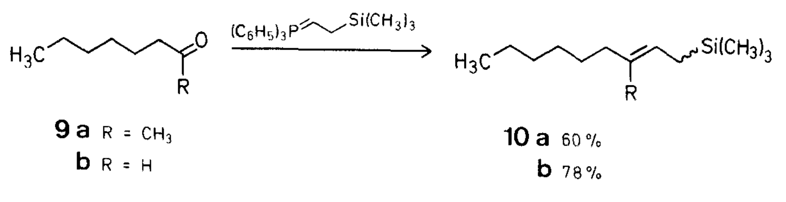
The allylsilanes **3**, **10a**, and **10b** were prepared from the ketones **2** and **9a** and the aldehyde **9b**, using the Wittig reaction developed by Seyferth and his co-workers[6]. Thus, the overall result of our reactions has been to replace the carbonyl oxygen by two carbon substituents in only two steps. To illustrate the synthetic potential of this method of "geminal alkylation", we also converted the allylsilane **3** into the ketones **6** and **7**, thus showing that functionality can easily be introduced into one of the alkyl groups one carbon (as in **6**), two carbons (as in **4**), and three carbons (as in **7**) from the carbon atom of the original carbonyl group. Finally, the allylsilanes undergo protodesilylation with boron trifluoride/acetic acid in chloroform at 20° for 5 min to give the products **8**[7], **13a**, and **13b** in excellent yield; we recommend these conditions for protodesilylation of allylsilanes in general. They are the best we have found.

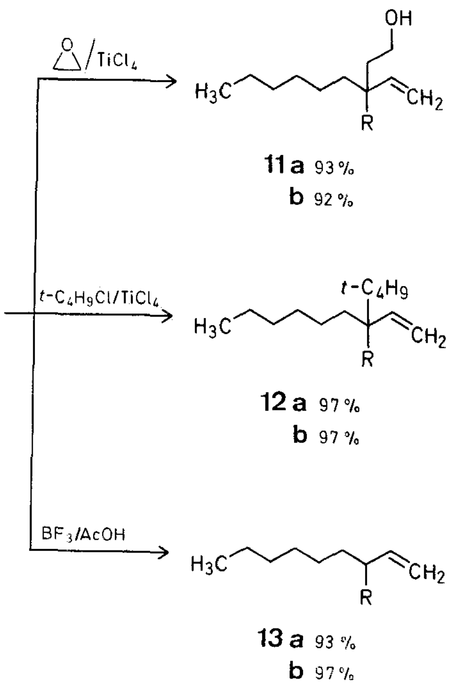




General, One-Pot Procedure for Synthesis of Allylsilanes from Aldehydes and Ketones:

n-Butyllithium (15.0 ml of a 1.66 molar solution in hexane, 25 mmol) is added dropwise with stirring over 0.5 h to a suspension of methyltriphenylphosphonium bromide (8.03 g, 22.5 mmol) in dry tetrahydrofuran (40 ml) at 0° under nitrogen. The mixture is warmed to room temperature and stirred for 1 h, recooled to 0°, and iodomethyltrimethylsilane (2.82 g, 22.5 mmol) is added over 10 min. The mixture is again allowed to come slowly to room temperature to precipitate the new phosphonium salt. After 1 h, the reaction mixture is treated with a second equivalent of *n*-butyllithium (15.0 ml of a 1.66 molar solution in hexane, 25 mmol) at −78°. The mixture is allowed to warm slowly to room temperature and stirred for a further 1.5 h to give the dark red solution of the ylid, β-trimethylsilylethylidenephosphorane. The carbonyl compound (20 mmol) in dry tetrahydrofuran (10 ml) is then added dropwise over 15 min to the ylid solution at −78° under nitrogen. After 0.5 h, the mixture is allowed to warm slowly to room temperature, stirred under nitrogen for a further 16 h, quenched by pouring into saturated ammonium chloride solution (100 ml) and extracted with ether (3 × 300 ml). The combined organic extracts are dried ($MgSO_4$) and evaporated in vacuo. The allylsilane is isolated (in >98 % purity, by G.L.C.) either by chromatography on silica gel, eluting with carbon tetrachloride, or by distillation. Yields were: **3**: 86 %, **10a**: 60 %, and **10b**: 78 %. These reactions are somewhat easier to perform and faster than those given in Lit. [6].





General Procedure for Allylsilane Alkylation Promoted by Titanium(IV) Chloride:

Titanium(IV) chloride (0.6 ml, 5.5 mmol) is added under nitrogen to dry dichloromethane (5 ml) and the resulting solution is stirred and cooled to −78°. The cooled titanium(IV) chloride solution is transferred, via syringe, to a stirred solution of the allylsilane (5 mmol) and the alkylating reagent (6 mmol) (either alkyl chloride or bromide, ethylene oxide, acetyl chloride, or methyl vinyl ketone)

Table 1. Preparation of Allylsilanes by Wittig Reaction

Carbonyl Compound	Allylsilane Product	Yield [%]	b.p./torr	Molecular Formula[a]	^{1}H-N.M.R. (CCl$_4$, 100 MHz) δ [ppm]
2	**3**	86	90–92°/17	$C_{11}H_{22}Si$ (182.3)	0.00 [s, 9H, $Si(CH_3)_3$]; 1.38 [d, 2H, $C\underline{H}_2Si(CH_3)_3$, $J=8$ Hz]; 1.40–1.67 (m, 6H, ring H); 1.88–2.20 (m, 4H, allylic ring H); 5.04 (bt, 1H, C=CH, $J=8$ Hz)
9a	**10a**[b]	60	112–114°/20	$C_{13}H_{28}Si$ (218.2)	−0.01 [s, 9H, $Si(CH_3)_3$]; 0.87 (bt, 3H, $CH_2-C\underline{H}_3$, $J=7$ Hz); 1.13–1.69 [m, 13H, CH_2 including $C\underline{H}_2Si(CH_3)_3$, and $C=C-CH_3$]; 1.82–2.07 (m, 2H, $C=CH-C\underline{H}_2$), 5.09 (bt, 1H, C=CH, $J=8$ Hz)
9b	**10b**	78	102–104°/18	$C_{12}H_{26}Si$ (198.2)	0.01 [s, 9H, $Si(CH_3)_3$]; 0.90 (bt, 3H, CH_3, $J=7$ Hz); 1.24–1.58 [m, 10H, CH_2 including $C\underline{H}_2Si(CH_3)_3$]; 1.82–2.13 (m, 2H, $C=CH-C\underline{H}_2$); 4.91–5.52 (m, 2H, olefinic H)

[a] The microanalyses were in satisfactory agreement with the calculated values (C ±0.1, H ±0.15).
[b] *E*/*Z* mixture.

Table 2. Preparation of Terminal Alkenes from Allylsilanes

Allylsilane Substrate	Alkene Product	Yield [%]	Molecular Formula	M.S. *m/e* (M$^+$) found	required	Reference
3	**4**	87	$C_{10}H_{18}O$ (154.3)[a]	—	—	—
3	**5a**	98	$C_{12}H_{22}$ (166.2)	166.1711	166.1721	—
3	**5b**	85	$C_{13}H_{24}$ (180.2)	180.1877	180.1877	
3	**5c**	98	$C_{15}H_{26}$ (206.2)	206.2048	206.2035	—
3	**5d**	83	$C_{16}H_{22}$ (214.2)	214.1723	214.1722	—
3	**6**	82	$C_{10}H_{16}O$ (152.2)[a]	—	—	—
3	**7**	55	$C_{12}H_{20}O$ (180.3)[a]	—	—	—
3	**8**	99	C_8H_{14} (110.2)	—	—	7
10a	**11a**	93	$C_{12}H_{24}O$ (184.3)[a]	—	—	
10b	**11b**	92	$C_{11}H_{22}O$ (170.3)[a]	—	—	—
10a	**12a**	97	$C_{14}H_{28}$ (196.2)	196.2198	196.2190	—
10b	**12b**	97	$C_{13}H_{26}$ (182.2)	182.2059	182.2034	—
10a	**13a**	93	$C_{10}H_{20}$ (140.3)	—	—	8
10b	**13b**	97	C_9H_{18} (126.2)	—	—	9

[a] Satisfactory microanalyses (C ±0.3, H ±0.3).

in dichloromethane (8 ml) under nitrogen at −78°. After 1 h, the reaction mixture is poured into saturated sodium hydrogen carbonate solution (25 ml) and extracted with ether (3 × 50 ml). The organic phase is dried ($MgSO_4$) and evaporated in vacuo to give, after chromatography on silica gel or distillation, the alkylation product (>98% purity by G.L.C.).

General Procedure for Allylsilane Protodesilylation by Boron Trifluoride/Acetic Acid:

A solution of the allylsilane (2 mmol) in dry chloroform (2 ml) is added in a single portion to boron trifluoride/acetic acid complex (0.2 ml, 280 mg, 2.2 mmol) with vigorous shaking until a single phase is obtained. After 5 min, the mixture is poured into saturated sodium hydrogen carbonate solution (10 ml) and extracted with ether (3 × 20 ml). The organic phase is dried ($MgSO_4$) and evaporated in vacuo to give the crude product (>95% purity by G.L.C.), which is purified by chromatography on silica gel or by distillation.

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