

Regiocontrolled Allylsilane Synthesis from Secondary Allylic Alcohol Derivatives†

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Unsymmetrical secondary allylic acetates and urethanes react with the dimethyl(phenyl)silylcuprate reagent to give allylsilanes with fair to good regioselectivity.

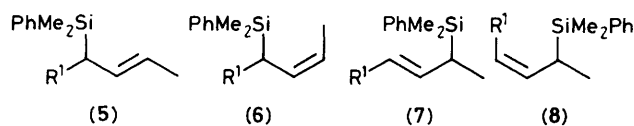
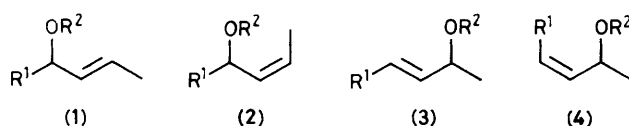
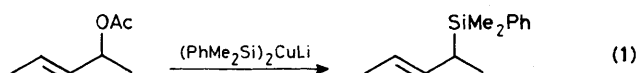
We reported earlier¹ a simple synthesis of allylsilanes from tertiary allylic acetates, using our silyl-cuprate reagent. This synthesis was completely regioselective and stereospecific, giving allylsilanes with the silyl group at the less-substituted

end of the allyl fragment. At that time, using the same conditions, we found that secondary allylic acetates were unreactive towards the silyl-cuprate reagent. In the meantime, Kitching has shown that primary and secondary allylic chlorides react with the silyl-cuprate reagent stereospecifically *anti* but with incomplete regiocontrol.² Smith has shown that silyl-cuprate and silyl-lithium reagents react with primary allyl

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Table 1. Yields and ratios of products (5–8) from the reaction of (PhMe₂Si)₂CuLi on the allylic alcohol derivatives (1–4).

Starting material	Entry	R ¹	R ²	Yield %	(5)	(6)	(7)	(8)
(1)	1	Ph	Ac	40	68		32	
	2	Pr ⁱ	Ac	83	26		74	
	3	Pr ⁱ	CONHPh	87			100	
(2)	4	Ph	Ac	51		18	82	
	5	Pr ⁱ	Ac	83			100	
	6	Pr ⁱ	CONHPh	87			100	
(3)	7	Ph	Ac	40	8	23	69	
	8	Ph	SO ₂ Me	71	12	13	75	
	9	Pr ⁱ	Ac	86	10		90	
	10	Pr ⁱ	CONHPh	87	67	9	23	
(4)	11	Ph	Ac	60	88	12		
	12	Pr ⁱ	Ac	55	73		8	18
	13	Pr ⁱ	CONHPh	66	95		5	



chlorides with high and opposite regioselectivity,³ and Trost has developed reagents, based on tris(trimethylsilyl)aluminum and transition metal catalysts, which react with secondary and tertiary allylic acetates with some useful but not always complete regiocontrol.⁴ We now report the extension of our silyl-cuprate reaction to secondary allylic acetates, with which we have now achieved quite high levels of regiocontrol in some cases.

Whereas secondary allylic acetates do not react with the silyl-cuprate reagent in tetrahydrofuran (THF), we find that they do react in a mixture of THF, Et₂O, and pentane. Thus *E*-pent-3-en-2-yl acetate gave a 70% yield of *E*-2-dimethyl(phenyl)silylpent-3-ene at 0 °C after 2 h [reaction (1)]. Using these conditions, we have examined the regioselectivity of the reaction using the four allylic acetates (1–4, R¹ = Ph, R² = Ac). We get moderate yields of three of the four possible products (5–8, R¹ = Ph) in different ratios from each of the starting materials (entries 1, 4, 7, and 11 in Table 1). Evidently the silyl group is transferred to carbon before complete equilibration of the allyl-copper intermediate has taken place, in contrast to Goering's results⁵ with the acetates (1) and (3) (R¹ = Ph, R² = Ac) reacting with lithium dimethylcuprate.[‡] This is consistent with our observation⁶ that a mixed methyl-silyl-cuprate transfers only the silyl group. Entries 1 and 7 show that the *E*-allylic acetates react largely without allylic shift, but the degree of selectivity is low (~2:1), and the methanesulphonate (entry 8) was little different from the corresponding acetate, except in giving a higher yield. In contrast, entries 4 and 11 show that the *Z*-allylic acetates react largely with allylic shift, and with higher levels of regiocontrol (>4:1).

In the aliphatic series (1–4, R¹ = Prⁱ, R² = Ac), the yields using these conditions were also low, but they were much improved by adding triphenylphosphine,⁷ without significantly affecting the regiochemistry. Entries 2 and 9 show that the *E*-allylic acetates react to give largely the allylsilane with

the silyl group at the less hindered end of the allyl fragment. In contrast, entries 5 and 12 show that the *Z*-allylic acetates react largely with allylic shift, especially (entry 5) when that places the silyl group at the less hindered end of the allyl fragment. Some hint that *Z*-allylic substrates might have a higher tendency to react with allylic shift is to be found in the work of Julia⁸ and of Claesson.⁹

Finally, using the urethane leaving group introduced by Gallina¹⁰ and improved by Goering,¹¹ we observe high levels of allylic shift when the silyl group enters at the less hindered end of the allyl fragment (entries 3 and 6), or when the allylic shift to the more hindered end replaces a *cis* by a *trans* double bond (entry 13).

Typically, the silyl-cuprate reagent was prepared, as usual,¹ from copper(I) cyanide (1.5 mmol) and phenyldimethylsilyllithium (3 mmol in THF), but with the addition of Et₂O (10 ml) and pentane (10 ml). After 15 min at 0 °C, the acetate (1 mmol) in Et₂O (2 ml) was added and the mixture kept for 3 h. Aqueous work up and chromatography on silica gel eluting with hexane gave the mixtures of allylsilanes, which were identified by their ¹H n.m.r. spectra. For those reactions with phosphine present, the phosphine (3 mmol) was added with the copper cyanide. For the reactions with the urethanes, *n*-butyl-lithium (1 mmol) was added to the urethanes (1 mmol) in THF (15 ml) at 0 °C, and this solution added to a mixture of copper(I) iodide (1 mmol) and triphenylphosphine (2 mmol) in Et₂O (5 ml) at 0 °C. After 5 min, the silyl-lithium solution (1 mmol in THF) was added, and kept for 2 h at 0 °C.

In conclusion, we have developed methods for the conversion of allylic alcohols into allylsilanes with useful levels of

[‡] Goering did not report the reaction of lithium dimethylcuprate with the *Z*-acetates (2) and (4) (R¹ = Ph, R² = Ac). We find that both of them give very largely *E*-3-methyl-1-phenylbut-1-ene, just as the *E*-acetates (1) and (3) (R¹ = Ph, R² = Ac) do.

regiocontrol. The allylsilanes are themselves valuable intermediates, because they are known to react with a wide range of electrophiles with high levels of regiocontrol.¹²

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