

Pentaco-ordinate Silicon Compounds in Synthesis: Regiospecific Allylation of Aldehydes by Use of Triethylammonium Bis(pyrocatecholato)allylsilicates

Akira Hosomi,* Shinya Kohra, and Yoshinori Tominaga

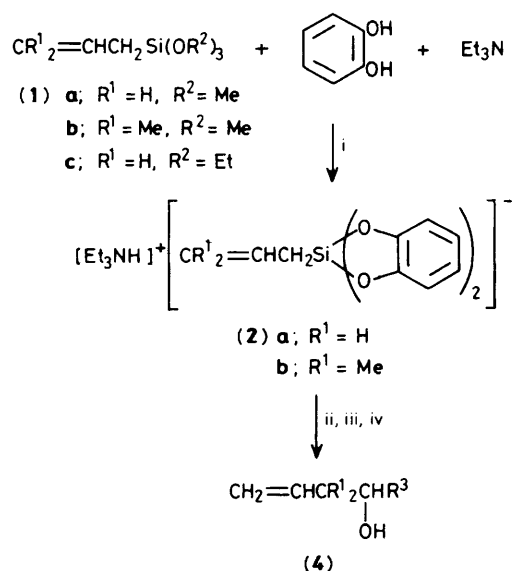
Faculty of Pharmaceutical Sciences, Nagasaki University, Nagasaki 852, Japan

The title compounds, readily prepared from allyltrimethoxysilane, pyrocatechol, and triethylamine, react with aldehydes regiospecifically and chemoselectively without catalyst under mild conditions: the allylation takes place even in protic solvents such as ethanol.

Much effort has been devoted to the regiospecific allylation of carbonyl compounds and efficient methods are highly desirable. Tetraco-ordinate allyltrialkylsilanes are excellent reagents for the regiospecific allylation of various electrophiles; however a stoichiometric amount of a Lewis acid is generally required for the activation of electrophiles.¹ Recently we have reported the reduction of carbonyl compounds by a pentaco-ordinate silane using a trialkoxy-silane–dilithium pinacolate.² In an extension of our studies on pentaco-ordinate organosilanes in synthesis,³ we now report that pentaco-ordinate allylsilicates (2), readily prepared from allyltrialkoxysilane (1),[†] pyrocatechol, and triethylamine,⁴ react with aldehydes (3) smoothly in dichloromethane or chloroform at reflux temperature to give the corresponding homoallyl alcohols (4) in high yield as illustrated in Scheme 1. Allylation takes place regiospecifically. This provides the first example of direct transfer of an organic ligand from a pentaco-ordinate silicon species to a carbon electrophile without catalyst.

Triethylammonium bis(pyrocatecholato)allylsilicate (2a) (decomp. 120 °C) was obtained by reaction of allyltrimethoxysilane (1a) (5 mmol) with pyrocatechol (10 mmol) in triethylamine (3 ml) for 5 h at 45 °C in quantitative yield after evaporation of volatile material under vacuum. The structure of (2a) was confirmed by spectroscopic and elemental analyses. The ²⁹Si n.m.r. (79.3 MHz) spectrum showed

δ –78.4 (p.p.m. from tetramethylsilane in CDCl₃). The negative ion fast atom bombardment mass spectrum showed *m/z* 285 for the anion. Similarly, (2b) was obtained from (1b) [m.p. 94 °C (decomp.), δ_{Si} –76.7, neg. ion f.a.b. *m/z* 313] in



Scheme 1. Reagents and conditions: i, 45 °C, 5 h; ii, R³CHO (3), reflux, 20 h, CH₂Cl₂ or CHCl₃; iii, 1 M-HCl, 1 h; iv, 1 M-NaOH, 1 h.

[†] Allyltrialkoxysilanes are commercially available or easily prepared by the monoallylation of tetra-alkoxysilanes with the allyl Grignard reagent.

Table 1. Reactions of allylsilicates (2) with aldehyde (3).^a

(2)	(3)		(4)		% Yield ^b
	R ³	R ¹	R ³		
(2a)	Ph	H	Ph		86 (84) ^{c,d}
(2b)	Ph	Me	Ph		72
(2b)	<i>p</i> -MeC ₆ H ₄	H	<i>p</i> -MeC ₆ H ₄		84
(2a)	<i>p</i> -ClC ₆ H ₄	H	<i>p</i> -ClC ₆ H ₄		97 ^d
(2a)	<i>p</i> -CNC ₆ H ₄	H	<i>p</i> -CNC ₆ H ₄		65 ^d
(2b)	<i>p</i> -CNC ₆ H ₄	Me	<i>p</i> -CNC ₆ H ₄		68
(2a)	<i>p</i> -OHCC ₆ H ₄	H	<i>p</i> -CH ₂ =CHCH ₂ CH(OH)C ₆ H ₄		62
(2a)	<i>p</i> -NO ₂ C ₆ H ₄	H	<i>p</i> -NO ₂ C ₆ H ₄		93
(2a)	PhCH=CH	H	PhCH=CH		77
(2a)	Pr	H	Pr		100 ^{c,d}
(2a)	CH ₃ [CH ₂] ₆	H	CH ₃ [CH ₂] ₆		67

^a All reactions were carried out in CHCl₃ at reflux, unless otherwise noted. ^b Not optimized. Yield after isolation by t.l.c. ^c In CH₂Cl₂.

^d Determined by g.l.c.

quantitative yield. A slightly higher temperature (60–80 °C) was necessary to complete the reaction with (1c).

The pentaco-ordinate allylsilicate (2a) reacted with aliphatic and aromatic aldehydes (3) smoothly to give the corresponding homoallyl alcohols (4) (Table 1).[‡] Allylation occurred even in the presence of the nitro and cyano functions. Reaction of an α,β-unsaturated aldehyde with (2a) proceeded entirely in the 1,2-addition mode. Allylation takes place slowly in THF or MeCN at reflux, and can also be carried out in protic solvents. Unfortunately, aliphatic, alicyclic, and aromatic ketones such as octan-2-one, cyclohexanone, and acetophenone did not give satisfactory results in the present reaction system.

The phenylsilicate (2b) reacted with (3a) entirely regio-specifically to afford 2,2-dimethyl-1-phenylbut-3-enol (3h) in 72% yield, in sharp contrast with the fluoride ion-promoted allylation with allyltrimethylsilane, in which regioselectivity could not be attained.⁵ The absence of the regioisomer in the reaction mixture was confirmed by spectroscopic and g.l.c. analyses. 2-Methyl-1-phenylbut-1-enol (*erythro*:*threo* 10:90) was also obtained regioselectively from the reaction of the crotylsilicate (*E*:*Z* 90:10) with benzaldehyde in 88% yield.

[‡] In a typical procedure the allylsilicate (2) (1.2 mmol) and an aldehyde (3) (1.0 mmol) were stirred in dichloromethane (1 ml) at room to reflux temperature for 20 h. Diethyl ether (20 ml) and hydrochloric acid (1 M; 5 ml) were then added and the mixture was stirred for 1 h. The usual work-up after treatment with aqueous sodium hydroxide (1 M; 10 ml) and separation by preparative t.l.c. gave the pure homoallyl alcohol (4).

This strongly suggests that the reaction proceeds *via* the cyclic transition state, as with allylic boron and aluminium reagents.⁶

These results present a striking contrast to the inability to prepare allylpentafluorosilicates owing to the ready cleavage of the allyl–silicon bond, in spite of the successful use of other organofluorosilicates in organic synthesis.⁷ Transfer of organic ligands from phenyl-, vinyl-, and *n*-butyl-bis(pyrocatecholato)silicates does not occur under conditions similar to those described here.

This work was supported in part by the Ministry of Education (Grants-in-Aid for Scientific Research), the Houan-sha, the Takeda Science Foundation, the Yamada Science Foundation, and the Mitsubishi Foundation.

Received, 23rd April 1987; Com. 549

References

- For reviews see E. Colvin, 'Silicon in Organic Synthesis,' Butterworths, London, 1981, ch. 9, pp. 97–124; W. P. Weber, 'Silicon Reagents for Organic Synthesis,' Springer Verlag, Berlin, 1983, Ch. 11, pp. 173–205; T. H. Chan and I. Fleming, *Synthesis*, 1979, 761; A. Hosomi and H. Sakurai, *J. Synth. Org. Chem. Jpn.*, 1985, **43**, 406. Recently Mukaiyama *et al.* reported that trityl salts were excellent activators of carbonyl compounds for allylation with allylsilanes: see T. Mukaiyama, H. Nagaoka, M. Mukaiyama, and M. Oshima, *Chem. Lett.*, 1985, 977; M. Hayashi and T. Mukaiyama, *ibid.*, 1987, 289, and references cited therein.
- A. Hosomi, H. Hayashida, S. Kohra, and Y. Tominaga, *J. Chem. Soc., Chem. Commun.*, 1986, 1411, and references cited therein; see also M. Kira, K. Sato, and H. Sakurai, *J. Org. Chem.*, 1987, **52**, 948.
- A. Hosomi, S. Iijima, and H. Sakurai, *Chem. Lett.*, 1981, 243; see also J. Boyer, C. Breliere, R. J. P. Corriu, A. Kpoton, M. Poirier, and G. Royo, *J. Organomet. Chem.*, 1986, **311**, C39; A. Bouldin, G. Cerveau, C. Chuit, and R. J. P. Corriu, *Angew. Chem.*, 1986, **98**, 472.
- C. L. Frye, *J. Am. Chem. Soc.*, 1964, **86**, 3170; 1966, **88**, 2727; 1970, **92**, 1205; see also R. Müller and L. Heinrich, *Chem. Ber.*, 1961, **94**, 1943; F. P. Boer, J. J. Flynn, and J. W. Turley, *J. Am. Chem. Soc.*, 1968, **90**, 6973; R. R. Holmes, R. O. Day, J. J. Harland, A. C. Sau, and J. M. Holmes, *Organometallics*, 1984, **3**, 365; A. Hosomi, S. Kohra, and Y. Tominaga, *Chem. Pharm. Bull.*, 1987, **35**, 2155.
- A. Hosomi, A. Shirahata, and H. Sakurai, *Tetrahedron Lett.*, 1978, 3043; G. Majetich, A. Casares, D. Chapman, and M. Behnke, *J. Org. Chem.*, 1986, **51**, 1745.
- R. W. Hoffmann and B. Kemper, *Tetrahedron Symposium*, 1984, **40**, 2219; Y. Yamamoto and K. Maruyama, *Heterocycles*, 1982, **18**, 357.
- K. Tamao, J. Yoshida, H. Yamamoto, T. Kakui, H. Matsumoto, M. Takahashi, A. Murata, and M. Kumada, *Organometallics*, 1982, **1**, 355; K. Tamao, J. Yoshida, and M. Kumada, *J. Synth. Org. Chem. Jpn.*, 1980, **38**, 769; R. Müller and C. Dathe, *Z. Anorg. Allg. Chem.*, 1965, **341**, 49.