



Stereoselective one-pot synthesis of vinylsilanes from aromatic aldehydes

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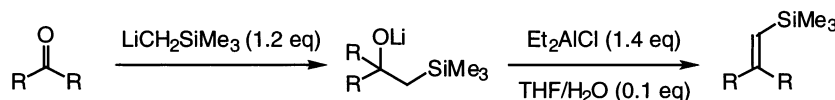
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Abstract—Vinylsilanes serve as convenient vinyl anion equivalents, but procedures for their stereoselective synthesis from aldehydes are scarce. A variety of aromatic aldehydes are converted to the corresponding vinylsilanes in a one-pot procedure involving the addition of (trimethylsilylmethyl)lithium to the aldehyde followed by treatment with $\text{Cp}_2\text{TiCH}_2\cdot\text{AlMe}_2\text{Cl}$ ('Tebbe's reagent'). Halide and alkoxide substituents are tolerated, and (*E*)-vinylsilanes are formed exclusively in good yield. © 2001 Elsevier Science Ltd. All rights reserved.

The development of stereospecific alkene synthesis methodology has been driven by the central role played by the alkene functionality in countless natural and unnatural products and synthetic intermediates. Vinylsilanes play important synthetic roles as vinyl anion equivalents for stereospecific electrophilic reactions.¹ However, few effective synthetic methods for the preparation of these versatile intermediates have been

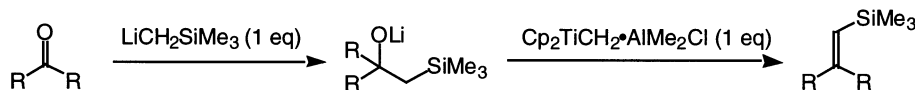
reported. Although routes from alkynes have been developed,² the obvious Wittig approach from ketones and/or aldehydes, using a substituted ylide, $\text{Ph}_3\text{P}=\text{CHSiMe}_3$, is ineffective.³ Battiste and Kwan have recently developed⁴ a protocol for the conversion of non-enolizable ketones to vinylsilanes based on the Peterson olefination reaction.⁵ Treatment of the lithium alkoxide resulting from addition of (trimethylsilyl-



Scheme 1.

Table 1. Conversion of benzaldehyde to β -trimethylsilylstyrene

Reagents	Conditions	Yield	<i>E</i> : <i>Z</i> ratio	Reference
$\text{Cp}_2\text{Ti}(\text{CH}_2\text{SiMe}_3)_2$	$(\text{EtOCH}_2)_2$, 110°C, 26 h	20	<1.5:1	6
$\text{Cp}^*\text{Ti}(\text{CH}_2\text{SiMe}_3)_3$	$(\text{EtOCH}_2)_2$, 110°C, 26 h	40	<1.5:1	6
$(\text{Me}_2\text{SiOMe})_2\text{CH}_2/t\text{-BuLi}$	100°C, 2 h	85	3:1	7
$\text{Me}_3\text{SiCHBr}_2/\text{CrCl}_2$	THF, 25°C, 24 h	82	1:0	8
$(\text{Me}_3\text{Si})_2\text{CHLi}$	THF, $-78^\circ\text{C} \rightarrow 25^\circ\text{C}$	70	1.4:1	9
$(2\text{-PyMe}_2\text{Si})_2\text{CHLi}$	Et_2O , $-78^\circ\text{C} \rightarrow 25^\circ\text{C}$	90	>99:1	10



Scheme 2.

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methyl)lithium to a ketone with diethylaluminum chloride in wet THF affords the corresponding vinylsilane in fair to good yield (Scheme 1).

This modified Peterson olefination approach fails with aromatic aldehydes, forming complex mixtures of desilylated, alkylated, and reduced materials together with the desired vinylsilanes. Other methods for the conversion of aldehydes to vinylsilanes generally suffer from low yields, poor stereoselectivity, and/or expensive or hazardous reagents, as summarized in Table 1.

Recognizing the ability of $\text{Cp}_2\text{TiCH}_2\text{AlMe}_2\text{Cl}$ ('Tebbe's reagent') to cleave a variety of carbon–oxygen bonds,¹¹ we explored its reactions with β -silylalkoxides, generated by the addition of (trimethylsilyl-methyl)lithium to aromatic aldehydes. Upon addition of the β -silylalkoxide to Tebbe's reagent at room temperature, a color change from brownish-red to purple-red is observed. ^1H NMR spectroscopy at this point suggests that an alkoxide analog of Tebbe's reagent has formed. No additional significant chemistry occurs at room temperature, but heating the reaction mixture to ca. 150°C in a sealed tube leads to the production of the corresponding (*E*)-vinylsilane (Scheme 2, Table 2).¹²

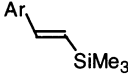
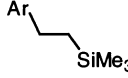
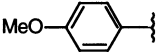
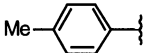
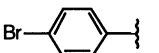
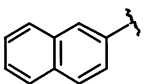
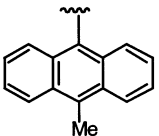
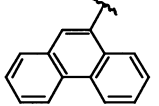
In the alumoxane-mediated synthesis of vinylsilanes from non-enolizable ketones, the presence of water appears to enhance the chemoselectivity of the reaction (affording the desired abstraction of a proton instead of

the trimethylsilyl group).⁴ In contrast, traces of water in the titanium-mediated reaction lead to desilylation, affording simple styrene derivatives. Drying of aldehyde substrates (solids—Abderhalden pistol at 10 – 15°C below the melting point of the aldehyde over P_2O_5 ; liquids—washing with 10% sodium bicarbonate, then distillation from CaH_2 , freeze–pump–thaw degassing, and storage over activated 3 Å molecular sieves) effectively eliminates the desilylation reaction.

The reaction appears to form the vinylsilane exclusively as the (*E*)-isomer, and yields range from 44 to 86%. An electronic effect seems apparent, with the electron-rich substrate, *p*-methoxybenzaldehyde, (Table 2, entry 1) reacting appreciably faster than the *p*-bromo derivative. The implications of this with regards to the mechanism of the reaction are under continuing investigation. Several aldehydes afford the (*E*)-vinylsilane cleanly (entries 1, 3, and 5). In other cases, however, formation of the corresponding alkylsilane (β -trimethylsilyl ethylarene) is also observed (entries 2, 4, and 6). Although separable (e.g. capillary gas chromatography on a fused silica column), we are continuing to explore the factors responsible for formation of the reduction products in order to minimize their formation.

Interestingly, whereas 10-methyl-9-anthraldehyde cleanly affords the anticipated (*E*)-vinylsilane in good yield (entry 5), 9-anthraldehyde itself undergoes an apparent dimerization reaction (as revealed by mass

Table 2. Vinylsilanes from aromatic aldehydes

Entry	Substrate ArCHO, Ar =	Reaction time (h)	Isolated yield (%)			Lit. Ref.
1 ^a		11.5	86	>99	<1	13
2 ^a		17	58	4.7	1	14
3 ^b		48	44	>99	<1	14
4 ^c		36	83	7.4	1	15
5 ^b		48	74	>99	<1	–
6 ^d		36.5	82	1.4	1	15

^a Toluene, 110°C .

^b Benzene, sealed tube, 150°C .

^c Tetrahydrofuran, sealed tube, 150°C .

^d Toluene, sealed tube, 150°C .

spectral and partial X-ray crystallographic analysis). The detailed structure of this product, whose formation may also prove suggestive with regards to the mechanism of the vinylsilane forming reaction, has proven elusive due to crystallographic problems, but is under continued investigation.

This procedure provides convenient and reliable access to a variety of vinylsilanes with excellent stereoselectivity. We are continuing to explore the versatility of this reaction, as well as the factors responsible for the formation of reduction products.

Acknowledgements

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- General procedure: Under an inert atmosphere, 1.1 equiv. of $\text{Me}_3\text{SiCH}_2\text{Li}$ (1.3 M solution in benzene) was added to a solution of 1.7 mmol of the aromatic aldehyde in 10 mL of dry benzene in a thick-walled tube with Teflon closure. After stirring the solution at room temperature for 2 h, a solution of 1.1 equiv. of $\text{Cp}_2\text{TiCH}_2\text{-AlMe}_2\text{Cl}$ in 40 mL of dry benzene was added, forming a deep-red solution. The tube was closed, then heated in a 150°C oil bath for 11–48 h (see Table 2). The resulting mixture was transferred in air to a 500 mL beaker containing excess sodium oxalate (ca. 15 g) and sodium bicarbonate (ca. 1 g). The mixture was stirred overnight, affording a brown paste, which was extracted with pentane. The resulting solution was washed with 0.5% aqueous sodium bicarbonate, dried over MgSO_4 , and evaporated.
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