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α-Lithioalkoxysilanes: applications to alkene synthesis

Tim F. Bates, Sushama A. Dandekar, Jon J. Longlet, Ruthanne D. Thomas *

Department of Chemistry, University of North Texas, Denton, TX 76203-5070, USA

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Abstract

α-Lithioalkoxysilanes [RO(Me_2)Si]CH(Li)(X), where R = Me or Et and X = H or $SiMe_3$, react with carbonyl compounds in hydrocarbon solution to produce alkenes in moderate to high yield via Peterson-type reactions. For X = $SiMe_3$, the corresponding vinylsilanes are isolated directly following work-up. The reaction is regiospecific and shows fair stereoselectivity. When the carbonyl substrates are cyclic ketones in six- or seven-membered rings, the products are exocyclic alkenes. For X = H, the initial product is a β-hydroxysilane, which is then efficiently converted to the corresponding terminal alkene by heating with sodium acetate in acetic acid. Both types of α-lithioalkoxysilane reagents are amenable to reaction with enolizable carbonyl compounds.

Keywords: Vinylsilanes; Exocyclic alkenes; Peterson olefination; α-Lithiosilanes; Alkoxysilanes; Terminal alkenes

1. Introduction

In the late 1940s, Whitmore et al. first observed that trimethylsilylmethylmagnesiumchloride reacts with acetaldehyde to yield propene after acid treatment [1]. It was not until some 20 years later that Peterson generalized this type of reaction to the alkene synthesis that bears his name [2]. Since its initial discovery, a great deal of work has been done to further exploit this methodology and it has been the subject of several reviews [3].

In general, the Peterson olefination involves the reaction of a carbonyl compound with a carbanion alpha to silicon. The alkene is formed by elimination of a silanolate from the initial adduct (Scheme 1). When X is a heteroatom, the elimination is usually spontaneous, directly affording the alkene upon mild hydrolytic work-up of the reaction mixture. However, when X = H (counterion = Li/Mg), the product initially isolated is a β-hydroxysilane [2], which undergoes elimination upon treatment with either acid or base. The elimination is stereospecific; anti in acid and syn in base [3,4a]. While the reaction is known to work well with a variety of alkyl and aryl substituents on silicon, the effects of other types of substituents have not been extensively investigated [5]. The Peterson reaction has proved to be complimentary to the Wittig olefination and is particularly useful in the synthesis of heteroatom-substituted alkenes [6–10].

Despite its widespread use, the Peterson reaction has several important limitations. The reaction is generally not applicable to enolizable ketones or aldehydes [10a]. Also, notwithstanding the stereospecific nature of the elimination step leading to the alkene, there is little or no overall stereoselectivity in the formation of the *E* and *Z* isomers [4a]. There is some evidence to suggest that the diastereomeric ratio is generally insensitive to changes in temperature and variations in solvent [4b]. However, solvent effects, temperature and the bulk of the silyl functionalities have been reported to be responsible for enhanced stereoselectivity in some Peterson reactions [4c].

We have reported preliminary results of our investigations regarding the synthesis of an α-lithioalkoxysilane, [(methoxydimethylsilyl)(trimethylsilyl)methyl]-lithium (**1a**), and its reactions with aldehydes and ketones to form vinylsilanes [11]. In this modified Peterson reagent, one of the alkyl groups on silicon has been replaced by a methoxy group. Interestingly, this reagent reacted even with enolizable carbonyl compounds, and

* Corresponding author. Fax: +1-940-5654318.
E-mail address: rthomas@unt.edu (R.D. Thomas).

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showed moderate stereoselectivity. Equally importantly, it was also amenable to the formation of exocyclic alkenylsilanes. Since our initial report, Avery and coworkers have successfully applied this methodology for preparing key exocyclic vinylsilane intermediates in the synthesis of the analogs of the potent antimalarial, (+)artemesinin [12]. We recently reported the regiospecific synthesis of several α-lithioalkoxysilanes [13]. We now report our findings on the reactions of some of these α-lithioalkoxysilanes, $[(RO)Me_2Si]CH(Li)(X)$, where R = Me or Et and $X = SiMe_3$ or H, with a number of carbonyl compounds to produce the corresponding alkenes.

2. Results and discussion

2.1. Reaction of (alkoxydimethylsilyl)(trimethylsilyl)methyllithium compounds with aldehydes and ketones

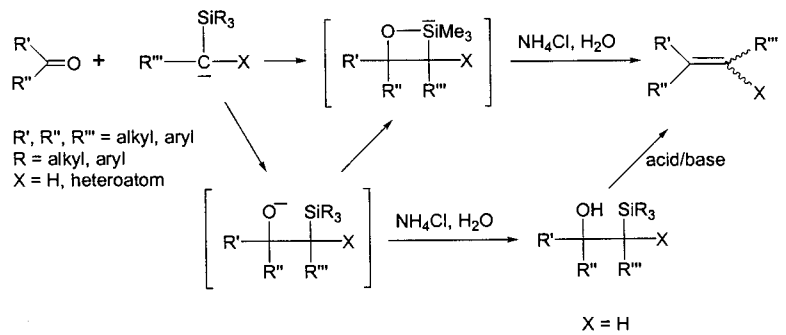
When pentane solutions of either (methoxydimethylsilyl)(trimethylsilyl)methyllithium (**1a**), or (ethoxydimethylsilyl)(trimethylsilyl)methyllithium (**1b**), are treated at −78°C with ketones or aldehydes, the corresponding vinylsilanes, **2**, are isolated directly after hydrolysis (Scheme 2).

In each case, ^{13}C-NMR spectra of the crude product indicated the absence of the other possible olefin, **3**. The results of these reactions are summarized in Table 1.

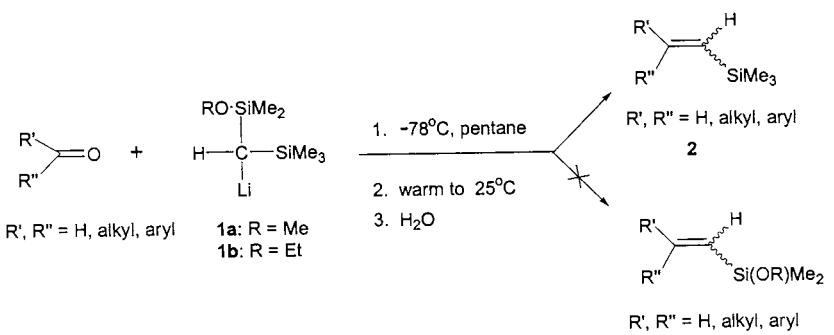
Of particular note, reagents **1a** and **1b** are effective for the conversion of enolizable ketones to alkenylsilanes. This is in contrast to bis(trimethylsilyl)methyllithium [8,9] and bis(trimethylsilyl)bromomethyllithium [10], which are suitable only for non-enolizable carbonyl compounds. It is not clear whether this is an inherent property of α-lithioalkoxysilanes, or perhaps merely due to our use of a non-polar solvent (pentane). However, our observation that reduced yields of vinylsilane **2a** are obtained when a diethyl ether solution of cyclohexanone is added to **1a**, suggests that solvent effects are important [11].

2.2. Formation of exocyclic vinylsilanes

Although there are a number of routes to vinylsilanes [7,14], most of the reported syntheses begin with an alkyne [14–17], thereby precluding the formation of exocyclic alkenylsilanes. Thus, there have been only a few reports documenting the preparation of this class of compounds [12,18–20]. Our results indicate that α-lithioalkoxysilanes provide a general means of preparing exocyclic vinylsilanes via the Peterson methodology. As shown in Table 1, vinylsilanes exocyclic to both six- and seven-membered rings have been prepared in moderate to good yields using reagents **1a** or **1b** and the corresponding cyclic ketone. As we noted earlier, the



Scheme 1.



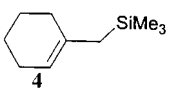
Scheme 2.

Table 1
Yields and isomer ratios of vinylsilanes

R	Carbonyl	Product	R_1	R_2	Yield (%) [a]	*E*/*Z*
Me	Cyclohexanone	**2a** [b]	$-(CH_2)_5-$		68 [c]	
Et	Cyclohexanone	**2a**	$-(CH_2)_5-$		71	
Me	Cycloheptanone	**2b**	$-(CH_2)_6-$		43 [c]	
Me	Cyclohexenone	**2c** [d]	$-CH=CH(CH_2)_3-$		61	2.0:1
Et	Cyclohexenone	**2c**	$-CH=CH(CH_2)_3-$		56	2.3:1
Me	Benzaldehyde	**2d** [e]	Ph	H	85	2.8:1
Et	Benzaldehyde	**2d**	Ph	H	71	2.4:1
Me	3-Pentanone	**2e** [d]	Et	Et	70	
Et	Benzophenone	**2f** [f]	Ph	Ph	81	

[a] Isolated yields.
[b] Ref. [19].
[c] Heated at 100°C for 2 h prior to chromatography.
[d] Ref. [11].
[e] Ref. [26].
[f] Ref. [8].

reaction of cyclohexanone with **1a** occasionally afforded a minor product, previously unidentified, in addition to the expected alkenylsilane [11]. We have since identified this product as (1-cyclohexenyl)-methyltrimethylsilane (**4**), an isomer of **2a** with an endocyclic double bond. An analogous isomeric product, (1-cycloheptenyl)methyltrimethylsilane (**5**), was also occasionally obtained during the reaction of **1a** with cycloheptanone. During attempts to optimize the yields of alkenes **2a**–**b**, it was found that when the crude product mixtures obtained after work-up were heated at 100°C for 2 h, no endocyclic isomers were detected or isolated. This procedure was therefore adopted as routine for subsequent experiments with these compounds.



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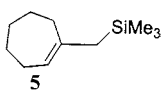

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2.3. Mechanism of elimination

As noted above, there was no evidence for the formation of an alkoxy-substituted alkenylsilane (**3**), indicating a regiospecific elimination from the initially formed adduct. The Peterson reaction has generally been assumed to take place via a β-oxidosilane intermediate, formed when C–C bond formation precedes Si–O bond formation. However, Hudrlik and coworkers have shown that, at least in a few cases, the β-oxidosilane is probably not formed at all, that C–C and Si–O bond formation is likely concerted, so that the oxasiletane anion is formed directly, and is the more likely major intermediate [21]. Two distinct pathways leading to the alkenylsilanes seemed possible, from either postulated intermediate, as depicted in Scheme 3 for the reaction of **1a** with cyclohexanone. Of the two possible siloxetane anions that could be formed, the one formed from the alkoxy-substituted silicon seemed more likely, since the lithium could be chelated to two oxygen atoms; the siloxetane anion formed from the trimethyl-substituted silicon, on the other hand, would have only one coordinated oxygen.

Path A represents a concerted elimination of an alkoxysilanolate to form **2a**, analogous to the mechanism proposed for other Peterson-type reactions, [2,3]. Path B involves an alternate path: an initial elimination of lithium alkoxide, leading to the formation of a second siloxetane intermediate. Under the reaction conditions, this intermediate would be likely to eliminate dimethylsilanone to yield the alkenylsilane **2a** [22,23]. Dimethylsilanone, in its turn, might be expected to produce some hexamethylcyclotrisiloxane, D_3, although the decomposition of a stable 1,2-siloxetane has also been shown to form polymeric material [23].

When the gas chromatographic retention times of samples from the reaction mixtures were compared to the retention time of an authentic sample of D_3, no evidence for D_3 was found, suggesting that path B was probably not the correct mechanistic pathway. In order to further differentiate between the two possible pathways leading to **2a**, we attempted to determine the identity of the lithium species eliminated, by trapping it with chlorotrimethylsilane; this was added to the adduct resulting from the addition of cyclohexanone to **1a**. Analysis of the product mixture revealed large amounts of methoxypentamethyldisiloxane, formed presumably from $LiOSi(Me)_2OMe$; no methoxytrimethylsilane was found, showing that LiOMe was not eliminated during the reaction. This provided direct evidence that path A was the likely route for the formation of the alkenylsilane.

Another aspect of the elimination determines the identity of the final reaction product: the regiospecificity. Loss of the alkoxy-substituted silicon would yield **2**, while elimination of the other silyl group would afford **3**. The fact that the reaction exclusively affords **2** may be due to two major differences between the two silyl groups. The alkoxy-substituted silicon is expected to be more electrophilic than the other silyl group, making it likely to be eliminated more readily. In addition, the alkoxy group is almost certainly coordinated intramolecularly to the lithium [24], a feature that is not possible with the trimethylsilyl group, further facilitating selective elimination of the alkoxydimethylsilyl group, leading to the formation of **2** as the only isolated alkene product.

2.4. Stereoinduction from the interaction of unsymmetrically substituted carbonyl compounds with (1a) or (1b)

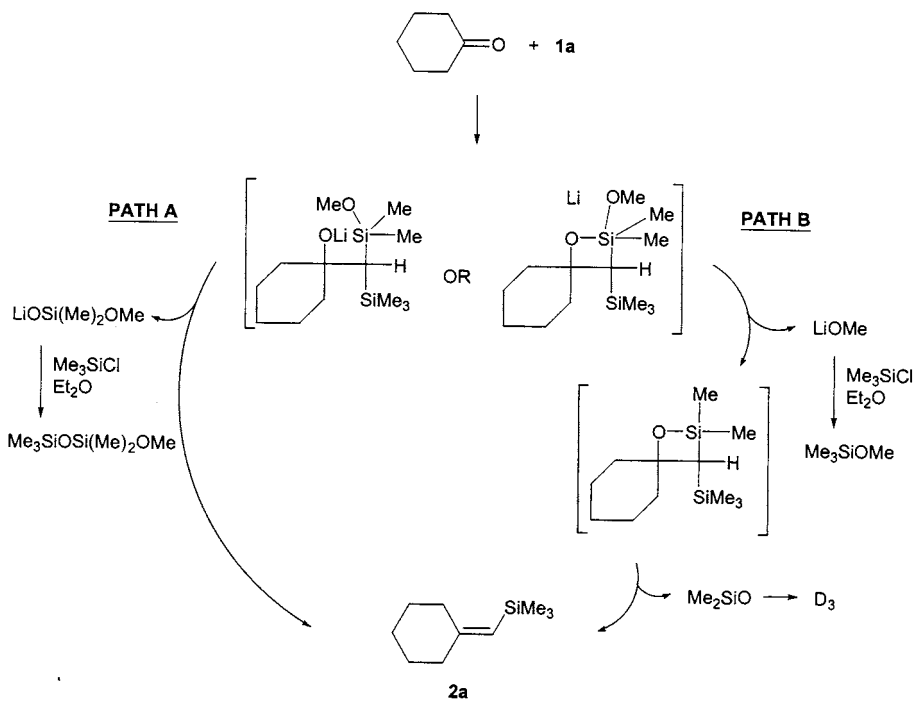
In general, Peterson reactions show very low stereoselectivity [3]. This has been attributed to low stereoselectivity in the formation of the initial adduct, since the elimination step leading to the alkene has been shown to be stereospecific. Thus, where the possibility of diastereomers exists, no significant stereoselectivity is observed in the addition of chiral, α-lithiated silanes to prochiral ketones or aldehydes [25].

There are some exceptions to this general observation, the most notable being the preparation of vinylsilanes from non-enolizable ketones via bis(trimethylsilyl)methyllithium [9] and the preparation of α-bromovinylsilanes from aldehydes via bis(trimethylsilyl)-bromomethyllithium [10]. The intermediates, in these special cases, have two possible routes for elimination from the β-hydroxysilanes and so stereoselectivity is not unexpected [9,10].

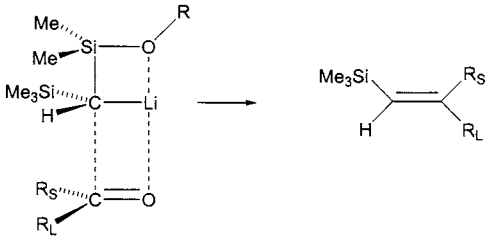
As shown in Table 1, modest stereoselectivity is observed with our reagents **1a** and **1b** when $R^1 \neq R^2$. The stereochemical assignments of compounds **E-2d** and **Z-2d** were made by comparing the ^{1}H-NMR spectra to those previously reported for each isomer [26], while the assignments of **E-2c** and **Z-2c** are based on the coupling patterns in the 300 MHz ^{1}H-NMR spectra [11]. Compound **Z-2c** shows a five-bond coupling of 1.5 Hz between H-3 and the olefinic proton geminal to silicon, consistent with the *trans–trans* configuration. No coupling was detected between the corresponding protons of **E-2c**. The fair selectivity observed for this reaction (2:1, E/Z) and that with benzaldehyde (3:1, E/Z) contrasts with the low stereoselectivity generally observed with other Peterson-type olefinations.

The elimination reaction of the lithium silanolate from the intermediate adduct, as shown in path A of Scheme 3, is usually a stereospecific and *syn* process [4a]. Therefore, any selectivity observed for the overall olefination must reflect an enhanced selectivity during the formation of the initial adduct from a chiral, α-lithiated alkoxysilane and a prochiral carbonyl compound.

Complexation of the carbonyl oxygen with the lithium atom is believed to be the initial interaction between an alkyllithium and a carbonyl compound [27].



Scheme 3.



Scheme 4.

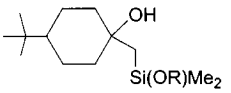
We speculate that the lithium atom in **1** is also coordinated intramolecularly to the alkoxy oxygen. Klumpp and coworkers have demonstrated the intramolecular complexation of alkyllithiums with $-NMe_2$ and have suggested a very similar lithium complexation propensity for –OMe [24]. Analogous intramolecular coordination to the nitrogen of the pyridyl group has been shown to occur in (2-pyridyl)dimethylsilylmethyllithium [28]. Due to chelation, the preferred face of attack for the carbonyl compound would be that which would result in the bulky trimethylsilyl group eclipsing the smaller of the two carbonyl alkyl groups, R_S; the H would then eclipse the larger of the two carbonyl alkyl groups, R_L (Scheme 4). Subsequent *syn*-elimination of lithium silanolate would lead to the *E*-isomer.

This mechanism would account for the observed stereochemistry. It would also account for the similarity in the stereoselectivity observed with reagents **1a** and **1b**. Since R is directed away from the carbonyl compound, there would be little difference in the steric effects of the two lithium reagents. With reagents such as bis(trimethylsilyl)methyllithium, no intramolecular coordination is possible, reducing selectivity in the formation of the adduct and leading ultimately to the absence of marked stereoselectivity typically observed in Peterson olefinations. This analysis treats the lithium compound as if it is monomeric. However, similar arguments should hold for lithium aggregates.

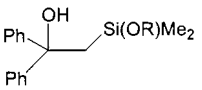
2.5. Methylenation reagents

We have also studied the reactions of several structurally simpler α-lithiated alkoxysilanes, $[RO(Me)_2Si]$-CH_2Li, where R = Me (**6a**), and R = Et (**6b**) (Scheme 5).

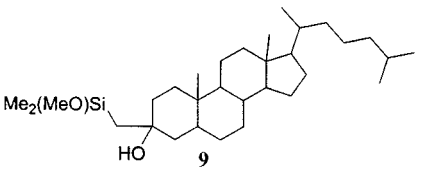
These undergo Peterson-like reactions with aldehydes and ketones to yield, initially, not alkenes, but β-hydroxy alkoxysilanes **7**, **8**, and **9**. These results are analogous to Peterson reactions with other primary lithium or magnesium compounds [2]. However, these β-hydroxy alkoxysilanes proved to be somewhat unstable upon standing at room temperature, eventually forming the corresponding terminal alkenes **10**, **11** and **12**, along with non-volatile material, presumed to be a silicone polymer from alkoxydimethylsilanol. Nevertheless, NMR spectra of the crude products were fully consistent with the assigned structures of the expected alcohols.



7a: R = Me
7b: R = Et



8a: R = Me
8b: R = Et



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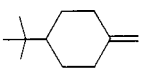

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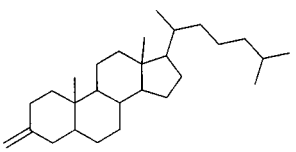

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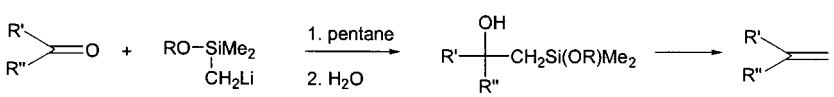
Freshly prepared **7b**, derived from the reaction of **6b** and 4-*tert*-butyl-cyclohexanone, was then used in a model study aimed at determining an efficient way for the conversion of β-hydroxy alkoxysilanes into the corresponding alkenes.

Since the alcohols isolated after work-up had been found to undergo slow elimination at room temperature, we first attempted to accelerate this process by the use of heat. However, **7b** remained unchanged when heated to 100°C for 1 h. Similarly, refluxing **7b** in a mixture of cyclohexane and pyridine left the alcohol



6a: R = Me
6b: R = Et

7-9

10-12

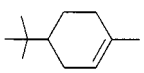
Scheme 5.

Table 2
Yields of terminal alkenes from carbonyl compounds and α-lithioalkoxysilanes, $[RO(Me)_2Si]CH_2Li$

Lithium compound	Carbonyl compound	β-Hydroxysilane	Product	Yield (%) [a]
6a	4-*tert*-Butylcyclohexanone	**7a**	**10** [b]	76
6b	4-*tert*-Butylcyclohexanone	**7b**	**10**	64
6a	Benzophenone	**8**	**11** [c]	91
6a	5-α-Cholestan-3-one	**9**	**12** [d]	48

[a] Isolated yields.
[b] Ref. [35].
[c] Ref. [37].
[d] Ref. [38].

unchanged. When treated with potassium metal in THF, as expected, the initially formed potassium alkoxide underwent spontaneous elimination to give **10** in moderate yield [2]. Elimination could also be brought about by refluxing a cyclohexane solution of **7b** containing trace amounts of conc. sulfuric acid. However, the product mixture was found to contain significant amounts of the endocyclic olefin, 1-methyl-4-*tert*-butylcyclohexene (**13**), presumably arising via acid-catalyzed isomerization of **10**. Although a modification of this procedure, i.e. removal of ethanol from the reaction as its cyclohexane azeotrope, helped to decrease the amount of **13** found in the alkene product, it did not completely prevent the secondary reaction. Heating **7b** in acetic acid, saturated with sodium acetate, to 50°C for 30 min proved to be the most effective of the various procedures tried, affording alkene **10** in good yield [4a].



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As shown in Table 2, this method also proved satisfactory for conversion of the other β-hydroxy alkoxysilanes to the desired alkenes. As with the reagents **1a** and **1b** described in the previous sections, both **6a** and **6b** are amenable to reaction with enolizable carbonyl compounds.

2.6. Conclusion

Our results clearly demonstrate the potential utility of α-lithioalkoxysilanes as excellent Peterson olefination reagents that do not suffer from the limitations common to many of the standard reagents used to carry out the reaction. Thus, alkenes may be prepared with moderate to good stereoselectivity in fair yields from various enolizable carbonyl compounds. These reagents also provide a new, excellent and direct route to two classes of compounds that have heretofore been somewhat difficult to prepare, vinylsilanes and exocyclic alkenes.

3. Experimental

3.1. General

All experiments were carried out under an atmosphere of argon. Glassware was assembled hot from the drying oven. Reagents were transferred by standard syringe or double-ended needle techniques. Methoxytrimethylsilane was either prepared by the literature procedure [29] or purchased from Aldrich. In either case, traces of methanol were removed by distillation from sodium metal [30]. Ethoxytrimethylsilane, purchased from Huls Scientific, was also distilled from sodium metal. The synthesis of (methoxydimethylsilyl)(trimethylsilyl)methane has been described earlier [11,13,32]. (Ethoxydimethylsilyl)(trimethylsilyl)methane was prepared similarly [13,29]. The *tert*-butyllithium solution in pentane, purchased from Aldrich, was titrated prior to use [31]. The 5-α-cholestan-3-one was purchased from Lancaster Synthesis Ltd. Pentane was dried over $LiAlH_4$ before transferring to a dry storage vessel under high vacuum. Diethyl ether and THF were distilled from $LiAlH_4$. All NMR spectra were obtained on a Varian VXR-300 NMR spectrometer (299.9 MHz for ^1H and 75.4 MHz for ^{13}C), with $CDCl_3$ as the solvent and internal standard (77.0 ppm). Chemical shifts are expressed in ppm relative to TMS. Results of ^{13}C APT (attached proton test) spectra are tabulated for each carbon resonance: (−), CH_3 or CH; (+), CH_2 or C. Mass spectra were obtained from a Hewlett–Packard 5970A GC/MS. Elemental analysis was performed by Schwarzkopf Microanalytical Laboratory (Woodside, NY). High resolution mass spectra were obtained from the Midwest Center for Mass Spectrometry, University of Nebraska, Lincoln, NE.

3.2. Synthesis of vinylsilanes (2)

All of the vinylsilanes listed in Table 1 were synthesized by procedures analogous to that described in Section 3.2.1 for the synthesis of **2a** from **1b**. All

spectroscopic data for **2c** and **2d** were determined from a mixture of *E* and *Z* isomers.

3.2.1. Preparation of (trimethylsilyl)methylenecyclohexane (2a)

3.2.1.1. Using (ethoxydimethylsilyl)(trimethylsilyl)-methane (1b). To a solution of (ethoxydimethylsilyl)-(trimethylsilyl)methane (**1b**), (1.14 g, 6.0 mmol) in pentane (10 ml) at room temperature (r.t.) was added *tert*-BuLi in pentane (3.53 ml, 6.0 mmol, 1.7 M) via syringe. After stirring for 2 h, the reaction mixture was cooled to −78°C and cyclohexanone (0.518 ml, 5.0 mmol) was added drop-wise, via syringe. The reaction mixture was allowed to warm to room temperature while stirring overnight. The pale yellow solution was then added to NH_4Cl (satd., aq., 12 ml) and the reaction vessel rinsed with water (12 ml). After extraction of the combined aqueous portions with pentane (2 × 10 ml), the combined organic layers were dried with anhydrous $MgSO_4$. The crude product, obtained after removal of the solvent under reduced pressure, was then heated for 2 h at 100°C. Flash chromatography (silica gel–pentane) afforded 0.60 g (71%) of **2a** [19]. ^{13}C-NMR: $\delta = 0.6(-)$; 26.3(+); 28.4(+); 28.8(+); 34.5(+); 40.5(+); 120.3(−); 160.1(+). MS, *m*/*z* (relative intensity): 168(18, P), 153(100, M-15), 125(43), 93(22), 73(37), 59(96), 45(25).

In a few instances, the NMR spectrum of the crude product revealed the presence of small amounts of an additional compound. Upon subsequent isolation by chromatography, this was identified as 1-trimethylsilymethyl cyclohexene (**4**) [33]. ^{13}C-NMR: $\delta = 1.0(-)$; 22.5(+); 23.0(+); 25.0(+); 28.0(+); 31.0(+); 119.0(+); 135.5(−). MS, *m*/*z* (relative intensity): 168(6, P), 94(8), 73(100), 59(10), 45(11).

In some experiments involving the synthesis of **2a** (and **2b**), when crude product isolated after work-up was heated (100°C, 2 h), prior to chromatography, NMR analysis showed absence of **4**. This procedure was therefore adopted as routine in subsequent experiments.

3.2.1.2. Using (methoxydimethylsilyl)(trimethylsilyl)-methane (1a). A similar reaction starting with (methoxydimethylsilyl)(trimethylsilyl)methane (**1a**), (12 mmol) afforded 1.15 g (68%) of **2a**.

3.2.2. Preparation of (trimethylsilyl)-methylenecycloheptane (2b)

In a manner similar to that described above for the formation of **2a**, *tert*-BuLi in pentane (2.61 ml, 12 mmol, 1.7 M) was added to a pentane (20 ml) solution of (methoxydimethylsilyl)(trimethylsilyl)methane (**1a**) (2.12 g, 12 mmol). Cycloheptanone (1.18 ml, 10 mmol) was added drop-wise at −78°C. Following aqueous work-up, the crude product, obtained after removal of the solvent under reduced pressure, was heated for 2 h at 100°C. Flash chromatography afforded 0.78 g (43%) of **2b**. ^{13}C-NMR: 0.2(−); 28.1(+); 28.5(+); 29.3(+); 29.5(+); 35.0(+); 41.0(+); 124.0(−); 162(+). MS, *m*/*z* (relative intensity): 182(8, P), 167(66, M − 15), 139(27), 79(34), 73(77), 59(100), 45(38). Molar mass from high resolution MS Anal. Calc. for $C_{11}H_{22}Si$: 182.1491. Found: 182.1488.

In a few instances, the NMR spectrum of the crude product obtained after work-up revealed small amounts of an additional compound. Isolation by flash chromatography, followed by NMR and MS analysis, showed this substance to be 1-trimethylsilymethyl cycloheptene, **5**. ^{13}C-NMR: $\delta = 1.2$, 26.7, 27.7, 28.5, 31.0, 32.7, 35.4, 123.6, 142.4. MS, *m*/*z* (relative intensity): 182(13, P), 108(17), 79(13), 73(100), 59(30), 45(49).

When the crude product was heated (100°C, 2 h) and analysed by NMR, only **2b** was detected.

3.2.3. Preparation of 3-[(trimethylsilyl)methyleno]cyclohexene (2c)

3.2.3.1. Using (methoxydimethylsilyl)(trimethylsilyl)-methane (1a). tert-BuLi in pentane (6.47 ml, 11.0 mmol, 1.7 M) was added to a pentane (20 ml) solution of (methoxydimethylsilyl)(trimethylsilyl)methane (**1a**) (1.94 g, 11.0 mmol). 2-Cyclohexenone (1.00 ml, 10.0 mmol) was added at −78°C. The reaction mixture was an intense yellow prior to hydrolysis. Flash chromatography of the crude product obtained upon aqueous work-up afforded 1.02 g (61%) of **2c** [11]. *E*-isomer: ^{1}H-NMR: $\delta = 0.13$ (s, $SiMe_3$), 1.72 (quintet, 2H), 2.11 (t, 2H), 2.42 (t, 2H), 5.27 (b, 1H), 5.81 (m, 1H), 6.07 (m, 1H). ^{13}C-NMR: $\delta = 0.04(-)$, 22.94(+), 25.23(+), 30.26(+), 125.80(−), 130.30(−), 133.08(−), 151.66(+). *Z*-isomer: ^{1}H-NMR: $\delta = 0.11$ (s, $SiMe_3$), 1.73 (quintet, 2H), 2.08 (t, 2H), 2.37 (t, 2H), 5.21 (b, 1H), 5.90 (m, 1H), 6.34 (m, 1H). ^{13}C-NMR: $\delta = 0.40(-)$, 23.21(+), 25.61(+), 35.43(+), 125.42(−), 128.65(−), 131.53(−), 151.25(+). MS: *m*/*z* (relative intensity) 166(31, P), 151(90), 149(34), 123(40), 121(48), 106(57), 91(42), 73(46), 59(100), 45(59), 43(85). The ratio of *E*/*Z*-isomers was determined from the ratio of the integrations of the proton resonances at 5.21 and 5.27 ppm and found to be 2.0:1. High resolution MS: Anal. Calc. for $C_{10}H_{18}Si$: 166.1178. Found: 166.1176.

3.2.3.2. Using (ethoxydimethylsilyl)(trimethylsilyl)-methane (1b). A similar reaction starting with (ethoxydimethylsilyl)(trimethylsilyl)methane (**1b**), (5.5 mmol) afforded 0.47 g (56%) of **2c** (*E*/*Z* = 2.3:1)

3.2.4. 1-Phenyl-2-trimethylsilylethene (2d)

3.2.4.1. Using (methoxydimethylsilyl)(trimethylsilyl)-methane (1a). tert-BuLi in pentane (3.53 ml, 6.0 mmol,

1.7 M) was added to a solution of (methoxydimethylsilyl)(trimethylsilyl)methane (**1a**) (1.06 g, 6.0 mmol). Benzaldehyde (0.51 ml, 5.0 mmol) was added drop-wise at −78°C. Following aqueous work-up, flash chromatography gave 0.75 g (85%) of **2d** [6a,26]. *E*-isomer: ^{1}H-NMR: $\delta = 0.18$ (s), 6.49 (d), 6.90 (d), 7.17–7.56 (m). ^{13}C-NMR: $\delta = -1.20(-)$, 126.38(−), 127.92(−), 128.49(−), 129.36(−), 138.38(+), 143.70(−). *Z*-isomer: ^{1}H-NMR: $\delta = 0.076$ (s), 5.85 (d), 7.17–7.56 (m). ^{13}C-NMR: $\delta = 0.20(-)$, 127.31(−), 127.88(−), 128.11(−), 132.78(−), 140.14(+), 146.67(−). The ratio of *E*/*Z*-isomers was determined from the ratio of the integrations of the proton resonances at 6.49 and 5.85 ppm and found to be 2.8:1.

*3.2.4.2. Using (ethoxydimethylsilyl)(trimethylsilyl)-methane (**1b**).* An analogous reaction starting with (ethoxydimethylsilyl)(trimethylsilyl)methane (**1b**) (6.0 mmol) gave 0.62 g (71%) of **2d** (*E*/*Z* = 2.4:1).

*3.2.5. Preparation of 1-ethyl-2-trimethylsilyl-1-butene (**2e**)*

tert-BuLi in pentane (3.53 ml, 6.0 mmol, 1.7 M) was added to a pentane (10 ml) solution of (methoxydimethylsilyl)(trimethylsilyl)methane (1.06 g, 6.0 mmol). 3-Pentanone (0.53 ml, 5.0 mmol) was added at −78°C. Following aqueous work-up, flash chromatography gave 0.55 g (70%) of **2e** [11]. ^{13}C-NMR: $\delta =$ 0.38(−), 12.53(−), 13.81(−), 29.13(+), 30.70(+), 120.60(−), 162.99(+). MS, *m*/*z* (relative intensity): 156(9, P), 141(81), 99(33), 73(71), 59(100), 45(44), 43(53). Anal. Calc. for $C_9H_{20}Si$: C, 69.14; H, 12.89. Found: C, 69.40; H, 12.96%.

*3.2.6. Preparation of 1,1-diphenyl-2-trimethylsilylethene, **2f***

tert-BuLi in pentane (3.53 ml, 6.0 mmol, 1.7 M) was added to a pentane (10 ml) solution of (ethoxydimethylsilyl)(trimethylsilyl)methane (1.14 g, 6.0 mmol). Benzophenone (0.91 g, 5.0 mmol), dissolved in diethylether (10 ml), was added from a dropping funnel at −78°C. The green reaction mixture turned reddish-brown overnight, but the color was discharged upon hydrolysis. Flash chromatography of the crude product afforded 1.02 g (81%) of **2f** [8,9]. ^{1}H-NMR: $\delta = 0.08$ (s), 6.48 (s), 7.38–7.47 (m); ^{13}C-NMR: $\delta = 0.03(-)$, 127.20(−), 127.34(−), 127.58(−), 127.87(−), 128.00(−), 129.62(−), 129.70(−), 142.67(+), 143.28(+), 157.22(+).

3.3. Mechanistic studies of the elimination step

3.3.1. Testing for presence of hexamethylcyclotrisiloxane, D_3, in crude product mixtures

Gas chromatograms of the crude products **2a** and **2b**, from experiments in Sections 3.2.2 and 3.2.1, respectively, were obtained under the same conditions as the gas chromatogram of an authentic sample of hexamethylcyclotrisiloxane, D_3. A comparison of the retention times of the various components indicated the absence of D_3 in the crude product mixtures **2a** and **2b**.

3.3.2. Trapping of silanolate with Me_3SiCl

The procedure described in Section 3.2.1.2 for the preparation of **2a** was repeated, using (methoxydimethylsilyl)(trimethylsilyl)methane (**1a**) (1.06 g, 6.0 mmol). Upon warming of the reaction mixture to r.t., instead of adding to NH_4Cl(aq.), freshly distilled Me_3SiCl (0.762 ml, 6.0 mmol) was added. There was no visible indication of reaction in the opaque mixture. When dry THF (3 ml) was added, the mixture clarified and then, almost immediately, formed a white precipitate (LiCl). The volatiles were transferred to another dry vessel under high vacuum ($< 10^{-5}$ Torr) and analyzed by GC–MS. The major component was found to be methoxypentamethylsiloxane [34]; there was no evidence of methoxytrimethylsilane [29]. MS, *m*/*z* (relative intensity): 163(100, M − 15), 133(95), 73(22), 59(29), 45(13).

3.4. Methylenation reactions

All of the terminal alkenes listed in Table 2, **10**–**12**, were previously known. The specific details of our synthetic procedures are described below. ^{13}C-NMR data are described for several of the intermediate β-hydroxysilanes. However, due to their instability, no attempt was made to acquire combustion data for these compounds.

*3.4.1. Preparation of 4-tert-butyl-methylenecyclohexane (**10**)*

The β-hydroxysilanes **7a** and **7b** were first made according to the typical procedure described in Section 3.4.1.1. Several methods were then explored to optimize the conversion **7a** and **7b** to **10**.

*3.4.1.1. Preparation of 1-ethoxydimethylsilylmethyl-4-tert-butyl-cyclohexanol (**7b**); treatment of **7b** with acetic acid–sodium acetate.* To a stirred solution of ethoxytrimethylsilane (1.25 ml, 0.80 mmol) in pentane (10 ml) at −78°C, was added *tert*-BuLi (3.53 ml, 6.0 mmol, 1.7 M in pentane) slowly, via syringe. After stirring for 3 h, the cooling bath was removed and stirring continued for an additional 4 h. The reaction mixture was then re-cooled to −78°C and a solution of 4-*tert*-butyl-cyclohexanone (0.771 g, 5.0 mmol) in pentane (12 ml) was added, drop-wise, from an addition funnel. Stirring was continued while the reaction mixture was allowed to warm up slowly, overnight. The reaction mixture was then added to NH_4Cl (satd., aq., 12 ml); the reaction vessel was rinsed with water (12

ml). After extraction of the combined aqueous portions with pentane (2 × 10 ml), the combined organic portions were dried with $MgSO_4$ (anhyd.) and the solvent removed under reduced pressure to afford **7b**. ^{13}C-NMR of impure alcohol (**7b**): $\delta = 0.1(-)$; 18.3(−); 22.9(+); 27.6(−); 32.2(+); 33.3(+); 41.1(+); 47.8(−); 58.4(+); 71.0(+).

The impure alcohol, **7b**, was mixed with acetic acid (saturated with sodium acetate, 60 ml) and heated to 50°C for 30 min. After cooling, it was carefully poured into $NaHCO_3$ (satd., aq., 40 ml); after the gas evolution had subsided, pentane (25 ml) was added, and the mixture was separated. The pentane layer was washed again with $NaHCO_3$ (satd., aq., 15 ml) and the combined aqueous portions extracted further with pentane (2 × 15 ml). The combined organic extract was dried over $MgSO_4$ (anhyd.) and the solvent was removed under reduced pressure. Flash chromatography (silica gel–pentane) gave 0.49 g of **10** (64%) [35]. ^{13}C-NMR: $\delta = 27.7(-)$; 29.0(+); 32.4(+); 35.4(+); 48.0(−); 106.2(+); 149.9(+).

*3.4.1.2. Preparation of 1-methoxydimethylsilylmethyl-4-tert-butyl-cyclohexanol (**7a**); treatment of **7a** with acetic acid–sodium acetate.* Alcohol **7a** was first made by the procedure described above, using methoxytrimethylsilane (1.10 ml, 8.0 mmol). ^{13}C-NMR of impure alcohol, **7a**: $\delta = -0.1(-)$; 22.9(+); 27.8(−); 32.1(+); 33.0(+); 41.0(+); 47.9(−); 50.2(−); 71.0(+).

Heating with acetic acid (saturated with sodium acetate, 40 ml) at 50°C for 30 min, was followed by aqueous work-up, as described in Section 3.4.1.1, after which, flash chromatography afforded 0.578 g of **10** (76%).

*3.4.1.3. Treatment of **7b** with potassium metal.* The impure alcohol **7b**, made as described in Section 3.4.1.1 from 5.0 mmol of 4-*tert*-butyl-cyclohexanone, was dissolved in THF (10 ml) and potassium metal (0.3 g) added. After stirring for 1 h, the undissolved potassium was removed and the reaction mixture was added to NH_4Cl (satd., aq., 10 ml); the reaction vessel was rinsed with water (10 ml). The combined aqueous portions were extracted with pentane (2 × 5 ml) and dried with $MgSO_4$ (anhyd.). NMR analysis of the product mixture, after removal of the solvents under reduced pressure, revealed that the major product was **10** (estimated yield 65%).

*3.4.1.4. Treatment of **7b** with H_2SO_4.* The alcohol **7b**, made as described above from 5.0 mmol of 4-*tert*-butyl-cyclohexanone, was dissolved in cyclohexane (20 ml). The solution was divided equally into two 50-ml round-bottom flasks containing boiling chips and one drop of H_2SO_4 was added to each flask. One was equipped with a reflux condenser (setup A) and the other with a short-path distillation head (setup B). Each flask was heated, at the same level, to reflux for 30 min. The ethanol–cyclohexane azeotrope (b.p. 64°C) was removed from setup B (approx. 0.09 ml EtOH) followed by cyclohexane (b.p. 81°C). The reaction mixtures were analyzed directly by ^{13}C- and ^{1}H-NMR. The reaction mixture from setup A contained an approximately 60:40 mixture of exocyclic alkene **10** and its endocyclic isomer, 4-*tert*-butyl-1-methylcyclohexene (**13**) [36]. The reaction mixture from setup B contained an approximately 85:15 mixture of **10** to **13**. In each case, there were a large number of smaller resonances between 0 and 4 ppm in the ^{13}C-NMR spectrum, attributed to silicone polymers.

*3.4.2. Preparation of 1,1-diphenylethylene (**11**)*

A pentane solution of **6a** was prepared as described above from 8.0 mmol of methoxytrimethylsilane and 6.0 mmol of *tert*-BuLi. After cooling to −78°C, a solution of benzophenone (0.911 g, 5.0 mmol) in diethylether (12 ml) was added, drop-wise, from a dropping funnel. The reaction mixture turned green, then dark brown; while stirring, it was allowed to warm slowly overnight. NMR analysis of the product, obtained after standard work-up, indicated a near quantitative yield of diphenyl(methoxydimethylsilylmethyl)-carbinol (**8**). ^{13}C-NMR: $\delta = -1.41(-)$; 31.4(+); 50.3(−); 77.6(+); 125.6(−); 126.4(−); 127.9(−); 149.0(+).

Alcohol **8** was then mixed with acetic acid (saturated with sodium acetate, 50 ml) and heated at 45–50°C for 30 min. Flash chromatography (silica gel–pentane) of the crude product obtained after standard work-up afforded 0.82 g (91%) of 1,1-diphenylethylene (**11**) [37]. ^{13}C-NMR: $\delta = 114.2(+)$; 127.7(−); 128.1(−); 128.2(−); 141.4(+); 150.0(+).

*3.4.3. Preparation of 3-methylene-5-α-cholestane (**12**)*

A pentane solution of **6a** was prepared from 3.2 mmol of methoxytrimethylsilane and 2.4 mmol of *tert*-BuLi and cooled to −78°C. 5-α-Cholestan-3-one (0.773 g, 2.0 mmol) was dissolved in 20–25 ml of pentane and added drop-wise via addition funnel. After warming to r.t. overnight, 15 ml of saturated NH_4Cl solution was added with ether to dissolve all solids. The organic layer was separated and washed with 15 ml H_2O. The combined aqueous portions were extracted with ether (3 × 10 ml) and the combined organic portions dried over $MgSO_4$. After removal of the solvent under reduced pressure, the crude alcohol **9** was mixed with 25 ml of acetic acid–sodium acetate and heated at 45–50°C for 30 min. After cooling, the reaction mixture was carefully poured into $NaHCO_3$ (aq., satd., 25 ml). It was extracted with pentane (25 ml). The pentane extract was then washed, first with $NaHCO_3$ (aq., satd., 15 ml), then with water (15 ml). The combined aqueous

portions were then further extracted with pentane (3 × 10 ml). The combined organic portions were dried with $MgSO_4$ (anhyd.) before removal of the solvent under reduced pressure. Subsequent flash chromatography (silica gel–pentane) afforded 0.369 g (48%) of **12** (> 95% pure by NMR) [38]; m.p. 64–65°C (recrystallized from MeOH; lit. m.p. 64–65°C [38]); ^{13}C-NMR: δ = 150.2(+); 105.9(+); 56.5(−); 56.3(−); 54.4(−); 48.1(−); 42.6(+); 40.1(+); 39.9(+); 39.5(+); 38.0(+); 36.2(+); 36.0(+); 35.8(−); 35.5(−); 32.0(+); 31.0(+); 28.9(+); 28.3(+); 28.0(−); 24.2(+); 23.8(+); 22.8(−); 22.5(−); 21.1(+); 18.7(−); 12.1(−); 11.8(−).

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