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Strained organosilacyclic compounds: synthesis of *anti*-Bredt olefins and *trans*-dioxasilacyclooctenes†

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Insertions of silylenes into the allylic carbon–oxygen bond of vinyl epoxides was shown to generate 1,2-silaoxetanes. These intermediates undergo highly diastereoselective additions to aldehydes to form *anti*-Bredt olefins and *trans*-dioxasilacyclooctenes. Additions of electrophiles could be performed selectively on the outside face of these strained *trans*-cycloalkenes to provide valuable functionalized compounds.

Introduction

Silacyclic compounds displaying strain–release Lewis acidity have found a number of applications in the stereoselective construction of carbon–carbon bonds.[1,2] Myers and Denmark pioneered this field by establishing that the rate of the uncatalyzed reaction between an enoxysilacyclobutane and an unactivated aldehyde was dramatically increased when the silicon atom was embedded in a four-membered ring.[3,4] These reactions were proposed to proceed by direct intramolecular silicon group transfer.[4] Oshima and Utimoto later described allylation of carbonyl compounds with allylsilacyclobutanes.[5] Chair-like transition states, bearing the allyl group and the hypervalent silicon atom bound to the carbonyl group, were invoked to rationalize the diastereoselectivities observed. More recently, Leighton reported uncatalyzed intramolecular allylsilylation of aldehydes involving oxasilacyclopentane intermediates.[6–9]

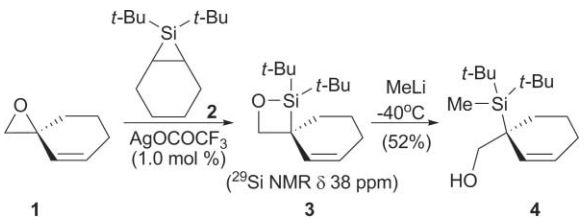
Our laboratory has offered some contributions to the field of strain–release Lewis acidity by developing a diastereoselective metal-catalyzed silylene transfer reaction that can give access to structurally diverse strained silacyclopropanes from alkenes.[10,11] These intermediates display Lewis acidic character at the silicon atom and have found application in the stereoselective construction of carbon–carbon bonds.[12] Silylene transfer under mild conditions was also performed on alkynes,[13] allenes,[14] α,β-unsaturated carbonyl compounds[15] and allylic ethers[16,17] to provide different reactive silacyclic compounds.

In a recent communication,[18] we reported that vinyl 1,2-silaoxetanes, obtained by metal-catalyzed silylene insertions into vinyl epoxides, undergo diastereoselective additions to aldehydes to give functionalized non-racemic *trans*-dioxasilacyclooctenes. These compounds display the same unique properties reported for *trans*-cyclooctene.[19] Like their all–carbon parent medium-ring *trans*-cycloalkenes,[20] *trans*-dioxasilacyclooctenes are configurationally stable at room temperature[19] and can undergo reactions selectively on the outside face of the olefin in the ring.[21] The high π-facial selectivity observed in these reactions allows for efficient transfer of planar chirality to chirality at stereogenic carbon atoms.[21] Reported herein is a full account on the preparation of *trans*-dioxasilacyclooctenes by silylene insertions into vinyl epoxides.

Results and discussion

Synthesis of spiro-1,2-silaoxetane and *anti*-Bredt olefins

In our initial studies, we examined silylene insertion into spiro-epoxide **1**. When **1** was treated with silacyclopropane **2** in the presence of a catalytic amount of silver trifluoroacetate at ambient temperature, we observed the formation of 1,2-silaoxetane **3** by ^{1}H, ^{13}C and ^{29}Si NMR spectroscopic analysis of the reaction mixture (eqn (1)). The ^{29}Si NMR resonance measured at δ 38 ppm for allylic silane **3** was indicative of a silicon atom embedded in a strained ring[22] and comparable to the value reported for Lewis acidic silanes (for allyl silyl triflates, δ 39 ppm[23]). As a point of comparison, unstrained allyl silyl ethers typically display a ^{29}Si NMR shift of δ 15–17 ppm.[24] The formation of allylic silane **4**, after addition of MeLi to the reaction mixture, supported the spectral assignments for **3** (eqn (1)).



(1)

The relative stability of silaoxetane **3** is noteworthy given that 1,2-silaoxetanes are generally too reactive to be observed. Structural information for this class of compounds is therefore limited.[22,25] Support for the formation of 1,2-silaoxetanes mostly rely on the isolation of products from Peterson-like eliminations of these intermediates to provide alkenes and siloxane oligomers.[26–29]

Because strained allylic silanes show enhanced reactivity towards unactivated aldehydes,[5] we explored application of the vinyl spiro-oxetane intermediate for carbon–carbon bond formation. Addition of isobutyraldehyde and benzaldehyde to the reaction mixture, after complete insertion of silylene into spiro-epoxide **1**, led to the formation of alkenes **5** and **6** as single diastereomers

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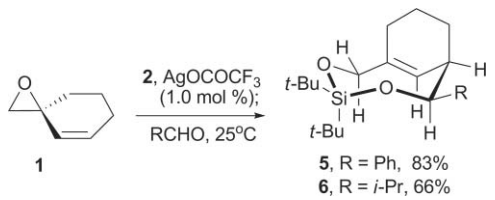
† Electronic supplementary information (ESI) available: NMR spectra and stereochemical proofs for compounds **7**, **8**, **9**, **11b**, **13b**, **23** and **26**. CCDC reference number 766307. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c003227a

(Scheme 1). Because they contain a bridgehead double bond that is the equivalent of having a *trans* double bond in an eight-membered ring, these alkenes are *anti*-Bredt olefins[30] and are related to medium-ring *trans*-cycloalkenes.[19,20,31]



Scheme 1 *anti*-Bredt olefins from vinyl spiro-epoxide.

X-Ray crystallography revealed that *anti*-Bredt alkene **6** adopts a crown conformation with substantial distortion of the bridgehead double bond.[18] The main type of distortion experienced by *anti*-Bredt olefins and *trans*-cycloalkenes is out-of-plane bending,[31,32] which typically translates into pyramidalization and twisting of the strained alkene (depicted separately in Fig. 1). Because both ends of the alkene have different substituents, each sp^2 carbon may experience different distortion angles. An average value for the pyramidalization ($\chi_{av} = \chi_1 + \chi_2$) and twisting ($\tau$) have therefore been defined.[31] The distortion angle determined for *anti*-Bredt olefin **6** ($\chi_{av} = 18.9°$ and $\tau = 20.5°$) closely relate to what is reported for similar bicyclo[5.3.1]undecene systems and, consequently, are indicative of a highly strained ring.[31]

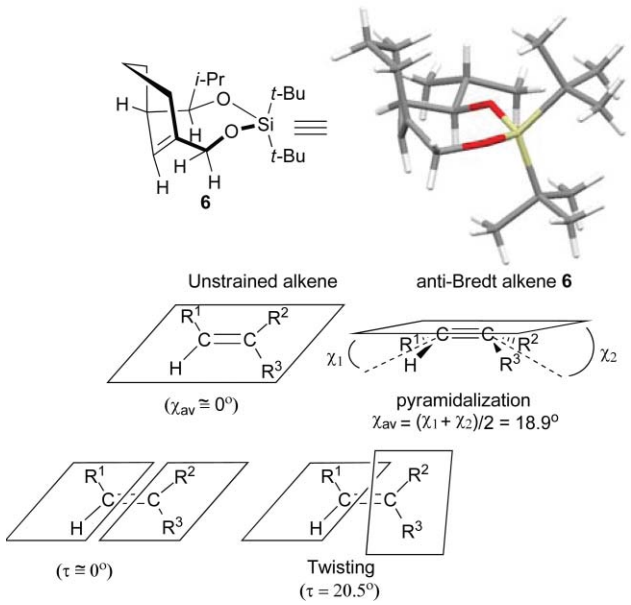


Fig. 1 Pyramidalization and twisting angles determined from X-ray spectroscopic analysis of *anti*-Bredt olefin **6**.

The stereochemical outcome of the addition of spiro-1,2-silaoxetane **3** to aldehydes is consistent with a mechanism involving chair-like six-membered ring transition states **A** and **B** (Fig. 2). In both of these transition states, the silicon atom binds to the aldehyde and forms a trigonal-bipyramidal Si–O(aldehyde) complex with the two bulky *t*-butyl groups in the basal positions. Transition state **A** should be favored over **B** based on the preferential pseudoequatorial position of the R group to avoid

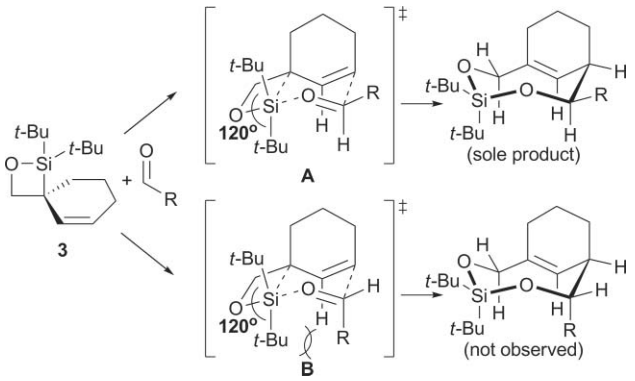
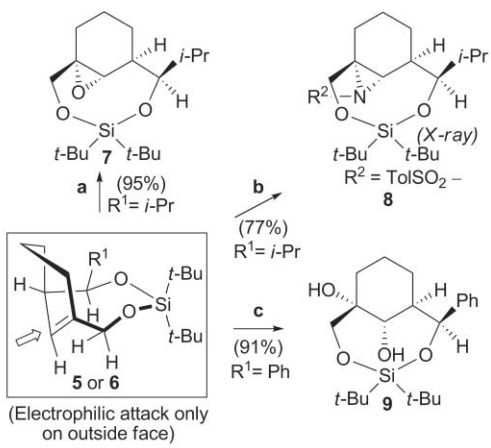


Fig. 2 Proposed transition states for the stereoselective formation of *anti*-Bredt olefins **5** and **6** from spiro-1,2-silaoxetanes.

developing *syn*-pentane interactions with the pseudoaxial *t*-Bu group.

The *anti*-Bredt compounds were oxidized diastereoselectively on the external face of the cyclic double bond with various electrophiles (Scheme 2). Epoxidation with MCPBA and copper(I)-catalyzed aziridination[33] of olefin **6** proceeded smoothly to provide **7** and **8**, respectively, as single diastereomers (Scheme 2). Strained olefin **5** was particularly reactive under osmium tetroxide-catalyzed dihydroxylation conditions (Scheme 2). While acyclic trisubstituted alkenes generally react sluggishly and unselectively with OsO_4,[34–37] catalytic dihydroxylation of alkene **6** reached completion in less than 10 min to give diol **9** as a single diastereomer (Scheme 2). Pyramidalization at the olefinic carbons of cyclic *trans*-alkene could explain why these reactions, where sp^2 carbons undergo rehybridization, are greatly accelerated.[38,39]



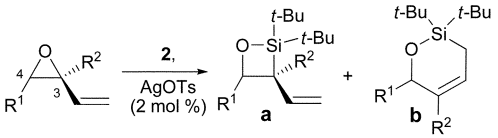
Conditions: (a) MCPBA, $NaHCO_3$, CH_2Cl_2, 5 min. (b) $Cu(CN)_4PF_6$ (5 mol %), $TolSO_2N$=IPh (1.2 equiv), $MeCN/CH_2Cl_2$, 5 min. (c) OsO_4 (5 mol %), acetone/H_2O, *N*-methylmorpholine-*N*-oxide, 10 min.

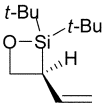
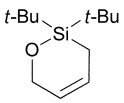
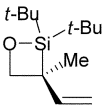
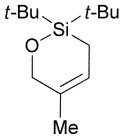
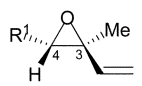
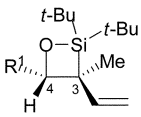
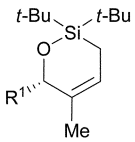
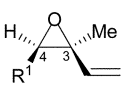
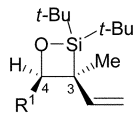
Scheme 2 Stereospecific *syn*-additions to *anti*-Bredt olefins

Synthesis of *trans*-dioxasilacyclooctenes

Acyclic vinyl epoxides also undergo silylene insertion. Treatment of butadiene monoxide **10** and isoprene monoxide **12** with silacyclopropane **2** in the presence of AgOTs gave silaoxetanes **11a** and **13a** in 78% and 63% yield, respectively (entry 1 and 2, Table 1).

Table 1 Silylene transfer to vinyl epoxides



	Epoxides	Product **a**	Product **b**	Yield [a] (**a** : **b**)
1	 **10**	 **11a**	 **11b**	96% **11a** : **11b** (80 : 20)
2	 **12**	 **13a**	 **13b**	93% **13a** : **13b** (68 : 32)
3	 **14**, 3,4-trans R_1= -CH_2CH_2Ph	 **15a**, 3,4-trans	 **15b**	91% **15a** : **15b** (46 : 54)
4	 **16**, 3,4-cis R_1= -CH_2CH_2Ph	 **17a**, 3,4-cis	*not observed*	97% **17a** : **17b** (>95 : 5)

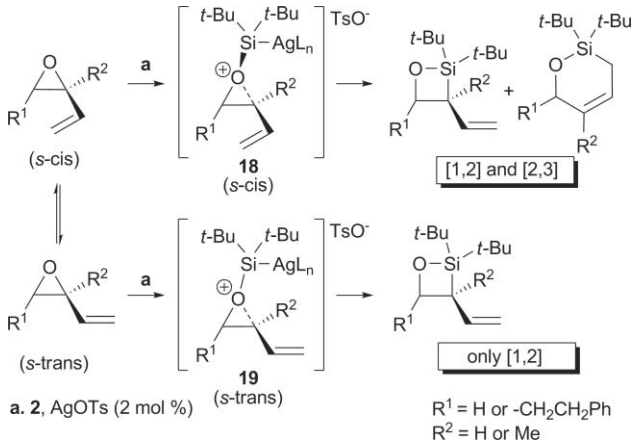
[a] Determined by ^{1}H NMR spectroscopic analysis of the reaction mixtures.

These products were formed along with oxasilacyclohexenes **11b** and **13b**, which we had not observed from spiro-epoxide **1**.

Insertion of silylenes into diastereomeric epoxides then indicated that the stereochemical integrity is preserved at the allylic C–O bond. 3,4-*trans*-Silaoxetane **15a** and 3,4-*cis*-silaoxetane **17a** were observed as single diastereomers from vinyloxiranes **14** and **16**, respectively (Table 1, entry 3 and 4). The oxasilacyclohexene product (**15b**) was only formed from 3,4-*trans*-vinyloxiranes **14** (Table 1, entry 4).

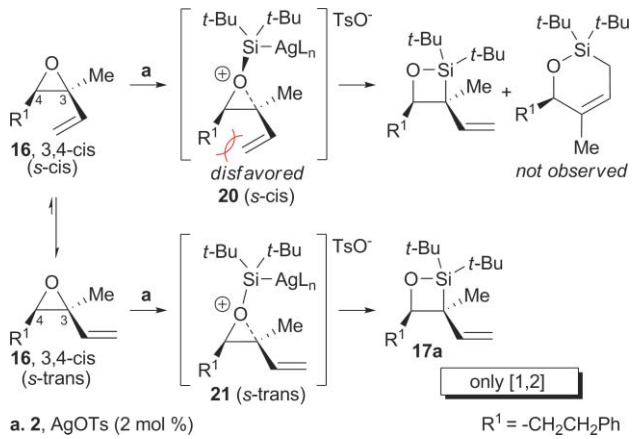
The formation of 1,2-silaoxetanes and oxasilacyclohexenes is rationalized by rearrangements of oxonium ylides,[16–17] which should exist mostly in the *s-cis* and *s-trans* conformations, **18** and **19**, respectively, where the π-bond adopts an orientation perpendicular to the epoxide C–O bond that is cleaving (Scheme 3).[40] Whereas formal [1,2]-rearrangement could proceed from *s-cis* or *s-trans* conformations to generate silaoxetanes products, the formal [2,3]-rearrangement should occur mainly in the *s-cis* conformation to provide cyclic *cis*-alkene products (Scheme 3).

The results presented in Table 1 suggest that the structure of the vinyl oxirane has a significant impact on the product distribution of the silylene insertion. Steric interactions present in the *s-cis* or *s-trans* conformations of the vinyl epoxides could explain the selectivity of the formation of silaoxetane *vs*. oxasilacyclohexene products. Silylene insertion into 3,4-*cis*-vinyl epoxides in the *s-cis*



Scheme 3 Insertions of silylene into vinyl epoxides **10**, **12** and **14**.

conformation are probably disfavored because of significant steric interactions between the vinyl moiety and alkyl R^1 group (**20**, Scheme 4).[40–41] Selective formation of silaoxetane **17a** from 3,4-*cis* epoxides **14** would therefore proceed favorably in the *s-trans* conformation to give selectively [1,2]-rearranged products (entry 4, Table 1 and Scheme 4). Conversely, lower selectivity for the formation of silaoxetane **13a** relative to formation of **11a** could be the result of destabilizing interactions between the methyl group and the vinyl moiety in *s-trans* intermediate **19** (Scheme 3). A higher proportion of products would therefore be formed through the less selective reaction path, involving intermediate **18**, when performing silylene insertions into **12** (Scheme 3).

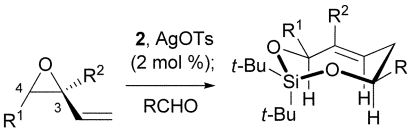


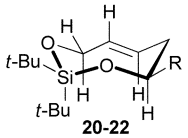
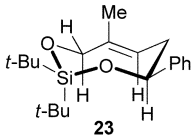
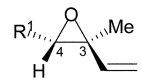
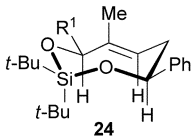
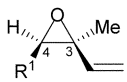
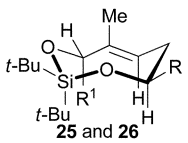
Scheme 4 Insertions of silylene into vinyl epoxide **16**.

After studying the insertions of silylenes into acyclic vinyl oxiranes, we examined allylation of aldehydes with the acyclic vinyl silaoxetanes obtained. *In situ* additions of benzaldehyde, isobutyraldehyde and isopropyl glyoxalate to **11a** led to the formation of the corresponding *trans*-dioxasilacyclooctenes **20–22** (Table 2, entry 1). Insertions of silylenes into vinyl epoxides **12**, **14** and **16** and subsequent allylation also provided dioxasilacyclooctenes **23–26** as single diastereomers (Table 2, entries 2–4).

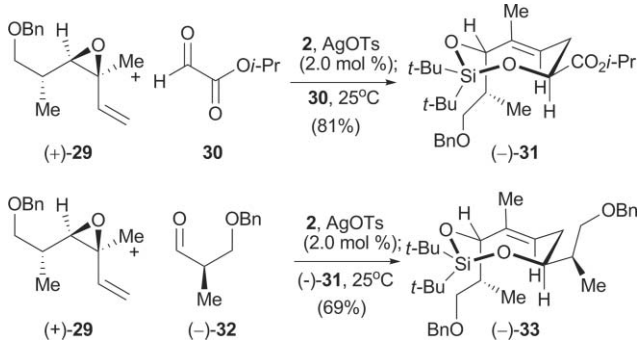
The scope of this silylene insertion and allylation sequence was further established with enantiomerically enriched vinyl epoxide (+)-**29**. Additions of aldehyde **30** and (–)-**32** to the reaction mixtures provided selectively the non-racemic *trans*-cycloalkenes (–)-**31** and (–)-**33** (Scheme 5).

Table 2 Silylene transfer into vinyl epoxides and allylation of aldehydes



Entry	Epoxides	*trans*-dioxasilacyclooctenes [a]	Yields
1	 **10**	 **20-22**	71% (**20**, R = Ph) 72% (**21**, R = *i*-Pr) 71% (**22**, R = -CO_2*i*-Pr)
2	 **12**	 **23**	62% [b]
3	 **14**, 3,4-trans	 **24** R_1= -CH_2CH_2Ph	39% [c]
4	 **16**, 3,4-cis	 **25** and **26** R_1= -CH_2CH_2Ph	71% (**25**, R = Ph) 80% (**26**, R = -CO_2*i*-Pr)

[a] The products were all obtained as one diastereomer. [b] Isolated along with 24% of **13b**. [c] Isolated along with 42% of **15b**.



Scheme 5 Formation of non-racemic *trans*-dioxasilacyclooctenes.

Six-membered transition states **C** and **D** are proposed to explain the diastereoselectivity obtained for addition of 1,2-silaoxetanes to aldehydes (Fig. 3). Binding the aldehyde to the silicon atom would give hypervalent complexes **27** and **28** with trigonal-bipyramidal geometry.[5] These complex would then collapse to the products through chair-like transition states. *trans*-Dioxasilacyclooctene would be formed selectively because of the preferential pseudo-equatorial position of the –CH_2– group of the silaoxetane ring in transition state **C**.[42] This transition state should also be favored by having two *t*-Bu groups in the basal position of the trigonal

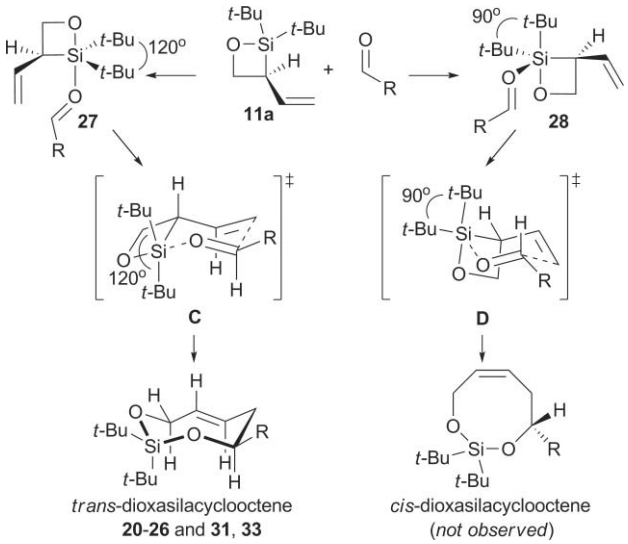
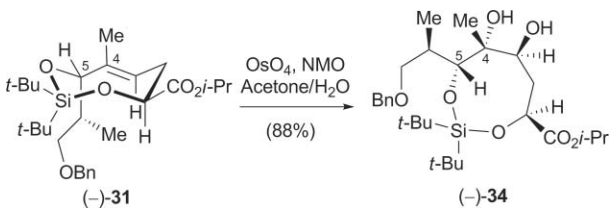


Fig. 3 Proposed transition states for *trans*-cycloalkenes.

bipyramidal complex to avoid the severe steric interaction between these two bulky groups in **D**, where one *t*-Bu occupies the apical position of the trigonal-bipyramidal complex (Fig. 3).

trans-Dioxasilacyclooctene (–)-**31** was dihydroxylated under osmium-tetroxide catalyzed conditions in the presence of *N*-methylmorpholine-*N*-oxide (NMO) to give (–)-**34** as the sole diastereomer (eqn (2)). This reaction represents an example of the efficient dihydroxylation of a trisubstituted alkene bearing an electron withdrawing group at the allylic position.[34–37] Moreover, the 4,5-*syn* stereochemical outcome of the dihydroxylation of **31** is complementary to substrate-controlled dihydroxylation of comparable acyclic systems, which provide diols with *anti* stereochemistry.[34–37]



(2)

Conclusions

anti-Bredt olefins and *trans*-dioxasilacyclooctenes can be prepared with complete diastereocontrol by insertions of silylenes into vinyl epoxides and subsequent additions to aldehydes. Efficient and highly diastereoselective transformations could be performed exclusively on the external face of the *trans*-alkene.

Experimental

General

^{1}H NMR, ^{13}C and ^{29}Si NMR spectra were recorded at room temperature using Bruker DRX 400 or DRX 500 spectrometers, as indicated. The data are reported as follows: chemical shift in ppm referenced to residual solvent (^{1}H NMR: C_6D_6, δ 7.16; d_8-toluene, δ 7.00; $CDCl_3$, δ 7.24. ^{13}C NMR: C_6D_6, δ 128.39; d_8-toluene, δ 137.86; $CDCl_3$, δ 77.23. ^{29}Si NMR: referenced to internal

tetramethylsilane δ 0.0), multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, sept = septuplet, m = multiplet), coupling constants (Hz), and integration. High resolution mass spectra were acquired on a VG analytical 7070E or Fisons Autospec spectrometer, and were obtained by peak matching. Microanalyses were performed by Atlantic Microlabs, Norcross, GA. Analytical thin layer chromatography was performed on EM reagents 0.25 mm silica gel 60-F plates. Liquid chromatography was performed using forced flow (flash chromatography) of the indicated solvent system on EM reagents silica gel (SiO_2) 60 (230–400). Optical rotations were calculated using the formula: $\alpha_D = 1000\alpha_{obs}/cl$, where c = (mg of substrate/mL of solvent) and l = 1 dm. Silacyclopropanes were stored and manipulated in an Innovative Technologies nitrogen or argon atmosphere dry box. All reactions were performed under an atmosphere of nitrogen in glassware that had been flame-dried under a stream of nitrogen or under vacuum. Solvents were distilled or filtered through alumina before use. Cyclohexene silacyclopropane was constructed by known methods.[12,43]

Characterization data and stereochemical proofs for compounds **3–6**, **11a**, **15a**, **15b**, **17a**, **20–22**, **24**, **25** and **31–34** have been previously reported.[18]

Preparation of compounds 7, 8, 9, 11b, 13a, 13b, 23, 26

Representative procedure for insertions of silylenes into vinyl epoxides (silaoxetane 13a and silacyclohexene 13b). To a cooled (–20 °C) solution of vinyl epoxide **12** (0.020 g, 0.24 mmol) and $PhSiMe_3$ (0.0378 M, internal standard) in d_6-benzene–THF (1 : 1, 2.4 mL) was added silacyclopropane **2** (0.069 g, 0.31 mmol) and AgOTs (0.0013 g, 0.0051 mmol). The reaction mixture was allowed to warm to ambient temperature over 2 h and then placed in a J. Young NMR tube to be analyzed by ^{1}H NMR spectroscopy (d_1 relaxation time was set to 20 s). Silaoxetane **13a** and oxasilacyclohexene **13b** were formed in 63% and 30% yields, respectively, based on comparison of the area of the standard $PhMe_3Si$ peak at δ 0.15 ppm and the area of the *t*-Bu and alkene peaks of the product. Characteristic NMR resonance for silaoxetane **13a**: ^{1}H NMR (400 MHz, C_6D_6) δ 6.34 (dd, J = 17.4, 10.7 Hz, 1H, $CCH{=}CH_2$), 4.78 (dd, J = 10.7, 1.2 Hz, 1H, $CH{=}CH_2$), 4.70 (dd, J = 17.4, 1.2 Hz, 1H, $CH{=}CH_2$), 4.36 (d, J = 7.6 Hz, 1H, OCHHC), 4.01 (d, J = 7.6 Hz, 1H, OCHHC), 1.40 (s, 3H, Me), 1.07 (s, 9H, Me_3C), 1.06 (s, 9H, Me_3C); ^{13}C NMR (126 MHz, C_6D_6) δ 147.0, 109.6, 80.0, 28.9, 28.5. The reaction mixture was concentrated *in vacuo* and the resulting residue was purified by flash chromatography (hexanes) to afford oxasilacyclohexene **13b** (0.0145 g, 27%) as a clear oil: ^{1}H NMR (400 MHz, C_6D_6) δ 5.58 (ddd, J = 6.4, 3.2, 1.6 Hz, 1H, CH=C), 4.27 (m, 2H, OCH_2C), 1.35 (m, 3H, Me), 1.18 (m, 2H, $SiCH_2CH$), 1.06 (s, 18H, 2 × Me_3C); ^{13}C NMR (101 MHz, C_6D_6) δ 135.0, 119.5, 67.7, 27.7, 20.8, 20.5, 5.4.; IR (thin film) 3111, 3073, 2858, 1458, 1265, 1100 cm^{-1}; HRMS (CI) m/z calc. for $C_{13}H_{27}OSi$ $(M + H)^+$ 227.1831, found 227.1834.

Representative procedure for the preparation of *trans*-dioxasilacyclooctenes from vinyl epoxides (*trans*-dioxasilacyclooctene 23). To a cooled (–20 °C) solution of vinyl epoxide 12 (0.0201 g, 0.238 mmol) in benzene–THF (1 : 1, 2.0 mL) was added silacyclopropane 2 (0.0694 g, 0.309 mmol) and AgOTs (0.0013 g, 0.0048 mmol) under a nitrogen atmosphere. The reaction mixture was allowed to warm to ambient temperature over 1 h before addition of freshly distilled benzaldehyde (0.0266 mL, 0.262 mmol). After stirring for 1 h, the resulting solution was concentrated *in vacuo*. ^{1}H NMR spectroscopic analysis of the unpurified product indicated that 23 was formed as a single diastereoisomer. The resulting oil was purified by flash chromatography (3 : 97 Et_3N–hexanes) to afford **23** as a thick oil (0.0489 g, 62%): ^{1}H NMR (400 MHz, C_6D_6) δ 7.33 (d, J = 7.2 Hz, 2H, Ph), 7.21 (t, J = 7.6 Hz, 2H, Ph), 7.09 (t, J = 7.4 Hz, 1H, Ph), 5.72 (ddq, J = 12.3, 3.4, 1.6 Hz, 1H, CH=C), 5.00 (dd, J = 10.5, 3.6 Hz, 1H, $OCHPhCH_2$), 4.42 (d, J = 9.4 Hz, 1H, OCHHC), 4.14 (d, J = 9.4 Hz, 1H, OCHHC), 2.40 (td, J = 12.2, 10.6 Hz, 1H, $CHCH_2CH$), 2.21 (dt, J = 12.1, 3.6 Hz, 1H, $CHCH_2CH$), 1.83 (d, J = 1.6 Hz, 3H, Me), 1.20 (s, 9H, Me_3C), 1.10 (s, 9H, Me_3C); ^{13}C NMR (126 MHz, C_6D_6) δ 145.7, 145.1, 129.7, 129.0, 127.7, 125.6, 80.4, 73.6, 41.1, 29.8, 28.9, 23.0, 21.9, 18.0; IR (thin film) 3062, 3027, 2933, 2858, 1473, 1084, 1045 cm^{-1}; HRMS (CI) m/z calc. for $C_{20}H_{33}O_2Si$ $(M + H)^{++}$ 333.2250, found 333.2252. Anal. Calc. for $C_{20}H_{32}O_2Si$: C, 72.23; H, 9.70. Found: C, 71.94; H, 9.70%.

Epoxide 7. To a cooled (0 °C) solution of *anti*-Bredt olefin **6** (0.050 g, 0.15 mmol) in CH_2Cl_2 (1.5 mL) was added $NaHCO_3$ (0.052 g, 0.62 mmol) and *m*-CPBA (0.053, 0.91 mmol). The reaction mixture was allowed to warm to ambient temperature over 10 min before addition of saturated $Na_2S_2O_3$ solution (2 mL). After stirring for 20 min, the layers were separated and aqueous layer was extracted with CH_2Cl_2 (3 × 3 mL). The combined organic layers were concentrated *in vacuo*. ^{1}H NMR spectroscopic analysis of the unpurified product indicated formation of **7** as a single diastereomer. The resulting oil was purified by flash chromatography (10 : 90 EtOAc–hexanes) to afford **7** as a white solid (0.050 g, 95%): mp = 108 °C; ^{1}H NMR (400 MHz, C_6D_6) δ 4.10 (d, J = 9.9 Hz, 1H, $SiOCH_2C$), 3.61 (dd, J = 9.6, 2.8 Hz, 1H, OCH(*i*-Pr)CH), 3.59 (d, J = 9.9 Hz, 1H, SiOCHHC), 3.04 (s, 1H, OCHCH), 2.11–2.02 (m, 2H, OCHCHCOSi and $CH_2CH_2CH_2CH$), 1.88 (dt, J = 14.5, 6.0 Hz, 1H, $CH_2CH_2CH_2CH$), 1.59 (ddt, J = 13.3, 9.6, 6.6 Hz, 1H, $CHMe_2$), 1.46–1.37 (m, 2H, $CH_2CH_2CH_2CH$), 1.36–1.24 (m, 2H, $CH_2CH_2CH_2CH$), 1.17 (d, J = 2.6 Hz, 9H, Me_3C), 1.04 (s, 9H, Me_3C), 1.02 (d, J = 6.6 Hz, 3H, $CHMe_2$), 0.59 (d, J = 6.7 Hz, 3H, $CHMe_2$); ^{13}C NMR (101 MHz, C_6D_6) δ 84.3, 73.6, 62.9, 57.9, 33.2, 32.6, 30.2, 29.2, 26.6, 24.0, 22.1, 21.3, 19.1, 18.9, 17.3; IR (thin film) 2937, 2859, 1473, 1115, 827 cm^{-1}; HRMS (ESI) m/z calc. for $C_{19}H_{36}NaO_3Si$ $(M + Na)^+$ 363.2332, found 363.2328. Anal. Calc. for $C_{19}H_{36}O_3Si$: C, 67.01; H, 10.65. Found: C, 67.07; H, 10.77%.

Aziridine 8. To a solution of *anti*-Bredt olefin **6** (0.065 g, 0.21 mmol) in MeCN (1.0 mL) was added $TolSO_2N{=}IPh$[44] (0.077 g, 0.24 mmol) and $Cu(CN)_4PF_6$ (0.0037 g, 0.010 mmol). The reaction mixture was stirred for 5 min before being concentrated *in vacuo*. ^{1}H NMR spectroscopic analysis of the unpurified product indicated formation of **8** as a single diastereomer. The resulting oil was purified by flash chromatography (10 : 90 EtOAc–hexanes) to afford **8** as a white solid (0.079 g, 77%): mp 174 °C (from AcOEt–hexanes); ^{1}H NMR (400 MHz, C_6D_6) δ 7.95 (d, J = 8.2 Hz, 2H, MeC_6H_4S), 6.75 (d, J = 8.0 Hz, 2H, MeC_6H_4S), 4.98 (d, J = 10.7 Hz, 1H, SiOCHH), 4.30 (d, J = 10.7 Hz, 1H, SiOCHH), 3.73 (dd, J = 9.5, 2.1 Hz, 1H, $SiOCHMe_2$), 3.56 (s, 1H, NCHCH), 2.06 (m, 2H), 1.92 (dt, J = 14.2, 4.7 Hz, 1H), 1.83 (s, 3H, MeC_6H_4S), 1.46 (m, 2H), 1.32 (m, 2H), 1.24 (s, 9H, Me_3C), 1.15 (s, 9H, Me_3C),

1.14 (m, 1H), 0.98 (d, $J = 6.5$ Hz, 3H, CHMe_2), 0.45 (d, $J = 6.7$ Hz, 3H, CHMe_2);^{13}C NMR (126 MHz, C_6D_6) δ 143.9, 139.5, 130.0, 127.9, 85.4, 68.2, 52.3, 51.3, 32.6, 32.1, 30.3, 29.1, 27.2, 23.9, 22.1, 21.5, 21.1, 18.7, 18.5, 17.3; IR (thin film) 2947, 2859, 1475, 1319, 1115 cm^{-1}; HRMS (ESI) m/z calc. for $C_{26}H_{43}NaNO_4SSi$ (M + Na)$^+$ 516.2580, found 516.2587.

Diol 9. To a cooled (0 °C) solution of *anti*-Bredt olefin **5** (0.0480 g, 0.134 mmol) in acetone–H_2O (10 : 1, 1.3 mL) was added *N*-methylmorpholine-*N*-oxide (0.047 g, 0.40 mmol) and a solution of osmium tetroxide in *tert*-butanol (0.084 mL, 2.5 wt%, 0.0067 mmol). The reaction mixture was allowed to warm to ambient temperature over 10 min before addition of saturated $Na_2S_2O_3$ solution (2 mL). After stirring for 20 min, the layers were separated and the aqueous layer was extracted with AcOEt (3 × 3 mL). The combined organic layers were washed with brine (10 mL), dried over $NaSO_4$, and concentrated *in vacuo*. ^{1}H NMR spectroscopic analysis of the unpurified product indicated formation of **9** as a single diastereomer. The resulting oil was purified by flash chromatography (30 : 70 EtOAc–hexanes) to afford **9** as a white solid (0.048 g, 91%): mp = 144 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, $J =$ 7.6 Hz, 2H, Ph), 7.39 (t, $J = 7.6$ Hz, 2H, Ph), 7.29 (t, $J = 7.3$ Hz, 1H, Ph), 5.54 (s, 1H, OC*H*Ph), 4.35 (s, 1H, HOCC*H*), 4.32 (d, $J =$ 12.7 Hz, 1H, SiOCH_2), 3.77 (d, $J = 12.7$ Hz, 1H, SiOCH_2), 2.52 (br s, 1H, OH), 2.35 (m, 1H), 1.76 (m, 2H), 1.59 (m, 1H), 1.44 (m, 1H), 1.31 (m, 2H), 1.21 (s, 9H, Me_3C), 1.16 (s, 9H, Me_3C), 1.08 (m, 1H);^{13}C NMR (101 MHz, C_6D_6) δ 143.1, 128.2, 126.9, 125.5, 78.4, 75.8, 74.3, 70.6, 49.1, 29.3, 28.8, 27.9, 22.0, 21.1, 18.7, 16.9; IR (thin film) 3412, 2935, 2860, 1475, 1124 cm^{-1}; HRMS (ESI) m/z calc. for $C_{22}H_{36}NaO_4Si$ (M + Na)$^+$ 415.2281, found 415.2285. Anal. Calc. for $C_{22}H_{36}O_4Si$: C, 67.30; H, 9.24. Found: C, 67.33; H, 9.43%.

Oxasilacyclohexene 11b. The representative procedure for insertion of silylenes into vinyl epoxides was followed using vinyl epoxide **10** (0.011 g, 0.15 mmol), silacyclopropane **2** (0.044 g, 0.196 mmol) and AgOTs (0.0008 g, 0.003 mmol) in benzene–THF (1 : 1, 1.0 mL). The reaction mixture was concentrated *in vacuo* and the resulting residue was purified by flash chromatography (hexanes 100%) to afford oxasilacyclohexene **11b** (0.0049 g, 15%) as a clear volatile oil: ^{1}H NMR (400 MHz, C_6D_6) δ 5.81 (m, 1H, OCH_2C*H*=CH), 5.38 (d, $J = 10.4$ Hz, 1H, OCH_2CH=C*H*), 4.36 (s, 2H, OCH_2), 1.13 (m, 2H, SiCH_2), 1.05 (s, 18H, 2 × Me_3C); ^{13}C NMR (126 MHz, C_6D_6) δ 129.6, 124.5, 64.3, 27.6, 21.1, 5.4; ^{29}Si NMR (99.3 MHz, C_6D_6) δ 6.2; IR (thin film) 3024, 2931, 2858, 1469, 1178, 825 cm^{-1}; HRMS (CI) m/z calc. for $C_{12}H_{25}OSi$ (M + H)$^+$ 213.1675, found 213.1673.

***trans*-Dioxasilacyclooctene 26.** The representative procedure for the formation of *trans*-dioxasilacycloctenes was followed using vinyl epoxide **16** (0.070 g, 0.37 mmol), silacyclopropane **2** (0.13 g, 0.56 mmol), AgOTs (0.002 g, 0.007 mmol) and isopropyl 2-oxoacetate[45] solution in benzene (0.52 mL, 0.095 g, 0.82 mmol) in toluene–THF (1 : 1, 2.7 mL). ^{1}H NMR spectroscopic analysis of the unpurified product indicated formation of **26** as a single diastereoisomer. The resulting oil was purified by flash chromatography (3 : 97 Et_3N–hexanes) to afford **26** as colorless oil (0.133 g, 80%): ^{1}H NMR (400 MHz, C_6D_6) δ 7.19 (m, 4H, Ph), 7.09 (m, 1H, Ph), 5.58 (ddq, $J = 12.3$, 3.6, 1.7 Hz, 1H, CH=C), 5.03 (sept, $J = 6.2$ Hz, 1H, OC*H*Me_2), 4.53 (dd, $J = 9.8$, 4.9 Hz, 1H, SiOC*H*(CO_2i-Pr)), 4.10 (dd, $J = 8.3$, 5.9 Hz, 1H, SiOC*H*CMe=C), 2.61 (m, 4H, CH_2CH_2Ph and CMe=CHCH_2CH), 2.17 (m, 1H, CH_2CH_2Ph), 1.90 (m, 1H, CH_2CH_2Ph), 1.69 (dd, $J = 1.6$, 0.8 Hz, 3H, CHC*Me*=CH), 1.20 (s, 9H, Me_3C), 1.11 (s, 9H, Me_3C), 1.05 (d, $J = 6.3$ Hz, 6H, OCHMe_2);^{13}C NMR (126 MHz, C_6D_6) δ 171.1, 149.7, 142.7, 129.2, 129.1, 126.6, 124.9, 78.9, 75.1, 68.3, 37.9, 34.2, 33.2, 29.3, 29.1, 29.0, 28.7, 22.1, 21.8, 19.9; IR (thin film) 3027, 2969, 2935, 1755, 1729, 1105 cm^{-1}; HRMS (CI) m/z calc. for $C_{26}H_{42}NaO_4Si$ (M + Na)$^+$ 469.2750, found 469.2753.

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