Chemistry of Enoxysilacyclobutanes: Highly Selective Uncatalyzed Aldol Additions

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*Received December 16, 1993. Revised Manuscript Received April 25, 1994**

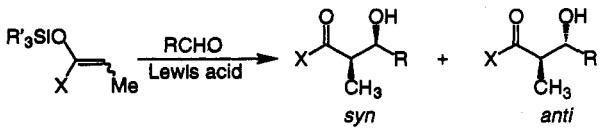
Abstract: *O*-(Silacyclobutyl) ketene acetals derived from esters, thiol esters, and amides underwent facile aldol addition with a variety of aldehydes at room temperature without the need for catalysts. The uncatalyzed aldol addition reaction of *O*-(silacyclobutyl) ketene acetals displayed the following characteristics: (1) the rate of reaction was highly dependent on the spectator substituent on silicon and the geometry of the ketene acetal, (2) the *O,O*-ketene acetal of *E* configuration afforded the *syn* aldol products with high diastereoselectivity (93/7 to 99/1), (3) conjugated aldehydes reacted more rapidly than aliphatic aldehydes, and (4) the reaction was mildly sensitive to solvent. In addition, the aldol reaction was found to be efficiently catalyzed by metal alkoxides. Labeling experiments revealed that the thermal aldol reaction proceeds by *direct intramolecular silicon group transfer*, while the alkoxide-catalyzed version probably proceeds via *in situ* generated metal enolates. Computational modeling of the transition states suggests that the boat transition structures are preferred, supporting the observed *syn* selectivity of the thermal aldol reaction. Both thermal and alkoxide-catalyzed Michael additions were investigated, revealing a competition between 1,2- and 1,4-addition favoring the former.

Introduction

The directed aldol reaction has emerged as one of the most powerful and selective methods for the construction of carbon–carbon bonds.[1] Of the myriad of variants on this basic theme, the Mukaiyama crossed aldol reaction (Scheme 1) is one which has been extensively utilized and developed.[2] This now-familiar transformation involves the reaction of enoxysilanes derived from ketones, acids, esters, thiol esters, amides, and thiol amides with aldehydes usually in the presence of a stoichiometric or catalytic amount of an activator. By far, the most common activators for this process are Lewis acids. Much of the motivation for the development of new Lewis acid catalysts derives from the successful demonstration of asymmetric catalysis by the use of chiral Lewis acids.[3] In addition, it has been demonstrated that the Mukaiyama aldol addition reaction is promoted by fluoride ion,[4] trityl salts,[5] high pressure,[6] water,[7] and elevated temperature.[8]

Despite the synthetic ease and utility of the Mukaiyama aldol addition reaction, it does not share the substrate generality and stereochemical complementarity of its enoxyborane counterpart.[1] Extensive studies have shown that the level of simple diastereoselection is dependent upon the substituents and reaction conditions.[9]

Scheme 1



The mechanistic basis for these types of addition reactions has not yet been firmly established.[10] However, apart from a limited number of exceptions, the stereochemical observations have been rationalized by an acyclic transition state with no interaction (either direct or mediated by a Lewis acid) between the enoxysilane and aldehyde.[11] In this formulation, the overriding stereocontrol feature is the avoidance of nonbonded interactions between the substituents on the reactive sp^2 carbons. One of the important exceptions to this general behavior is the addition of *O*-silyl *N,O*-ketene acetals with aldehydes reported by Myers.[12] Reaction of the siloxane derived from (*S*)-prolinol propanamide with aldehydes afforded nine-membered ring, silicon-bridged *anti* aldol products with high diastereoselectivity. It was proposed that the reaction proceeds in the absence of an external catalyst via a cyclic transition state involving a trigonal bipyramidal silicon.

* Abstract published in *Advance ACS Abstracts*, June 1, 1994.

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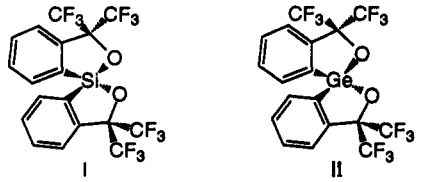
Chart 1



I II

The silicon-based, Lewis acid-promoted aldol reaction is mechanistically distinct from the aldol reactions of enoxyboranes and titanates wherein the metal atom serves the critical role as organizational node for nucleophile, electrophile, and (in some cases) chiral adjuvants. While the metal-centered reactions are of unquestionable power and utility, it is difficult to imagine how they could be rendered catalytic. We were intrigued by the possibility of developing a thermal aldol reaction that used the silicon atom as an organizational node and also was susceptible to nucleophilic catalysis. Since this implicates a pentacoordinate (and ultimately hexacoordinate) silicon,[13] we chose to assay the potential of "strain release Lewis acidity"[14] to promote reaction via this pathway.

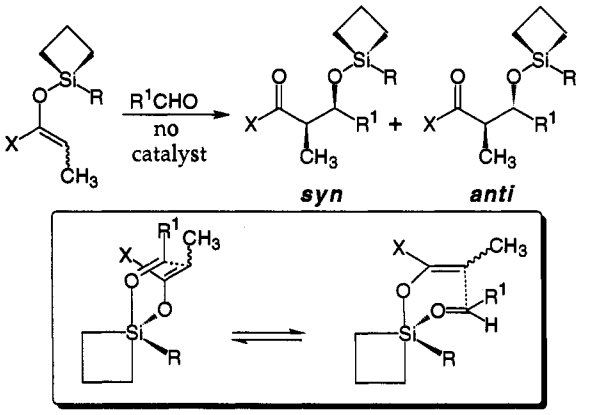
The concept of strain release Lewis acidity was enunciated by Martin[15] to explain the observed electrophilicity of the silicon in the spirosilane i (Chart 1). The electrophilicity of the silicon is a consequence of the release of strain which accompanies coordination by a Lewis base. We rationalized that if the C–M–O angle were decreased even closer to the optimal angle between the apical and basal positions in a trigonal pyramid, then the Lewis acidic properties would increase. This hypothesis was demonstrated by the preparation of the complex ii containing germanium; the longer Ge–O bonds decrease the endocyclic C–Ge–O angle to 91.4°. The structure of a 5-Ge-10 *n*-butyl ate complex exhibited the expected trigonal bipyramidal geometry by X-ray crystallography wherein the O-Ge–O angle expanded to 173.8°.

The effect of angle strain on the chemistry of organosilanes has already been well documented in the classic studies of stereochemistry and mechanism of nucleophilic substitution at silicon.[16,17] Under normal circumstances, organosilanes undergo invertive substitution. However, if the silicon is incorporated in a strained ring (four or five membered), the reaction usually proceeds with retention of configuration.[18] This dichotomy has been explained by the formation of a stable pentacoordinate siliconate intermediate which undergoes a pseudorotation mechanism resulting in a net retention of configuration. These observations suggested the notion that enoxysilacyclobutanes might react with aldehydes by silicon group transfer via trigonal bipyramidal (tbp) intermediates.

The potential for silicon to act as an organizational node derives from the ability to expand its coordination number to form penta- and hexacoordinate compounds.[19] Hypervalent silicon intermediates of this type have been proposed in the allylation of carbonyl compounds.[13] It is proposed that a pentacoordinate allylsiliconate is formed which subsequently undergoes reaction via a six-membered, cyclic transition state involving hexacoordinate silicon. Hypervalent silicon species have also been proposed as intermediates in the reaction of *O*-silyl *N,O*-ketene acetals with aldehydes.[12]

In addition to investigating the potential of enoxysilacyclobutanes in uncatalyzed aldol reactions we proposed a novel aldol addition on the principle of "ligand-accelerated catalysis".[20] This concept comprises an amalgamation of the strain release Lewis acidity in silacyclobutanes with the demonstration of nucleophilic catalysis of substitution at silicon.[21] The crucial event is an asymmetric, catalytically activated transfer of an achiral silyl group. The advantage of this strategy over the asymmetric aldol addition using chiral boron enolates is the ability to use substoichiometric amounts of the chiral activator. The advantage over the classic Mukaiyama aldol addition with chiral Lewis acids is the high degree of organization of the transition structure and attendant diastereoselectivity.

Scheme 2



Thus, the essence of our proposal, formulated in Scheme 2, was to evaluate the ability of a silicon atom, constrained in a four-membered ring and attached to an enolate oxygen, to behave like a coordinatively unsaturated group III element. In other words, is the strain imparted by compressing the tetrahedral silicon atom valencies into a four-membered ring sufficient to promote the coordination of a Lewis basic aldehyde oxygen, thus allowing rehybridization to trigonal bipyramidal silicon accommodating the acute C–Si–C angle of the silacyclobutane? If so, would the siliconate complex be sufficiently reactive to promote the aldol addition reaction, having brought the aldehyde and enoxysilane α-carbons within bonding proximity?

In our preliminary communication, we reported the successful realization of this concept in the uncatalyzed, room temperature aldol addition reaction of *O*-(silacyclobutyl) ketene acetals, ketene thioacetals, and ketene aminals with aldehydes.[22] Independently, Myers et al. also reported dramatic rate accelerations in the *anti* aldol addition reaction of proline-derived *N,O*-ketene silyl acetals. These workers noted rate increases in reactions with benzaldehyde of 10-fold for silacyclopentane and *ca.* 10^6 for silacyclobutane compared to dimethylsilyl derivatives.[23] In this account, we disclose in full our studies on (1) the effect of the spectator ligand on silicon on the rate of reaction, (2) the effect of *O*-(silacyclobutyl) ketene acetal geometry on the rate and selectivity of the reaction, (3) the origin of the diastereoselectivity, (4) asymmetric nucleophilic catalysis, (5) Michael addition reactions, and (6) general Lewis acidity of silacyclobutanes.

Results

Preparation of Precursors. A significant number of substituted silacyclobutanes are known, and the general procedures established for their preparation were followed.[24] The compounds required for this investigation were prepared by either a ring closure reaction or a substitution reaction with the appropriate

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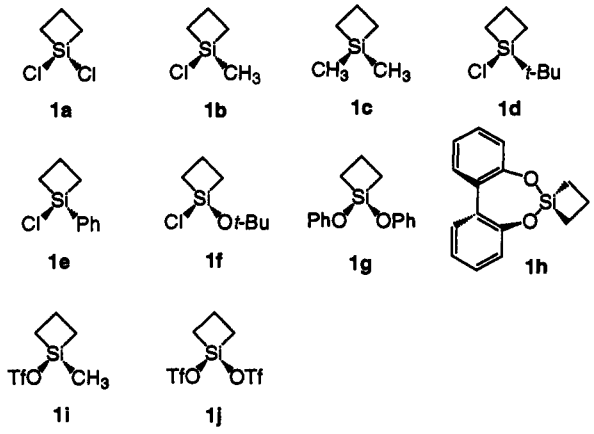
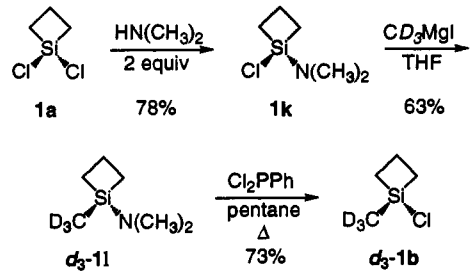
Chart 2



Scheme 3



reagent on a preformed silacyclobutane. 1,1-Dichlorosilacyclobutane (**1a**) (Chart 2) and 1-chloro-1-methylsilacyclobutane (**1b**) were easily synthesized via Wurtz-type coupling of (3-chloropropyl)trichlorosilane and (3-chloropropyl)methyldichlorosilane, respectively.[25]

Preparation of the derivatives **1c**, **1d**, and **1e** followed directly from the literature procedures by addition of organometallic reagents to 1,1-dichlorosilacyclobutane (**1a**).[26] It was noted that a significant amount of a by-product, presumably from double addition, was formed in the synthesis of **1d**. The formation of this side-product could be eliminated by using an excess of **1a** in THF instead of hexane as the reaction solvent.

The alkoxy derivatives **1f**, **1g**, and **1h** were prepared by reaction of **1a** with the corresponding alcohol or diol in the presence of an amine base. In the preparation of **1f** difficulties arose in the separation of the desired product from the amine hydrochloride salts when pyridine was used, but the problem was circumvented by the use of *N,N*-dimethylaniline. The reaction of bisfunctional silanes with diols can afford either monomeric or dimeric products;[27] the monomeric nature of the spirosilane **1h** was confirmed by mass spectrometry. The compounds containing the triflate moiety, **1i** and **1j**, were synthesized from the chlorosilacyclobutanes **1b** and **1a**, respectively, by treatment with silver triflate.

For a number of mechanistic studies, the deuterium-labeled substrates methyl-d_3-**1b**, *tert*-butyl-d_9-**1d**, and *tert*-butoxy-d_9-**1f** were prepared. Since direct addition of methyl nucleophiles to **1a** is not selective, methyl-d_3-**1b** was prepared using a temporary blocking group strategy as depicted in Scheme 3. Following the literature precedent,[26a] first 1-chloro-1-(*N,N*-dimethylamino)-silacyclobutane (**1k**) was prepared in 78% yield by the addition of dimethylamine to **1a**. Then 1-(*N,N*-dimethylamino)-1-methyl-d_3-silacyclobutane (d_3-**1l**) was prepared in 63% yield from **1k** by the addition of methyl-d_3-magnesium iodide. Finally, removal of the dimethylamino moiety and replacement with a chloride by treatment with dichlorophenylphosphine gave methyl-d_3-**1b** in 73% yield. The related substrates *tert*-butyl-d_9-**1d** and *tert*-butoxy-d_9-**1f** were synthesized as described above using **1a** with *tert*-butyl-d_9-lithium[28] and *tert*-butanol-d_9/*N,N*-dimethylaniline, respectively.

The enoxysilane derivatives **2–10** (Chart 3) were prepared by standard enolization/silylation protocols for those functional groups.[9,29] To examine the effect of the strain associated with the silacyclobutane ring, the corresponding dimethylsilyl analogs **12–18** were also synthesized for control reactions.[30] For the preparation of ketone-derived enoxysilanes, the use of lithium tetramethylpiperide was required to minimize competitive reaction of the amine with the highly reactive chlorosilane **1b**. The small size and high reactivity of **1b** also presented problems in the preparation of enoxysilane derivatives from esters. Under standard silylation conditions, reaction with **1b** led to substantial amounts of *C*-silylation products such as **11**. This undesirable side reaction could be suppressed by the use of tripiperidinephosphoric triamide (TPPA) as a polar cosolvent for the preparation of **5**. Moreover, TPPA allowed the generation of (*Z*)-**4** exclusively when used as a cosolvent in the enolization of methyl propanoate.[31] For the preparation of **4**, the more sterically demanding *tert*-butylsilyl chloride **1d** had to be used to suppress the formation of the *C*-silylated by-product. We were gratified to find that **1d** was more reactive than *tert*-butyldimethylsilyl chloride for trapping ester enolates, obviating the need for TPPA or other polar cosolvents.[32] The crude silacyclobutyl *O,O*-ketene acetals were prone to thermal rearrangement to the *C*-silylated analogs at elevated temperatures, although in typical distillations very little (<2%) of the *C*-silylated isomers were observed.

The formation of *O*-silyl *S,O*-ketene acetal (*Z*)-**9** followed literature analogy.[29b] None of the silacyclobutane derivatives (**1b**, **1d**, **1e**) gave *C*-silylated by-products. The *O*-silyl *S,O*-ketene acetal (*E*)-**9** was obtained by enolization using tritylllithium.[33] As expected, the enolization of *N,N*-dimethylpropanamide gave exclusively the (*Z*)-enolate; however, *tert*-butylsilyl chloride **1d** again had to be used to suppress the formation of the *C*-silylated by-product observed with **1b**. The configurational assignments for the geometrical isomers of enoxysilanes **2–10** were made according to literature precedent.[30a,c,d] *C*-Silylated analogs were identified by the diagnostic singlet in the ^{1}H NMR spectrum for the methyl groups on C(3) (see the supplementary material).

Deuterated analogs d_6-**5**, d_{12}-**6**, and d_{12}-**7** were synthesized for crossover studies following the above protocols starting from methyl-d_3 isobutyrate and the corresponding deuterated silylchlorides methyl-d_3-**1b**, *tert*-butyl-d_9-**1d**, and *tert*-butoxy-d_9-**1f**.

Uncatalyzed Aldol Addition. Ketone Derived. To compare the reactivity of enoxysilacyclobutanes relative to enoxytrialkylsilanes, orienting experiments were performed by combining **2** with benzaldehyde. The reaction of enolsilane **2** with benzaldehyde (1 M, C_6D_6) was extremely slow and required heating for prolonged periods for completion (100 °C, $t_{1/2}$ 800 min; *syn*/*anti* 85/15). Although **2** reacted disappointingly slowly, the control enolsilane **12** showed absolutely no sign of reaction under the

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Chart 3

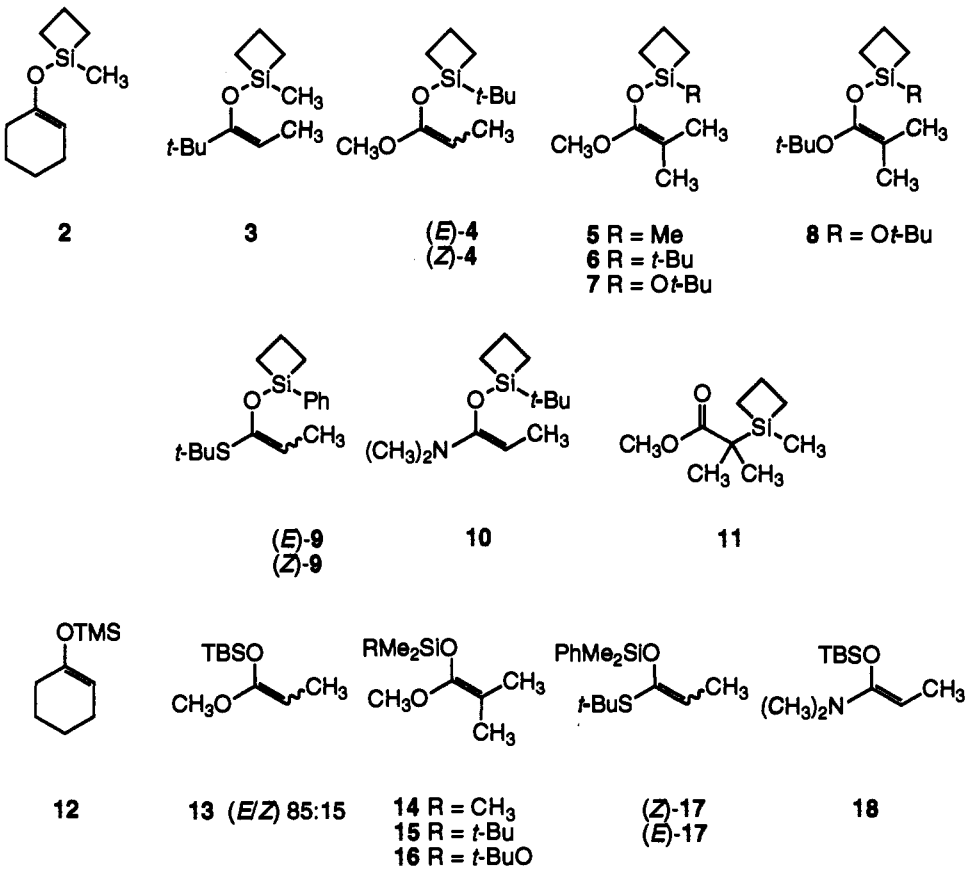
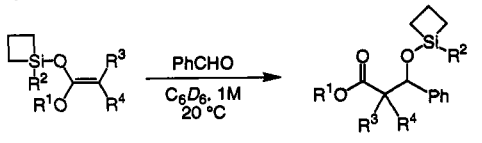


Table 1. Uncatalyzed Aldol Reactions of *O,O*-Ketene Acetals with Benzaldehyde[a]



entry	ketene acetal	R^1	R^2	R^3	R^4	product	$t_{1/2}$ (min)
1	**5**	CH_3	CH_3	CH_3	CH_3	**19**	5
2	**7**	CH_3	*tert*-butoxy	CH_3	CH_3	**21**	33
3	**6**	CH_3	*tert*-butyl	CH_3	CH_3	**20**	2100
4[b]	**8**	*tert*-butyl	*tert*-butyl	CH_3	CH_3		
5	(*E*)-**4**	CH_3	*tert*-butyl	H	CH_3	**22**	42
6	(*Z*)-**4**	CH_3	*tert*-butyl	CH_3	H	**22**	24 000

[a] All reactions were run in sealed tubes using degassed C_6D_6. [b] Neat reaction run at 20 °C.

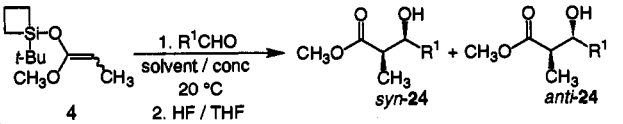
same conditions after 66 h. Thus, a significant enhancement in reactivity for enoxysilacyclobutanes was demonstrated, although the practical utility was still unclear.

Preliminary reactions with **3** were extremely capricious, sometimes proceeding to completion in minutes, sometimes not at all. The hydrolytic lability of enoxysilacyclobutanes was taken into consideration more carefully from then on; hydrolysis was noted in these preliminary trials.

Ester Derived. In contrast to the ketone-derived enoxysilacyclobutanes, the silacyclobutyl *O,O*-ketene acetals were extremely reactive toward aldehydes. For example, **5** underwent rapid and clean aldol addition with benzaldehyde (1 M, C_6D_6, 20 °C) to afford the corresponding β-silyloxy ester **19** as the only product (Table 1, entry 1). More importantly, in a control experiment, **14** *showed no sign of reaction under the same conditions after 15 days*!

The generality of the uncatalyzed aldol addition of enoxysilacyclobutanes was explored using *O,O*-ketene acetal **4** as a test substrate. To evaluate the effect of medium, (*E*)-**4** was combined

Table 2. Aldol Reactions of Silacyclobutyl *O,O*-Ketene Acetal **4**[a]



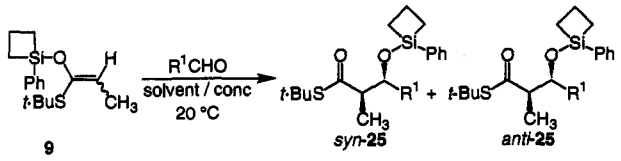
entry	**4**, *E/Z*	R^1	solvent[b]	$t_{1/2}$ (h)[b]	product	yield[c] (%)	*syn/anti*[d]
1	89/11	Ph	$CDCl_3$	2.8	**23a**		98/2[e]
2	89/11	Ph	C_6D_6	0.7	**23a**		98/2[e]
3	89/11	Ph	THF-d_8	1.1	**23a**		97/3[e]
4	0/100	Ph	C_6D_6	408.0	**23a**		43/57
5	0/100	Ph	$CDCl_3$	28.3	**24a**	80	42/58
6	95/5	Ph	$CDCl_3$	2.2	**24a**	94	95/5
7	89/11	cinnamyl	$CDCl_3$	6.7	**24b**	95	93/7
8	89/11	*n*-pentyl	$CDCl_3$	17.0	**24c**	91	93/7
9	89/11	cyclohexyl	$CDCl_3$	38.3	**24d**	85	>99/1

[a] All reactions run at room temperature in 1.0 M solution. [b] Reactions monitored by ^1H NMR. [c] Yield of isolated, desilylated product. [d] Ratio determined by ^1H NMR on purified, desilylated products. [e] Ratio by ^1H NMR of silyl products. After 8 h, the majority of the *Z* isomer still remained.

with benzaldehyde in a variety of solvents at 20 °C (Table 2). The effect on the rate was modest, but was notable for the order C_6D_6 > THF-d_8 > $CDCl_3$. Control experiments with (*E*)-**13** and benzaldehyde in THF-d_8 or C_6D_6 also showed no reaction after 120 h. To determine the level of stereoselectivity, the aldol products **23a** were desilylated with HF/THF and the purified hydroxy esters **24a** were analyzed by ^1H NMR in comparison to the known stereoisomers.[34] The product **24a** was formed highly diastereoselectively from (*E*)-**4** (*up to 96% de*). Moreover, entries 1–3 show that an 89/11 *E/Z* mixture of **4** afforded a 98/2 *syn/anti* mixture of **24a**. This observation is most certainly due to the more rapid reaction of (*E*)-**4**. Indeed, as was demonstrated

(34) (a) Harada, T.; Kurokawa, H.; Kagamihara, Y.; Tanaka, S.; Inoue, A.; Oku, A. *J. Org. Chem.* **1992**, *57*, 1412. (b) Gennari, C.; Bernardi, A.; Colombo, L.; Scolastico, C. *J. Am. Chem. Soc.* **1985**, *107*, 5812.

Table 3. Aldol Reactions of Silacyclobutyl *S,O*-Ketene Acetal **9**[a]



9

entry	**9**, *E*/*Z*[b]	R¹	solvent[c]	*t*[d] (h)	product	conv[d] (%)	*syn*/*anti*[e]
1	4/96	Ph	$CDCl_3$	50.5	**25a**	84	98/2
2	4/96	Ph	C_6D_6	50.5	**25a**	97	97/3
3	4/96	Ph	THF-d_8	49.5	**25a**	93	89/11
4	4/96	Ph	neat		**25a**		99/1
5	100/0	Ph	neat		**25a**		85/15
6	4/96	cinnamyl	$CDCl_3$	51	**25a**	91	70/30
7	4/96	*n*-pentyl	$CDCl_3$	50.5	**25c**	42	90/10
8	4/96	*n*-pentyl	neat	24.0	**25c**	68	90/10
9	4/96	cyclohexyl	$CDCl_3$	50.0	**25d**	NR	

[a] All reactions run at room temperature. [b] (*Z*)-**9** has cis *t*-BuS//CH_3. [c] Solution reactions run at 0.5 M. [d] Reaction progress and selectivity monitored by ^1H NMR. [e] Ratio of silylated aldols.

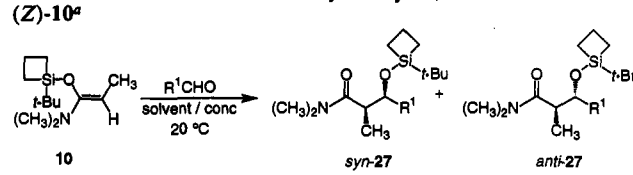
earlier, pure (*Z*)-**4** reacted sluggishly and with opposite, albeit weak, *anti* selectivity. The fact that (*Z*)-**4** reacted faster in $CDCl_3$ than in C_6D_6 is probably due to adventitious catalysis by trace HCl in the $CDCl_3$.

To evaluate the importance of enoxysilacyclobutane structure and geometry on rate, we examined the reaction of ketene acetals **4-8** with benzaldehyde by ^1H NMR analysis in sealed tubes (1 M, C_6D_6, 20 °C). The data for reaction half-lives are compiled in Table 1. The effect of the silicon "spectator ligand" was dramatic as the rate of reaction dropped precipitously in the order Me > O-*t*-Bu ≫ *t*-Bu (compare compounds **5**, **6**, and **7** derived from methyl isobutyrate). Control experiments with all three dimethylsilyl analogs (**14**, **15**, and **16**) showed no sign of reaction under identical conditions, thus clearly supporting the special influence of the silacyclobutane ring. The effect of ketene acetal geometry was still more dramatic, as the comparison between (*E*)-**4** and (*Z*)-**4** clearly illustrates (Table 1, entries 5 and 6); *the E isomer reacted nearly 600 times faster than the Z isomer.* Again, control experiments with **13** (*E*/*Z* 85/15) showed absolutely no sign of reaction. It is interesting to note that (*E*)-**4** is 50 times more reactive than **6**, which in turn is more than 10 times more reactive than (*Z*)-**4**. This difference in reactivity between *E* and *Z* isomers has practical consequences for stereoselection and theoretical consequences for interpretation of transition structure geometry. Finally, the effect of the ester substituent was evaluated in the comparison of **6** and **8**. Whereas **6** reacted sluggishly, we could detect no sign of reaction of **8** with benzaldehyde neat after 80 h at room temperature.

To evaluate the scope of the aldol reaction, (*E*)-**4** was combined with representative aldehydes in $CDCl_3$ (Table 2). The more basic and less hindered aldehydes reacted faster, but none of these partners reacted as rapidly as benzaldehyde. Nevertheless, the reactions did go to completion and were extremely clean and diastereoselective. The *syn*/*anti* ratios were determined on the desilylated aldol products **24a-d**, by comparison of the spectral data to that of the authentic compounds, specifically the diagnostic ^1H NMR resonances for the C(3) methine protons in the aldol products.[34]

Thiol Ester Derived. The results from the *O*-silyl *S,O*-ketene acetals (*Z*)-**9** and (*E*)-**9** are collected in Table 3. As was the case with the *O,O*-ketene acetals, the substituent on silicon had a dramatic effect on reactivity. Orienting experiments with the methylsilacyclobutyl analog showed a very slow reaction with benzaldehyde at 1 M concentration in $CDCl_3$ with 10% conversion to the desired products in 30 h. The *tert*-butylsilacyclobutane derivative failed to react with benzaldehyde neat after 30 h at room temperature. Replacement of the alkyl substituent on silicon with a phenyl group increased the reactivity of **9**, as illustrated by the successful aldol reactions in Table 3.

Table 4. Aldol Reactions of Silacyclobutyl *N,O*-Ketene Acetal (*Z*)-**10**[a]



10

entry	R¹	solvent	product	$t_{1/2}$[b] (h)	*syn*/*anti*[b,c]
1	Ph[d]	$CDCl_3$	**27a**	0.67	9/91
2	Ph[d]	C_6D_6	**27a**	3.6	31/69[e]
3	Ph[d]	THF-d_8	**27a**	3.8	33/67
4	*n*-pentyl[f]	C_6D_6	**27b**	4.6	40/60
5	cyclohexyl[f]	C_6D_6	**27c**	12.8	50/50

[a] Reactions run at 0.5 M. [b] Reaction progress and selectivity monitored by ^1H NMR. [c] Ratio determined by ^1H NMR on **27**. [d] Reactions run at room temperature. [e] Yield of isolated, purified **27a**, 84%. [f] Reactions run at 52 °C.

The effect of the solvent on the reaction was examined using benzaldehyde in combination with (*Z*)-**9** (Table 3, entries 1–3). The rate of reaction was dependent on the solvent, with the fastest reaction being observed in C_6D_6, as was the case for the *O*-silyl *O,O*-ketene acetals. High *syn* selectivity was obtained in both $CDCl_3$ and C_6D_6, but there was a noticeable erosion of selectivity in THF-d_8. The stereochemical outcome of the reaction was confirmed by desilylation of product **25** using tetra *n*-butylammonium fluoride (TBAF) and comparison of ^1H NMR data from the *syn* and *anti* aldols **26** to the literature values.[29b]

The reaction of (*Z*)-**9** with a number of different aldehydes was then surveyed (Table 3, entries 6–9). A moderate reaction rate was observed in $CDCl_3$ solution with cinnamaldehyde, yielding the *syn* isomer with modest selectivity. Higher selectivity was observed in the reaction of (*Z*)-**9** with hexanal; however, the reaction was sluggish, with less than 50% conversion in 50 h. Cyclohexanecarboxaldehyde did not react at all in $CDCl_3$ solution. Reaction was observed when (*Z*)-**9** was mixed with the aldehydes neat; however, ^1H NMR analysis indicated that a number of competing processes were occurring with hexanal. The effect of the silyl ketene acetal geometry on the reaction was examined using (*Z*)-**9** and (*E*)-**9** in a neat reaction with benzaldehyde (entries 4 and 5). In this series, changing from the *Z* to the *E* isomer did not alter the configuration of the product but did reduce the *syn* selectivity. Overall, the sulfur analogs were less reactive than the corresponding *O,O*-ketene acetals. Nevertheless, control experiments with the dimethylphenyl derivative **17** and each aldehyde (both neat and in C_6D_6 solution) showed no trace of product after 24 h.

Amide Derived. The reactions of (*Z*)-**10** with a number of different aldehydes are presented in Table 4. The reactions with benzaldehyde were rapid, but the rate and the level of stereoselection observed were dependent upon the solvent used (entries 1–3). In $CDCl_3$, an extremely fast reaction occurred to afford the *anti* product **27** with high selectivity. However, close inspection of the ^1H NMR spectrum indicated traces of hydrolysis, and therefore adventitious catalysis in this solvent could not be excluded. In C_6D_6 and THF-d_8 the half-life of the reaction was *ca.* 5 times greater than that in $CDCl_3$ and the level of *anti* selectivity was compromised. From the reaction in C_6D_6 the desilylated aldol product **28a** was obtained in 84% yield by treatment of **27a** with HF in THF at room temperature. Comparison of the ^1H NMR spectrum **28a** with published data allowed the assignment of configuration.[35]

In contrast to the control experiments with *O*-silyl ketene acetals derived from esters and thiol esters, (*Z*)-**18** underwent reaction with aldehdyes in the absence of an external catalyst. The results are collected in Table 5. The effect of the solvent on the reaction was determined by studying the reaction with benzaldehyde

(35) (a) Fujii, H.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1991**, *32*, 6147. (b) Crouse, D. N.; Seebach, D. *Chem. Ber.* **1968**, *101*, 3113.

Scheme 4

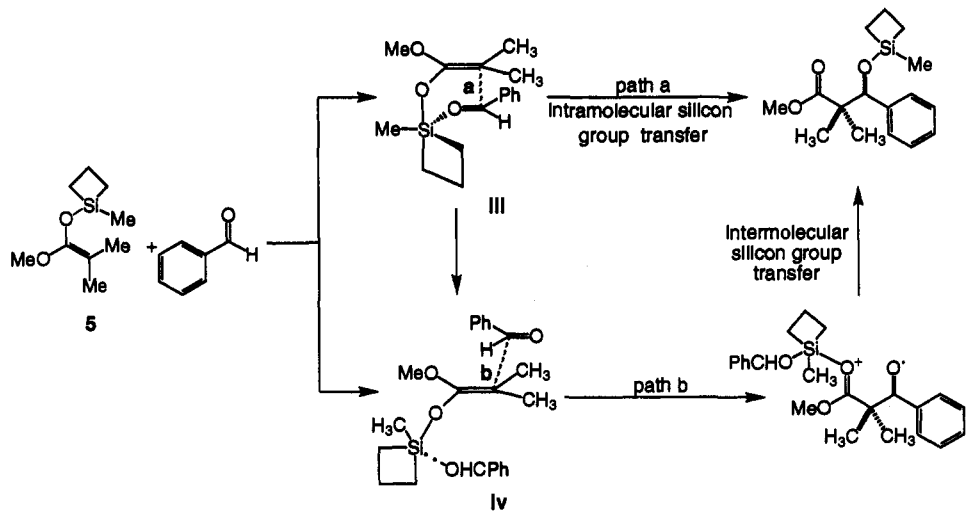
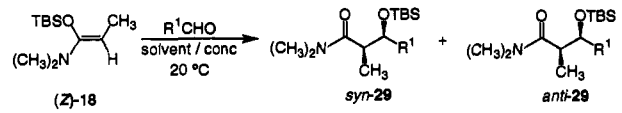


Table 5. Control Reactions with *N,O*-Ketene Acetal (*Z*)-**18**[a]



entry	R^1	solvent	product	$t_{1/2}$[b] (h)	*syn/anti*[b,c]
1	Ph[d]	$CDCl_3$	**29a**	0.75	11/89
2	Ph[d]	C_6D_6	**29a**	26.7	17/83
3	Ph[d]	THF-d_8	**29a**	33.3	22/78
4	*n*-pentyl[e]	C_6D_6	**29b**	46.7	23/77
5	cyclohexyl[e]	C_6D_6	**29c**	199.0	30/70

[a] Reactions run at 0.5 M. [b] Reaction progress and selectivity monitored by ^{1}H NMR. [c] Ratio determined by ^{1}H NMR. [d] Reactions run at room temperature. [e] Reactions run at 52 °C.

(entries 1–3). The reference compound (*Z*)-**18** revealed a comparable reactivity to the silacyclobutane derivative (*Z*)-**10** only in $CDCl_3$. However, as for the enoxysilacyclobutane, trace amounts of *N,N*-dimethylpropanamide could be detected. When the reaction of (*Z*)-**18** with benzaldehyde was performed in C_6D_6 or THF-d_8, the rate was *ca.* 8 times slower than with (*Z*)-**10**. A similar difference in the reactivity between (*Z*)-**10** and the control compound (*Z*)-**18** was observed with other aldehydes when compared in C_6D_6.

Mechanistic Studies. The basic hypothesis for the enhanced reactivity of the silacyclobutane derivatives requires the intermediacy of a pentacoordinate siliconate. Given the fact that (*E*)-ketene acetals afford *syn* aldol products with high diastereoselectivity, this further requires a boat-like transition structure through a trigonal bipyramid. To provide experimental support for the proposed mechanism and understand the origin of stereocontrol, it was deemed critical to establish the nature of the silicon group transfer. If reaction of silacyclobutyl *O,O*-ketene acetals with aldehydes proceeds via a closed transition structure about a trigonal bipyramidal silicon **iii** (Scheme 4), then a *direct silicon group transfer* from the *O,O*-ketene acetal to its aldehyde partner is mechanistically mandated. Herein, the silicon moiety and the ester group never become disconnected. However, if the reaction proceeds by any open transition structure such as **iv** (even involving hypercoordinate silicon), then the silicon group transfer to the aldol product is not coupled with the new C–C bond forming event and is thus an intermolecular group transfer.[11]

To distinguish these limiting possibilites, a double-label crossover experiment was designed (Figure 1). First, a d_6 analog of **5** was synthesized from methyl-d_3 isobutyrate and 1-chloro-1-methyl-d_3-silacyclobutane (d_3-**1b**).[36] One equivalent each of

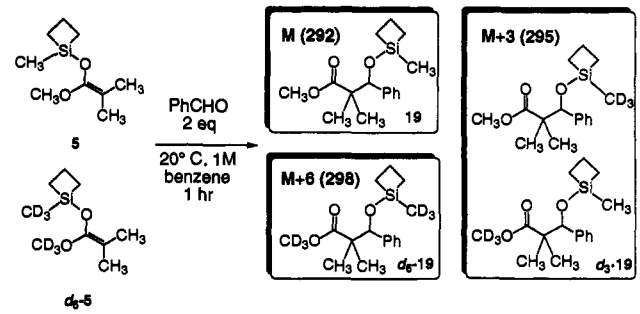


Figure 1. Uncatalyzed aldol reaction crossover test.

5 and d_6-**5** (96.8% d_6) were combined with 2 equiv of benzaldehyde in C_6D_6 (1 M, 18 °C, $t_{1/2}$ 4.5 min). The reactions were very clean and afforded quantitative yields of the analytically pure aldol products. The products were analyzed by field ionization mass spectrometry. The nondeuterated aldol product has *m/z* 292, the aldol-d_6 has *m/z* 298, and any intermolecular silicon transfer in the reaction would produce an aldol product of *m/z* 295. The aldol products were analyzed for the relative ratio of *m/z* 292, 295, and 298. Intermolecular silicon group transfer would give a statistical 1.0/2.0/1.0 ratio of the M^+, $M^+ + 3$, and $M^+ + 6$ ions, respectively, while intramolecular silicon group transfer would give a 1.0/0/1.0 ratio of the M^+, $M^+ + 3$, and $M^+ + 6$ ions, respectively. The mass spectral analysis revealed that only 0.54% of the $M^+ + 3$ ion was present (M^+ (46.9%); $M^+ + 3$ (0.54%), $M^+ + 6$ (52.5%)), unambiguously establishing that these uncatalyzed aldol reactions proceed through *direct intramolecular silicon group transfer.*

Catalyzed Aldol Addition. Having established the ability of silacyclobutyl *O,O*-ketene acetals to undergo uncatalyzed aldol reactions with aldehydes through direct silicon group transfer, the possibility of nucleophilic catalysis of the aldol reaction between silacyclobutyl *O,O*-ketene acetals with aldehydes was examined. Early in our studies it was found that the aldol reactions of both (*E*)-**4** and (*Z*)-**4** were highly susceptible to catalysis. For example, both ketene acetals reacted rapidly with benzaldehyde in the presence of 5 mol % of KO-*t*-Bu at low temperature (<7 min, –78 °C, THF-d_8, 0.25 M, 88/12 (*E/Z*)-**4**) to cleanly[37] give the corresponding β-silyloxy aldol products **23a** (33/67 *syn/anti*). The control reaction with **15** and benzaldehyde (0.25 M, 5 mol % KO-*t*-Bu) showed no reaction after 64 h at 20 °C.

While the silacyclobutyl ketene acetal was again unique in its reactivity under catalysis, the precise mechanism of reaction again had to be determined. Since the hypothesis for ligand-accelerated catalysis in the aldol reaction required high-energy, hexacoor-

(36) Methyl-d_3 isobutyrate was synthesized from isobutyryl chloride and methanol-d_3.

(37) After aqueous workup, ether extraction, and concentration *in vacuo*, the aldol products were obtained in analytically pure form.

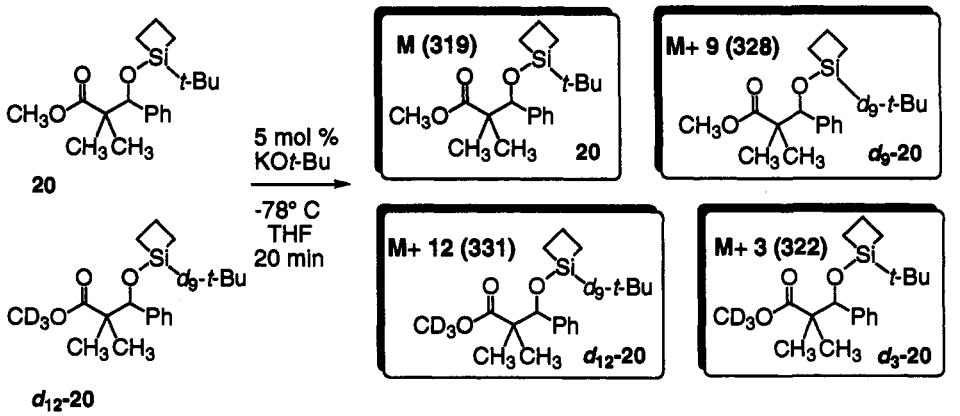


Figure 2. Catalyzed aldol reaction product control experiment.

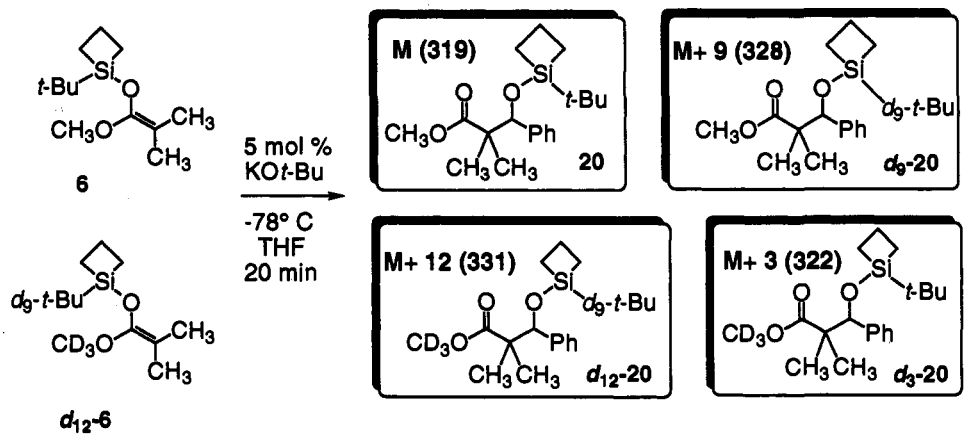


Figure 3. Catalyzed aldol reaction crossover test.

dinate siliconates as intermediates, we chose to test the nature of the silicon group transfer. Once again, a double-label crossover was devised to probe the nature of the silicon group transfer in the alkoxide-catalyzed aldol reaction.

The "isotopic stability" of the products needed to be established first. The *tert*-butyl derivative **6** was selected instead of the previously employed methyl analog **5** because control experiments revealed that the silylated aldol products **19** from **5** suffered silicon group scrambling in the presence of potassium *tert*-butoxide. Thus, to be sure that the products **20** from **6** were stable under reaction conditions, the following product-crossover control reaction was performed (Figure 2). One equivalent each of the analytically pure β-silyloxy aldols **20** and d_{12}-**20** (98.1% d_{12}, 0.1% d_9, 0.1% d_3, and 1.7% d_3) were combined in THF (0.25 M, −78 °C), and 5 mol % of KO-*t*-Bu (0.46 M in THF) was added. After 20 min, the reaction was quenched at −78 °C with pH 7 phosphate buffer, extracted with diethyl ether, dried, and concentrated. The aldol products were then analyzed by field ionization mass spectrometry, which indicated that no exchange of the deuterium labels had occurred; that is, none of the ions *m/z* 322 or 328 were detected.[38]

Figure 3 depicts the double-label crossover method used to study the catalyzed aldol reactions. One equivalent each of **6** and d_{12}-**6** (98.1% d_{12}, 0.1% d_9, 0.1% d_3, and 1.7% d_3) were combined with 2 equiv of benzaldehyde in THF (0.25 M, −78 °C), and 5 mol % of potassium *tert*-butoxide (0.46 M in THF) was added. After isolation the analytically pure β-silyloxy aldol products **20** were analyzed by field ionization mass spectrometry. The nondeuterated aldol product **20** has an *m/z* 319, while the d_{12}-**20** has *m/z* 331. Any *intermolecular* silicon transfer in the reaction would produce two other aldol products, d_3-**20** *m/z* 322 ($M^+ + 3$) and d_9-**20** *m/z* 328 ($M^+ + 9$). The mixture of labeled products was analyzed for the relative ratio of *m/z* 319, 322, 328, and 331. From the stoichiometry of **6** and d_{12}-**6** used in the reaction and the isotope content analysis for d_{12}-**6**, the theoretical distribution for the four ions was calculated for intramolecular transfer (no crossover) and intermolecular transfer (crossover). The theoretical ion distribution for the intermolecular transfer scenario was M^+(30.4%), $M^+ + 3$ (24.7%), $M^+ + 9$ (24.7%), $M^+ + 12$ (20.1%). The mass spectral analysis showed complete scrambling of the deuterium labels: M^+(30.9%), $M^+ + 3$ (25.2%), $M^+ + 9$ (24.1%), $M^+ + 12$ (19.8%).

(38) Aldol product **20** did not give a molecular ion when analyzed by field ionization mass spectrometry, but rather a mass distribution corresponding to a loss of "methyl" or 15 amu. The ion composition was found: calculated M^+ (54.6%), $M^+ + 3$ (0%), $M^+ + 9$ (0%), $M^+ + 12$ (45.4%); found M^+ (53.8%), $M^+ + 3$ (0.3%), $M^+ + 9$ (0.2%), $M^+ + 12$ (45.7%).

Table 6. Catalyzed Aldol Reaction of 6, Crossover Study Results

catalyst[a]	solvent	temp[b] (°C)	$t_{1/2}$ (min)[b]	time[b] (min)	% yield[c]	crossover?
KO-*t*-Bu	THF	−78		20	90	yes
KO-*t*-Bu[d]	benzene[d]	20		15	81	yes
LiO-*t*-Bu	THF	20	22	90	85	yes
LiOPh	THF	0	31	120	92	yes
LDA	THF	0	90	480	79	yes

[a] All reactions were run at 0.25 M using 5 mol % of the indicated catalyst. [b] All reaction conditions were developed initially by VT ^{1}H NMR studies. [c] Yield of the β-silyloxy ester aldol product. [d] Due to the limited solubility of the catalyst in benzene, the exact stoichiometry was not definite.

A number of other nucleophilic reagents were shown to catalyze the aldol addition. The double-label crossover method was applied to the reactions of **6** and benzaldehyde catalyzed by these reagents as well. The catalysts, reaction conditions, and results of the crossover experiments are listed in Table 6. In all trials, complete scrambling of the deuterium labels was observed. Changing the catalyst counterion from potassium to lithium served only to slow the reaction. The less nucleophilic and sterically less encumbering phenoxide anion was found to be an efficient catalyst; lithium diisopropylamide also served as a catalyst, but the reaction was sluggish.

On the basis of the initial crossover studies, it appeared that

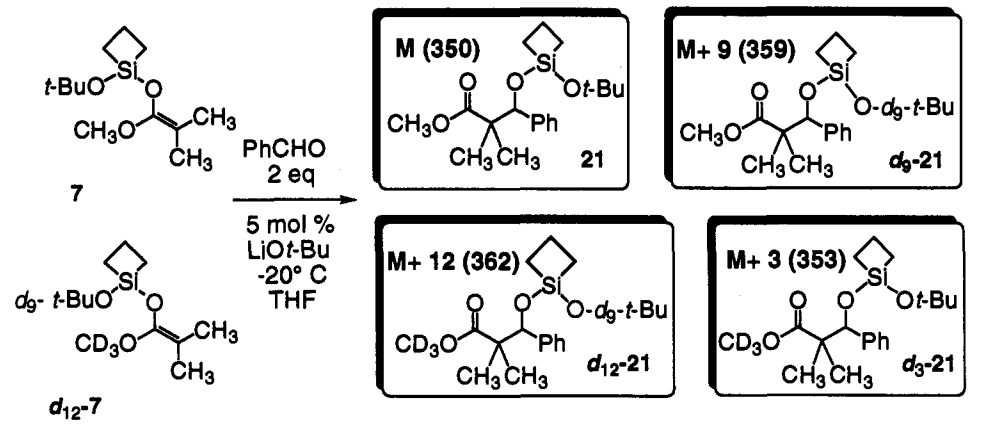


Figure 4. Catalyzed aldol reaction crossover test, alkoxy-substituted silacyclobutane.

Table 7. Catalyzed Aldol Reaction of 7, Crossover Study Results

catalyst[a]	solvent	temp[b] (°C)	$t_{1/2}$ (min)[b]	time[b] (min)	% yield[c]	crossover?
LiO-*t*-Bu	THF	−20	9.2	30	80	yes
LiOPh	THF	−20	6.5	20	82	yes

[a] All reactions were run at 0.25 M using 5 mol % of the indicated catalyst. [b] All reaction conditions were developed initially by VT ^{1}H NMR studies. [c] Yield of the β-silyloxy ester aldol product.

the alkoxide-catalyzed aldol reaction of **6** with benzaldehyde proceeded via free potassium or lithium enolates. Thus, to stabilize the putative hexacoordinate siliconate intermediate, an alkoxy-substituted silacyclobutane was considered.

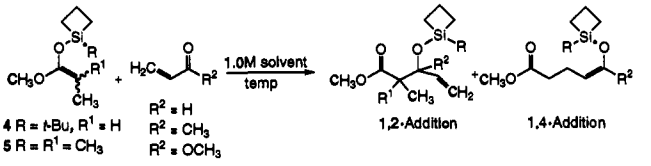
Silacyclobutyl *O,O*-ketene acetal d_{12}-**7** (Chart 3) was synthesized in deuterium-labeled form (from d_9-**1f** and methyl-d_3 isobutyrate), and the double-label crossover method was used to assess the presence of direct silicon group transfer in the alkoxide-catalyzed reaction with benzaldehyde, Figure 4. One equivalent each of **7** and d_{12}-**7** (94.9% d_{12}, 2.4% d_9, 1.8% d_3, and 0.9% d_3) were combined with 2 equiv of benzaldehyde in THF (0.25 M, −20 °C), and 5 mol % of lithium *tert*-butoxide or lithium phenoxide was added. After workup the analytically pure β-silyloxy aldol products were analyzed as previously described, this time comparing the relative ratios of ions with *m/z* 350 (M^+), 353 ($M^+ + 3$), 359 ($M^+ + 9$), and 362 ($M^+ + 12$). From the mass spectral data there was, as in previous trials, complete scrambling of the deuterium labels: M^+ (27.2%), $M^+ + 3$ (28.3%), $M^+ + 9$ (20.5%), $M^+ + 12$ (23.9%). The same result was obtained with lithium phenoxide.

Table 7 contains the reaction conditions employed and rate data for the crossover trials with **7**. The reactions proceeded smoothly at −20 °C; the *tert*-butoxy moiety on silicon accelerated the reaction relative to the *tert*-butyl moiety, as was observed in the uncatalyzed aldol reaction studies. A similar product control experiment was performed, subjecting a mixture of the aldol products **21** and d_{12}-**21** to the catalyzed reaction conditions, and once again there was no scrambling of the label.

Although the double-label, crossover studies showed that there was no direct silicon group transfer in these versions of the catalyzed aldol reaction, we nonetheless felt that at least empirical asymmetric catalysis studies were warranted. Thus, **4** (88/12 *E/Z*) was combined with benzaldehyde (0.25 M, THF, −78 °C, 20 min) using a catalytic amount (5 mol %) of a potassium alkoxide derived from a variety of scalemic alcohols ((1*R*,2*S*,5*R*)-(−)-menthol, (−)-methylborneol, (−)-(1*R*)-2,2-diphenylcyclopentanol, and (+)-(1*S*,2*R*)-phenylcyclohexanol). The reactions were quenched at −78 °C with pH 7 phosphate buffer, followed by extractive workup and desilylation (dilute HF/THF) to afford the aldol products **24a**. In all cases the aldol reactions were efficiently catalyzed (yields 80–90%), but there was no indication of enantiomeric excess in the aldol products.

Michael Addition. The feasibility of using enoxysilacyclobutanes in Michael-type reactions was examined by combining

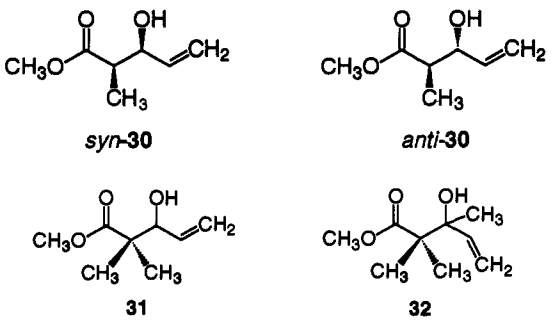
Table 8. Attempted Michael Additions with 4 or 5[a]



entry	acetal	R^2	solvent	temp (°C)	$t_{1/2}$ (min)[b]	1,2/1,4[c]	yield (%)
1	4	H	C_6D_6	20	8	100/0	84
2	5	H	C_6D_6	20	160	100/0	75
3	4	CH_3	C_6D_6	20			
4	5	CH_3	C_6D_6	20	10 560	100/0	
5	5	CH_3	CD_3CN	20			
6	5	CH_3	C_6D_6	100	138	100/0	66
7	5	CH_3	d_8-THF	−60[d]		60/40	
8	5	OCH_3	d_8-THF	−60[d]	*e*		

[a] All reactions run at 1.0 M. [b] Reactions monitored by ^{1}H NMR. [c] Ratio determined by ^{1}H NMR. [d] Reaction performed in the presence of KO-*t*-Bu. [e] Disappearance of methyl acrylate was observed.

Chart 4



4 (*E/Z*, 80/20) or **5** with representative α,β-unsaturated carbonyl compounds. The results are presented in Table 8. In initial experiments the acetal **4** reacted rapidly with acrolein with complete consumption of the *E* isomer. However, the addition reaction was exclusively of the aldol type (1,2-addition). This was confirmed by desilylation of the material using HF and comparison of the isolated allylic alcohol **30** (Chart 4) with an authentic[39] sample, which also revealed that the addition occurred with *syn* selectivity (*syn/anti* 94/6). A similar reaction was observed with the acetal **5**, entry 2. In this case the reaction was extremely fast ($t_{1/2}$ 8 min) as expected. The regiochemical outcome of the reaction was again confirmed by desilylation and isolation of the allylic alcohol **31**.

The reactions of **4** or **5** with other types of α,β-unsaturated carbonyl compounds, methyl vinyl ketone (MVK), and methyl acrylate were investigated. Surprisingly, the reaction with MVK

(39) Dodd, D. S.; Oehlschlager, A. C.; Georgopapadakou, N. H.; Polak, A.-M.; Hartman, P. G. *J. Org. Chem.* **1992**, *57*, 7226.

and acetal **5** at room temperature in C_6D_6 or CD_3CN[40] at 1 M concentration was extremely slow ($t_{1/2}$ 176 h). Repetition of the reaction of **5** in C_6D_6 at an elevated temperature (100 °C) did result in reaction; however, the only observable product, **32**, was the consequence of 1,2-addition. The potential for nucleophilic catalysis was examined in this type of reaction as well. The acetal **5** was combined with either MVK or methyl acrylate in THF-d_8 in the presence of KO-*t*-Bu (10 mol %) at −60 °C, Table 8, entries 7 and 8. The reaction of **5** with MVK was rapid and afforded a mixture of 1,2- and 1,4-addition products from analysis of the ^{1}H NMR spectrum, most likely via a different mechanism from that which occurs under thermal conditions.

Complexation Studies. Our hypothesis for the enhanced reactivity of enoxysilacyclobutanes derives from "strain-release Lewis acidity" expressed by the silicon atom in forming a reactive trigonal bipyramid with the substrate aldehyde. To garner experimental support for this hypothesis and evaluate the Lewis acidity of substituted silacyclobutanes in general, a spectroscopic study of their ability to complex with carbonyl compounds was undertaken. Three different silanes, **1c**, **1g**, and **1h**, were chosen for the study. The Lewis acidic properties were initially assayed by ^{13}C NMR spectroscopy.[41] The ^{1}H and ^{13}C NMR spectra of stoichiometric mixtures of the silacyclobutane derivatives and 4-(dimethylamino)benzaldehyde displayed no significant shift in the signals corresponding to the aldehydic proton or carbonyl carbon.

To enhance the Lewis acidity of the silicon atom, the trifloxy derivatives **1i** and **1j** were next investigated. Stimulated by the recent report[42] of "uncatalyzed" aldol reactions of trifloxysilyl enol ethers with aldehydes, the silacyclobutanes **1i** and **1j** were combined with benzaldehyde and studied by NMR spectroscopy. When either **1i** or the corresponding control compound TMSOTf was mixed with benzaldehyde, there was no observable shift in the NMR resonances. However, with the bis(trifluoromethanesulfonyl) derivative **1j** and dimethylsilyl bis(trifluoromethanesulfonate)[43] significant downfield shifts in the ^{13}C resonances of benzaldehyde could be seen. However, the resonances returned to their original locations when 0.5 equiv of the hindered base, 2,6-di-*tert*-butylpyridine, was introduced. *Thus, the observed effects of both bis(triflate) reagents were due to traces of triflic acid. These changes in the NMR spectra of benzaldehyde could be reproduced by the addition of triflic acid followed by 2,6-di-tert-butylpyridine.*

Computational Studies. The remarkable observation of high *syn* diastereoselectivity with (*E*)-silyl ketene acetals stands in contrast to the normal, geometry-independent, Lewis acid-promoted *anti* selectivity seen for these species. The lack of crossover in the double-label experiment assures an intramolecular silicon group transfer and, in light of the *syn* selectivity, requires that boat-like transition structures be invoked. To gain more quantitative insights, transition structures for the reaction of (*E*)-**4** with benzaldehyde were calculated with MOPAC version 6.1 employing the PM3 Hamiltonian.[44]

Four initial conditions were set for computational simplicity under the following assumptions: (1) the reactions were all formulated to proceed via prior aldehyde complexation to silicon, (2) complexation of the aldehyde was assumed to be nonlinear and *syn* to the aldehyde hydrogen, (3) complexation at the silicon was assumed to induce a trigonal bipyramidal geometry, and (4) the products were assumed to initially arise as silicon-chelated six-membered-ring aldolates. The first assumption derives from the special reactivity of (*E*)-**4** and the lack of crossover found with d_6-**5**. The second assumption was based on overwhelming spectroscopic, crystallographic, and computational evidence available for complexation of Lewis acids to aldehydes.[41,45] For the silicon configuration (assumption 3), both apical (denoted "a") and basal (denoted "b") locations of the aldehyde were considered. Additionally for each silicon configuration, both boat (denoted "B") and chair (denoted "C") conformations (affording the *syn* and *anti* products, respectively) were considered. The fourth assumption was required to facilitate the location of transition structures. On the basis of a pericyclic mechanism, the aldolate products must be created as six-membered rings from coordination of the silicon to the carbonyl oxygen of the resultant ester moiety. Thus, the relative orientation of the substituents on the reacting partners (or in the products) becomes more well-defined, *i.e.* whether two particular substituents are on the same (proximal, denoted "p") or opposite (distal, denoted "d") sides of the ring in question. Because their relative orientations were found to give rise to important interactions, we chose the phenyl ring of benzaldehyde and the *tert*-butyl group on silicon to be used as part of our descriptive nomenclature. Therefore, considering the three key variables, apical/basal, chair/boat, proximal/distal, the eight limiting (four boats and four chairs) transition-state structures were evaluated. As depicted in Scheme 5, we chose a three-letter designation for each of the eight possible starting geometries, the first letter designating the apical or basal aldehyde orientation (a or b), the second letter designating boat or chair (B or C), and the third letter designating the relative orientation of the phenyl and *tert*-butyl moieties about the presumed six-membered ring, proximal or distal (p or d). The products formed from each of the starting trigonal bipyramidal silicon complexes are also shown. In the following discussion of our results, each of the transition structures will be identified by its corresponding starting geometry with the appropriate three-letter designation.[46]

As an aid to describing the computed transition-state models, we have selected key dihedral angles and steric interactions for discussion, Chart 5. The structures in Chart 5 reveal that twist boats were located for the *syn* manifold, and half-chairs were found for the *anti* pathway. The apparent computational difficulty in reaching idealized closed six-membered transition states is borne out when one considers the importance of the steric interactions in such a tightly organized transition state. The calculated transition structures possessed square pyramidal (sp) geometry for silicon. The first important dihedral angle depicted is α ((C(1)–C(2)–Si(3)–C(4)), which defines the orientation of the methyl groups (of the *tert*-butyl) with respect to the silacyclobutane ring. The two designated orientations (Chart 5) for α are (1) eclipsed (e), which designates that the acute C–Si-C bond angle of the silacyclobutane ring is contained within the CH_3–C–CH_3 bond angle of the *tert*-butyl moiety, and (2) staggered (s), which designates that one of the methyl groups of the *tert*-butyl moiety resides over the silacyclobutane ring system. The second important dihedral angle depicted is β ((C(5)–C(6)–C(7)–C(8)), which describes the torsional interactions between the phenyl and methyl moieties on the incipient bonding carbon centers. Another important interaction is γ, the closest contact between the hydrogens on the *tert*-butyl moiety and the hydrogens on the aldehyde (either the formyl hydrogen (f) or one of the ortho hydrogens (o) of the phenyl ring). Also, depicted in Chart 5 is δ, the interaction between methyl ether and *tert*-butyl moieties. The top two structures (v and vi) represent the methyl

(40) Kita, Y.; Segawa, J.; Haruta, J.-I.; Yasuda, H.; Tamura, Y. *J. Chem. Soc., Perkin Trans. 1* **1982**, 1099.
(41) Denmark, S. E.; Almstead, N. G. *J. Am. Chem. Soc.* **1993**, *115*, 3133.
(42) Kobayashi, S.; Nishio, K. *J. Org. Chem.* **1993**, *58*, 2647.
(43) Matyjaszewski, K.; Chen, Y. L. *J. Organomet. Chem.* **1988**, *340*, 7.
(44) (a) Stewart, J. J. P., Frank J. Seiler Research Laboratory, United States Air Force Academy, Colorado Springs, CO 80840. (b) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 221.
(45) For excellent reviews on Lewis acid carbonyl complex structures see: (a) Shambayati, S.; Crowe, W. E.; Schreiber, S. L. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 256. (b) Shambayati, S.; Schreiber, S. L. In *Comprehensive Organic Synthesis, Vol. 1, Additions to C-X π Bonds, Part 1*; Schreiber, S. L., Ed.; Pergamon Press: Oxford, 1991; pp 283–324.
(46) Transition state geometries for each of the eight transformations depicted in Scheme 8 were located from saddle calculations and optimized by the eigenvector-following (EF) method. All stationary points were characterized by harmonic vibrational frequency analysis and confirmed as a transition state by having only one negative eigenvalue. Intrinsic reaction coordinate (IRC) searches were performed to confirm that the points were on the reaction coordinate.

Scheme 5

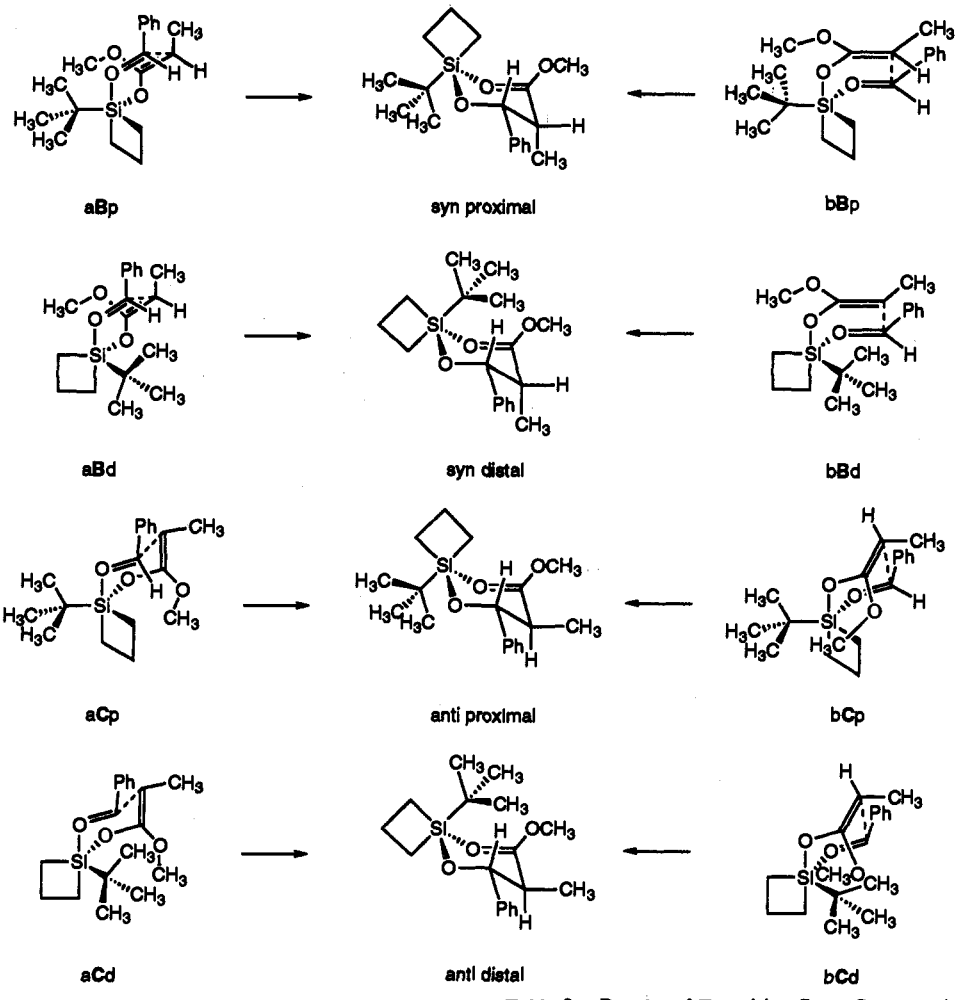
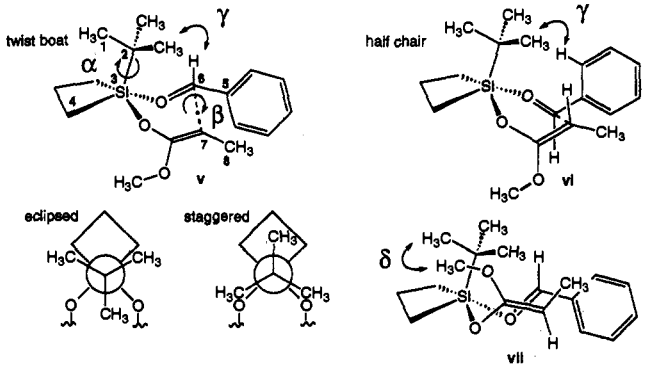


Chart 5



ether/*tert*-butyl groups on opposite sides of the ring system, and the bottom structure (vii) depicts the methyl ether/*tert*-butyl interactions when both occupy the same side of the six-membered-ring chelate. In the boat transition structures, the methyl ether resides on the same side as phenyl, and thus proximal and distal describe also the methyl ether/*tert*-butyl moiety relative orientations. In the chair transition structures, the methyl ether resides on the side opposite the phenyl group, and thus proximal and distal describe the converse for the methyl ether/*tert*-butyl moiety relative orientations. Listed in Table 9 are some of the results of our computational studies.

Several generalizations can be made from the calculated transition structures (Figure 5, boats, and Figure 6, chairs). First, in all cases, the ketene acetal maintains the orientation in which the methyl ether is disposed away from the C(3) methyl group but still in the plane of the ketene acetal π system, the so-called "pinwheel effect".[47] Second, the starting orientation of the

Table 9. Results of Transition-State Computational Studies

starting geometry	transition-state energy (kcal/mol)	TS $\Delta E^{\ddagger}_{rel}$	α	β (deg)	γ^a (Å)	δ (Å)
aBp	−128.54	5.83	e	−12.2	1.77, o	1.76
bBp	−133.38	0.99	e	−40.3	1.79, o	2.39
aBd	−133.35	1.02	e	+24.2	1.75, f	5.22
bBd	−134.37	0.00	s	+32.2	1.78, f	4.88
aCp	−133.69	0.68	s	−60.4	1.71, o	4.47
bCp	−134.27	0.10	e	−51.3	1.71, o	4.37
aCd	−132.37	2.00	e	+56.0	2.34, f	1.70
bCd	−133.23	1.14	e	+58.4	2.37, f	1.72

[a] The "o" denotes an ortho hydrogen on the aldehyde phenyl ring; an "f" denotes the formyl or aldehydic hydrogen.

aldehyde is an important factor. In all cases wherein the starting geometry involved an apical aldehyde, the resultant transition state had a higher energy than when starting from the corresponding geometry with a basal aldehyde. This observation suggests that a *basal* aldehyde orientation is preferred in the transition state.[12b]

Orientation of the methyl ether proximal to the *tert*-butyl substituent results in an approximately 1.0 kcal/mol energy penalty over the distal orientation (compare bBd/bBp or bCp/bCd); the energy cost of the phenyl and *tert*-butyl moiety being proximal seems to be insignificant in comparison (compare bBd/bCp). If we compare directly the two lowest transition states resulting from starting geometries bBd and bCp, we see that for bBd both the values for γ and δ indicate less interaction (distance) between the *tert*-butyl substituent and either the methyl ether or the aldehyde. Therefore, the *tert*-butyl substituent is an important

(47) Wilcox, C. S.; Babston, R. E. *J. Org. Chem.* **1984**, *49*, 1451.

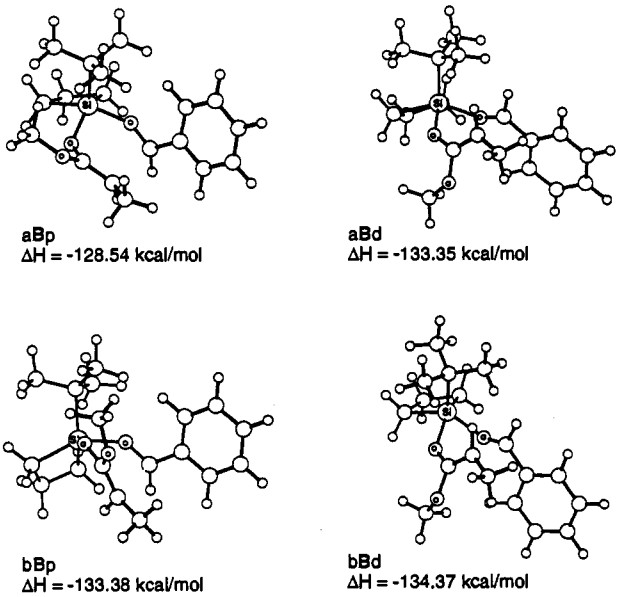


Figure 5. Calculated boat-like transition structures for reaction of (*E*)-4 and benzaldehyde.

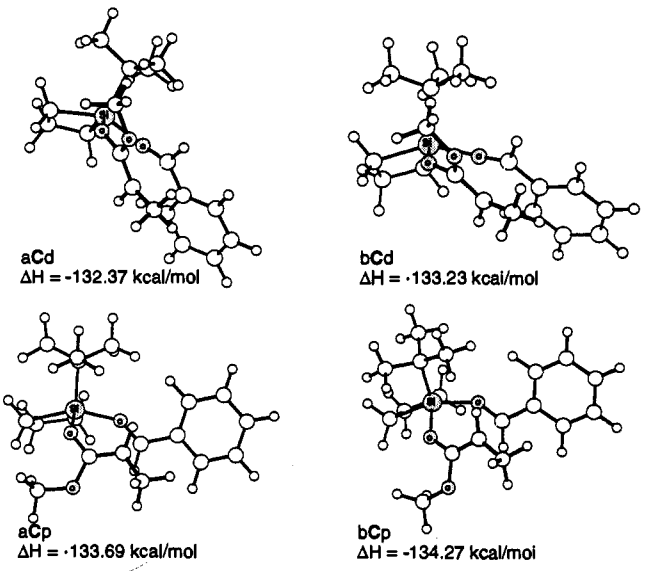


Figure 6. Calculated chair-like transition structures for reaction of (*E*)-4 and benzaldehyde.

steric parameter in the energy of the transition states. Having a methyl group of the *tert*-butyl substituent directly over the silacyclobutane ring (staggered, see Chart 5) seems to lend some energy savings in the boat conformations (compare aBd with bBd); however, such an orientation for the chair conformation does not seem to impart any lowering of overall energy (compare aCp/bCp and note identical γ values). For the chairs, having the phenyl and *tert*-butyl moieties distal serves only to orient the methyl ether and *tert*-butyl moieties proximal, which invokes a higher energy penalty.

If we consider boat and chair conformations in general, we see that two boat conformations can allow for both the phenyl and ketene acetal C(3) methyl to be distal to the *tert*-butyl moiety. In the chair conformations there must *always* be either a phenyl or a ketene acetal C(3) methyl steric interaction with the *tert*-butyl moiety, which may account for the inaccessibility of a true chair conformation. The lowest energy boat, bBd, displays a 32.2° staggering of the phenyl and ketene acetal C(3) methyl groups. Comparison of the values for γ shows that although the chair conformations can allow the phenyl group to be distal to the *tert*-butyl moiety in two of the cases, in the lowest energy chair the closest contact interaction is actually *worse* than in the lowest energy boat.

Discussion

Enoxysilacyclobutanes. The preparation of enoxysilacyclobutanes follows in direct analogy to that of conventional enoxysilanes. Silacyclobutyl chlorides tend to be more reactive than their dimethylsilyl chloride counterparts. In addition, we have found that the less sterically demanding silacyclobutyl chlorides, *e.g.* **1b** and **1f**, give proportionately more *C*-silylation in their reaction with ester enolates. This undesirable side reaction can usually be overcome by the use of polar cosolvents. Also, these less sterically congested silacyclobutyl chlorides were found to react competitively with diisopropylamine in the presence of preformed enolates. This problem could be overcome by the use of lithium tetramethylpiperidide in the enolization event.

Aldol Reaction. In every case examined, the enoxysilacyclobutanes underwent uncatalyzed aldol addition (except compound **8**, Table 1, entry 4) with aldehydes, albeit at drastically variable rates. Moreover, with the exception of the *N,O*-ketene acetals, the corresponding acyclic silicon derivatives failed to react at all. The origin of this reactivity is intriguing and may be rationalized by considering both the geometric constraints and electronic structure of the silacyclobutane ring system.

The high reactivity of silacyclobutanes toward nucleophiles has been well documented,[21,24,48] and the structure of the silacyclobutane ring system has been studied spectroscopically[25a,49] as well as computationally.[50] The C–Si-C bond angle for these systems is approximately 80°, and the strain energies of silacyclobutanes have been calculated to be quite high. The current consensus for the enhanced reactivity of silacyclobutanes identifies the ability of silicon to rehybridize. Specifically, for silacyclobutanes, the reaction with nucleophiles allows for relief of the strain energy via rehybridization of the geometry at silicon from tetrahedral to trigonal bipyramidal upon formation of a pentacoordinate species. This reorganization allows the four-membered ring to span one apical and one basal position, thus relieving the strain. In addition, studies on the electronic nature of silacyclobutane ring systems suggest that there is a lowering in energy of the LUMO compared to cyclobutanes.[51]

Clearly from the above results, incorporation of a silacyclobutane moiety into enoxysilanes imparts strain energy sufficient to allow the aldol reaction with aldehydes. The dramatic rate effects observed in the aldol reaction when the ketene acetal geometry or substituents are varied (Table 1) suggest that an associative (pericyclic) reaction mechanism and thus entropically demanding transition states are involved. The steric limits for the *O,O*-ketene acetal system were delineated with acetals **5-8** (Table 1, entries 1–4). Small groups on silicon can accommodate the increase in steric interactions that attend the change in coordination number from 4 to 5, thus giving rise to greatly enhanced reaction rates.

In evaluating the reactivity of enoxysilacyclobutanes, the primary consideration is the choice of enolate derivative. The spectrum of this reactivity is defined by simple ketone enolsilanes as the least reactive and ketene aminals as the most reactive. We have found that a balance of high reactivity and selectivity can be obtained by using *O,O*-ketene acetals in the thermal aldol reaction. The second factor to consider is the environment at silicon. There is a clear manifestation of electronic and steric influences of the substituent at silicon in enoxysilacyclobutane aldol reactions with aldehydes. In the *O,O*-ketene acetal rate study (Table 1) the larger the substituent on silicon, the slower

(48) (a) Matsumoto, K.; Aoki, Y.; Oshima, K.; Utimoto, K. *Tetrahedron* **1993**, *49*, 8487. (b) Matsumoto, K.; Miura, K.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1991**, *32*, 6383.

(49) (a) Laane, J.; Lord, R. C. *J. Chem. Phys.* **1968**, *48*, 1508. (b) Laane, J. *Spectrochim. Acta* **1970**, *26A*, 517. (c) Aleksanyan, V. T.; Kuz'yants, G. M.; Vdovin, V. M.; Grinberg, P. L.; Kuz'min, O. V. *J. Struct. Chem.* **1969**, *10*, 397.

(50) Boatz, J. A.; Gordon, M. S.; Hilderbrandt, R. L. *J. Am. Chem. Soc.* **1988**, *110*, 352.

(51) Krapivin, A. M.; Măgi, M.; Svergun, V. I.; Zaharjan, R. Z.; Babich, E. D.; Ushakov, N. V. *J. Organomet. Chem.* **1980**, *190*, 9.

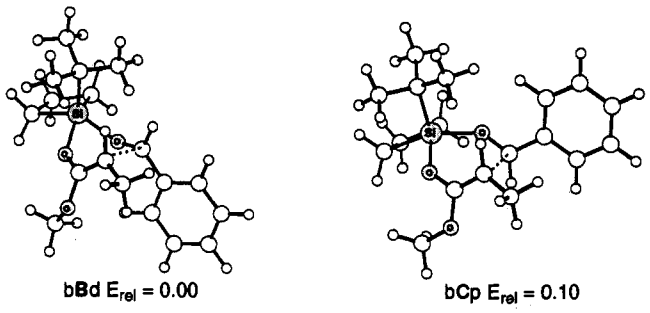


Figure 7. Lowest energy calculated boat-like and chair-like transition structures.

the reaction. There does seem to be an electronic factor involving the substituent at silicon as well. For example the *S,O*-ketene acetals substituted with alkyl groups (methyl or *tert*-butyl) reacted sluggishly or not at all with benzaldehyde; while the phenyl silyl analog **9** did react at room temperature.

Enolate geometry also has important consequences with regard to the reactivity of enoxysilacyclobutanes. For example, although *(E)*-**4** reacted 600 times faster than the presumably more stable *(Z)*-**4**, the more sterically demanding α-disubstituted analog **6** was found to be 10 times more reactive than *(Z)*-**4**. Presumably, the extra methyl group on **6** makes this acetal more electron rich and thus more reactive than *(Z)*-**4**. This observation might also be explained by the assumption that the thermodynamic stability of **6** is probably more similar to that of *(E)*-**4** rather than *(Z)*-**4**. The nature of the aldehyde has dramatic consequences on the rate of reaction for all of the enoxysilacyclobutanes studied. The more basic and less hindered aldehydes reacted faster.

Finally, solvent studies revealed that aromatic solvents seemed to give the fastest rates in most cases. We believe that in chloroform adventitious catalysis is taking place, given the difficulty in removing acidic species. We have demonstrated the high reactivity of enoxysilacyclobutanes, and any trace amounts of acidic impurities would likely accelerate the aldolization event.

Mechanism and Diastereoselectivity for the Thermal Aldol Reaction. The thermal aldol reaction of enoxysilacyclobutanes with aldehydes proceeds via direct intramolecular silicon group transfer, a fact that strongly implicates the intermediacy of pentacoordinate trigonal bipyramidal silicon. Our results are in accord with those of Myers,[12] which advocate not only the intermediacy of trigonal bipyramidal silicon but also a pseudorotational mechanism in silicon-directed aldol reactions.

The computational studies provided clues to the origin of the diastereoselectivity for the silacyclobutyl *O,O*-ketene acetals. Of primary importance is orientation of the silacyclobutane ring and the spectator (*tert*-butyl) substituent relative to the enol moiety and aldehyde. The steric contributions from each of these factors ultimately determine the relative energies for the transition structures.

Although the calculated heats of formation for the lowest energy chair and boat transition structures that were located are within 0.1 kcal/mol, the identification of the key contributing factors as discussed above provides valuable insights for explaining the observed *syn* selectivity. Shown in Figure 7 are the lowest boat (bBd) and chair (bCp) transition-state structures. The structures shown are Chem3D representations of the MOPAC-optimized geometries. The salient features of the boat transition structure are the following: (1) the boat has the phenyl, α-methyl, and methyl ether moieties all oriented distally with respect to the *tert*-butyl moiety, as would be expected considering the steric importance of the *tert*-butyl moiety, (2) the α-methyl and phenyl moieties are gauche, with a dihedral angle of 32.2°, (3) the C(1)-O-CH_3 bond angle of the ketene acetal is 118.4°,[52] but interestingly the methyl ether is bent out of the plane of the ketene acetal π system by 23.0°, and (4) one of the methyl groups of the *tert*-butyl moiety is directly over the silacyclobutane ring, which allows the α-hydrogen of the ketene acetal to point in between the other two methyl groups. The salient features of the chair transition structure are the following: (1) the chair has the α-methyl and methyl ether moieties oriented distally to the *tert*-butyl moiety, but the phenyl is proximal, (2) the interaction of the phenyl ring with the *tert*-butyl moiety leaves one of its methyl groups disposed 39.4° away from the silacyclobutane ring while another *directly eclipses* one of the silacyclobutane ring Si–C bonds, (3) the α-methyl and phenyl moieties are staggered, with a dihedral angle of 51.3°, and (4) the C(1)-O-CH_3 bond angle of the ketene acetal is 119.3°, but in this case the methyl ether deviates from the plane of the ketene acetal π system by only 0.5°.

The fundamental difference between these boat and chair systems and those of group I, II, or III metal enolates is that they contain a pentacoordinate metal atom, rather than the traditional four-coordinate metal center. The reasons for the normal preference for chair-like structures in idealized Zimmerman–Traxler closed transition states (primarily avoidance of vicinal nonbonding interactions) most certainly do apply here. However, these calculations have identified additional nonbonding interactions of the enolate and aldehyde partners with the spectator (*tert*-butyl group) on the silicon atom. Thus, in these systems, the unfavorable eclipsing interactions in conventional boat transition states do not constitute an extreme energy penalty where other more important steric interactions may dominate.

In his early analysis of closed aldol addition reactions, Evans considered the possible intervention of boat-like transition structures in the enolate-geometry-independent *syn*-selective reactions of zirconium enolates.[53] Evans has postulated that the acute O–Zr–O bond angle and the bulk of the cyclopentadienyl rings in the five-coordinate, 18-electron zirconium enolate/aldehyde complexes severely distort the chelated transition state in an aldol reaction. Our calculated transition structures for five-coordinate silicon bear striking resemblance to the transition structures proposed in the zirconium systems in that the silicon provides a similar distorting element.

The insights provided by this modeling study highlight the *nature* of the interactions involved and not necessarily their magnitude. Also it is clear that we can eschew the conventional wisdom for evaluation of the steric interactions in closed six-membered transition states in such systems.

Catalyzed Aldol Additions. Our crossover studies of the alkoxide-catalyzed aldol addition reaction of enoxysilacyclobutanes suggest that free metal enolates are the true reactive species adding to the aldehydes. The hoped-for hexacoordinate siliconates bearing the aldehyde, enolsilane, and the catalyst were thus not putative intermediates as was found in nucleophile-promoted allylations. Even when a less nucleophilic, more stabilized alkoxide (such as lithium phenoxide) was used, the reaction rate merely slowed, requiring higher temperatures, and resulted in complete scrambling in the crossover test. Attempts to further stabilize the putative hexacoordinate siliconate species by attachment of the more electron withdrawing *tert*-butoxy moiety also failed, as did promotion with nonanionic nucleophiles. Although we were not able to demonstrate asymmetric catalysis with enoxysilacyclobutane systems, we have found an efficient catalytic system which is not accessible with conventional enoxysilanes and offers an alternative to the Lewis acid-catalyzed systems. The catalytic cycle is most likely similar to that proposed by Noyori for fluoride-catalyzed reactions of enol silanes.[4]

Michael Addition Studies. From the uncatalyzed reactions performed using (*E*)-**4** and **5** with α,β-unsaturated carbonyl compounds, it is evident that the 1,2-addition reaction is the favored reaction pathway. This is a consequence of the direct silicon group transfer: a 1,2-addition process occurs via a six-membered transition state, which would be anticipated to be more

(52) All eight transition-state structures deviate no more than 1.6° from the ideal 120° angle, as would be expected for the "pinwheel" effect in ketene acetals; see ref 47.

(53) Evans, D. A.; McGee, L. R. *Tetrahedron Lett.* **1980**, *21*, 3975.

energetically accessible than the eight-membered transition state necessary for the conjugate addition process to occur. The fact that no reaction was observed with methyl acrylate, a species where a 1,2-addition reaction cannot occur, may indicate that in the trigonal bipyramid assembly it is not possible to arrange the α,β-unsaturated ester and silyl ketene acetal into the requisite eight-membered ring. However, it should be noted that cyclic transition states of this type have been proposed for the group transfer polymerization process.[54]

Complexation Studies. The documentation of an uncatalyzed aldol reaction using enoxysilacyclobutanes supports the notion of "strain release Lewis acidity" associated with a silacyclobutane. However, this Lewis acidic property was not spectroscopically detectable in the complexation of aldehydes to a variety of silacyclobutanes. The disappearance of the initially observed shifts for the bis(triflate) **1j** on the introduction of a substoichiometric quantity of a sterically hindered base indicated the effect was a spurious consequence of the presence of triflic acid.

To reconcile the observed rate enhancement for uncatalyzed aldol additions with enoxysilacyclobutanes and their, at best, modest Lewis acidity requires that the intermediate pentacoordinate complexes be formed in trace amounts. However, due to the simultaneous electronic activation of both partners (partially negative silicon and partially positive carbonyl oxygen) and concatenation of the reactive centers, reaction takes place uniquely and selectively from this complex. Thus, while traditionally, Lewis acid-activated termolecular processes are not suitable candidates for study, many other reactions of organosilanes can conceivably benefit from the special opportunities offered by replacement of the silicon moiety with a silacyclobutyl group.

Summary

We have demonstrated that enoxysilacyclobutanes derived from esters and thiol esters engage in uncatalyzed, *syn*-selective aldol additions with a range of aldehydes at ambient temperatures. From double-label crossover experiments we have shown unambiguously that this thermal aldol reaction proceeds via direct intramolecular silicon group transfer. Modeling studies suggest (and the stereochemical consequences require) that the boat transition state is preferred over the chair, which explains the origin of the diastereoselectivity. A unique catalytic reaction for enoxysilacyclobutanes has been demonstrated; however, attempts at asymmetric catalysis have thus far been unsuccessful. Complexation studies of silacyclobutanes with aldehydes revealed no spectroscopically detectable coordinated species. Michael addition reaction studies showed a clear competition between 1,2- and 1,4-addition modes. Silacyclobutanes hold promise for future carbon–carbon bond forming strategies, which potentially involve the intermediacy of hypervalent silicon.

Experimental Section

General. (See the supplementary material.)

Preparation of 1,1-Dichlorosilacyclobutane (1a) and 1-Chloro-1-methylsilacyclobutane (1b). 1,1-Dimethylsilacyclobutane and 1-chloro-1-methylsilacyclobutane were prepared following a procedure by Laane[25a] and using a modification of a procedure of Brown[25c] for the activation of the magnesium metal. The general procedure is as follows: Magnesium (50 g, 2.06 mol, Aldrich 50 mesh) was placed in a 3-L, three-neck, round-bottomed flask with a mechanical stirrer fitted with a large Teflon paddle. The magnesium was stirred under nitrogen for at least 8 h or until a finely divided black powder was formed. It is important that the Teflon paddle gently scrapes the magnesium against the inner surface of the flask and that one does not use too much nitrogen pressure (*i.e.* mercury bubbler) on the flask, as this will drive the finely divided magnesium into the stirring mechanism. After activation of the magnesium was complete, the stirrer was stopped momentarily while the flask was fitted with a reflux condenser and a 250-mL pressure-equalizing addition funnel. The stirrer was then restarted, and 250 mL of anhydrous diethyl ether was added along with ~0.5 g of iodine crystals. The ether/magnesium slurry was brought to reflux, and 100 g (0.47 mol) of (3-chloropropyl)-trichlorosilane (Huls America) was added over 30 min via an addition funnel. The reaction began to thicken after 1–3 h, and an additional 500 mL of ether was added. The reaction was stirred for 3 days, and ether was added (for a total of 2.0–2.5 L) periodically as the reaction became very thick. After 3 days the reaction was allowed to cool to room temperature, and the magnesium chloride/excess magnesium was removed via suction filtration through a large sintered-glass funnel. Fractional distillation of the filtrate provided 44 g (66%) of **1a** (bp 110–114 °C) as a clear slightly pink (trace iodine) liquid. 1-Chloro-1-methylsilacyclobutane **1b** (bp 102–104 °C) was prepared using the same general procedure starting with (3-chloropropyl)dichloromethylsilane (Aldrich); the yield for this reaction was generally 50–65%.

Preparation of 1-(*N,N*-Dimethylamino)-1-methyl-d_3-silacyclobutane (d_3-1l). In a flame-dried 250-mL, three-neck, round-bottomed flask equipped with a stir bar, internal thermometer, and a 50-mL pressure-equilibrating addition funnel under N_2 was placed 1-chloro-1-(*N,N*-dimethylamino)silacyclobutane[26] (6.7 g, 45 mmol, 1.0 equiv) via syringe. Dry THF (100 mL) was added via syringe, and the solution was cooled to −15 °C (internal). Slowly, via a pressure-equilibrating addition funnel was added methyl-d_3 magnesium iodide (49.2 mL, 49 mmol, 1.1 equiv, Aldrich 1.0 M) in diethyl ether, maintaining the internal temperature at −15 °C. After complete addition, the reaction was allowed to slowly warm to room temperature. The reaction was then recooled to 0 °C before filtration with a Schlenk tube (medium porosity frit) to remove the magnesium salts. The filtrate was then fractionally distilled to afford 3.72 g (63%) of d_3-**1l** as a clear colorless oil: bp 135 °C; ^{1}H NMR (400 MHz) δ 2.58 (s, 6H, $(CH_3)_2$N), 1.90 (m, 1H), 1.50 (m, 1H), 1.25 (m, 2H), 1.02 (m, 2H); ^{13}C NMR (100.6 MHz) δ 37.8 ($(CH_3)_2$N), 17.8 (CH_2), 13.7 (CH_2); IR (neat) 2961 (s), 2930 (s), 2863 (s), 2793 (s), 1464 (m), cm^{-1}. Anal. Calcd for $C_6H_{12}D_3SiN$: C, 54.47; H, 11.43; N, 10.59. Found: C, 54.34; H, 11.49; N, 10.58.

Preparation of 1-Chloro-1-methyl-d_3-silacyclobutane (d_3-1b). In a flame-dried 50-mL two-neck, round-bottomed flask equipped with a stir bar and reflux condenser was placed 1-(*N,N*-dimethylamino)-1-methyl-d_3-silacyclobutane (4.23 g, 32.0 mmol, 1.0 equiv) via syringe, followed by 25 mL of dry pentane. Slowly, via syringe was added dichlorophenylphosphine (6.94 mL, 51.2 mmol, 1.6 equiv, Aldrich). A white precipitate was noted, and after complete addition the reaction mixture was refluxed for 1 h before cooling to room temperature. The volatile pentane/silylchloride mixture was removed *in vacuo* (0.03 Torr, until the reaction flask had warmed to room temperature, and then 20 min more) and trapped with a liquid N_2 trap, leaving the less volatile by-products behind. The pentane/silylchloride mixture was fractionally distilled to afford 2.9 g (73%) of d_3-**1b** as a clear colorless oil: bp 103–106 °C; ^{1}H NMR (400 MHz) δ 2.22 (m, 1H), 1.96 (m, 1H), 1.44 (m, 4H); ^{13}C NMR (100.6 MHz) δ 20.6 (CH_2), 15.8 (CH_2); IR (neat) 2934 (m), 2874 (m) m^{-1}; FIMS at 25 °C *m/z* (M^+, 123). Anal. Calcd for $C_4H_6D_3SiCl$: C, 38.85; H, 7.34; Cl, 28.67. Found: C, 38.84; H, 7.37; Cl, 28.49.

Preparation of 1-Chloro-1-(1,1-dimethyl-d_9-ethyl)silacyclobutane (d_9-1d). In a flame-dried 250-mL, three-neck, round-bottomed flask equipped with a stir bar and internal thermometer was added 1,1-dichlorosilacyclobutane (6.3 g, 45 mmol, 1.5 equiv) followed by 160 mL of dry THF via syringe. The reaction mixture was cooled to −78 °C and slowly *tert*-butyl-d_9-lithium (28 mL, 30 mmol, 1.07 M in pentane) was added via syringe pump over a 2-h period. A localized yellow color formed as each drop of *tert*-butyllithium was added; the color quickly faded early in the addition process, and as the end of the addition was reached, the color persisted for longer periods. After complete addition the reaction was allowed to slowly warm to room temperature (without removal of the cooling bath). The THF was removed by distillation, and the product/LiCl slurry was triturated with 50 mL of dry pentane. The LiCl was removed by filtration of the slurry with a Schlenk tube (medium porosity frit) and the pentane removed *in vacuo* (100 Torr). The resulting clear colorless oil was distilled *in vacuo* to afford 4.44 g (87%) of d_3-**1d** as a clear colorless oil: bp 95 °C (90 Torr); ^{1}H NMR (400 MHz) δ 2.20 (m, 1H), 1.92 (m, 1H), 1.44 (m, 4H); ^{13}C NMR (100.6 MHz) δ 17.3 (CH_2), 15.9 (CH_2); IR (neat) 2979 (m), 2934 (m), 2876 (w), cm^{-1}; FIMS at 25 °C *m/z* (M^+, 171). Anal. Calcd for $C_7H_6D_9SiCl$: C, 48.94; H, 8.80; Cl, 20.64. Found: C, 48.97; H, 8.86; Cl, 20.60.

Preparation of 1-Chloro-1-(1,1-dimethylethoxy)silacyclobutane (1f) and 1-Chloro-1-(1,1-dimethyl-d_9-ethoxy)silacyclobutane (d_9-1f). In a flame-dried, 250-mL, round-bottomed flask was weighed 1,1-dichlorosilacyclobutane (**1a**) (5.0 g, 35.4 mmol), and the chlorosilane was diluted with 100 mL of dry methylene chloride. A few crystals of 4-(*N,N*-

(54) Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1983**, *105*, 5706.

dimethylamino)pyridine were added, the solution was chilled to 0 °C, and *N,N*-dimethylaniline (4.5 mL, 35.4 mmol, freshly distilled over CaH_2) was added slowly via syringe. Finally, freshly distilled *tert*-butyl alcohol (3.35 mL, 35.4 mmol (or the equivalent amount of *tert*-butyl-d_9 alcohol)) was added as a solution in 6 mL of methylene chloride slowly over a 20-min period (syringe pump). After complete addition the reaction was stirred for 12 h, allowing the reaction to slowly warm to room temperature over that period. The methylene chloride was distilled off, and to the slurry of salts was added 50 mL of dry pentane. The salts were removed via Schlenk filtration, and the pentane solution was concentrated to give a clear colorless oil. After a short time, white needles formed in the crude oil, and it was triturated with an additional 20 mL of dry pentane with removal of the needles via filtration. The pentane was removed via distillation to provide a clear colorless oil. Kugelrohr distillation provided 5.2 g (83%) of **1f** as a clear colorless oil.

1-Chloro-1-(1,1-dimethylethoxy)silacyclobutane (1f). bp 70 °C (15 Torr); ^{1}H NMR (400 MHz) δ 1.60 (m, 6H), 1.24 (s, 9H); ^{13}C NMR (100.6 MHz) δ 76.3 ($(CH_3)_3C$), 31.6 ($(CH_3)_3C$), 26.6 (CH_2), 12.7 (CH_2); IR (neat) 2979 (s), 2932 (m), 2874 (m) cm^{-1}; FIMS at 100 °C *m/z* (M^+, 178). Anal. Calcd for $C_7H_{15}ClOSi$: C, 47.04; H, 8.46. Found: C, 47.38; H, 8.55.

1-Chloro-1-(1,1-dimethyl-d_9-ethoxy)silacyclobutane (d_9-1f). From 6.9 g (48.7 mmol) of 1,1-dichlorosilacyclobutane, 6.2 mL (48.7 mmol) of *N,N*-dimethylaniline, and 4.05 g (48.7 mmol) of *tert*-butyl-d_9 alcohol was obtained 7.7 g (84%) of d_9-**1f** after distillation: bp 70 °C (15 Torr); ^{1}H NMR (400 MHz) δ 1.60 (m, 6H); ^{13}C NMR (100.6 MHz) δ 26.6 (CH_2), 12.7 (CH_2); IR (neat) 2982 (m), 2936 (m), 2874 (m), 2230 (s) cm^{-1}; FIMS at 25 °C *m/z* (M^+, 187). Anal. Calcd for $C_7H_6D_9ClOSi$: C, 44.77; H, 8.05. Found: C, 45.10; H, 8.21.

Preparation of 1,1-Diphenoxysilacyclobutane (1g). A solution of 1,1-dichlorosilacyclobutane (1.17 g, 8.29 mmol) in dry dichloromethane (8 mL) was added dropwise to a stirred solution of phenol (1.56 g, 16.58 mmol), pyridine (1.34 mL, 1.31 g, 16.58 mmol) and a catalytic amount of DMAP in dry dichloromethane (32 mL) at 0 °C under an atmosphere of nitrogen over a period of 0.75 h. The resultant white suspension was allowed to warm to room temperature slowly and then stirred for *ca.* 10 h. The solvent was evaporated *in vacuo* and the residue suspended in dry hexane (30 mL). After stirring for 30 min the white suspension was filtered via a Schlenk tube and the clear filtrate evaporated. Recrystallization of the residue from pentane afforded 1.16 g (55%) of **1g** as a white solid: mp 45–47 °C; ^{1}H NMR (400 MHz) δ 7.31–7.24 (m, 2H, *H*Ar), 7.07–6.96 (m, 3H, *H*Ar), 1.87–1.76 (m, 2 H, CH_2), 1.74–1.67 (m, 4H, 2 × CH_2); ^{13}C NMR (100 MHz) δ 153.25 (*C*(Ar)), 129.62 (*C*H-(Ar)), 122.39 (*C*H(Ar)), 119.67 (*C*H(Ar)), 21.53 (C(2,4)), 11.61 (C(3)); IR (KBr disc) 1595 (s), 1491 (s) cm^{-1}; MS (70 eV) *m/z* 257 (M^+ + 1, 28), 256 (M^+, 100). Anal. Calcd for $C_{15}H_{16}O_2Si$: C, 70.27; H, 6.29. Found: C, 69.92; H, 6.36.

Preparation of Spiro[dibenzo(*d,f*)(1,3,2)dioxasilepin-2,1′-silacyclobutane] (1h). A solution of 1,1-dichlorosilacyclobutane (0.515 g, 3.64 mmol) in dry dichloromethane (5 mL) was added dropwise to a stirred solution of 2,2′-dihydroxybiphenyl (0.679 g, 3.64 mmol), pyridine (0.59 mL, 0.576 g, 7.28 mmol), and a catalytic amount of DMAP in dry dichloromethane (30 mL) at 0 °C under an atmosphere of nitrogen. The reaction mixture was allowed to warm to room temperature slowly and then stirred for *ca.* 11 h. The solvent was evaporated *in vacuo* and the residue suspended in dry hexane (25 mL). The white suspension was stirred for 0.5 h and then filtered via a Schlenk tube. The clear filtrate was evaporated *in vacuo* and then transferred to a Kugelrohr bulb via a cannula using dry hexane (*ca.* 2 mL). The solvent was removed and the residue distilled to afford 0.572 g (62%) of **1h** as a thick colorless oil: bp 180–185 °C (0.5 Torr); ^{1}H NMR (400 MHz) δ 7.50–7.41 (m, 2H, *H*Ar), 7.40- 7.31 (m, 2H, *H*Ar), 7.25 -7.18 (m, 2H, *H*Ar), 7.15–7.10 (m, 2H, *H*Ar), 2.00–1.83 (m, 2H, CH_2), 1.80–1.68 (m, 2H, 2 × CH_2); ^{13}C NMR (100 MHz) δ 150.98 (*C*(Ar)), 131.11 (*C*H(Ar), 129.77 (*C*(Ar)), 129.21 (*C*H(Ar)), 123.59 (*C*H(Ar)), 121.03 (*C*H(Ar)), 22.13 (C(2,4)), 11.06 (*C*(3)); IR (neat) 3063 (m), 3026 (m), 2934 (m), 2870 (m), 1564 (s), 1497 (s), 1478 (s), 1437 (s) cm^{-1}; MS (70 eV) *m/z* 255 (M^+ + 1, 26), 254 (M^+, 100). Anal. Calcd for $C_{15}H_{14}O_2Si$: C, 70.83; H, 5.55. Found: C, 70.67; H, 5.52.

Preparation of 1-Methyl-1-[(trifluoromethyl)sulfonyl]silacyclobutane (1i). A solution of 1-chloro-1-methylsilacyclobutane **1b** (0.917 g, 7.60 mmol) in dry dichloromethane (2 mL) was added dropwise to a stirred suspension of silver triflate (1.95 g, 7.60 mmol) in dry dichoromethane (10 mL) at room temperature under an atmosphere of nitrogen and protected from the light. The reaction mixture was allowed to stir for *ca.* 18 h and then filtered through a plug of oven-dried Celite under an atmosphere of nitrogen. The solvent was removed by distillation at atmospheric pressure and the residue transferred via a cannula to a Kugelrohr bulb. Distillation afforded 0.784 g (44%) of **1i** as a pale brown liquid: bp 80–85 °C (50 Torr); ^{1}H NMR (400 MHz) δ 2.30–2.16 (m, 1H, C*H*), 2.06–1.93 (m, 1H, C*H*), 1.72–1.62 (m, 2H, 2 × C*H*), 1.52–1.40 (m, 2H, 2 × C*H*), 0.69 (s, 3H, CH_3); ^{13}C NMR (100.7 MHz) δ 118.29 (q, *J* = 318, CF_3), 19.30 (*C*(2,4)), 14.66 (*C*(3)), 0.66 (CH_3); ^{19}F NMR (376.3 MHz) δ -77.92 (CF_3).

Preparation of 1,1-Bis[(trifluoromethyl)sulfonyl]silacyclobutane (1j). A solution of 1,1-dichlorosilacyclobutane (**1a**) (1.286 g, 9.18 mmol) in dry dichloromethane (2 mL) was added dropwise to a stirred suspension of silver triflate (4.72 g, 18.36 mmol) in dry dichloromethane (10 mL) at 0 °C under an atmosphere of nitrogen. The resultant suspension was shielded from the light, allowed to warm to room temperature slowly, and stirred overnight (*ca.* 18 h). The reaction mixture was filtered through a plug of oven-dried Celite under an atmosphere of nitrogen and the plug washed with dichloromethane (5 mL). The solvent was removed by distillation at atmospheric pressure and the residue transferred via a cannula to a Kugelrohr bulb. Distillation afforded 1.615 g (48%) of **1j** as a pale yellow liquid: bp 85–90 (1 Torr); ^{1}H NMR (400 MHz) δ 2.22–2.10 (m, 6H, 3 × CH_2); ^{13}C NMR (100.6 MHz) δ 118.11 (q, *J* = 318, CF_3), 24.56 (*C*(2,4)), 11.40 (*C*(3)); ^{19}F NMR (376.3 MHz) δ -77.18 (CF_3).

Preparation of 1-(1-Cyclohexenyloxy)-1-methylsilacyclobutane (2) and (*Z*)-1-[(1-(1,1-Dimethylethyl)propenyl)oxy]-1-methylsilacyclobutane (3). A solution of *n*-butyllithium in hexanes (14.3 mL, 2.11 M solution, 29.6 mmol, 1 equiv) was added dropwise to a stirred solution of 2,2,6,6,-tetramethylpiperidine (5 mL, 29.6 mmol, 1 equiv) in dry THF (45 mL) at 0 °C under an atmosphere of nitrogen. After stirring for 30 min at 0 °C the clear solution was cooled to −78 °C and stirred for an additional 15 min. A solution of the ketone (29.6 mmol) in dry THF (10 mL) was added dropwise over a period of 10 min. After 10 min at −78 °C, 1-methyl-1-chlorosilacyclobutane (3.8 g, 32.0 mmol, 1.05 equiv) was added dropwise. The resulting clear solution was allowed to warm very slowly to 25 °C over a 3 h period. The clear solution was evaporated *in vacuo* and the residue suspended in dry hexane (50 mL). After being stirred for 1 h at 25 °C, the white suspension was filtered with a Schlenk tube and the clear filtrate evaporated *in vacuo*. The clear, slightly yellow oil was transferred via cannula to an assembled Kugelrohr apparatus and distilled to afford the enol silane as a clear colorless oil.

1-(1-Cyclohexenyloxy)-1-methylsilacyclobutane (2). From 2.96 g (30 mmol) of cyclohexanone, 4.4 g (30 mmol) of lithium tetramethylpiperidide, and 3.80 g (30 mmol) of 1-chloro-1-methylsilacyclobutane (**1b**) was obtained 4.2 g (84%) of **2** after distillation: bp 53–55 °C (0.03 Torr); ^{1}H NMR (400 MHz) δ 4.95 (t, *J* = 3.6, 1H, *H*C(2)), 2.05 (m, 6H), 1.69–1.50 (m, 4H), 1.35 (m, 2H), 1.18 (m, 2H), 0.33 (s, 3H, H_3CSi); ^{13}C NMR (75.5 MHz) δ 149.93 (C(1)), 104.69 (C(2)), 29.72, 23.73, 23.04, 22.23, 19.05, 13.55, −1.50; IR (neat) 2930 (s), 1671 (s) cm^{-1}. Anal. Calcd for $C_{10}H_{18}OSi$: C, 65.87; H, 9.55. Found: C, 65.85; H, 10.04.

(*Z*)-1-[(1-(1,1-Dimethylethyl)propenyl)oxy]-1-methylsilacyclobutane (3). From 3.38 g (29.6 mmol) of 2,2-dimethyl-3-pentanone, 4.35 g (29.6 mmol) of lithium tetramethylpiperidide, and 3.80 g (29.6 mmol) of 1-chloro-1-methylsilacyclobutane (**1b**) was obtained 4.2 g (72%) of **3** after distillation: bp 60 °C (0.03 Torr); ^{1}H NMR (300 MHz) δ 4.65 (q, *J* = 6.8, 1H, *H*C(2)), 2.00 (m, 2H), 1.51 (d, *J* = 6.8, 3 H, H_3C(3)), 1.50–1.15 (m, 4H), 1.05 (s, 9H, $(H_3C)_3C$), 0.31 (s, 3H, H_3CSi); ^{13}C NMR (75.5 MHz) δ 158.78 (C(1)), 97.99 (C(2)), 36.03 (CH_2), 28.36 ($(CH_3)_3C$), 20.75 (*C*(3)), 12.63 (CH_3Si), 11.56 (CH_2), −2.06 ($C(CH_3)_3$); IR (neat) 2967 (s), 1667 (s) cm^{-1}. Anal. Calcd for $C_{11}H_{22}OSi$: C, 66.60; H, 11.18. Found: C, 66.76; H, 11.20.

Preparation of (*E*)-1-[(1-Methoxy-1-propenyl)oxy]-1-(1,1-dimethylethyl)silacyclobutane ((*E*)-4). A solution of *n*-butyllithium in hexanes (5.6 mL, 2.17 M, 12.1 mmol) was added dropwise to a stirred solution of diisopropylamine (1.7 mL, 12.1 mmol) in dry THF (40 mL) at 0 °C under an atmosphere of nitrogen. After being stirred for 20 min at 0 °C, the LDA solution was cooled to −78 °C and was stirred vigorously. Methyl propanoate (1.16 mL, *ca.* 1.06 g, 12.1 mmol) was added dropwise over a 10-min period, and the mixture was stirred an additional 30 min at −78 °C after complete addition. To the enolate solution was added 1-*tert*-butyl-1-chlorosilacyclobutane (2.0 g, 12.3 mmol) dropwise over a 5-min period. The reaction mixture was allowed to slowly warm to 25 °C over a 3-h period. The clear solution was evaporated *in vacuo* and the residue suspended in dry hexane (40 mL). After stirring for 1 h at 25 °C, the white suspension was filtered via a Schlenk tube and the clear filtrate evaporated *in vacuo*. The clear, slightly yellow oil was transferred via cannula to an assembled Kugelrohr apparatus and distilled to afford 1.8 g (72%) of the *O*-silyl *O,O*-ketene acetal (*E*)-**4** as a clear, colorless oil.

The *E* and *Z* isomers were identified by comparison to Ireland's NMR analysis.[30b] (*E*)-4: bp 50–55 °C (0.03 Torr); ^{1}H NMR (400 MHz) δ 3.79 (q, *J* = 6.6, 1 H, *H*C(2)), 3.57 (s, 3H, C*H*$_3$O), 2.20 (m, 1H), 1.64 (m, 1H), 1.52 (d, *J* = 6.6, 3H, *H*$_3$C(3)), 1.42 (m, 2H, C*H*$_2$), 1.29 (m, 2H, C*H*$_2$), 1.01 (s, 9 H, (C*H*$_3$)$_3$C); ^{13}C NMR (100.6 MHz) δ 153.62 (*C*(1)), 79.44 (*C*(2)), 54.75 (O*C*H$_3$), 24.99 ((*C*H$_3$)$_3$C), 15.19 (*C*H$_2$), 13.9 (*C*H$_2$), 9.36 (*C*(3)); IR (neat) 2930 (s), 2859 (s), 1688 (s) cm^{-1}; MS (10 eV) *m/z* 214 (M$^+$, 5), 101 (100); Anal. Calcd for $C_{11}H_{22}SiO_2$: C, 61.63; H, 10.34. Found: C, 61.66; H, 10.32.

Preparation of (*Z*)-1-[(1-Methoxy-1-propenyl)oxy]-1-(1,1-dimethylethyl)silacyclobutane ((*Z*)-4). A solution of *n*-butyllithium in hexanes (3.12 mL, 2.51 M, 7.83 mmol) was added dropwise to a stirred solution of diisopropylamine (1.1 mL, 7.83 mmol) in dry THF (10 mL) at 0 °C under an atmosphere of nitrogen. After being stirred for 20 min at 0 °C, tripiperidinephosphoric triamide (19.3 mL of a 2.44 M solution in THF, 47 mmol, 6 equiv) was added via syringe and the mixture stirred at 0°C for 20 min. The LDA/tripiperidinephosphoric triamide solution was cooled to −78 °C and was stirred vigorously. A solution of methyl propanoate (690 mg, 7.83 mmol) in THF (1 mL) was added dropwise over a 10-min period, and the mixture was stirred an additional 30 min at −78 °C after complete addition. To the enolate solution was added 1-*tert*-butyl-1-chlorosilacyclobutane (1.3 g, 7.99 mmol, 1.02 equiv) dropwise over a 5-min period. The reaction mixture was allowed to slowly warm to 25 °C over a 3-h period. The clear solution was evaporated *in vacuo* and the residue suspended in dry pentane (40 mL). After stirring for 1 h at 25 °C, the white suspension was filtered via a Schlenk tube and the clear filtrate evaporated *in vacuo*. The clear, slightly yellow oil was transferred via cannula to an assembled Kugelrohr apparatus and distilled to afford 785 mg (47%) of (*Z*)-4 as a clear, colorless oil; bp 45–50 °C (0.03 Torr); ^{1}H NMR (400 MHz) δ 3.55 (q, *J* = 6.8, 1 H, *H*C(2)), 3.52 (s, 3H, C*H*$_3$O), 2.00 (m, 1H), 1.62 (m, 1H), 1.52 (d, *J* = 6.8, 3 H, *H*$_3$C(3)), 1.32 (m, 4H), 1.01 (s, 9H, (*H*$_3$C)$_3$C); ^{13}C NMR (100.6 MHz) δ 156.5 (C(1)), 70.5 (C(2)), 54.7 (*C*H$_3$O), 25.0 ((*C*H$_3$)$_3$C), 15.9 (*C*H$_2$), 14.1 (*C*H$_2$), 9.6 (H$_3$*C*(3)); IR (neat) 2930 (s), 1686 (s) cm^{-1}; MS (70 eV) *m/z* 214 (M$^+$, 5), 101 (100). Anal. Calcd for $C_{11}H_{22}SiO_2$: C, 61.63; H, 10.34. Found: C, 61.31; H, 10.44.

Preparation of 1-[(1-Methoxy-2-methyl-1-propenyl)oxy]-1-methylsilacyclobutane (5), 1-[(1-methoxy-*d*$_3$-2-methyl-1-propenyl)oxy]-1-methyl-*d*$_3$-silacyclobutane (*d*$_6$-5), 1-[(1-methoxy-2-methyl-1-propenyl)oxy]-1-(1,1-dimethylethyl)silacyclobutane (6), 1-[(1-methoxy-*d*$_3$-2-methyl-1-propenyl)oxy]-1-(1,1-dimethyl-*d*$_9$-ethyl)silacyclobutane (*d*$_{12}$-6), 1-[(1-methoxy-2-methyl-1-propenyl)oxy]-1-(1,1-dimethylethoxy)silacyclobutane (7), and 1-[(1-methoxy-*d*$_3$-2-methyl-1-propenyl)oxy]-1-(1,1-dimethyl-*d*$_9$-ethoxy)-silacyclobutane (*d*$_{12}$-7). General Procedure. A solution of *n*-butyllithium in hexanes (5.45 mL, 2.35 M, 12.8 mmol) was added dropwise to a stirred solution of diisopropylamine (1.8 mL, 12.8 mmol) in dry THF (40 mL) at 0 °C under an atmosphere of nitrogen. After the LDA solution had stirred for 20 min at 0 °C, tripiperidinephosphoric triamide in THF (3.35 mL, 4.22 M, 14.1 mmol) was added dropwise, giving an orange solution. After stirring for 20 min at 0 °C, the LDA/tripiperidinephosphoric triamide solution was cooled to −78 °C and stirred vigorously. Methyl isobutyrate (1.47 mL, 12.8 mmol) was added dropwise over a 10-min period, and the mixture was stirred an additional 30 min at −78 °C after complete addition. To the enolate solution was added the 1-substituted-1-chlorosilacyclobutane (13.1 mmol, 1.02 equiv) in 5 mL of THF dropwise over a 5-min period. The reaction mixture was allowed to slowly warm to 25 °C over a 3-h period. The clear colorless solution was evaporated *in vacuo* and the residue (slurry of salts in oil) suspended in dry hexanes (40 mL). After stirring for 1 h at 25 °C, the white suspension was filtered via a Schlenk tube and the clear filtrate evaporated *in vacuo*. The clear, slightly yellow oil was transferred via a cannula to an assembled Kugelrohr apparatus and distilled to afford the silyl *O,O*-ketene acetal as a clear, colorless oil.

1-[(1-Methoxy-2-methyl-1-propenyl)oxy]-1-methylsilacyclobutane (5). From 12.8 mmol of LDA, 4.2 g (14.1 mmol) of tripiperidinephosphoric triamide, 1.31 g (12.8 mmol) of methyl isobutyrate, and 1.7 g (14.1 mmol) of 1-chloro-1-methylsilacyclobutane was obtained 1.4 g (58%) of **5** as a clear colorless oil: bp 40 °C (0.1 Torr); ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 3.30 (s, 3H), 1.95 (m, 1H), 1.68 (s, 3H), 1.60 (s, 3H), 1.45 (m, 3H), 1.13 (m, 2H), 0.24 (s, 3H); ^{13}C NMR (75.5 MHz, C$_6$D$_6$) δ 149.75, 90.37, 56.23, 19.39, 17.13, 16.42, 13.95, −1.54; IR (neat) 2940 (s), 2845 (s), 1700 (s) cm^{-1}; MS (70 eV) *m/z* 186 (M$^+$, 3), 145 (100). Anal. Calcd for $C_9H_{18}SiO_2$: C, 58.02; H, 9.74. Found: C, 58.28; H, 9.92.

1-[(1-Methoxy-*d*$_3$-2-methyl-1-propenyl)oxy]-1-methyl-*d*$_3$-silacyclobutane (*d*$_6$-5). From 10.3 mmol of LDA, 3.4 g (11.3 mmol) of tripiperidinephosphoric triamide, 1.08 g (10.3 mmol) of methyl-*d*$_3$ isobutyrate, and 1.4 g (11.3 mmol) of 1-chloro-1-methyl-*d*$_3$-silacyclobutane was obtained 1.03 g (52%) of *d*$_6$-5 as a clear colorless oil: bp 40 °C (0.1 Torr); ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 1.95 (m, 1H), 1.68 (s, 3H, (C*H*$_3$-α)), 1.61 (s, 3H, (C*H*$_3$-α), 1.44 (m, 3H), 1.12 (m, 2H); ^{13}C NMR (75.5 MHz, C$_6$D$_6$) δ 149.7 (C(1)), 90.3, 20.5, 19.3, 17.1, 16.4, 13.9, 13.7; IR (neat) 2973 (s), 2923 (s), 2859 (s), 1707 (s) cm^{-1}; MS (70 eV) *m/z* 192 (M$^+$, 13), 94 (100). Anal. Calcd for $C_9H_{12}D_6SiO_2$: C, 56.19; H, 9.43. Found: C, 56.14; H, 9.55.

1-[(1-Methoxy-2-methyl-1-propenyl)oxy]-1-(1,1-dimethylethyl)silacyclobutane (6). From 5.7 mmol of LDA, 1.9 g (6.3 mmol) of tripiperidinephosphoric triamide, 0.6 g (5.7 mmol) of methyl isobutyrate, and 0.95 g (6.3 mmol) of 1-chloro-1-(1,1-dimethylethyl)silacyclobutane was obtained 0.64 g (49%) of 6 as a clear colorless oil: bp 45–50 °C (0.1 Torr); ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 3.33 (s, 3H, (C*H*$_3$O)), 2.05 (m, 1H), 1.72 (s, 3H, (C*H*$_3$-α)), 1.64 (s, 3H, (C*H*$_3$-α), 1.53 (m, 3H), 1.30 (m, 2H), 1.04 (s, 9H, (C*H*$_3$)$_3$CSi)); ^{13}C NMR (75.5 MHz, C$_6$D$_6$) δ 149.8 (*C*(1)), 90.7 (*C*(2)), 56.2 (*C*H$_3$O), 25.5, 25.1 (*C*H$_3$)$_3$CSi), 17.1 (*C*H$_3$-α), 16.5 (*C*H$_3$-α), 16.1 (*C*H$_2$), 14.5 (*C*H$_2$); IR (neat) 2930 (s), 2858 (m), 1705 (s) cm^{-1}; MS (70 eV) *m/z* 228 (M$^+$, 9), 101 (100). Anal. Calcd for $C_{12}H_{24}SiO_2$: C, 63.10; H, 10.59. Found: C, 63.18; H, 10.71.

1-[(1-Methoxy-*d*$_3$-2-methyl-1-propenyl)oxy]-1-(1,1-dimethyl-*d*$_9$-ethyl)-silacyclobutane (*d*$_{12}$-6). From 6.3 mmol of LDA, 1.9 g (6.3 mmol) of tripiperidinephosphoric triamide, 0.66 g (6.3 mmol) of methyl-*d*$_3$ isobutyrate, and 1.10 g (6.4 mmol) of 1-chloro-1-(1,1-dimethyl-*d*$_9$-ethyl)-silacyclobutane was obtained 1.0 g (67%) of *d*$_{12}$-6 as a clear colorless oil: bp 45–50 °C (0.1 Torr); ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 2.00 (m, 1H), 1.70 (s, 3H, (C*H*$_3$-α)), 1.62 (s, 3H, (C*H*$_3$-α), 1.48 (m, 3H), 1.25 (m, 2H); ^{13}C NMR (75.5 MHz, C$_6$D$_6$) δ 149.8 (*C*(1)), 90.6 (*C*(2)), 17.1 (*C*H$_3$-α), 16.5 (*C*H$_3$-α), 16.1 (*C*H$_2$), 14.5 (*C*H$_2$); IR (neat) 2969 (m), 2924 (m), 2861 (m), 1705 (s) cm^{-1}; MS (70 eV) *m/z* 240 (M$^+$, 14), 104 (100). Anal. Calcd for $C_{12}H_{12}D_{12}SiO_2$: C, 59.93; H, 10.06. Found: C, 59.78; H, 10.22.

1-[(1-Methoxy-2-methyl-1-propenyl)oxy]-1-(1,1-dimethylethoxy)silacyclobutane (7). From 6.3 mmol of LDA, 1.9 g (6.3 mmol) of tripiperidinephosphoric triamide, 0.64 g (6.3 mmol) of methyl isobutyrate, and 1.14 g (6.4 mmol) of 1-chloro-1-(1,1-dimethylethoxy)-silacyclobutane was obtained 0.875 g (57%) of 7 as a clear colorless oil: bp 40–50 °C (0.5 Torr); ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 3.36 (s, 3H, (C*H*$_3$O)), 1.69 (s, 3H, (C*H*$_3$-α)), 1.67 (s, 3H, (C*H*$_3$-α), 1.65 (m, 3H), 1.50 (m, 3H), 1.28 (s, 9H, (C*H*$_3$)$_3$C)); ^{13}C NMR (75.5 MHz, C$_6$D$_6$) δ 149.2 (*C*(1)), 90.6 (*C*(2)), 74.3 ((CH$_3$)$_3$*C*), 56.6 (*C*H$_3$O), 31.8 (*C*H$_3$)$_3$C), 23.4 (*C*H$_2$), 17.2 (*C*H$_3$-α), 16.4 (*C*H$_3$-α), 12.3 (*C*H$_2$); IR (neat) 2977 (s), 2932 (s), 1707 (s) cm^{-1}; MS (70 eV) *m/z* 244 (M$^+$, 11), 229, 90 (100). Anal. Calcd for $C_{12}H_{24}SiO_3$: C, 58.97; H, 9.90. Found: C, 58.75; H, 9.83.

1-[(1-Methoxy-*d*$_3$-2-methyl-1-propenyl)oxy]-1-(1,1-dimethyl-*d*$_9$-ethoxy)silacyclobutane (*d*$_{12}$-7). From 12.3 mmol of LDA, 3.7 g (12.3 mmol) of tripiperidinephosphoric triamide, 1.29 g (12.3 mmol) of methyl-*d*$_3$ isobutyrate, and 2.4 g (12.5 mmol) of 1-chloro-1-(1,1-dimethyl-*d*$_9$-ethoxy)silacyclobutane was obtained *d*$_{12}$-7 as a clear colorless oil: 2.37 g (75%); bp 40–50 °C (0.5 Torr); ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 1.70 (s, 3H, (C*H*$_3$-α)), 1.69 (s, 3H, (C*H*$_3$-α), 1.66 (m, 3H), 1.50 (m, 3H); ^{13}C NMR (75.5 MHz, C$_6$D$_6$) δ 149.3 (*C*(1)), 90.5 (*C*(2)), 23.4 (*C*H$_2$), 17.3 (*C*H$_3$-α), 16.5 (*C*H$_3$-α), 12.3 (*C*H$_2$); IR (neat) 2979 (m), 2926 (m), 1707 (s), cm^{-1}; MS (70 eV) *m/z* 256 (M$^+$, 14), 94 (100). Anal. Calcd for $C_{12}H_{12}D_{12}SiO_3$: C, 56.19; H, 9.43. Found: C, 56.06; H, 9.50.

1-[(1-*tert*-Butoxy-2-methyl-1-propenyl)oxy]-1-(1,1-dimethylethyl)-silacyclobutane (8). From 9.0 mmol of LDA, 1.30 g (9.0 mmol) of *tert*-butyl isobutyrate, and 1.5 g (9.2 mmol) of 1-chloro-1-*tert*-butylsilacyclobutane was obtained 1.7 g (70%) of 8 as a clear colorless oil: bp 100 °C (0.05 Torr); ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 1.98 (m, 1H), 1.60 (s, 3H, *H*$_3$C(3)), 1.50 (s, 3H, *H*$_3$C(3′)), 1.42 (m, 3H), 1.29 (s, 9H, (*H*$_3$C)$_3$-CO), 1.25 (m, 2H), 1.02 (s, 9H, (*H*$_3$C)$_3$CSi); ^{13}C NMR (75.5 MHz, C$_6$D$_6$) δ 146.2 (*C*(1)), 95.7 (*C*(2)), 78.7 (O*C*(CH$_3$)$_3$), 29.1 (OC(*C*H$_3$)$_3$), 25.2 (SiC(*C*HCH$_3$)$_3$), 17.9 (H$_3$*C*(3)), 17.1 (H$_3$*C*(3′)), 16.2 (*C*H$_2$), 14.0 (*C*H$_2$); IR (neat) 2940 (s), 2845 (s), 1700 (s) cm^{-1}; MS (70 eV) *m/z* 270 (M$^+$, 3), 57 (100). Anal. Calcd for $C_{15}H_{30}SiO_2$: C, 66.61; H, 11.18. Found: C, 66.54; H, 11.40.

Preparation of Dimethyl-*tert*-butoxy[(1-methoxy-2-methyl-1-propenyl)oxy]silane (16). A solution of *n*-butyllithium in hexanes (4.13 mL, 2.64 M, 10.9 mmol) was added dropwise to a stirred solution of diisopropylamine (1.53 mL, 10.9 mmol) in dry THF (50 mL) at 0 °C under an atmosphere of nitrogen. After being stirred for 20 min at 0 °C the solution was cooled to −78 °C and was stirred vigorously. A solution of methyl isobutyrate (1.11 g, 10.9 mmol) in THF (3 mL) was added dropwise over a 10-min period, and the mixture was stirred an additional 30 min at −78 °C after complete addition. To the enolate solution was

added *tert*-butoxydimethylchlorosilane (2 g, 12.0 mmol, 1.1 equiv) dropwise over a 5-min period. The reaction mixture was allowed to slowly warm to 25 °C over a 3-h period. The clear colorless solution was evaporated *in vacuo* and the residue suspended in dry pentane (40 mL). After stirring for 30 min at 25 °C, the white suspension was filtered via a Schlenk tube and the clear filtrate evaporated *in vacuo*. The clear, slightly yellow oil was transferred via cannula to an assembled Kugelrohr apparatus and distilled to afford 1.7 g (68%) of **16** as a clear colorless oil: bp 30–35 °C (0.05 Torr); ^{1}H NMR (400 MHz, C_6D_6) δ 3.36 (s, 3H, (H_3CO)), 1.70 (s, 3H, (H_3C(3))), 1.68 (s, 3H, (H_3C(3′))), 1.24 (s, 9H, ((H_3C)$_3$C), 0.23 (s, 6H, ((H_3C)$_2$Si); ^{13}C NMR (100.6 MHz, C_6D_6) δ 149.9 (*C*(1)), 90.4 (*C*(2)), 73.1 (*C*(CH$_3$)$_3$), 56.6 (*C*H$_3$O), 31.9 ((*C*H$_3$)$_3$C), 17.2 (*C*(3)), 16.5 (*C*(3′)), 0.5 ((*C*H$_3$)$_2$Si); IR (neat) 2976 (s), 2930 (m), 2861 (m), 1705 (s) cm^{-1}; MS (70 eV) *m/z* 232 (9), 75 (100). Anal. Calcd for $C_{11}H_{24}SiO_3$: C, 56.85; H, 10.41. Found: C, 56.81; H, 10.43.

Preparation of (*Z*)-1-[(1-((1,1-Dimethylethyl)thio)-1-propenyl)oxy]-1-phenylsilacyclobutane ((*Z*)-9). A solution of *n*-butyllithium in hexanes (2.84 mL, 2.19 M solution, 6.22 mmol) was added dropwise to a stirred solution of 2,2,6,6-tetramethylpiperidine (1.05 mL, 0.879 g, 6.22 mmol) in dry THF (15 mL) at 0 °C under an atmosphere of nitrogen. After being stirred for 30 min at 0 °C the clear solution was cooled to −78 °C and was stirred for an additional 15 min. A solution of *tert*-butyl thiopropanoate (0.912 g, 6.24 mmol) in dry THF (10 mL) was added dropwise over a period of 10 min. After 30 min a solution of 1-phenyl-1-chlorosilacyclobutane (**1e**) (1.137 g, 6.22 mmol) in dry THF (5 mL) was added dropwise. The resultant clear solution was allowed to warm very slowly to room temperature over 4 h. The clear solution was evaporated *in vacuo* and the residue suspended in dry hexane (30 mL). After stirring for 2 h at room temperature the white suspension was filtered via a Schlenk tube and the slightly cloudy filtrate evaporated *in vacuo*. The residue was transferred via cannula to an assembled Kugelrohr apparatus and distilled to afford 1.074 g (59%) of (*Z*)-**9** as a colorless oil: bp 135–140 °C (0.2 Torr); ^{1}H NMR (400 MHz) δ 7.77–7.65 (m, 2H, *H*Ar), 7.49–7.35 (m, 3H, *H*Ar), 5.47, 5.33 (two quartets, 96/4, J = 6.8, 1H, *H*C(2)), 2.22–2.08 (m, 2H, CH_2), 1.81–1.38 (m, 16H, (CH_3)$_3$C, 3 × *H*C(3), 2 × CH_2); ^{13}C NMR (100.6 MHz) δ 144.92 (*C*(l)), 133.49 (*C*(Ar)), 130.06 (*C*H(Ar)), 129.89 (*C*H(Ar)), 127.85 (*C*H(Ar)), 127.81 (*C*H(Ar)), 116.94 (*C*(2)), 35.00 (*C*(CH$_3$)$_3$), 31.61 ((*C*H$_3$)$_3$C), 19.78 (*C*H$_2$), 18.41 (*C*H$_2$), 14.74 (*C*(3)), 14.05 (*C*H$_2$), 13.75 (*C*H$_2$); IR (neat) 2967 (m), 2926 (m), 1688 (m) cm^{-1}; MS (CI) *m/z* 293 (M$^+$ + 1, 2), 147 (100). Anal. Calcd for $C_{16}H_{24}OSSi$: C, 65.70; H, 8.27. Found: C, 66.17; H, 8.43.

Preparation of (*Z*)-Dimethylphenyl[(1-((1,1-dimethylethyl)thio)-1-propenyl)oxy]silane ((*Z*)-17). A solution of *n*-butyllithium in hexanes (2.87 mL, 2.19 M, 6.29 mol) was added dropwise to a stirred solution of diisopropylamine (0.88 mL, 0.635 g, 6.28 mmol) in dry THF (20 mL) at 0 °C under an atmosphere of nitrogen. After 10 min the clear solution was cooled to −78 °C and stirred for an additional 5 min. A solution of *tert*-butyl thiopropanoate (0.918 g, 6.28 mmol) in dry THF (10 mL) was added dropwise over a period of 10 min. After an additional 30 min dimethylphenylsilyl chloride (1.04 mL, 1.07 g, 6.28 mmol) was added dropwise. The resultant mixture was allowed to warm slowly to room temperature over *ca.* 2 h. After being cooled to 0 °C, aqueous phosphate buffer (1 mL, pH 7.8) was added dropwise. The mixture was partitioned between pentane (75 mL) and phosphate buffer (50 mL). The organic phase was washed with phosphate buffer (50 mL) and dried (Na_2SO_4) and the solvent evaporated *in vacuo*. The residue was Kugelrohr distilled to afford 1.46 g (82%) of (*Z*)-**17** as a colorless oil: bp 100–105 °C (0.1 Torr); ^{1}H NMR (400 MHz) δ 7.66–7.57 (m, 2H, *H*Ar), 7.45–7.33 (m, 3H, *H*Ar), 5.26 (q, J = 6.8, 1H, *H*C(2)), 1.69 (d, J = 6.8, 3H, *H*C(3)), 1.37 (s, 9H, (CH_3)$_3$C), 0.47, 0.41 (each s, 6H, 2 × CH_3Si); ^{13}C NMR (100.6 MHz) δ 145.33 (*C*(1)), 133.41 (*C*(Ar)), 132.91 (*C*H(Ar)), 129.52 (*C*H(Ar)), 127.78 (*C*H(Ar)), 127.64 (*C*H(Ar)), 116.08 (*C*(2)), 46.84 (*C*(CH$_3$)$_3$), 31.60 ((*C*H$_3$)$_3$C), 14.71 (*C*(3)), −1.18 (2 × *C*H$_3$Si); IR (neat) 2961 (m), 2921 (w), 1626 (m) cm^{-1}; MS (CI) *m/z* 280 (M$^+$, 39), 147 (100). Anal. Calcd for $C_{15}H_{24}OSSi$: C, 64.23; H, 2.62; S, 11.43. Found: C, 64.11; H, 8.56, S, 11.40.

Preparation of (*Z*)-1-[(1-(*N*,*N*-Dimethylamino)-1-propenyl)oxy]-1-(1,1-dimethylethyl)silacyclobutane ((*Z*)-10). A solution of *n*-butyllithium in hexanes (5.6 mL, 2.17 M, 12.05 mmol) was added dropwise to a stirred solution of diisopropylamine (1.7 mL, 12.05 mmol) in dry THF (40 mL) at 0 °C under an atmosphere of nitrogen. After stirring for 20 min at 0 °C, *N*,*N*-dimethylpropanamide (1.32 mL, 12.05 mmol) was added dropwise over a 10-min period. After 35 min at 0 °C the enolate solution was cooled to −78 °C, and *tert*-butyl-1-chlorosilacyclobutane (2.0 g, 12.28 mmol) was added over a 5-min period. The reaction mixture was allowed to warm slowly to 25 °C over a 3-h period. The clear, slightly yellow solution was evaporated *in vacuo* and the residue suspended in dry hexane (40 mL). After being stirred for 1 h at 25 °C, the white slurry was filtered with a Schlenk tube, and the clear, slightly yellow oil was transferred via cannula to an assembled Kugelrohr apparatus and distilled to afford 2.0 g (74%) of (*Z*)-**10** as a clear, colorless oil: bp 60–65 °C (0.03 Torr); ^{1}H NMR (400 MHz) δ 3.67 (q, J = 6.6, 1H, *H*C(2)), 2.51 (s, 6H, (CH_3)$_2$N), 1.95 (m, 1H), 1.55 (m, 1H), 1.52 (d, J = 6.6, 3H, H_3C(3)), 1.41–1.19 (m, 4H), 1.05 (s, 9H, (CH_3)$_3$C); ^{13}C NMR (100.6 MHz) δ 153.90 (*C*(1)), 79.41 (*C*(2)), 40.06 ((CH$_3$)$_2$N), 25.16 ((*C*H$_3$)$_3$C), 15.79 (*C*H$_2$), 14.24 (*C*H$_2$), 10.64 (*C*(3)); IR (neat) 2928 (s), 2859 (s), 1665 (s) cm^{-1}; MS (70 eV) *m/z* 229 (M$^+$ + 2, 6). Anal. Calcd for $C_{12}H_{25}NOSi$: C, 63.38; H, 11.08; N, 6.16. Found: C, 63.26; H, 11.06; N, 6.02.

General Procedure for Uncatalyzed Reaction of *O*-Silyl *O*,*O*-Ketene Acetals (4–7) and *O*-Silyl *N*,*O*-Ketene Acetals (10 or 18) with Aldehydes or α,β-Unsaturated Carbonyl Compounds. An oven-dried 5 mm × 9 in. NMR tube was fitted with a septum and cooled under a nitrogen atmosphere. The acetal was added to the tube via syringe followed by approximately one-half of the required volume of the appropriate solvent to make a 1.0 M solution. The NMR tube was immersed in liquid nitrogen to a depth sufficient to freeze the acetal solution. The appropriate carbonyl compound was then added in one portion via syringe followed by the remaining amount of solvent. The tube was then immersed further into the liquid nitrogen bath to a depth sufficient to freeze the entire contents of the tube. The tube was then evacuated to 0.03 Torr and sealed with a torch. The reaction tubes were kept at liquid nitrogen temperature just prior to thawing for NMR analysis of the reactions. The uncatalyzed crossover experiments were run following this procedure and using 1 equiv each of the labeled and nonlabeled ketene acetals to 2 equiv of benzaldehyde. After completion of the crossover reactions, the solvent was removed *in vacuo* to afford the corresponding analytically pure β-siloxy aldol products. For all other uncatalyzed aldol reactions, the authentic aldol products were isolated by desilylation with dilute HF in THF solution followed by extractive workup and silica gel column chromatography.

***syn*-Methyl 3-Hydroxy-2-methyl-3-phenylpropanoate (24a).** From 206 mg (0.96 mmol) of (*E*)-1-[(1-methoxy-1-propenyl)oxy]-1-(1,1-dimethylethyl)silacyclobutane ((*E*)-**4**) and 102 mg (0.96 mmol) of benzaldehyde was obtained 175 mg (94%) of **24a** as a clear colorless oil: ^{1}H NMR (400 MHz) δ 7.35 (m, 3H, *H*C(Ar)), 7.25 (m, 2H, *H*C(Ar)), 5.11 (dd, J = 2.2, 2.2, 1H, *H*C(3)), 3.68 (s, 3H, H_3CO), 2.95 (s, 1H, *H*O), 2.79 (dq, J_q = 7.2, 4.0, 1H, *H*C(2)), 1.12 (d, J = 7.2, 3H, H_3C); ^{13}C NMR (100.6 MHz) δ 176.3 (*C*(1)), 141.3 (*C*(Ar)), 128.2 (*C*H(Ar)), 127.5 (*C*H(Ar)), 125.9 (*C*H(Ar)), 73.5 (*C*(3)H), 51.9 (*C*H$_3$O), 46.3 (*C*(2)H), 10.6 (*C*H$_3$); IR (neat) 3476 (m), 2986 (m), 2949 (m), 1734 (s) cm^{-1}; MS (70 eV) *m/z* 194 (5), 88 (100). Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 67.92; H, 7.34

(*E*)-*syn*-Methyl 3-Hydroxy-2-methyl-5-phenyl-4-pentenoate (24b). From 187 mg (0.87 mmol) of (*E*)-1-[(1-methoxy-1-propenyl)oxy]-1-(1,1-dimethylethyl)silacyclobutane ((*E*)-**4**) and 119 mg (0.87 mmol) of *trans*-cinnamaldehyde was obtained 181 mg (95%) of **24b** as a clear colorless oil: ^{1}H NMR (400 MHz) δ 7.37 (m, 2H, *H*C(Ar)), 7.30 (m, 2H, *H*C(Ar)), 7.24 (m, 1H, *H*C(Ar)), 6.65 (dd, $J_{5,4}$ = 15.6, $J_{5,3}$ = 1.2, 1H, *H*C(5)), 6.20 (dd, $J_{4,5}$ = 15.6, $J_{4,3}$ = 6.0, 1H, *H*C(4)), 4.58 (dd, J = 4.8, 4.8, 1H, *H*C(3)), 3.71 (s, 3H, H_3CO), 2.96 (s, 1H, *H*O), 2.73 (dq, J_q = 7.2, J_d = 4.4, 1H, *H*C(2)), 1.23 (d, J = 7.2, 3H, H_3C); ^{13}C NMR (100.6 MHz) δ 175.7 (*C*(1)), 136.4 (*C*(Ar)), 131.4 (*C*H(Ar)), 128.6 (*C*(5)H), 128.5 (*C*H(Ar)), 127.7 (*C*H(Ar)), 126.4 (*C*(4)H), 72.9 (*C*(3)H), 51.8 (*C*H$_3$O), 44.9 (*C*(2)H), 11.4 (*C*H$_3$); IR (neat) 3463 (m), 2984 (m), 2950 (m), 1732 (s) cm^{-1}; MS (70 eV) *m/z* 220 (5), 133 (100). Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.88; H, 7.32. Found: C, 71.05; H, 7.38.

***syn*-Methyl 3-Hydroxy-2-methyloctanoate (24c).** From 188 mg (0.88 mmol) of (*E*)-1-[(1-methoxy-1-propenyl)oxy]-1-(1,1-dimethylethyl)-silacyclobutane ((*E*)-**4**) and 88 mg (0.88 mmol) of hexanal was obtained 150 mg (91%) of **24c** as a clear colorless oil: ^{1}H NMR (400 MHz) δ 3.87 (m, 1H, *H*C(3)), 3.68 (s, 3H, H_3CO), 2.57 (s, 1H, *H*O), 2.51 (dq, J_q = 7.2, J_d = 3.2, 1H, *H*C(2)), 1.50–1.20 (m, 8H, H_2C(4, 5, 6)), 1.15 (d, J = 7.2, 3H, H_3C), 0.86 (t, J = 6.8, 3H, H_3C(8)); ^{13}C NMR (100.6 MHz) δ 176.6 (*C*(1)), 71.7 (*C*(3)H), 51.8 (*C*H$_3$O), 44.1 (*C*(2)H), 33.7 (*C*(4)-H$_2$), 31.7 (*C*(5)H$_2$), 25.6 (*C*(6)H$_2$), 22.5 (*C*(7)H$_2$), 13.9 (*C*(8)H$_3$), 10.5 (*C*H$_3$); IR (neat) 3852 (w), 3744 (w), 3445 (m), 2934 (s), 1736 (s) cm^{-1}; MS (CI) *m/z* 189 (64), 171 (100). Anal. Calcd for $C_{10}H_{20}O_3$: C, 63.79; H, 10.71. Found: C, 63.72; H, 10.76.

***syn*-Methyl 3-Cyclohexyl-3-hydroxy-2-methylpropanoate (24d).** From 180 mg (0.84 mmol) of (*E*)-1-[(1-methoxy-1-propenyl)oxy]-1-(1,1-dimethylethyl)silacyclobutane ((*E*)-**4**) and 95 mg (0.84 mmol) of cyclohexanecarboxaldehyde was obtained 143 mg (85%) of **24d** as a clear colorless oil: ^{1}H NMR (400 MHz) δ 3.67 (s, 3H, H_3CO), 3.60 (ddd, J

= 4.0, 4.0, 4.0, 1H, HC(3)), 2.65 (dq, J_q = 7.2, J_d = 3.6 , 1H, HC(2)), 2.56 (d, J = 4.4, 1H, HO), 2.02 (dt, J_d = 14.4, J_t = 1.6, 1H, HC(4)), 1.72 (m, 2H), 1.62 (m, 1H), 1.52 (m, 1H), 1.31 (m, 1H), 1.18 (m, 3H), 1.13 (d, J = 7.2, 3H, H_3C), 0.93 (qd, J_q = 12.4, J_d = 3.2, 2H, H_2C); ^{13}C NMR (100.6 MHz) δ 176.9 (C(1)), 75.5 (C(3)H), 51.7 (CH_3O), 40.9 (C(2)H), 39.9 (C(4)H), 28.9 (CH_2), 26.0 (CH_2), 25.7 (CH_2), 9.7 (CH_3); IR (neat) 3478 (m), 2928 (s), 2851 (s), 1734 (s) cm^{-1}; MS (CI) m/z 201 (29), 151 (100). Anal. Calcd for $C_{11}H_{20}O_3$: C, 65.97; H, 10.07. Found: C, 66.00; H, 10.10.

Methyl 2,2-Dimethyl-3-[1-(1-methylsilacyclobutoxy)]-3-phenylpropanoate (19). From 132.2 mg (0.71 mmol) of 1-[(1-methoxy-2-methyl-1-propenyl)oxy]-1-methylsilacyclobutane (**5**) and 75.4 mg (0.71 mmol) of benzaldehyde was obtained 207 mg (99%) of **19** as a clear colorless oil: ^{1}H NMR (400 MHz, C_6D_6) δ 7.23 (d, J = 6.7, 2H), 7.05 (m, 3H), 5.26 (s, 1H, HC(3)), 3.34 (s, 3H, (CH_3O)), 1.85 (m, 1H), 1.40 (m, 3H), 1.26 (s, 3H, (H_3C-α)), 1.05 (m, 1H), 0.99 (s, 3H, (H_3C-α)), 0.95 (m, 1H), 0.14 (s, 3H, H_3CSi); ^{13}C NMR (100.6 MHz, C_6D_6) δ 176.4 (C(1)), 140.7, 128.2, 127.7, 80.0 (C(3)), 51.4 (CH_3O), 49.1 (C(2)), 22.1 (CH_3-α), 19.2 (CH_3-α and CH_2), 18.6 (CH_2), 13.9 (CH_2), -1.40 (CH_3Si); IR (neat) 2928 (m), 2857 (m), 1742 (s) cm^{-1}; MS (70 eV) m/z 292 (M$^+$, 3), 191 (100). Anal. Calcd for $C_{16}H_{24}SiO_3$: C, 65.71; H, 8.27. Found: C, 65.74; H, 8.29.

Methyl-d_3 2,2-Dimethyl-3-[1-(1-methyl-d_3-silacyclobutoxy)]-3-phenylpropanoate (d_6-19). From 130.0 mg (0.68 mmol) of 1-[(1-methoxy-d_3-2-methyl-1-propenyl)oxy]-1-methyl-d_3-silacyclobutane (d_6-**5**) and 72 mg (0.68 mmol) of benzaldehyde was obtained 200 mg (99%) of d_6-**19** as a clear colorless oil: ^{1}H NMR (400 MHz, C_6D_6) δ 7.24 (d, J = 6.8, 2H), 7.05 (m, 3H), 5.26 (s, 1H, HC(3)), 1.85 (m, 1H), 1.40 (m, 3H), 1.25 (s, 3H, (H_3C-α)), 1.05 (m, 1H), 0.99 (s, 3H, (H_3C-α)), 0.95 (m, 1H); ^{13}C NMR (100.6 MHz, C_6D_6) δ 176.6 (C(1)), 140.9, 128.2, 127.8, 80.2 (C(3)), 49.3 (C(2)), 22.2 (CH_3-α), 19.3 (CH_3-α and CH_2), 18.7 (CH_2), 14.0 (CH_2); IR (neat) 2973 (m), 2934 (m), 1740 (s) cm^{-1}; MS (70 eV) m/z 298 (M$^+$, 3), 105 (100). Anal. Calcd for $C_{16}H_{18}D_6SiO_3$: C, 64.39; H, 8.11. Found: C, 64.38; H, 8.45.

***N,N*-Dimethyl-3-hydroxy-2-methyl-3-phenylpropanamide (28a).** From 85 mg (0.37 mmol) of (*Z*)-1-[(1-(*N,N*-dimethylamino)-1-propenyl)oxy]-1-(1,1-dimethylethyl)silacyclobutane ((*Z*)-**10**) and 40 mg (0.37 mmol) of benzaldehyde was obtained 77 mg (86%) of **28a** as a white solid: ^{1}H NMR (400 MHz) δ 7.39–7.22 (m, 5H, HAr), 5.11 (s, 0.33H, *syn* HC(3)), 5.09 (d, J = 2.4, 0.33H, *syn* OH), 4.77 (dd, J = 6.3, 6.3, 0.67H, *anti* HC(3)), 4.52 (d, J = 6.6, 0.67H, *anti* OH), 3.07–2.97 (m, 2.65H, *anti* HC(2), *syn* (CH_3)$_2$N), 2.87–2.82 (m, 4.35H, *syn* HC(2), *anti* (CH_3)$_2$N), 1.18 (d, J = 7.1, 2.01H, *anti* CH_3C(2)), 1.02 (d, J = 7.1, 0.99H, *syn* CH_3C(2)); ^{13}C NMR (100.6 MHz) δ 177.36 (*syn* CO), 175.72 (*anti* CO), 142.91 (*anti* C(Ar)), 141.64 (*syn* C(Ar)), 128.21 (*anti* CH(Ar)), 128.04 (*syn* CH(Ar)), 127.41 (*anti* CH(Ar)), 127.03 (*syn* CH(Ar)), 126.03 (*anti* CH(Ar)), 125.94 (*syn* CH(Ar)), 76.61 (*anti* C(3)), 73.07 (*syn* C(3)), 42.53 (*anti* C(2)), 41.43 (*syn* C(2)), 37.30 (*syn* CH_3N), 37.15 (*anti* CH_3N), 35.37 (*syn* CH_3N), 35.32 (*anti* CH_3N), 15.25 (*anti* CH_3C(2)), 9.41 (*syn* CH_3C(2)); IR (CCl_4) 3399 (m), 2936 (w), 1632 (s) cm^{-1}; MS (CI) m/z 208 (M$^+$ + 1, 17), 190 (57), 72 (100). Anal. Calcd for $C_{12}H_{17}NO_2$: C, 69.54; H, 8.27; N, 6.76. Found: C, 69.35; H, 8.31; N, 6.60.

***N,N*-Dimethyl-3-hydroxy-2-methyloctanamide (28b).** ^{1}H NMR (400 MHz) δ 4.60 (s, 0.46H, *syn* OH), 4.05 (d, J = 7.6, 0.54H, *anti* OH), 3.88–3.79 (m, 0.46H, *syn* HC(3)), 3.62–3.50 (m, 0.54H, *anti* HC(3)), 3.03, 3.025 (each s, 2.76H, *syn* (CH_3)$_2$N), 2.93, 2.92 (each s, 3.24H, *anti* (CH_3)$_2$N), 2.73–2.65 (m, 0.54H, *anti* HC(2)), 2.65–2.57 (m, 0.46H, *syn* HC(2)), 1.62–0.77 (m, 14H, CH_3C(2), 4 × CH_2, CH_3C(7)); ^{13}C NMR (100.6 MHz) δ 177.84 (*syn* CO), 176.71 (*anti* CO), 74.25 (*anti* C(3)), 71.01 (*syn* C(3)), 40.04 (*anti* C(2)), 38.56 (*syn* C(2)), 37.30 (CH_3N), 35.45 (CH_2), 35.29 (CH_3N), 35.24 (CH_3N), 33.65 (CH_2), 31.82 (CH_2), 31.78 (CH_2), 25.67 (CH_2), 25.64 (CH_2), 22.58 (CH_2), 15.08 (*anti* CH_3C-(2)), 14.02 (CH_3C(7)), 9.45 (*syn* CH_3C(2)); IR (film) 3411 (m), 2934 (s), 2861 (s), 1624 (s) cm^{-1}; MS (CI) m/z 202 (M$^+$ + 1, 100). Anal. Calcd for $C_{11}H_{23}NO_2$: C, 65.62; H, 11.52; N, 6.96. Found: C, 65.45; H, 11.57; N, 6.99.

***N,N*-Dimethyl-3-cyclohexyl-3-hydroxy-2-methylpropanamide (28c).** ^{1}H NMR (400 MHz) δ 4.77 (s, 0.5H, OH), 4.25 (d, J = 8.5, 0.5H, OH), 3.46 (dd, J = 9.0, 1.5, 0.5H, HC(3)), 3.28–3.19 (m, 0.5H, HC(3)), 3.04, 3.03 (each s, 3H, (CH_3)$_2$N), 2.94 (s, 3H, (CH_3)$_2$N), 2.90–2.79 (m, 1H, HC(2)), 2.13, 1.95 (each m, each 0.5H, HC-(cyclohexyl)), 1.82–0.77 (m, 13H, CH_3C(2), 5 × CH_2); ^{13}C NMR (100.6 MHz) δ 177.92 (CO), 177.16 (CO), 79.08 (C(3)), 75.32 (C(3)), 41.86 (C(2)), 39.44 (C(2)), 37.31 (CH_3N), 37.24 (CH_3N), 35.98 (CH), 35.38 (CH_3N), 35.24 (CH_3N), 35.13 (CH), 30.01 (CH_2), 29.76 (CH_2), 28.69 (CH_2), 28.56 (CH_2), 26.38 (CH_2), 26.33 (CH_2), 26.24 (CH_2), 25.98 (CH_2), 25.96 (CH_2), 25.76 (CH_2), 15.47 (CH_3C(2)), 9.32 (CH_3C(2)); IR (film) 3409 (br m), 2926 (s), 2851 (s), 1622 (s) cm^{-1}; MS (CI) m/z 214 (M$^+$ + 1, 100). Anal. Calcd for $C_{12}H_{23}NO_2$: C, 67.55; H, 10.87; N, 6.57. Found C, 67.40; H, 10.92; N, 6.52.

Methyl 3-Hydroxy-2,2-dimethyl-4-pentenoate (31). From 124 mg (0.67 mmol) of 1-[(1-methoxy-2-methyl-1-propenyl)oxy]-1-methylsilacyclobutane (**5**) and 37 mg (0.67 mmol) of acrolein was obtained 75 mg (75%) of **31** as a colorless oil: bp 60–65 °C (0.5 Torr); ^{1}H NMR (400 MHz) δ 5.90–5.80 (m, 1H, HC(4)), 5.33–5.20 (m, 2H, HC(5)), 4.16 (dd, J = 6.3, 6.3, 1H, HC(3)), 3.70 (s, 3H, CH_3O), 2.69 (d, J = 6.1, 1H, OH), 1.19 (s, 3H, CH_3C(2)), 1.17 (s, 3H, CH_3C(2)); ^{13}C NMR (100.6 MHz) δ 177.68 (C(1)), 136.95 (C(4)), 117.57 (C(5)), 77.83 (C(3)), 51.88 (OCH_3) 46.57 (C(2)), 22.46 (CH_3), 19.73 (CH_3); IR (neat) 3480 (br s), 2982 (s), 2953 (s), 1727 (s) cm^{-1}; MS (CI) m/z 141 (M$^+$ - OH, 100). Anal. Calcd for $C_8H_{14}O_3$: C, 60.74; H, 8.92. Found: C, 60.67; H, 8.99.

Methyl 3-Hydroxy-2,2,3-trimethyl-4-pentenoate (32). From 114 mg (0.61 mmol) of 1-[(1-methoxy-2-methyl-1-propenyl)oxy]-1-methylsilacyclobutane (**5**) and 43 mg (0.61 mmol) of methyl vinyl ketone was obtained 69 mg (66%) of **32** as a colorless oil: bp 60–65 °C (0.5 Torr); ^{1}H NMR (400 MHz) δ 5.95 (dd, J = 17.1, 10.7, 1H, HC(4)), 5.31 (dd, J = 17.1, 1.5, 1H, HC(5)), 5.11 (dd, J = 10.7, 1.7, 1H, HC(5)), 3.82 (s, 1H, OH), 3.68 (s, 3H, CH_3O), 1.23, 1.21 (each s, 6H, 3H, 2 × CH_3-C(2), CH_3C(3)); ^{13}C NMR (100.6 MHz) δ 178.52 (C(1)), 140.78 (C(4)), 114.16 (C(5)), 75.65 (C(3)), 52.03 (OCH_3) 49.51 (C(2)), 22.86 (CH_3), 21.14 (CH_3); IR (neat) 3497 (br m), 2986 (s), 2953 (m), 1709 (s), 1472 (s) cm^{-1}; MS (CI) m/z 155 (M$^+$ - OH, 100). Anal. Calcd for $C_9H_{16}O_3$: C, 62.77; H, 9.36. Found: C, 62.61; H, 9.30.

General Procedure for Reaction of *O*-Silyl *S,O*-Ketene Acetal 9 and 17 with Aldehydes. An oven-dried ignition tube (7 × 50 mm, neat reactions) or a 5-mm NMR tube (dilute reactions) was fitted with a septum and cooled under a nitrogen atmosphere. To the tube was added the acetal via syringe followed (in the case of solution reactions) by the appropriate solvent to make a 1.0 M solution. The appropriate aldehyde was then added in one portion via syringe. The tube was gently shaken and then allowed to stand. The neat reactions were followed by ^{1}H NMR analysis of aliquots. The aldol products were isolated by desilylation with tetrabutylammonium fluoride and the sample washed with D_2O (0.35 mL). Assignment of the stereochemistry of the products was made by comparison of the characteristic signals of HC(3) in the ^{1}H NMR spectra of the crude material with the literature values.[29b] The aldol products were obtained by silica gel chromatography.

(*S*)-1,1-Dimethylethyl 3-Hydroxy-2-methyl-3-phenylpropanethioate (26a): ^{1}H NMR (400 MHz) δ 7.34–7.25 (m, 5H, HAr), 5.07 (dd, J = 3.9, 2.4, 0.94H, *syn* HC(3)), 4.77 (dd, J = 8.1, 4.4, 0.06H, *anti* HC(3)), 3.00 (d, J = 2.2, OH), 2.84–2.77 (m, 1H, HC(2)), 1.46 (s, 0.54H, *anti* (CH_3)$_3$C), 1.43 (s, 8.46H, *syn* (CH_3)$_3$C), 1.13 (d, J = 7.1, 2.82H, *syn* CH_3), 1.01 (d, J = 7.1, 0.18H, *anti* CH_3); ^{13}C NMR (100.6 MHz) *syn* isomer δ 205.18 (CO), 141.21 (C(Ar)), 128.19 (CH(Ar)), 127.44 (CH-(Ar)), 126.07 (CH(Ar)), 73.81 (C(3)), 54.99 (C(2)), 48.27 ((CH_3)$_3$C), 29.65 ((CH_3)$_3$C), 11.44 (CH_3C(2)); IR (CCl_4) 3528 (br w), 2967 (m), 1663 (s) cm^{-1}; MS (CI) m/z 253 (M$^+$ + 1, 100). Anal. Calcd for $C_{14}H_{20}O_2S$: C, 66.63; H, 7.99. Found: C, 66.24; H, 7.92.

(*S*)-1,1-Dimethylethyl 3-Hydroxy-2-methyl-5-phenyl-4-pentenethioate (26b): ^{1}H NMR (400 MHz) δ 7.40–7.20 (m, 5H, HAr), 6.63 (overlapping d, each J = 15.8, 1H, HC(5)), 6.22–6.12 (m, 1H, HC(4)), 4.60–4.55 (m, 0.70H, *syn* HC(3)), 4.39 (dd, J = 12.7, 6.1, 0.3H, *anti* HC(3)), 2.81–2.72 (m, 1H, HC(2)), 2.62 (d, J = 5.9, OH), 1.46 (s, 2.7H, *anti* (CH_3)$_3$C), 1.45 (s, 6.3H, *syn* (CH_3)$_3$C), 1.24 (d, J = 7.1 2.1H, *syn* CH_3C(2)), 1.21 (d, J = 7.1, 0.9H, *anti* CH_3C(2)); ^{13}C NMR (100.6 MHz) δ 204.51 (*syn* CO), 204.29 (*anti* CO), 136.53 (*syn* C(Ar)), 136.39 (*anti* C(Ar)), 131.85 (*anti* CH(Ar)), 131.33 (*syn* CH(Ar)), 129.39 (*anti* CH(Ar)), 128.61 (*syn* CH(Ar)), 128.53 (*anti* CH(Ar)), 128.51 (*syn* CH(Ar)), 127.78 (*anti* CH(Ar)), 127.65 (*syn* CH(Ar)), 126.53 (*anti* CH(Ar)), 126.48 (*syn* CH(Ar)), 74.99 (*anti* C(3)), 73.14 (*syn* C(3)), 53.92 (*anti* C(2)), 53.52 (*syn* C(2)), 48.41 (*anti* (CH_3)$_3$C), 48.36 (*syn* (CH_3)$_3$C), 29.68 (*anti* (CH_3)$_3$C), 29.66 (*syn* (CH_3)$_3$C), 15.09 (*anti* CH_3C(2)), 12.08 (*syn* CH_3C(2)); IR (film) 3447 (br m), 2965 (s), 2924 (m), 1676 (s) cm^{-1}; MS (70 eV) m/z 278 (M$^+$ + 1, 2), 133 (100). Anal. Calcd for $C_{16}H_{22}O_2S$: C, 69.03; H, 7.96. Found: C, 69.30; H, 8.04.

(*S*)-1,1-Dimethylethyl 3-Hydroxy-2-methyloctanethioate (26c): ^{1}H NMR (400 MHz) δ 3.90–3.87 (m, 0.88H, *syn* HC(3)), 3.66–3.58 (m, 0.12H, *anti* HC(3)), 2.65–2.52 (m, 1H, HC(2)), 2.48 (d, J = 3.4, 0.88H, OH), 2.41 (d, J =7.6, 0.12H, OH), 1.48–1.23 (m, 17H, (CH_3)$_3$C, 4 × CH_2), 1.21 (d, J = 7.1, 0.36H, *anti* CH_3C(2)), 1.17 (d, J = 7.1 2.64H, *syn* CH_3C(2)), 0.91–0.85 (m, 3H, CH_3); ^{13}C NMR (100.6 MHz) *syn* isomer δ 205.47 (CO), 71.96 (C(3)), 52.92 (C(2)), 48.18 ((CH_3)$_3$C),

34.01 (CH_2), 31.72 (CH_2), 29.71 ((CH_3)$_3$C), 25.58 (CH_2), 22.58 (CH_2), 14.05 (C(8)), 11.32 (CH_3C(2)); IR (film) 3454 (m), 2959 (s), 2930 (s), 2861 (m), 1676 (s) cm^{-1}; MS (CI) *m/z* 247 (M^+ + 1, 47), 157 (100).

General Procedure for Catalyzed Reaction of *O*-Silyl *O,O*-Ketene Acetals (4–7) with Benzaldehyde. An oven-dried 5 mm × 9 in. NMR tube was fitted with a septum and cooled under a nitrogen atmosphere. To the tube was added the acetal via syringe followed by the appropriate solvent to make a 0.5 M solution. The benzaldehyde was then added in one portion via syringe, the tube was introduced into the NMR probe (at the appropriate temperature), and a spectrum was taken. The tube was ejected, the catalyst (5 mol %) added, and the tube quickly reintroduced into the probe, keeping track of the total time since addition of the catalyst. The reactions were followed by ^{1}H NMR to determine the half-lives.

The bench-top reactions were performed in the same manner, except that they were quenched (at the appropriate time) with 0.05 M pH 7 phosphate buffer and allowed to warm (in the case of cold reactions) to room temperature before addition of diethyl ether and aqueous extraction. The ether layer was dried over anhydrous potassium carbonate and concentrated to give the analytically pure silylated aldol product. The catalyzed crossover experiments were run following this procedure and using 1 equiv each of the labeled and nonlabeled ketene acetals to 2 equiv of benzaldehyde. The product crossover control reactions were run following this same reaction and workup procedure and using 1 equiv each of the analytically pure labeled and nonlabeled β-silyloxy aldol products and 5 mol % of the alkoxide catalyst.

Methyl 2,2-Dimethyl-3-[(1-(1,1-dimethylethyl)silacyclobut-1-yl)oxy]-3-phenylpropanoate (20). From 89 mg (0.39 mmol) of 1-[(1-methoxy-2-methyl-1-propenyl)oxy]-1-(1,1-dimethylethyl)silacyclobutane (6), 41.3 mg (0.39 mmol) of benzaldehyde, and 2.20 mg (0.02 mmol) of potassium *tert*-butoxide was obtained 76 mg (58%) of **20** as a clear colorless oil: ^{1}H NMR (400 MHz, C_6D_6) δ 7.23 (d, *J* = 7.1, 2H), 7.05 (m, 3H), 5.26 (s, 1H, *H*C(3)), 3.34 (s,3H, (C*H*$_3$O)), 1.80 (m, 1H), 1.45 (m, 2H), 1.26 (s, 3H, (*H*$_3$C-α)), 1.20 (m, 1H), 1.00 (s, 12H, (*H*$_3$C-α) and ((*H*$_3$C)$_3$C)), 0.99 (m, 1H), 0.80 (m, 1H); ^{13}C NMR (100.6 MHz, C_6D_6) δ 176.4 (*C*(1)), 140.7, 128.1, 127.8, 79.9 (*C*(3)), 51.3 (*C*H$_3$O), 49.2 (*C*(2)), 25.3 ((*C*H$_3$)$_3$C), 22.2 (*C*H$_3$-α), 19.1 (*C*H$_3$-α), 16.0 (CH_2), 14.6 (CH_2), 14.4 (CH_2); IR (neat) 2930 (s), 2857 (s), 1742 (s) cm^{-1}; MS (70 eV) *m/z* 334 (M^+, 2), 319 (100). Anal. Calcd for $C_{19}H_{30}SiO_3$: C, 68.22; H, 9.04. Found: C, 67.98; H, 9.23.

Methyl-d_3 2,2-Dimethyl-3-[(1-(1,1-dimethyl-d_9-ethyl)silacyclobut-1-yl)oxy]-3-phenylpropanoate (d_{12}-20). From 154 mg (0.64 mmol) of 1-[(1-methoxy-d_3-2-methyl-1-propenyl)oxy]-1-(1,1-dimethyl-d_9-ethyl)silacyclobutane (d_{12}-6), 67.9 mg (0.64 mmol) of benzaldehyde, and 3.6 mg (0.03 mmol) of potassium *tert*-butoxide was obtained 87 mg (78%) of d_{12}-**20** as a clear colorless oil: ^{1}H NMR (400 MHz, C_6D_6) δ 7.24 (d, *J* = 6.8, H), 7.05 (m, 3H), 5.26 (s, 1H, *H*C(3)), 1.80 (m, 1H), 1.46 (m, 2H), 1.26 (s, 3H, (*H*$_3$C-α)), 1.20 (m, 1H), 1.00 (s, 3H, (*H*$_3$C-α)), 0.99 (m, 1H), 0.83 (m, 1H); ^{13}C NMR (100.6 MHz, C_6D_6) δ 176.4 (*C*(1)), 140.7, 128.2, 127.8, 79.9 (*C*(3)), 49.2 (*C*(2)), 22.2 (*C*H$_3$-α), 19.1 (*C*H$_3$-α), 16.0 (CH_2), 14.6 (CH_2), 14.4 (CH_2); IR (neat) 2969 (m), 2932 (m), 1740 (s) cm^{-1}; MS (70 eV) *m/z* 346 (M^+, 4), 331 (100). Anal. Calcd for $C_{19}H_{18}D_{12}SiO_3$: C, 65.84; H, 8.73. Found: C, 65.91; H, 8.72.

Methyl 2,2-Dimethyl-3-[(1-(1,1-dimethylethoxy)silacyclobut-1-yl)-oxy]-3-phenylpropanoate (21). From 100 mg (0.41 mmol) of 1-[(1-methoxy-2-methyl-1-propenyl)oxy]-1-(1,1-dimethylethoxy)silacyclobutane (7), 43.8 mg (0.41 mmol) of benzaldehyde, and 1.6 mg (0.02 mmol) of lithium *tert*-butoxide was obtained 102 mg (71%) of **21** as a clear colorless oil: ^{1}H NMR (400 MHz) δ 7.30 (m, 5H), 5.20 (s, 1H, *H*C(3)), 3.66 (s, 3H, (C*H*$_3$O)), 1.58 (m, 1H), 1.40 (m, 5H), 1.29 (s, 9H, ((*H*$_3$C)$_3$C)), 1.19 (s, 3H, (C*H*$_3$-α)), 1.03 (s, 3H, (C*H*$_3$-α)), 0.92 (m, 1H); ^{13}C NMR (100.6 MHz) δ 177.0 (*C*(1)), 140.0 (*C*(Ar)), 127.8 (H*C*(Ar)), 127.5 (H*C*(Ar)), 127.4 (H*C*(Ar)), 79.0 (C(3)), 73.8 ((H$_3$C)$_3$*C*)), 51.7 (*C*H$_3$O), 48.9 (*C*(2)), 31.9 ((*C*H$_3$)$_3$C), 22.7 (CH_2), 21.8 (CH_2 and *C*H$_3$-α), 19.1 (*C*H$_3$-α), 11.7 (CH_2); IR (neat) 2975 (m), 1742 (m) cm^{-1}; MS (70 eV) *m/z* 350 (M^+, 1), 87 (100). Anal. Calcd for $C_{19}H_{30}SiO_4$: C, 65.10; H, 8.63. Found: C, 64.84; H, 8.40.

Methyl-d_3 2,2-Dimethyl-3-[(1-(1,1-dimethyl-d_9-ethoxy)silacyclobut-1-yl)oxy]-3-phenylpropanoate (d_{12}-21). From 100 mg (0.39 mmol) of 1-[(1-methoxy-d_3-2-methyl-1-propenyl)oxy]-1-(1,1-dimethyl-d_9-ethoxy)-silacyclobutane (d_{12}-7), 41.8 mg (0.39 mmol) of benzaldehyde, and 1.4 mg (0.02 mmol) of lithium *tert*-butoxide was obtained 94 mg (67%) of d_{12}-**21** as a clear colorless oil: ^{1}H NMR (400 MHz) δ 7.30 (m, 5H), 5.20 (s, 1H, *H*C(3)), 1.57 (m, 1H), 1.40 (m, 5H), 1.19 (s, 3H, (C*H*$_3$-α)), 1.03 (s, 3H, (C*H*$_3$-α)), 0.93 (m, 1H); ^{13}C NMR (100.6 MHz) δ 177.0 (C(1)), 140.0 (*C*(Ar)), 127.8 (H*C*(Ar)), 127.5 (H*C*(Ar)), 127.4 (H*C*(Ar)), 78.9 (*C*(3)), 48.8 (*C*(2)), 22.7 (CH_2), 21.9 (*C*H$_3$-α), 21.7 (CH_2), 19.1 (*C*H$_3$-α), 11.6 (CH_2); IR (neat) 2979 (m), 2934 (m), 1740 (s) cm^{-1}; MS (70 eV) *m/z* 362 (M^+, 1), 65 (100). Anal. Calcd for $C_{19}H_{18}D_{12}SiO_4$: C, 62.93; H, 8.34. Found: C, 63.21; H, 8.46.

Acknowledgment. We are grateful to the National Science Foundation (CHE-8818147 and CHE-9121631) for generous financial support. D.M.C. thanks the Fulbright Commission for a travel grant. Mr. Robert Harlan and Mr. Michael Van Brunt are thanked for the large scale preparation of **1a** and **1b**.

Supplementary Material Available: General experimental procedures, a table of characteristic NMR resonances for the enoxysilacyclobutanes, and a full listing of IR bands and mass spectral fragments (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.