Sakurai Addition and Ring Annulation of Allylsilanes with α,β-Unsaturated Esters. Experimental Results and ab Initio Theoretical Predictions Examining Allylsilane Reactivity

Michael G. Organ,*,† Vladimir Dragan,† Michael Miller,† Robert D. J. Froese,‡ and John D. Goddard‡

Department of Chemistry, York University, 4700 Keele Street, Toronto, Ontario, Canada M3J 1P3, and Guelph-Waterloo Centre for Graduate Work in Chemistry, Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1

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Trimethylallylsilane has been shown to add to methyl acrylate in good yield when catalyzed by $TiCl_4$ at room-temperature despite literature reporting to the contrary. Further, even with these small alkyl ligands on the metal, ring annulation occurs to a large extent, in addition to simple allylation (Sakurai addition). The kinetic product is the ((trimethylsilyl)methyl)cyclobutane derivative which can be isomerized to cyclopentanoid, the thermodynamic product, if left in the presence of the catalyst. Consistent with other literature in this area, increasing the size of the ligands on silicon increases both the rate of product formation and the proportion of ring annulation relative to allylation. To develop a predictive model for allylsilane reactivity, ab initio gas-phase calculations have been made on the parent allylsilane with different ligands on the metal and on the reaction between these allylsilanes and acrolein, acrylic acid, and methyl acrylate. Predictions indicate that as the length of *n*-alkyl ligands on silicon increase, so does the *apparent* ability of the Si−Cα bond of the allylsilane to hyperconjugate with developing vacant p orbital on C*β* as the allylsilane begins to attack an electrophile. This is corroborated by a gradually increasing HOMO in the ground-state allylsilane as the ligands are changed from methyl through to *n*-hexyl and an increasing Si−Cα bond length and decreasing Si−Cα−C*β* bond angle in the protonated species. These results in the gas phase mirror the reactivity of these *n*-alkyl-substituted allylsilanes in experiment; i.e., as the length of the alkyl chain increases, reactivity increases significantly. Triisopropylallylsilane, a very reactive silane, appears to anomalous in charge distribution and geometrical features compared with other substituted allylsilane systems which is due, presumably, to steric effects. The calculations on the protonated species would indicate that almost no hyperconjugative stabilization can occur on the basis of the bond lengths and angles necessary to promote good orbital overlap between the Si−Cα bond and the empty p orbital on C*β*. However, the gas-phase reaction of the triisopropylallylsilane with acrolein and methyl acrylate led to comparatively low energy barriers of 13.1 and 24.5, respectively, which is consistent with its high experimental reactivity. Together, this computational analysis has produced a useful model for predicting allylsilane reactivity and some possible explanations for this reactivity.

Introduction

This report discusses the reactivity of allylsilanes and the mechanism of addition of these compounds to α,*β*-unsaturated ester and carbonyl substrates. In our synthetic program, we are interested in exploring the use of allylsilanes in multireaction sequences that involve cycloaddition chemistry.[1] The formation of four-membered rings using allylsilane precursors via photocycloaddition or Lewis acid catalysis, followed by ring cleavage or expansion, is a useful approach to compounds of considerable complexity. Our approach to these cyclobutane structures has uncovered information concerning the reactivity of a variety of allylsilanes in such additions and the kinetic vs thermodynamic stability of the cycloadducts which result.

Since the seminal work on the allylation reaction between allyltrimethylsilane and α,*β*-unsaturated ketones was disclosed by Hosomi and Sakurai,[2] there has been a great deal published expanding the scope and utility of allylsilanes in such reactions in synthesis.[3] This methodology has been expanded to include ring formation when the allylsilanes involved possess "bulky groups" on silicon to provide cyclobutane and cyclopentane products via net [2 + 2][4] and [3 + 2][5,6] annulation, respectively. The general addition process for allylsilanes onto unsat-

*To whom correspondence should be addressed. Phone: (416) 736-5313. Fax: (416) 736-5936. E-mail: organ@yorku.ca.

† York University.

‡ University of Guelph.

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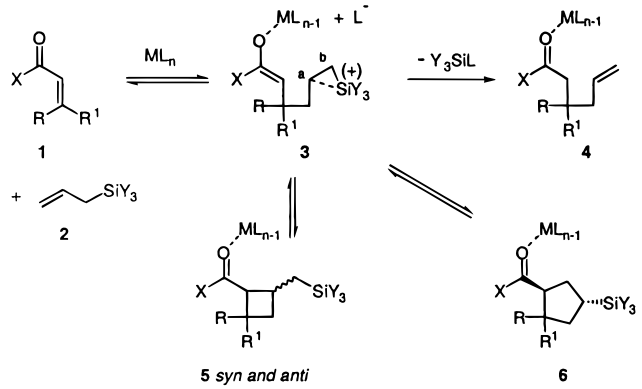
Scheme 1



urated substrates is illustrated in Scheme 1. Siliranium ion intermediate **3** is central to all possible products of initial conjugate addition. In the case of enone substrates (X = alkyl), if Y is large (e.g., isopropyl) the principal product isolated is the five-membered ring adduct **6** which appears to be both the thermodynamic and kinetic product.[7] When Y is methyl, the allylation product **4**, i.e., the Sakurai product, is the major adduct isolated. However, there has been one recent report detailing the formation of a (trimethylsilyl)methyl-substituted cyclobutane adduct, in addition to some of the trimethylsilyl-substituted cyclopentanoid, from the reaction of naphthaquinone and allyltrimethylsilane in the presence of the mild Lewis acid Me_2AlCl.[8]

Since the release of Sakurai's paper (1977),[2] it has been generally accepted that allyltrimethylsilane is unreactive in such additions to analogous ester substrates.[9] Therefore, it was believed that allylsilanes in general were unreactive in additions to α,β-unsaturated esters until the work of Knölker and co-workers was communicated in 1994.[10] They were able to show that when "bulky groups", i.e., isopropyl or phenyl, were placed on the silicon of an allylsilane, the reactivity of the allyl moiety toward conjugate addition to α,β-unsaturated esters (X = OCH_3; $TiCl_4$ catalyst) *appeared* to be enhanced and ring annulation adducts were isolated. Further, closure of the titanium enolate onto the siliranium ion of **3** (in their study) provided cyclobutane adducts **5** (syn and anti with respect to silylmethyl and carbonyl moieties) as the major products, with minor amounts of the *anti* cyclopentanoid **6**.

That allyltriisopropylsilane and allyltriphenylsilane added to the α,β-unsaturated esters in Knölker's study[10] (100% combined cycloadduct yield reported for the addition of triisopropylallylsilane to methyl acrylate, 48% for allyltriphenylsilane) while allyltrimethylsilane failed to add at all to the same electrophile[2] is puzzling! The ability of silicon to stabilize a developing β carbocation is believed to be responsible for the rate of such reactions.[11,12] Presumably, this stabilization would be mainly an electronic effect. Thus, electron-donating ligands on silicon such as methyl, have an accelerating effect on the rate, while electron-withdrawing groups, such as chlorine, decrease the rate. It is well documented that large alkyl groups on silicon have an even greater accelerating effect on the overall rate of allylsilane substitution/addition.[13] Mayr and co-workers studied the addition of a large number of allyltrialkylsilanes to *p*-anisylphenylcarbenium tetrachloroborate and their results show a definite correlation between increasing size of the alkyl group on silicon and the corresponding second-order rate constant. However, if one accepts that the increase in rate is the sole result of an electronic change in the silicon ligands,[14] it is not clear how the rate constants in Mayr's study could increase from 313 for triethylallylsilane to 507 for tri-*n*-butylallylsilane and increase yet again for trihexylallylsilane (542). Presumably, electronic stabilization drops off appreciably beyond two carbons on each ligand on silicon. Further, from this same study the rate

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Scheme 2

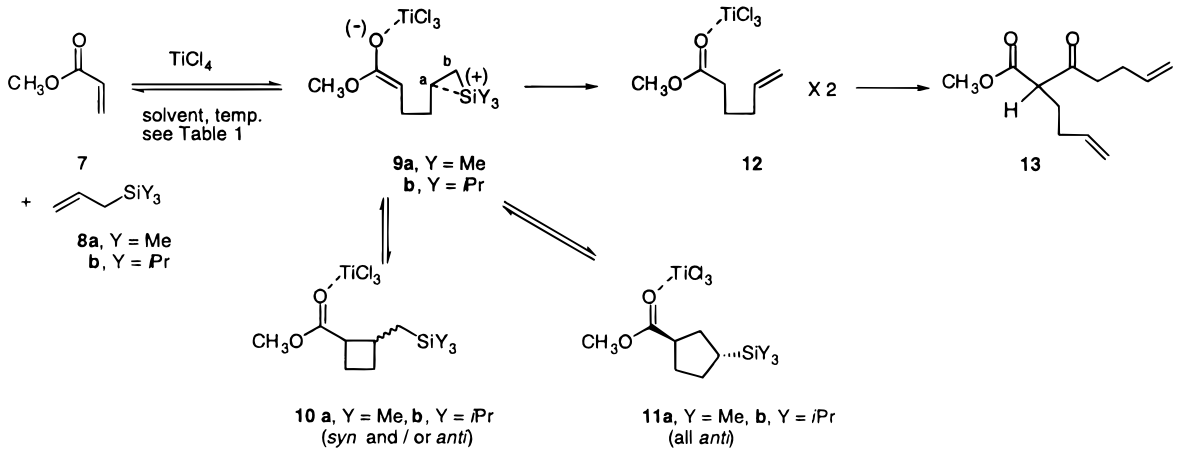

Table 1. Reaction Conditions for $TiCl_4$-Catalyzed Addition of Allyltrimethylsilane to Methyl Acrylate

	no. of equiv							product ratios			
entry	**7**	**8a**	$TiCl_4$	solvent	temp (°C)	time (h)	combined yield	**10a**-*syn*	**10a**-*anti*	**11a**	**13**
1	1	1.1	1	CH_2Cl_2	−78 to 25	5.5	74	2.5	1.7	1.3	1
2	1	1.1	1.1	CH_2Cl_2	40	19	60	1.1	0.1	1.2	1
3	1	1.1	1.1	$CHCl_3$	65	14.5	17	2	1	0.9	1
4	1	1.1	1.1	CH_2Cl_2	25	14.5	74	1.8	0.9	0.9	1
5	1	1.2	2	CH_2Cl_2	25	5.5	74	2.6	0.9	1.7	1
6	1	1.2	1.5	CH_2Cl_2	25	5.5	74	2.8	1.3	1.7	1

constant for allyltriphenylsilane was reported to be 3.21, whereas allyltrimethylsilane was 197. The rate constant for allyltriisopropylsilane (439) relative to allyltrimethylsilane is consistent for the *apparent* reactivity seen in Knölker's study,[10] but the rate constant for allyltriphenylsilane is inconsistent with the fact that allyltrimethylsilane is unreactive in such additions to α,β-unsaturated esters. The electron-deficient phenyl groups on silicon should slow the rate because they destabilize the positive charge forming β to silicon. With this in mind, it does not seem logical that allyltrimethylsilane would not be reactive in such additions.

A number of fundamental aspects of allylsilane reactivity have come into question, and we address them herein. We reinvestigated Sakurai's study regarding the reactivity of allyltrimethylsilane toward addition to methyl acrylate. This single experiment led into a broad study of the factors that determine allylsilane reactivity and how this effects the formation of adducts in reactions with α,β-unsaturated ketone and ester electrophiles. We have synthesized some new allylsilanes to compare reactivities with that of the other derivatives discussed above. All of these studies provide product ratios which, although perhaps indicative, do not give any indication of relative reactivity; thus we have also developed a computational model to evaluate allylsilane reactivity and product stability.

Results and Discussion

Following Sakurai's conditions,[2] methyl acrylate was stirred at −20 °C in CH_2Cl_2 with freshly distilled $TiCl_4$ (1.0 equiv), the solution further cooled to −78 °C, and the silane (1.1 equiv) added (see Scheme 2 and Table 1, entry 1). The initial Lewis acid/ester complex is deep burgundy in color and upon cooling to −78 °C came out of solution as a yellowish precipitate. No reactivity was observed until the suspension was warmed to RT (room temperature) at which time a homogeneous yellow solution was observed and product spots appeared on TLC. This experiment was also conducted in an NMR tube and the reaction's progress monitored by ^1H NMR spectroscopy. After 1 h at 25 °C, the only products seen in the ^1H NMR spectrum were **10a** and **13**,[15] in addition to starting materials. Interestingly, syn cyclobutane adducts are the major products derived from ester substrates despite being less stable than the corresponding anti adducts.[16] Compound **13** could be formed by a Claisen-type condensation of **9a** onto **12**, presumably following silicon loss, which implies that there must be an internal source of H^+ to protonate the Ti−enolate of **9a**. It is possible that only the trace of acid present in $TiCl_4$ is necessary to initiate this side reaction as the acidic proton on **13** could serve as the proton source once formed. This condensation must be a very rapid process because we do not see **12** in the NMR spectra of the reaction mixture. After 4 h, the first noticeable amount of **11a** began to form. Structural elucidation was carried out by comparison of ^1H and ^{13}C NMR data with the analogous triisopropylsilyl adducts prepared in this study (vide infra) and by Knölker who confirmed their connectivity by X-ray analysis.[10] The NMR data are quite diagnostic for all syn and anti cyclobutane and anti cyclopentane structures in this series.

We also performed a number of experiments where reaction conditions were varied. $TiCl_4$ seems to be necessary for this reaction to proceed because analogous experiments under $SnCl_4$ and $AlCl_3$ catalysis only returned starting materials. Increasing the reaction time had the general effect of increasing the percentage of **11a** and **13** relative to the cyclobutane adducts **10a** (see Table

(15) Compound **13** has been prepared previously by another route and the spectral characterization corresponded well; see: Nakahara, Y.; Fujita, A.; Ogawa, T. *Agric. Biol. Chem.* **1987**, *51*, 1009−1015.

(16) This study; see the Theoretical Considerations section and also ref 10.

1, entry 4). Further, heating the reaction also had the same effect (see Table 1, entry 2). Compounds **9a** and **10a** exist in a readily reversible equilibrium, and **10a** is clearly the kinetic product of this reaction. Ring strain present in **10a** is responsible for the facile fragmentation of the cyclobutane which is not present in the case of the cyclopentane; thus, formation of **11a** is likely nonreversible. Further, **12** reacts rapidly when formed providing **13** which also serves as another sink in this reaction. Therefore, time and heat simply promote the formation of the thermodynamic products **11a** and **13**. Finally, we dissolved **10a** (both isomers) in CH_2Cl_2 and added 1 equiv of $TiCl_4$ and observed quantitative conversion of **10a** to **11a** and **13** in approximately equal proportions which further supports this idea.

The fact that the cyclobutane adducts could be completely isomerized to the cyclopentanoid (in addition to the formation of **13**) prompted us to further investigate the addition of allyltriisopropylsilane to methyl acrylate. Knölker et al. performed this transformation under two sets of reaction conditions.[10] In the first case, the temperature was kept at or below 0 °C for 19 h, and the second reaction was performed at 40 °C for 3 h. The ratios of **10b**-*syn*:**10b**-*anti*:**11b** were 11.9:9.5:1 and 6.3:1.7:1, respectively. As with the allyltrimethylsilane addition in our study, the syn cyclobutane adduct dominates under both sets of conditions with methyl acrylate electrophile. Further, higher temperature, more so than time, increases the percentage of the cyclopentane adduct which is presumably the thermodynamic product. Compounds **7** (1.0 equiv) and **8b** (1.2 equiv) were loaded into an NMR tube along with CD_2Cl_2 (0.5 mL, 0.34 M in **7**), the solution was cooled to 0 °C, and 2 equiv of $TiCl_4$ was added (see Scheme 2 for structures). The mixture was then warmed to 40 °C and the reaction's progress followed by ^{1}H NMR spectroscopy (see Figure 1). Formation of adducts **10b** is considerably more rapid than with allyltrimethylsilane addition. The spectrum taken at 3 h had a ratio of 6:1:1 for **10b**0*syn*:**10b**-*anti*:**11b**, which is consistent with Knölker's result at 3 h. The remaining spectra demonstrate smooth conversion of **10b** to **11b** over the span of 24 h. In an analogous experiment, **10b** was treated with 2 equiv of $TiCl_4$ in CD_2Cl_2 and the conversion to **11b** was quantitative as well. The bulky nature of the isopropyl groups prevents nucleophilic displacement of the silyl moiety at the siliranium ion stage (i.e., **9b**) which would lead to the product of Sakurai addition (i.e. **12**).

These results indicated that our proposed ring expansion strategy to provide cyclopentane-containing natural products from cyclobutane precursors could well be successful. Allyltrimethylsilane does in fact add to methyl acrylate via stepwise ring annulation. The overall yield and *apparent* reactivity of allyltrimethylsilane in this reaction were consistent with what we would have expected. That is, general reactivity and isolated yields of reactions employing this silane with methyl acrylate lie between that of allyltriisopropylsilane and allyltriphenylsilane as reported by Knölker.[10]

With these results in hand, we had hope for our synthetic studies employing unsaturated ester substrates. However, there were two concerns regarding the trimethyl and triisopropyl derivatives for synthetic work. First, the triisopropylsilyl group on **11b** cannot be oxidized readily rendering this product of little use.[17] Second, while the trimethylsilyl group on **11a** can be

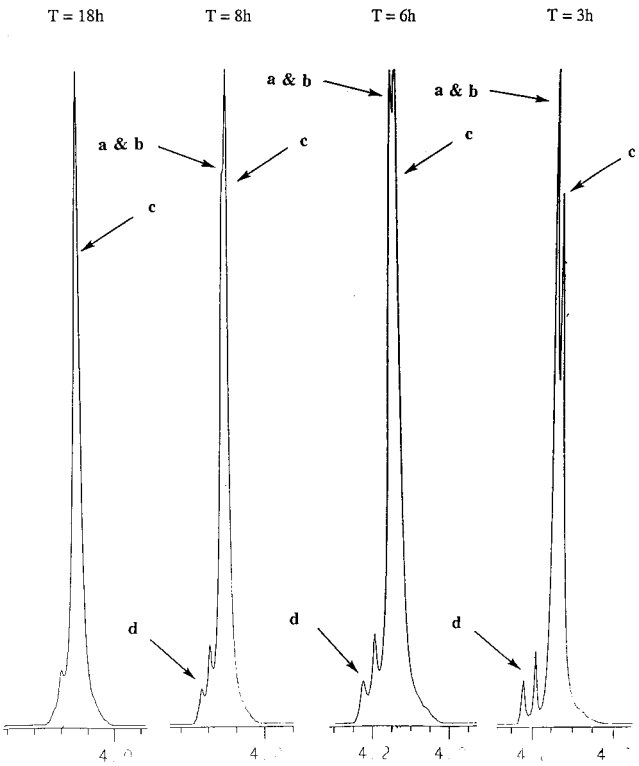

Figure 1. NMR spectra of the reaction between methyl acrylate (**7**, 1.0 equiv) and triisopropylallylsilane (**8b**, 1.2 equiv) in the presence of $TiCl_4$ (2.0 equiv) in CD_2Cl_2. The reagents were combined at 0 °C, the tube was warmed to 40 °C, and the reaction's progress was followed over 18 h. Signals indicated are those of the methyl ester which have been shifted downfield of 4 ppm due to coordination to the titanium catalyst. Key: a = *syn*-cyclobutane adduct; b = *anti*-cyclobutane adduct; c = *anti*-cyclopentane adduct; d = methyl acrylate.

oxidized easily using Tamao conditions,[18] the isolated yield of **11a** is modest, largely due to the formation of side product **13**. We reasoned that we could compromise and design an allylsilane that was suitably reactive in the ring annulation reaction and that the resultant silane product could be readily oxidized. We hypothesized that dihexylphenylallylsilane would be a reactive partner in ring annulation and the phenyl group would make oxidation possible.[19] Although the phenyl group would be expected to decrease reactivity, we reasoned that the two hexyl substituents would compensate on the basis of Mayr's rate studies which showed that trihexylallylsilane had the largest second-order rate constant in his addition studies.[13]

We began this study using trihexylallylsilane to compare the reactivity of this derivative with allyltriisopropylsilane. On the basis of Mayr's studies, we expected

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(19) Just following the completion of the work for this manuscript, two reports were disclosed on the oxidation of diphenyl-*tert*-butylsilane and diisopropylphenylsilane; see ref 5i and the following: Knölker, H.-J.; Jones, P. G.; Wanzel, G. *Synlett* **1998**, 613−616.

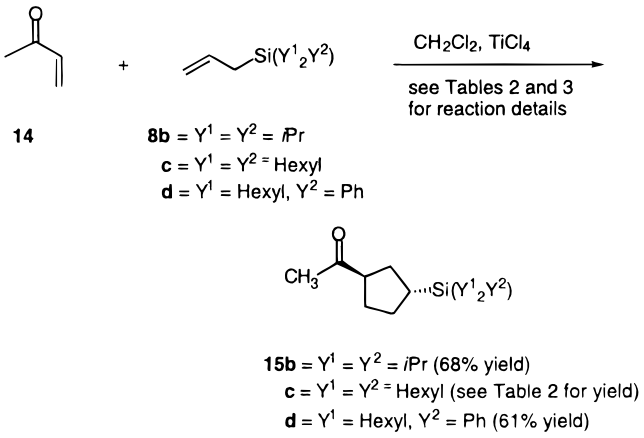
Table 2. Reaction Conditions for $TiCl_4$-Catalyzed Addition of Trihexylallylsilane to Methyl Vinyl Ketone

	no. of equiv					time (h)	yield of
entry	**14**	**8c**	$TiCl_4$	Me_2AlCl	temp (°C)	at each temp	**15c** (%)
1	1	2.0	2.0	1.3	−78	16.0	33
2	1	1.0	1.0	0	−70	2.0	>5
3	1	0.5	1.1	1.2	−78	15.0	26
4	1	2.0	1.1	0.15	−78	15.0	7
5	1	2.0	1.05	0.15	−78 to −5	1.0, 0.5	16
6	1	2.0	1.05	0	−78	1.5	10
7	1	2.1	1.1	0.2	40	5.0	0

Table 3. Reaction Conditions for $TiCl_4$-Catalyzed Addition of Dihexylphenylallylsilane to Methyl Vinyl Ketone

	no. of equiv					time (h)	yield of
entry	**14**	**8d**	$TiCl_4$	Me_2AlCl	temp (°C)	at each temp	**15c** (%)
1	1	0.9	2.0	0	−78 to 25	2.0, 40.0	27
2	1	1.0	1.0	0	−78 to 25	1.5, 23.0	28
3	1	0.5	2.0	1.1	−78 to 25	5.0, 20.0	40
4	1	2.1	2.0	1.3	−78 to 25	20.0, 1.0	60

Scheme 3



the trihexyl derivative would be considerably more reactive in additions to methyl acrylate and MVK than the triisopropyl case, but the opposite proved to be true. Reaction of MVK (**14**) with **8c** was sluggish, and if the reaction was heated, no product (**15c**) was isolated whatsoever (see Scheme 3 and Table 2). The comparable run with allyltriisopropylsilane provided 68% yield (**15b**). It is instructive to note that the best product recoveries were reported when at least 1 equiv of Me_2AlCl cocatalyst was included in the reaction mixture. We have studied the effects of using this cocatalyst with $TiCl_4$ during allylsilane substitution chemistry, and it has shown to have remarkable effects on reaction yield.[1b] The principal role of Me_2AlCl is believed to be that of a proton sponge which helps to prevent protodesilylation of the allylsilane starting material, thus allowing more of the desired reaction to take place.[20] This usually results in significantly higher yields when Me_2AlCl is used.

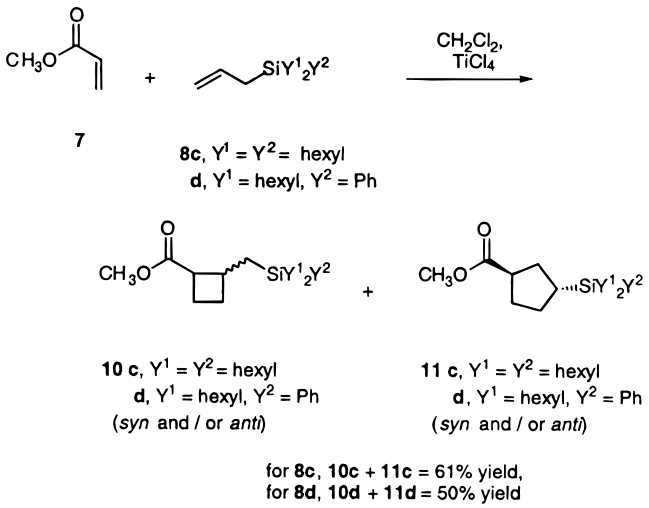
Dihexylphenylallylsilane (**8d**) provided consistently higher yields than the trihexyl case with MVK, even though it is surely less reactive toward initial attack on the enone (see Scheme 3 and Table 3). In Mayr's study of allylsilane rate constants, he reported that replacing one methyl of allyltrimethylsilane with one phenyl ring reduces the reactivity of the allyl moiety by a factor of 5.[13] However, allylsilanes possessing at least one phenyl group on silicon are noticeably less prone to protodesilylation.[1b] One possible explanation for the poor result using trihexylallylsilane is that the rates of nucleophilic attack of both the triisopropyl and trihexyl derivatives on the enone are comparable but increased susceptibility of trihexylallylsilane to protodesilylation is responsible for the lower "*observed*" or "*desired*" reactivity with the electrophile. Of course, another possibility is that allyltriisopropylsilane is simply much more reactive toward electrophilic addition than trihexylallylsilane, despite Mayr's conclusions, and that this heightened reactivity is kinetically much faster than protodesilylation. This would lead to more product formation before protodesilylation has a chance to occur. Slower addition of the trihexyl derivative to the electrophile would lead to more protodesilylation, which may be the favored kinetic process with that particular silane. We are unable to suggest which hypothesis, if either, is operative although we do address it in the computational section (see Theoretical Considerations).

The presence of an acidic proton on MVK (from the methyl ketone, pK_a 20−25) can promote enolization in titanium's presence thus providing an in situ source of H^+.[1b] Further, allylsilanes can behave as the Brönsted base resulting in protodesilylation.[21] This would dramatically affect product recovery from these reactions because such a process removes both MVK and the allylsilane from the mixture before any desired addition can take place between them. To confirm that protodesilylation was occurring during the reaction and not during the workup, MVK, $TiCl_4$, and **8c** were loaded into an NMR tube (CD_2Cl_2 solvent), the tube was quickly sealed, and the reaction's progress was followed by NMR spectroscopy. As suspected, protodesilylation occurred to a large extent during the reaction as evidenced by the significant presence of propene. The identical NMR experiment with methyl acrylate showed propene formation initially upon addition of $TiCl_4$, likely owing to the presence of trace HCl in the catalyst, and this did not increase over the course of 2 days. In a control experiment, trihexylallylsilane was treated with $TiCl_4$ (1.0 equiv) in an NMR tube and the result was the same as that which contained

(20) (a) Snider, B. B.; Rodini, D. J.; Conn, R. S. E.; Sealfon, S. *J. Am. Chem. Soc.* **1979**, *101*, 5285−5293. (b) Snider, B. B.; Rodini, D. J. *Tetrahedron Lett.* **1980**, *21*, 1815−1818.

(21) For reports dealing with acid-catalyzed protodesilylation, see: (a) Coughlin, D. J.; Salomon, R. G. *J. Org. Chem.* **1979**, *44*, 3784−3790. (b) Pennanen, S. I. *Synth. Commun.* **1980**, *10*, 373−379. (c) Hosomi, A.; Iguchi, H.; Sasaki, J.-I.; Sakurai, H. *Tetrahedron Lett.* **1982**, 551−554. (d) Ireland, R. E.; Varney, M. D. *J. Am. Chem. Soc.* **1984**, *106*, 3668−3670. (e) Shibasaki, M.; Fukasawa, E.; Ikegami, S. *Tetrahedron Lett.* **1983**, *24*, 3497−3500. (f) Corey, E. J.; Letavic, M. A. *J. Am. Chem. Soc.* **1994**, *117*, 9616−9617.

Scheme 4



methyl acrylate, i.e., some initial propene formation upon catalyst addition only. This result supports our suspicion that MVK is facilitating protodesilylation and that trihexylallylsilane is especially sensitive to this side reaction.

If that which has been proposed above is true, one would expect that product recovery from experiments with methyl acrylate (which lacks the acidic proton) to be higher than for MVK, despite being a less electrophilic substrate. Treatment of methyl acrylate (**7**) with **8c** (2.0 equiv) in the presence of $TiCl_4$ (1.1 equiv) at 40 °C provided a 61% combined yield of cycloadducts **10c** and **11c** (Scheme 4). At the end of this reaction, which had been heated for 22 h, some starting allylsilane was also recovered. The analogous reaction with **8d** provided a 50% yield of ring annulated products **10d** and **11d**. In light of the fact that starting materials can be recovered from this reaction, we are confident that the yields can be increased significantly. As hypothesized, dihexylphenylallylsilane provided promising recovery of ring-annulation products when compared to that obtained with triphenylallylsilane reported by Knölker.[10]

As anticipated, methyl acrylate has provided a nicely controllable system to study the relative reactivity of a number of allylsilane derivatives. It is interesting to note that the best results in all reactions attempted are with the allyltriisopropylsilane. Further, reactions with this silane appear to be kinetically much faster (when monitored by NMR spectroscopy) than with other allylsilanes, although the appearance of cycloadduct in the spectra is not an accurate measure of reaction rate. This has inspired us to take a look at some of these systems computationally to see if any trends emerge to assist in predicting the order of reactivity of different allylsilanes. Further, we can validate these computational estimates by comparing them with the experimental results obtained in this study and those of other scientists who have studied allylsilane reactivity by other methods.

Theoretical Considerations

We have undertaken theoretical studies of some of the allylsilane systems to determine if gas-phase computational approaches can give any rationalization for the reactivities observed. More specifically, we have examined the charges and geometries of a variety of substituted allylsilanes, both as neutral and cationic species, to determine if the observed reactivities can be explained on the basis of these properties. In addition, we have studied the formation of intermediate cation **3** using acrolein, acrylic acid, and methyl acrylate as our electrophile together with trimethyl-, triethyl-, and triisopropylallylsilane in order to determine the effect of the silicon ligands on the activation barrier. While solvation effects surely must play an important role for these ions and since ab initio calculations will not properly take these into account, we are most interested in the trends and not the absolute numbers. Theoretical predictions were performed with the GAUSSIAN suite of programs.[22] The geometry optimizations of the intermediate cations were performed without symmetry constraints at the Hartree−Fock level (HF) using the 3-21G* basis set.[23] Calculations on the neutral and cationic allylsilanes were done at both the Hartree−Fock level and the hybrid density functional theory level, B3LYP[24] using the 6-31G*[25] basis set. Some calculations were also tested using second-order perturbation theory, MP2.[26] Mulliken charges were predicted using the 3-21G* and 6-31G* basis sets.

Figures 2 and 3 depict important geometrical features of eight different allylsilanes. The three substituents on the silicon range from hydrogen, to electron-withdrawing chlorine (−I), to a variety of electron-donating alkyl groups (+I, +R) including isopropyl and *n*-hexyl. The different geometrical features and Mulliken charges are shown for both the ground-state species (Figure 2) and the cationic complex that would be obtained by protonation of the allylsilane (Figure 3) that we are using to model the reaction intermediate.

Considerable effort has been expended to explain how substituents on silicon increase or decrease the nucleophilicity of the olefin of an allylsilane.[12,14] To the extent that ground-state structure can be used or extrapolated to predict reactivity of any chemical species, examination of the data in Figure 2 is interesting. Certainly such considerations must be viewed critically for molecules generally react from the most reactive conformation and not the most stable one. However, if the reactivity of an allylsilane is dependent on the extent to which the Si−Cα bond is parallel to p orbitals of the olefin as nucleophilic attack begins,[3] these minimized structures, relative to each other, should provide useful information for the lowest energy conformation for all structures are in fact

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(25) (a) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724−728. (b) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257−2261. (c) Hariharan, P. C.; Pople, J. A. *Mol. Phys.* **1974**, *27*, 209−214. (d) Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163−168. (e) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213−222.

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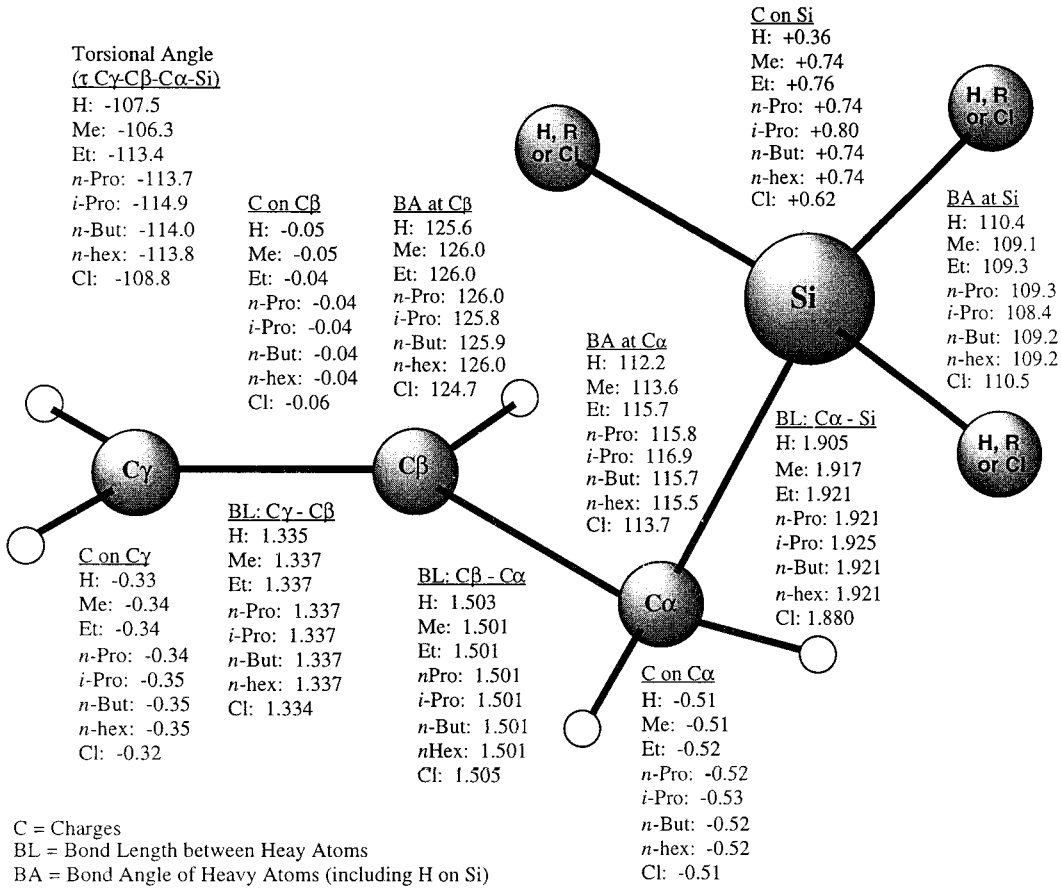

Figure 2. Important geometrical parameters and charges of eight allyl silanes for the ground state. Geometries were optimized at the B3LYP/6-31G* level of theory.

close to the proposed reacting conformation. Aside from methyl, the Si−Cα−Cβ−Cγ torsional angle does not vary substantially among all other *n*-alkyl ligands indicating that there are no pronounced steric effects by elongating the chain length of the groups on silicon. These observations lend support to the "cone angle" analysis presented by Panek and co-workers, who hypothesized that the cone angle of bulkier silicon ligands does not vary appreciably from nonbulky ones.[14b] Further, these results also support the work by Mayr's group, who observed a steady increase in allylsilane reactivity as the ligand chain-length on silicon is lengthened from methyl through to *n*-hexyl and that this increase in reactivity is primarily the result of electronic considerations.[13] The increased steric requirement of the paddling isopropyl moieties causes noticeable twisting of the Si−Cα bond away from a reacting conformation, relative to the other alkyl ligand groups.

For the protonated structures, which are intended to model the cation intermediate of nucleophilic attack (Figure 3), R = H would appear to have the best torsional geometry for hyperconjugative stabilization (−93.5°). However, careful inspection of the Si−Cα−Cβ angle (97.4°) indicates that the Si−Cα bond is also bent away from the adjacent Cβ p orbital. The largest deviants in this regard are triisopropyl and trichloro at 102.3 and 106.6°, respectively, which suggests Cα is closer to sp^3 hybridized. These two results are in themselves very interesting for they demonstrate steric and electronic extremes that separately lead to similar structural results. The chloro-substituted allylsilane, where Cl is smaller than the effective van der Waals radius of a methyl group, resists hyperconjugation of the Si−Cα bond due to the electron-withdrawing Cl ligands. The isopropyl group, a pronounced electron donor, is too large to allow the necessary rehybridization of Cα to take place to pull the Si−Cα bond closer to the vacant p orbital on Cβ. The significantly shorter Si−Cα bond lengths for R = H (2.086 Å) and Cl (2.037 Å) and the slightly shorter triisopropyl case (2.214 Å), relative to the other alkyl-substituted allylsilanes, further suggests that little hyperconjugation of the Si−Cα bond appears to be taking place in the cation. Conversely, the Si−Cα−Cβ angle gets progressively smaller and the Si−Cα bond length progressively longer as the *n*-alkyl series progresses from methyl through to *n*-hexyl. This is highly suggestive that as the length of the ligand chain increases on Si, hyperconjugation also increases which mirrors measured allylsilane reactivity for this series.[13] Although this analysis nicely accounts for the increasing reactivity of the tri-*n*-alkylallylsilanes, it is anomalous in its apparent treatment of triisopropyl. If hyperconjugation is an accurate measure of reactivity, owing from a lowered energy intermediate (i.e., more stable), triisopropyl would appear to be a poor candidate, yet it is clearly one of the most reactive nucleophiles of all the allylsilanes.

In an attempt to better understand the relationship between sterics and hyperconjugation, a series of calculations was performed whereby the ligands on the silicon were replaced with three hydrogen atoms for the other allylsilanes studied, and the data are listed in Table 4. The new structures were designed to maintain the same angular and torsional values possessed by the original silanes. The Si−H bond lengths were fixed at the

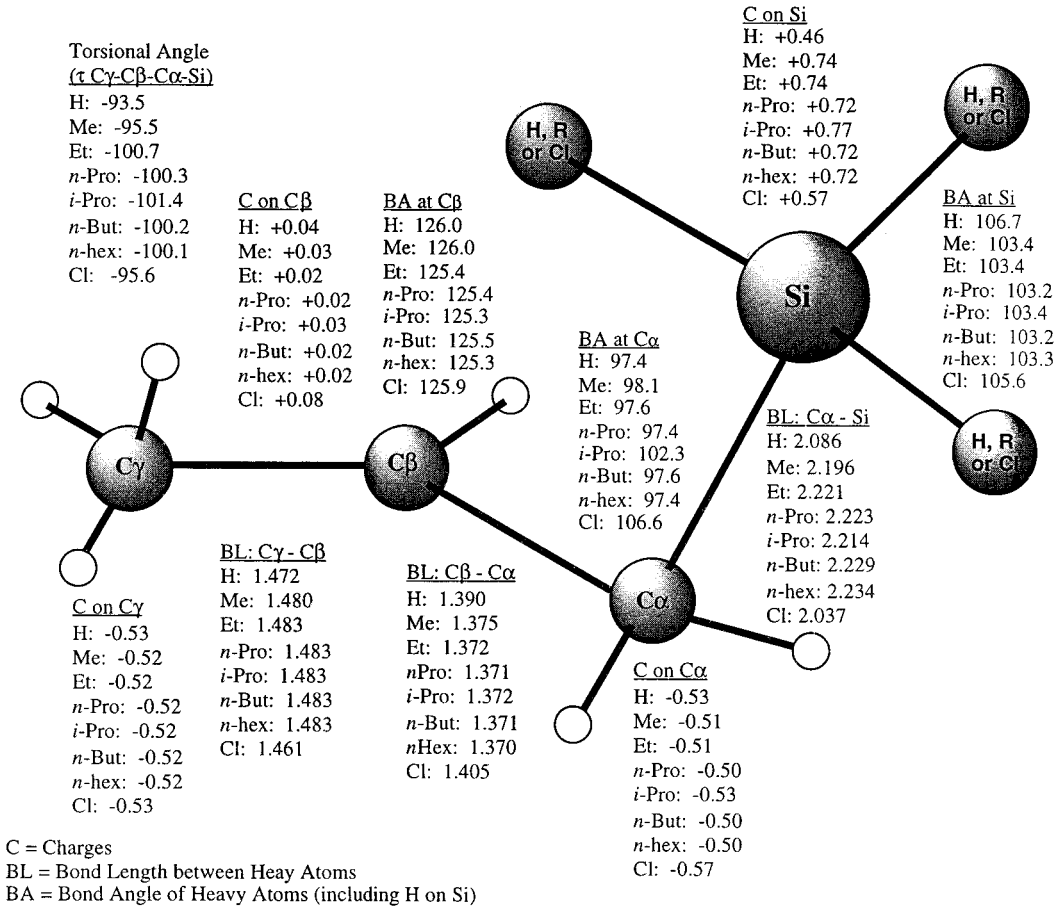

Figure 3. Important geometrical parameters and charges of eight allyl silanes for the cationic species. Geometries were optimized at the B3LYP/6-31G* level of theory.

Table 4. Effect of the C−C−C−Si Torsion Angle on the Energies of the Ground-State and Charged Allylsilanes[a]

	R_3 group							
	H	Me	Et	*n*-Prop	*i*-Prop	*n*Bu	*n*Hex	Cl
				Torsion Angles and Energies				
C−C−C−Si (−t)	−107.5	−106.3	−113.4	−113.7	−114.9	−114.0	−113.8	−108.8
DE (ground state)	0.0	0.2	0.4	0.4	0.8	0.4	0.4	0.2
C−C−C−Si (−t)	−93.5	−95.5	−100.7	−100.3	−101.4	−100.2	−100.1	−95.6
DE (cations)	0.0	1.2	2.1	2.3	2.4	2.2	2.4	0.9
				Relative Energies of the HOMO (eV)				
ground state	0.61	0.98	1.00	1.00	1.00	1.00	1.01	0.00

[a] The energies of the eight species are in kcal/mol relative to the R = H structure as shown in Figures 2 and 3. The B3LYP/6-31G* level of theory was employed where the R groups on the allylsilane were replaced with hydrogens at a bond length of 1.4890 Å for cations and 1.4738 Å for neutral isomers, and all other bond, angle, and torsion values remained the same as those optimized on the full system at the B3LYP/6-31G* level. The relative energies of the HOMO for the ground-state species at the B3LYP/6-31G* level are also shown with the HOMO of the tri-Cl being most stable and the others listed relative to thos system in eV.

optimized bond lengths of 1.4890 and 1.4738 Å for the neutral and cationic species (R = H), respectively. The relative energies (kcal/mol) at the B3LYP/6-31G* level should tell us what the "energetic cost" is of steric effects that force the Si−Cα bond away from hyperconjugation with Cβ, assuming the most ideal Si−Cα−Cβ−Cγ torsional value is 90° (or −90°). Since R = H corresponds to the minimum and represents our energy zero, the optimized ground-state torsional angle is −107.5° and deviations from this value will increase the energy. For the R = H cation, the torsion angle of −93.5° is close to the ideal perpendicular orientation desired for hyperconjugation. There is a clear correlation between a torsional angle τ varying further from 90° and an energy increase. The torsional angle differing furthest from perpendicular is the isopropyl case (−101.4°). Here, the deviation from the ideal hyperconjugative geometry is 7.9° (relative to R = H) which leads to a cost of 2.4 kcal/mol. These numbers clearly indicate that hyperconjugative effects are significant and energetically stabilizing. For the *n*-alkyl ligands on Si, there is a gradual increase in energy as you proceed from trimethyl to tri-*n*-hexyl for the cation that results, presumably, from a loss of hyperconjugation. The high reactivity of allylsilanes with larger alkyl ligands suggests that the increasing +R effect of the longer chains overcomes poorer orbital overlap that forces orbitals out of ideal overlap alignment to impart electronic stability.

In addition to charges and geometries, we have also examined the relative energies of the highest occupied orbitals (B3LYP/6-31G*) for the ground-state isomers (Table 4). The chlorine HOMO has the lowest energy

Table 5. Energetic Data for the Addition of Three Allylsilanes (a, Tri-Me; b, Tri-Et; c, Tri-*i*-Prop) to the Lithiated Acrolein (15), Acrylic Acid (16), and Methyl Acrylate (17) Species

reactants	tot. energy (Hartree)	ZPVE	ΔE	species
15	−196.976 72	43.5		$C_3H_4LiO^+$
16	−271.455 016	47.1		$C_3H_4LiO_2^+$
17	−310.273 146	66.2		$C_4H_6LiO_2^+$
a	−521.586 815	122.0		$C_6H_{14}Si$
b	−638.027 243	180.8		$C_9H_{20}Si$
c	−754.470 112	238.7		$C_{12}H_{26}Si$
15 + **a**	−718.563 540	165.5	0.0	$C_9H_{18}LiOSi^+$
transition state	−718.540 799	167.5	16.3	
intermediate	−718.544 060	168.5	15.2	
16 + **a**	−793.041 830	169.1	0.0	$C_9H_{18}LiO_2Si^+$
transition state	−793.002 628	170.8	26.3	
intermediate	−793.002 686	170.8	26.3	
17 + **a**	−831.859 827	188.2	0.0	$C_{10}H_{20}LiO_2Si^+$
transition state	*a*			
intermediate	−831.814 322	190.1	30.5	
15 + **b**	−835.003 967	224.3	0.0	$C_{12}H_{24}LiOSi^+$
transition state	−834.982 853	226.2	15.1	
intermediate	−834.987 907	227.2	13.0	
16 + **b**	−909.482 257	227.9	0.0	$C_{12}H_{24}LiO_2Si^+$
transition state	−909.445 324	229.1	24.4	
intermediate	−909.446 200	229.7	24.4	
17 + **b**	−948.300 388	247.0	0.0	$C_{13}H_{26}LiO_2Si^+$
transition state	−948.257 362	248.8	28.8	
intermediate	−948.257 467	248.8	28.7	
15 + **c**	−951.446 837	282.2	0.0	$C_{15}H_{30}LiOSi^+$
transition state	−951.430 627	285.1	13.1	
intermediate	−951.430 728	285.2	13.1	
16 + **c**	−1025.925 127	285.8	0.0	$C_{15}H_{30}LiO_2Si^+$
transition state	−1025.888 628	287.5	24.6	
intermediate	−1025.889 047	287.6	24.4	
17 + **c**	−1064.743 258	304.9	0.0	$C_{16}H_{32}LiO_2Si^+$
transition state	−1064.706 889	*b*	24.5[c]	
intermediate	−1064.707 312	*b*	24.4[c]	

[a] Transition state could not be located. [b] Frequency calculations were not performed due the size of the molecules. [c] These relative energies include zero point corrections estimated from the frequency analysis of **16** + **c**.

because its electron-withdrawing power creates a HOMO which is electron-deficient. This makes it more difficult to remove electrons thus lowering the energy and decreasing reactivity. As the *n*-alkyl ligands on silicon go from methyl to hexyl, there is a slight, but gradual, increase in the HOMO energy. This slight destabilization could play a role in increasing the reactivity for these systems.

We have studied theoretically the addition of three allylsilanes with acrolein, acrylic acid, and methyl acrylate. To minimize electron count, we have used a Li cation in place of $TiCl_3$ cation as the Lewis acid in this study. The energetic data for the additions to the substituted allylsilanes, $CH_2{=}CH_2{-}CH_2{-}SiR_3$, where R = Me, Et, and *i*-Prop, are summarized in Table 5.

Although calculations are done at the HF/3-21G* level of theory, the general trends should give us an idea of which species are predicted to be most reactive. Figure 4 depicts important geometrical features and charges of the transition states for the addition of trimethyl-, triethyl-, and triisopropylallylsilane to acrylic acid in the presence of Li cation. By examination of the structural and energetic trends, the effect of the alkyl substitution of the allylsilane and the acrolein group (H, OH, OCH_3) can be determined.

For the addition of the three allylsilanes to the lithiated acrylic acid species, the forming C−C bond in the three transition state structures has lengths of 1.748 (**16a**), 1.799 (**16b**), and 1.786 (**16c**) Å (see Figure 4 for representative structures). The bond which has formed in the intermediate is extremely long at distances of 1.686, 1.644, and 1.661 Å, respectively, indicative of a very weakly bound intermediate. The energetics in Table 5 indicate the transition state energies lie only between 0 and 0.2 kcal/mol above the minima indicating again that this intermediate is weakly bound. The highly endothermic nature of this reaction by ca. 25 kcal/mol is helping lead to this result. Thus, the relative reactivities can be accurately judged thermodynamically by the energetic height of the intermediate rather than kinetically by the activation energies.

There are some interesting trends which can be observed in the energetics from Table 5. First, as the R group is changed in the allylsilane, there are slight changes in the transition state barriers. On going from R = Me, Et, and *i*-Prop, the activation barrier typically decreases for any given reaction. For example, for the addition of the three allylsilanes to lithiated acrolein, the barrier (kcal/mol) goes from 16.3 (R = Me) to 15.1 (R = Et) to 13.1 (R = *i*-Prop). These energy differences qualitatively support the rate increase reported in Mayr's work of 67% on going from R = Me to R = Et and 40% from R = Et to R = *i*Prop.[13] It is interesting that this series of calculations indeed predict a decrease in activation energy when the substitution on Si changes from Me to Et to *i*-Prop in agreement with experimental data in this report and others,[13] although these substituents are some distance from the reacting center.

This last series of calculations clearly shows the potential danger of relying on just one computational model. The reaction models demonstrate that triisopropylallylsilane has energy differences in both the TS barriers and intermediates that are consistent with the apparent high reactivity demonstrated by this reagent experimentally. However, while the data in Figures 2 and 3 and Table 4 provide a nicely explainable trend to follow

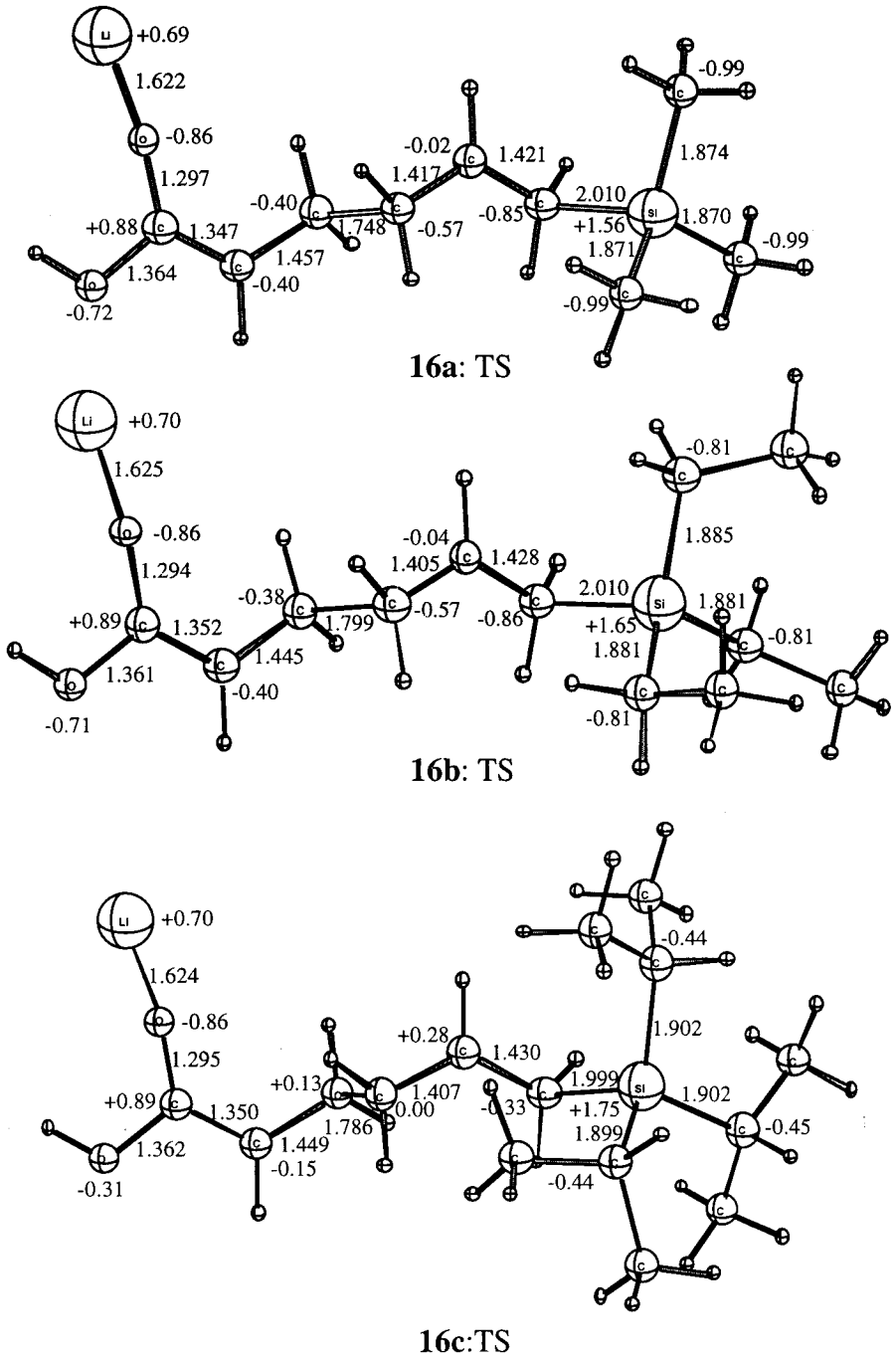

Figure 4. Important geometrical features and Mulliken charges for the transition state structures for the addition of the lithiated acid (**16**) to three allyl silanes, the Me (**a**), Et (**b**), and *i*-Prop (**c**) substituted systems. Geometries and charges came from the HF/3-21G* level of theory.

for the *n*-alkyl substituted silanes, as well for H and Cl, isopropyl always sat outside of the trends. These data would have indicated lower reactivity for isopropyl than is observed experimentally. We believe that this combination of computational models has provided a useful method for analyzing allylsilane reactivity, and we are continuing our studies on this system.

Conclusions

Trimethylallylsilane adds effectively to methyl acrylate in the presence of $TiCl_4$. The intermediate siliranium ion thus produced (**9a**) can undergo desilylation to give the Sakurai addition product (**12**) or the titanium enolate can close onto the carbocation, thereby maintaining the silicon-containing moiety in the structure, giving rise to either (**10a**) or five-membered-ring (**11a**) annulation products. Products **11a** and **12** (which self-condenses when formed) are thermodynamic sinks and do not react further. The ring strain in **10a** makes it susceptible to fragmentation in the presence of $TiCl_4$, and equilibration takes place eventually converting all of **10a** to **11a** and **12**.

When larger ligands on Si are employed, such as triisopropyl- or di-*n*-hexylphenylallylsilane, ring annulation similarly occurs with MVK to yield the five-membered-ring product exclusively with no observed

Sakurai product. However, when tri-*n*-hexylallylsilane was reacted under identical conditions, protodesilylation of the starting material occurred to a major extent in the presence of MVK and $TiCl_4$ and we believe this to be the result of heightened sensitivity of this reagent relative to other silanes used, but the origin of this sensitivity is not understood. When all of the above silanes were reacted with methyl acrylate, all added smoothly, the four-membered ring products dominated kinetically, and all equilibrated to the more stable 5-membered ring product over time.

A series of ab initio gas phase predictions has been made. The parent allylsilane with different substituents on the silicon was examined, and then the reaction between the allylsilane and different α,*β*-unsaturated carbonyl systems was investigated. It was determined that the triisopropyl group is anomalous in charge and geometrical features compared with other alkyl substituted systems. The bulky *i*-Prop groups lead to a C═C−C−Si torsion angle differing from the H-substituted species by about 8° in both the ground state and cation. Steric effects appear to be important since the Si−Cα−C*β* angle of 116.9° in the ground state structure is also noticibly larger than the other seven species which have a small range of 112.2−115.8°.

The charge on the silicon atom for the *i*-Prop system is the largest at +0.80 and +0.77 on the ground-state silane and cationic species, respectively. This result appears to be consistent with the high reactivity observed with this silane experimentally but appears to contradict other computational results. These charge data would suggest that hyperconjugation occurs to the largest extent with triisopropylallylsilane which should place the maximum amount of positive charge on the Si atom. However, the orbital overlap analysis with this very electron-rich silane appears to be the worst of all the silanes studied, despite the charge on Si. This is supported by the torsional angle analysis discussed above, the fact that Cα for the cationic triisopropyl case (Figure 3) is much closer to sp^3 hybridized than the other alkyl ligands, and the Si−Cα bond is comparatively short indicating higher bond order.

For the reaction of the allylsilanes with the unsaturated aldehyde, acid, and ester, two different trends were observed from the energetic data. First, as the size alkyl group of the allylsilane is increased, there is a decrease in the activation barrier, in agreement with experiment. In addition, on changing from methyl acrylate to acrolein, the reactivity of the system is predicted to dramatically increase which also agrees with experimental data. Clearly, more study is required here to probe the origin of reactivity with allylsilanes so that useful predictions can be made about the practical synthetic application of this very useful family of nucleophiles.

Experimental Section

General Procedure. All reactions were carried out under a positive atmosphere of dry argon. Solvents were distilled prior to use: THF was distilled from sodium benzophenone; CH_2Cl_2 was distilled from CaH_2. All $TiCl_4$ used in these studies was drawn from a sample that had been distilled and stored in an air-free storage flask equipped with a glass 14/20 joint (sealed with fluorine-based grease) through which needles were inserted while the flask was under a positive pressure of dry argon which was supplied through a side arm equipped with a Teflon needle valve. A distilled sample of $TiCl_4$ was used over a maximum period of 3 weeks at which time it would be redistilled.

Allyl-tri-*n*-hexylsilane (8c). To a solution of chloro-tri-*n*-hexylsilane (500 mg, 574 mL, 1.57 mmol) in dry THF (3 mL) at 0 °C was added allylmagnesium bromide (2.56 mL, 1.10 M in ether, 2.82 mmol). After being stirred for 1 h, the reaction was quenched by the addition of saturated $NaHCO_3$. The mixture was diluted with diethyl ether and the organic layer separated. The aqueous layer was extracted 3× with ether, and the combined organic layers were dried over anhydrous $MgSO_4$. Following solvent removal in vacuo, the crude product was purified by flash chromatography (straight hexanes) to provide 514.0 mg (99.1%) of **8c** as a clear oil: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.86−5.68 (m, 1H), 4.82 (d, J = 15.4 Hz, 1H), 4.78 (d, J = 8.8 Hz, 1H), 1.52 (d, J = 8.1 Hz, 2H), 1.39−1.14 (m, 24H), 0.93−0.82 (m, 9H), 0.61−0.42 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz, APT pulse sequence, evens up (+), odds down (−)) δ 135.53 (−), 112.43 (+), 33.55 (+), 31.56 (+), 23.75 (+), 22.65 (+), 20.57 (+), 14.12 (−), 12.17 (+); IR (neat) 3078 cm^{-1}; HRMS calcd for $[C_{21}H_{44}Si - (C_3H_5)]^+$ 283.2823, found 283.2830.

Allyl-di-*n*-hexylphenylsilane (8d). To a suspension of magnesium turnings (67.7 mg, 2.78 mmol) in dry THF (5 mL) was added bromobenzene (205 μL, 306 mg, 1.95 mmol). The solution was refluxed 1 h, cooled to 0 °C, and then transferred by cannula to a solution of dichloro di-*n*-hexylsilane (520 mL, 500 mg, 1.86 mmol) in dry THF (4 mL) at 0 °C. The solution was allowed to warm to RT overnight and then heated to 40 °C for 45 min. After cooling of the solution to 0 °C, allylmagnesium bromide (4.31 mL, 0.56 M in hexanes, 2.41 mmol) was added dropwise. After warming of the mixture gradually to room temperature, saturated NH_4Cl was added to quench the reaction. The mixture was diluted with diethyl ether and the organic layer separated. The aqueous layer was extracted 3× with ether, and the combined organic layers were dried over anhydrous $MgSO_4$. Following solvent removal in vacuo, the crude product was purified by flash chromatography (straight pentane) to provide 307.3 mg (52.1%) of **8d** as a clear oil: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.61−7.52 (m, 2H), 7.45−7.37 (m, 3H), 5.96−5.79 (m, 1H), 4.96 (d, J = 15.5 Hz, 1H), 4.92 (d, J = 11.0 Hz, 1H), 1.90 (d, J = 8.1 Hz, 2H), 1.49−1.26 (m, 16H), 0.92−0.89 (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz, APT pulse sequence, evens up (+), odds down (−)) δ 137.16 (+), 134.76 (−), 134.10 (−), 128.82 (−), 127.64 (−), 113.35 (+), 33.42 (+), 31.47 (+), 23.59 (+), 22.62 (+), 20.49 (+), 14.11 (−), 12.09 (+); IR (neat) 3071 cm^{-1}; HRMS calcd for $[C_{21}H_{36}Si - (C_3H_5)]^+$ 275.2197, found 275.2202.

Reaction of Methyl Acrylate with Trimethylallylsilane (10a-*syn* and -*anti*, 11a, and 13). Into an NMR tube was added 0.5 mL of distilled CD_2Cl_2 followed by $TiCl_4$ (20.1 μL, 34.8 mg, 0.18 mmol, 1.1 equiv) and the solution cooled to −78 °C. To this was then added methyl acrylate (15.0 μL, 14.3 mg, 0.17 mmol) followed by trimethylallylsilane (26.5 μL, 19.0 mg, 0.17 mmol) and the temperature taken to 40 °C in an oil bath. The tube was cooled with a stream of air above the level of the liquid inside the NMR tube. The progress of the reaction was monitored periodically by ^{1}H NMR spectroscopy. After 19 h, the reaction was then cooled to RT and the contents of the tube were poured into a flask containing saturated NH_4Cl. The mixture was diluted with diethyl ether and the organic layer separated. The aqueous layer was extracted 3× with ether, and the combined organic layers were dried over anhydrous $MgSO_4$. Following solvent removal in vacuo, the crude product was purified by flash chromatography (2% ether in pentane) to provide 20.0 mg (60.0%) of adducts **10a** and **11a** as pale yellow oils. All ring annulation products were pooled together after flash chromatography and the ratio of products determined by ^{1}H NMR spectroscopy. The ratio of **10a**-*syn*:**10a**-*anti*:**11a**:**13** was 1.1:0.1:1.2:1. C and H analysis was performed on the mixture to confirm yield. Anal. Calcd for $C_{10}H_{20}O_2Si$: C, 59.95; H, 10.06. Found: C, 59.76; H, 10.20. Compound **13** is known, and spectra conform with the literature.[15]

***syn*-Methyl 2-((Trimethylsilyl)methyl)cyclobutanecarboxylate (10a-*syn*):** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.59 (s, 3H), 2.70 (m, 1H), 2.05−1.00 (m, 5H), 0.88 (dd, J = 14.5, 5.0 Hz, 1H), 0.67 (dd, J = 14.5, 10.0 Hz, 1H), −0.10 (s, 9H);

^{13}C NMR ($CDCl_3$, 75 MHz,) δ 175.31, 51.38, 47.87, 36.98, 27.87, 25.04, 21.59, −1.14.

***anti*-Methyl 2-((Trimethylsilyl)methyl)cyclobutanecarboxylate (10a-*anti*):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.62 (s, 3H), 3.12 (m, 1H), 2.14 (m, 1H), 2.05−1.00 (m, 6H), −0.09 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 174.96, 51.09, 44.49, 34.78, 28.14, 20.08, 19.61, −1.08.

***anti*-Methyl 3-(trimethylsilyl)cyclopentanecarboxylate (11a):** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.59 (s, 3H), 2.60 (m, 1H), 2.05−1.00 (m, 6H), 0.58 (m, 1H), −0.08 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 177.38, 51.56, 44.37, 31.82, 31.71, 28.70, 25.79, −3.08.

Reaction of Methyl Acrylate with Triisopropylallylsilane (10b-*syn* and -*anti* and 11b). Into an NMR tube was added methyl acrylate (15.3 μL, 14.6 mg, 0.17 mmol), triisopropylallylsilane (53.0 μL, 44.0 mg, 0.22 mmol), $TiCl_4$ (37.3 μL, 64.5 mg, 0.34 mmol), and 0.5 mL of distilled CD_2Cl_2. The tube was warmed in an oil bath at 40 °C for 18 h while the tube was cooled with a stream of air above the level of the liquid in the NMR tube. The progress of the reaction was monitored periodically by ^{1}H NMR spectroscopy. The reaction was then cooled to RT, and the contents of the tube were poured into a flask containing saturated NH_4Cl. The mixture was diluted with diethyl ether and the organic layer separated. The aqueous layer was extracted 3× with ether, and the combined organic layers were dried over anhydrous $MgSO_4$. Following solvent removal in vacuo, the crude product was purified by flash chromatography (2% ether in pentane) to provide 31.0 mg (64.0%) of **11b** as a pale yellow oil.

The above reaction was performed on the same scale in CH_2Cl_2 and halted after 4 h. It was found that the ratio of syn and anti cyclobutane adducts to *anti*-cyclopentane was 6:1:1. All ring annulation products were pooled together after flash chromatography. The ratio of products was determined by ^{1}H NMR spectroscopy. Representative NMR spectra for the cyclobutane isomers are given below, and C and H analysis was performed on the mixture to confirm yield. Anal. Calcd for $C_{16}H_{32}O_2Si$: C, 67.55; H, 11.34. Found: C, 67.95; H, 11.06.

***syn*-Methyl 2-((Triisopropylsilyl)methyl)cyclobutanecarboxylate (10b-*syn*):** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.66 (s, 3H), 2.59 (m, 1H), 2.50−1.60 (m, 8H), 1.00 (br s, 18H), 0.74 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 175.12, 51.24, 48.22, 37.08, 28.28, 21.12, 18.71, 17.27, 11.07.

***anti*-Methyl 2-((Triisopropylsilyl)methyl)cyclobutanecarboxylate (10b-*anti*):** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.69 (s, 3H), 3.17 (m, 1H), 2.50−1.60 (m, 8H), 1.20−0.90 (m, 2H), 1.01 (br s, 18H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 174.80, 50.92, 44.77, 34.65, 28.52, 19.90, 18.71, 11.94, 11.12.

***anti*-Methyl 3-(Triisopropylsilyl)cyclopentanecarboxylate (11b):** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.64 (s, 3H), 2.79 (m, 1H), 2.15−1.18 (m, 10H), 1.07 (br s, 18H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 177.43, 51.60, 44.04, 32.60, 31.72, 30.13, 22.43, 19.17, 11.30; IR (neat) 1722 cm^{-1}.

Reaction of Methyl Acrylate with Trihexylallylsilane (10c and 11c). Into a 10 mL round-bottom flask were added 3.0 mL CH_2Cl_2 and 34.7 μL of methyl acrylate (0.39 mmol) followed by 47 μL of freshly distilled $TiCl_4$ (0.43 mmol) at room temperature. Allyl-tri-*n*-hexylsilane (250 mg, 0.73 mmol) was then added dropwise. The mixture was heated to reflux for 16 h and then cooled to room temperature. A 10 mL volume of saturated NH_4Cl was then added and the organic layer separated. The aqueous layer was then extracted twice with diethyl ether, and the organic fractions were combined and dried over anhydrous $MgSO_4$. Following solvent removal in vacuo, the crude residue was purified by flash chromatography (1% ether in pentane) to yield 97.0 mg of three isomeric ring annulation products (61% yield). Characterization, including C and H analysis, was performed on the mixture of the three isomers, i.e., **10c** *syn*- and *anti*-cyclobutanes and **11c** *anti*-cyclopentane. For ^{1}H NMR the number of protons reported has been normalized to one isomer. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.67, 3.65, 3.64 (3 s, 3H), 2.82−2.44 (m, 1H), 2.15−1.37 (m, 6H), 1.36−1.11 (m, 24H), 0.86 (t, J = 6.6 Hz, 9H), 0.74−0.56 (m, 1H), 0.54−0.34 (m, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 177.32, 175.21, 174.85, 51.47, 51.26, 50.96, 48.02, 44.67, 44.29, 37.00, 34.81, 33.68, 33.60, 33.55, 33.48, 32.11, 31.71, 31.53, 31.50, 31.43, 29.69, 29.25, 28.28, 28.04, 24.02, 23.83, 23.78, 23.70, 22.60, 21.42, 20.74, 20.06, 15.43, 14.08, 12.82, 12.77, 11.75, 11.34 (one peak could not be found due to overlap). IR (neat): 1738 cm^{-1}. Anal. Calcd for $C_{25}H_{50}O_2Si$: C, 73.10; H, 12.27. Found: C, 72.98; H, 12.19.

Reaction of Methyl Acrylate with Allyl-di-*n*-hexylphenylsilane (10d and 11d). Into a 10 mL round-bottom flask were added 2.0 mL CH_2Cl_2 and 23 μL of methyl acrylate (0.253 mmol) followed by 33 μL of freshly distilled $TiCl_4$ (0.303 mmol) at room temperature. Allyl-di-*n*-hexylphenylsilane (200 mg, 0.632 mmol) was then added dropwise. The mixture was heated to reflux for 16 h and then cooled to room temperature. A 10 mL volume of saturated NH_4Cl was then added and the organic layer separated. The aqueous layer was then extracted twice with diethyl ether, and the organic fractions were combined and dried over anhydrous $MgSO_4$. Following solvent removal in vacuo, the crude residue was purified by flash chromatography (straight hexanes) to yield 50.0 mg of 3 isomeric ring annulation products (49% yield). Characterization, including C and H analysis, was performed on the mixture of the three isomers, i.e., **10d** *syn*- and *anti*-cyclobutanes and **11d** *anti*-cyclopentane. For ^{1}H NMR the number of protons reported has been normalized to one isomer. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.48−7.40 (m, 2H), 7.35−7.28 (m, 3H), 3.70, 3.63, 3.60 (3S, 3H), 3.12 (tt, J = 5.2, 4.4 Hz, 1H), 2.82−2.46 (m, 1H), 2.24−2.09 (m, 1H), 2.07−1.64 (m, 3H), 1.61−1.40 (m, 1H), 1.38−1.15 (m, 15H), 1.03−0.65 (m, 12H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (only signals for **10d**-*syn* and **11d** were strong enough to be detected in ^{13}C NMR spectrum, and these signals are presented here) 177.29, 175.08, 137.57, 136.66, 134.40, 134.00, 128.74, 128.69, 127.59, 127.58, 51.54, 51.29, 47.79, 44.06, 36.58, 33.58, 33.45, 31.98, 31.55, 31.45, 31.42, 29.67, 29.14, 27.85, 23.84, 23.70, 23.67, 23.62, 22.58, 21.52, 20.76, 14.08, 12.56, 11.33. IR (neat): 3070, 1738, 1732 cm^{-1}. Anal. Calcd for $C_{25}H_{42}O_2Si$: C, 74.57; H, 10.51. Found: C, 74.61; H, 10.65.

1-Acetyl-3-(tri-*n*-hexylsilyl)cyclopentane (15c). Dimethylaluminum chloride (193 μL, 1 M in hexanes, 0.193 mmol) and $TiCl_4$ (42.3 μL, 0.386 mmol) were added to dry CH_2Cl_2 (3 mL), and the resultant solution was stirred for 1 h. After cooling of the solution to 20 °C, MVK (16.1 μL, 0.193 mmol) was added and the reaction cooled to −78 °C. In a separate flask, Me_2AlCl (58 mL, 1 M in hexanes, 0.058 mmol) was dissolved in dry CH_2Cl_2 (4 mL), to this was added **8c** (125 mg, 0.386 mmol), and the mixture was cooled to −78 °C. The silane solution was transferred to the mixture containing MVK by cannula. After being stirred for 17 h at −75 °C, the mixture was allowed to warm to RT at which time it was quenched with saturated NH_4Cl. The mixture was diluted with diethyl ether and the organic layer separated. The aqueous layer was extracted 3× with ether, and the combined organic layers were dried over anhydrous $MgSO_4$. Following solvent removal in vacuo, the crude product was purified by flash chromatography (2% ether in pentane) to provide 25.4 mg (33.4%) of **15c** as a pale yellow oil: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.85 (tt, J = 12.50, 5.15 Hz, 1H), 2.13 (s, 3H), 2.00−1.76 (m, 3H), 1.74−1.52 (m, 2H), 1.31−1.18 (m, 24H), 1.12−0.94 (m, 2 H), 0.86 (t, J = 6.62 Hz, 9H), 0.53−0.42 (m, 6 H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 211.10, 52.89, 33.69, 31.51, 30.72, 30.51, 29.50, 28.75, 24.04, 23.83, 22.62, 14.09, 11.76; IR (neat): 1713 cm^{-1}; HRMS calcd for $C_{25}H_{50}OSi$ 394.3633, found 394.3621. Anal. Calcd for $C_{25}H_{50}OSi$: C, 76.07; H, 12.76. Found: C, 76.14; H, 12.57.

1-Acetyl-3-(di-*n*-hexylphenylsilyl)cyclopentane (15d). To 8 mL of dry CH_2Cl_2 was added Me_2AlCl (172 μL, 1 M in hexanes, 0.172 mmol) and $TiCl_4$ (37.7 μL, 65.3 mg, 0.344 mmol), and the solution was stirred 20 min at RT. The solution was cooled to −20 °C and MVK (14.32 μL, 12.06 mg, 0.172 mmol) added dropwise. In a separate flask, 3 mL of dry CH_2Cl_2 was stirred with Me_2AlCl (52 μL, 1 M in hexanes, 0.052 mmol) for 20 min at RT and allyl-di-*n*-hexylphenylsilane (130 μL, 114 mg, 0.361 mmol) added dropwise. Both flasks were cooled to −78 °C, and the silane solution was transferred via cannula (flask rinsed 3 × 4 mL with dry CH_2Cl_2) to the catalyst mixture. After being stirred at −50 °C for 21 h, the solution

was warmed to RT and quenched by the addition of saturated $NaHCO_3$. The organic layer was separated and the aqueous layer extracted 3× with ether. The combined organic layers were dried over anhydrous $MgSO_4$. Following solvent removal in vacuo, the crude product was purified by flash chromatography (3% ether in hexanes) to provide 40.0 mg (60%) of **15d** as a pale yellow oil: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.50−7.42 (m, 2H), 7.37−7.29 (m, 3H), 2.84−2.71 (m, 1H), 2.11 (s, 3H), 2.04−1.93 (m, 1H), 1.93−1.77 (m, 2H), 1.74−1.53 (m, 3H), 1.44−1.09 (m, 17H), 0.96−0.70 (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz, APT pulse sequence, evens up (+), odds down (−)) δ 210.99 (+), 136.62 (+), 134.39 (−), 128.74 (−), 127.59 (−), 52.59 (−), 33.56 (+), 32.40 (+), 31.40 (+), 30.27 (+), 29.30 (+), 28.80 (−), 23.83 (+), 23.65 (−), 22.58 (+), 14.08 (−), 11.33 (+); IR (neat) 3069, 1713 cm^{-1}; HRMS calcd for $C_{25}H_{42}OSi$ 386.3007, found 386.3011. Anal. Calcd for $C_{25}H_{42}OSi$: C, 77.65; H, 11.00. Found: C, 77.80; H, 11.50.

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