Tetrahedron Vol. 48, No. 27, pp. 5565-5578, 1992
Printed in Great Britain

0040-4020/92 $5.00+.00
Pergamon Press Ltd

Spectroscopic Studies on the $TiCl_4$-Promoted Reaction of Allylsilanes with Aldehydes and α,β-Enones

Scott E. Denmark*, and Neil G. Almstead

Roger Adams Laboratory, Department of Chemistry, University of Illinois, Urbana, IL 61801, USA

(*Received in Germany* 27 *January* 1992)

Key Words: *Allylsilanes; Lewis Acid; Aldehyde Complex; α,β-Enones*

Abstract: *The complexation of n-heptanal and 4-(n-heptyl)benzaldehyde with $TiCl_4$ was studied spectroscopically. It was observed that the nature of the complex formed was dependent upon the stoichiometry of $TiCl_4$ present. The 2:1 (Lewis base /$TiCl_4$) complex was preferred at sub-stoichiometric quantities of $TiCl_4$ while the 1:1 complex formed preferentially when excess $TiCl_4$ was present. Reaction of the pre-complexed aldehyde with allyltrimethylsilane led to the formation of a titanium alkoxide, the structure of which was independently established by metathesis of the corresponding silyl ether. No metathesis of the allylsilane occurred before addition. The reaction of allyltrimethylsilane with $TiCl_4$-complexed enones was also studied. A titanium enolate was observed spectroscopically as the intermediate in this reaction. No metathesis of the allylsilane occurred before addition to the complexed enone.*

INTRODUCTION

Allylsilanes have emerged as one of the most useful organosilicon reagents in organic synthesis.[1] The reaction of allylsilanes with carbonyl compounds, as first reported by Calas,[2] required the use of activated substrates such as perfluoroacetone and chloroacetone in order for the reaction to proceed when $AlCl_3$, $GaCl_3$ or $InCl_3$ were used as Lewis acids. The utility of this reaction was greatly expanded by the discovery that $TiCl_4$ could promote the regioselective addition of allylic silanes to unactivated carbonyl groups in high yield.[3] Since that time, $TiCl_4$ has been widely used as the Lewis acid of choice to promote the reactions of allylic silanes with various electrophiles including epoxides, aldehydes, acetals, and acid chlorides.[1c]

The conjugate addition of allylsilanes to α,β-enones, first demonstrated by Sakurai[4] (and now commonly known as the Sakurai reaction), has also proven to be of great synthetic interest.[5] Before the development of this reaction the method of choice was the conjugate addition of allylic copper reagents, a reaction which proceeded with modest regioselectivity at best, due primarily to the instability of the copper reagent.[6] The Lewis acid promoted conjugate addition of allylsilanes to α,β-enones has proven to be completely regioselective and the stereoselectivity of these additions is often higher than the corresponding copper catalyzed Grignard additions.[7] The addition of allylsilanes to α,β-enones results in the formation of an enolate intermediate that can further be trapped by another carbon electrophile to yield doubly alkylated products.[8] The exact nature of this intermediate has not been rigorously established, but it is thought to be a titanium enolate.

In our previous studies on the mechanism and origin of stereocontrol in the reactions of allylmetals with aldehydes and acetals we focused on the importance of the Lewis acid and the structure of the complexes formed with the electrophilic substrates.[9] We found that the stereochemical outcome is highly dependent upon the stoichiometry and concentration of the Lewis acid as well as other factors which change the effective bulk of the

Lewis acid-aldehyde complex. Through extensive ^{13}C NMR experiments we have demonstrated that complexation of aldehydes to $SnCl_4$ always occurred in a 2:1 stoichiometry (aldehyde / $SnCl_4$) regardless of the amount of $SnCl_4$ present. In the subsequent reactions of these aldehyde-$SnCl_4$ complexes with allylstannanes, it was observed that metathesis of the stannanes was faster than addition to the precomplexed aldehyde in most cases.[10,11]

In continuation of these studies we have chosen to investigate the behavior of $TiCl_4$ since it is the most often employed promoter of the reaction of allylic silanes with carbonyl compounds. Remarkably, only a few studies on the complexation of $TiCl_4$ to aldehydes have been reported, none of which, however, employ ^{13}C NMR spectroscopy.[12,13] Our experience has demonstrated the value of the technique to examine the complexation of aldehydes with Lewis acids and the subsequent reactions of these complexes with allyltrimethylsilane. The addition of allylsilanes to α,β-enones has also never been examined spectroscopically. Thus, we describe herein ^{13}C NMR studies on the nature of complexation of carbonyl compounds with $TiCl_4$, and the subsequent reactions of these complexes.

RESULTS

To provide a firm foundation for an understanding of how $TiCl_4$ promotes the addition of allylsilanes to carbonyl compounds it was essential to establish how this reagent interacts with the two reaction components. Therefore, two sets of control experiments were performed to determine: (1) if the allyl reagents would undergo metathesis when exposed to $TiCl_4$ and (2) the mode of complexation of $TiCl_4$ with aldehydes and α,β-enones. In addition, the structure of the intermediates formed during reaction needed to be established by independent synthesis. For purposes of comparison, all of the complexation experiments were carried out with both $TiCl_4$ and $SnCl_4$. These reagents were added in 0.25 equivalent portions to the aldehydes to generate a set of reference spectra. Two different aldehydes were chosen for this study: *n*-heptanal and 4-(*n*-heptyl)benzaldehyde. These aldehydes were chosen because the $TiCl_4$ complexes were found to be quite soluble in CD_2Cl_2 at -80 °C. Simple aldehydes such as benzaldehyde formed insoluble precipitates upon complexation with $TiCl_4$ and therefore could not be used in this study.

1. *Control Experiments.* 1.1. *Metathesis of Allylstannanes.* As a control experiment we first carried out the reaction between the Lewis acid $TiCl_4$ and the allyl reagents tetraallylstannane and allyltri*n*-butylstannane. Upon addition of $TiCl_4$ to either allyltributylstannane or tetraallylstannane at -80 °C it was immediately observed that the ^{13}C NMR signals broadened significantly and the solution became deep purple in color. No signals for the starting material remained, but the new signals which were observed were very broad. No discrete, identifiable species could be discerned from the spectra. It was apparent that the stannanes were behaving as reducing reagents with $TiCl_4$ providing some paramagnetic Ti (III) species, thus prohibiting the study of this reaction by ^{13}C NMR spectroscopy. We therefore abandoned the study of the stannane reagents with $TiCl_4$ and concentrated on allyltrimethylsilane.

1.2. *Metathesis of Allylsilanes.* The metathesis of allylsilanes was studied using allyltrimethylsilane in a 1:1 solution of CD_2Cl_2:$CDCl_3$ (Figure 1). *The addition of $TiCl_4$ to the 0.1 M solution of allyltrimethylsilane at -80 °C resulted in no change in the ^{13}C NMR spectra.* The solution was warmed in 20 °C intervals and no change was observed in the resulting spectra of allyltrimethylsilane. Even after several hours at room temperature there was no metathesis of the allyltrimethylsilane. It is therefore clear that reaction of allyltrimethylsilane with $TiCl_4$ is a very slow process and that $TiCl_4$-promoted reactions of allylsilanes do not involve allyltrichlorotitanium species. Previous attempts to prepare allyltrichlorotitanium itself were unsuccessful as the in-situ generated reagent is reported to decompose below -50 °C.[14]

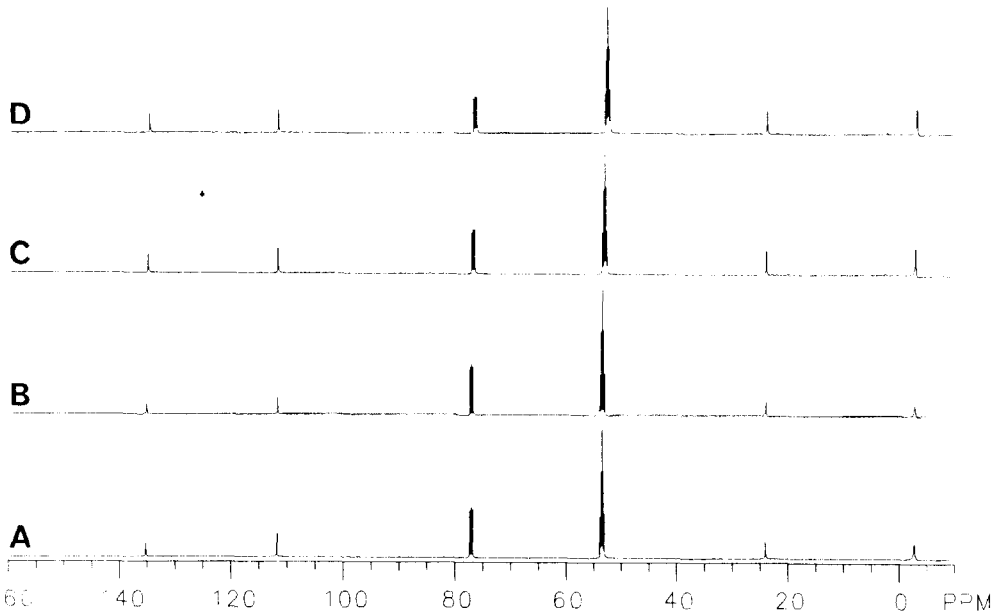


Figure 1. ^{13}C NMR spectra of allyltrimethylsilane, **1**, at -80 °C (spectrum A), **1** and $TiCl_4$ at -80 °C (spectrum B), **1** and $TiCl_4$ at -40 °C (spectrum C), **1** and $TiCl_4$ at 20 °C (spectrum D).

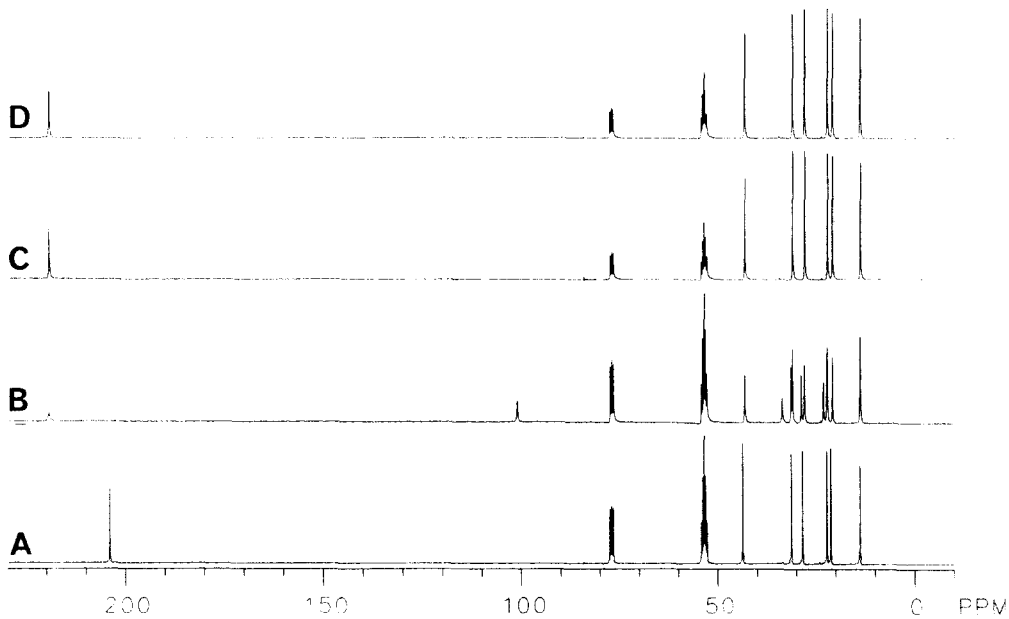


Figure 2. ^{13}C NMR spectra of *n*-heptanal, **2**, at -80 °C (spectrum A), **2** and 0.25 equiv $SnCl_4$ at -80 °C (spectrum B), **2** and 0.5 equiv $SnCl_4$ at -80 °C (spectrum C), **2** and 1.0 equiv $SnCl_4$ at -80 °C (spectrum D).

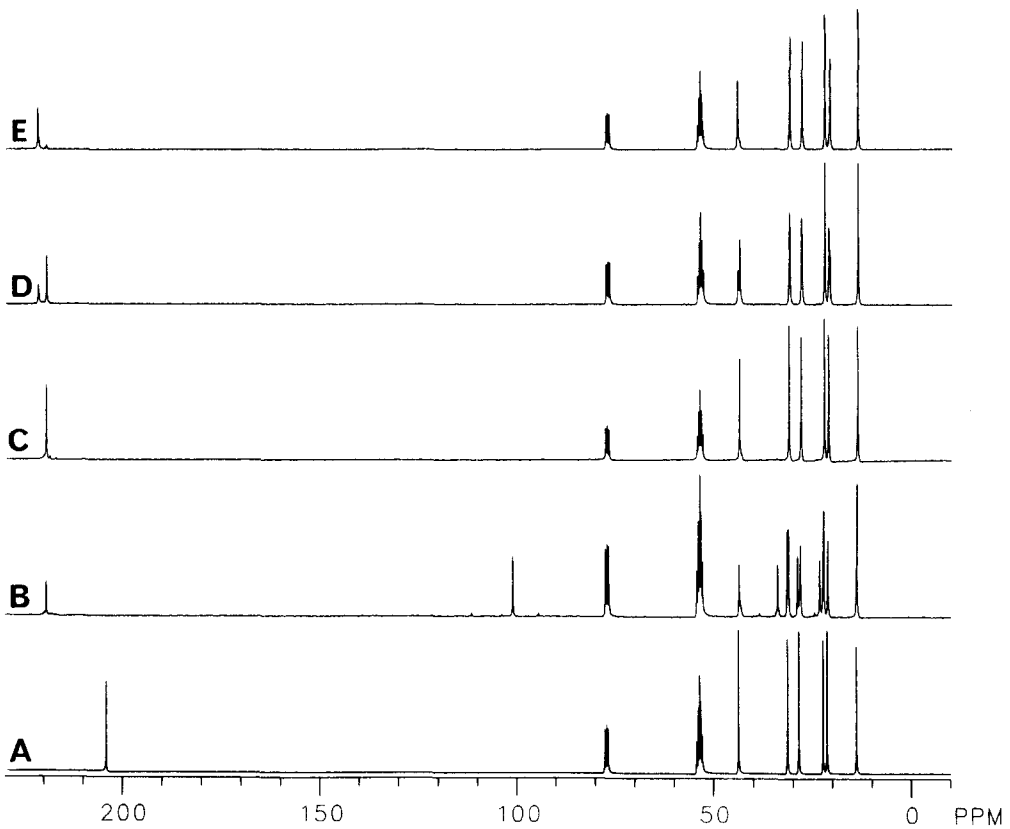


Figure 3. ^{13}C NMR spectra of *n*-heptanal, **2**, at -80 °C (spectrum A), **2** and 0.25 equiv $TiCl_4$ at -80 °C (spectrum B), **2** and 0.5 equiv $TiCl_4$ at -80 °C (spectrum C), **2** and 0.75 equiv $TiCl_4$ at -80 °C (spectrum D), **2** and 1.0 equiv $TiCl_4$ at -80 °C (spectrum E).

1.3. *Complexation of n-Heptanal* (**2**). 1.3.1. *$SnCl_4$* The complexation of *n*-heptanal and 4-(*n*-heptyl)benzaldehyde with $TiCl_4$ and $SnCl_4$ were studied by ^{13}C NMR spectroscopy. These experiments were performed by adding the Lewis acid to the aldehyde (0.2 M in a 1:1 solution of CD_2Cl_2:$CDCl_3$, spectrum A in all Figures) at -80 °C and observing the change in chemical shift of the various carbon signals. First, the complexation of *n*-heptanal with $SnCl_4$ was examined as a reference (Figure 2). Upon addition of 0.25 equivalents of $SnCl_4$ to *n*-heptanal the signals for the free aldehyde disappeared (spectrum B). The only observable signals were assigned to the 2:1 complex of *n*-heptanal and $SnCl_4$ (C(1), 219.55 ppm) and the aldehyde cyclic trimer (C(1), 101.13 ppm). When 0.5 equivalents of $SnCl_4$ were present, spectrum C, complete formation of the 2:1 complex was observed (C(1), 219.51 ppm). This complex was found to be very stable, as warming the colorless homogeneous solution to 0 °C did not result in any decomposition and only minimal changes in chemical shift were observed at elevated temperatures. Further addition of $SnCl_4$ (1.0 equiv, spectrum D) did not affect the stoichiometry of complexation nor did it change the NMR chemical shifts of the complex. The only observable species was $(2)_2$•$SnCl_4$.

1.3.2. *$TiCl_4$* The complexation of *n*-heptanal with $TiCl_4$ was performed in an identical manner (Figure 3). At 0.25 equivalents of $TiCl_4$ only the 2:1 complex (C(1), 219.46 ppm) and the aldehyde trimer (C(1), 101.02

ppm) were present in solution (spectrum B). When 0.5 equivalents of $TiCl_4$ were present, the 2:1 complex (C(1), 219.49 ppm) again was the only observed species. However, when 0.75 equivalents of $TiCl_4$ was added, a new species with a carbonyl resonance at 221.63 ppm was observed in coexistence with $(2)_2$•$TiCl_4$ (spectrum D). This new species rose to dominance to the exclusion of $(2)_2$•$TiCl_4$ at an equimolar stoichiometry of $TiCl_4$ and **2** (spectrum E). On the basis of spectral similarity and stoichiometry dependence we have tentatively assigned the new species as the 1:1 complex, **2**•$TiCl_4$. Addition of excess $TiCl_4$ (up to 10 equivalents) did not affect the stoichiometry of complexation. This behavior is dramatically different from that observed with $SnCl_4$. With $TiCl_4$, the nature of the complex formed with an aldehyde seems to be *dependent upon the stoichiometry of the reagents present*. All of the $TiCl_4$ complexes formed with *n*-heptanal were slightly yellow, homogeneous solutions. At no time did any precipitation of the complex occur at these concentrations.

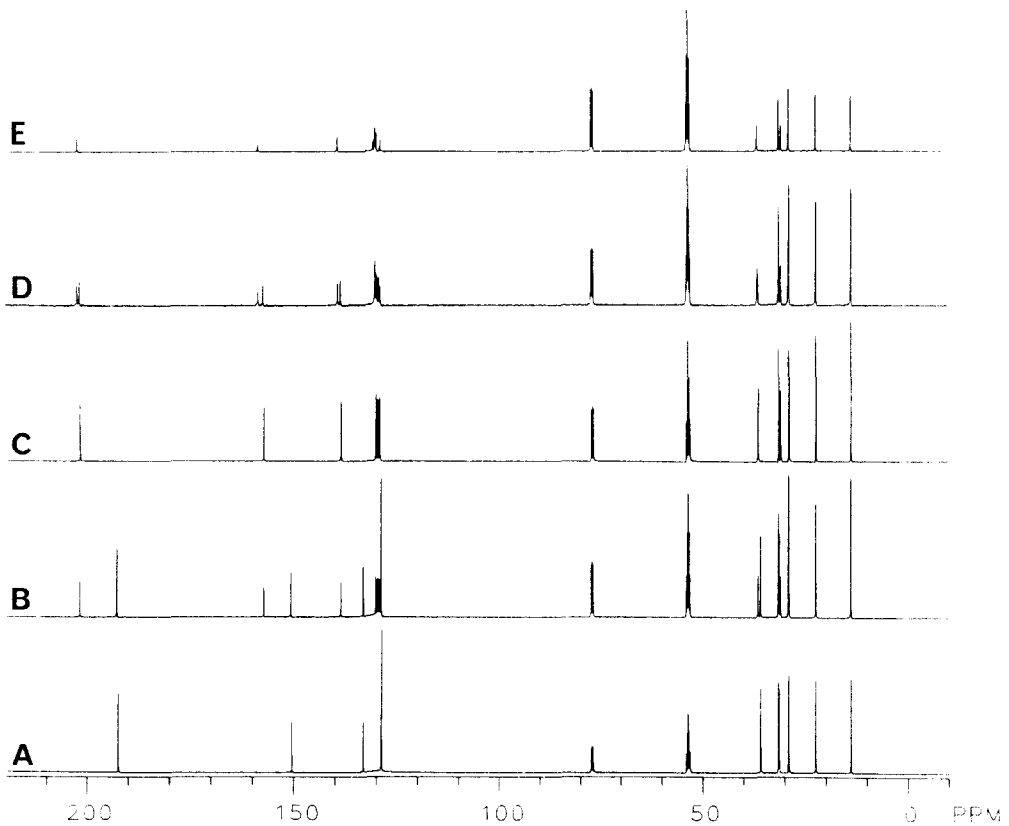


Figure 4. ^{13}C NMR spectra of 4-(*n*-heptyl)benzaldehyde, **3**, at -80 °C (spectrum A), **3** and 0.25 equiv $TiCl_4$ at -80 °C (spectrum B), **3** and 0.5 equiv $TiCl_4$ at -80 °C (spectrum C), **3** and 0.75 equiv $TiCl_4$ at -80 °C (spectrum D), **2** and 1.0 equiv $TiCl_4$ at -80 °C (spectrum E).

1.4. *Complexation of 4-(n-Heptyl)benzaldehyde* (**3**). 1.4.1. *$SnCl_4$*. The complexation studies were next repeated with 4-(*n*-heptyl)benzaldehyde. This aromatic aldehyde was chosen because of the solubility of its complexes with $TiCl_4$. The results obtained from the complexation of $SnCl_4$ to 4-(*n*-heptyl)benzaldehyde were identical to those obtained previously with 4-(*t*-butyl)benzaldehyde[10] and differ from those with *n*-heptanal in

that no aldehyde trimer was observed at 0.25 equivalents of $SnCl_4$; only the free aldehyde (C(1), 192.80 ppm) and the 2:1 complex (C(1), 199.67 ppm). Adding excess $SnCl_4$ resulted only in the quantitative formation of the 2:1 complex (C(1), 199.64 ppm).

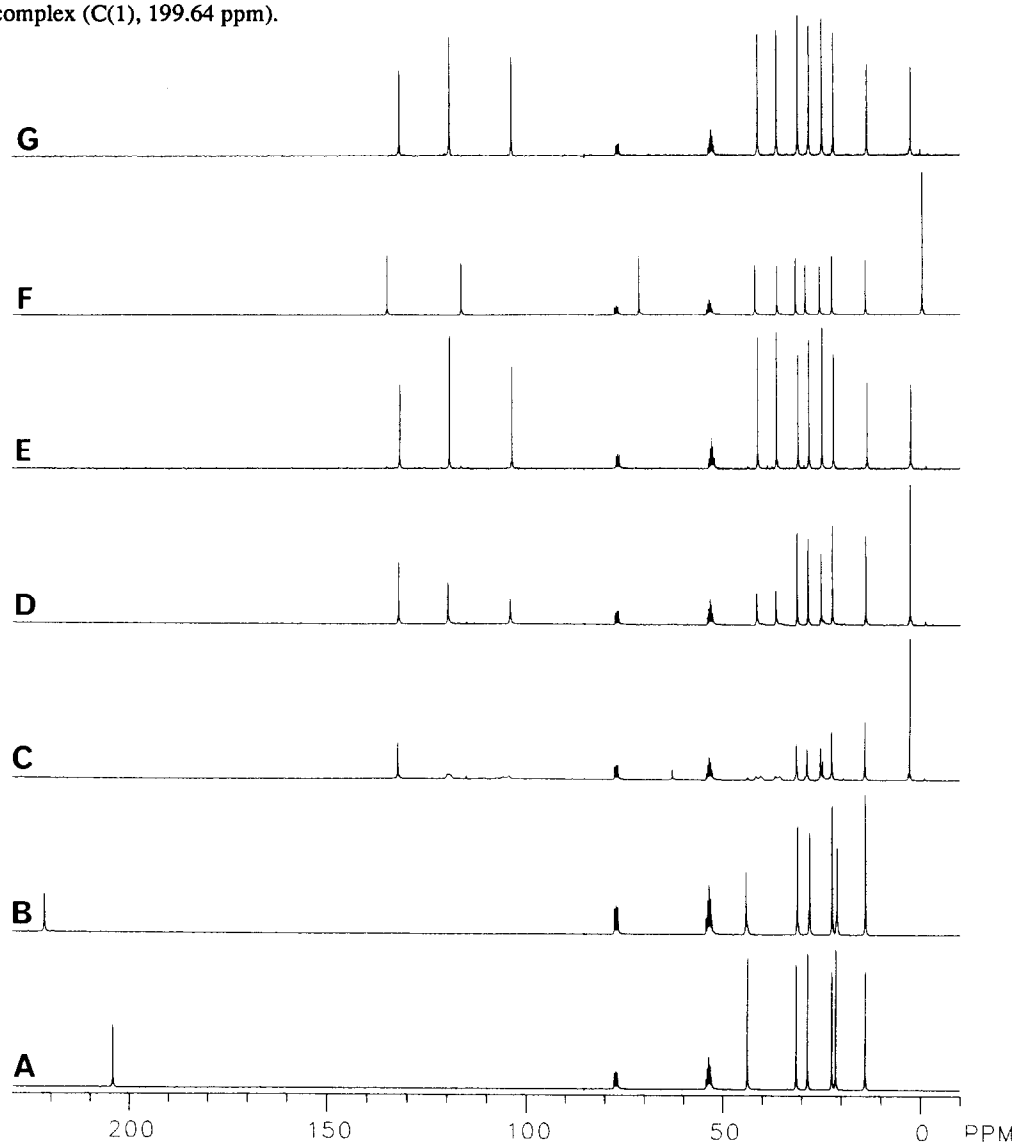


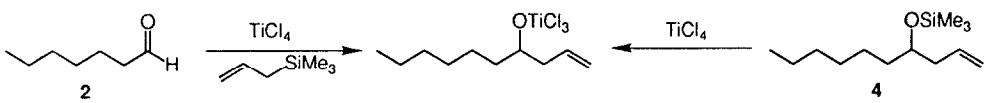
Figure 5. ^{13}C NMR spectra of *n*-heptanal, **2**, at -80 °C (spectrum A), **2** and 1.0 equiv $TiCl_4$ at -80 °C (spectrum B), **2**·$TiCl_4$ and allyltrimethylsilane **1** at -80 °C (spectrum C), **2**·$TiCl_4$ and allyltrimethylsilane **1** at -60 °C (spectrum D), **2**·$TiCl_4$ and allyltrimethylsilane **1** at -20 °C (spectrum E), silyl ether, **4** at -80 °C (spectrum F), **4** and $TiCl_4$ at -20 °C (spectrum G).

1.4.2. *$TiCl_4$*. The results in this series were now easily understood on the basis of the forgoing experiments. When 0.25 equivalents of $TiCl_4$ were added to 4-(*n*-heptyl)benzaldehyde only the free aldehyde (C(1), 192.64 ppm) and the 2:1 complex (C(1), 201.60 ppm) were observed (spectrum B, Figure 4). At 0.5

equivalents of $TiCl_4$ only the 2:1 complex $(\mathbf{3})_2$•$TiCl_4$ (C(1), 201.59 ppm) was present in solution (spectrum C). Further addition of $TiCl_4$ led to the formation of a new species (in roughly equivalent concentration with $(\mathbf{3})_2$•$TiCl_4$) which we preliminarily have tentatively assigned as the 1:1 complex **3**•$TiCl_4$ (spectrum D). This new complex (C(1), 202.20 ppm) was the only species observed when 1.0 equivalents of $TiCl_4$ were employed (spectrum E). All of the complexes formed with $TiCl_4$ and 4-(*n*-heptyl)benzaldehyde were yellow homogeneous solutions at -80 °C. Increasing the concentration of the solution above 0.2 M resulted in the formation of an insoluble precipitate. When excess $TiCl_4$ was present and the temperature of the solution was warmed above -60 °C new signals appeared in the ^{13}C NMR spectra.

2. *Reaction of Allyltrimethylsilane with n-Heptanal.* We were now in a position to investigate the reaction of *n*-heptanal with allyltrimethylsilane promoted by $TiCl_4$. The reference spectra and reaction course are shown in Figure 5. A solution of *n*-heptanal (0.2 M in 1:1 CD_2Cl_2:$CDCl_3$, spectrum A) was treated with 1.0 equivalent of $TiCl_4$ at -80 °C to form **2**•$TiCl_4$ (spectrum B) and then 1.0 equivalent of allyltrimethylsilane was added (spectrum C). The allyltrimethylsilane was instantaneously consumed at -80 °C generating TMSCl (2.97 ppm) but the resonances for the addition product were not visible. However, upon warming the solution to -60 °C (spectrum D) and then -20 °C (spectrum E) clean spectra containing all ten signals of the of the allylation product could be recorded. The nature of this species could be easily be established by two spectroscopic comparisons. That the product was not silyl ether **4** was readily apparent from comparison of the two ^{13}C NMR spectra E and F, Figure 5. Moreover, it was possible to independently generate the same product by treatment of silyl ether **4** with $TiCl_4$ (Scheme 1). Reaction of **4** with $TiCl_4$ generated a product that was spectroscopically identical to the product formed from addition of allyltrimethylsilane to the titanium complex of *n*-heptanal (compare spectra E and G, Figure 5). Therefore, the product from direct addition is a titanium alkoxide and not a silyl ether. Interestingly, the $TiCl_3$ moiety significantly shifted the ^{13}C NMR signal for the alkoxide carbon 33 ppm downfield compared to the silyl ether **4**.

Scheme 1



2 **4**

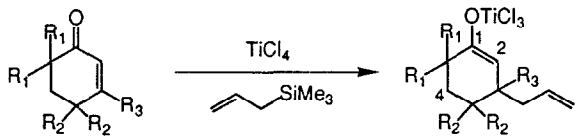
3. *Addition of Allyltrimethylsilane to α,β-Enones.* The addition of allyltrimethylsilane to conjugated enones was studied next using ^{13}C NMR spectroscopy. Since it was established that no metathesis occurs with $TiCl_4$ and allylsilanes, we were primarily interested in the nature of the intermediate formed in this reaction. We therefore chose to examine the reactions of several α,β-enones with allyltrimethylsilane.

Initially we studied the conjugate addition of allyltrimethylsilane to 2-cyclohexenone. Reaction with the unsubstituted cyclohexenone proceeded rapidly, but no intermediate could be observed. In fact, the addition of allyltrimethylsilane was so rapid at -80 °C that the reaction was complete before we were able to acquire any data. It had already been established that trichlorotitanium enolates derived from unsubstituted cycloalkanones decomposed rapidly.[15] We therefore focused our studies on the more highly substituted α,β-enones. All of the α,β-enones studied ($\Delta^{1,9}$-octalone[16a] **5**, 4,4-dimethyl-2-cyclohexenone[16b] **6**, 6,6-dimethyl-2-cyclohexenone[16c] **7**, and 3,6,6-trimethyl-2-cyclohexenone[16d] **8**) were prepared by literature procedures.

For all of the reactions, the α,β-enone was first combined with 1.0 equivalent of $TiCl_4$ at -80 °C in CD_2Cl_2. The allyltrimethylsilane (1.0 equivalent) was then added at -80 °C and the solution was placed in the spectrometer. Spectra were obtained at 20 °C intervals (approximately every 20 minutes). No metathesis of the allyltrimethylsilane was observed before addition to the α,β-enone occurred. As expected, the reactions were

slower with the more highly substituted enones. In all of the reactions, signals corresponding to the formation of a titanium enolate were detected. The diagnostic resonances for the titanium enolate were observed in the range of 170-182 ppm. Kuwajima had previously generated trichlorotitanium enolates by the addition of $TiCl_4$ to trimethylsilyl enol ethers and had established that the ^{13}C NMR signals for a trichlorotitanium enolate were significantly further downfield than those for the corresponding silyl enol ether.[15] Selected ^{13}C NMR data for the reaction of the substituted enones with allyltrimethylsilane are shown in Table 1.

Table 1. Addition of Allyltrimethylsilane to Substituted α,β-Enones. Selected ^{13}C NMR Data.



				δ ^{13}C, ppm at 20 °C	
Enone	R_1	R_2	R_3	C(1)	C(2)
5	H	$CH_2(CH_2)_2CH_2$		172.46	122.95
6	H	CH_3	H	172.80	115.03
7	CH_3	H	H	181.43	123.29
8	CH_3	H	CH_3	180.61	124.73

As a representative example of these reactions, the spectra obtained from the addition of allyltrimethylsilane to 3,6,6-trimethyl-2-cyclohexenone (**8**) are shown in Figure 6. When $TiCl_4$ was added to the α,β-enone (spectrum B) several different complexes were obtained, possibly due to either a mixture of 1:1 and 2:1 complexes or geometrically different sigma complexes of the carbonyl group. The addition of the silane to the pre-complexed α,β-enone proceeded slowly, with no apparent metathesis of the allyltrimethylsilane. The reaction progress could be conveniently monitored by the appearance of TMSCl corresponding to the consumption of the allyltrimethylsilane During the addition, the formation of a dark purple titanium enolate was observed which was *stable over a 24 hour period at room temperature*. The characteristic signal for the titanium enolate was observed at 180.61 ppm (Table 1 and Figure 6, spectrum F).

To confirm the nature of this species, we attempted to generate the titanium enolate by reaction of the corresponding silyl enol ether with $TiCl_4$. The silyl enol ether was easily prepared by silylation of the lithium enolate of **10**. Combination of $TiCl_4$ with this silyl enol ether bearing an allyl substituent produced many different products, none of which could be identified as the titanium enolate. Significantly, the resonances for the allyl unit disappeared indicating that some competitive process exists for reaction with $TiCl_4$ involving the participation of the double bond. The major product isolated from this reaction arose from an interesting cyclization/rearrangement pathway.[17] These processes could not be suppressed even at -100 °C. Therefore, a model of the putative titanium enolate formed during the addition reaction was generated for comparison. We reasoned that the silyl enol ether **9** containing a propyl group at C(3) instead of an allyl group (Scheme 2) should behave normally and that the resonances for the enolate moiety should not be significantly shifted. Thus, $TiCl_4$ was added to **9** at -80 °C resulting in the slow metathesis of the silyl group. The solution was warmed to 25 °C and the titanium enolate was clearly observed after 4 hours. The titanium enolate formed had characteristic ^{13}C NMR signals at 180.87 and 125.10 ppm, nearly identical to those observed from the conjugate addition to the α,β-enone. This enolate was also found to be stable for more than 24 hours at room temperature.

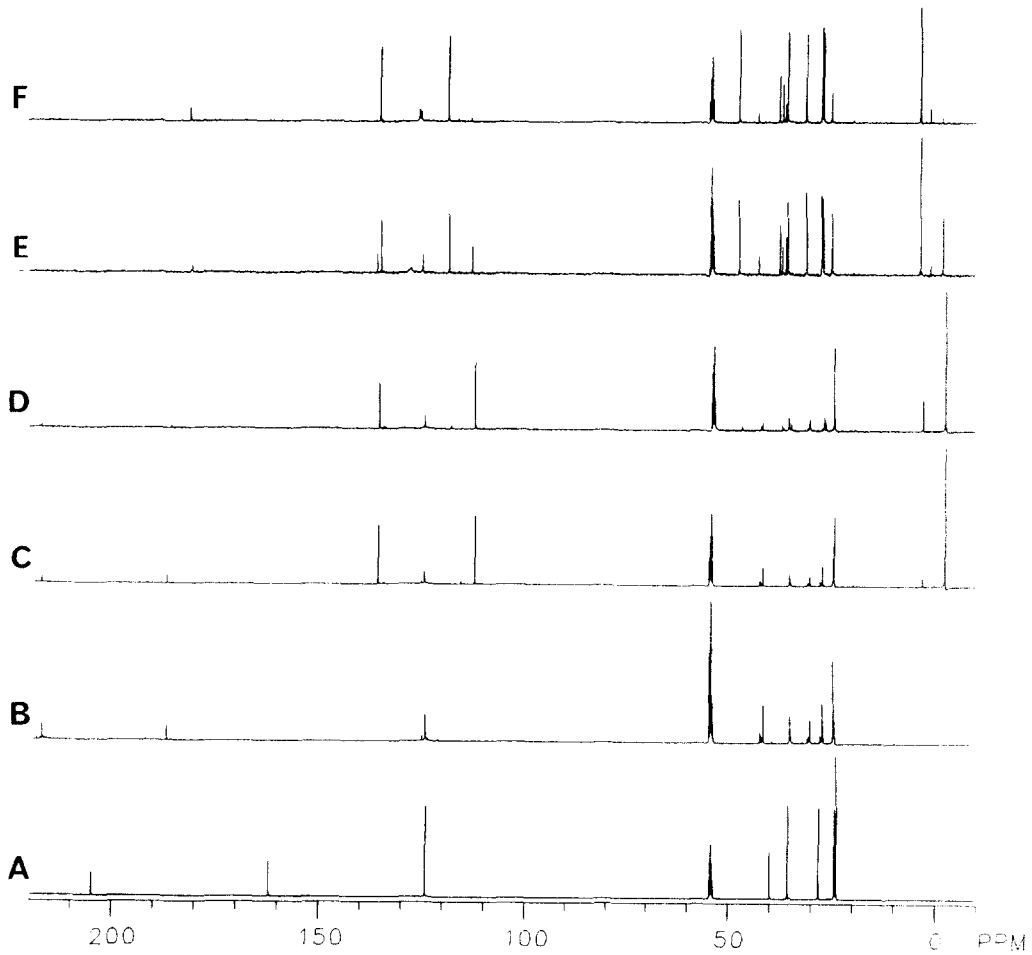
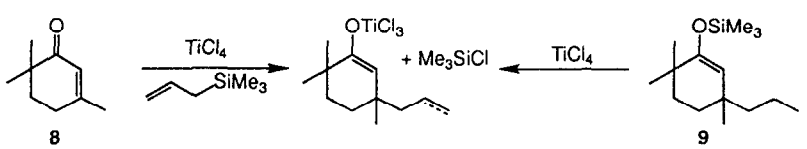


Figure 6. ^{13}C NMR spectra of 3,6,6-trimethyl-2-cyclohexenone, **8**, at -80 °C (spectrum A), **8** and 1.0 equiv. $TiCl_4$ at -80 °C (spectrum B), **8**·$TiCl_4$ and allyltrimethylsilane **1** at -80 °C (spectrum C), **8**·$TiCl_4$ and allyltrimethylsilane **1** at -20 °C (spectrum D), **8**·$TiCl_4$ and allyltrimethylsilane **1** at 20 °C (spectrum E), **8**·$TiCl_4$ and allyltrimethylsilane **1** at 20 °C, 12 h. (spectrum F).

Scheme 2



DISCUSSION

Their thermal stability combined with latent nucleophilic reactivity make allylsilanes ideal reagents for organic synthesis. It has long been known that organosilanes undergo redistribution reactions more slowly than their lower group 14 counterparts.[18] This is particularly evident for the important allyl derivatives. Whereas the metathesis of allyltrimethylstannane with $SnCl_4$ is quantitative and instantaneous at -80 °C in 0.5 M solution,[10] the reaction of allyltrimethylsilane is only 22% complete under the identical conditions after 2 minutes.[19] Thus, while it was expected that allylstannanes would react rapidly with $TiCl_4$,[20] it was somewhat surprising that no reaction whatsoever was detected between allyltrimethylsilane and $TiCl_4$. This may well be a manifestation of the small size and high charge of the titanium atom in $TiCl_4$ which make it a poor electrophile for olefinic carbon.

The complexation of carbonyl compounds with Lewis acids has been extensively studied by calorimetry, infrared and NMR spectroscopy, electron and X-ray diffraction and by computational methods as well. Due to their reactivity, aldehydes have not been employed as often as other Lewis bases. Nevertheless, it is precisely for that reason that they are of considerable interest. The results of complexation described above highlight important differences in the behavior of $SnCl_4$ and $TiCl_4$. Unlike $SnCl_4$ for which only the 2:1 complex $L_2 \cdot SnCl_4$ was observed, $TiCl_4$ can form two different kinds of complexes, the nature of which is dependent upon the stoichiometry of $TiCl_4$ and the aldehyde present. That $TiCl_4$ is capable of forming 1:1 and 2:1 complexes with aldehydes has been known for some time. In 1970, Susz prepared crystalline complexes of both types using aromatic and aliphatic aldehydes and compared their infrared spectra.[12e] In 1972, Azzaro measured the enthalpies of complexation of $TiCl_4$ with several cyclic ketones and determined that both 1:1 and 2:1 complexes were formed.[21] Interestingly, for many of the Lewis bases, the first and second complexation enthalpies were similar. This fact nicely explains the stoichiometry dependent equilibria we have observed spectroscopically. By contrast, only one type of aldehyde complex has been characterized for $SnCl_4$ and complexation enthalpies for similar carbonyl compounds are significantly smaller.[22] It is interesting to note in passing that 1:1 complexation with $SnCl_4$ has been claimed for di(*t*-butyl) ketone on the basis of low temperature ^{119}Sn NMR measurements.[23]

The structure of the titanium-aldehyde complexes in solution was not unambiguously established though reasonable analogies to the solid state may be made. The initially formed species at low $TiCl_4$ concentration is presumed to be a 2:1 complex whose structure is most likely monomeric and octahedral. Structural analogs can be found in the X-ray crystallographic analyses of (4-(*t*-butyl)benzaldehyde)$_2SnCl_4$[9b], and chelates of $TiCl_4$ with ethyl acryloyl lactate,[24a] 3,3-dimethyl-2,4-pentanedione,[24b] and acetic anhydride,[24c] and di(*i*-butyl) phthalate.[24d] Upon addition of excess $TiCl_4$ a new complex was observed which is assumed to possess a 1:1 stoichiometry of $TiCl_4$ to aldehyde. The 1:1 complexes can be either monomeric or dimeric in nature, though the dimeric, chloride-bridging, edge-fused octahedra are well precedented crystallographically in the $TiCl_4$ adducts of ethyl acetate,[25a] ethyl anisate,[25b] and dimethyl terephthalate.[24d] The solution structure is probably best established by colligative measurements.

The striking differences between $TiCl_4$ and $SnCl_4$ in their in behavior toward allyltrimethylsilane and various aldehydes provide reasonable explanations for the remarkable reversal in stereochemical outcome for the intramolecular addition of an alkoxyallylsilane to a chiral aldehyde reported by Reetz.[26] The change in stereochemical course was accompanied by a change from intramolecularity (with $TiCl_4$) to intermolecularity (with $SnCl_4$). This is nicely explained by a prior metathesis with $SnCl_4$. The authors' explanation on the basis of different complex structure is also consistent with our results as well as those of Keck who showed that 3-alkoxybutanals are weak chelators towards $SnCl_4$.[11]

The reaction of substituted α,β-enones with allyltrimethylsilane was also amenable to examination by ^{13}C NMR spectroscopy. Complexation of the substituted α,β-enones was not as uniform as for the aldehydes since

several different complexes were detected. Previously, the complexation of substituted 2-cyclohexenones has been studied by Azzaro using BF_3 as the Lewis acid. It was found that two rapidly interconverting forms of the complex can exist (syn or anti to the double bond) and that the equilibrium is highly dependent on substitution around the carbonyl group.[27] Given the steric hindrance at the carbonyl group in **8** it is likely that one geometry is strongly preferred. We found that the rate of addition of allyltrimethylsilane to the complexed α,β-enone was very dependent on the substitution at the double bond. Substrate **8** proved very suitable as the addition was sufficiently slow to allow spectroscopic monitoring . We observed that reaction of this complexed enone with allyltrimethylsilane led to the formation of a titanium enolate and TMSCl. The resulting titanium enolate was sufficiently stable to allow its characterization. For all of the enones we studied (with the exception of 2-cyclohexenone which decomposed rapidly) we observed signals that could be assigned to titanium enolates. At no point were silyl enol ethers detected. By direct correlation with an independently generated sample, we can confirm that a titanium enolate is the intermediate formed during the conjugate addition of allylsilanes to α,β-enones.

In summary, this study has established the divergent behavior of $TiCl_4$ and $SnCl_4$ as promoters of reactions between allylmetals and carbonyl acceptors. The differences lie in the nature of interaction with the allylmetal reagent and the structure of the complexes formed with the carbonyl electrophiles. Finally it was unambiguously established that titanium alkoxides and enoxides are the direct products of reaction of allylsilanes with $TiCl_4$ complexed carbonyl compounds. This provides an alternative access to titanium trichloride enolates, the synthetic utility of which is still incompletely explored.[28]

EXPERIMENTAL

General Methods. ^1H NMR and ^{13}C NMR spectra were recorded on General Electric GN-300NB (300 MHz for ^1H, 75.5 MHz for ^{13}C) or GN 500 (500 MHz for ^1H and 125.7 MHz for ^{13}C) spectrometers in deuteriochloroform with chloroform as an internal standard. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), integration, and interpretation. Infrared spectra (IR) were obtained on an IBM FTIR-32 spectrophotometer. Peaks are reported in units of cm^{-1} with the following relative intensities: s (strong), m (medium), or w (weak). Mass spectra were obtained on a Varian MAT CH-5 spectrometer with ionization voltages of 70 eV. Data are reported in the form m/e (intensity relative to base=100). Elemental analyses were performed by the University of Illinois Microanalytical Service Laboratory. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel plates with QF-254 indicator. Visualization was accomplished with UV light, iodine, vanillin. Silica gel column chromatography was performed with 32-63 μm silica gel (Woelm). Medium pressure liquid chromatography (MPLC) was performed using Merck Lobar columns. Bulb-to-bulb distillations were done on a Buchi GKR-50 Kugelrohr; boiling points (bp) refer to air bath temperatures and are uncorrected.

2,2,5-Trimethyl-5-(2-propenyl)-cyclohexanone (10) 3,5,5,-Trimethyl-2-cyclohexenone **8** (2.65 g, 19.2 mmol) in CH_2Cl_2 (40 mL) was cooled to -80 °C. $TiCl_4$ (4.00 g, 21.1 mmol, 1.1 equiv) was added at -80 °C, resulting in the formation of a reddish-yellow solution. Allyltrimethylsilane (8.70 g, 76.7 mmol, 4.0 equiv) was slowly added at -80 °C over a 10 minute period. The solution became deep purple-red in color during this time. The solution was warmed to 0 °C and stirred for 1.5 h. The reaction was quenched by the addition of water. The solution was poured into water (50 mL) and then extracted with CH_2Cl_2 (3 × 75 mL). The organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure to leave a colorless oil. The crude product was purified by silica gel chromatography (hexane/EtOAc, 19/1) to afford the desired ketone **10** (2.66 g, 77 %) as a clear colorless oil. An analytical sample was obtained by Kugelrohr distillation. Data for **10**: bp 100 °C (1 Torr) (air bath); ^1H NMR: (400 MHz) 5.76 (m, 1 H, HC(8)), 5.02 (m, 2 H, $H_2C(9)$), 2.28 (m, 1 H, HC(6)), 2.06 (m, 1 H, HC(6)), 1.96 (d, J = 7.3, 2 H, $H_2C(7)$), 1.65 (m, 3 H), 1.07 (s, 3 H, $H_3C(10)$), 1.05 (s, 3 H, $H_3C(10)$), 0.86 (s, 3 H, $H_3C(11)$) ppm; ^{13}C NMR (100.58 MHz) 216.09 (C(1)), 133.73 (C(8)), 118.02 (C(9)), 46.49 (C(7)), 46.03, 44.10 (C(2)), 39.23 (C(5)), 36.29, 32.14, 25.12(C(10)); IR: (neat) 3102 (w), 2953 (s), 2924 (s), 2865 (m), 1705 (s), 1640 (w), 1456 (m), 1385 (m), 1302 (m), 1105

(m), 997)m), 914 (m); MS (70 eV) 140 (2.5), 139 (26), 111 (48), 69 (100), 67 (11), 55 (51), 43 (10), 41 (35), 39 (14). Anal. Calcd for $C_{12}H_{20}O$ (180.30): C, 79.94; H, 11.18. Found: C, 79.90; H, 11.20.

2,2,5-Trimethyl-5-propylcyclohexanone (11) 2,2,5-Trimethyl-5-(2-propenyl)-cyclohexanone **10** (1.15 g, 6.38 mmol) was added to a suspension of PtO_2 (50 mg) in EtOH (20 mL) in an atmosphere of hydrogen. The solution was stirred at room temperature for 1.5 h and then filtered through Celite with the aid of ether. The solvent was removed under reduced pressure to leave a colorless oil. The product was purified by Kugelrohr distillation to afford 1.02 g (88 %) of **11** as a clear, colorless oil. Data for **11**: bp 150 °C (20 Torr) (air bath); ^{1}H NMR: (500 MHz) 2.18 (ABq, J = 14, 38, 2 H, $H_2C(6)$), 1.63 (m, 3 H), 1.48 (m, 1 H), 1.19 (m, 4 H), 1.08 (s, 3 H, $H_3C(10)$), 1.06 (s, 3 H, $H_3C(10)$), 0.87 (t, J = 6.8, 3 H, $H_3C(9)$) ppm; ^{13}C NMR (125.8 MHz) 216.49 (C(1)), 54.09 (C(2)), 50.08 (C(6)), 44.17 (C(3)), 39.16 (C(5)), 36.49 (C(4)), 32.47 (C(7)), 25.23 (C(10)), 25.10 (C(8)), 24.99 (C(10)), 16.57 (C(11)), 14.77 (C(9)); IR: (neat) 2959 (s), 2872 (s), 1701 (s), 1458 (m), 1424 (m), 1383 (m), 1364 (m), 1302 (m), 1217 (w), 1167 (m), 1105 (m); MS (10 eV) 139 (87), 138 (100), 112(10), 111 (96), 109 (12), 95 (12), 70 (24), 69 (61), 56 (15), 55 (10). Anal. Calcd for $C_{12}H_{22}O$ (182.30): C, 79.06; H, 12.16. Found: C, 79.13; H, 12.18.

2,2,5-Trimethyl-5-propyl-1-trimethylsiloxy-1-cyclohexene (9) 2,2,5-Trimethyl-5-propylcyclohexanone (500 mg, 2.74 mmol) was added to a solution of lithium diisopropylamide (prepared from *n*-BuLi (2.15 mL, 2.90 mmol, 1.06 equiv) and diisopropylamine (0.33 g, 3.30 mmol, 1.20 equiv) in THF (15 mL)) at -78 °C. The resulting solution was stirred at -78 °C for 30 min. and then trimethylsilyl chloride (0.368 g, 3.30 mmol, 1.2 equiv) was added. The solution was warmed to room temperature and stirred for one hour. The reaction mixture was poured into saturated $NaHCO_3$ solution (50 mL) and then extracted with ether (3 × 50 mL). The organic extracts were quickly washed with 0.5 M HCl (50 mL) and then saturated $NaHCO_3$ solution (50 mL). The organic extracts were dried (Na_2SO_4) and then concentrated under reduced pressure to an oil. The crude product was purified by silica gel chromatography (hexanes) to afford 0.48 g (68 %) of the desired silyl enol ether **9**. Data for **9**: bp 100 °C (1 Torr) (air bath); ^{1}H NMR: (500 MHz, CD_2Cl_2) 4.42 (s, 1 H, HC(2)), 1.51 (m, 3 H), 1.27 (m, 5 H), 0.98 (s, 3 H, $H_3C(10)$), 0.97 (s, 3 H, $H_3C(10)$), 0.93 (s, 3 H, $H_3C(11)$, 0.86 (t, J = 6.8, 3 H, $H_3C(9)$), 0.17 (s, 9 H, $Si(CH_3)_3$) ppm; ^{13}C NMR (125.8 MHz, CD_2Cl_2) 155.85 (C(1)), 112.50 (C(2)), 46.47 (C(6)), 35.76, 35.09, 31.93, 28.16, 27.34, 26.84, 17.90, 15.23 (C(9)), 0.54 ($Si(CH_3)_3$); IR: (neat) 2959 (s), 1651 (m), 1456 (m), 1252 (m), 1194 (m), 1130 (m), 968 (w), 911 (w), 893 (m), 843 (m); CI-MS (CH_4) 256 (14), 255 (62), 254 (44), 253 (40), 240 (20), 239 (100), 212 (10), 211 (57), 186 (16), 165 (48). Anal. Calcd for $C_{15}H_{30}O$ (254.48): C, 70.79; H, 11.88. Found: C, 70.80; H, 11.89.

NMR Studies. General Procedure for the Formation of Lewis Acid-Aldehyde Complexes. Into an oven dried 10mm NMR tube sealed with a septum was added the aldehyde (0.8 mmol) by syringe. The tube was charged with $CDCl_3$ (2.0 mL and CD_2Cl_2 (2.0 mL). Th resulting 0.2 M solution was cooled to -80 °C and then placed into the probe of the NMR. Reference spectra at -80 °C were obtained and then freshly distilled, neat Lewis acid was added to the solution and the tube was gently swirled and shaken in a -80 °C cooling bath. The sample was inserted into the probe of the NMR and ^{13}C spectra were recorded. After accumulation of the FID was complete the sample was removed and an additional quantity of Lewis acid was added and the procedure was repeated.

General Procedure for the Reaction of Aldehydes or Enones with Lewis acids and Allylsilanes. The aldehyde or enone (0.2 M in CD_2Cl_2) was cooled to -80 °C. $TiCl_4$ (1 equiv) was added, and the resulting solution was placed in the cooled probe (-80 °C) of the NMR. Spectra were acquired for the Lewis acid complex, and then the sample was removed and allyltrimethylsilane was added (1 equiv). The sample was immediately re-inserted into the probe of the NMR, and spectra were acquired for the resulting sample. Additional spectra were recorded at this temperature and at 20 °C intervals up to 20 °C.

Acknowledgment: We gratefully acknowledge financial support for this project from the National Science Foundation (NSF CHE 881847 and CHE 9121631).

REFERENCES AND NOTES

1. Reviews: (a) Sakurai, H. *Pure Appl. Chem.* **1982**, *54*, 1-22. (b) Majetich, G. In *Organic Synthesis: Theory and Applications*; Hudlicky, T., Ed.; JAI Press: Greenwich, 1989; Vol. 1, pp 173-240. (c) Fleming, I.; Dunogués, J.; Smithers, R. *Org. React.* **1989**, *37*, 57-575. (d) Hosomi, A. *Acc. Chem. Res.* **1988**, *21*, 200. (e) The intramolecular reactions of allylsilanes have also been reviewed: Schinzer, D. *Synthesis* **1988**, 263-273.

2. (a) Calas, R.; Dunogues, J.; Deleris, G.; Piscioti, F. *J. Organomet. Chem.* **1974**, *69*, C15-C17. (b) Deleris, G.; Dunogues, J.; Calas, R. *J. Organomet. Chem.* **1975**, *93*, 43-50.

3. Hosomi, A.; Sakurai, H. *Tetrahedron Lett.* **1976**, 1295-1298.

4. Hosomi, A.; Sakurai, H. *J. Am. Chem. Soc.* **1977**, *99*, 1673-1675.

5. (a) Sakurai, H.; Hosomi, A.; Hayashi, J. *Org. Synth.* **1984**, *62*, 86-94. (b) Yamamoto, Y.; Sasaki, N. In *Chemical Bonds: Better Ways to Make Them and Break Them*; Bernal, I., Ed.; Elsevier, 1989, pp 363-441.

6. House, H. O.; Wilkins, J. M. *J. Org. Chem.* **1978**, *43*, 2443-2454. Recently, the use of allylcopper reagents has been re-investigated: Bertz, S. H.; Dabbagh, G. *Tetrahedron* **1989**, *45*, 425-434.

7. Blumenkopf, T. A.; Heathcock, C. H. *J. Am. Chem. Soc.* **1983**, *105*, 2354-2358.

8. Hosomi, A.; Hashimoto, H.; Kobayashi, H.; Sakurai, H. *Chem. Lett.* **1979**, 245-248.

9. (a) Denmark, S. E.; Weber, E. J. *Helv. Chim. Acta* **1983**, *66*, 1655-1660. (b) Denmark, S. E.; Henke, B. R.; Weber, E. *J. Am. Chem. Soc.* **1987**, *109*, 2512-2514.

10. (a) Denmark, S. E.; Wilson, T.; Willson, T. M. *J. Am. Chem. Soc.* **1988**, *110*, 984-986. (b) Denmark, S. E.; Weber, E. J.; Wilson, T. M.; Willson, T. M. *Tetrahedron* **1989**, *45*, 1053-1065.

11. This conclusion has been challenged by Keck, though the discrepancy in these studies remains to be resolved. (a) Keck, G. E.; Andrus, M. B.; Castellino, S. *J. Am. Chem. Soc.* **1989**, *111*, 8136-8141. (b) Keck, G. E.; Castellino, S.; Andrus, M. B. In *Selectivities in Lewis Acid Promoted Reactions*; Schinzer, D., Ed.; Kluwer Academic Publishers: Dodrecht; 1989, pp 73-105.

12. (a) Childs, R. F.; Mulholland, D. L.; Nixon, A. *Can. J. Chem.* **1982**, *60*, 801-808. (b) Dabrowski, J.; Katcka, M. *J. Mol. Structure* **1972**, *12*, 179-183. (c) Paul, R. C.; Singal, H. R.; Chadha, S. L. *Ind. J. Chem.* **1971**, *9*, 985-988. (d) Filippini, F.; Susz, B.-P. *Helv. Chim. Acta* **1971**, *54*, 1175-1178. (e) Susz, B.-P.; Weber, R. *Helv. Chim. Acta* **1970**, *53*, 2085-2097. (f) Weber, R.; Susz, B. P. *Helv. Chim. Acta* **1967**, *50*, 2226-2232.

13. Recently, a thorough study of the complexation of $TiCl_4$ and alkoxytitanium halides with ketones has appeared. Bachand, B.; Wuest, J. D. *Organometallics* **1991**, *10*, 2015-2025.

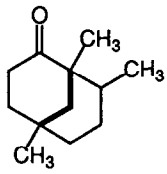
14. Panse, M.; Thiele, K.-H. *Z. Anorg. Allg. Chem.* **1982**, *485*, 7-14.

15. Nakamura, E.; Shimada, J.; Horiguchi, Y.; Kuwajima, I. *Tetrahedron Lett.* **1983**, *24*, 3341-3342.

16. (a) Augustine, R.L.; Caputo, J. A. *Org. Synth.* **1973** Coll Vol. 5, p 869-871. (b) Chan, Y.; Epstein, W.W.; *Org. Synth.* **1975**, *53*, 48-52. (c) Bergman, R.; Magnusson, G. *J. Org. Chem.* **1986**, *51*, 212-217. (d) Dauben, W. G.; Michno, D. M. *J. Org. Chem.* **1977**, *42*, 682-685.

17. The rearranged product is thought to be a bicyclic ketone. The structure **i** is most compatible with all of the spectroscopic data collected. However, it is not to be considered an unambiguous assignment. Mechanistic rationalization is left as an exercise for the reader. Data for **i**: b.p. 120 °C (1 Torr)(air bath); ^{1}H NMR (300 MHz) 2.23 (m, 1 H), 2.18 (m, 1 H), 2.04 (m, 2 H), 1.75 (m, 1 H), 1.60-1.40 (m, 5 H),

1.17 (m, 1 H), 0.98 (s, 3 H), 0.88 (s, 3 H), 0.77 (d, J = 7, 3 H); ^{13}C NMR (75.5 MHz) 216.62 (C=O), 51.41 (CH_2), 50.25 (C), 43.23 (CH_2), 40.89 (CH_2), 39.79 (CH_2), 35.59 (CH_2), 32.62 (C), 32.52 (CH_3), 22.60 (CH_3), 22.60 (CH_2), 21.94 (CH_3), 22.60 (CH_3); IR (neat) 2921 (s), 2859 (s), 1703 (s), 1456 (s), 1404 (m), 1374 (s), 1360 (m), 1327 (w), 1287 (w), 1260 (w), 1240 (w), 1188 (m), 1157 (m), 1098 (m), 1055 (m), 982 (m).; MS (70 eV) 181 (7), 180 (51), 165 (17), 138 (10), 137 (47), 136 (14), 124 (11), 123 (31), 121 (13), 111 (98), 110 (36), 109 (100), 108 (12), 107 (20), 98 (15), 97 (15), 96 (47), 95 (87), 83(33), 82 (99), 81 (86), 69 (58), 68 (59), 67 (86), 55 (98), 53 (38).; HRMS Calcd for $C_{12}H_{20}O$: 180.151415. Found: 180.151393.



I

18. (a) Grant, D.; van Wazer, J. R. *J. Organomet. Chem.* **1965**, *4*, 229-236. (b) Fishwick, M. W.; Wallbridge, M. G. H. *Ibid.* **1977**, *136*, C46-C48.

19. Wilson, T. M. M. S. Thesis, University of Illinois, Urbana IL, 1988.

20. The reaction of *alkyl*stannanes with $SnCl_4$ is well documented: (a) Baker, W. R. *J. Org. Chem.* **1985**, *50*, 3942-3943. (b) Goswami, R. *J. Org. Chem.* **1985**, *50*, 5907-5909. (c) Lee, T. V.; Boucher, R. J; Ellis, K. L.; Richardson, K. A. *Tetrahedron Lett.* **1988**, *29*, 685-688.

21. Elegant, L.; Pagliardini, A.; Torri, G.; Azzaro, M. *Bull. Chim. Soc. Fr.* **1972**, 4422-4424.

22. (a) Paul, R. C.; Singal, H. R.; Chanda, S. L. *J. Inorg. Nucl. Chem.* **1970**, *32*, 3205-3208. (b) Ganyushin, L. A.; Romm, I. P.; Gur'yanova, E. N.; Isaeva, E. S.; Ryaboi, V. M.; Shcherbakova, E. S. *J. Gen. Chem USSR (Engl. Transl.)* **1980**, *50*, 1735-1739. (c) Childs, R. F.; Mulholland, D. L.; Nixon, A. *Can. J. Chem.* **1982**, *60*, 809-812.

23. Reetz, M. T. In *Selectivities in Lewis Acid Promoted Reactions*; Schinzer, D., Ed.; Kluwer Academic Publishers: Dordrecht; 1989, pp 107-125.

24. (a) Poll, T.; Metter, J. O.; Helmchen, G. *Angew. Chem. Int Ed. Engl.* **1985**, *24*, 112-114. (b) Maier, G.; Seipp, U.; Boese, R. *Tetrahedon Lett.* **1987**, *28*, 4515-4516. (c) Viard, B.; Poulain, M.; Grandjean, D.; Amaudrut, J. *J. Chem. Res. Synop.* **1983**, 84-85. (d) Sobota, P.; Utko, J.; Lis, T. *J. Organomet. Chem.* **1990**, *393*, 349-358.

25. (a) Brun, L. *Acta Cryst.* **1966**, *20*, 739-749. (b) Bassi, I. W.; Calcaterra, M.; Intrito, R. *J. Organomet. Chem.* **1977**, *127*, 305-313.

26. Reetz, M. T.; Jung, A.; Bolm, C. *Tetrahedron* **1988**, *44*, 3889-3898.

27. (a) Paris, C.; Torri, G.; Elégant, L.; Azzaro, M. *Bull Chim Soc Fr.* **1974**, 1449-1452. (b) Torri, J.; Azzaro, M. *Bull Chim Soc Fr.* **1978**, II-283-291.

28. (a) Evans, D. A.; Bilodeau, M. T.; Somers, T. C.; Clardy, J.; Cherry, D.; Kato, Y. *J. Org. Chem.* **1991**, *56*, 5750-5752. (b) Evans, D. A.; Urpí, F.; Somers, T. C.; Clark, J. S.; Bilodeau, M. T. *J. Am. Chem. Soc.* **1990**, *112*, 8215-8216. (c) Evans, D. A.; Rieger, D. L.; Bilodeau, M. T.; Urpí, F. *J. Am. Chem. Soc.* **1991**, *113*, 1047-1049. (d) Evans, D. A.; Clark, J. S.; Metternich, R.; Novack, V. J.; Sheppard, G. S. *J. Am. Chem. Soc.* **1990**, *112*, 866-868.