

CLEAVAGE REACTIONS OF β -TRIMETHYLSILYLSTYRENE
WITH ACETYL CHLORIDE USING PRECIOUS
METAL CATALYSTS

THESIS

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Master of Science

By

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TABLE OF CONTENTS

	Page
LIST OF FIGURES	iii
LIST OF TABLES	iv
ACKNOWLEDGEMENTS	v
 Chapter	
I. INTRODUCTION	1
A. General Principles.	1
B. Comparison of Reactivity of Allyl- and Vinylsilanes.	2
C. Reactions of Allylsilanes and Vinylsilanes with Electrophiles	4
D. Purpose of Thesis	19
II. EXPERIMENTAL	22
A. Purification of Solvents and Reagents.	22
B. Analytical Procedures	23
C. Preparation of Reagents	24
D. Preparation of Catalysts.	25
E. Reactions of β -Trimethyl- silylstyrene with Acetyl Chloride	28
F. Gas Chromatographic Analyses: Methodology and Calculations.	30
III. DISCUSSION.	33
A. Allylsilanes and Vinylsilanes Used in the Synthesis of Unsaturated Ketones	33
B. Reaction Results.	34
C. Proposed Mechanisms	39
D. Reactions that Failed	47
E. Summary	48
F. Suggestions for Further Research.	49
APPENDIX I	51
LIST OF REFERENCES.	54

LIST OF FIGURES

Figure	Page
1. σ - π Hyperconjugation	2
2. Uncoordinated Vinylsilane	39
3. Complexed Vinylsilane	40

LIST OF TABLES

Table	Page
1. Reactions of Allylsilanes with Electrophiles.	8
2. Reactions of Vinylsilanes with Electrophiles.	16
3. Reactions of β -Trimethylsilylstyrene (22.6 mmol) with Acetyl Chloride (0.07 mol). .	35
4. Summary of Effect of Concentration and Temperature on Catalyst Effectiveness	38

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Chapter I

INTRODUCTION

A. General Principles

Within the last fifteen years the use of organometallic compounds in organic synthesis has significantly increased. Organosilicon compounds in particular have received a great deal of attention.¹ Several explanations for the interest in these compounds as synthons have been presented.

In general, organosilicon compounds are much more stable than other organometallic compounds. Their stability arises because of the low polarity in the silicon to carbon σ -bond. Consequently, they are rather unreactive toward many electrophiles and nucleophiles, and it is this attenuated reactivity that gives silicon its primary advantage over other metals in organic synthesis. Because of the stability of these compounds to air and water, the need to use anhydrous solvents or inert atmospheres is eliminated.

Organosilicon compounds will, however, react with both electrophiles and nucleophiles when the appropriate

conditions are observed.² The carbon-silicon bond is more polar than the carbon-hydrogen bond, and organosilanes are, therefore, usually more reactive than corresponding hydrocarbons. For example, halogen or oxygen nucleophiles (in contrast to carbon or nitrogen nucleophiles) attack a silyl group faster than they attack a hydrogen atom in the corresponding silicon-free compound.³ In addition, a carbon-silicon bond stabilizes a carbonium ion beta to it more than does a hydrogen-carbon or a carbon-carbon bond.⁴ This second observation is of paramount importance in discussing the reactivity of allyl- and vinylsilanes toward electrophiles.

B. Comparison of Reactivity of Allyl- and Vinylsilanes

A thorough comparison of the reactivity of allyl- and vinylsilanes has not been made. However, allylsilanes would be expected to be more reactive than vinylsilanes because the silicon-carbon bond of an allylsilane can overlap with the orbitals of the π -bond (σ - π hyperconjugation) as illustrated in Figure 1. This overlap results in a rise

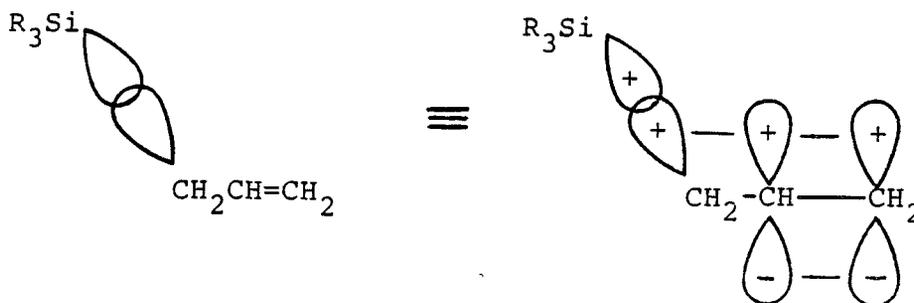
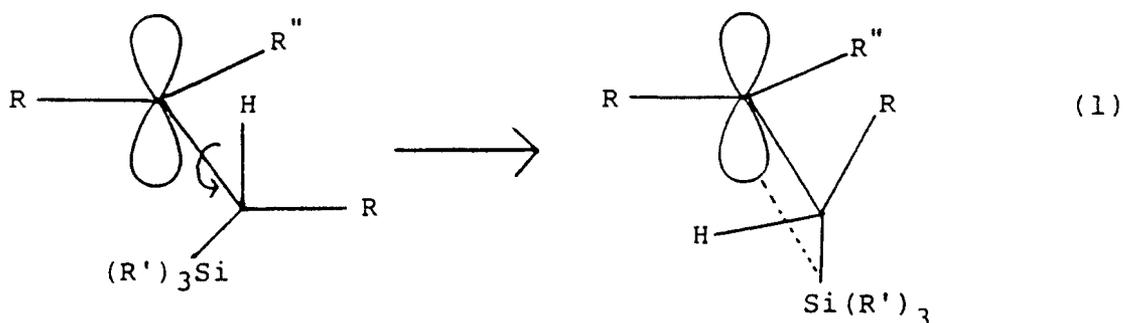
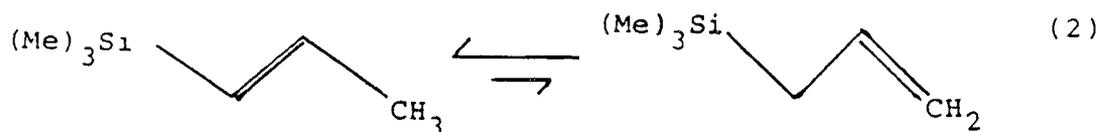


Fig. 1. σ - π Hyperconjugation

in energy of the HOMO of the π -bond and causes the molecule to be more susceptible toward electrophilic attack. In addition, the overlap causes stabilization of the developing positive charge of the carbon atom beta to the silicon atom if a carbonium ion is generated at that site. In vinylsilanes the developing positive charge of a carbonium ion resulting from electrophilic attack is stabilized by hyperconjugation only after a 90° rotation of the central carbon-carbon bond as shown in equation 1.



Additionally, it has been shown by studying equilibration reactions that vinylic silanes are thermodynamically more stable than their allylic isomers (equation 2 below). In the case of the silanes shown below,

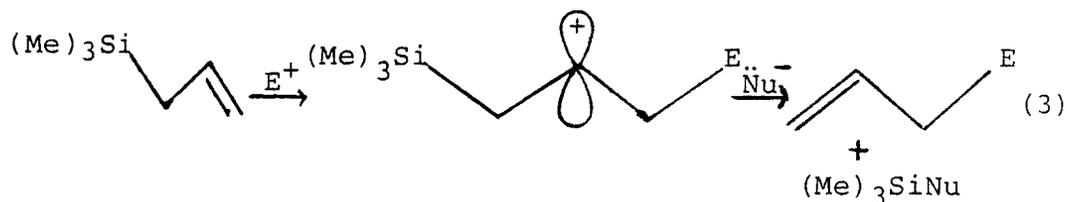


the vinylic isomer is about 8 kJ mol^{-1} lower in energy than the allylic isomer.⁵ Since protonation of both

isomers lead to the same intermediate, the allylsilane would be expected to be more reactive. Experimental observations verify this suggestion.⁶ Among molecules that contain both allyl- and vinylsilanes, reaction takes place preferentially at the allylic group.

C. Reactions of Allylsilanes and Vinylsilanes with Electrophiles

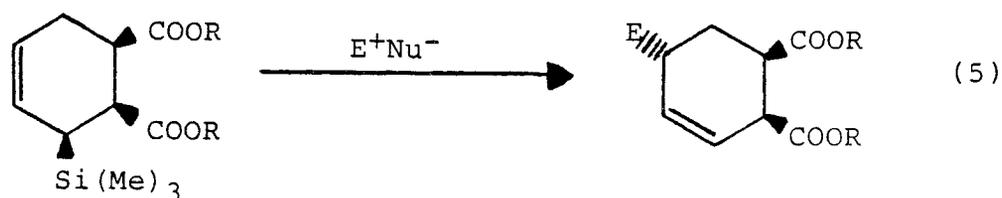
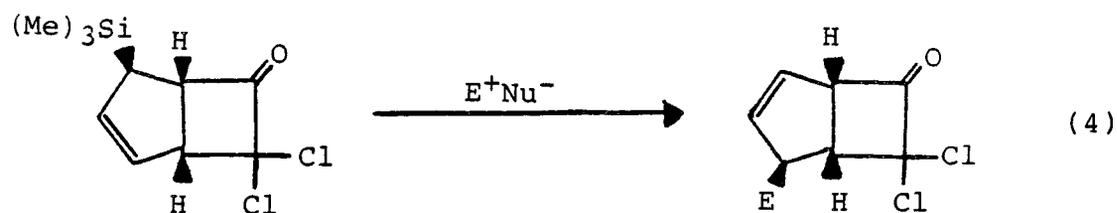
Allylsilanes are much more reactive toward both electrophiles and nucleophiles than are saturated organosilanes.¹ They are therefore very important compounds synthetically. They react with carbon electrophiles as shown below in equation 3. Attack at the terminal



carbon of the allyl system generates a cation intermediate which is stabilized by the carbon-silicon bond. The displacement of silicon is then fast. In addition, allylsilanes only rearrange at relatively high temperatures; this behavior contrasts to that of other allyl-metal compounds which readily undergo allylic rearrangements.⁵ Therefore, the reaction of an unsymmetrical allylsilane with an electrophile is usually stereospecific and gives a single product. In contrast, the corresponding

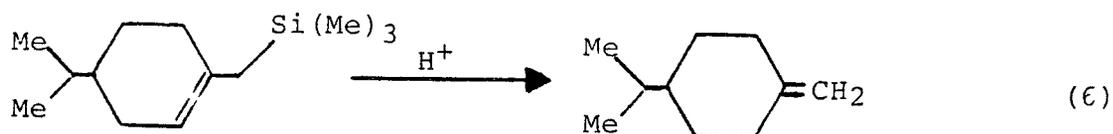
unsymmetrical allyl Grignard reagent may give a mixture of rearranged allylic products.⁷

Electrophilic substitution of allylsilanes can result in two possible stereochemical consequences, syn⁸ or anti,⁹ and both have been observed (equations 4 and 5). The data suggest that the directing effect of the

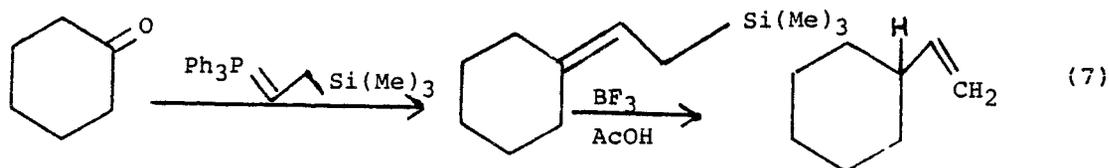


silyl group, if it exists at all, is not particularly strong, and the stereochemistry of the reaction is influenced more by the stereochemical bias of the whole molecule than by the silyl substituent.⁷

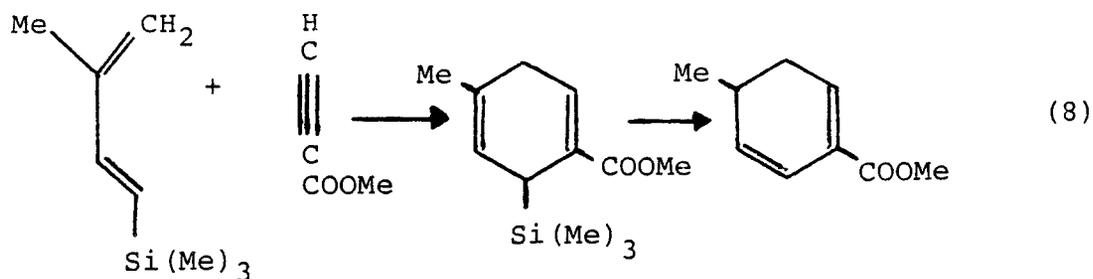
Allylsilanes react with a wide range of electrophiles, and protodesilylation, which can be used to shift the position of a double bond, is very common.¹⁰ An example of this reaction is the shift of a double bond from an endocyclic to an exocyclic position as shown in equation 6. The reaction can be applied to reductive



vinylation of carbonyls if the carbonyl compound is first converted to an allylsilane (by the Wittig reaction, for example) which is then readily protodesilylated¹¹ as shown in equation 7. The usefulness of the Diels-Alder



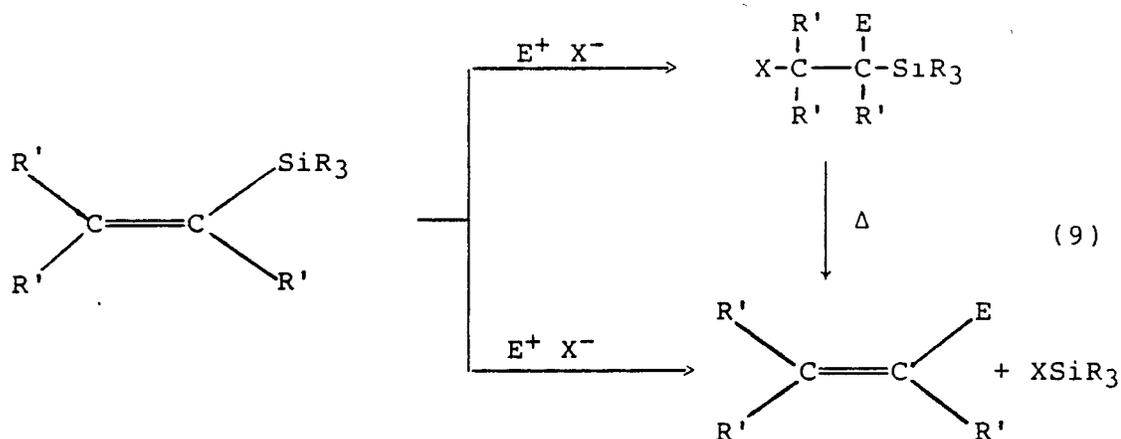
reaction can also be extended using protodesilylation¹² which can be used to shift the double bond position of the original adduct as in equation 8.



In addition to protodesilylation, allylsilanes also react with a wide variety of carbon electrophiles

to give carbon-carbon bond formation with a high degree of regioselectivity. The predictability of the site of electrophilic attack can be explained by the fact that cleavage of the carbon-silicon bond may be concerted with the build-up of electrophilic character beta to the silicon atom (equation 3). Because of this predictability, and the high nucleophilicity of allylsilanes, they have been used extensively for carbon-carbon bond formation. Several research groups have developed many effective procedures which utilize allylsilanes in organic synthesis. Some of these are listed in Table 1.

When vinylsilanes react with electrophiles both addition to the double bond and desilylation are possible²⁵ (equation 9). The addition product can subsequently



undergo elimination either thermally or on treatment with a good nucleophile for silicon.

Table 1
Reactions of Allylsilanes with Electrophiles

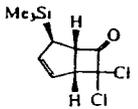
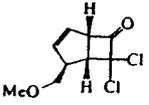
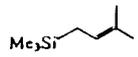
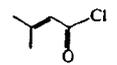
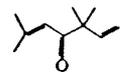
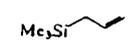
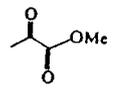
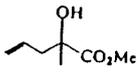
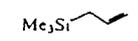
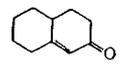
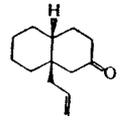
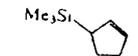
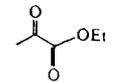
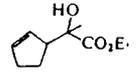
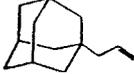
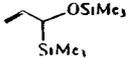
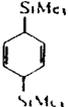
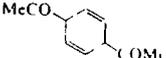
Substrate	Electrophile	Catalyst/Conditions (Stoichiometric Amount)	Product	Reference
	MeOCH_2Cl	$\text{SnCl}_4/25^\circ$		13
		$\text{AlCl}_3/-60^\circ$		14
		$\text{BF}_3\text{OEt}_2/25^\circ$		15
		$\text{TiCl}_4/-30^\circ$		16
		$\text{TiCl}_4/-15^\circ$		17

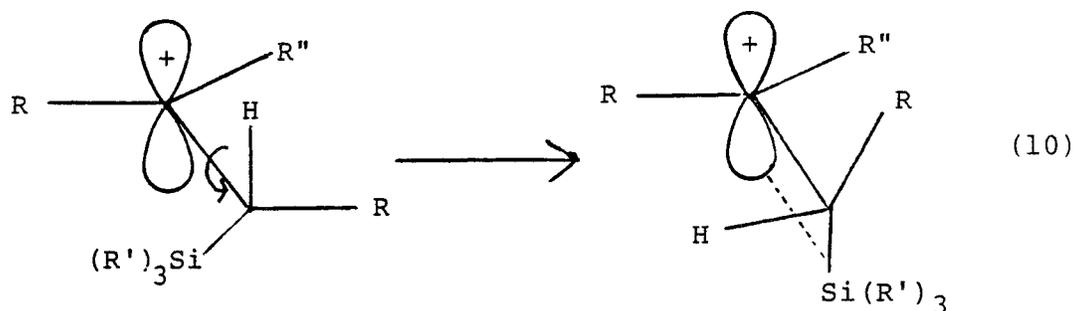
Table 1 (Continued)

Substrate	Electrophile	Catalyst/Conditions (Stoichiometric Amount)	Product	Reference
	1. ClSO ₂ NCO 2. Pyridine	1. 0° 2. 25°	1. 2.	18
	--	SnCl ₄ /25°		13
		SnCl ₄ /0°	 4 + 1	19
	Bu ^t Cl	TiCl ₄ /25°		11
		TiCl ₄ /25°		19

Table 1 (Continued)

Substrate	Electrophile	Catalyst/Conditions (Stoichiometric Amount)	Product	Reference
		TiCl ₄ /25°		20
	RCOCl	TiCl ₄ /25°		21
	RCHO	AlCl ₃ /25°		22
		AlCl ₃ /25°		23
	2 MeCOCl	AlCl ₃ /25°		24

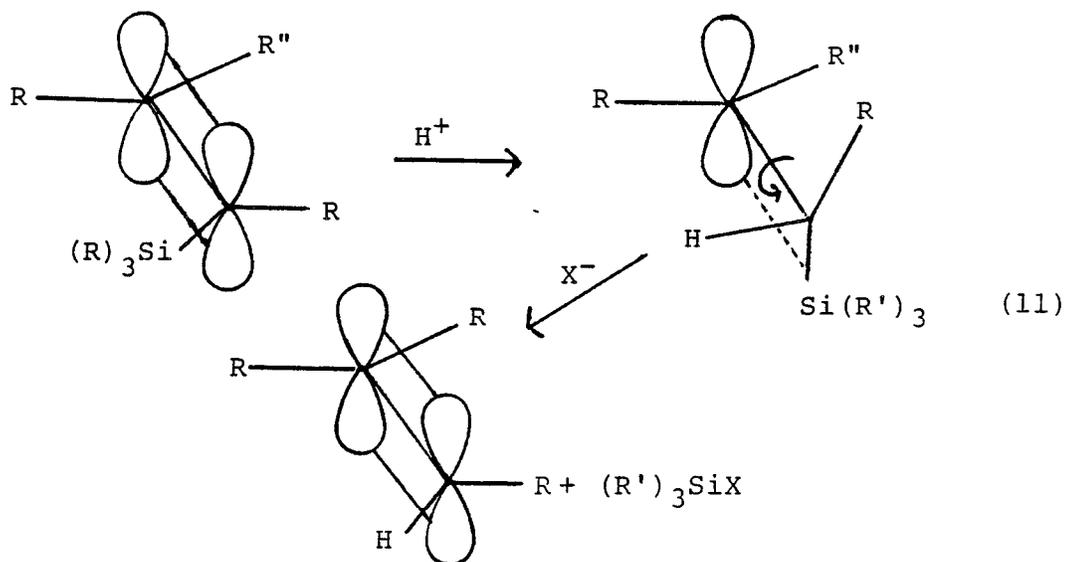
The addition of an electrophile to a vinylsilane causes a build-up of positive charge beta to the carbon-silicon bond just as in allylsilanes.²⁶ The intermediate electron deficient species is stabilized either by bridging²⁷ or by hyperconjugation.²⁸ The developing cation at the β -position is especially stabilized if the developing positive charge is contained in a $2p_z$ orbital which is coplanar with the carbon-silicon σ -bond. This geometric requirement usually presents no problem with acyclic systems. As the electrophile approaches the vinylsilane π -system, rotation about the central carbon-carbon bond brings the incipient β -carbonium ion center into the same plane as the carbon-silicon bond²⁹ (equation 10). However, for cyclic vinylsilanes, it may be



difficult or impossible for the carbon-silicon bond to move into the same plane as the $2p_z$ orbital carrying

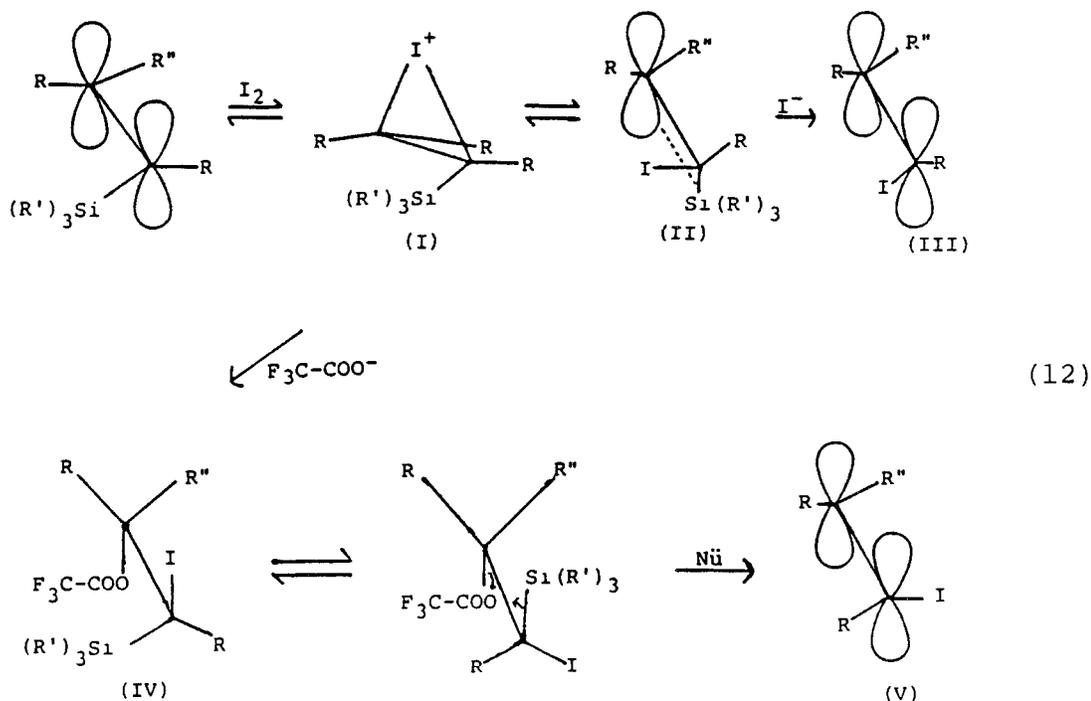
the positive charge. In such cases the silyl group is not lost.³⁰

The replacement of the silyl group in vinylsilanes by an electrophile (a desilylation reaction) usually takes place stereospecifically. Retention or inversion of configuration, however, depends on the electrophile and the reaction conditions. When the electrophile is a proton, retention of configuration occurs in all cases. For example, Koenig and Weber^{31,32} showed that complete retention of stereochemistry is observed when (Z)- and (E)- β -trimethylsilylstyrene were converted to (Z)- and (E)- β -deuterostyrene by deuterium chloride or bromide. The stereospecificity of the reaction has been found to be general with vinylsilanes. A mechanism explaining retention of stereochemistry was proposed by Koenig and Weber and is shown below (equation 11). As the proton



approaches the double bond, the central carbon-carbon bond rotates by the shortest possible path in the direction which permits the trimethylsilyl group to stabilize the β -carbonium ion. If the nucleophile attacks silicon before any further rotation can occur (equation 11), retention of configuration will result.

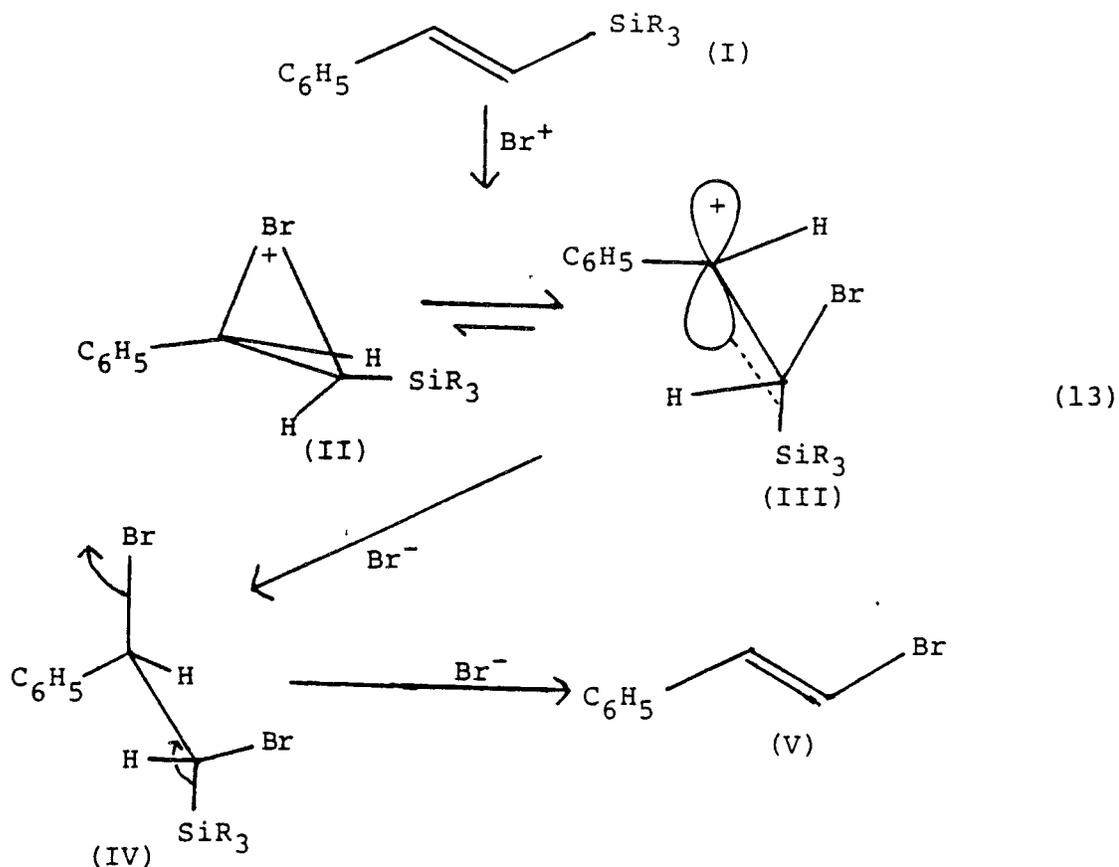
The stereochemical results are more complicated when halogens are used as electrophiles.^{33,34,35} The complication arises from the high nucleophilicity of halide ions which gives them the ability to open a bridged halonium ion intermediate. For example, iodine attacks the double bond to give intermediate I reversibly as shown in equation 12 below. If iodide ion is the



only available counter ion, substitution rather than addition will occur because the diiodo adduct is unstable. Therefore, with iodine, I will rotate to give II, after which elimination occurs to give III with retention of configuration. However, if other counter ions such as trifluoroacetate or chloride ion are present, V, which has an inverted configuration about the double bond, is isolated. The inverted product arises from an intermediate addition product IV which can be isolated. Product IV arises stereospecifically from anti-addition. Stereospecific anti-elimination of the trimethylsilyl group and the trifluoroacetate or chloride ion then gives V.

Chlorine and bromine follow the same addition-elimination sequence resulting in inversion of configuration. However, retention of stereochemistry is observed with cyanogen bromide and aluminum chloride.³³ This result can be attributed to the weak nucleophilicity of the complex formed from the counter ion with aluminum chloride. Therefore, the addition reaction is avoided and retention of configuration is observed.

β -Silylstyrenes react with bromine with retention of configuration although the reaction proceeds by the addition-elimination mechanism. The intermediate adducts of β -triphenylsilylstyrene have been isolated and shown to be the result of syn-addition.³⁶ Equation 13 below shows the overall retention of configuration results from unusual syn-addition (I—IV) followed by the usual anti-elimination (IV — V). It has been suggested³⁶



that the phenyl group stabilizes the intermediate cation so that it (III) is less symmetrical than the conventional bridged structure (II). Bromide ion therefore adds syn to the existing bromine. Additional support for this mechanism might be obtained by using β -silyl-p-nitrostyrenes.⁷ Less stabilization of the intermediate and consequently more stereochemical inversion would be the expected result. Several specific examples of the reactions just discussed as well as several others are collected in Table 2.

Table 2
Reactions of Vinylsilanes with Electrophiles

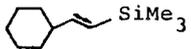
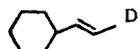
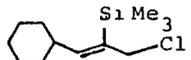
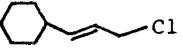
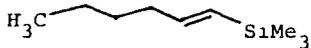
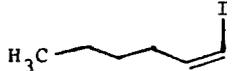
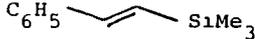
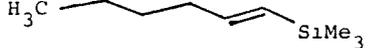
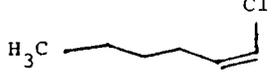
Substrate	Electrophile	Catalyst/Conditions (Stoichiometric amount)	Product	Reference
	DCl or DBr in CH ₃ CN	25°		31
	HCl	25°		37
	1. ICl 2. KF	25°		38
	1. Br ₂ /CS ₂ , -100° 2. CH ₃ CN, r.t.	25°		29
	1. Cl ₂ 2. NaOCH ₃	25°		35

Table 2 (Continued)

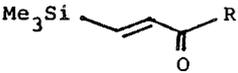
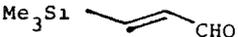
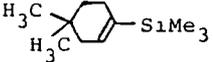
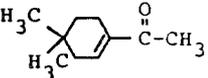
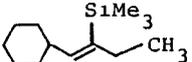
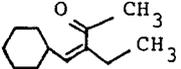
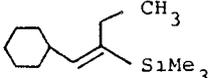
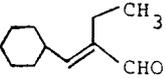
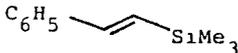
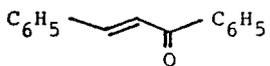
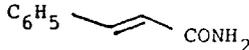
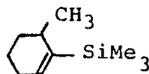
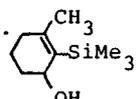
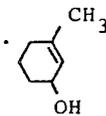
Substrate	Electrophile	Catalyst/Conditions (Stoichiometric Amount)	Product	Reference
	RCOCl	AlCl ₃ /25°		39
	1. H ₃ COCHCl ₂ 2. H ₂ O	1. AlCl ₃ 25°		39
	AcCl	AlCl ₃ /25°		40
	AcCl	AlCl ₃ /25°		33
	1. H ₃ CO-CHCl ₂ 2. H ₂ O	1. AlCl ₃ 25°		33

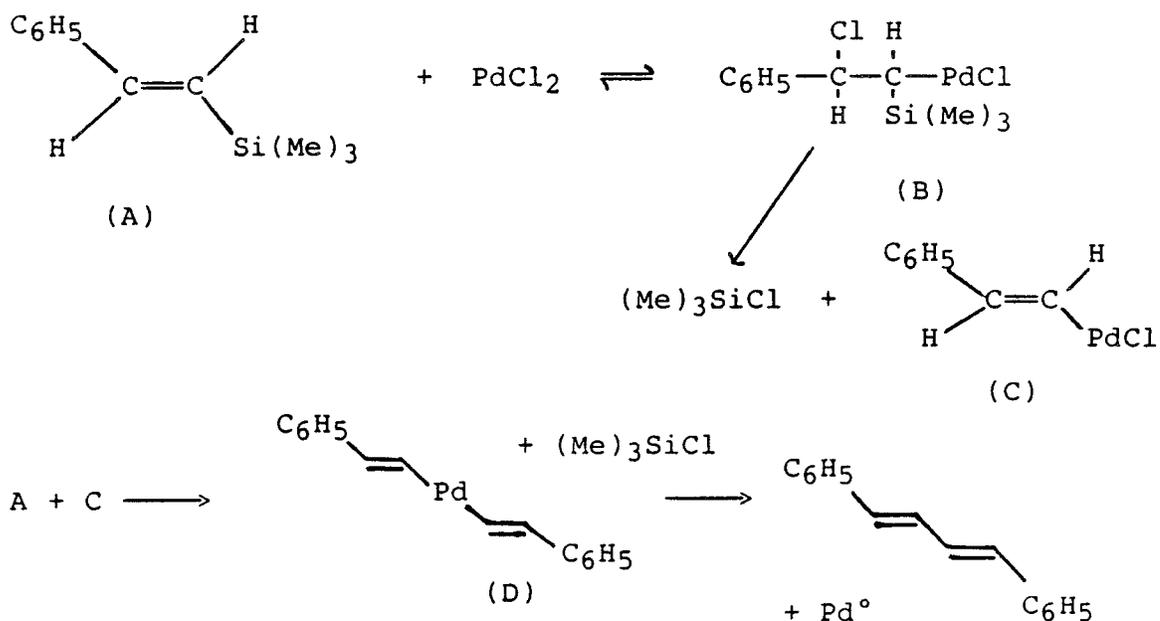
Table 2 (Continued)

Substrate	Electrophile	Catalyst/Conditions (Stoichiometric Amount)	Product	Reference
	C_6H_5COCl .	$AlCl_3/25^\circ$		40
	1. $ClSO_2NCO$ 2. H_3O^+	25°		41
	1. $O_2, NaBH_4$ 2. $Bu_4NF, MeCN$	25°	1.  2. 	42

D. Purpose of Thesis

One of the most thoroughly studied and potentially useful electrophilic cleavage reactions of both allyl- and vinylsilanes is the Friedel-Crafts acylation reaction. It typically yields α,β -unsaturated ketones with vinylsilanes⁴⁰ and β,γ -unsaturated ketones with allylsilanes.⁴³ However, the reaction suffers from the disadvantage that molar quantities of the Lewis Acid catalyst must be used. The Lewis Acids most commonly employed in this reaction, SnCl_4 ,¹³ TiCl_4 ,²⁰ and AlCl_3 ,⁴⁰ are inconvenient to handle since they are very water sensitive and release large quantities of hydrochloric acid upon hydrolytic workup of reaction mixtures. Therefore, it was decided to determine if an alternate air and water stable catalyst could be found for these reactions. The investigations have focused on noble metal catalysts with the long term goal of the research effort being development of other catalysts based on less expensive metals after the mechanism of the noble metal catalyzed reaction is understood.

Recently, compounds of mercury,⁴⁴ palladium,⁴⁵ and platinum⁴⁶ have been observed to catalyze cleavage of allyl- and vinylsilanes. Various mechanistic interpretations have been suggested to explain these catalytic processes. The mechanism proposed⁴⁵ for the reaction of β -trimethylsilylstyrene with palladium(II) chloride is typical and is shown in Scheme 1. The palladium(II)



Scheme 1

chloride is thought to form an initial addition compound, B, with the vinylic silane. β -Elimination then gives chlorotrimethylsilane and the β -styrylpalladium complex C. C reacts with another molecule of A to give the bis- β -styrylpalladium(II) intermediate D. Oxidative coupling of the two styryl groups with concurrent reductive elimination of palladium(0) gives 1,4-diphenyl-1,3-butadiene. The reaction is stoichiometric in palladium(II) chloride, although the addition of copper(I) chloride reoxidizes

palladium(0) to palladium(II) chloride, and makes the reaction catalytic in palladium(II) chloride.

A hydrolysis reaction of β -trimethylsilylstyrene (TMSS) in the presence of trichloro(ethylene)platinate(II) (Zeise's Salt) in wet acetone has also been observed.⁴⁷ When Zeise's Salt and excess TMSS are allowed to react, the silane is totally "consumed" within 3 hours to yield: hexamethyldisiloxane (78-100 mole % conversion based on TMSS); styrene (40-80 mole % conversion based on TMSS, 139-310 mole % conversion based on Zeise's Salt); 1,4-diphenyl-1,3-butadiene (13-15 mole % conversion based on TMSS); K_2PtCl_4 (24-33 mole % conversion based on Zeise's Salt); and an uncharacterized, dark brown, acetone-soluble solid. In this reaction the styrene is catalytically formed, the silicon-carbon bond is cleaved quantitatively, and no elemental platinum is formed.

These results suggest activation of the silane to electrophilic cleavage in the presence of platinum or palladium complexes. In particular, it is suggested that platinum and palladium complexes should function as Friedel-Crafts catalysts for cleavage reactions of unsaturated silanes.

Chapter II

EXPERIMENTAL

A. Purification of Solvents and Reagents

1,2-Dimethoxyethane - 1,2-dimethoxyethane obtained from Aldrich Chemical Company was tested for peroxides by shaking with an equal volume of two percent potassium iodide containing a trace of dilute hydrochloric acid. The presence of peroxides was indicated by a rapid color change from clear to yellow. If peroxides were detected, they were removed from the 1,2-dimethoxyethane by a column containing activated alumina.

Acetyl Chloride - Reagent grade acetyl chloride (6.5 mL, 0.092 mol) purchased from Eastman Organic Chemicals Company was added to 1,2-dimethoxyethane (25 mL) containing 1,8-bis(dimethylamino)naphthalene (10 g). The solution was stirred for 30 minutes under nitrogen and then flash distilled into a 50 mL Airlessware reaction flask.

1,8-Bis-(dimethylamino)naphthalene - This reagent was purchased from Aldrich Chemical Company and used without further purification.

Tetrahydrofuran - Water was removed from tetrahydrofuran by refluxing the solvent for 3 to 5 hours over calcium hydride. The dry solvent was then distilled from the calcium hydride.

β -Bromostyrene - Reagent grade β -bromostyrene obtained from Aldrich Chemical Company was used without additional purification.

Chlorotrimethylsilane - Reagent grade chlorotrimethylsilane was purchased from Petrarch Systems, Inc. and flash distilled immediately before use.

B. Analytical Procedures

Carbon and Hydrogen Analysis - Carbon and hydrogen analyses were obtained from Galbraith Laboratories in Knoxville, Tennessee or were performed locally with a Perkin-Elmer 240-C Elemental Analyzer.

Gas Chromatography - Qualitative and quantitative analyses of liquid compounds were performed on a Gow-Mac Model 69-550 Gas Chromatograph with a thermal conductivity detector. A stationary phase of 5% OV-101 (6'x1/8") was used. An Omniscribe recorder manufactured by Industrial Scientific, Inc. was used. Integration was accomplished by weight comparison of the product peak to that of a standard product peak. The procedure required that product peaks from both the reaction mixture and standard chromatograms be cut out and accurately weighed. Analyses were also performed using a Varian Model 3700 Gas Chromatograph

with a thermal conductivity detector. The stationary phase used was 10% SP-2100 (6'x1/8"). A Hewlett-Packard 3390A Integrator was used in conjunction with the Varian instrument.

Infrared Analysis - Infrared spectra were obtained on a Perkin-Elmer Model 683 with a Perkin-Elmer Model 3600 Data Station. Liquid samples were analyzed neat between sodium chloride plates.

Nuclear Magnetic Resonance - Proton NMR spectra were obtained on a Perkin-Elmer Model R-12A. Liquid samples were analyzed neat and were referenced to tetramethylsilane (δ 0.00) which was added as the internal standard.

C. Preparation of Reagents

β -Trimethylsilylstyrene - β -Trimethylsilylstyrene was prepared by a modified version of the procedure outlined by Seyferth, et al.⁴⁸

In a typical reaction, a three-liter three-necked round-bottomed flask containing magnesium turnings (25 g., 1.0 mol, previously washed with ethyl ether and dried in vacuo) was fitted with a 250 mL dropping funnel, condensor, and Waco stirrer. The system was purged with nitrogen before dry ethyl ether (800 mL) was added through the dropping funnel. The dropping funnel was removed, and ethylene dibromide (2.25 mL) along with several crystals of iodine were added to the mixture.

β -Bromostyrene (128 mL, 1.0 mol) and dry, peroxide-free tetrahydrofuran (100 mL) were added dropwise over a period of 4 to 5 hours. The mixture was refluxed for 15 hours, after which time the solution turned brown. After cooling, dry benzene (220 mL) was added to the flask and chlorotrimethylsilane (127 mL, 1.0 mol) was added by syringe at a rate to maintain a gentle reflux. The solution was refluxed for 24 hours, cooled, and hydrolyzed with saturated aqueous ammonium chloride (1500 mL). The aqueous layer was discarded, and the organic layer was washed with two portions (500 mL each) of water. After the solution was dried with magnesium sulfate, the coupling product (1,4-diphenyl-1,3-butadiene) was removed by filtration, and the filtrate was vacuum distilled to yield β -trimethylsilylstyrene (73-75°/4.0mm Hg). The product obtained (80 g, 45% yield) was identified by its IR and NMR spectra which were compared to authentic spectra. Gas chromatography showed the product to be 90% pure, with the principle contaminant being styrene.

D. Preparation of Catalysts

Potassium trichloro(ethylene)platinate(II) - Potassium trichloro(ethylene)platinate(II)(Zeise's Salt) and its precursors were prepared by standard literature methods.^{49,50} In a typical preparation platinum metal (21.0 g, 0.11 mol) was digested in aqua regia (600 mL). The mixture was heated until all the platinum was in solution while adding

aqua regia to maintain a constant volume. Concentrated hydrochloric acid (600 mL) was added and the solution was concentrated to about 150 mL. Distilled water (400 mL) and ethanol (400 mL) were added to the solution while it was being stirred. Potassium chloride (20 g in 200 mL of water) was added to precipitate yellow crystals of K_2PtCl_6 . The mixture was finally cooled in ice and filtered (39.4 g, 74% yield).

K_2PtCl_6 was reduced to K_2PtCl_4 according to the procedure of Kauffman and Cowan.⁵¹ Yellow crystals of K_2PtCl_6 (39.4 g, 0.08 mol) were added to distilled water (300 mL) in a one liter beaker. Hydrazine hydrochloride (4.25 g, 0.04 mol in 400 mL of water) was placed in a dropping funnel. The beaker was placed in an oil bath, and the solution was magnetically stirred while the temperature was maintained at 40-45°. The hydrazine hydrochloride was added dropwise over a period of several hours after which time the redish solution was concentrated to about 70 mL at a temperature of 80-90°. The solution was then filtered to remove trace amounts of platinum and unreacted K_2PtCl_6 .

Cold acetone (500 mL) and cold ethyl ether (400 mL) were added to precipitate K_2PtCl_4 , and the solution was allowed to stand in an ice bath for 5 minutes. The supernatant layer was then decanted through a filter, and the remaining slurry of pink crystals of K_2PtCl_4 was filtered and dried in vacuo (31.0 g, 92% yield).

To prepare Zeise's Salt, K_2PtCl_4 (20 g) was dissolved in 3N hydrochloric acid (100 mL) and placed in a shaker bottle with tin(II) chloride dihydrate (0.05 g). Argon was bubbled through the solution for 30 minutes to remove the oxygen. The shaker bottle was next attached to a Parr Pressure Reaction apparatus and charged with ethylene (50 psi). The solution was then shaken for 24 hours; ethylene was added when required to maintain the pressure. The resulting yellow solution was transferred to a rotary evaporation apparatus, and water was removed until a slush remained (evaporation to dryness at this point causes formation of Zeise's Dimer). The slush was dried completely in a sulfuric acid desiccator containing potassium hydroxide pellets. Zeise's Salt was separated from trace amounts of potassium chloride by extraction with acetone. The acetone was removed by evaporation under reduced pressure to leave bright yellow crystals of Zeise's Salt (16.9 g, 95% yield).

Other Catalysts - The following potential catalysts were prepared earlier by the indicated methods and were on hand in the laboratory: Di- μ -chloro-1,3-dichloro-2,4-bis(triphenylphosphine)diplatinum(II),⁵² allyl(chloro)-pyridine platinum(II),⁵³ trans-dichloro(propene) pyridine platinum(II),⁵⁴ cis-dichloro(propene)pyridine platinum(II),⁵⁵ acetylacetonato bis(ethylene)rhodium(I),⁵⁶ bis(ethylene)-(η^5 -indenyl)rhodium(I),⁵⁷ cis-dichloro(propene)triphenylphosphine platinum(II),⁵⁸ chloro tris-triphenylphosphine rhodium(I),⁵⁹ palladium (II) acetate (Spex Industries,

Inc., Metuchen, New Jersey), cis-dichloro(propene)
n-tributyl phosphine platinum(II).⁵⁸

E. Reactions of β -Trimethylsilylstyrene
with Acetyl Chloride

Catalyzed (0.543 mmol) Reactions (24 hours at reflux temperature). In a typical reaction, Zeise's Salt (0.543 mmol) was placed in a 50 mL Airlessware flask which was then evacuated and filled with nitrogen. In another 50 mL Airlessware flask, 1,2-dimethoxyethane (25 mL) was added to acetyl chloride (6.5 mL, 0.092 mol), and the solution was stirred for 30 minutes. The flask containing the catalyst was placed in a Dry Ice-ethanol bath (-78°), and the solution of acetyl chloride in 1,2-dimethoxyethane was flash distilled into it. The mixture was allowed to warm to room temperature while stirring, and β -trimethylsilylstyrene (5 mL, 22.6 mmol) was added slowly (30 minutes) through a septum using a syringe.

The flask was fitted with a condenser while it was being purged with a counter-current of nitrogen. The solution was refluxed for 24 hours after which time the volatiles were removed in vacuo. The flask was then washed several times with ethyl acetate; the washings were combined, and additional ethyl acetate was added until the total volume of solution occupied 10 mL. The solution was

then analyzed by gas chromatography, and the only product detected was styrene. In all subsequent reactions 1,8-bis-(dimethylamino)naphthalene (10 g) was added to the 1,2-dimethoxyethane-acetyl chloride solution prior to flash distillation.

The product obtained from these reactions was identified as 4-phenyl-3-buten-2-one by comparison of its infrared and nuclear magnetic resonance spectra to authentic spectra (Appendix 1). Carbon and hydrogen analysis gave the following results: 82.00% C, 7.06% H; calculated - 82.16% C, 6.89 H.

Yields of 4-phenyl-3-buten-2-one obtained with various catalysts are listed below in the format: Catalyst (percent yield of 4-phenyl-3-buten-2-one). $[\text{P}\emptyset_3(\text{Pt}(\text{Cl}_2))_2]$ (0%), $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$ (49%), $[(\text{C}_3\text{H}_5)\text{PtCl}(\text{py})]$ (79%), trans- $[\text{Pt}(\text{py})(\text{CH}_3\text{CH}=\text{CH}_2)\text{Cl}_2]$ (60%), cis- $[\text{Pt}(\text{py})(\text{CH}_3\text{CH}=\text{CH}_2)\text{Cl}_2]$ (78%), $[(\text{acac})\text{Rh}-(\text{CH}_2=\text{CH}_2)]_2$ (0%), $[(\text{Ind})\text{Rh}(\text{CH}_2=\text{CH}_2)_2]$ (0%), cis- $[\text{Pt}(\text{P}\emptyset_3)(\text{CH}_3\text{CH}=\text{CH}_2)\text{Cl}_2]$ (22.4%), $[(\text{P}\emptyset_3)_3\text{RhCl}]$ (0%), $\text{Pd}(\text{OAc})_2$ (30%), cis- $[\text{Pt}(\text{P}\text{Bu}_3)(\text{CH}_3\text{CH}=\text{CH}_2)\text{Cl}_2]$ (0%).

Catalyzed (0.543 mmol) Reactions (24 hours at room temperature.) In a procedure identical to that just described, several catalysts were studied for 24 hours at room temperature. Only those catalysts which gave product yields greater than 35% when the reaction was refluxed for 24 hours with the use of 0.543 mmol of catalyst were utilized. Yields for the catalysts are

listed below in the format: Catalyst (percent yield of 4-phenyl-3-buten-2-one). $K[PtCl_3(C_2H_4)]$ (64%), $[(C_3H_5)PtCl(py)]$ (15%), trans- $[Pt(py)(CH_3CH=CH_2)Cl_2]$ (39%), cis- $[Pt(py)CH_3CH=CH_2]Cl_2$ (92%).

Catalyzed (0.224 mmol) Reactions (24 hours at reflux temperature or 24 hours at room temperature). Only those catalysts which gave product yields greater than 35% when the reaction was refluxed for 24 hours with the use of 0.543 mmol of catalyst were utilized. Whether the reaction was refluxed for 24 hours or stirred at room temperature for 24 hours was determined by which condition gave the higher yield when 0.543 mmol of catalyst was used. Yields for various catalysts and the corresponding reaction conditions are listed below in the format: Catalyst (percent yield of 4-phenyl-3-buten-2-one) reaction condition. $K[PtCl_3(C_2H_4)]$ (51%) 24 hours at room temperature, $[(C_3H_5)PtCl(py)]$ (35%) 24 hours at reflux temperature, trans- $[Pt(py)CH_3CH=CH_2]Cl_2$ (40%) 24 hours at reflux temperature, cis- $[Pt(py)CH_3CH=CH_2]Cl_2$ (50%) 24 hours at room temperature.

F. Gas Chromatographic Analyses:

Methodology and Calculations

Several techniques were used in the laboratory in the attempt to separate the product ketone from the

reaction mixtures. These included vacuum distillation, product derivitization, thin layer chromatography, and column chromatography. However, only vacuum distillation was successful in isolating the unsaturated ketone from the reaction of β -trimethylsilylstyrene with acetyl chloride. Redistillation of the crude product yielded slightly yellow crystals identified as 4-phenyl-3-buten-2-one (m.p. 39° , literature: $40-42^\circ$).

It was subsequently determined that a convenient and effective method to monitor the product yield of the reaction was gas chromatography. This method required the use of the ketone product (via vacuum distillation) as a reference standard. This reference standard was injected into the gas chromatograph followed by injection of a reaction mixture sample. Several injections of each were chromatographed until reproducibility was established. The yield of the reaction was determined by comparison of the integration value (weight or area) of the standard and reaction mixture product peaks representing the ketones. Calculation of product yield from a typical reaction is shown below.

Standard Reference Ketone Sample:

Sample size = 0.5 μ L (91.87% pure)

Product peak area = 1.806×10^7 unit area (u.a.)

$$\frac{0.9187\%}{1.806 \times 10^7 \text{ u.a.}} = 5.087 \times 10^{-8} (\text{u.a.})^{-1}$$

$$5.087 \times 10^{-8} (\text{u.a.})^{-1} (0.5 \mu\text{L}) = 2.544 \times 10^{-8} \mu\text{L} (\text{u.a.})^{-1}$$

Reaction Mixture Sample:

Sample size = 1.0 μL

Total reaction mixture volume = $1.0 \times 10^4 \mu\text{L}$

Initial amount of substrate = $2.260 \times 10^{-2} \text{ mol}$

Product peak area = $6.118 \times 10^6 \text{ u.a.}$

$$(6.118 \times 10^6 \text{ u.a.}) 2.544 \times 10^{-8} \mu\text{L} (\text{u.a.})^{-1} = 1.556 \times 10^{-1} \mu\text{L}$$

$$\frac{1.556 \times 10^{-1} \mu\text{L}}{1.0 \mu\text{L}} (1.0 \times 10^4 \mu\text{L}) = 1.556 \times 10^3 \mu\text{L}$$

$$(1.556 \times 10^3 \mu\text{L}) 1.0 \times 10^{-3} \text{ mL} (\mu\text{L})^{-1} = 1.556 \text{ mL}$$

$$(1.556 \text{ mL}) 1.0377 \text{ g} (\text{mL})^{-1} = 1.614 \text{ g}$$

$$\frac{1.614 \text{ g}}{146.19 \text{ g} (\text{mol})^{-1}} = 1.104 \times 10^{-2} \text{ mol}$$

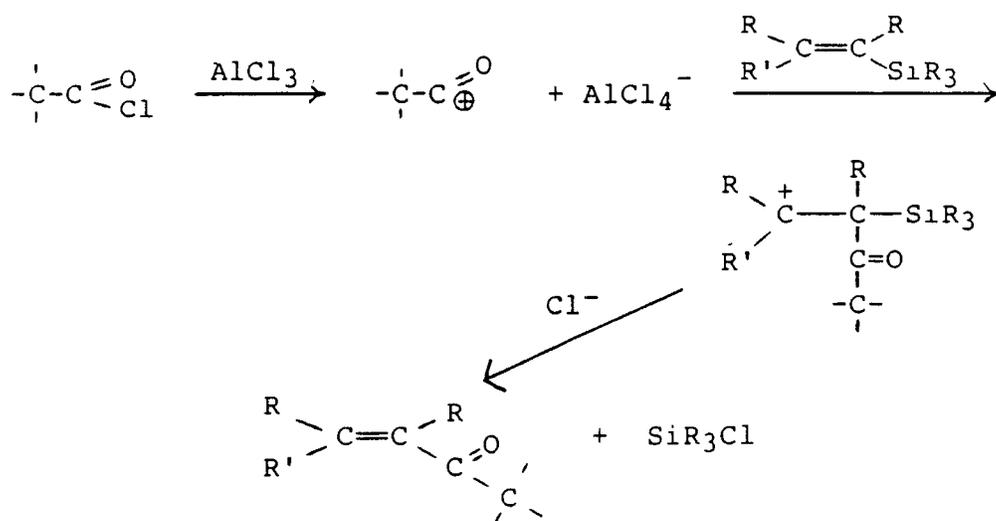
$$\frac{1.104 \times 10^{-2} \text{ mol}}{2.260 \times 10^{-2} \text{ mol}} (100\%) = 48.86\%$$

Chapter III

DISCUSSION

A. Allylsilanes and Vinylsilanes Used in the Synthesis of Unsaturated Ketones

As noted in Chapter I, both allyl- and vinylsilanes react with acyl halides under Friedel-Crafts conditions to form β,γ and α,β unsaturated ketones, respectively. The reaction with vinylsilanes usually occurs with retention of configuration about the double bond, whereas corresponding syntheses using Grignard reagents can give a mixture of products.⁷ The mechanism of the reaction is as expected and is shown for a vinylsilane in Scheme 2.



Scheme 2

Under the Friedel-Crafts conditions, an acyl cation is formed from the reaction of the acyl halide with a Lewis Acid, usually aluminum chloride. The cation then reacts with the allyl- or vinylsilane in the same manner as a proton (equations 1 and 3, Chapter I). As noted before, one disadvantage of this reaction and all Friedel-Crafts acylations is that the Lewis Acid catalyst must be added stoichiometrically.

Recent work has shown that certain transition metal complexes of mercury,⁴⁴ palladium,⁴⁵ and platinum⁴⁶ can also promote cleavage reactions of allyl- and vinylsilanes. These catalysts differ from the typical Lewis Acid catalysts in that they are true catalysts which function at low concentration and give high turnover numbers. Therefore, this investigation has focused on a study of the ability of several transition metal compounds to catalyze the acylation reaction of a typical vinylsilane, β -trimethylsilylstyrene. Table 3 summarizes the data obtained from the reactions catalyzed by several of the transition metal compounds examined.

B. Reaction Results

Eleven compounds containing the transition metals platinum, rhodium, and palladium were initially tested for catalytic activity. Each compound (0.543 mmol) was allowed to reflux for 24 hours with β -trimethylsilylstyrene (mole ratio of substrate to catalysts - 42:1)

Table 3

Reactions of β -Trimethylsilylstyrene (22.6 mmol) with Acetyl Chloride (0.07 mol)

Reaction No.	Catalyst	Catalyst Concentration (mmol)	Reaction Conditions	Yield (%)	Catalyst Turnovers
1	$[\text{P}\phi_3(\text{Pt})(\text{Cl}_2)]_2$	0.543	24 hours at reflux temp.	0	0
2	$\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$	0.543	24 hours at reflux temp.	49	20
3	$[(\text{C}_3\text{H}_5)\text{PtCl}(\text{py})]$	0.543	24 hours at reflux temp.	79	33
4	<u>trans</u> - $[\text{Pt}(\text{py})(\text{CH}_3\text{CH}=\text{CH}_2)\text{Cl}_2]$	0.543	24 hours at reflux temp.	60	25
5	<u>cis</u> - $[\text{Pt}(\text{py})(\text{CH}_3\text{CH}=\text{CH}_2)\text{Cl}_2]$	0.543	24 hours at reflux temp.	78	33
6	$[(\text{acac})\text{Rh}(\text{CH}_2=\text{CH}_2)_2]$	0.543	24 hours at reflux temp.	0	0
7	$[(\text{Ind})\text{Rh}(\text{CH}_2=\text{CH}_2)_2]$	0.543	24 hours at reflux temp.	0	0
8	<u>cis</u> - $[\text{Pt}(\text{P}\phi_3)(\text{CH}_3\text{CH}=\text{CH}_2)\text{Cl}_2]$	0.543	24 hours at reflux temp.	22	9
9	$[(\text{P}\phi_3)_3\text{RhCl}]$	0.543	24 hours at reflux temp.	0	0
10	$\text{Pd}(\text{OAc})_2$	0.543	24 hours at reflux temp.	30	13
11	<u>cis</u> - $[\text{Pt}(\text{P}\text{Bu}_3)(\text{CH}_3\text{CH}=\text{CH}_2)\text{Cl}_2]$	0.543	24 hours at reflux temp.	0	0
12	$\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$	0.543	24 hours at room temp.	64	27
13	$[(\text{C}_3\text{H}_5)\text{PtCl}(\text{py})]$	0.543	24 hours at room temp.	15	6
14	<u>trans</u> - $[\text{Pt}(\text{py})(\text{CH}_3\text{CH}=\text{CH}_2)\text{Cl}_2]$	0.543	24 hours at room temp.	39	17

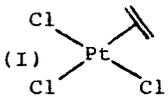
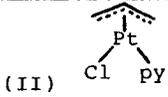
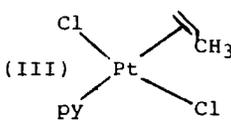
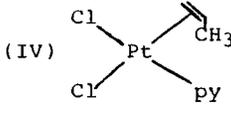
Table 3 (continued).

Reaction No.	Catalyst	Catalyst Concentration (mmol)	Reaction Conditions	Yield (%)	Catalyst Turnovers
15	<u>cis</u> -[Pt(py)(CH ₃ CH=CH ₂)Cl ₂]	0.543	24 hours at room temp.	92	38
16	K[PtCl ₃ (C ₂ H ₄)]	0.226	24 hours at room temp.	51	51
17	[(C ₃ H ₅)PtCl(py)]	0.226	24 hours at reflux temp.	35	35
18	<u>trans</u> -[Pt(py)(CH ₃ CH=CH ₂)Cl ₂]	0.226	24 hours at reflux temp.	40	40
19	<u>cis</u> -[Pt(py)(CH ₃ CH=CH ₂)Cl ₂]	0.226	24 hours at room temp.	50	50

and acetyl chloride (mole ratio of reagent to substrate-3:1) in 1,2-dimethoxyethane. Six of the complexes (five containing platinum and one containing palladium) gave yields of 4-phenyl-3-buten-2-one which ranged from 22-79 percent. The four best catalysts contained platinum and are $K[PtCl_3(C_2H_4)]$ (49%), $[(C_3H_5)PtCl(py)]$ (79%), trans- $[Pt(py)CH_3CH=CH_2)Cl_2]$ (60%), and cis- $[Pt(py)(CH_3CH=CH_2)Cl_2]$ (78%). Catalyst concentration, reaction temperature, product yield, and catalyst turnover number for the four best catalysts are summarized in Table 4. The four best catalysts were next compared to each other by changing the reaction temperature from reflux to room temperature. Finally, a different concentration (0.226 mmol) of the catalysts was used in the reaction to determine their relative catalytic effectiveness by increasing the substrate to catalyst molar ratio. The reaction temperature selected for the study of the effect of the reduced catalyst concentrations was determined by which temperature gave the higher yield when 0.543 mmol of the catalyst was used.

As can be seen in Table 3, only four π -complexes of platinum(II) and palladium(II) acetate yielded detectable product. Curiously, two π -complexes of rhodium and one π -complex of platinum failed to catalyze the reaction at all. Table 4 shows that catalysts I and IV were more effective at room temperature while catalysts II and III gave better product yields at reflux

Table 4
Summary of Effect of Concentration and Temperature on Catalyst Effectiveness

Catalyst	Reaction Number	Catalyst Concentration (mmol)	Reaction Temperature	Yield (%)	Catalyst Turnovers
 (I) $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$	1	0.543	Reflux	49	20
	2	0.543	25 °	64	27
	3	0.226	25 °	51	51
 (II) $[(\text{C}_3\text{H}_5)\text{PtCl}(\text{py})]$	4	0.543	Reflux	79	33
	5	0.543	25 °	15	6
	6	0.226	Reflux	35	35
 (III) $\text{trans-}[\text{Pt}(\text{py})(\text{CH}_3\text{CH}=\text{CH}_2)\text{Cl}_2]$	7	0.543	Reflux	60	25
	8	0.543	25 °	39	17
	9	0.226	Reflux	40	40
 (IV) $\text{cis-}[\text{Pt}(\text{py})(\text{CH}_3\text{CH}=\text{CH}_2)\text{Cl}_2]$	10	0.543	Reflux	78	33
	11	0.543	25 °	92	38
	12	0.226	25 °	50	50

temperature. Additionally, catalysts I, III, and IV exhibited relatively similar yields for both reaction temperatures while catalyst II yields varied over 60% with reaction temperature. Catalyst I gave the greatest turnover number (51) while catalyst IV had the highest yield (92%). Catalyst II had both the lowest turnover number (6) and yield (15%) at room temperature. All catalysts gave the greatest turnover numbers when reduced concentrations were used.

C. Proposed Mechanisms

The polarity of the carbon-silicon bond in vinylsilanes (Figure 2) is altered as the transition metal is coordinated to the π -bond of the ligand. Two factors

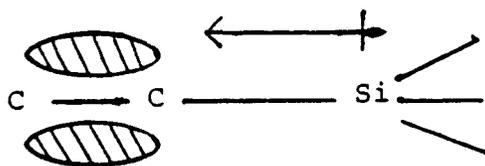


Fig. 2. Uncoordinated Vinylsilane

determine the degree of labilization of the carbon-silicon bond to cleavage (Figure 3). These factors are forward

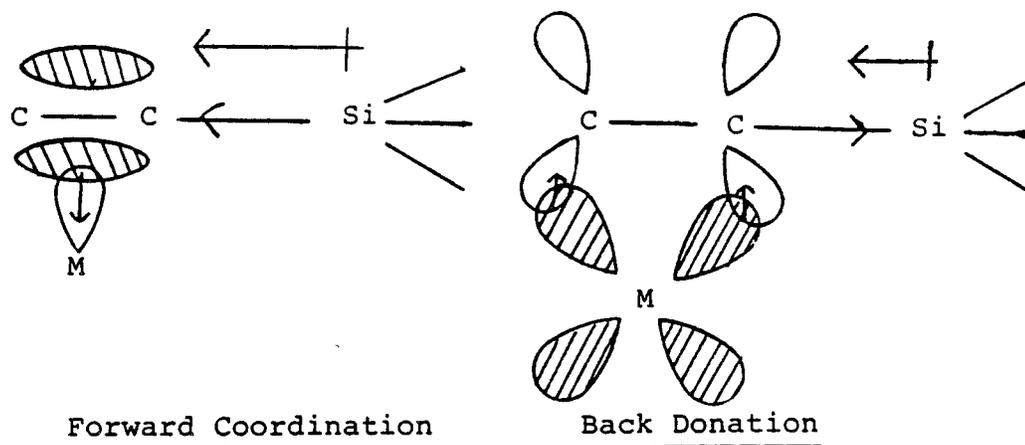


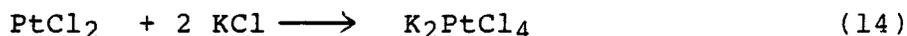
Fig. 3. Complexed Vinylsilane

coordination of electron density from the π -bond to the metal, and back donation of electron density from the metal to the π^* -bond of the vinylsilane. If forward coordination dominates the metal-vinylsilane bonding, then the carbon-silicon bond polarity is intensified and the bond should be labilized to cleavage by diplar reagents. The silicon atom is made more susceptible to attack by a nucleophile while the adjacent carbon atom is activated to attack by an electrophile according to this scheme. However, as back donation approaches forward coordination in importance, the carbon-silicon bond polarity is decreased, and cleavage is predicted to be less likely to occur.

While the exact role of the transition metal compound in catalyzing the cleavage reactions of allyl- and vinyl-

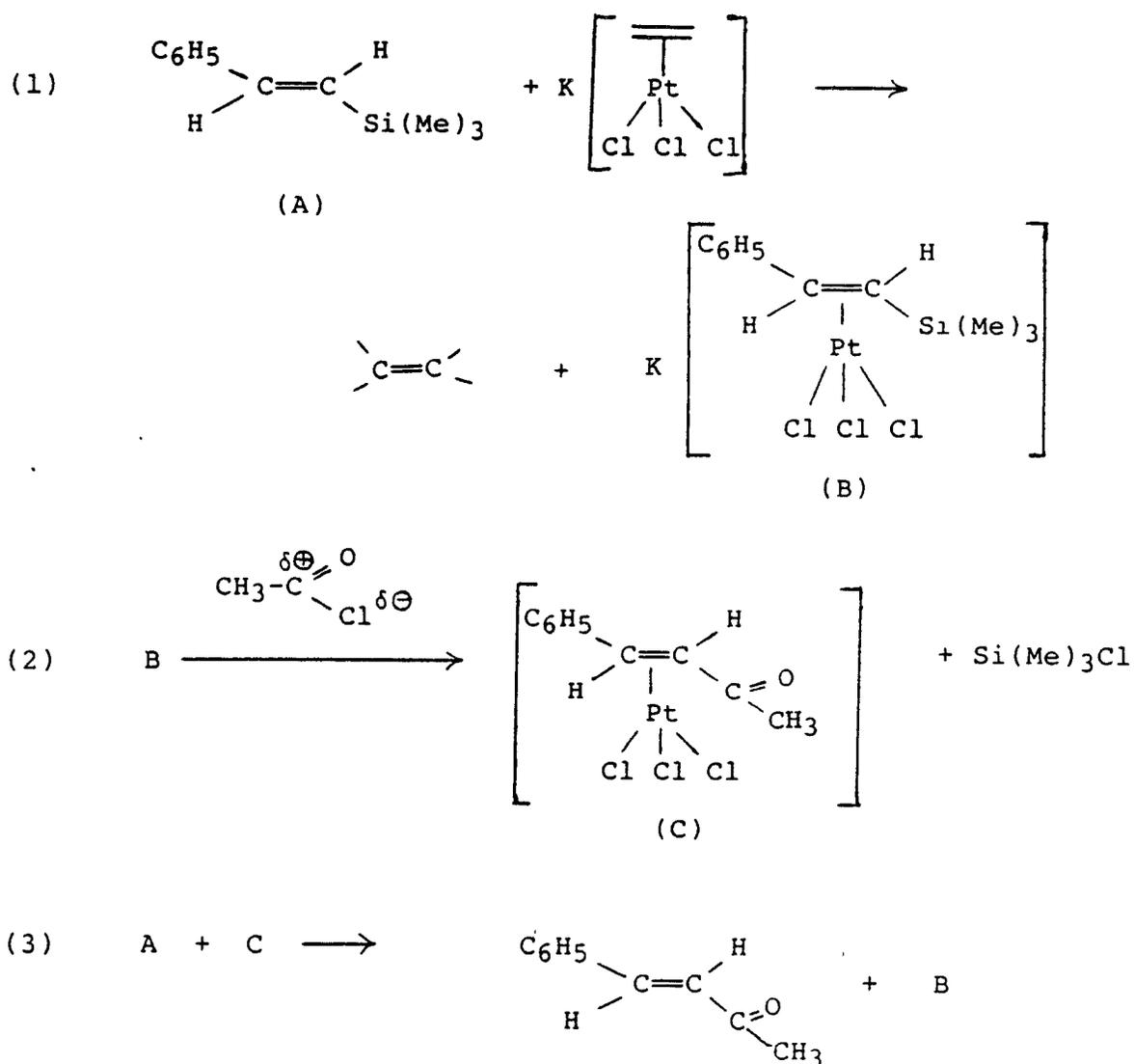
silanes is not yet fully understood, three mechanisms are considered possible because of earlier work.^{45,46} These mechanisms are: (1) the transition metal complex behaves simply as a Lewis Acid toward the acyl halide, (2) a metal-complexed silane is cleaved by the dipolar acyl halide in either an ionic or concerted process and (3) the reaction may proceed by an oxidative addition-reductive elimination pathway. The oxidative addition-reduction elimination mechanism is suggested because all of the effective catalysts studied are coordinatively unsaturated and thus able to undergo oxidative addition. However, there is no evidence for oxidative addition of acyl halides to the complexes studied, and therefore the mechanism is not considered likely. The other two suggested mechanisms will, however, be discussed in some detail.

The first suggested mechanism involves the well-documented ability of transition metal compounds to behave as Lewis Acids (see equation 14 below). The Lewis Acid



behavior of coordinatively unsaturated transition metal complexes has been suggested by various mechanistic investigations.⁴⁶ However, if the transition metal complex functioned simply as a Lewis Acid it would seem that any transition metal complex should catalyze the reaction,

in palladium(II) chloride. This mechanism cannot explain the catalytic turnovers (up to 50) exhibited by the transition metal compounds examined in this laboratory since no reoxidizing agent was required in the current study. However, a similar mechanism involving complexation of β -trimethylsilylstyrene with the transition metal compound seems reasonable and is shown in Scheme 4.



Scheme 4

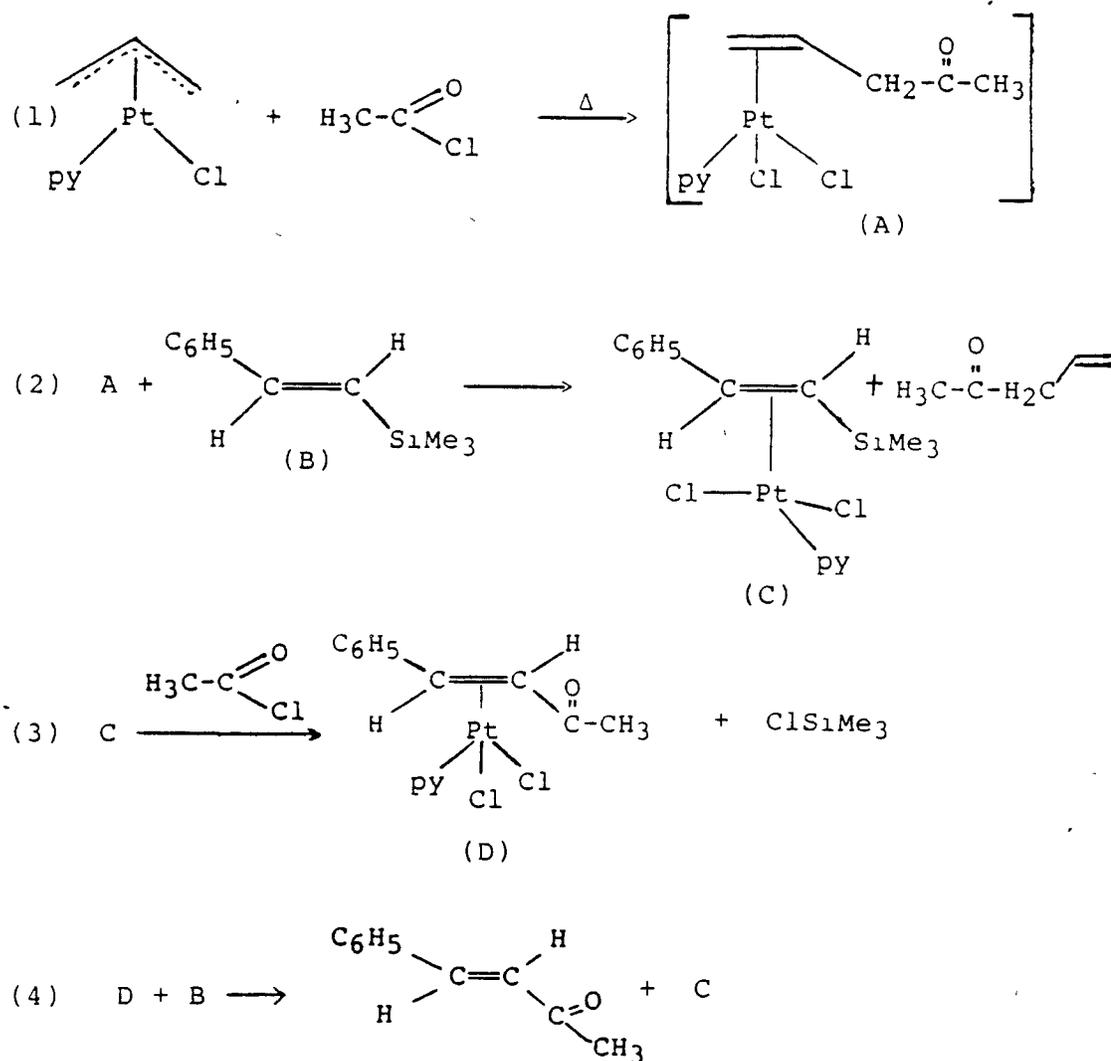
Electrophilic replacement of the silyl group by solvolytically formed acyl cation or concerted cleavage through a four centered mechanism involving the molecular acyl halide are both enhanced by the increase in polarity of the carbon-silicon bond. Either variation of the mechanism results ultimately in the displacement of the halosilane molecule. The transition metal complexed vinyl ketone intermediate could then react with another molecule of the vinylsilane to free the unsaturated ketone and regenerate another molecule of the transition metal complexed silane. The transition metal complex would theoretically remain catalytically active indefinitely in this mechanism.

This second mechanistic view is generally consistent with the observed yield data summarized in Table 4 for complexes I, III, and IV (Zeise's Salt and trans- and cis-[Pt(py)CH₃CH=CH₂]Cl₂], respectively). However, under each condition studied compound IV was observed to be a more effective catalyst than its trans-isomer. This observation is at first glance puzzling since the steric crowding of the alkene coordination site is certainly greater in IV than in III. The data can be understood, however, by comparing and analyzing the relative trans effects of the chloro and pyridine ligands.

The trans effect⁶⁰ can be described as the relative ability of a ligand (A) to facilitate substitution of a ligand in the position trans to itself. This effect

is due, in part, to the ability of the ligand (A) to perturb the transition metal's $d\pi$ electron density. If ligand (A) is electron withdrawing (generally associated with strong trans effect ligands) there is a resulting decrease in electron density between the transition metal and the ligand trans to ligand (A). Since chlorine exhibits a larger trans effect than does pyridine, the polarization of the carbon-silicon bond (because of the imbalance of forward coordination and back donation (Figure 3)) is more pronounced for the cis-isomer. The result of this effect is the prediction that the carbon-silicon bond is more easily cleaved when the vinylsilane is complexed in the cis-isomer (trans to chlorine). As expected, a higher yield is obtained from the reaction catalyzed by the cis-isomer (Table 3, reaction No. 11) than from the reaction catalyzed by the trans-isomer (Table 3, reaction No. 8). Analogously, the cis-isomers of $[\text{Pt}(\text{P}\emptyset_3)(\text{CH}_3\text{CH}=\text{CH}_2)\text{Cl}_2]$ and $[\text{Pt}(\text{PBu}_3)(\text{CH}_3\text{CH}=\text{CH}_2)\text{Cl}_2]$ would be predicted to give product yields (see Table 3, reaction No. 8 and 11) similar to those of cis- $[\text{Pt}(\text{py})(\text{CH}_3\text{CH}=\text{CH}_2)\text{Cl}_2]$ based on arguments involving the trans effect. However, a significantly lower yield was obtained with cis- $[\text{Pt}(\text{P}\emptyset_3)(\text{CH}_3\text{CH}=\text{CH}_2)\text{Cl}_2]$ (22%) and no reaction occurred with cis- $[\text{Pt}(\text{PBu}_3)(\text{CH}_3\text{CH}=\text{CH}_2)\text{Cl}_2]$. These results suggest that the larger phosphine ligands may sterically interfere with coordination of the bulky ligand, β -trimethylsilylstyrene. Further work is needed in this area with less bulky vinylsilanes.

A minor variation of the second mechanism seems reasonable for the reactions catalyzed by $[(C_3H_5)Pt(py)Cl]$ (see Table 4, reaction No. 4 and 5). The wide variations of yield with reaction temperature (reflux temperature = 79%, room temperature = 15%) exhibited with this catalyst's activity may be explained by the suggestion that it must first form a reactive intermediate before catalytic activity is observed (Scheme 5). At room temperature, the



Scheme 5

initial formation of an intermediate complex (A) is probably slow, and the product yield is low (15%). However, at reflux temperature the formation of the intermediate can likely occur more easily, and high product yield (92%) results. Again additional work is required to verify formation of the proposed vinyl ketone complex intermediate.

D. Reactions that Failed

Initially, this investigation was to include a survey of the reactions of various allyl- and vinylsilanes with several dipolar reagents using Zeise's Salt as the catalyst. The reactions attempted utilized the following substrates and reagents: allyltrimethylsilane with benzoyl chloride, β -trimethylsilylstyrene with benzoyl chloride, vinyltrimethylsilane with benzoyl chloride, allyltrimethylsilane with acetyl chloride, β -trimethylsilylstyrene with trimethyl acetyl chloride, and β -trimethylsilylstyrene with acetyl chloride. Of these reactions, only that of β -trimethylsilylstyrene with acetyl chloride yielded an isolatable product.

There are several possible explanations for the failure to isolate the expected ketones from the other attempted reactions. One possibility is that hydrochloric acid generated from the hydrolysis of acyl chlorides causes protodesilylation of the substrates to yield ethylene and propene from vinyl- and allyltrimethylsilanes, respectively, before the ketones can be formed. In the case

of β -trimethylsilylstyrene, protodesilylation gives styrene. Confirmation of this competing reaction was achieved in the laboratory by allowing unpurified acetyl chloride to react with the silane substrate. The only product detected from the reaction was styrene. The reaction was repeated with 1,8-bis-(dimethylamino)naphthalene used to scavenge protons originating from impure (hydrolyzed) acetyl chloride before it was used, and the unsaturated ketone was obtained. Therefore, acetyl chloride was routinely purified (as described in Chapter II) prior to use for all subsequent reactions.

Another competing reaction involves the formation of coupling products. It has been shown⁴⁵ that the reaction of β -trimethylsilylstyrene with palladium(II) chloride in methanol gives trans, trans-1,4-diphenyl-1,3-butadiene in good yield. The proposed mechanism for this reaction is shown in **Scheme 3** (page 42). Perhaps some similar coupling mechanism is responsible for the failure to detect the unsaturated ketones from the reactions of other allyl- and vinylsilanes with various acyl halides.

E. Summary

Several transition metal complexes were shown to catalyze the reaction of β -trimethylsilylstyrene with acetyl chloride to yield 4-phenyl-3-buten-2-one. These catalysts were added in trace amounts and gave turnover numbers of up to fifty. Although the mechanism of the

reaction is not fully understood, several possible schemes have been suggested.

F. Suggestions for Further Research

Several ideas involving transition metal catalysis deserve further investigation. Since many of the attempted reactions of allyl- and vinylsilanes with acyl halides in the presence of a transition metal complex gave evidence of reaction, (evolution of gas, color change, etc.), the purification of acetyl chloride and the monitoring of reaction products by gas chromatography could yield successful results.

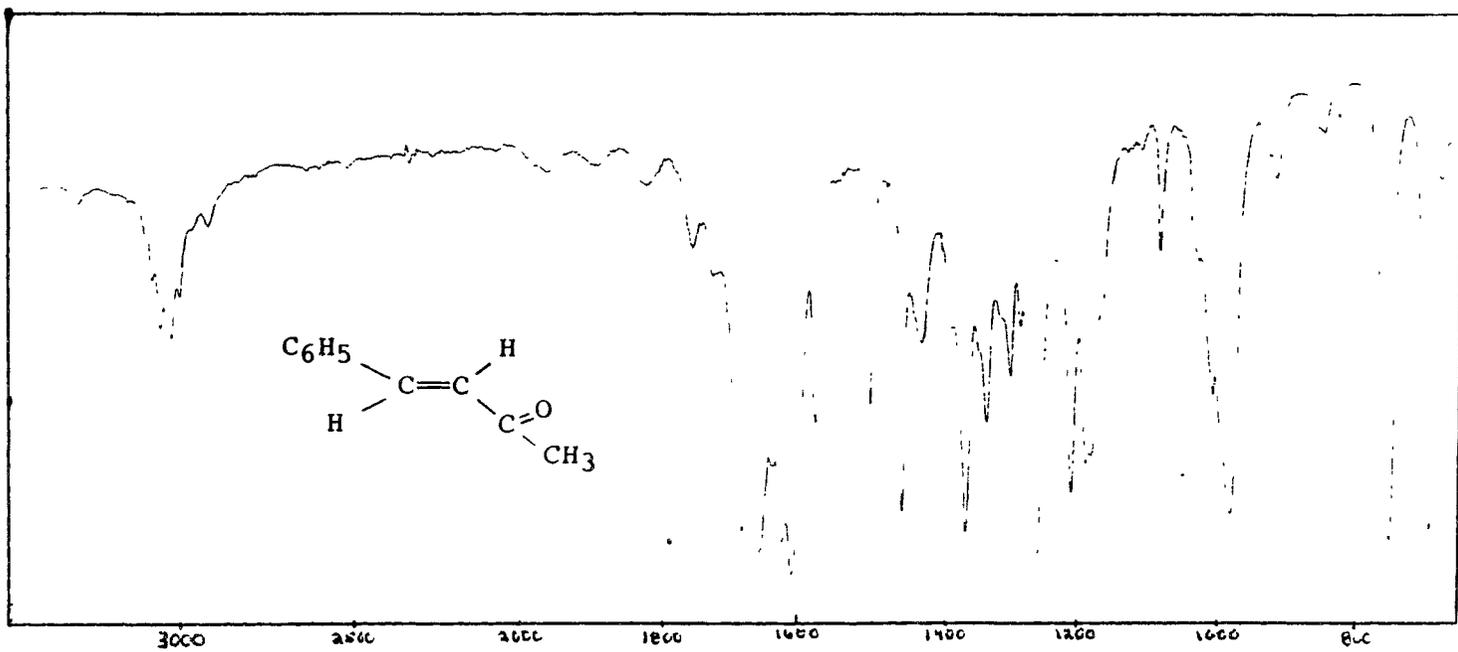
Another future investigation could involve the use of a co-catalyst in conjunction with the transition metal complex in an effort to increase catalytic turnover numbers. Milstein and Stille⁶¹ have demonstrated that various tetraorganotin compounds can be added stoichiometrically as co-catalysts to acid chlorides with a catalytic amount of benzylchloro-bis-(triphenylphosphine)palladium(II) to give unsaturated ketones in quantitative yields. Perhaps this co-catalyst could be used in combination with the transition metal catalysts studied in this laboratory to produce the high catalyst turnover numbers (14,000) reported by Milstein and Stille.⁶¹

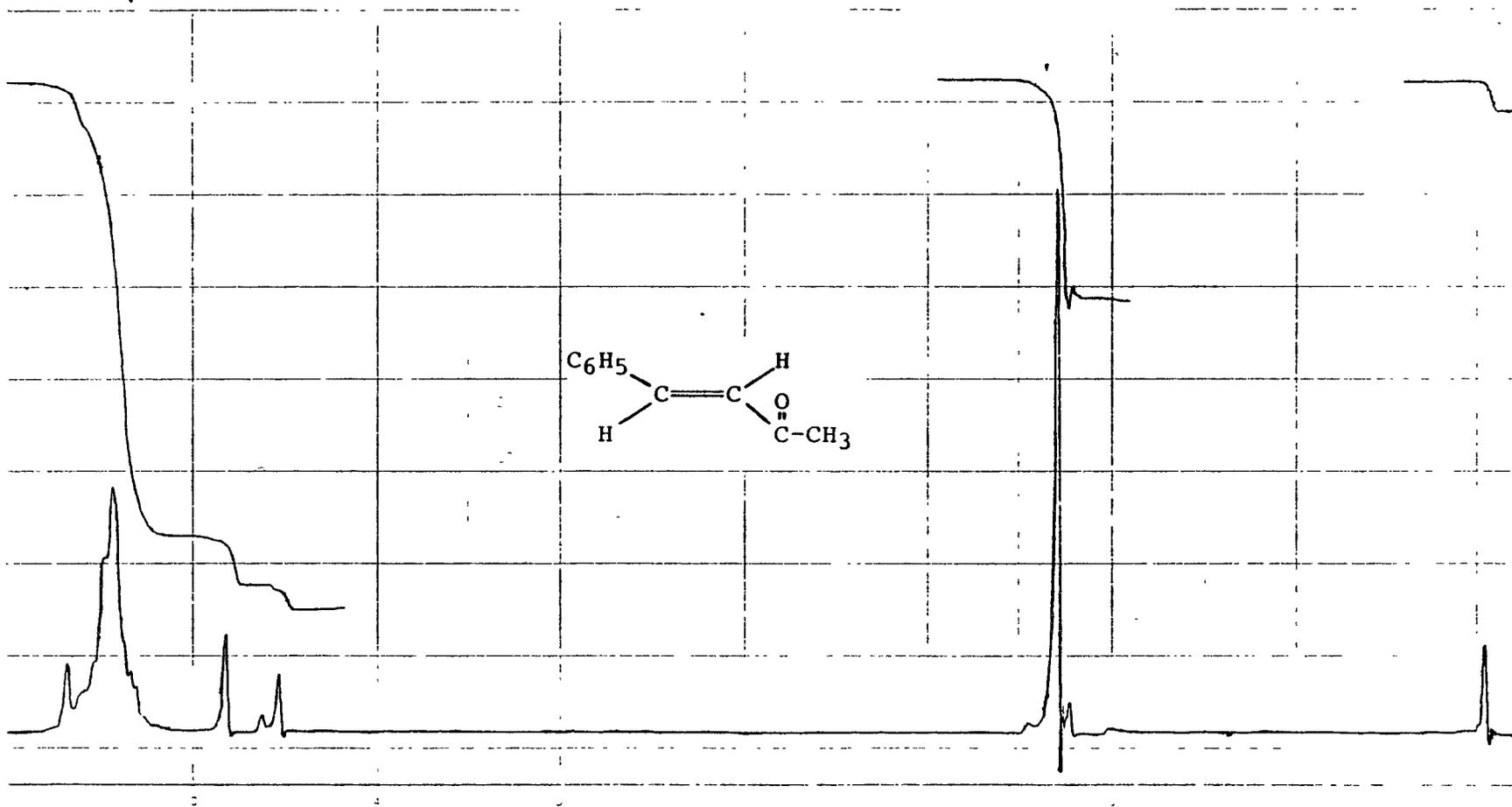
Additionally, in view of the numerous applications of transition metal complexes as catalysts, compounds of Cu(I) or Ag(I) may also be active catalytically.

Some vinylsilane complexes of Cu(I) have been synthesized and characterized in this laboratory.⁶² The substantially lower cost of these complexes gives them their potential attractiveness over precious metal complexes.

It is generally accepted that the reaction of allyl- and vinylsilanes with acyl halides is successful largely due to the dipolar nature of the acyl halide. A future research goal could be an investigation to determine whether other dipolar reagents (such as N-chlorosuccinimide) would be effective in metal catalyzed cleavage reactions of allyl- and vinylsilanes. These investigations could lead to additional applications in organic synthesis for allyl- and vinylsilanes.

Appendix I
Infrared
and
Nuclear Magnetic Resonance
Spectra





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