STUDY OF 1-METALATED-2-(TRIMETHYLSILYL)VINYL CATIONS:
AN EXAMINATION OF THE β-EFFECT
FOR SILYL, GERMYL AND STANNYL GROUPS

By

CAROL DALLAIRE, M.Sc.

A Thesis
Sudmitted to the School of Graduate Studies
in Partial Fulfilment of the Requirements
for the Degree
Ph. D.

McMaster University

STUDY OF 1-METALATED-2-(TRIMETHYLSILYL)VINYL CATIONS:
AN EXAMINATION OF THE β-EFFECT
FOR SILYL, GERMYL AND STANNYL GROUPS

À mon père Lucien

et à la mémoire de

ma mère Rose-Hélène

DOCTOR OF PHILOSOPHY (1991)
(Chemistry)

McMASTER UNIVERSITY
Hamilton, Ontario

TITLE: Study of 1-Metalated-2-(trimethylsilyl)vinyl Cations: An Examination of the β-Effect for Silyl, Germyl and Stannyl Groups

AUTHOR: Carol Dallaire, B. Sc. (Université de Sherbrooke)
M. Sc. (Université de Sherbrooke)

SUPERVISOR: Dr. Michael A. Brook

NUMBER OF PAGES: xvi, 157

ABSTRACT

The ability of silicon, germanium and tin elements (group 14) to stabilize a vinyl cation intermediate was investigated upon proton addition to metalated (trimethylsilyl)acetylene compounds to lead, after demetalation, to monometalated acetylenes. The reactions were followed by ^1H NMR spectroscopy. A bimolecular addition mechanism is obtained and nucleophilic participation in the reaction is observed.

The reaction rates showed that vinyl cations are stabilized by hyperconjugation of the carbon-metal bond (β-effect) in the order of magnitude Sn (10^8)> Ge (500)> Si (1). The magnitude of the β-effect on vinyl cation is altered to a degree by the groups born by the metal.

The vinyl cations are also stabilized, in a lower extent, by inductive effects of the metalated group to the electron-deficient carbon (α-effect).

ACKNOWLEDGEMENTS

I am extremely grateful to my supervisor, Dr. Michael A. Brook for his encouragement, enthusiasm, guidance and expert advice throughout the course of this present work. I do not have enough words to thank him for his extreme patience, friendship and the confidence he had in me throughout the entire course of my graduate study.

I express my gratitude to Brian Sayer and Dr. Don Hughes for their patience and expert advice in the NMR spectroscopic analysis.

Thanks to Faj Ramalan and Dr. Richard Smith for their help in the MS spectroscopic analysis.

Thanks are also due to all my co-workers, especially to Graham McGibbon for his fruitful discussions of this project and to Thomas Sebastian for his help in the initial stage of my graduate study.

I thank McMaster University for financial support.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF SCHEMES

LIST OF TABLES

LIST OF EQUATIONS

LIST OF GRAPHS

CHAPTER 1

INTRODUCTION

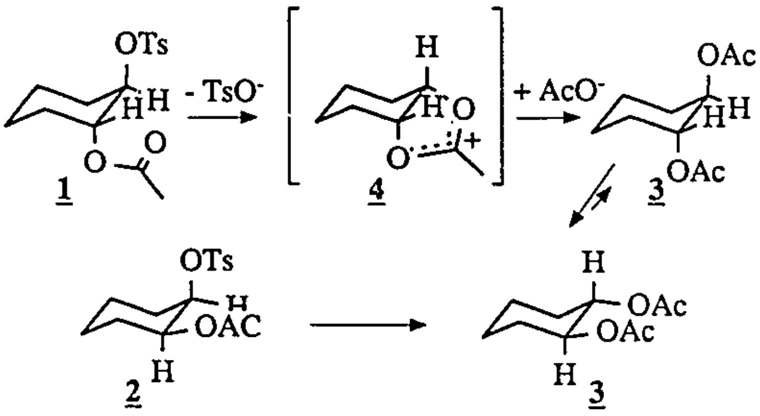
The study of vinyl cation intermediates have been the subject of many works in Organic Chemistry[1]. Stabilization of these high energy carbonium ions with the help of stabilizing substituents has allowed the development of many organic reactions. Recently, the stabilization of vinyl cation intermediates by some silyl and stannyl groups has increased further their utilities in organic synthesis. Many studies have demonstrated the ability of silyl and stannyl groups (group 14 elements) to stabilize a β-carbonium ion. However, few studies have been performed on unsaturated carbonium ions even though interesting synthetic applications should result from these studies.

In this first chapter, we will introduce the chemistry of vinyl cation intermediates and the stabilizing abilities of the Group 14 elements on carbonium ions. Afterwards, some synthetic applications of vinyl cation intermediates stabilized by silyl or stannyl groups will be presented.

1.1) Vinyl Cation Intermediates

Carbocations are interesting species which occur in many reactions in organic chemistry[1]. Although many of these species are so unstable that they have never been detected even as intermediates of reactions, some of them have indeed shown remarkable stability. Between these two extremes, there are a series of carbonium ions which are more or less stable and/or detectable. The conjugation of π or n electrons with the electron-deficient center is well known to stabilize carbonium ions to a high degree. The commercially available triphenylmethyl tetrafluoroborate is a good example of a stable carbocation. Stabilization by a remote neighboring group which possesses π or n electrons has also been demonstrated. Hence, the acetolysis of the *trans* 1 and the *cis* 2 tosylates gave the same *trans* diacetate 3 isomer (Scheme 1-1)[2]. However, the *trans* tosylate 1 acetolyzed approximately 700 times faster than the *cis* tosylate 2 since it occurred through a stabilized cyclic acetoxonium intermediate 4 by neighboring-group participation (anchimeric assistance).

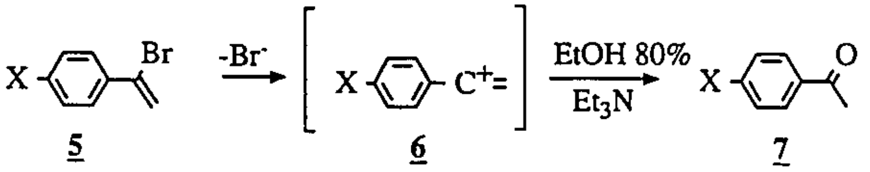
Scheme 1-1



The substitution of alkyl groups for hydrogen on the electron-deficient center also stabilizes these species. The typical order of stability of carbonium ion, tertiary> secondary> primary> methyl cation, is well known. This order of stability is explained by both inductive and hyperconjugative effects. These stabilizing effects are less important than the conjugation of π or n electrons but play an important role in the chemistry of carbonium ions.

Among the carbonium ions, vinyl cations are less stable than their saturated counterparts[1,3]. For many years, these unsaturated carbonium ions were not considered as attractive intermediates in organic chemistry. They were thought to be extremely difficult to generate and too unstable to be observed. However, in 1964 Grob and Csek proved that these intermediates were not imaginary[4]. They showed that α-bromo-*p*-substituted-styrenes 5 could be solvolyzed, by a S_N1 process, to produce *p*-substituted-styrylmethyl ketones 7 via a vinyl cation intermediate 6 (Scheme 1-2). Since these first reported solvolyses of vinylic compounds, numerous studies of vinyl cation intermediates have been made[1]. Vinyl cation intermediates are now proposed for many organic reactions and interest in them is still growing.

Scheme 1-2



The first part of this introduction will not be an extensive review on the work published on vinyl cations. We refer the reader to several reviews which cover most of the field[1,5-7]. We will instead present an overview of some aspects of these species: their stabilities, geometries, generation, and methods by which they are stabilized.

1.1.1) Thermodynamics and Theoretical Calculations

Vinyl cations are now well established as intermediates in many organic reactions[1]. Despite active research, few workers have observed these species using spectroscopy[8,9]. The energies and the geometries of vinyl cation intermediates have been investigated by theoretical calculations. Mayr and co-workers have compared the heats of formation for some vinyl cation intermediates evaluated from ab initio calculations with those obtained from solvolysis experiments[10]. They found that the experimental values were only one-quarter of those obtained from the theoretical calculations. The use of experimental measurements to deduce the relative stability of a vinyl cation intermediate is complicated by ground state and solvation effects[5,6,9,10] and their very short lifetime in solution.

A few values for gas-phase heats of formation are available. These values are for the parent vinyl cation ($CH_2{=}CH^+$), the propenyl cation ($CH_3\text{-}^+CH{=}CH_2$), the butenyl cation ($CH_3\text{-}^+C{=}CH\text{-}CH_3$), and some other pentenyl cations ($C_5H_9^+$)[1,11]. The isodesmic proton transfer reactions are used to calculate the relative stabilities of two ions (Eq. 1-1).

$$CH_3CH_2^+ + HC{\equiv}CH \longrightarrow CH_2{=}CH_2 + H_2C{=}CH^+ \qquad \text{Eq. 1-1}$$

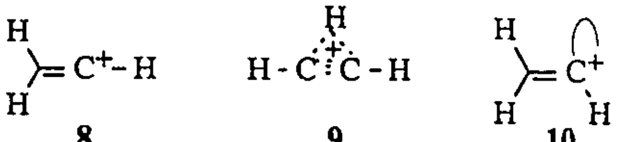
From such calculations in the gas phase, it was shown that the parent vinyl cation ($H_2C{=}CH^+$) is 15 kcal/mol less stable than the ethyl cation but is 25 kcal/mol more stable than the methyl cation. The propenyl cation is comparable in stability to the 1-propyl cation but 15 kcal/mol less stable than the isopropyl cation. It is expected that the energy difference, in the gas phase, between a vinyl cation and its saturated counterpart decreases with the size of the molecular ion[3,12]. Moreover, the differences in stabilities in solution are expected to be smaller due to solvation[13,14].

Even though calculations have shown that vinyl cation intermediates are less stable than their aliphatic counterparts, the ease of protonation of double and triple bonds is comparable[3,14]. The proton transfer reaction endotherm shows that it is more difficult to protonate acetylene than ethylene (Eq. 1-1). However, a triple bond has a higher ground state energy than a double bond ($C{\equiv}C$ bond energy is less than 3/2 $C{=}C$ bond energy), and this compensates for the higher strain (energy) in vinyl cation species relative to alkyl cation species.

An α-alkyl substituent on a vinyl cation intermediate makes it more stable. For example, the propenyl cation (CH_3-^+C=CH_2) is some 26 kcal/mol more stable than the parent vinyl cation (CH_2=CH^+)[12]. A more detailed understanding of the stabilities of the larger vinyl cation intermediates has been provided by ab initio molecular orbital calculations[3,10,12,15,16].

Recently, aryl cations, another kind of vinyl cation, have elicited interest[17]. Ab initio calculations (MP2/6-31G*) have shown the parent structure phenyl cation ($C_6H_5^+$) to be approximately 51 kcal/mol less stable than the parent vinyl cation (H_2C=CH^+).

The structure of vinyl cation intermediates has attracted considerable theoretical interest. Calculations done on the parent structure (CH_2=CH^+) brought divergent results between a classical (linear) 8 and a nonclassical (bridge) 9 structure[1] (Figure 1-1). However, the latest calculations predict the nonclassical structure to be only 1 to 2 kcal/mol more stable than the classical one[16]. In this nonclassical form, the vinyl cation 9 is planar with small C=C-H angle (i.e. almost linear). Usually, substitution of vinyl cations favors the classical structure. Calculations on the classical form 8 predict a linear sp-hybridized carbon with an empty p orbital located in the molecular plane. Calculations on the parent vinyl cation with a bent form 10[18], which has sp^2-hybridized carbon, reveal it is some 50 kcal/mol higher in energy than the classical structure 8.



8 9 10

Figure 1-1: Geometries of the Parent Vinyl Cations

1.1.2) Methods of Generation of Vinyl Cation Intermediates

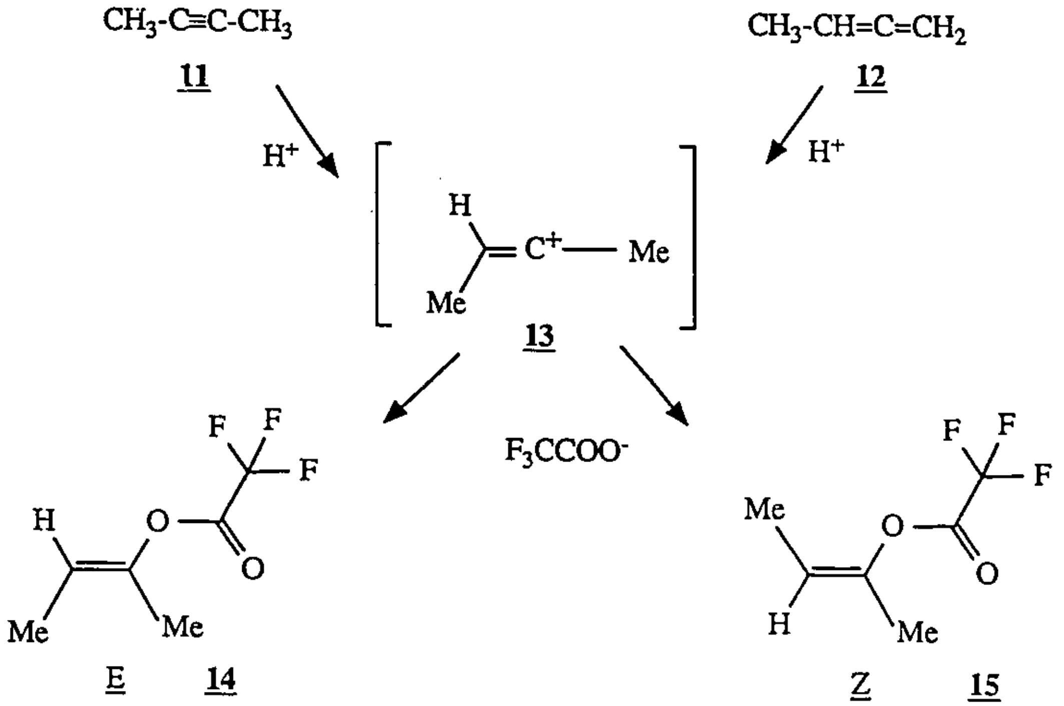
Interest in the stabilities of differently substituted vinyl cations and their chemical reactivities brought chemists to develop a variety of methods to generate them in solution. The purpose of this section is to summarize the principal methods used to produce vinyl cation intermediates in solution[1].

1.1.2a) Electrophilic Addition to Allenic and Acetylenic Bonds.

Electrophilic addition to allenes[1,19] or alkynes[1] is an easy process for generating vinyl cations as intermediates and provides a large number of possible reactions.

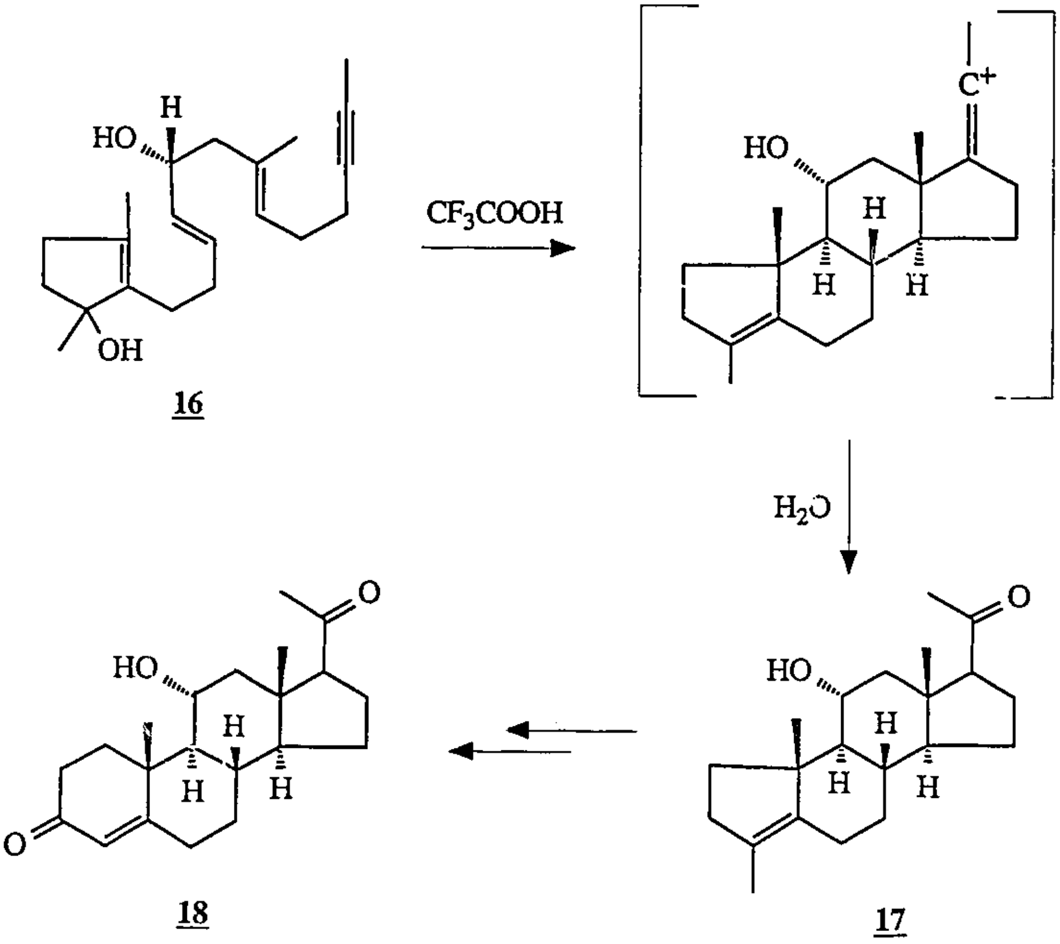
The E and Z 2-buten-2-yl trifluoroacetates 14 and 15 are prepared, via the same vinyl cation intermediates 13, by addition of CF_3COOH to 2-butyne 11 or to 1,2-butadiene 12[20] (Scheme 1-3).

Scheme 1-3



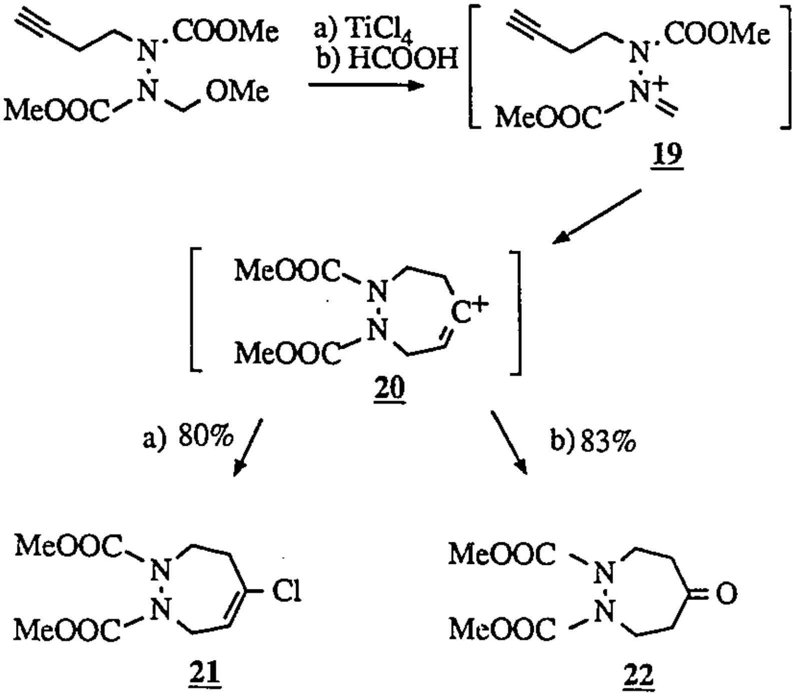
Intramolecular triple bond addition to a carbonium ion, to generate a vinyl cation intermediate, has been shown to be a useful method of annulation in organic synthesis. Johnson and co-workers have synthesized several steroids and terpenes by biomimetic cyclizations[21] with systems involving triple bond addition to a carbonium ion. The asymmetric synthesis of 11α-hydroxyprogesterone has been done with this methodology. The optically active polyene substrate 16 was converted by biomimetic cyclization to the polycyclic product 17, which was readily converted to corticoid 18 (Scheme 1-4)[22].

Scheme 1-4



In recent years, Hiemstra, Speckamp and co-workers have been interested in the ring closure reaction of iminium ions[23], oxonium ions[24] and hydrazinium ions[25] with olefins or acetylenes (Scheme 1-5). An interesting example is the synthesis of cyclic hydrazide compounds. Intramolecular electrophilic addition of a terminal alkyne to N,N-di(methoxycarbonyl)hydrazinium ion 19 leads to the formation of a cyclic vinyl cation intermediate 20. Depending on the acid used, the cyclic vinyl cation intermediate afforded in high yield the 1,2-diaza-5-chloro-cyclohept-4-ene 21 ($TiCl_4$) or the 1,2-diazacycloheptan-5-one 22 (HCOOH)[25].

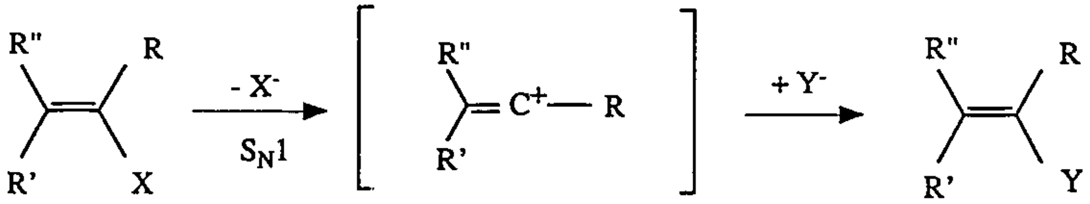
Scheme 1-5



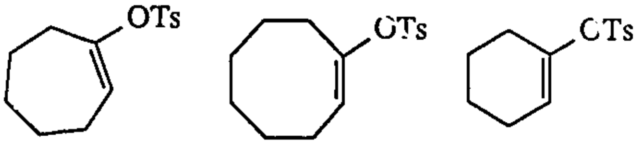
1.1.2b) Bond Heterolysis

The most common method used to generate vinyl cation species is the solvolysis of vinylic compounds[1,4,5,20] (Scheme 1-6). A necessary requirement for the solvolytic generation of vinyl cation species is either an appropriate leaving group or stabilizing neighboring groups in the molecule. The super leaving-groups trifluoromethanesulfonate (Tf= triflate) and nonafluorobutanesulfonate (Nf= nonaflate) are the best ones[26].

Schem 1-6



The generation of cyclic vinyl cation intermediates was possible from the solvolysis of cycloalkenyl triflates[27,28]. The rate of solvolysis of the cycloalkenyl triflates was shown to depend on the size of the ring. Hence, it was demonstrated that the seven-membered 23 and eight-membered 24 rings solvolyze about 10^4 to 10^5 times faster than the six-membered ring 25 (Figure 1-2). These differences in rates are due to the fact that the six-membered ring vinyl cation intermediate has a bent vinylic geometry whereas the larger rings can better accommodate the linear geometry of a vinyl cation.

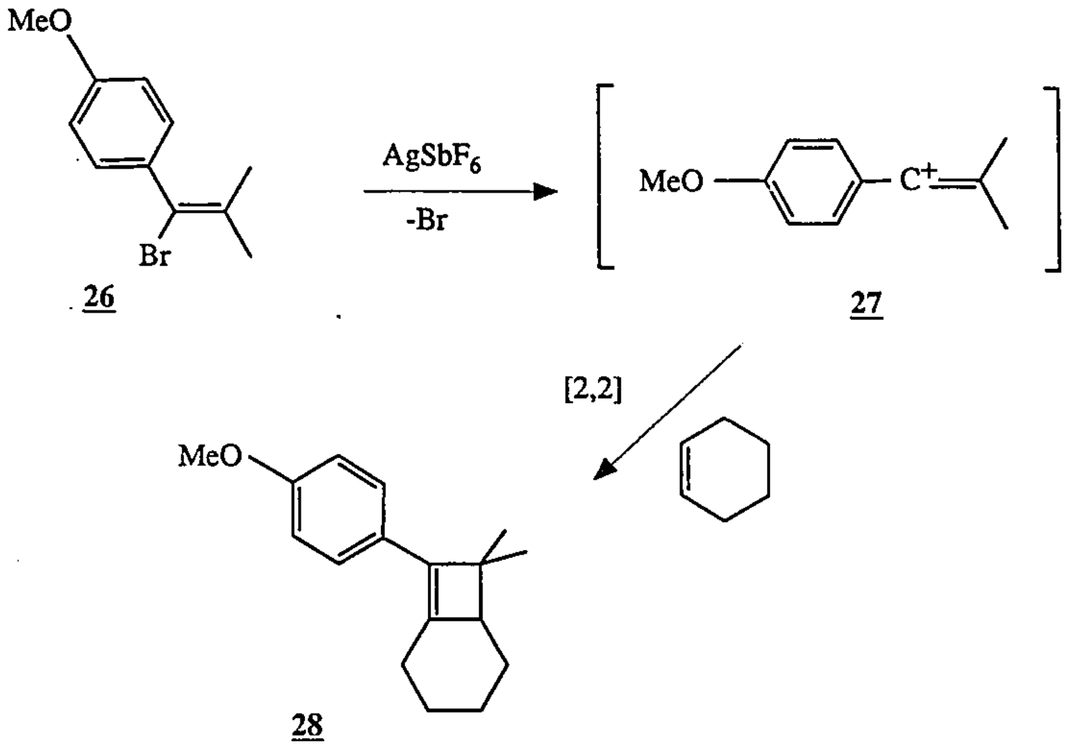


23 24 25

Figure 1-2: Cyloalkene triflates

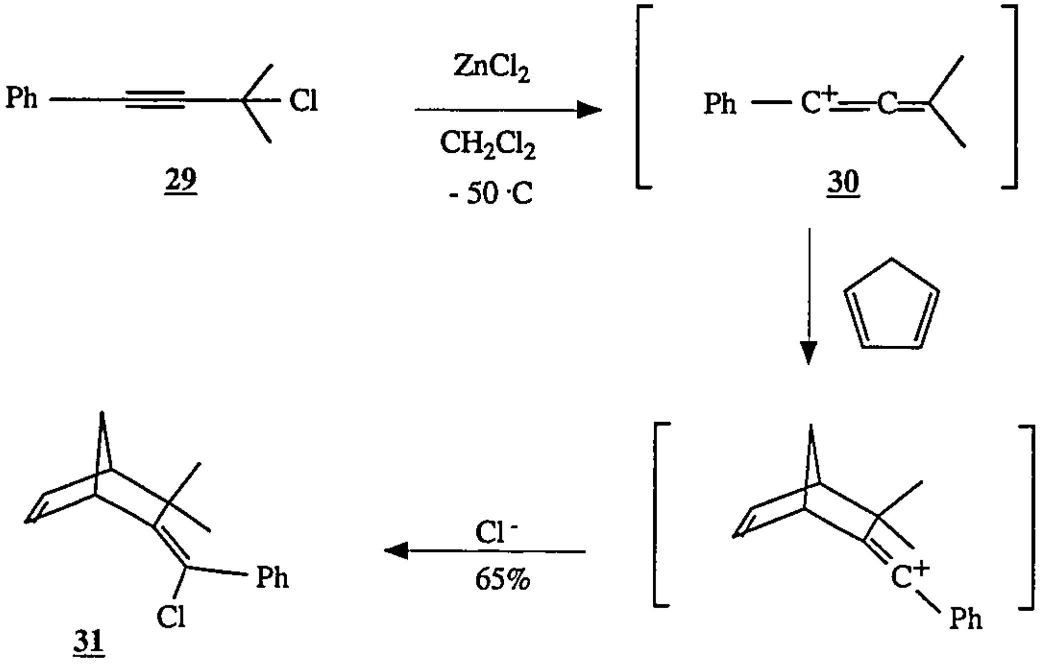
Solvolytic generation is also possible using other leaving groups, such as tosylate and halide ions, if the electron-deficient center is stabilized by neighboring electron-donating groups[1,4-6]. The bond heterolysis can be catalyzed by a Lewis acid. This method of generation of vinyl cation intermediates has been used in the synthesis of polycyclic compounds. Thus, 1-bromo-1-(*p*-methoxyphenyl)-2-methyl-1-propene 26 reacts with cyclohexene in presence of $AgSbF_6$, via the vinyl cation intermediate 27, to produce by formal [2+2] cycloaddition the bicyclo[4,2,0] compound 28 in excellent yield[7,29] (Scheme 1-7).

Scheme 1-7



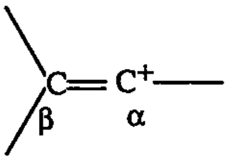
Another example is the bond heterolysis of 1-chloro-1,1-dimethyl-3-phenylpropyne 29 with zinc chloride to generate an intermediate allenyl cation 30 (Scheme 1-8). This intermediate undergoes a stepwise [2+4] cycloaddition with cyclopentadiene to form the bicyclo[2.2.1] vinyl chloride compound 31[30].

Scheme 1-8



1.1.3) Stabilization of Vinyl Cations

As we have seen in the previous section, the generation of vinyl cation intermediates depends, in most cases, on the stabilizing groups present in the molecule. Since a vinyl cation with the classical geometry is a disubstituted carbonium ion 32, the stabilizing groups can be linked to the positively charged carbon atom in two different ways: by a single bond to the α-carbon to produce a secondary vinyl cation and/or by substitutions at the β-carbon of the vinylic structure. Of course, all stabilizing groups with electron-donating abilities which are effective in stabilizing saturated carbonium ions are also suitable for stabilizing vinyl cation intermediates.



32

The magnitude of stabilization for differently substituted vinyl cation intermediates has been clearly determined by numerous solvolysis studies. For example, the solvolysis of a series of vinylic bromides has been reported by different authors (Figure 1-3). Thus the α-bromo-4-methoxystyrenes 33 and 34[31], 2-bromo-1,3-butadienes 35 and 36[32], β-bromocyclopropylidenes 37 and 38[6,33], the bromoallene 39[34] were solvolyzed in aqueous ethanol under almost the same conditions. The relative rates of solvolysis were found to be in increasing order 38< 36< 33< 37< 34< 35< 39. This order reflects the relative stabilities of the vinyl cation intermediates formed.

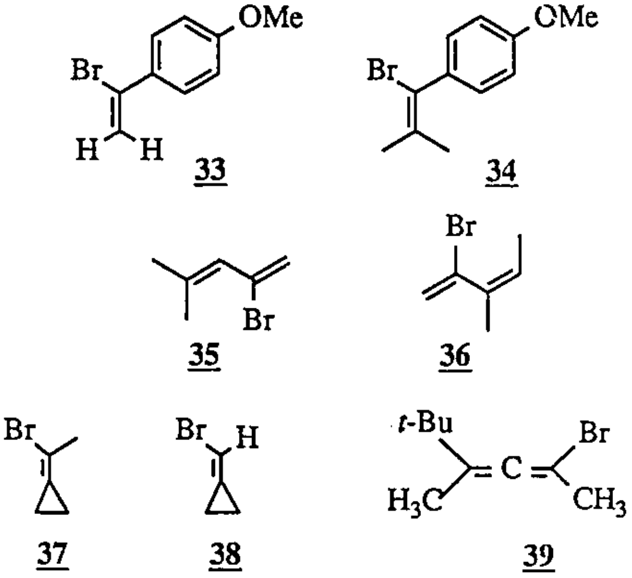
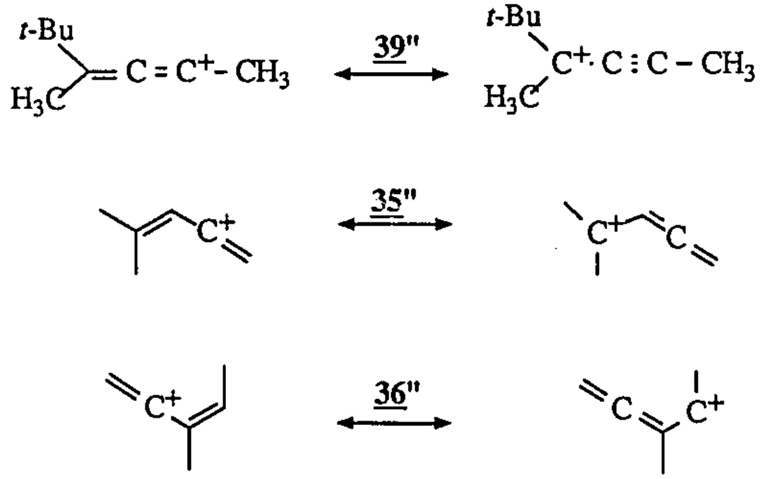
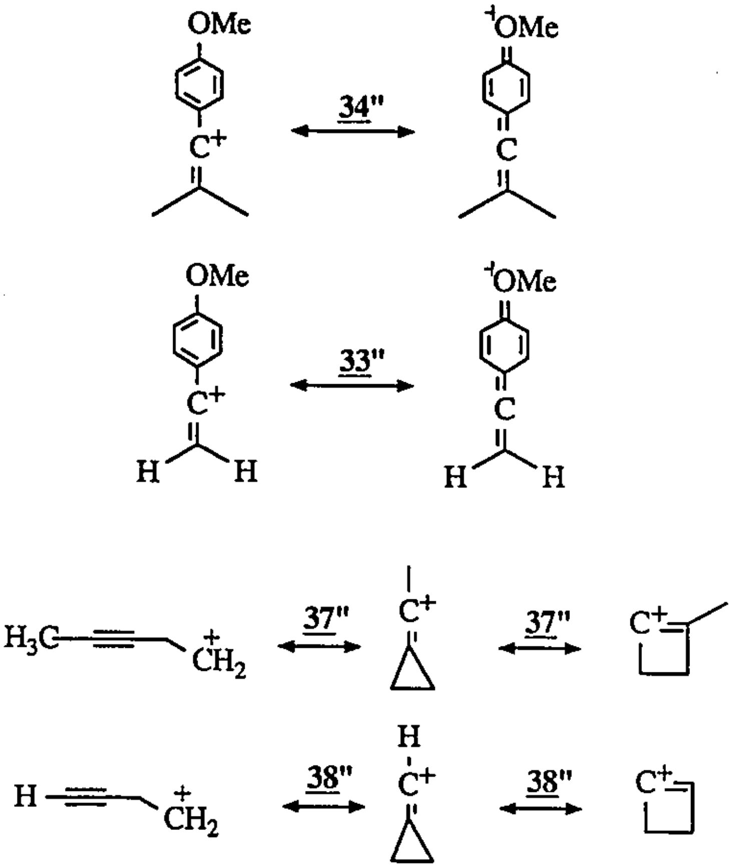


Figure 1-3: Vinylic Bromide Compounds

Of course, substituents which can delocalize an electron-pair to the empty p orbital via a π-type interaction, as in 39" and 35", to form a conjugated tertiary carbonium ion are the most stabilizing (Scheme 1-9). The *p*-methoxyphenyl group is also a good stabilizing substituent by conjugation of the electron-pair to the empty p orbital (33" or 34"). The cyclopropylidenevinyl cations 37" and 38", are stabilized in a non-classical manner. The short C=C bond allows an overlap between the C-C bond of the planar cyclopropyl ring and the empty p orbital which can rearrange to a cyclobutenylvinyl cation. On the other hand, the cyclopropylidenevinyl cations 37" and 38" could rearrange to the homopropargylic cation. The difference in stabilities within the pairs 33" and 34", 35" and 36", and 37" 38" are due to the inductive and/or the hyperconjugative stabilization from a methyl substituent compared to hydrogen.

Scheme 1-9





The use of the rate of solvolysis to deduce the stability provided by a substituent to a vinyl cation intermediate has some limitations. The solvolysis is subject to phenomena such as steric acceleration or inhibition and to solvent effects.

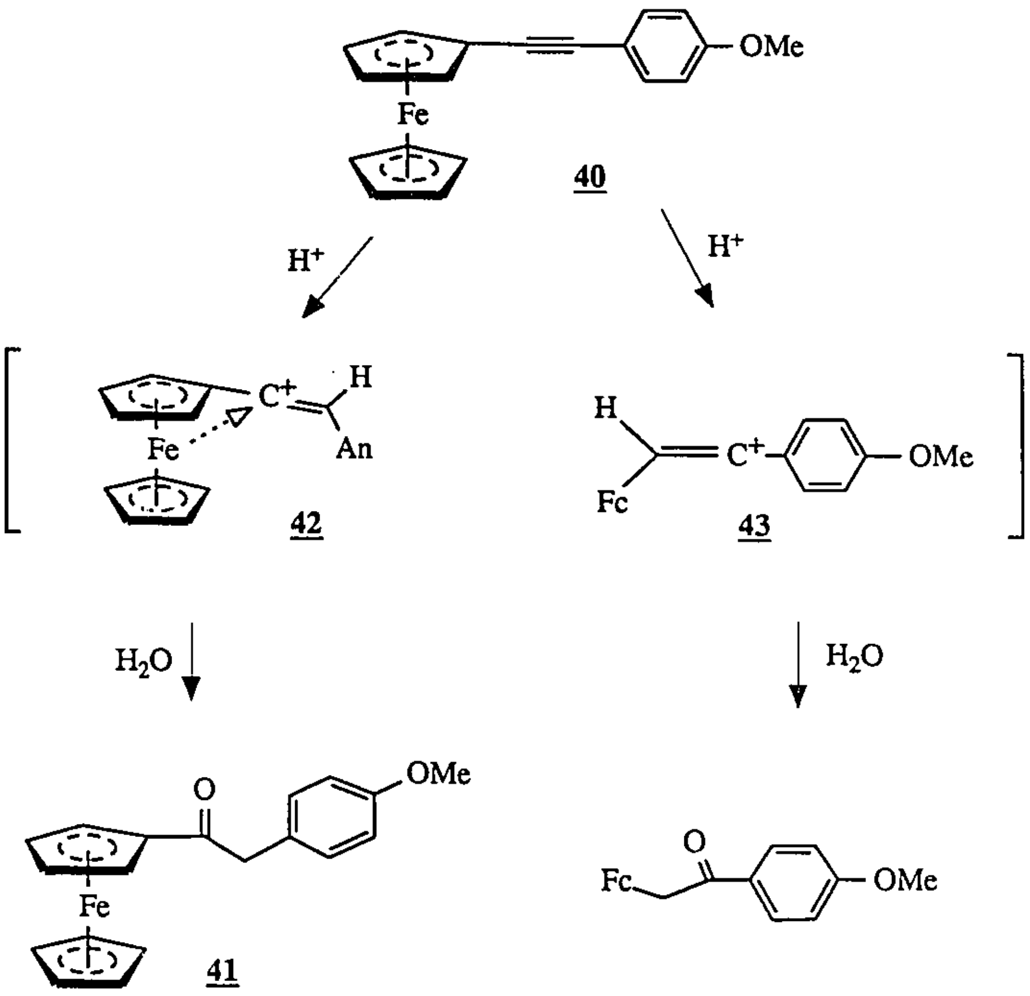
Apeloig and co-workers have used ab initio calculations to deduce the degree of stabilization provided by some substituents to a vinyl cation[12]. They determined that the relative efficiency of an α-substituent (R) in stabilizing the vinyl cation $H_2C{=}C^{+}\text{-}R$ followed the decreasing order phenyl> cyclo-C_3H_4 ~ $CH{=}CH_2$>> $C{\equiv}CH$ ~ CH_3>> H. It was suggested that the low degree of stabilization provided by an α-acetylene group by π-conjugation was cancelled by a destabilizing σ-withdrawing effect from the acetylene.

Vinyl cations are strongly stabilized in some transition-metal complexes. Depending on the resonance forms, which place the positive charge on the metal or on the α-carbon, these complexes are called "Cationic vinylidene complexes" ($M^{+}{=}C{=}CR_2$) or "Metal-stabilized vinyl cations" ($M\text{-}C^{+}{=}CR_2$)[35].

The chemistry of iron-stabilized vinyl cations has been well investigated[36]. The stabilization provided by some complexes is so high that their structures have been confirmed by X-ray analysis[37]. Molecular modeling calculations have been carried out on $L_2CpFe^{+}{=}C{=}CH_2$ (L= CO or PPh_3 as group ligands)[38]. Bonding to the metal atom occurs via a vinyl-metal σ-donor bond and metal-vinyl p-bond. The stabilization is therefore the result of a strong back donation of electron density to the empty p orbitals.

Considerable attention has been paid to the ability of the ferrocenyl group (ferrocenyl= Fc) to stabilize a carbocation[37]. The ferrocenyl vinyl cation is easily generated on protonation of ferrocenylacetylene. Kaufman and co-workers reported the acid-catalyzed hydration of the ferrocenyl-*p*-methoxyphenylacetylene <u>40</u> compound to produce quantitatively the ferrocenyl *p*-methoxybenzylketone <u>41</u>[39] (Scheme 1-10). The result indicates that a vinyl cation intermediate is much better stabilized by an α-ferrocenyl moiety <u>42</u> than an α-*p*-methoxyphenyl group <u>43</u>. The stabilization of this vinyl cation species <u>42</u> is provided by a strong electron release from the cyclopentadienyl ring and by electron density donation from the iron d orbital to the empty p orbital.

Scheme 1-10

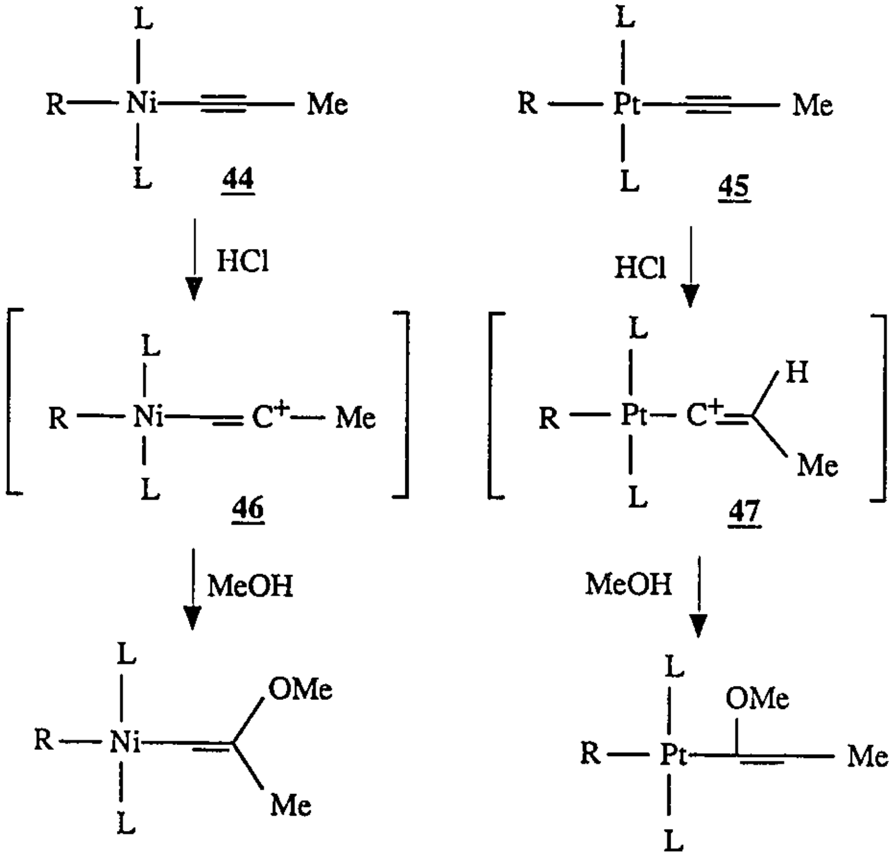


Fc = ferrocenyl

Other vinylidene cation complexes of ruthenium[40,41], osmium[40,41], tungsten[42] and iridium[43] have been described and shown to have almost the same chemistry as the iron vinylidene cation complexes. These complexes are very stable and the X-ray analysis indicates a considerable degree of back-bonding from the metal to the α-carbon.

Chisholm and co-workers have shown that electrophilic addition to propynyl complexes of nickel 44 occurred on the α-carbon to form the complex 46[44], whereas it occurred on the β-carbon with the platinum complex 45 to form the complex 47[45] (Scheme 1-11). These results demonstrated that the stabilizing ability of nickel and platinum moieties for vinyl cation intermediates was in the decreasing order Pt> CH_3> Ni. The difference between the metal was explained by the better ability of the heavy metal to stabilize the cation by back-bonding.

Scheme 1-11

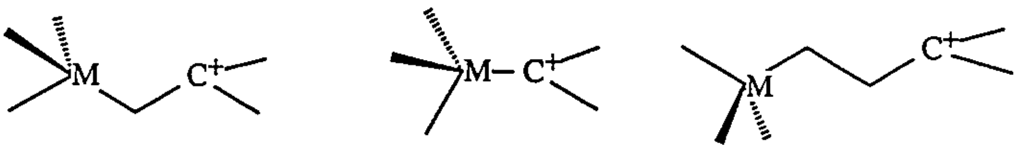


Vinyl cation intermediates are also stabilized by the main group elements silicon, germanium and tin. The nature of the stabilization of carbocations by the Group 14 elements will be the subject of the next part of the introduction.

1.2) Stabilization of Carbonium Ions by Group 14 Elements

During the last twenty years, many studies have demonstrated the ability of the lower elements of Group 14 to stabilize carbocations. This stabilization, which does not involve the participation of π or n electrons, has stimulated much research interest. Most of these studies have been done on silicon and have recently been well reviewed[46,47].

It has been shown that the Group 14 elements can stabilize a carbocation in three different ways. The most important one involves a C-M bond (M= Si, Ge, Sn and Pb) in the beta position to the electron-deficient center 48 (β-effect) (Figure 1-4). Stabilization also occurs to a lower degree when the element is linked directly to the electron-deficient center 49 (called the α-effect)[48]. Finally, it was recently demonstrated that a carbocation can be stabilized by a gamma-silyl group 50 (γ-effect)[49].



48 49 50

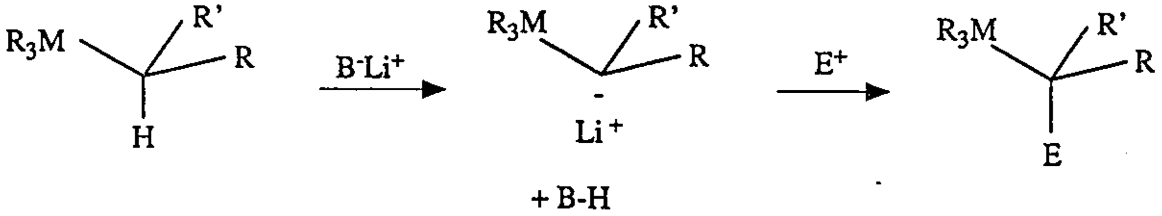
Figure 1-4: Carbocation Stabilized by Group 14 Elements

In the next parts of this introduction, we will see the nature of the stabilization for the β-effect and the α-effect provided by the Group 14 elements. We will also review some studies that explained these stabilizing effects in vinyl cation species.

1.2.1) The α-Effect

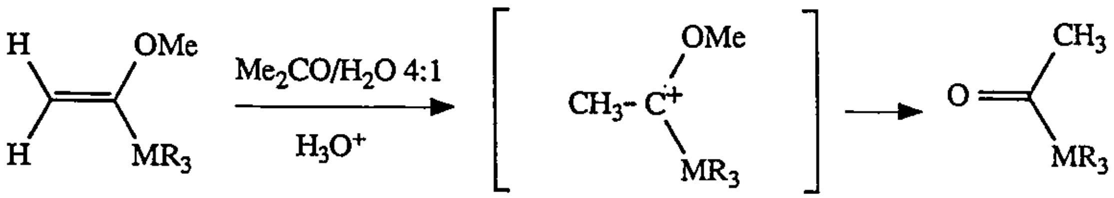
It is well known that the Group 14 elements stabilize an alpha anion[47]. The nature of this stabilizing effect (α-effect) is still controversial. It is generally thought to be the result of electronic density transmission from the filled p-orbital of the α-anion to the *anti* sigma C-M bond, a $(p\text{-}\sigma^*)_\pi$ conjugation[50,51]. Other authors believe it results from the interaction of the filled p orbital with the empty d orbital of the element, a $(p\text{-}d)_\pi$ conjugation[47]. This effect plays an important role in the α-alkylation of organometalloid compounds[47] (Scheme 1-12). Therefore, it is not surprising that many studies on α-halosilanes have demonstrated the ability of silyl groups to inhibit the formation of an α-carbonium ion[46,47]. However, Soderquist and Hassner showed in a recent study that the Group 14 elements also have the ability to stabilize an alpha-carbenium ion, which they also called the α-effect[48].

Scheme 1-12



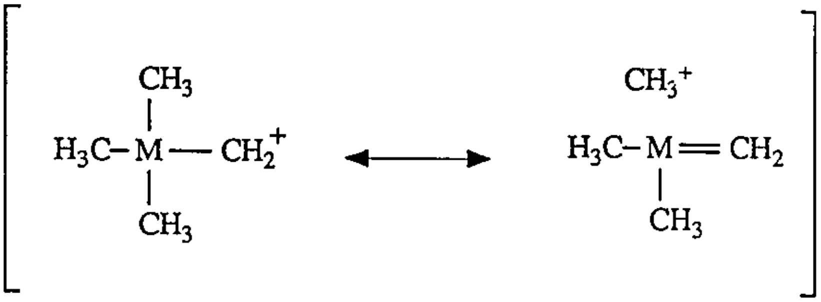
The hydrolysis of a number of α-metalated methylvinyl ethers were done in 4:1 acetone-water solution (Scheme 1-13). The relative rate of hydrolysis for the trimethylsubstituted series was compared to the parent methylvinylether (MR_3= H). The degree of stabilization provide by these α-substituents is, from the relative rate, in the order H< $SiMe_3$< $GeMe_3$< $SnMe_3$< CMe_3 (1, 1.8, 4.3, 12, 100 respectively). Further comparison with the triphenylsubstituted series gave a similar order. However, it was showed that the trimethylsilyl derivative hydrolyzes 30 times faster than its triphenylsilyl counterpart.

Scheme 1-13



M= C, Si, Ge, Sn
R= Me, Ph

The large degree of stabilization of the *t*-butyl group is explained by hyperconjugative effects. This hyperconjugative stabilization is absent with the lower elements since it leads to a resonance form with a carbon-metal double bond which is known to be weak (Figure 1-5)[46]. The minor stabilization by the metalated group when compared to a hydrogen atom is explained by increasing field/inductive effects with diminishing electronegativity from the carbon to the tin atom.

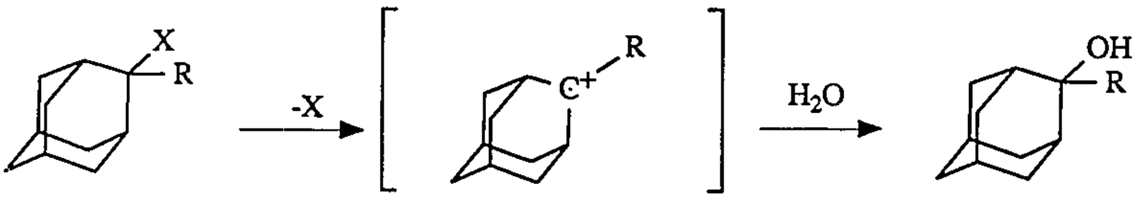


M= C, Si, Ge, Sn

Figure 1-5: C^+/M=C Hyperconjugation

Apeloig and Stanger have recently solvolyzed a series of tertiary 2-adamantyl esters[52] (Scheme 1-14). Experimental data combined with ab initio calculations showed that the methyl group stabilizes the 2-adamantyl cation by 6 to 8 kcal/mol more than the trimethylsilyl group. However, the trimethylsilyl group is 12 to 14 kcal/mol more stabilizing than a hydrogen atom.

Scheme 1-14



R= H, CH_3, $SiMe_3$
X= p-$O_2NC_6H_4COO$

High level ab initio calculations (MP3/6-31G*) have been carried out by Jorgensen and co-workers[53]. The stabilization energies resulting from substitution of the methyl group were evaluated by means of the isodesmic reaction (Eq. 1-2). They found

$$XCH_2^+ + CH_4 \longrightarrow XCH_3 + CH_3^+ \qquad \text{Eq. 1-2}$$

that the $H_3SiCH_2^+$ carbonium ion is 6.2 kcal/mol less stable than the ethyl cation ($CH_3CH_2^+$) but 17.8 kcal/mol more stable than the methyl cation (CH_3^+). However, the silicenium ions CH_3-Si^+H_2 and CH_3-Si^+R_2, have been found to be more stable in many studies[54-56].

1.2.2) The α-effect on Vinyl Cation Species

Solvolytic studies on α-silylvinyl triflates in aqueous ethanol were performed by Schiavelli and co-workers[57]. The solvolysis reaction did not show a perfect E1 mechanism and it was suggested that an E2-type elimination occurred with the participation of the solvent. Nevertheless, it was concluded from the solvolytic data that an α-trimethylsilyl group was more stabilizing for the vinyl cation intermediate than a hydrogen atom or a methyl group, but less stabilizing when compared with an α-*t*-butyl group.

Ab initio calculations were used to study an α-silylvinyl system through the isodesmic reaction (Eq. 1-3). An initial study using a small basic set concluded that H_3Si

$$CH_2{=}C^{+}R + CH_2{=}CHR' \longrightarrow CH_2{=}CHR + CH_2{=}C^{+}R' \qquad \text{Eq. 1-3}$$

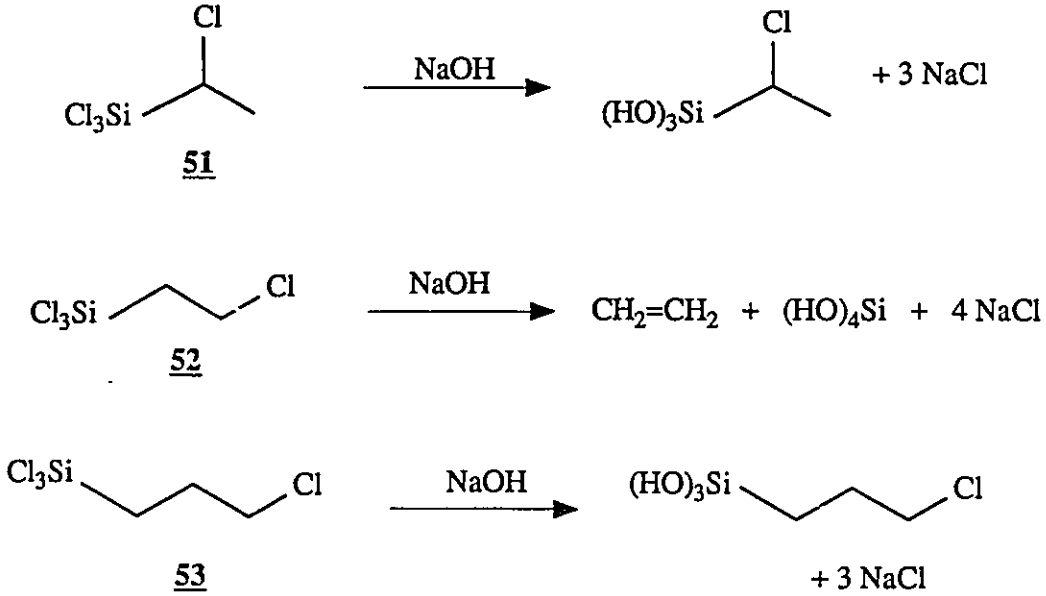
and CH_3 groups stabilize a vinyl cation intermediate to the same degree compared to hydrogen[58]. Moreover, they also proposed that the trimethylsilyl group is slightly more stabilizing a vinyl cation than a *t*-butyl group (3-21G//3-21G basic set). Another ab initio calculation using the MP3/6-31G*//3-21G* basis set concluded that an α-methyl group stabilizes a vinyl cation by only 3 kcal/mol more than an α-H_3Si group[53]. The small difference in the stabilization between silicon and carbon atoms in vinyl cation species compared to the saturated parent has been explained by two effects. First, the demand for C-H hyperconjugation from an α-methyl group has been suggested to be diminished for vinyl cation species. Second, a cationic center on an sp carbon is more susceptible to inductive effects than on a cationic center sp^2 carbon. An electropositive silicon atom provides more effective stabilization by inductive effects than a carbon atom. Both effects may contribute to lower this difference of stabilization.

1.2.3) The β-Effect

The ability of the lower Group 14 elements to stabilize a β-carbonium ion has been studied in detail over the last 50 years[46,47]. Sommer, Whitmore and co-workers reported 45 years ago the unusually high reactivity of a β-chloroalkylsilane <u>52</u> in contrast to the inactivity of the analogous α- and γ-chloroalkylsilanes <u>51</u> and <u>53</u>[59] (Scheme 1-15).

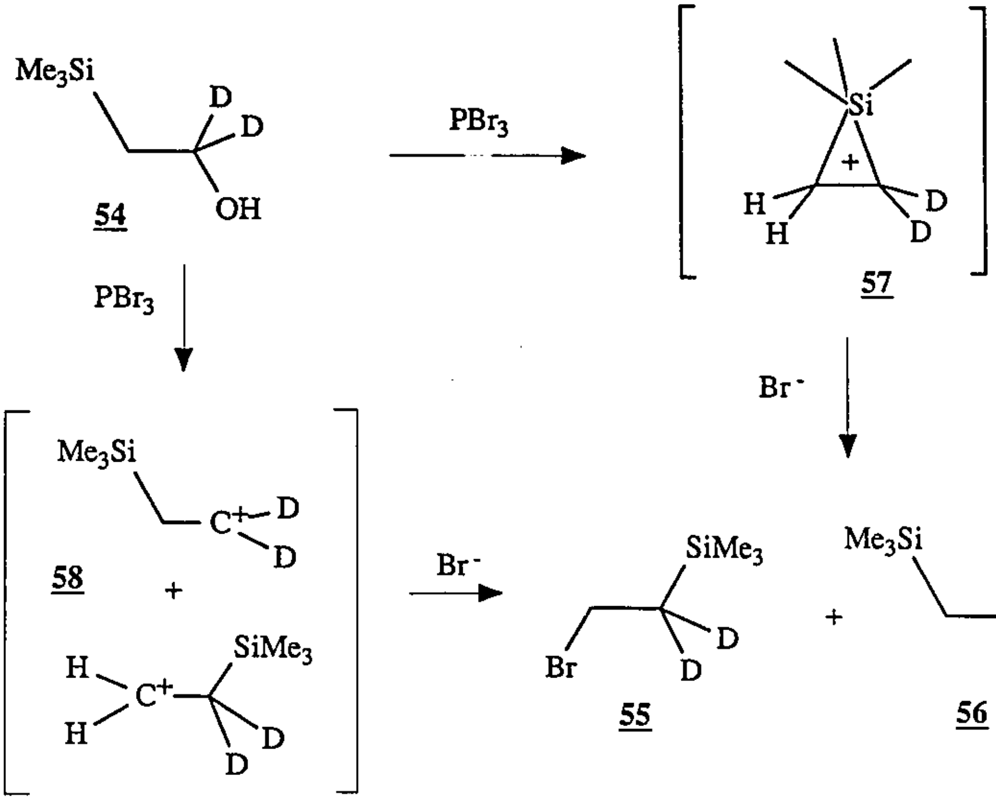
Many mechanistic processes have been suggested for the elimination of the β-silyl group[46,47]. However, most of them have now been ruled out.

Scheme 1-15



Controversy about the mechanism of carbonium ion stabilization by a β-silyl group was initiated when Jarvie's group[60] and Eaborn's group[61] reported independently that the reaction of the dideuterio-β-hydroxysilane 54 with phosphorus bromide gives a mixture of the β-bromoethylsilanes 55 and 56 (Scheme 1-16). The results were interpreted in term of anchimeric assistance by the trimethylsilyl group to produce a silacyclopropenium ion 57 as an intermediate of reaction which was afterwards trapped by bromide ion. However, the initial formation of a classical carbonium ion 58, which could rapidly undergo a 1,2-silyl migration, was not ruled out.

Scheme 1-16



From observations of many experiments, Traylor and co-workers suggested a theory for the stabilization of carbonium ions by neighbouring groups: vertical and non-vertical stabilization[62]. The non-vertical stabilization process is described by nuclear movement and/or a large change of geometry to reach the transition state. The stabilization of a β-silylethyl cation by formation of a silacyclopropenium 57 ion is a good example. In contrast, vertical stabilization is described by electronic conjugation without nuclear movement and little geometric change in the transition state. Stabilization of a carbonium ion by a beta silicon-carbon bond 58 is a good example.

Traylor and co-workers described many effects which contribute to increase the magnitude of the hyperconjugative stabilization (β-effect)[62]. We summarize these effects in four points as shown in the Figure 1-6:

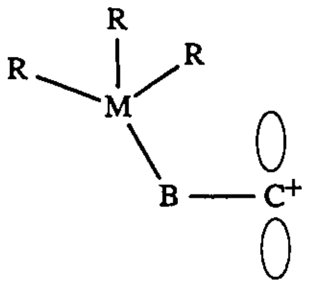


Figure 1-6: The Hyperconjugative Stabilization

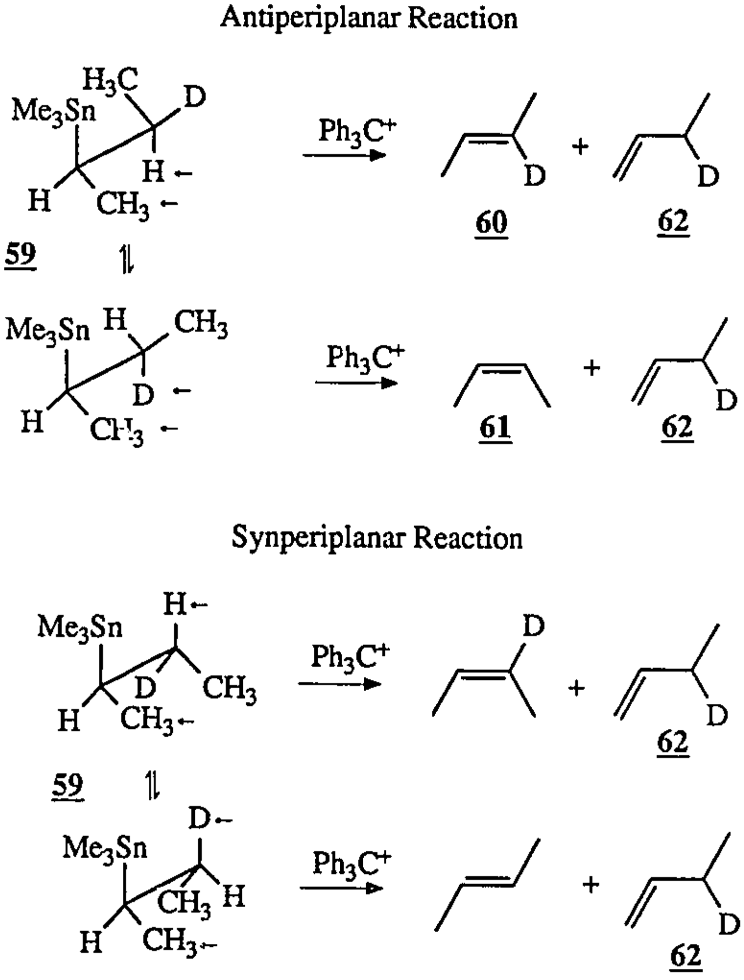
1) coplanarity of the M-B bond with the p orbital of the C atom maximizes the hyperconjugation.
2) lower electronegativity of the element M than the atom B makes the polar bond M-B more delocalizable.
3) the atoms B and C should form a strong π-bond.
4) inductive donation to M by the substituents R increases the electron density in the M-B bond and thus increases the hyperconjugation.

We will now review some studies discussing the importance of these points on the magnitude of the β-effect.

1.2.3a) Geometrical Dependence of the β-Effect

Traylor and co-workers have demonstrated in many studies that the maximum stabilization of a carbenium ion by hyperconjugation of a carbon-metal bond occurs with coplanarity of the orbitals[62,63]. In a mechanistic study, they have also shown that the dehydrometalation of organometallic compounds proceeded with stereoselectivity[63]. The reaction of trityl tetrafluoroborate with *threo*-3-deuterio-2-(trimethylstannyl)butane 59 could occur either by syn or antiperiplanar mechanisms (Scheme 1-17). Examination of the reaction by GC-MS spectroscopy showed that the elimination was antiperiplanar as *trans*-2-deuterio-2-butene 60, *cis*-2-butene 61 and 3-deuterio-1-butene 62 were produced as products[63a].

Scheme 1-17

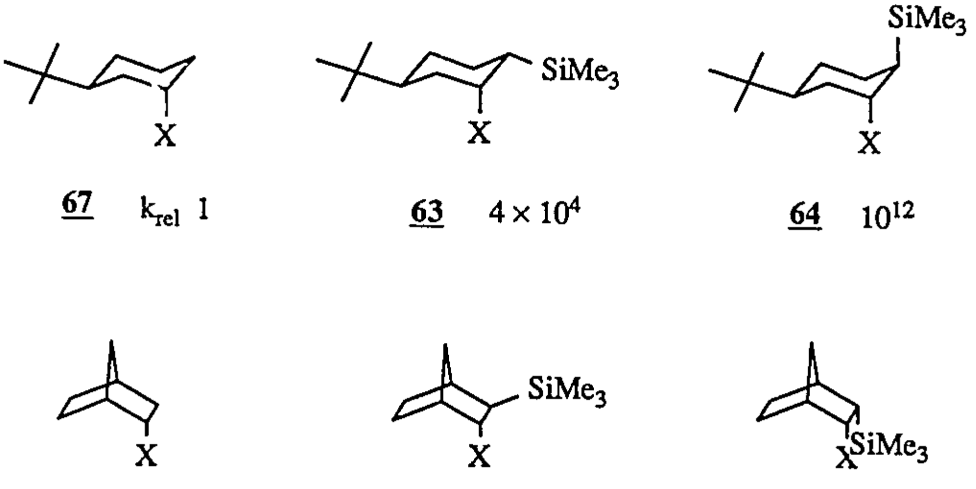

Antiperiplanar Reaction

Synperiplanar Reaction

In further experiments, they suggested that the reaction occurs through a carbonium ion intermediate stabilized by hyperconjugation of the carbon-metal bond and not by bridged ion formation[63b].

Lambert and co-workers have done an extensive study involving the measurement of the β-effect by solvolysis reactions of conformationally constrained compounds[64-67]. The series of β-substituted silane compounds, shown in Scheme 1-18, was solvolyzed in trifluoroethanol/water and ethanol/water solutions. Each compound has its own well-defined stereochemistry for the dihedral angle of the Si-C-C-X fragment (X is the nucleofuge). The compound 63 has a dihedral angle of 60° (gauche conformation), 64 has 180° (antiperiplanar geometry), 65 has 120° (anticlinal conformation), and 66 has 0° (synperiplanar geometry).

Scheme 1-18



67 k_{rel} 1

63 4×10^4

64 10^{12}

68 k_{rel} 1

65 $\cong 1.7 \times 10^5$

66 10^5

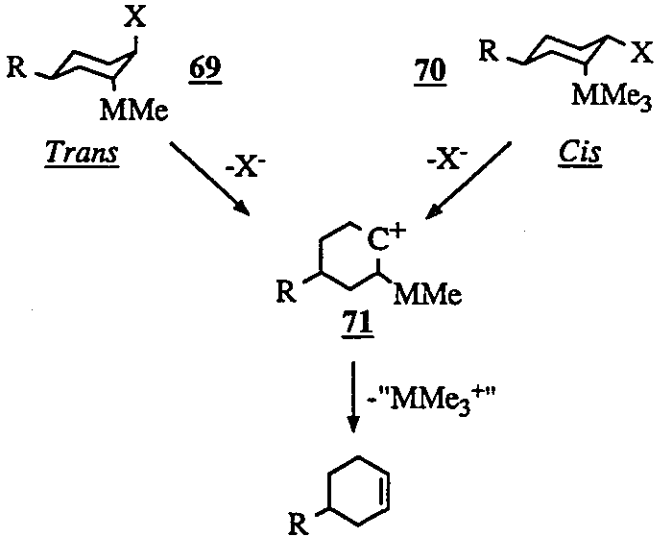
X= $MeSO_3^-$

The relative rate of solvolysis for these compounds towards their unsubstituted parent compounds 67 and 68 were found to be in the order 64 (anti)10^{12}, 65 (anticlinal)1.7×10^5, 66 (syn) 10^5, and 63 (cis) 4×10^4. The anticlinal compound 65 was observed to follow a bimolecular solvolytic pathway. However, its rate of solvolysis was estimated to be similar to the synperiplanar compound 66.

An inductive contribution to the rate of solvolysis, which is independent of the dihedral angle and occurs primarily through the bonds, has been calculated to be only 10^2 in magnitude[65]. Therefore the rate acceleration of solvolysis for these β-silylated compounds cannot be explained by a non-vertical process but is consistent with a vertical process (β-effect).

The antiperiplanar 69 and the cis-conformation 70 have the same β-silyl carbonium ion intermediate 71 in the solvolysis reaction (Scheme 1-19; M= Si, R= *t*-Bu, X= nucleofuge). However, the β-effect-assistance of the C-Si bond to the rate of solvolysis are 10^{10} and 4×10^2 respectively in magnitude (inductive assistance is 10^2)[65] (Scheme 1-18). This large difference is due to the maximum of overlap between the C-Si and the C-X bonding orbitals approaching the transition state during the solvolysis of the antiperiplanar compound 69. Overlap of these orbitals for the cis-conformation 70 is lower which reduces the β-effect-assistance in the solvolysis reaction.

Scheme 1-19



The antiperiplanar and the synperiplanar geometries should have the same overlap of the C-Si and C-X bonds. However, steric and electronic factors may cause a poor overlap of the orbitals and reduce the observed β-effect[66]. Moreover, it is well known that the antiperiplanar overlap is superior to the synperiplanar overlap of orbitals[63,68].

Ab initio calculations at the MP3/6-31G* level have also been carried out for β-silyl ethyl cation by Jorgensen and co-workers using the isodesmic reaction[53] (Eq. 1-4):

$$H_3SiCH_2CH_3 + CH_3^+ \longrightarrow H_3SiCH_2CH_2^+ + CH_4 \quad \text{Eq. 1-4}$$

The calculations indicate that in the conformation 72 the SiH_3 group is 8.9 kcal/mol more stablilizing than hydrogen in the ethyl cation (Figure 1-7). This was suggested to be a measure of the inductive and polarization effects due to the β-silyl group. In conformation 73 the SiH_3 group provides a total stabilizing energy of 38 kcal/mol due to the coplanarity of the orbitals. This energy of stabilization is similar to the value of 39 kcal/mol obtained by Hajdasz and Squires in a gas phase study for the $Me_3Si(CH_2CH_2)^+$ ion relative to the ethyl cation[55]. Since the inductive and polarization effects are also present in this conformer, the hyperconjugative contribution to the stabilization $(\sigma\text{-p})_\pi$ is 29.1 kcal/mol. The non-vertical stabilized silacyclopropyl cation 74 was found to be 2.4 kcal/mol more stable than the open structure 73.

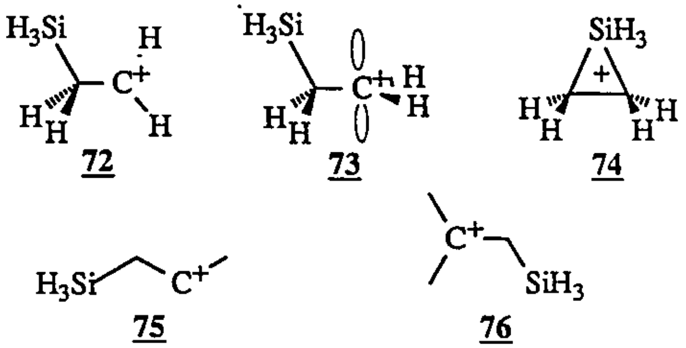


Figure 1-7: β-Silyl Carbonium Ions

Further calculation at the MP2/6-31G(d) level was also done by Jorgensen and co-workers[69]. The stabilizing energy provided by a β-SiH_3 group is 22.1 kcal/mol for the 2-propyl cation 75 and 15.9 kcal/mol for the *t*-butyl cation 76 (Figure 1-7). In these cases, the bridged conformation was found to be higher in energy.

1.2.3b) Electronegativity of the Element

Apeloig and co-workers have studied by ab initio calculations the hyperconjugative stabilization of the first-period elements on ethyl and vinyl cations[70]. The calculated stabilizing energies from the isodesmic reactions parallel the electronegativity of the substituents (Eq. 1-5 and 1-6). The data in Table 1-1 show that the

$$XCH_2CH_2^+ + CH_3CH_3 \longrightarrow XCH_2CH_3 + H_3CCH_2^+ \quad \text{Eq. 1-5}$$

$$XCH{=}CH^+ + H_2C{=}CH_2 \longrightarrow XCH{=}CH_2 + CH_2{=}CH^+ \quad \text{Eq. 1-6}$$

cations are more stabilized by the less electronegative elements, and less stabilized by the more electronegative elements. These results are consistent with the resonance representations of hyperconjugation 78 and 79 (Figure 1-8). The resonance contribution 79 dominates more for substituents "X" which accommodate a positive charge better.

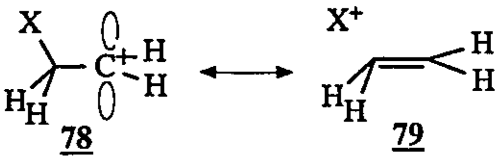


Figure 1-8: Resonance Contribution of the β-Effect

Table 1-1: Stabilization Energies of β-Substituted Cations

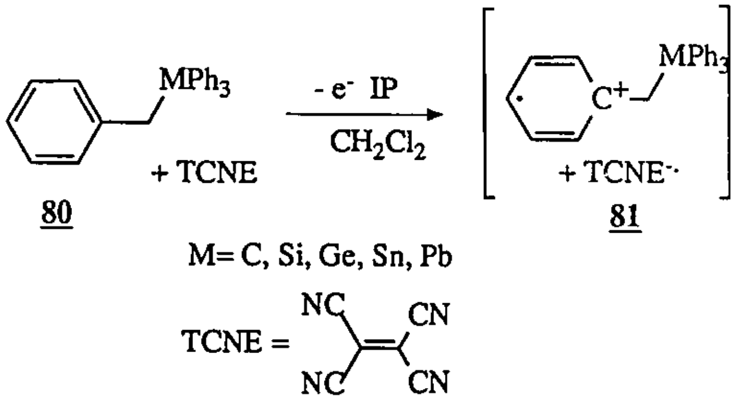
Substituent X	EN@	Ethyl cation*	Vinyl cation*
H	2.1	0	0
Li	1.0	88.9	89
BeH	1.5	27.1	26.4
BH_2	2.0	12.2	17.5
CH_3	2.5	7.4	10.9
NH_2	3.0	3.1	5.4
OH	3.5	-17.0	-10.8
F	4.0	-31.0	-32.0

@ Pauling electronegativity of the substituent X.
* Total energy in kcal/mol calculated at RHF/4-31G level.

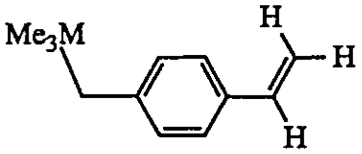
We have seen earlier that Traylor and co-workers suggested that the low electronegativity of the element M towards the atom B in the M-B bond increases the magnitude of the β-effect[62] (Figure 1-6). Therefore, in the group 14 elements, one might expect that the magnitude of the β-effect should increase in the order C< Si< Ge< Sn< Pb, which follows the order of decreasing electronegativity[71-73]. (Although the scale of electronegativity for the lower elements is controversial, it seems reasonable to accept a slight progressive decrease from silicon to lead[71,72]).

The hyperconjugative stabilization of an electron-deficient π-system by a carbon-metal bond was demonstrated by observing the low ionization potentials of benzylic metal compounds[74] 80 (Scheme 1-20). The charge transfer frequencies of substituted benzene tetracyanoethylene (TCNE) molecular complexes 81 are related to a Hammett constant σ^+_Y. A negative value of this constant σ^+_Y is proportional to the polarizability of the C-M bond and it is well correlated with the stabilization of an adjacent electron-deficient center. The values of these constants for the CH_2MPh_3 groups relative to benzene (σ^+_Y=0) are for M= C(-0.2), Si(-0.42), Ge(-0.60), Sn(-0.81), and Pb(-1.0)[75]. These data show that the β-effect increases as the element M becomes more electropositive.

Scheme 1-20



Reynolds and co-workers used the ^1H and ^{13}C chemical shifts from the NMR spectra of some 4-substituted styrenes 82 (Figure 1-9) to estimate the field/inductive (σ_I) and the resonance (σ_R) constants for the CH_2MMe_3 derivatives (M= Si, Ge, Sn, Pb)[76]. The calculated negative values of σ_R are consistent with previous studies which showed that the polar C-M bond releases electrons to the phenyl π-orbitals by a σ-π or $(\sigma\text{-}p)_\pi$ hyperconjugation in the same trend C<< Si, Ge< Sn, Pb.



82

M= C, Si, Ge, Sn, Pb

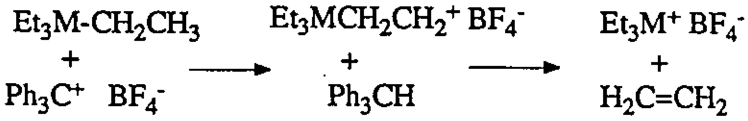
Figure 1-9: Metalated Methylene-4-styrenes

Lambert and co-workers have also investigated the β-effect of the trimethyl silyl, germyl, and stannyl groups by the solvolysis reaction of the 1,2-disubstituted cyclohexyl compounds discussed above[64] (Scheme 1-19; where M= Si, Ge, Sn, R= H, X= trifluoroacetate). The accelerating rates of solvolysis for these compounds, shown in Table 1-2, are consistent with the general trend of the β-effect decreasing in the order Sn>> Ge> Si. The relative rate of solvolysis for the trans-cyclohexyl stannane compound was too fast to be accurately measured and was estimated from the trans/cis ratio.

Table 1-2: Rate of Solvolysis of 1,2-disubstituted Cyclohexanes

Group	k_{rel}	trans/cis
Cyclohexyl	1.0	
Si(cis)	3.3×10^4	1.7×10^5
Si(trans)	5.7×10^9	
Ge(cis)	4.6×10^5	2.2×10^5
Ge(trans)	1.0×10^{11}	
Sn(cis)	$> 1.3 \times 10^{11}$	$>>>10^3$
Sn(trans)	$>>>10^{14}$	

Traylor and co-workers reported the hydride abstraction reaction of a series of tetraethylmetaloid compounds with the trityl cation[77] (Eq. 1-7). The relative rate of reaction follows the order Si< Ge<< Sn< Pb (1/ 70/ ~10^5/ 9 × 10^6). The authors suggested that cations such as $Et_3SnCH_2CH_2^+$ and $Et_3PbCH_2CH_2^+$, although primary, should be more stable than the trityl cation.



$$\begin{array}{c} Et_3M\text{-}CH_2CH_3 \\ + \\ Ph_3C^+\ \ BF_4^- \end{array} \longrightarrow \begin{array}{c} Et_3MCH_2CH_2^+\ BF_4^- \\ + \\ Ph_3CH \end{array} \longrightarrow \begin{array}{c} Et_3M^+\ BF_4^- \\ + \\ H_2C{=}CH_2 \end{array}$$

Eq. 1-7

An extensive review on the application of frontier orbitals in organic reactions has been published by Fleming[78]. The analysis of the lowest unoccupied molecular orbital (LUMO) of an empty p orbital and the highest occupied molecular orbital (HOMO) of the carbon-M sigma-bond (M= H, C, Si) is sufficient to explain the β-stabilization of a carbonium ion (Figure 1-10). The magnitude of the β-effect is inversely proportional to the energy separation of these orbitals. The energy of $\sigma_{Si\text{-}C}$ molecular orbital is higher than that of $\sigma_{C\text{-}C}$ or $\sigma_{C\text{-}H}$[51]. Thus the HOMO of a C-Si bond has a higher energy and a better interaction with the LUMO of the empty p orbital compare to those of the C-C and C-H bonds. Therefore, the stabilizing energy E_1 from the C-Si bond is greater than E_2 from the C-C or C-H bonds. The effect of the HOMO of the C-Ge and C-Sn bonds on the stabilizing energy should follow the order of the β-effect[51].

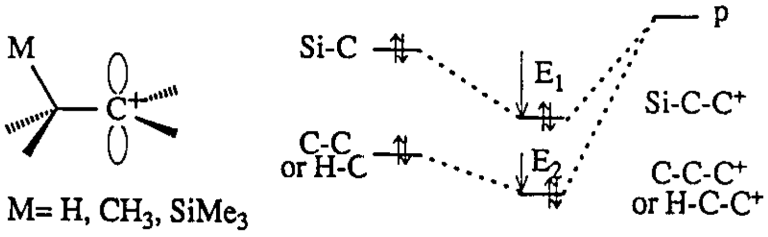
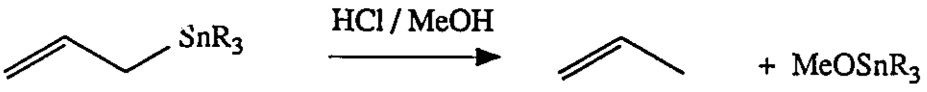


Figure 1-10: Diagram of Energy for the p and C-M Orbitals

1.2.3c) Inductive Effect of the Ligands

As mentioned, the substituents borne by the element play a role in the magnitude of the β-effect. Early studies on the protonolysis of allyltin compounds with diluted hydrogen chloride in methanol showed that the replacement of methyl substituents by phenyl groups decreased the reactivity by one hundred-fold[79] (Scheme 1-21).

Scheme 1-21



R= Me , Ph

Studies of the β-effect in addition reactions with differently substituted silyl compounds have been recently reported. Brook and co-workers reported the addition of bromine to a series of (E)-β-silylstyrenes[80,81] (Scheme 1-22). It is well known that bromine adds in *anti*-fashion to olefins via a bromonium ion intermediate. However, the reaction of the bromine with (E)-β-silylstyrenes <u>83</u> generates products which result from both *anti*- and *syn*-addition. It was demonstrated that substituents on the silicon atom with electron-donating abilities favor the formation of the *trans*-bromostyrenes <u>87</u> via the *syn*-addition to (E)-β-silylstyrenes <u>83</u> due to the β-stabilization of the carbonium ion <u>85</u> by the silyl group (Table 1-3). On the other hand, substituents with increased electronegativities reduced the abilities of the silyl groups to stabilize the carbonium ion <u>85</u> and favored the formation of the *cis*-bromostyrenes <u>86</u> via the bromonium ion <u>84</u>. The degree of *syn*-addition of bromine to a (E)-β-silylstyrene was used as a relative measure of the β-effect for a silyl group. The result of this study showed that the magnitude of the β-effect is directly related to the electron-withdrawing ability of the substituents on the silicon atom. A linear relationship was demonstrated between the degree of *syn*-addition and the group electronegativity of the silyl groups SiXYZ with the exception of the case when XYZ were alkoxy groups[81].

Scheme 1-22

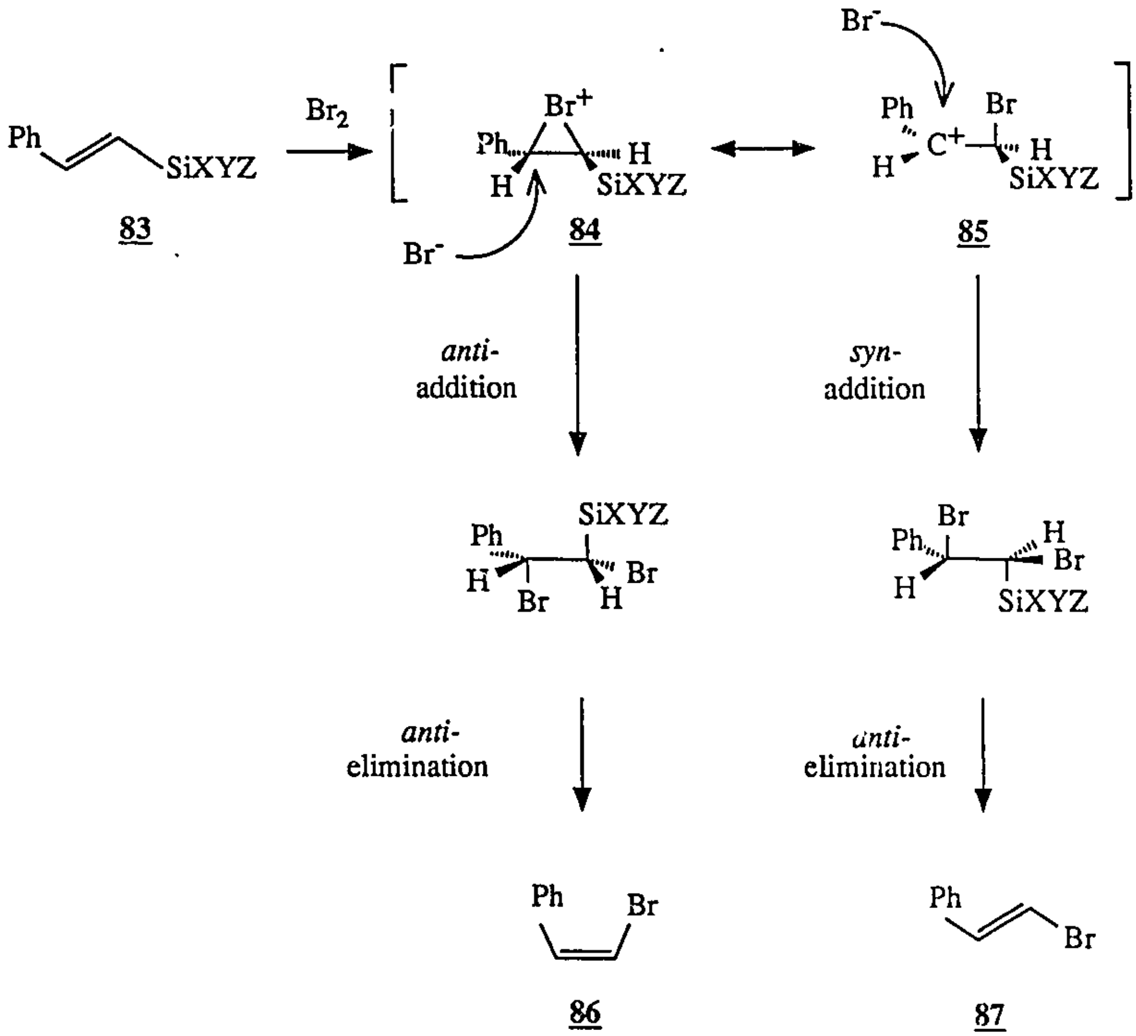


Table 1-3: Degree of *syn*-Addition of Bromine to (E)-β-Silylstyrenes

SiXYZ	%*syn*-Addition	Group Electronegativity@
$SiMe_3$	100	2.06
$SiMe_2Cl$	100	2.12
$SiMe_2F$	87	2.18
$Si(OMe)_3$	81	2.46
$SiMeCl_2$	68	2.19
$SiCl_3$	57	2.26
$SiMeF_2$	40	2.41
SiF_3	17	2.47

@ Calculated from the equation and values of J. Mullay

Mayr and Hagen reported a kinetic measurement for the reactivity of a series of allylsilanes 88 towards the *p*-anisylphenylcarbonium ions 89[82-83] (Scheme 1-23). The results show that the reactivity of allylsilanes 88 strongly depends on the nature of the substituents on the silicon atom (Table 1-4).

Scheme 1-23

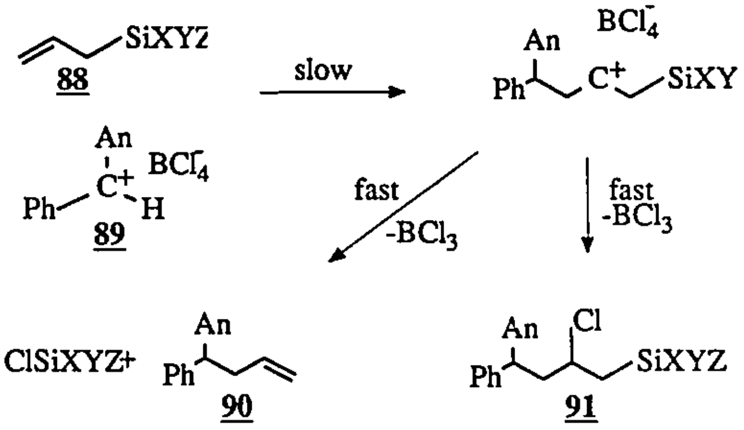


Table 1-4: Effects of the Substituents on the Relative Rate Constants and the Products of Electrophilic Additions on Allylsilanes

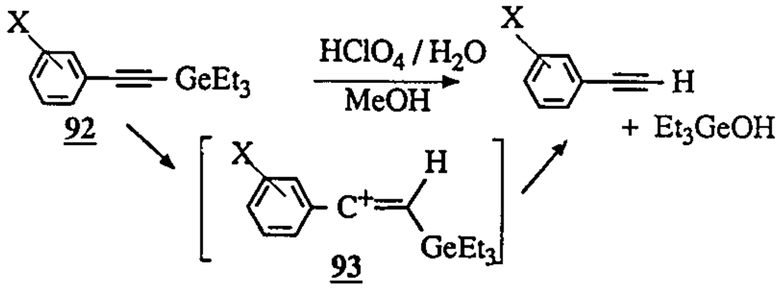
XYZ	k_{rel}	Products
Cl_3	No Rx	
Me_2Cl	1.5×10^{-3}	90
Ph_3	0.016	90
Me_2Ph	0.2	90, 91
Me_3	1	90
t-$BuMe_2$	1.04	91
Et_3	1.59	90
iso-Pr_3	2.29	91
n-Bu_3	2.57	90
n-Hex_3	2.75	90

Replacement of a methyl group by a larger alkyl group (branched or unbranched) leads to an increase of the reactivity of the allylsilane 88, whereas the exchange of a methyl group by phenyl or chloride groups reduces its reactivity. This study, like the previous study, demonstrates that the relative magnitude of the β-effect for a silyl group is related to the inductive effect of each substituent borne on the silicon atom.

1.2.4) Study of the β-Effect in the Stabilization of Cation

Few studies have been done on the degree of stabilization provided to a vinyl cation intermediate by the β-effect of Group 14 elements. The first experiment was reported 25 years ago by Bott, Eaborn and Walton[84]. They described the effect of substituents, X, on the rate of cleavage of some substituted (phenyl)ethynyltriethylgermanes 92 by aqueous methanolic perchloric acid (Scheme 1-24). They assumed that the reaction involves, in the rate determining step, the formation of the carbonium ion 93 as an intermediate. The cleavage of the triethylgermyl group, via nucleophilic attack by the solvent on the germanium atom, was shown to be faster than the hydration of the acetylene moiety. This result was explained by the large release of electrons of which the trialkylgermyl groups are capable.

Scheme 1-24



They did not compare quantitatively the ease of cleavage between the Si, Ge and Sn, but they observed that phenylethynyltrimethylsilane required a higher concentration of acid than the triethylgermyl compounds for the cleavage of the trimethylsilyl group. At this concentration, cleavage of the silyl compound as well as hydration of the phenylacetylene occurred, which prevented rate measurements. On the other hand, the phenylethynyltrimethylstannane was cleaved by neutral aqueous methanol.

Therefore, only the expected order of the β-effect, Si< Ge <<Sn, was obtained from this work.

Cochran and Kuivila[85] reported the kinetics of protiodestannylation of allenyltin compounds <u>**94**</u>. The reaction involved a competition between S_E2 and S_E2' mechanisms leading to a mixture of allenic <u>**97**</u> and acetylenic <u>**98**</u> products, respectively (Scheme 1-25). These two compounds are formed from two different vinyl cation intermediates <u>**95**</u> and <u>**96**</u>. They have shown in the S_E2' mechanism, that the reactivity of the allenyltins were comparable to the reactivity of allyltin compounds[79,86], whereas in the S_E2 mechanism the reactivity of the allenyltins were greater than those of vinyltin compounds[87]. This increase of reactivity was assumed to arise from the preferential β-effect caused by the orientation of the C-Sn bond and the developing empty p orbital.

The kinetic results (Table 1-5) of these protonation reactions with hydrochloric acid in methanol-4% water solution show, first of all, that the S_E2' mechanism (formation of acetylenic products) for the triethyl and triphenylstannyl allenes (Scheme 1-25) is more important than the S_E2 mechanism (formation of allenic products). The S_E2' mechanism is fully controlled by the developing β-effect of the C-Sn bond to the coplanar empty p orbital. The change of the substituents on the tin element from phenyl, to ethyl and methyl groups, increased the rate of both reactions in favor of the S_E2 mechanism . This difference of reactivity was attributed to steric hindrance around the tin atom increasing from methyl, to ethyl and phenyl that prevents proximal attack of a proton, and also to the electron-withdrawing effect of the phenyl groups. The increase of the reaction rate for the S_E2' reaction from the triethyl to trimethylstannyl groups is unexpected on the basis of inductive effects of the substituents to the tin element[80,82]. This difference was also explained by steric effects of the bulky stannyl moiety, which is disputable, but provides evidence for solvent participation in the transition state.

Scheme 1-25

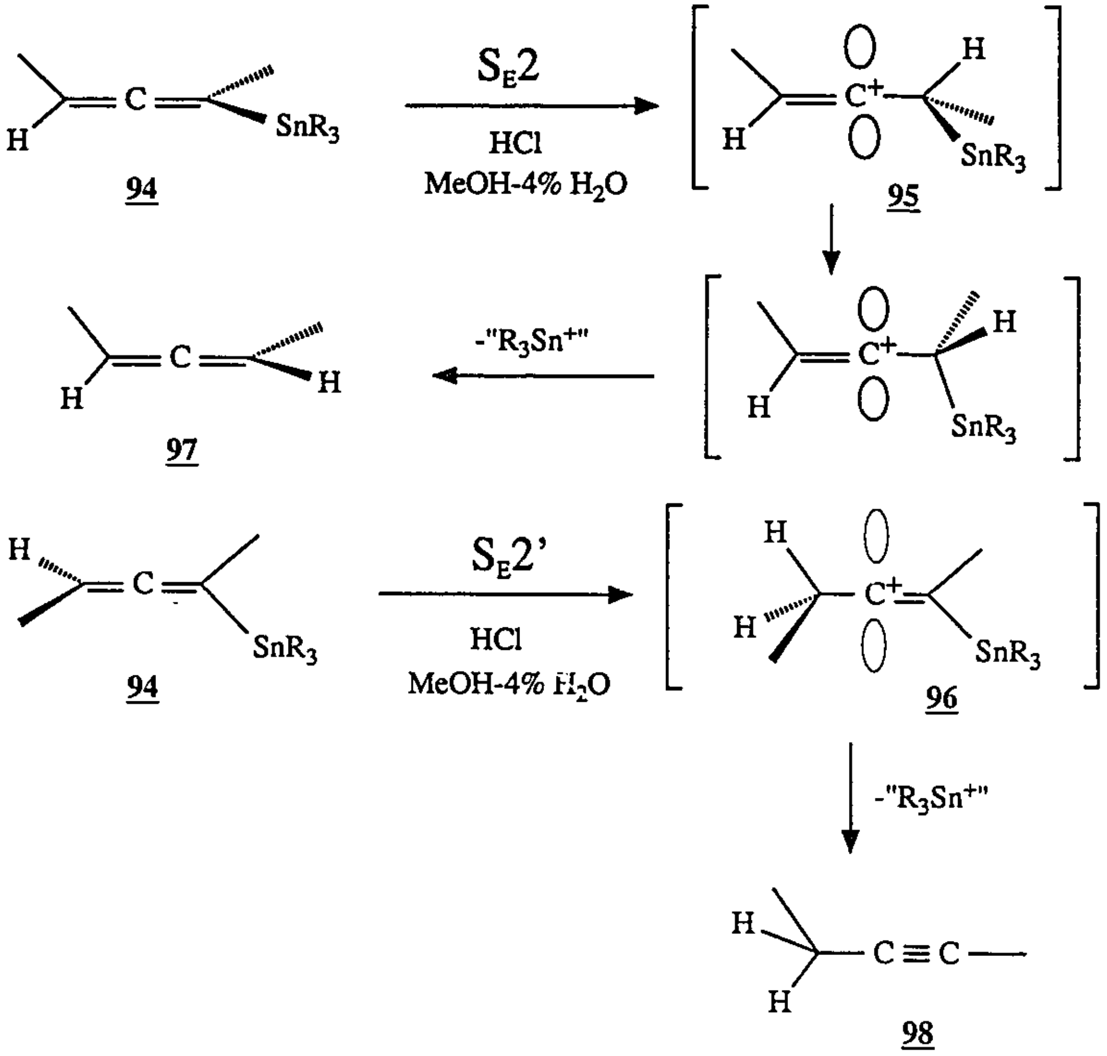


Table 1-5: Relative Second-Order Rate Constants and Relative Partial Rate Constants of S_E2 and S_E2'

SnR_3	k_{rel}	$k_{rel}(S_E2)$	$k_{rel}(S_E2')$
$SnMe_3$	4.8	2.46	2.34
$SnEt_3$	1.77	1	1.77
$SnPh_3$	0.069	0.005	0.064

Jorgensen and co-workers have also carried out ab initio calculations on β-methyl and β-H_3Si vinyl cations[53] <u>99</u> and <u>100</u> (Figure 1-11). The stabilizing energies calculated for the isodesmic reaction (Eq. 1-6) at the MP3/6-31G* level are 8.1 and 28.6 kcal/mol respectively. The C-C=C^+ angle of <u>99</u> was estimated to be 124.6° while the Si-C=C^+ angle of <u>100</u> was 107.9°. The smaller angle for the β-Si vinyl cation <u>100</u> shows a larger interaction between the empty p orbital and the C-Si bond.

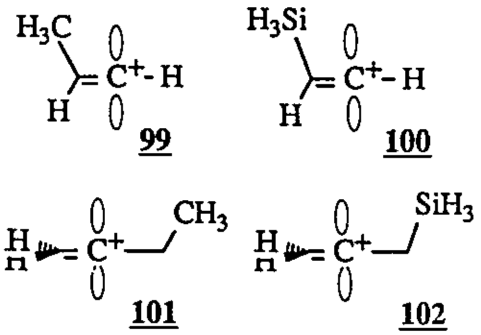
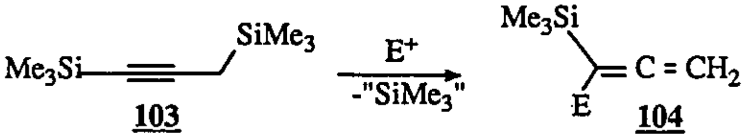


Figure 1-11: Vinyl Cation Intermediates

Examination of the allylic methyl <u>101</u> and silyl vinyl cation and <u>102</u> species (Figure 1-11) at the MP2/6-31G* and HF/6-31G* levels show higher stabilizing energies of 29.8 and 42.8 kcal/mol respectively[53]. These carbonium ions enjoy α-methylene stabilization in addition to C-C and Si-C hyperconjugation. In fact, it has been proven experimentally that electrophilic addition to 1,3-*bis*(trimethylsilyl)propyne <u>103</u> (Scheme 1-26) afforded in high regioselectivity the allenic product <u>104</u> with the cleavage of the most stabilizing group, the propargylic trimethylsilyl group[88]. However, the magnitude of the β-effect for these vinyl cations species is less effective by about 5 kcal/mol since the interaction is across a longer C-C single bond[53].

Scheme 1-26



1.3) Vinyl Cation Intermediates Stabilized by the β-Effect in Organic Reactions.

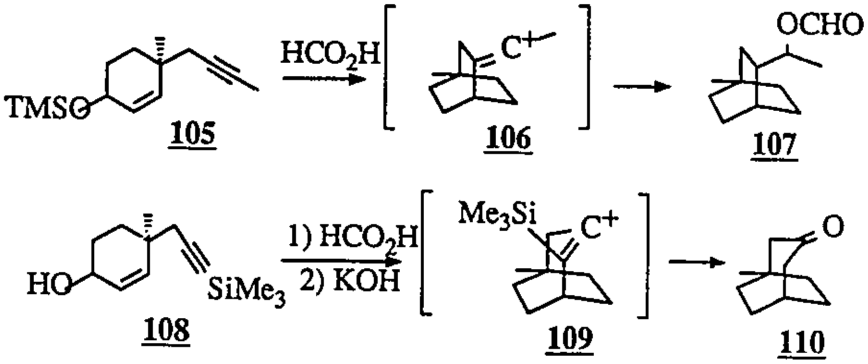
There are many reactions in the literature which involve carbonium ion intermediates stabilized by a β-Group 14 element[47]. Among them, the trimethylsilyl group has been the favorite choice of chemists to stabilize a vinyl cation intermediate. However, the tri-*n*-butylstannyl group has also become popular in the last five years. To the best of our knowledge, no organic reaction involving β-germyl or β-plombyl vinyl cations as intermediates has been published.

The goal of this last part of the introduction is to demonstrate the power of the β-effect on vinyl cation intermediates as a tool to control the regioselectivity of some organic reactions. Afterwards, we will look at some reactions which compare the strength of the β-effect between some silyl and stannyl groups.

1.3.1) Directing Effect of the β-Effect on Vinyl Cation in Organic Reactions

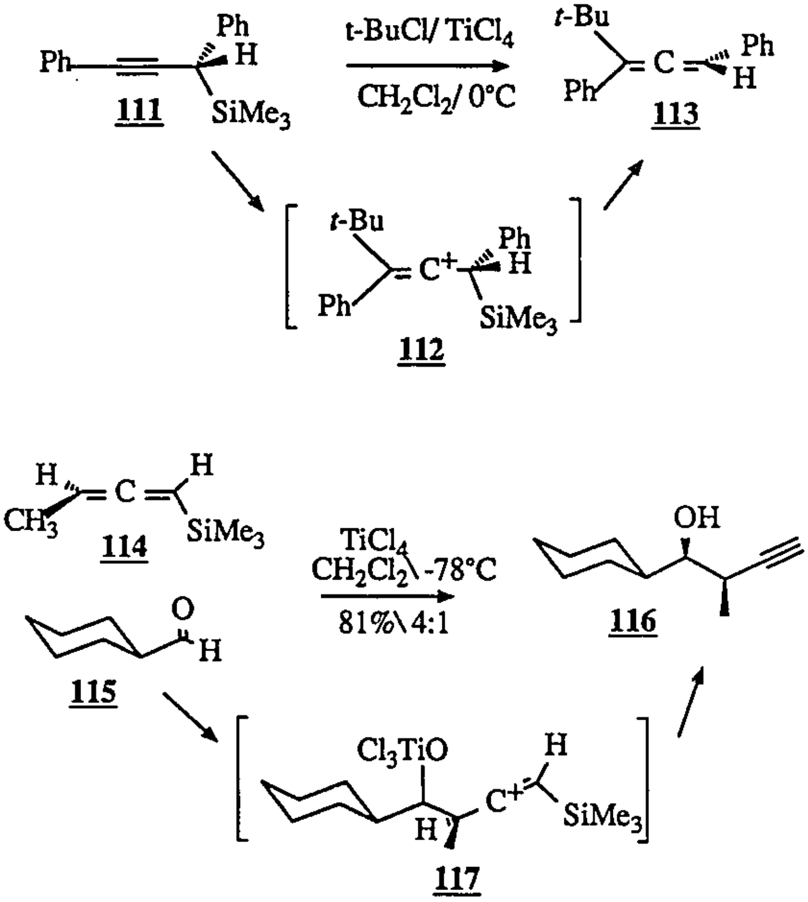
In the synthesis of bicyclic compounds, Heathcock and co-workers were the first group to report the different directing effect between a β-trimethylsilyl substituent and a β-methyl substituent when a vinyl cation intermediate was postulated in the reaction mechanism[89] (Scheme 1-27). In an electrophilic intramolecular π-cyclization of the methylpropargylic chain with the allylic alcohol 105, bicyclo[2.2.2]octene 107 was obtained via an exocyclic vinyl cation intermediate 106. However, by simple modification of the propargylic chain 108, the same reaction provided a bicyclo[3.2.2]nonenone 110 via an endocyclic β-trimethylsilyl vinyl cation intermediate 109. The β-effect of the silyl group is sufficiently powerful to stabilize a bent vinyl cation intermediate.

Scheme 1-27



Propargyl and allenyl silanes are interesting reagents in organic chemistry for the synthesis of various compounds. Propargylsilanes react with a variety of electrophiles to produce substituted allenes[23,88,90] whereas allenylsilanes react under the same conditions to produce alkynes[91,92] (Scheme 1-28). Kumada and co-workers[93] have shown that the optically active (S)-1,3-diphenyl-3- trimethylsilylpropyne 111 reacts with *t*-butyl chloride in presence of titanium chloride to give (S)-1,3-diphenyl-4,4-dimethyl-1,2-pentadiene 113. The reaction proceeds via S_E2' mechanism by an electrophilic attack on the double bond conjugated with the C-Si bond, from the side opposite to the silyl group (*anti* attack), to form the vinyl cation intermediate 112. On the other hand, Danheiser and coworkers[94] have shown that the chiral 1,2-butadienyltrimethylsilane 114 reacts with the cyclohexanecarboxaldehyde **115** to afford with modest diastereoselectivity (4:1) the homopropargylic alcohol **116** (erythro) via the β-silyl vinyl cation intermediate **117**.

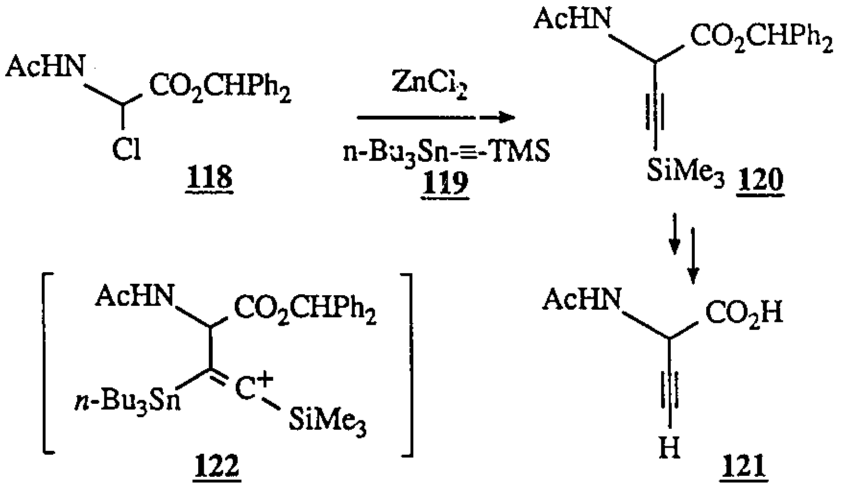
Scheme 1-28



1.3.2) The Comparative β-Effect of Silyl and Stannyl Groups on Vinyl Cations in Organic Reactions

Williams and co-workers[95] have recently published the synthesis of the racemic N-acetyl ethynylglycine 121 (Scheme 1-29). The coupling of the (tri-*n*-butylstannyl)(trimethylsilyl)acetylene 119 with the chloroglycinate 118 in the presence of zinc chloride afforded the ethynylglycinate 120 which showed that the stannyl group has a better stabilizing β-effect on vinyl cation intermediates 122 than the silyl group.

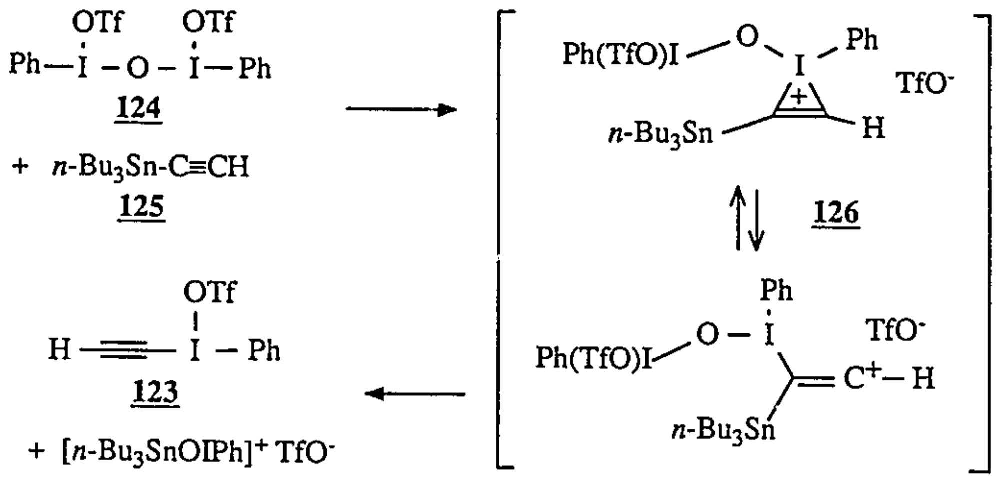
Scheme 1-29

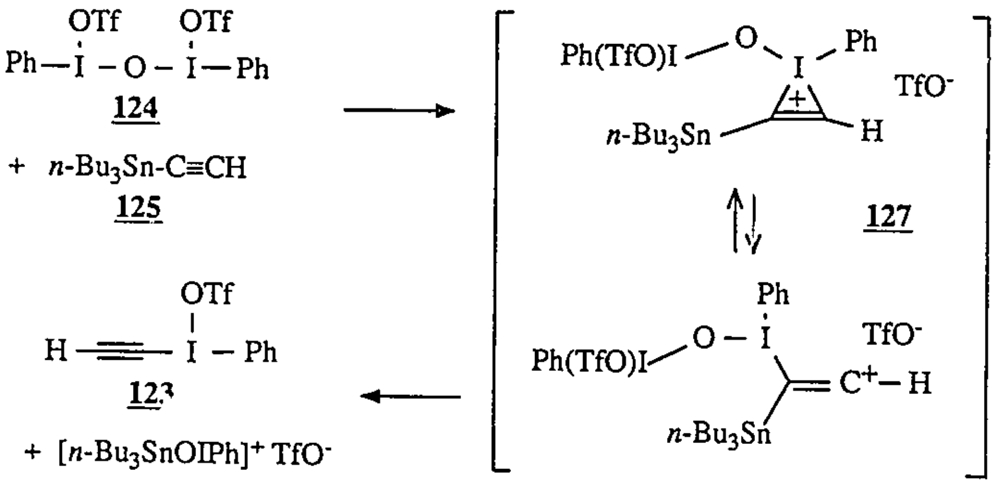


The alkynylaryliodonium salts are interesting new reagents in organic chemistry[96]. The synthesis of these hypervalent organoiodine compounds from alkynyltrimethylsilanes involves the formation of β-(trimethylsilyl)vinyl cation intermediates[97]. Stang and co-workers[98] have recently reported the synthesis of the simplest structure ethynyl(phenyl)iodonium triflate, $HC{\equiv}C\text{-}I^+\text{-}Ph\ CF_3SO_3^-$ 123 (Scheme

1-30). Zefirov's reagent 124 was shown to be unreactive with (trimethylsilyl)acetylene, TMS-C≡CH. However, the electrophilic addition of the reagent to (tri-*n*-butylstannyl)acetylene 125 was successful.

Scheme 1-30





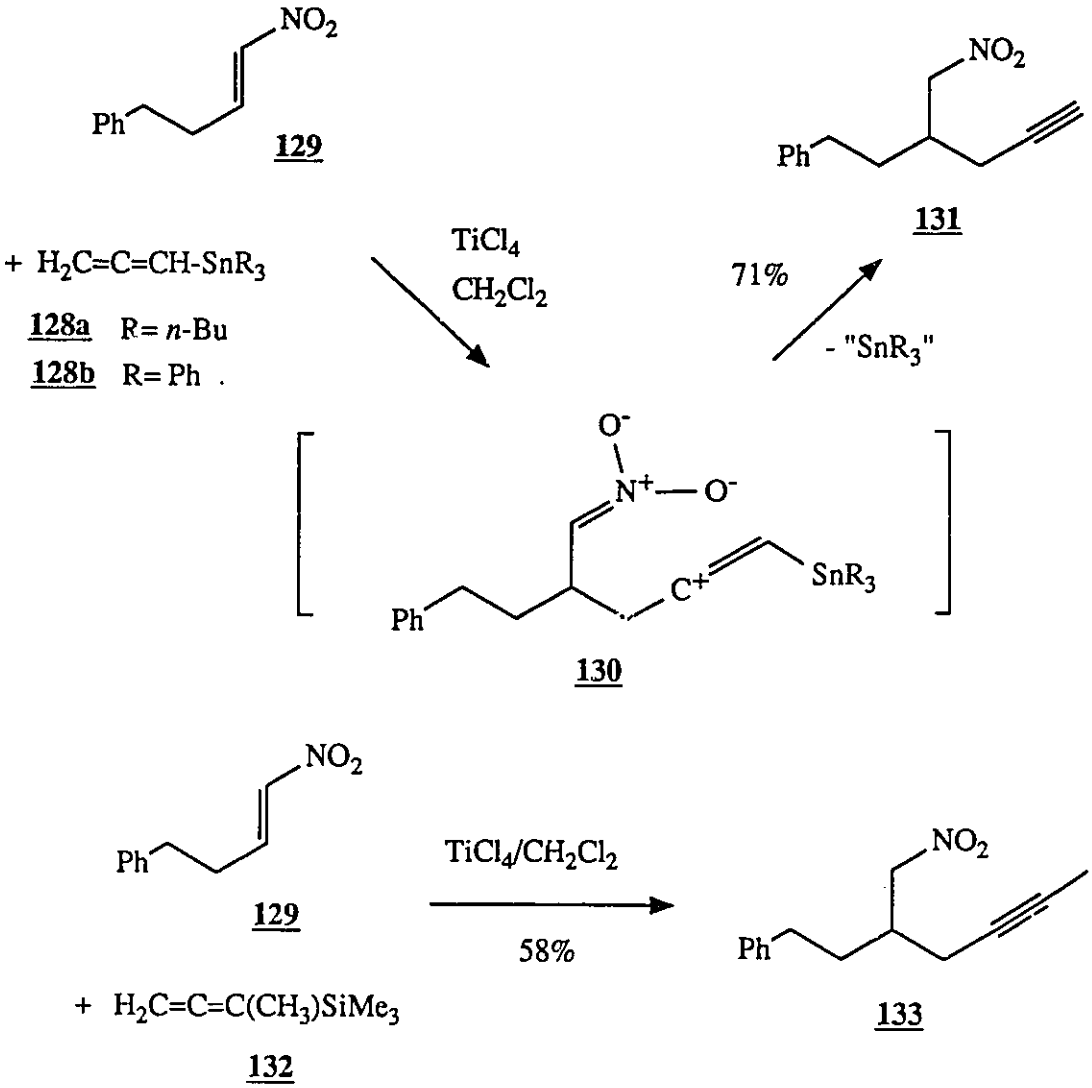
The initial formation of an unsubstituted vinyl cation intermediate **126**, high in energy, accounts for the lack of reactivity of the (trimethylsilyl)acetylene. The ionic intermediates **126** and **127** needed a stronger stabilizing effect from the β-stannyl group to be accessible. This synthesis showed that the β-effect of the tri-*n*-butylstannyl group on vinyl cation species is much stronger than for the trimethylsilyl group.

Huruta and co-workers have recently reported the conjugate propargylation reaction of stannylallenes to α-nitro olefins[99] (Scheme 1-31). It is presumed that a vinyl cation intermediate **130** stabilized by the Sn-C σ-bond (β-effect) occurs in the mechanism of the reaction.

The addition of (tri-*n*-butylstannyl)allene **128a** to 1-nitro-4-phenyl-1-butene **129** in the presence of a Lewis acid ($TiCl_4$) gave the β-propargylic nitro alkane **131** in 76% yield (Scheme 1-31). It was found that the addition of (triphenylstannyl)allene **128b** to α-nitro olefins **129** under the same conditions proceeded slowly. These results suggest that the tri-*n*-butylstannyl group has a stronger β-effect on vinyl cation species **130** than the triphenylstannyl group, as expected from the inductive effect of the substituents[80,82,83].

A similar reaction was reported by Danheiser and co-workers[92]. 1-Methyl-1-(trimethylsilyl)allene **132** reacted with α-nitro olefins **129** in the presence of a Lewis acid ($TiCl_4$) to give the 5-(nitromethyl)-7-phenyl-2-heptyne **133** in lower yield (58%) (Scheme 1-31). Relative comparison of the yields of this reaction again suggests that the tri-*n*-butylstannyl group has a stronger β-effect on vinyl cation species than the trimethylsilyl group.

Scheme 1-31


NO2
Ph
129
+ $H_2C{=}C{=}CH\text{-}SnR_3$
128a R= *n*-Bu
128b R= Ph
$TiCl_4$
CH_2Cl_2
NO2
Ph
131
71%
- "SnR_3"
O-
N+ — O-
C+
SnR_3
Ph
130
NO2
Ph
129
+ $H_2C{=}C{=}C(CH_3)SiMe_3$
132
$TiCl_4/CH_2Cl_2$
58%
NO2
Ph
133

1.4) Goal of the Study

As we have seen, chemists have used the strength of the β-effect from some silyl and stannyl groups as a powerful tool to stabilize vinyl cation intermediates in organic chemistry. From recent synthetic work, qualitative comparisons of the relative magnitude of the β-effect on vinyl cation species between silyl and stannyl groups could be made. However, comparisons done from different organic reactions are not as extensive as those on saturated carbonium ion species. In fact, most of these comparisons were non-existent in the beginning of our work.

Quantitative studies of the magnitude of the β-effect have been reported on saturated carbonium ion, however, no quantitative data has been provided for the analogous vinyl cation species. We have therefore undertaken a study which allows a comparison between the relative magnitude of the β-effect on vinyl cation species for the elements silicon, germanium and tin. We will also investigate the effect of the substituents borne by the elements on the magnitude of the β-effect on vinyl cations. Moreover, this study allows a comparison between the α-effect on vinyl cation species for some silyl groups.

This new relative scale of the β-effect for the Group 14 elements on vinyl cation species will be, afterwards, a useful reference in organic synthesis.

CHAPTER 2

STRATEGY OF THE STUDY

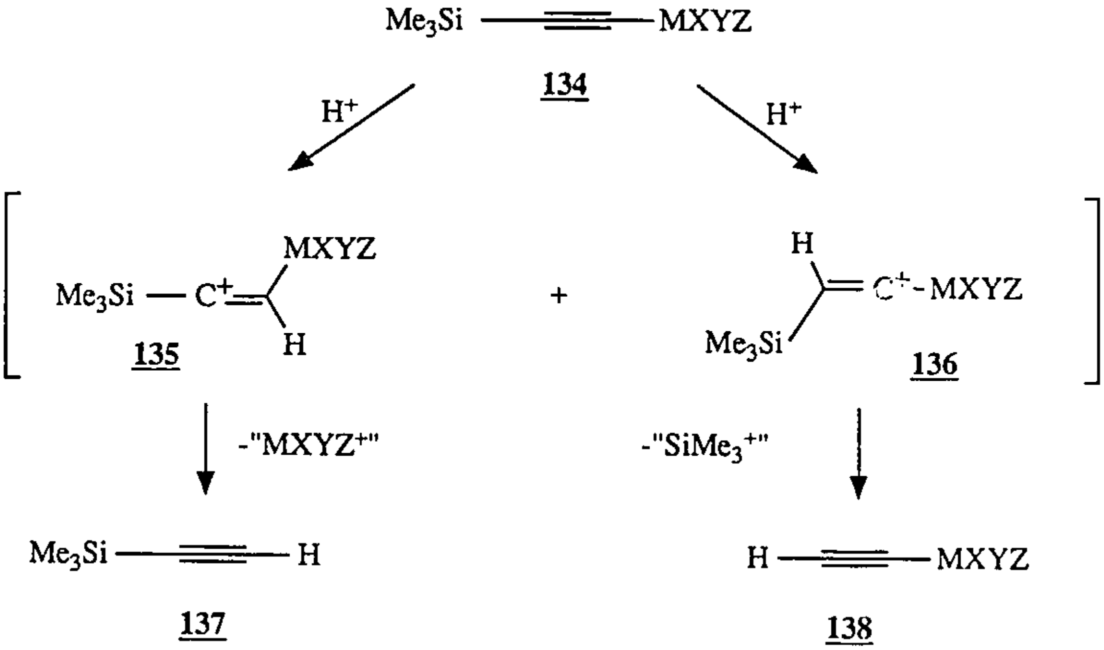
Comparing the two general methods available for generating a vinyl cation intermediate, we anticipated that the electrophilic addition to a metalated alkyne or metalated allene would be a better pathway than the solvolysis of β-substituted vinylmetalloid compounds. The synthesis and the stabilities of the latter compounds will certainly bring much trouble.

It is well known that propargyl germanes and stannanes undergo isomerization to their corresponding allenyl germanes and stannanes[100]. The equilibrium favors the allenyl derivatives in a protic solvent. The synthesis of alkynyl[47,101-104] and allenyl[47,94,105] organometallic compounds of the Group 14 elements are well described in the literature. However, upon electrophilic addition, especially on protonation, some allenylic compounds are ambident nucleophiles, which is manifested by their participation in both S_E2 and S_E2' mechanisms[19,85] (Scheme 1-25). On the other hand, metalated acetylenes are stable compounds and easily accessible[47,101-104].

Therefore, a metalated acetylene compound is a good model to study the β-effect on vinyl cation intermediates generated by electrophilic addition on the triple bond. A similar model, the substituted phenylethynyltriethylgermane 92 discussed previously (Scheme 1-24), was used by Eaborn and co-workers, to study only the effect of the substituent on the phenyl ring on protonation of the triple bond in aqueous methanolic solution[84]. They did not investigate fully the analogous silane and stannane.

The model chosen in our work consists of a dimetalated acetylene compound. The premise of this model is that competitive electrophilic addition on the dimetalated acetylene will proceed via the cation with the most hyperconjugative stabilization (stronger β-effect) and lead, after the loss of the better stabilizing group to a monometalated acetylene (Scheme 2-1). For a coherent study, we must keep constant one metalated group in the molecule. This will minimize any change of the inductive effect on the triple bond due to this metalated group[106] and keep constant the stabilizing or destabilizing α-effect on this side of the acetylene. We chose to use the trimethylsilyl group as the constant reference group in the molecule.

Scheme 2-1: Competitive Protonation of a Metalated (trimethylsilyl)acetylene



M = Si,Ge,Sn

A competitive protonation of a metalated (trimethylsilyl)acetylene **134** might proceed via two possible vinyl cation intermediates **135** and/or **136** (Scheme 2-1). The protonation reaction which proceeds via the vinyl cation **135** shows that the metalated group "MXYZ" has a stronger β-effect than the trimethylsilyl group. The loss of the stabilizing metalated group affords the (trimethylsilyl)acetylene **138**. On the other hand, the protonation which proceeds via the vinyl cation **136** shows that the trimethylsilyl group has a stronger β-effect than the other metalated group. The loss of this stabilizing metalated group affords the monometalated acetylene **137**.

This experiment will allow us to compare the magnitude of the β-effect of one metalated group relatively to the internal reference trimethylsilyl group as well as to other metalated groups from other compounds.

The protonation reaction of the metalated (trimethylsilyl)acetylene **134** (Scheme 2-1) will be followed by NMR spectroscopy. The proton signal of the trimethylsilyl group is especially characteristic in the ^1H NMR spectra and will be used as a reference point to gauge the degree of completion of the reaction. Moreover, this method allows us to carry out the reaction in an organic solvent. This is an advantage since most of the synthetically useful reactions which involve the formation of a vinyl cation intermediate occur in non-polar organic solvents. Most of the studies on the β-effect of group 14 elements have been carried out in aqueous solution. We are not saying that the results of these studies in aqueous solution cannot be extrapolated for use in organic synthesis involving non-aqueous media. However, we believe that a study in organic solvent is more appropriate for applications in organic synthesis.

CHAPTER 3

RESULTS AND DISCUSSION

We have synthesized a large series of metalated (trimethylsilyl)acetylene compounds. Four new compounds have been synthesized, (triphenylgermyl)(trimethylsilyl)acetylene (Ph_3Ge-C≡C-$SiMe_3$), (triphenylgermyl)(*t*-butyldimethylsilyl)acetylene (Ph_3Ge-C≡C-$SiMe_2$*t*-Bu), [bis(N,N-dimethylamino)methylsilyl](trimethylsilyl)acetylene (($Me_2N)_2MeSi$-C≡C-$SiMe_3$) and [tris(N,N-dimethylamino)silyl](trimethylsilyl)acetylene (($Me_2N)_3Si$-C≡C-$SiMe_3$). The synthesis and the spectroscopic data of these new compounds as well as other compounds are available in the experimental section (Chapter 4).

Interest on these metalated (trimethylsilyl)acetylene compounds brought us to performed X-Ray crystal structure analysis on tetrakis(trimethylsilylacetylide)germane and tetrakis(trimethylsilylacetylide)stannane. The data for the structure determination are presented in Appendix 1 and will not be discussed further in this work.

We have looked at the protonation reactions of these metalated (trimethylsilyl)acetylene compounds. All protonations were carried out with 0.05M solutions of the compounds in deuterated chloroform ($CDCl_3$) and were followed by ^1H NMR spectroscopy. The full kinetic procedure and kinetic measurements of all protonation reactions are available in the experimental section. Only the kinetic data (plot of the reaction rate) necessary to deduce the rate constants and to elucidate the reaction mechanism are presented in this chapter.

3.1) The Relative Magnitude of the β-Effect on Vinyl Cation Ion of Silicon, Germanium and Tin Elements

3.1.1) Results

A series of stannyl, germyl and silyl (trimethylsilyl)acetylene compounds (0.05M solution in chloroform-*d*) was reacted with different acids (concentrations varied from 0.05 to 1.3M in $CDCl_3$). The reactions are of second order over this acid concentration range. The ionic strength of the organic solution was not kept constant by addition of salt. Therefore, the rate constants for these metalated (trimethylsilyl)acetylene compounds are given for a equimolar concentration of acid (0.05M in $CDCl_3$) (Table 3-1). The standard deviations, obtained from a least-squares program, were generaly less than 5% of the rate constants observed (k_{obs}) for each reaction (Appendix 2). Error on the rate constants was estimated by a systematical 5% error in addition to the standard deviation.

The deuterium isotopic effect k_{H^+}/k_{D^+} of 2.8 obtained for the reaction of (trimethylstannyl)(trimethylsilyl)acetylene ($Me_3Sn\text{-}C{\equiv}C\text{-}SiMe_3$) with chloroacetic acid (entries 1 and 2) shows that the proton transfer from the acid to the acetylene is the rate determining step (Graph 3-1). The reaction are first order in both the acid and the acetylene (Eq. 1-1). Moreover, the rate of reaction for a given compound follows the order

$$-\frac{d[C]}{dt} = k\,[C]\,[A] \qquad \text{Eq. 3-1}$$

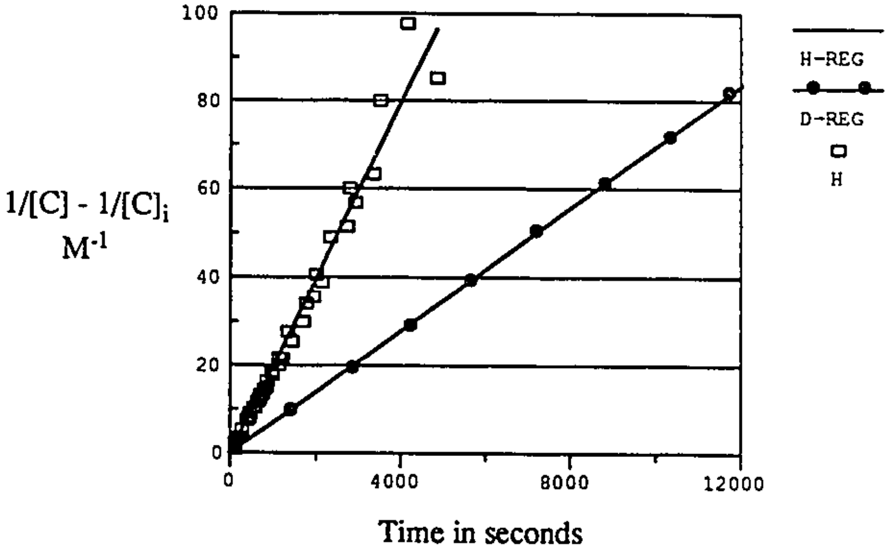
of acidity of the acid used and not the nucleophicility of the acid counterions (entries 5,6 and 7). This result confirms that the breaking of H-O bond of the acid by the triple bond (acting as a base) is really the rate determining step of the reaction and not the addition of the acid counterion to a metalated group.

Table 3-1: Second-Order Rate Constants for the Reaction of Me_3Si-C≡C-MXYZ 0.05M with Different Acids 0.05M in Chloroform-*d*@

Entries	MXY	Acid*	pKa#	k × 10^2 $M^{-1}s^{-1}$	r
1	Me_3Sn	$ClCH_2COOH$	2.85	1.98 ± .15	.9881
2	Me_3Sn	$ClCH_2COOD$		0.70 ± .05	.9911
3	*n*-Bu_3Sn	$ClCH_2COOH$	2.85	0.70 ± .05	.9932
4	*n*-Bu_3Sn	$Cl_2CHCOOH$	1.48	65 ± 8	.9820
5	Ph_3Sn	$Cl_2CHCOOH$	1.48	0.38 ± .03	.9948
6	Ph_3Sn	CCl_3COOH	0.70	18 ± 2	.9725
7	Ph_3Sn	CF_3COOH	0.23	54 ± 6	.9876
8	Me_3Ge^{ϵ}	CF_3COOH	0.23	0.094 ± .007	.9987
9	Me_3Si^{ϵ}	CF_3COOH	0.23	0.00018 ± .00003	.9811
10	Me_3Si^{ϵ}	CH_3SO_3H	~ -2	0.076 ± .009	.9935

@ The reaction was followed with ^1H NMR AC200 Bruker spectrometer
& MXYZ is the leaving group
* The acid is added as a solution in $CDCl_3$ to the NMR tube
# pKa in water
∈ The compound was reacted with different concentrations of acid solution in $CDCl_3$

GRAPH 3-1: Deuterium Isotopic Effect for the Reaction of Me_3Sn-C≡C-$SiMe_3$ (0.05M in $CDCl_3$) with $ClCH_2COOH/D$ (0.05M in $CDCl_3$)

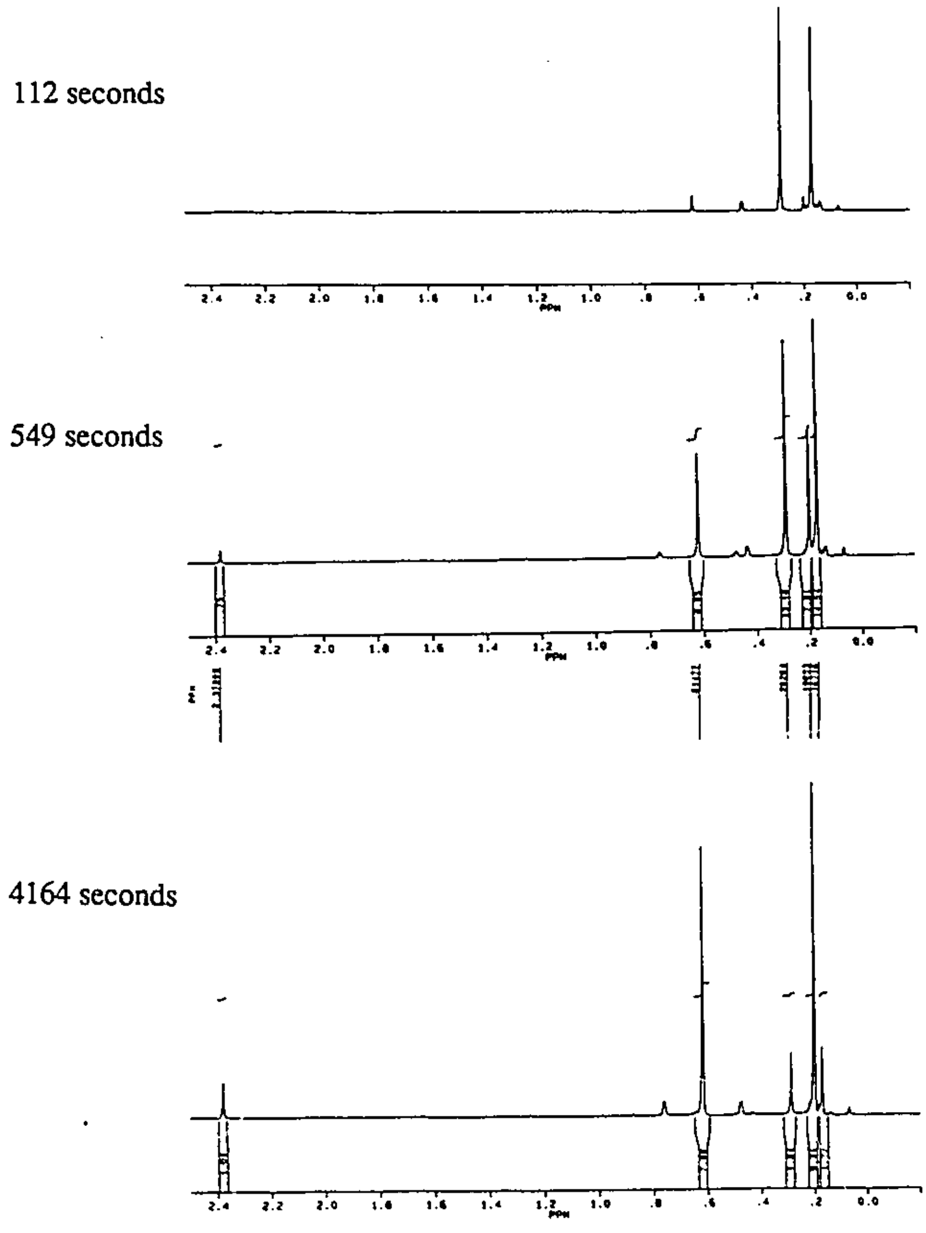


The competitive protonation reaction of the metalated (trimethylsilyl)acetylene compounds (TMS-C≡C-MXYZ from the Table 3-1) proceeded via the vinyl cation intermediate <u>**135**</u> (Scheme 2-1) with the loss of the most stabilizing metalated group MXYZ (except for the entries 9 and 10 where both metalated groups are Me_3Si groups). The product of these reactions could be followed by ^1H NMR spectroscopy. For example, the reaction of (trimethylstannyl)(trimethylsilyl)acetylene ($Me_3Sn-C{\equiv}C-SiMe_3$, 0.28 and 0.17 ppm) with chloroacetic acid (entry 1) led to the production of (trimethylsilyl)acetylene ($Me_3Si-C{\equiv}C-H$, 0.20 and 2.38 ppm) and trimethylstannyl chloroacetate ($ClCH_2COOSnMe_3$, 0.61 ppm) (Scheme 3-1) which shows the trimethylstannyl group to have a better stabilizing ability (β-effect) than the trimethylsilyl group.

The metalated (trimethylsilyl)acetylene compounds (Table 3-1) show different degrees of reactivity and it was impossible to determine the reaction rate with a single acid. Thus, several acids were used. Unfortunately, the pKa's of these acids in chloroform-*d* have not been determined. However, Rumeau has shown that the general order of pK of these acids in chloroform ($CHCl_3$) is in the same order as in water[107]. Therefore, it was possible to establish a relative order of reaction rates by comparing the absolute reaction rates of these compounds for a given acid. The metalated groups MXYZ in Table 3-1 have been ordered by decreasing relative rate with which the group is lost with a given acid: the faster the reaction, the better the β-effect.

Scheme 3-1: Reaction of $Me_3Sn\text{-}C{\equiv}C\text{-}SiMe_3$ (0.05M in $CDCl_3$) with One Equivalent of $ClCH_2COOH$ (0.05M) with Respect to the Time and Monitored by ^1H NMR Spectroscopy

$$Me_3Sn\text{-}C{\equiv}C\text{-}SiMe_3 + ClCH_2COOH \rightarrow ClCH_2COOSnMe_3 + Me_3Si\text{-}C{\equiv}C\text{-}H$$


112 seconds

549 seconds

4164 seconds

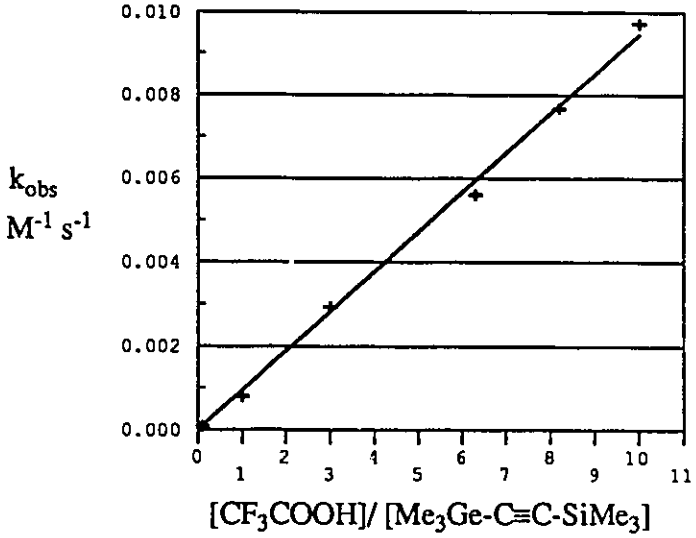
We measured the rate of reaction for (tri-*n*-butylstannyl)(trimethylsilyl)acetylene (n-Bu_3Sn-C≡C-$SiMe_3$) with one equivalent of dichloroacetic acid ($CHCl_2COOH$) (entry 4) and our most reliable data, which fitted the second order law, indicate that the half-life (Eq. 3-2) was approximately 30 seconds. However, our NMR spectroscopy method is not very accurate when the reactions occur too quickly (i.e. $t_{1/2} \leq 60$ seconds).

$$t_{1/2} = \frac{1}{k\,[C_o]} \qquad \text{for } [C_o] = [A_o] \qquad \text{Eq. 3-2}$$

The reaction of (triphenylstannyl)(trimethylsilyl)acetylene (Ph_3Sn-C≡C-$SiMe_3$) with one equivalent of acid (entries 5,6 and 7) gives a small amount of benzene (7.37 ppm) from the protonation of the phenyl ring (*ipso* β-effect). This side reaction causes the rate plot to deviate from linearity and it is more important with the weaker dichloroacetic acid ($CHCl_2COOH$) than the stronger trifluoroacetic acid (CF_3COOH). The rate constant for the reaction with CF_3COOH (entry 7) has been obtained from the best measurement which fitted the second order law. Our NMR spectroscopy method is not very accurate for this fast reaction ($t_{1/2} \leq 60$ seconds).

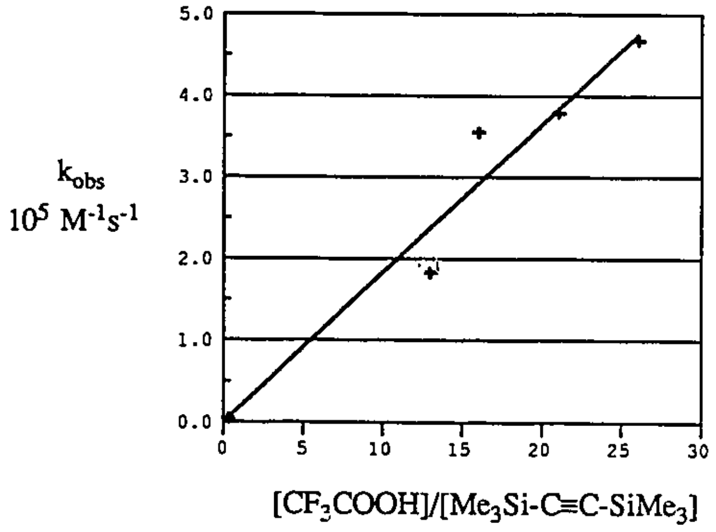
In contrast, the reaction of (trimethylgermyl)(trimethylsilyl)acetylene (Me_3Ge-C≡C-$SiMe_3$) with one equivalent of CF_3COOH (0.05M) was very slow. The rate constant was found to be $0.078 \pm 0.009 \times 10^{-2}\ M^{-1}s^{-1}$. In order to determine accurately the second-order rate constant of this reaction, several reaction rates were measured with different concentrations of CF_3COOH. These new reaction rates followed the second order law but showed an increase of the rate constants with the increase of the concentration of the acid used. Reactions involving a neutral molecule and a charged ion species in a non-polar solvent are subject to ionic strength effects. Increase of ionic strength with increasing acid concentration better stabilizes the charged ion intermediates in the reaction and results in an increase of rate constant[13,111]. The rate constants observed (k_{obs}) depend, therefore, on the CF_3COOH concentration. A plot of the rate constants observed versus the concentration ratio $[CF_3COOH]/[Me_3Ge\text{-}C{\equiv}C\text{-}SiMe_3]$ gives a straight line with a standard deviation of 2.5%. The new second-order rate constant for the reaction is obtained from the line for the corresponding ratio $[CF_3COOH]/[Me_3Ge\text{-}C{\equiv}C\text{-}SiMe_3]= 1$ (Table 3-1, entry 8; Graph 3-2) (See appendix 3).

Graph 3-2: Linear Relationship Between the Rate Constants Observed and the Concentration Ratio $[CF_3COOH]/[Me_3Ge\text{-}C{\equiv}C\text{-}SiMe_3]$



The bis(trimethylsilyl)acetylene ($Me_3Si\text{-}C{\equiv}C\text{-}SiMe_3$; Table 3-1, entries 9 and 10) is still less reactive but has been shown to react slowly with one equivalent of methanesulfonic acid ($MeSO_3H$, 0.05M) or with a high concentration of trifluoroacetic acid (CF_3COOH). The rate constants for the reaction with these acids have been determined with the same procedure as the previous reaction between the $Me_3Ge\text{-}C{\equiv}C\text{-}SiMe_3$ and CF_3COOH (Appendix 3). The reactions of $Me_3Si\text{-}C{\equiv}C\text{-}SiMe_3$ at high concentrations of CF_3COOH follow the second order law (Eq. 3-1). A linear relationship is obtained with a the standard deviation of 12% (Graph 3-3). Only four reaction rates were measured which caused a poor degree of linearity of the plot. The determination of the rate constant for the reaction of $Me_3Si\text{-}C{\equiv}C\text{-}SiMe$ with $MeSO_3H$ will be discussed in the second part of this Chapter.

Graph 3-3: Linear Relationship Between the Rate Constants Observed and the Concentration Ratio $[CF_3COOH]/[Me_3Si\text{-}C{\equiv}C\text{-}SiMe_3]$



3.1.2) Comparison of the Relative Magnitude of the β-Effect on Vinyl Cation Intermediates

The protonation reaction on the triple bond of these metalated (trimethylsilyl)acetylene compounds *could* be controlled by inductive effects alone (basicity of the triple bond[106]). However based on the electronegativity of the silicon, germanium and tin elements[71-73], the inductive effects of the Me_3Si, Me_3Ge and Me_3Sn groups to the triple bond should be "almost the same". Clearly this effect cannot explain alone the large difference in rate constants between the $Me_3Sn\text{-}C{\equiv}C\text{-}SiMe_3$ (Table 3-1; entry 1), $Me_3Ge\text{-}C{\equiv}C\text{-}SiMe_3$ (entry 8) and $Me_3Si\text{-}C{\equiv}C\text{-}SiMe_3$ (entries 9 and 10). Therefore, we believe that the inductive and β-effects act cooperatively in the control of the protonation reaction on the triple bond. This large difference in rate constants between these compounds (entries 1, 8, 9 and 10) has also been found to be the case in alkyl β-carbocation stabilization studies[63,64,77]. Moreover, since the inductive effect should be quite similar for all metalated groups in the acetylene compounds (Table 3-1), the relative rate constant is a relative measurement of the magnitude of β-effect on vinyl cation intermediates for each leaving group MXYZ.

The reaction of $Me_3Ge\text{-}C{\equiv}C\text{-}SiMe_3$ with one equivalent of $MeSO_3H$ was too fast to be measured accurately by our NMR spectroscopy method. The reaction was complete in less than 150 seconds, i.e. the time typically required to record the first spectrum of the reaction. From this time of reaction completion, it is reasonable to assume a half time between 10 and 40 seconds. Thus according to Eq. 3-2, the rate constant would be between 2 and 0.5 $M^{-1}s^{-1}$, respectively. This assumption leads, therefore, to a relative rate constant difference with the $Me_3Si\text{-}C{\equiv}C\text{-}SiMe_3$ from 2.6×10^3 to 6.6×10^2 in magnitude (Table 3-1; entry 10). Experiments carried out with CF_3COOH (Graphs 3-2 and 3-3) relate more accurately the rate constants of both compounds (entries

8 and 9). The difference in the rate constant of 5.2×10^2 in magnitude is in agreement with the previous assumption.

A comparison of the rate constants between the reactions of Ph_3Sn-C≡C-$SiMe_3$ (entry 7) and Me_3Ge-C≡C-$SiMe_3$ (entry 8) with CF_3COOH shows a difference of 5.7×10^2 in magnitude. Moreover, the difference of the rate constants between the reactions of *n*-Bu_3Sn-C≡C-$SiMe_3$ (entry 4) and Ph_3Sn-C≡C-$SiMe_3$ (entry 5) with $Cl_2CHCOOH$ has a magnitude of 1.7×10^2. We assume that the difference in the rate constants observed for the reaction of Ph_3Sn-C≡C-$SiMe_3$ with different acids depends largely on the pKa of each acid (entries 5,6 and 7). Then, the difference in the relative rate constants between the reaction of *n*-Bu_3Sn-C≡C-$SiMe_3$ with $Cl_2CHCOOH$ and Me_3Ge-C≡C-$SiMe_3$ with CF_3COOH is of the order 9.7×10^4. We have also obtained a difference of 2.8 in the rate constants between the reaction of Me_3Sn-C≡C-$SiMe_3$ (entry 1) and *n*-Bu_3Sn-C≡C-$SiMe_3$ (entry 3) with $ClCH_2COOH$. Therefore, Me_3Sn-C≡C-$SiMe_3$ has a relative rate constant larger in magnitude by 2.7×10^5 than Me_3Ge-C≡C-$SiMe_3$ and 1.4×10^8 larger than Me_3Si-C≡C-$SiMe_3$.

From these analyses, we found that the Me_3Sn group (entry 1) provides a relative rate acceleration in the approach to the transition state of the reaction approximately 10^5 and 10^8 greater in magnitude than the Me_3Ge group (entry 8) and Me_3Si group (entries 9 and 10), respectively. We propose that these large differences in the relative rate constants are provided by the stronger β-effect of the Me_3Sn group on the developing vinyl cation intermediate. It is interesting to note that the relative difference of magnitude in the β-effect of 5×10^2 to 10^3 between Me_3Ge and Me_3Si groups is larger than those found in saturated carbonium ions by a solvolysis[64] and hydride extraction[63,77].

As expected, the change of methyl (entry 1) substituents to phenyl (entry 5) groups on tin decreased the relative magnitude of the β-effect on the vinyl cation intermediate by more than 480 times. This result is due to the higher electronegativity of the phenyl compared to the methyl substituent[79,80,82]. Comparable studies on allylstannanes (Scheme 1-2.) has shown a decrease in the magnitude of the β-effect of 100-fold[79]. However, the difference of 2.8 in the rate constants between the $Me_3Sn\text{-}C{\equiv}C\text{-}SiMe_3$ (entry 1) and $n\text{-}Bu_3Sn\text{-}C{\equiv}C\text{-}SiMe_3$ (entry 3) compounds is unexpected. The results show the Me_3Sn to have a better β-effect than the $n\text{-}Bu_3Sn$ group. A similar result was obtained by Cochran and co-workers[85] on the protonation studies of trimethyl and triethylstannyl allenes (Table 1-4, Scheme 1-25). We believe that this result has to be handled with care and will be discussed later.

3.1.3) Mechanism of the Protonation of Triple Bond

A characteristic of the metalated (trimethylsilyl)acetylene compound is that the p orbitals of the π-bond and the carbon-metal σ-bonds are all orthogonal. Thus no stabilizing interaction is possible between the carbon-metal σ-bonds and the π system in the ground state[108]. It has been demonstrated[63-67] that the magnitude of the β-effect of a C-M bond on a β electron-deficient carbon center is geometrically dependent: a dihedral angle of 180° leads to a maximum magnitude whereas a dihedral angle of 90° leads to a minimum. In a rigid linear acetylenic compound, therefore, the β-effect of a C-M bond has no control on the protonation step. We must examine the mechanism of the electrophilic addition on the acetylenic compound to understand how the β-effect of the C-M bond occurs in the control of the reaction.

The reaction of alkynes with electrophilic reagents, especially protons, has been described by several groups[1,14,84,109,110]. Noyce and Schiavelli[110] have shown that the acid-catalyzed hydration (H_2SO_4/H_2O) of phenylacetylene involves the formation of a benzylic vinyl cation intermediate which reacts afterwards with water to give the enol of acetophenone. The solvent isotope effect k_{H2O}/k_{D2O} of 2 suggested that the proton was largely transferred from the solution to the terminal carbon in the rate-determining step. Furthermore, hydration of phenylacetylene-*d* (Ph-C≡C-D) was slower than phenylacetylene. The secondary isotope effect k_H/k_D of 1.1 in the hydration reaction was unexpected: rehybridization of the terminal carbon atom (from sp to sp^2) is predicted by an α-secondary isotope effect to be less than unity[111]. Hyperconjugative interaction (β-secondary isotope effect), in the transition state, of the isotopically C-H bond with the developing empty p orbital was proposed to explain this effect (Figure 3-1). The combination of these two effects gave the positive secondary isotopic effect. It was also observed that the secondary isotopic effect k_H/k_D for 4-ethynyl-*d*-anisol was closer to unity (1.07), showing that the hyperconjugative effect decreases as the degree of carbonium ion character decreases.

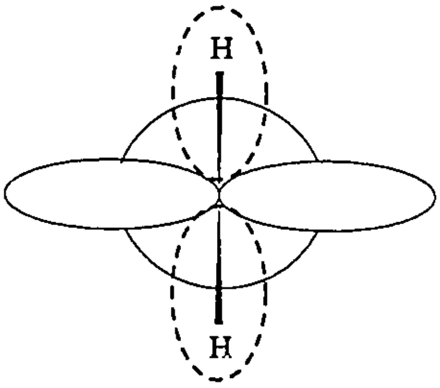


Figure 3-1: Hyperconjugative Overlaps in the Vinyl Cation Transition State

Melloni and co-workers have reported an extensive study on the reactivities of carbon-carbon multiple bonds toward electrophiles[14]. They suggested, in accord with other work, that the mechanism of the proton addition to alkyne proceeds via rate-limiting protonation of the triple bond and that the transition state of the reaction resembles a vinyl cation intermediate.

Eaborn and co-workers have used the same mechanism to describe the protiodegermylation reaction of (phenylethynyl)triethylgermanes 94 in aqueous methanolic solution (Scheme 1-24)[84]. Upon protonation, rehybridization of the carbon atom (sp to sp^2) bends the C-Ge bond and allows hyperconjugative overlap with the empty p orbital (β-effect) to take place in the transition state. The vinyl cation intermediate loses the triethylgermyl group, in nucleophilic attack by the solvent on germanium, faster than its hydrolysis. In this experiment, the magnitude of the β-effect depends also on the ability of the substituents on the phenyl ring to delocalize, in the transition state, a relative amount of positive charge from the carbonium ion center.

These studies have shown that the protonation step is controlled by inductive and hyperconjugative stabilization cooperatively. The mechanism proposed does not involve a vertical stabilization process but a non-vertical process due to the nuclear movement and the change of geometry in the approach of the transition state[62]. However, the β-effect on the developing carbonium ion is still relevant. We are using the same kinetic mechanism to explain our results (Table 3-1).

The electron density of the π bonds of the alkyne is greatest between the two carbon centers. Stereoelectronic considerations suggest that the most favorable approach for the electrophile is in the electron-rich regions, that is, perpendicular to the axis of the σ bonds. For the unsymmetrical alkynes, the electron density between the two carbon centers is not necessarily shared equally. Nevertheless, it is proposed that upon electrophilic addition, particularly on protonation, the alkyne bends slightly from its linear geometry[1].

In our metalated (trimethylsilyl)acetylene model (Scheme 2-1), upon protonation, the bending of the carbon-metal bonds leads to a competitive β-effect between the trimethylsilyl and the other metalated group. The most stabilizing group (stronger β-effect) gets a better overlap with the deficient-electron center in the transition state. Then, the rate of reaction is a measure of the magnitude of the activating β-effect in the protonation step to reach the transition state. Since the inductive effect of silicon, germanium and tin is almost similar[71-73], the regiocontrol of protonation is largely done by the β-effect.

It is worthwhile emphasizing here that the mechanism of the reaction controlled by the bending of the most stabilizing metalated group (stronger β-effect) leads to the thermodynamic vinyl cation intermediate and thus to the thermodynamic products (Scheme 2-1). The measure of the magnitude of β-effect on the vinyl cation intermediate for a metalated group cannot be done since this intermediate is not detectable. Therefore, we assume that the rate of reaction which is a measure of the magnitude of the activating β-effect to reach the transition state, reflects also a relative magnitude of the β-effect on vinyl cation intermediate for a metalated group. This assumption holds as long as the β-effect largely controls the rate-determining step. The important participation of any other effect in the control of the protonation step will give an incorrect value of the relative magnitude of β-effect for the metalated group on the vinyl cation intermediate. Moreover, any change in the mechanism of the reaction might lead to the kinetic products.

3.1.4) Effect of Alkyl Substitution on Tin

Mayr and co-workers have demonstrated that the larger alkyl group substituents (better electron-donating ability) on silicon atom increase the magnitude of the β-effect on a carbonium ion compared to the methyl group[82,83] (Scheme 1-23; Table 1-3). However, Cochran, Kuivila and co-workers have shown the reverse trend in the protiodestannylation of allyl[79], vinyl[87] and allenyl[85] tin compounds (Scheme 1-25; Table 1-5). The effect of alkyl substitution on tin in order of decreasing reactivity is Me > Et > *n*-Pr ≈ *n*-Bu. In the protiodestannylation of trialkylstannyl allenes, which involve the formation of vinyl cation intermediates <u>95</u> and <u>96</u>, the methyl substituents showed an increase of 2.46-fold (partial reaction rate for a S_E2 process) compared to the ethyl substituents. We have obtained the same trend: the substitution of methyl groups (Table 3-1; entry 1) by *n*-butyl groups (entry 3) in trialkylstannyl (trimethylsilyl)acetylene decreases the rate constant by 2.8-fold.

In contrast to (trialkylstannyl)(trimethylsilyl)acetylene, trialkylstannyl allene has C-Sn bond coplanar with a π orbital in its ground state. However, higher reactivity in this case is also obtained with the methyl subtituent on tin compared to the larger ethyl groups (Table 1-5). Moreover, a greater partial rate constant is obtained for the S_E2 mechanism (orthogonal position between C-Sn bond and the π orbital in the ground state) with the Me_3Sn group compared to the S_E2' mechanism (optimal position of the C-Sn bond and the π orbital). This result is unexpected given the geometrical dependence of the β-effect[64-66]. Baekelmans and co-workers[112] have explained this effect by suggesting that solvation of the leaving tin atom is required to stabilize the transition state. The larger alkyl substituents on tin spatially hinder stabilization of the transition state by the solvent. An increased hindrance in the approach of the electrophile was also proposed.

In our experiment, we used a non-polar aprotic solvent ($CDCl_3$). While the stabilization of the polar transition state by solvation with the chloroform-*d* might not be negligible, nucleophilic interaction with the acid or the anion of the acid should be more effective. From the result of Beakelmans and co-workers[112] and our results we propose an open transition state of the developing vinyl cation ion having the structure shown in the Figure 3-2; the protonation step occurs concomitantly with a nucleophilic interaction between the counterion and the tin atom of the stannyl group. Such a nucleophilic effect should increase the stabilization of the transition state and, therefore, increase the reaction rate.

The magnitude of this nucleophilic interaction should also depend on the steric hindrance and the electron-donating ability from the substituents on the tin atom. For a series of alkyl substituents where the electron-donating abilities are quite similar, the magnitude of the nucleophilic interaction depends on their bulkiness. The *n*-butyl substituent might, therefore, destabilize the transition state compared to the methyl substituent (Table 1-1, entries 1 and 3) by decreasing the magnitude of the nucleophilic interaction. However, the magnitude of the nucleophilic effect in the rate-determining step is negligible compared to the magnitude of the β-stabilization of the C-Sn bond.

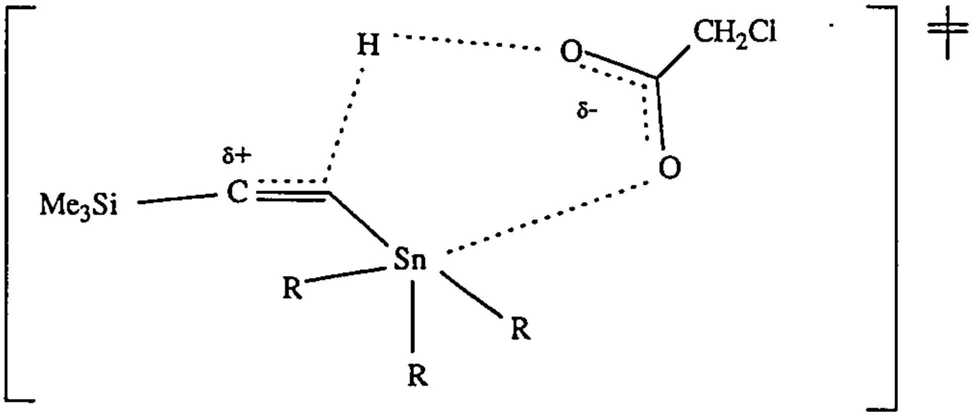


Figure 3-2: Open Transition State of the Developing Vinyl Cation Ion

The large difference of 5.2×10^2 in the rate constant found between the reaction of $Me_3Ge-C\equiv C-SiMe_3$ and $Me_3Si-C\equiv C-SiMe_3$ in high concentrations of CF_3COOH (Table 3-1, entries 8 and 9) might suggest the possibility of a similar transition state. The germanium atom is slightly more electropositive[71,72] and has a better ability to expand its coordination sphere* compared to the silicon atom[113,114]. Therefore, the difference in the rate constant could have been increased by a stabilizing nucleophilic interaction with the Me_3Ge group in the transition state. However, the magnitude of the nucleophilic interaction between CF_3COOH and the Me_3Ge group must be small compared to that between $ClCH_2COOH$ and the Me_3Sn group.

* There are few comparative studies on the ability of germanium and silicon atoms to expand their coordination sphere. However, Tandura and co-workers suggested that although germanium atom differs only slightly from silicon atom in its chemical and physical properties, there is an increasing tendency down the column of Group 14 elements for the stabilization of a trigonal-bipyramidal intermediate relative to the tetrahedral species[113].

3.2) The β-Effect Versus the α-Effect on Vinyl Cation Ions

We have studied, as described in the first section, some metalated (trimethylsilyl)acetylene compounds where the proton addition to the triple bond was controlled largely by the β-effect of one metalated group, either a stannyl, germyl or silyl group, on the developing vinyl cation intermediate. We could thus compare by competition the magnitude of the β-effect on vinyl cation species for those elements relative to the internal trimethylsilyl group as well as the effect of the substituents borne on the element. We will now study the competitive proton addition on silylated (trimethylsilyl) acetylene compounds in which only the substituents borne by one silicon atom change.

3.2.1) Results

The disilylated acetylene compounds showed low degrees of reactivity compared to the previous metalated (trimethylsilyl)acetylene compounds (Table 3-1). Therefore, strong acids were used in order to obtain a reaction with a 0.05 M solution of acetylene in chloroform-*d* ($CDCl_3$) (Table 3-2).

For all compounds studied, the trimethylsilyl group was always the unique leaving group (trimethylsilyl trifluoromethanesulfonate, TMSOTf= 0.50ppm; trimethylsilyl methanesulfonate, TMSOMs= 0.43ppm) to afford the metalated acetylene compound <u>138</u> (Scheme 2-1). However, the addition of one equivalent or trifluoromethanesulfonic acid (triflic acid= CF_3SO_3H) to the (chlorodimethylsilyl)(trimethylsilyl)acetylene ($ClMe_2Si\text{-}C{\equiv}C\text{-}SiMe_3$ 0.05M in $CDCl_3$;

Table 3-2, entry 6) affords two acetylenes ($Me_2XSi\text{-}C\equiv C\text{-}\underline{H}$= 2.62 and 2.73ppm). We propose that $Me_2ClSi\text{-}C\equiv C\text{-}H$ (probably at 2.62ppm) is formed by protiodesilylation reaction whereas $Me_2(TfO)Si\text{-}C\equiv C\text{-}H$ might result from a ligand exchange between the chloride atom and the acid counterion.

Due to its low solubility in $CDCl_3$, triflic acid was used neat (0.025mmol). Although no reaction rate was measured with this acid, the relative magnitude of reactivity of silylated (trimethylsilyl)acetylenes with triflic acid, as estimated by ^1H NMR spectroscopy, are shown in decreasing order in the Table 3-2 (entries 1,4,6,7).

Table 3-2: Reaction of $Me_3Si\text{-}C\equiv C\text{-}SiXYZ$ 0.05M in $CDCl_3$[@] with Different Acids

$$\text{TMS-C}\equiv\text{C-SiXYZ} \xrightarrow{+H^+} \text{H-C}\equiv\text{C-SiXYZ}$$

Entries	SiXYZ	Acid*	pKa#	$k \times 10^4\ sec^{-1}M^{-1}$	r
1	$t\text{-}BuMe_2Si$	CF_3SO_3H	~ -7		
2	$t\text{-}BuMe_2Si$	CH_3SO_3H	~ -2	$9.6 \pm .7^{\epsilon}$	.9997
3	Me_3Si	CH_3SO_3H	~ -2	$7.6 \pm .9^{\epsilon}$	.9935
4	Ph_3Si	CF_3SO_3H	~ -7		
5	Ph_3Si	CH_3SO_3H	~ -2	$0.32 \pm .07^{\epsilon}$	.9686
6	$ClMe_2Si$[&]	CF_3SO_3H	~ -7		
7	Cl_3Si	CF_3SO_3H	~ -7		

@ The reaction was followed with ^1H NMR AC200 Bruker spectrometer

* The CH_3SO_3H is added as a solution in $CDCl_3$ to the NMR tube whereas the CF_3SO_3H is added neat

\# Approximate pKa in water

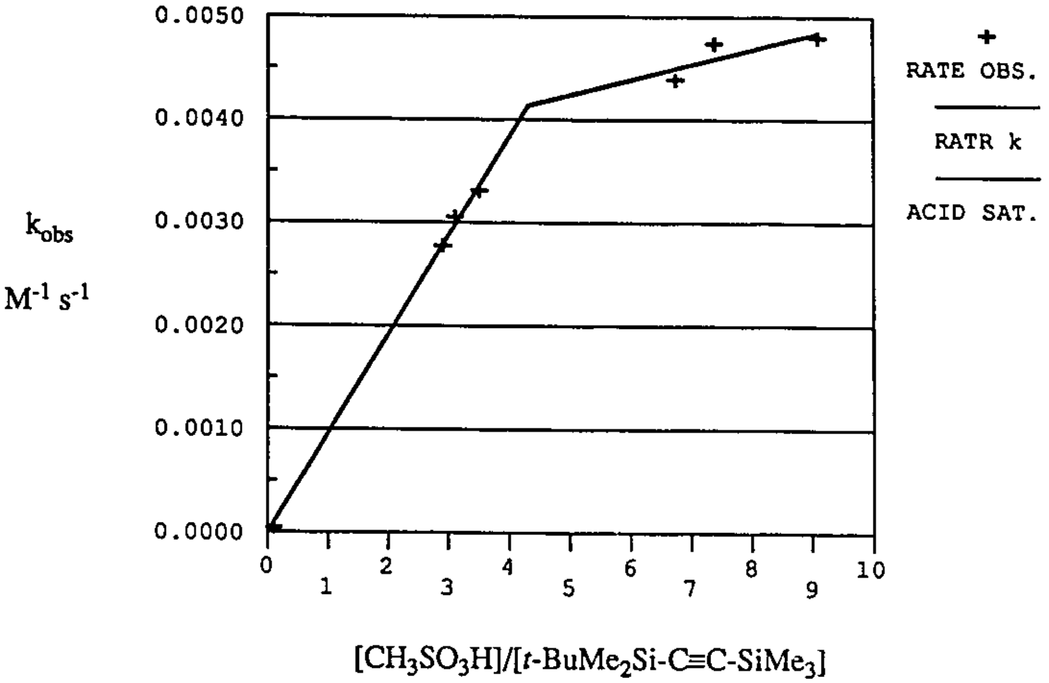
& Formation of two acetylenes, but no $Me_3Si\text{-}C\equiv C\text{-}H$ was detected

ϵ The second-order rate constant is estimated for a 0.05M CH_3SO_3H solution in $CDCl_3$

The (chlorodimethylsilyl)(trimethylsilyl)acetylene ($ClMe_2Si\text{-}C\equiv C\text{-}SiMe_3$) and the (trichlorosilyl)(trimethylsilyl)acetylene ($Cl_3Si\text{-}C\equiv C\text{-}SiMe_3$) showed little reaction with methanesulfonic acid (CH_3SO_3H) even at high concentration of the acid in the solution. The other silylated (trimethylsilyl)acetylenes (Table 3-2; entries 2, 3 and 5) react very slowly with one equivalent of methanesulfonic acid (0.05M solution of CH_3SO_3H in $CDCl_3$). In order to determine the rate constant of the reaction, these compounds were reacted with several high concentration of the acid. The reactions are of second-order and the standard deviations, obtained from a least-squares program, were generally less than 5% of the rate constants observed (Appendix 2). Error on the rate constants was estimated by a systematical 5% error in addition to the standard deviation.

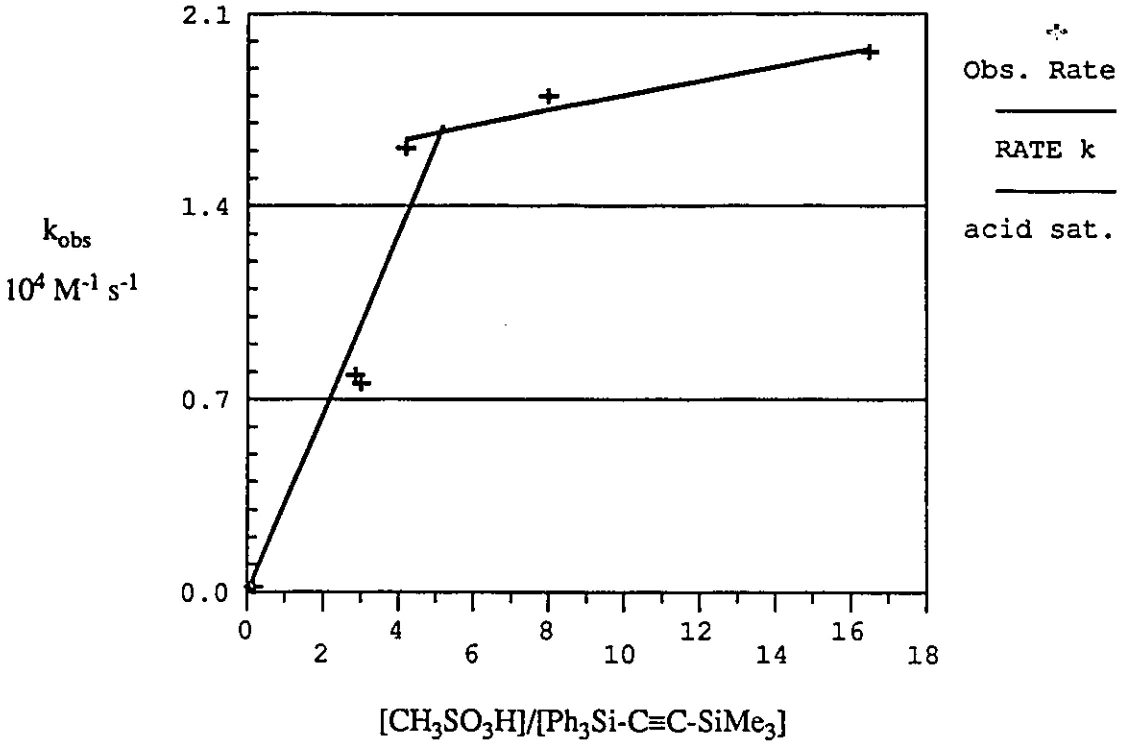
We have demonstrated previously for the reaction between the (trimethylgermyl)(trimethylsilyl)acetylene ($Me_3Ge\text{-}C{\equiv}C\text{-}SiMe_3$) and trifluoroacetic acid (CF_3COOH) that there is a linear relationship between the rate constant observed (k_{obs}) and the concentration ratio [acid]/[acetylene] (Graph 3-2). Therefore, the rate constants observed for the reaction of CH_3SO_3H with the (*t*-butyldimethylsilyl)(trimethylsilyl)acetylene (*t*-$BuMe_2Si\text{-}C{\equiv}C\text{-}SiMe_3$; Graph 3-4), (triphenylsilyl)(trimethylsilyl)acetylene ($Ph_3Si\text{-}C{\equiv}C\text{-}SiMe_3$; Graph 3-5) and bis(trimethylsilyl)acetylene ($Me_3Si\text{-}C{\equiv}C\text{-}SiMe_3$; Graph 3-6) were plotted. These plots show that the rate constants observed are not all in a straight line. However, the data for *t*-$BuMe_2Si\text{-}C{\equiv}C\text{-}SiMe_3$ (Graph 3-4) and $Ph_3Si\text{-}C{\equiv}C\text{-}SiMe_3$ (Graph 3-5) were treated in two parts, both by least squares fitting to a linear expression. The slopes obtained have in both cases a break which occurs around 4.2 to 5.2 equivalent of $[MeSO_3H]/[acetylene]$ (0.21 M to 0.26 M).

Graph 3-4: Linear Relationship Between the Rate Constants Observed and the [$MeSO_3H$]/[*t*-$BuMe_2Si$-C≡C-$SiMe_3$] Ratio



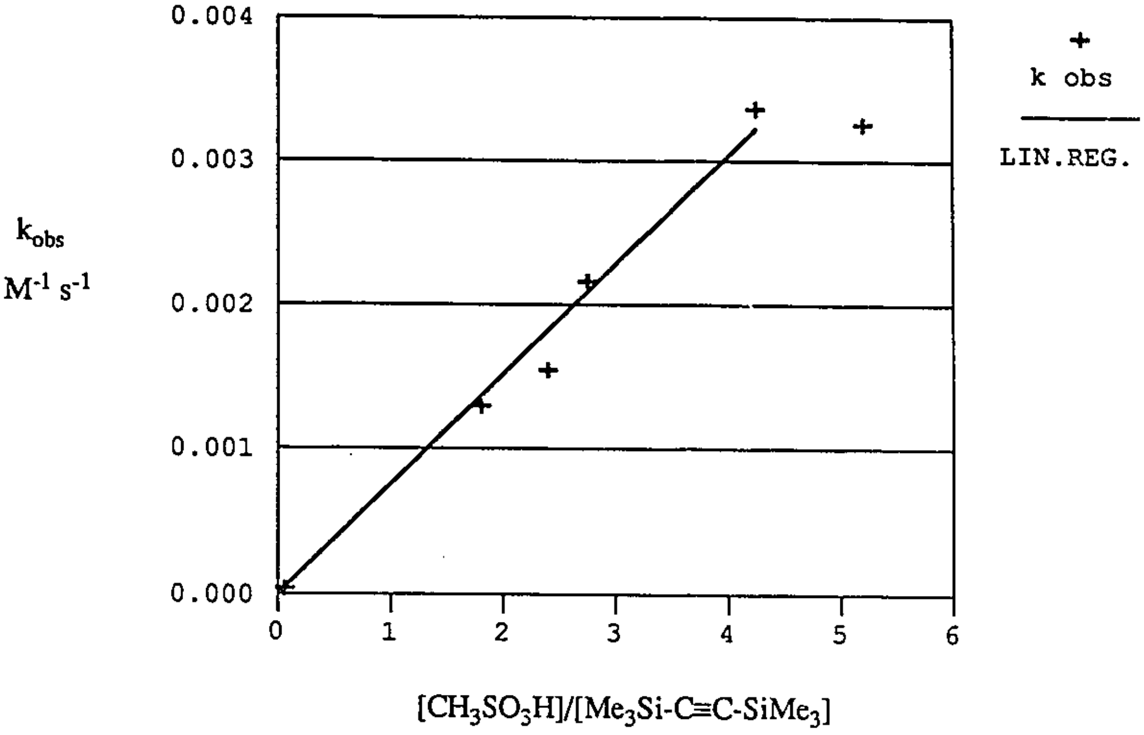
Titrimetric analysis of saturated methanesulfonic acid in $CDCl_3$ solution gives a saturation concentration of 0.27M ([$MeSO_3H$]/[acetylene]= 5.4). This concentration coincides well with the area where the break occurs in the slope. Therefore, the insolubility of $MeSO_3H$ in $CDCl_3$ can explain the slow increase of the rate constant observed with the increase of [$MeSO_3H$]/[acetylene] ratio. The rate constant of the reaction with CH_3SO_3H (0.05M in $CDCl_3$) is thus obtained from the slope of the first linear expression.

Graph 3-5: Linear Relationship Between the Rate Constants Observed and the [MeSO$_3$H]/[Ph$_3$Si-C≡C-SiMe$_3$] Ratio



The rate constants observed for the reaction of CH$_3$SO$_3$H with Me$_3$Si-C≡C-SiMe$_3$ (Graph 3-6) were also treated by least squares fitting to a linear expression. In this case, one rate constant observed was discarded due to experimental error (see Experimental section). The rate constant observed at [MeSO$_3$H]/[Me$_3$Si-C≡C-SiMe$_3$]= 5.2 (0.26M CH$_3$SO$_3$H in CDCl$_3$) was considered to be at the saturated area.

Graph 3-6: Linear Relationship Between the Rate Constants Observed and the [$MeSO_3H$]/[Me_3Si-C≡C-$SiMe_3$] Ratio



In addition to the compounds listed in the Table 3-2, we have also examined [bis(dimethylamino)methylsilyl](trimethylsilyl)acetylene ($(Me_2N)_2MeSi$-C≡C-$SiMe_3$, [tris(trimethylamino)silyl](trimethylsilyl)acetylene ($(Me_2N)_3Si$-C≡C-$SiMe_3$, (dimethoxymethylsilyl)(trimethylsilyl)acetylene ($(MeO)_2MeSi$-C≡C-$SiMe_3$ and (methoxydimethylsilyl)(trimethylsilyl)acetylene ($(MeO)Me_2Si$-C≡C-$SiMe_3$. For these compounds, the amino or methoxy groups underwent protonation followed by competitive nucleophilic substition with the acid counterion. Therefore, no information could be obtained about the stabilization of a vinyl cation.

3.2.2) The Effect of the Substituents Borne on the Silicon

For all compounds listed in Table 3-2, following acid addition, the trimethylsilyl group is always the leaving group. Therefore, no information about the magnitude of the β-effect of these groups on vinyl cation species can be obtained. However, we can look at the effect of the substituents on the silylated groups SiXYZ compared to the internal reference trimethylsilyl group for each compound.

The exchange of methyl groups by other substituents with higher electronegativity like phenyl (entries 4 and 5) or chloride (entries 6 and 7) decreases the ability of these silyl groups to compete with the trimethylsilyl group in the internal stabilization by the β-effect on the developing vinyl cation intermediate. These results are in agreement with the previous studies[80,82,83]. The exchange of a methyl group by the larger *t*-butyl group (better electron-donating ability) led also to the loss of Me_3Si group (entries 1 and 2). From the study of Mayr and Hagen[82,83] on allyl silanes, the larger alkyl substituents on the silicon atom enhance the reactivity (better β-effect) compare to the methyl substituents (Scheme 1-23, Table 1-4). However, the difference of the relative rate constants between the *t*-$BuMe_2Si$ group and the Me_3Si group is negligible (Table 1-4; k_{rel} *t*-$BuMe_2Si/Me_3Si$ of 1.04).

On the other hand, this result shows the same ligand effect on the magnitude of the β-effect as our previous results between $Me_3Sn\text{-}C{\equiv}C\text{-}SiMe_3$ and *n*-$Bu_3Sn\text{-}C{\equiv}C\text{-}SiMe_3$ (Table 3-1; entries 1 and 3). This result might also be explained by a nucleophilic assistance on the less hindered trimethylsilyl group (Figure 3-2) although the interaction between a silyl group with $CH_3SO_3^-$ or $CF_3SO_3^-$ should be negligible compared to a stannyl group with $ClCH_2COO^-$.

3.2.3) The α-Effect Versus the β-Effect

The kinetic results obtained for the protonation of the silylated (trimethylsilyl)acetylene compounds (Table 3-2) show that the protonation step is not largely controlled by the β-effect of the leaving trimethylsilyl group; otherwise the reaction rate would be similar for all of them. Therefore, other effects becomes more important in the mechanism of the reaction.

Nucleophilic interaction between the acid counterion and the silicon atom of the trimethylsilyl group does not explain these results. In fact, based on the substituent electronegativities or on the tendency of silicon compounds to expand the coordination sphere of the silicon atom, the trimethylsilyl group should not have more ability to interact with the acid counterion compared to the trichlorosilyl, dimethylchlorosilyl and triphenylsilyl groups[113,115].

In contrast to the first series of metalated (trimethylsilyl)acetylene compounds (Table 3-1) where there was a constant α-trimethylsilyl substituent in the vinyl cation intermediate (135; Scheme 2-1), we have now different silylated groups SiXYZ as α-subtituent (136; Scheme 2-1). The stability of a vinyl cation ion depends first of all on the magnitude of the inductive effect from the α-substituent. The reactivity of the silylated (trimethylsilyl)acetylene compounds shown in the Table 3-2 decreases with the order of the inductive ability (α-effect) provided by the silylated groups SiXYZ. The high electronegativity of the substituents borne on the silicon atom decreases the α-effect of the silylated groups and thus reduces the reactivity of the triple bond (basicity) towards protonation. On the other hand, the larger *t*-butyl group with a better electron-donating ability than the methyl group increases both the α-effect of the silylated group and the reactivity of the triple bond.

A comparison of the rate constants for *t*-BuMe$_2$Si-C≡C-SiMe$_3$ (Table 3-2; entry 2), Me$_3$Si-C≡C-SiMe$_3$ (entry 3) and Ph$_3$Si-C≡C-SiMe$_3$ (entry 5) reveals that *t*-BuMe$_2$Si and the Me$_3$Si groups have an α-effect 30 and 24 times stronger than Ph$_3$Si group respectively. These ratios are consistent with the work of Soderquist and Hasser on saturated carbonium ions which shows a difference of 30 between the Me$_3$Si and Ph$_3$Si groups[48] (Scheme 1-13).

The *t*-BuMe$_2$Si-C≡C-SiMe$_3$ (entry 2) has a rate constant larger in magnitude than Me$_3$Si-C≡C-SiMe$_3$ (entry 3) by a factor of 1.3. Since the difference of the relative magnitude of the β-effect between the *t*-BuMe$_2$Si and Me$_3$Si groups on a carbonium ion is small, this larger rate constant difference shows that the activating α-effect of the *t*-BuMe$_2$Si group on the developing vinyl cation ion is more predominant in the rate determining step than the activating β-effect of both silyl groups.

3.3) Parallel Competitive Reactions with the (Triphenylgermyl)(trimethylsilyl)acetylene

We have seen in the first section that the rate-determining step for the protonation of metalated (trimethylsilyl)acetylene (Table 3-1) was largely controlled by the strongest β-effect of one metalated group. However, the rate-determining step for the protonation of silylated (trimethylsilyl)acetylene (Table 3-2) was controlled by a stabilization provided by the β-effect, α-effect and the inductive effects of both silylated groups on the developing vinyl cation. In this section, we have the interesting possibility of studying the competition between these effects and nucleophilic effects on the developing vinyl cation.

3.3.1) Results

(Triphenylgermyl)(trimethylsilyl)acetylene ($Ph_3Ge\text{-}C\equiv C\text{-}SiMe_3$) is the only dimetalated acetylene studied which showed the production of both possible monometalated acetylenes <u>137</u> and <u>138</u> (Scheme 2-1). The formation of (trimethylsilyl)acetylene ($Me_3Si\text{-}C\equiv C\text{-}H$; 2.39 and 0.21 ppm) is favored over (triphenylgermyl)acetylene ($Ph_3Ge\text{-}C\equiv C\text{-}H$; 2.66 ppm) upon proton addition (Table 3-3).

The reaction of $Ph_3Ge\text{-}C\equiv C\text{-}SiMe_3$ (0.05M in $CDCl_3$) with one equivalent of triflic acid (CF_3SO_3H; entry 1) was not reproducible and different $[Ph_3Ge\text{-}C\equiv C\text{-}H]/[Me_3Si\text{-}C\equiv C\text{-}H]$ ratios were obtained which always favor the loss of the triphenylgermyl group (Ph_3Ge) compared to the trimethylsilyl group (Me_3Si). These different results might be due from the high hygroscopicity of this acid which must be handled carefully under a dry and inert atmosphere or from some other impurties.

Ph_3Ge-C≡C-$SiMe_3$ reacts slowly with one equivalent of methanesulfonic acid ($MeSO_3H$) (Table 3-3; entry 2) to produce a [Ph_3Ge-C≡C-H]/[Me_3Si-C≡C-H] ratio of approximately 1/2. An increase in the concentration of CH_3SO_3H decreases the relative quantity of Ph_3Ge-C≡C-H formed compared to Me_3Si-C≡C-H (entries 2, 3 and 4). The Ph_3Ge-C≡C-$SiMe_3$ reacts slowly with 10 equivalents of trifluoroacetic acid to produce (trimethylsilyl)acetylene as the unique acetylenic compound (entry 5).

Table 3-3: Formation of H-C≡C-MXYZ Mixture in the Reaction of Ph_3Ge-C≡C-$SiMe_3$$^{@}$ 0.05 M in $CDCl_3$ with Acids*.

Entries	[Acid]/[acetylene]	MXYZ	Ratio
1	1 eq. TfOH$^{\#}$	Ph_3Ge/Me_3Si	1/3$^{\&}$
2	1 eq. CH_3SO_3H	Ph_3Ge/Me_3Si	1/2
3	2.65 eq. CH_3SO_3H	Ph_3Ge/Me_3Si	1/3
4	CH_3SO_3H sat.	Ph_3Ge/Me_3Si	1/5
5	10 eq. CF_3COOH	Ph_3Ge/Me_3Si	0/1

@ Ph_3Ge-C≡C-$SiMe_3$ 0.05M solution in $CDCl_3$.
* The acids are added in different concentrations.
# TfOH is added neat.
& This ratio for the reaction with triflic acid was not reproducible. In fact, the ratios obtained with this acid change from 1/9 to 1/3. We believe that the presence of water in the acid altered the reaction in favor of the loss of Ph_3Ge group due to nucleophilic assistance.

The reaction of Ph_3Ge-C≡C-$SiMe_3$ with 2.65 equivalents of CH_3SO_3H (entry 3), with CH_3SO_3H at saturation in $CDCl_3$ solution (entry 4) and with 10 equivalents of CF_3COOH (0.50M; entry 5) followed the second order kinetics (Table A.2-24 and Table A.2-25). On the other hand, the competitive reaction of this compound for the loss of the Ph_3Ge group with 1 equivalent of CH_3SO_3H (entry 2) did not followed the second order kinetics (Eq. 3-1). The partial rate constant for the reaction of Ph_3Ge-C≡C-$SiMe_3$ with one equivalent of CH_3SO_3H in $CDCl_3$ solution could not be evaluated. However, from the relative reaction rates, as estimated by ^1H NMR spectroscopy, this compound has a lower reactivity than (trimethylgermyl)(trimethylsilyl)acetylene (Me_3Ge-C≡C-$SiMe_3$; Table 3-1, entry 8) but has a higher reactivity than (*t*-butyldimethylsilyl)(trimethylsilyl)acetylene (*t*-$BuMe_2Si$-C≡C-$SiMe_3$; Table 3-2, entry 2).

3.3.2) The β-Effect Versus the α-Effect

The product ratios obtained in the reaction of Ph_3Ge-C≡C-$SiMe_3$ with acid (Table 3-3; entries 1 and 2) are best analyzed by first considering the β-effect and the α-effect of the triphenylgermyl and trimethylsilyl groups on carbonium ion stability. These effects are predominant in the mechanism of the protonation step. However, other possible effects will be considered later in this section.

From the hydrolyses of α-metalated methylvinyl ethers (Scheme 1-13), Soderquist and Hassner[48] have shown that the relative difference of the α-effect between Me_3Ge and Me_3Si was 2.4 in magnitude. Moreover, the substitution of methyl groups by phenyl groups on the silicon atom reduced by a factor of 30 the α-effect on the carbonium ion whereas ours results with vinyl cations have shown a reduction of 24 in magnitude (Table 3-2; entries 3 and 5). A similar reduction in the magnitude of the α-effect should be expected upon change of substituents on germanium atom. Therefore, the α-effect of the Me_3Si and Ph_3Ge groups on vinyl cation intermediates might be of comparable magnitude.

The product ratios obtained from the parallel reactions of Ph_3Ge-C≡C-$SiMe_3$ with one equivalent of CF_3SO_3H or CH_3SO_3H (Table 3-3; entries 1 and 2) give no information about the relative magnitude of the β-effect and the α-effect on the developing vinyl cation intermediate of both Me_3Si and Ph_3Ge groups. The protonation of Ph_3Ge-C≡C-$SiMe_3$ could be controlled by the β-effects and/or the α-effects of the Ph_3Ge and Me_3Si groups. A "change" in the magnitude of the β-effect or the α-effect of the germyl or silyl groups would change the product ratio obtained in the parallel reactions (entries 1 and 2).

We have found previously that the *t*-BuMe$_2$Si group has an α-effect on the developing vinyl cation intermediate 1.3 times larger in magnitude than the α-effect of the Me$_3$Si group whereas the β-effect on carbonium ion of both silyl groups can be considered to be the same[82]. Thus, (triphenylgermyl)(*t*-butyldimethylsilyl)acetylene (Ph$_3$Ge-C≡C-SiMe$_2$*t*-Bu) was protonated with 1 equivalent of TfOH or CH$_3$SO$_3$H, upon the same conditions, to produce the (*t*-butyldimethylsilyl)acetylene (H-C≡C-SiMe$_2$*t*-Bu; 2.36, 0.96 and 0.14 ppm) as unique acetylenic compound and triphenylgermyl triflate or mesylate (Table 3-4). Therefore, the *t*-BuMe$_2$Si group has a much better α-effect on the developing vinyl cation intermediate compared to the Ph$_3$Ge group but no information on the relative magnitude of the β-effect of both groups can be obtained.

Table 3-4: Formation of H-C≡C-SiMe$_2$*t*-Bu in the Reaction of Ph$_3$Ge-C≡C-SiMe$_2$*t*-Bu@ 0.05M with Acids*.

Entries	Acid	MXYZ	Ratio
1	1 eq. TfOH#	Ph$_3$Ge/*t*-BuMe$_2$Si	0/1
2	1 eq. CH$_3$SO$_3$H	Ph$_3$Ge/*t*-BuMe$_2$Si	0/1

@ The reaction was followed with ^{1}H NMR AC200 Bruker spectrometer
# TfOH is added neat.

This last result demonstrates that the Me$_3$Si group might have an α-effect on the developing vinyl cation intermediate comparable in magnitude to the Ph$_3$Ge group. If so, a comparable magnitude of the β-effect on the developing vinyl cation intermediate for both Ph$_3$Ge and Me$_3$Si groups would explain the product ratio obtained in the parallel reaction (entries 1 and 2). However, further experiments need to be done in order to evaluate the order of magnitude of the β-effect on the developing vinyl cation intermediate for both Me$_3$Si and Ph$_3$Ge groups.

This result led us to believe that it is possible to reverse the order of the magnitude of the β-effect for silicon and germanium elements with the change of the substituents borne by them. After completion of our work, Hagen and Mayr[83] reported that the trimethylsilyl group has a slightly better β-effect towards an alkyl carbonium ion than the triphenylgermyl group. This result was obtained by reaction of allylic compounds with diarylcarbonium tetrachloroborate ($Ar_2CH^+BCl_4^-$) of triflate ($CF_3SO_3^-$) ions in dichloromethane (Scheme 1-23).

3.3.3) Ion Strength Effect and Nucleophilic Assistance

The various product ratios obtained in the parallel reactions (Table 3-4) demonstrate that upon protonation of $Ph_3Ge\text{-}C{\equiv}C\text{-}SiMe_3$, the stabilization of the developing vinyl cation ion involves other effects than the β-effects and the α-effects of both Me_3Si and Ph_3Ge groups.

The increase of the ionic strength of the solution increases the reaction rate by the stabilization of the developing vinyl cation ion and should also level the stability of the two possible ions in the transition state. However, the different ratios of the parallel reactions with different acid concentrations (Table 3-3) show that these charged transition states are not stabilized by the same effect.

The increase of the polarity of the solution with the acid concentration of the solution is accompanied by an increase of the nucleophilicity of the chloroform-*d* ($CDCl_3$) solution. Interaction of the acid counterion should be stronger with the germanium atom of the triphenylgermyl group compared to the silicon atom of the trimethylsilyl group[113]. This involvement of nucleophilic assistance in the mechanims of the reaction $Ph_3Ge\text{-}C{\equiv}C\text{-}SiMe_3$ with acid favors the loss of the triphenylgermyl group and the production of (trimethysilyl)acetylene ($Me_3Si\text{-}C{\equiv}C\text{-}H$).

Table 3-3 (entries 2,3 and 4) shows that the increase in the CH_3SO_3H concentration leads to a decrease in the [Ph_3Ge-C≡C-H]/[Me_3Si-C≡C-H] ratio. The reaction of the alkyne with higher concentrations of the weaker acid CF_3COOH (entry 5), the counterion of which is a stronger nucleophile, shows only the production of Me_3Si-C≡C-H and triphenylgermyl trifluoroacetate ($CF_3COOGePh_3$). Therefore, the nucleophilic effect controls the degree of each parallel reactions. The [Ph_3Ge-C≡C-H]/[Me_3Si-C≡C-H] ratio clearly becomes smaller for reactions involving greater nucleophilic assistance in the kinetics of the reaction.

The slow reaction rate obtained with the high concentration of weak acid CF_3COOH (entry 5; for more detail, see Table A.2-25 in Appendix 2) shows that a nucleophilic attack of the acid counterion on the germanium atom of the Ph_3Ge group is not the mechanism of the reaction. This slow reaction rate suggests instead that the proton transfer from the acid to the triple bond is still the rate-determining step which occurs concomitantly with the nucleophilic assistance of the acid counterion to break the C-Ge bond. The transition state should have the similar structure (Figure 3-2) as proposed earlier for the analoguous protiodestannylation of stannyl (trimethylsilyl)acetylenes (Table 3-1).

We have mentioned above the difficulty in reproducing the results of the reaction between the (triphenylgermyl)(trimethylsilyl)acetylene with one equivalent of triflic acid (Table 3-3; entry 1). The different [Ph_3Ge-C≡C-H]/[Me_3Si-C≡C-H] ratios obtained (from 1/9 to 1/3) might be explained by the presence of some impurities in the acid. The possible presence of water in hygroscopic triflic acid would increase the nucleophicility of the $CDCl_3$ solution and thus stabilize the transition state of the reaction. The parallel reaction products would be affected to different degrees depending on the concentration of the water in the $CDCl_3$ solution. The water impurity could also arise from the Ph_3Ge-C≡C-$SiMe_3$ 0.05M $CDCl_3$ solution sample.

3.4) Tetrakis(trimethylsilylacetylide)metaloid Compounds

The tetrakis(trimethylsilylacetylide)metaloid compounds (Table 3-5) have been shown to be symmetric by NMR spectroscopy and X-ray analysis (for details see the Appendix 1 and experiment part, Chapter 4). The interest in these compounds is that all carbon substituents borne by the central element are hybridized sp. Four successive electrophilic addition reactions with these compounds might follow one or many pathways which eventually lead at the end to $(TMS\text{-}C{\equiv}C\text{-})_mM(\text{-}C{\equiv}C\text{-}H)_nL_{4\text{-}n\text{-}m}$, where L is the counterion of the electrophile used. Further addition might lead to the final compound ML_4.

Unfortunately, the kinetic study of these compounds in the protonation reaction was impossible by ^1H NMR spectroscopy. Slow addition of the acid used did not react stoichiometrically and many species were formed in the solution from parallel reactions. However, information about the β-effect and the α-effect on vinyl cation intermediates can be obtained from the products of the reaction. Table 3-5 shows only the major acetylene products obtained from the two first proton addition reactions. To minimize any nucleophilic assistance in the kinetics of the reaction, the compounds were all studied with triflic acid (CF_3SO_3H) (entries 1, 3 and 5).

Table 3-5: Successive Proton Additions to Tetrakis(trimethylsilylacetylide)metaloids 0.05M in $CDCl_3$

$$(TMS\text{-}C{\equiv}C\text{-})_4M \xrightarrow{H^+} H\text{-}C{\equiv}C\text{-}W$$

Entries	M	ACID	W^1	W^2
1	Sn	CF_3SO_3H	Me_3Si	Me_3Si
2	Sn	CF_3COOH	Me_3Si	Me_3Si
3	Ge	CF_3SO_3H	$(TMS\text{-}C{\equiv}C\text{-})_3Ge$	$(TMS\text{-}C{\equiv}C\text{-})_2Ge\text{-}C{\equiv}C\text{-}H$
4	Ge	$MeSO_3H$	$(TMS\text{-}C{\equiv}C\text{-})_3Ge$	$(TMS\text{-}C{\equiv}C\text{-})_2Ge\text{-}C{\equiv}C\text{-}H/Me_3Si$
5	Si	CF_3SO_3H	$(TMS\text{-}C{\equiv}C\text{-})_3Si$	$(TMS\text{-}C{\equiv}C\text{-})_2Si\text{-}C{\equiv}C\text{-}H$
6	Si	$MeSO_3H$	$(TMS\text{-}C{\equiv}C\text{-})_3Si$	$(TMS\text{-}C{\equiv}C\text{-})_2Si\text{-}C{\equiv}C\text{-}H$

W^1= product from the first protonation.

W^2= product from the second protonation.

3.4.1) Tetrakis(trimethylsilylacetylide)stannane

The protonation of tetrakis(trimethylsilylacetylide)stannane, (TMS-C≡C-)$_4$Sn, with triflic acid (Table 3-5; entry 1) led only to the formation of (trimethylsilyl)acetylene (Me$_3$Si-C≡C-H; 0.20 and 2.38 ppm) as a metalated acetylide species. The formation of trimethylsilyltriflate (Me$_3$SiOTf; 0.50 ppm) and acetylene (C_2H_2; 1.90 ppm) occurred after addition of two equivalents of triflic acid, and were the unique products upon addition of an excess of eight equivalents. Similar results were obtained upon addition of trifluoroacetic acid (CF_3COOH) (entry 2).

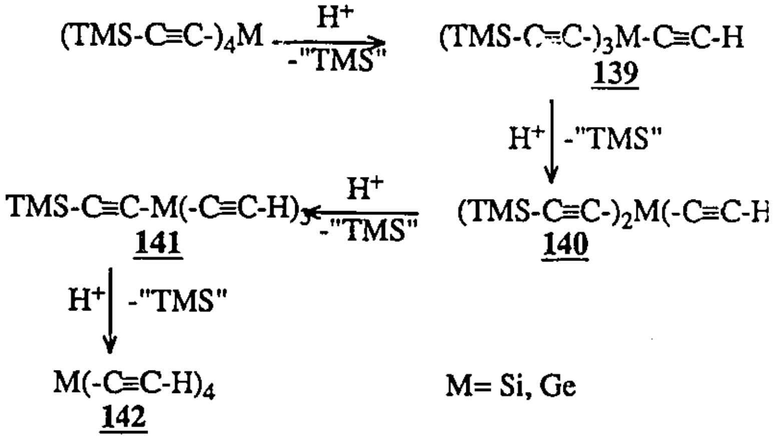
By analogy with the stannyl (trimethylsilyl)acetylene compounds (Table 1-1), the ease of the trimethylsilyl group (Me$_3$Si) loss shows that the (TMS-C≡C-)$_3$Sn group and the theoretical (TMS-C≡C-)$_2$SnL and (TMS-C≡C-)SnL$_2$ groups (L= CF_3SO_3 and CF_3COO) have a larger β-effect on the developing vinyl cation intermediates than a Me$_3$Si group. However, the substitution of (trimethylsilyl)acetylide groups by a second triflate or trifluoroacetate substituents lead to a decreased magnitude of the β-effect of the stannyl moiety, Me$_3$SiOTf and acetylene are produced from the decomposition of the stannyl species (black solution) and/or Me$_3$Si-C≡C-H.

The reactivity of the (TMS-C≡C-)$_4$Sn with CF_3COOH, as estimated by ^{1}H NMR was slower than (triphenylstannyl)(trimethylsilyl)acetylene and faster than (trimethylgermyl)(trimethylsilyl)acetylene (Table 1-1, entries 7 and 8). Therefore, the relative magnitude of the β-effect on vinyl cation intermediates for the (TMS-C≡C-)$_3$Sn group is between the Ph$_3$Sn and the Me$_3$Ge groups, which follows the order of electronegativity of the substituents[80,82,83] borne by the tin atom (Csp^3> Csp^2> Csp). From this trend, the change of a (trimethylsilyl)acetylide group with a triflate or a trifluoroacetate substituents (high electronegativity) is expected to decrease the ability of the stannyl group to stabilize vinyl cations arising from subsequent protonation steps.

3.4.2) Tetrakis(trimethylsilylacetylide)germane

The protonation of the tetrakis(trimethylsilylacetylide)germane with less than one equivalent of triflic acid (Table 3-5, entry 3) gave predominantly trimethylsilyltriflate (0.50 ppm) and many metalated acetylide proton signals (2.45, 2.48, 2.51, 2.54 and 2.55 ppm). With further addition of acid, the ^1H NMR intensity of the metalated acetylide goes from 2.45 ppm to 2.48 and 2.51 ppm after three equivalents of acid, and leads to a major signal at 2.54 ppm after four equivalents accompanied by the formation of acetylene (1.90 ppm). Only a trace of (trimethylsilyl)acetylene (2.38 ppm) and three other signals (2.8-2.7 ppm) are detected. From the ^1H NMR spectra, we suggest that the signals at 2.45, 2.48, 2.51 and 2.54 represent the <u>139</u>, <u>140</u>, <u>141</u> and <u>142</u> germyl compounds (Scheme 3-2).

Scheme 3-2: Competitive Protonation of a Tetrakis(trimethylsilylacetylide)metaloid



The electronegativity of the alkynyl substituent of a trialkynylgermyl group must reduce the ability of the germanium atom to stabilize an α-carbonium ion (α-effect) compared to the triphenylgermyl and the trimethylsilyl groups. Thus this result (entry 3) demonstrates that the trimethylsilyl group has a better β-effect for the developing vinyl cation ion than any other germyl group present in the solution (Scheme 3-2). Therefore, the order of magnitude of the β-effect between silicon and germanium atoms can be reversed by substitution of the three methyl groups on germanium atom by three alkyne groups.

The protonation reaction of the tetrakis(trimethylsilylacetylide)germane with methanesulfonic acid (Table 3-5, entry 4) showed an increase in production of (trimethylsilyl)acetylene in comparison with the previous experiment (entry 3). This result can be explained, as in the case of (triphenylgermyl)(trimethylsilyl)acetylene (Table 3-3), by a nucleophilic effect in the protonation step (Figure 3-2). In fact, the magnitude of the interaction beween the acid counterion and the germanium atom in the transition state must increase with the decrease of hindrance around the germyl group due to the loss of Me_3Si groups.

3.4.3) Tetrakis(trimethylsilylacetylide)silane

The protonation reaction of the tetrakis(trimethylsilylacetylide)silane with triflic acid (Table 3-5, entry 5) led to a clean formation of trimethylsilyltriflate (0.50 ppm) and four acetylide compounds **139**, **140**, **141** and **142** (2.56, 2.59, 2.62 and 2.65 ppm) (Scheme 3-2). After four equivalents of acid, a unique acetylene compound **142** is obtained (2.65 ppm). Similar results are obtained with methanesulfonic acid (entry 6). However, the reaction is very slow and an excess of acid was used. Therefore, trimethylsilyl group has a better β-effect on the developing vinyl cation intermediate than a trialkynylsilyl group.

CONCLUSION

This study on the protonation of metalated (trimethylsilyl)acetylenes has allowed the establishment of the first scale of the relative magnitude of the β-effect on vinyl cation provided by some silyl, germyl and stannyl groups. The order obtained for the elements relative to silicon is Sn> Ge> Si (10^8> 5 × 10^2> 1). The large activating β-effect on the developing vinyl cation ion of 10^8 in magnitude observed for tin compared to silicon agrees with the previous solvolytic study of Lambert and co-workers[64] (Scheme 1-9, Table 1-2) and the dehydrometalation study (Eq. 1-7) of Traylor and co-wokers[77]. However, the relative difference of 500-fold in the activating β-effect between germanium and silicon is larger than reported in previous studies[63,64,77]. This difference might be the real extent of the activating β-effect on the developing vinyl cation ion between both elements or might be due to some of the assumptions used in our study.

We evaluated the relative order of the activating β-effect on the developing vinyl cations for the elements through the rate constants observed for a series of metalated (trimethylsilyl)acetylene with different acids. These acids have different ionic strength and nucleophilicity in $CDCl_3$ solution. These effects for a series of carboxylic acids were consided to be negligible compared to the large magnitude of the β-effect, but they are important for the groups with similar magnitude of the β-effect (Ph_3Ge and Me_3Si, Table 3-3). The nucleophilic effect (Figure 3-1) is more important on the germanium atom (Me_3Ge and Ph_3Ge groups) compared to the silicon atom (Me_3Si group) and, therefore, might increase the relative difference of the observed activating β-effect on the developing vinyl cation.

The results demonstrate that the ligands reduce the magnitude of the activating β-effect on the developing vinyl cation ion for a given metal in the order Cl> Csp> Csp^2> Csp^3, a trend that parallels their relative electronegativity as expected. However, the better activating β-effect of a Me group compares to a larger alkyl group is due to effects other than their of electron-donating ability.

In the internal competitive study upon proton addition to the metalated (trimethylsilyl)acetylene, we have found that some groups have a lower β-effect than the Me_3Si group. We have also demonstrated that it is possible to interchange the order of the β-effect between germanium and silicon with appropriate ligands. For these metalated groups, no further information on the magnitude of the β-effect could be obtained. The relative magnitude of the β-effect on the developing vinyl cation for the series of metalated groups studied follows the order:

Me_3Sn> *n*-Bu_3Sn> Ph_3Sn> (Me_3Si-C≡C-$)_3Sn$> Me_3Ge> Ph_3Ge ≈ Me_3Si ≈ *t*-$BuMe_2Si$> (Me_3Si-C≡C-$)_3Ge$> Ph_3Si> (Me_3Si-C≡C-$)_3Si$> $ClMe_2Si$> Cl_3Si

The compounds in which the Me_3Si group is the leaving group upon protonation showed the importance of the α-effect and the inductive effects of both metalated groups on the basicity of the triple bond. This experiment demonstrated that the relative α-effect on a vinyl cation ion for a series of silyl groups is in the order: *t*-$BuMe_2Si$> Me_3Si> Ph_3Si> $ClMe_2Si$> Cl_3Si, which follows the electron-donating ability of the substituents. The activating α-effect on the developing vinyl cation for the *t*-$BuMe_2Si$, Me_3Si and Ph_3Si groups is of magnitude 30, 24 and 1, respectively.

We believe that this scale of relative magnitude of the β-effect for the vinyl cation by these groups might be an useful tool in organic chemistry and our laboratory is interested in the development of some synthetic applications based on these results.

CHAPTER 4

EXPERIMENTAL METHODS

Abbreviations

m.p.: melting point

b.p.: boiling point

IR: Infrared Spectrometry

- υ: frequency in cm^{-1}
- st: strong intensity
- m: medium intensity
- w: weak intensity

NMR: Nuclear Magnetic Resonance Spectrometry

- δ: chemical shift
- s: singlet
- d: doublet
- t: triplet
- d-d: doublet of doublet
- m: multiplet

MS: Mass Spectrometry

- EI: Electron impact mass spectra
- CI: Chemical ionization mass spectra
- M^+: molecular ion
- HRMS: High Resolution Mass Spectrometry

Kinetic experiment

k: rate constant
k_{obs}: rate constant observed
Int.: relative integretion in NMR spectra
s: second
M: concentration in mol/liter
r^2: root square
r: correlation coefficient
σ: standard deviation on the slop

4.1) Instrumental Techniques

The boiling points (b.p.) obtained by distillation under vacuum are rough estimates only.

^{1}H , ^{13}C NMR spectra were obtained on Bruker AC-200 (200 MHz) and WM-500 (500 MHz) spectrometers. For preliminary quality checks a Varian EM-390 (90 MHz) was used. Spectra were referenced either by TMS signal, residual solvent signal on $CDCl_3$, or by an internal CH_2Cl_2 signal at 5.3 ppm. ^{29}Si, ^{73}Ge, ^{119}Sn and ^{207}Pb NMR spectra were performed on a Bruker WR-250 (250 MHz) spectrometer using the signal of Me_4Si, Me_4Ge, Me_4Sn and Me_4Pb, respectively, as external reference (0 ppm).

Solid state ^{207}Pb NMR spectra were recorded on a Bruker MLS-100 (100 MHz) spectrometer operating without spinning.

Infrared spectra were run on a Perkin-Elmer 283 spectrometer in $CHCl_3$ or CH_2Cl_2 solution, in neat film on a NaCl cell or in KBr pellet.

Electron impact (EI) and chemical ionization (CI) mass spectra were recorded at 70 eV with a source temperature ca. 200°C either on a VG Micromass 7070-F mass spectrometer equipped with a data system comprised of a PDP8A with VG2000 software or a VG analytical ZAB E mass spectrometer equipped with a VG11-250 data system. High resolution mass spectral (HRMS) data were obtained with the VG-ZAB-E instrument by the EI method.

Elemental Analysis were done by Guelph Chemical Laboratories Ltd., Guelph, Ontario, Canada. N1H 1E7.

X-Ray crystal structure analysis was performed by Dr. Christopher H. Frampton and Dr. James F. Britten, McMaster University, Hamilton, Ontario. The data for the structure determination of tetrakis(trimethylsilylacetylide)germane and tetrakis(trimethylsilylacetylide)stannane are presented in Appendix 1.

4.2) Purification of Solvents

All syntheses of compounds were performed under anhydrous conditions. Therefore, the tetrahydrofuran (THF) and diethyl ether were freshly distilled under a nitrogen atmosphere over benzophenone/potassium.

Dichloromethane (CH_2Cl_2) was freshly distilled under a nitrogen atmosphere over calcium hydride (CaH_2) or phosphorus pentaoxide (P_2O_5).

Benzene was distilled under a nitrogen atmosphere over benzophenone/potassium.

4.3) Sources of Materials

The chloroacetic acid ($ClCH_2COOH$), dichloroacetic acid ($Cl_2CHCOOH$), trichloroacetic acid (CCl_3COOH), trifluoroacetic acid (CF_3COOH) and chloroacetic anhydride [$(ClCH_2CO)_2O$], were obtained from Aldrich.

Trifluoromethanesulfonic acid (CF_3SO_3H) and methanesulfonic acid (CH_3SO_3H) were obtained from Aldrich and were used from a fresh bottle without purification.

(Trimethylsilyl)acetylene ($Me_3SiC{\equiv}CH$) was obtained from Aldrich or prepared according to the experimental procedure[116].

Bis(trimethylsilyl)acetylene ($Me_3SiC{\equiv}CSiMe_3$), chlorotrimethylgermane (Me_3GeCl), chlorotriphenylgermane (Ph_3GeCl) and germanium tetrachloride ($GeCl_4$) were obtained from Aldrich.

Silicon tetrachloride ($SiCl_4$) and the tin tetrachloride ($SnCl_4$) were obtained from Aldrich or BDH and were purified by distillation from calcium hydride (CaH_2) under a nitrogen atmosphere.

Dimethyldichlorosilane (Me_2SiCl_2) and trimethylchlorosilane (Me_3SiCl) were obtained from Dow Corning and were purified by distillation from calcium hydride (CaH_2) under nitrogen atmosphere.

Tris(dimethylamino)chlorosilane [$(Me_2N)_3SiCl$] and bis(dimethylamino)methylchlorosilane [$(Me_2N)_2MeSiCl$] were obtained from Petrarch Systems and were purified by distillation under nitrogen atmosphere .

Chloroform-*d* ($CDCl_3$, 99.8 atom % D) and deuterium oxide-d_2 (D_2O, 99.9 atom % D) were obtained from Merck Frosst Canada (MSD Isotopes) and were used without purification from a new fresh bottle.

4.4) General Experimental Procedures of Synthesis

Due to the instability of the reagents towards hydrolysis we dealt with, all syntheses were performed with dry glassware, under a nitrogen atmosphere, using syringe techniques or in a glove-bag which was dried with anhydrous phosphorus pentoxide (P_2O_5) and continuously purged with dry nitrogen.

4.4.1) Chloroacetic acid deuterated

$ClCH_2COOD$

The hydrolysis of chloroacetic anhydride with deuterium oxide (D_2O) in THF under nitrogen atmosphere. The solvent was removed by simple distillation and excess D_2O was removed by azeotropic distillation with benzene to give a white solid (NMR analysis showed 94% + atom % D).

4.4.2) (Triphenylgermyl)(trimethylsilyl)acetylene

$Ph_3Ge\text{-}C{\equiv}C\text{-}SiMe_3$

A solution of *n*-BuLi 2.32 M in hexane (1.80 mmol, 0.78 ml) was added to a solution of trimethylsilylacetylene (1.81 mmol, 0.26 ml) in tetrahydrofuran (THF; 10 ml) at -78°C. The solution was stirred 30 minutes from -78°C to 0°C. Then, a solution of chlorotriphenylgermane (Ph_3GeCl; 0.613g, 1.75 mmol) in THF (5 ml) was added slowly at -78°C to the lithium salt of trimethylsilylacetylide (addition at 0°C would be more appropriate). The reaction was stirred 30 minutes at -78°C and at room temperature overnight.

Afterwards, the reaction was quenched with water and extracted three times with ether. The combined organic layers were dried over magnesium sulfate, filtered and the solvent was removed to give a white-yellowish solid. Recrystallization from isopropanol at -5°C gave 0.87g (1.42 mmol, 81%) of a white compound. This compound was stable in air for many months.

m.p. 68-69°C

^{1}H **NMR** ($CDCl_3$, 200 MHz): δ(ppm)= 7.75-7.6 (m, 6H), 7.5-7.35 (m, 9H), 0.3 (s, 9H)

^{13}C **NMR** ($CDCl_3$, 50.3 MHz): δ(ppm)= 135.1, 134.5, 129.5, 128.4, 117.2, 107.3, 0.05

^{29}Si **NMR** ($CDCl_3$, 49.69 MHz): δ(ppm)= -18.9

IR ($CHCl_3$) υ(cm^{-1})= 3060 m, 3010 m, 2970 m, 1960 w, 1890 w, 1820 w, 1770 w, 1480 w, 1435 m, 1300 w, 1245 m, 1200, 1085 m, 840 st, 730 st, 720 st, 710 st, 690 st, 660 st.

MS (EI, m/z reported for ^{74}Ge isotope): 402 (M^+, 20), 387 (62), 325 (46), 228 (100), 159 (12), 135 (11)

Analysis calculated for $C_{23}H_{24}GeSi$: C, 68.87; H, 6.03; Si, 7.00. Found: C, 68.74; H, 6.30; Si, 7.25.

HRMS: (M^+ reported for ^{74}Ge isotope) mass observed: 402.0842, mass calculated: 402.0859

4.4.3) (*t*-Butyldimethylsilyl)acetylene[117]

t-BuMe$_2$Si-C≡C-H

The synthesis of this compound has been done with a similar procedure to that used by Fitzmaurize and coworkers[117].

In a 500 ml three neck flask under an acetylene atmosphere (flow of acetylene gas), tetrahydrofuran (THF; 170 ml) was introduced. After chilling the flask to 0°C, a solution of *n*-butyllithium in hexane (2.5M, 75 mmols, 30 ml) was added. A white solid of lithium acetylide was immediately formed and the mixture was stirred for one hour at 0°C. Then, a solution of *t*-butyldimethylsilylchloride (10.92g, 72.45 mmol) in THF (40 ml) was added and stirred for 1.5 hour at 0°C. Afterwards, the mixture was warmed up at room temperature and the flask was left sealed overnight (12 hours) (closed system to keep the acetylene atmosphere).

The clear yellowish solution was quenched at 0°C with hydrochloric acid 10% (300 ml). The solution was extracted with ether (6 times). The combined organic layers were washed successively with a solution of sodium bicarbonate 5% and brine, and dried over anhydrous magnesium sulfate. The solvent was removed and the compound was distilled to get 9.16g.

Yield: 90 %; literature: 86 %

b.p.: 117-119 °C; literature[117]: 110 °C

^{1}**H NMR** ($CDCl_3$, 200 MHz): δ(ppm)= 2.32 (s, 1H), 0.92 (s, 9H), 0.11 (s, 6H); literature[117] (60 MHz): 2.5 (s, 1H), 1.0 (s, 9H), 0.2 (s, 6H)

^{13}**C NMR** ($CDCl_3$, 50.32 MHz): δ(ppm)= 93.71, 88.22, 25.68, 16.28, -4.77

4.4.4) (Triphenylgermyl) (*t*-butyldimethylsilyl)acetylene

$Ph_3Ge\text{-}C\equiv C\text{-}SiMe_2t\text{-}Bu$

A solution of *n*-BuLi 2.5 M in hexane (1.57 mmol, 0.63 ml) was added to a solution of (*t*-butyldimethylsilyl)acetylene (1.57 mmol, 221 mg) in tetrahydrofuran (THF; 2 ml) at 0°C. The solution was stirred 30 minutes at 0°C. Then, a solution of chlorotriphenylgermane (Ph_3GeCl; 0.50 g, 1.43 mmol) in THF (3 ml) was added and the reaction was stirred one hour at 0°C. The reaction was further stirred at room temperature overnight.

The reaction was quenched with water and extracted three times with ether. The combined organic layers were washed with brine, dried over anhydrous magnesium sulfate, filtered and the solvent was removed to give a white solid. Recrystallization from hot hexane gave 582mg (92%) of a white compound. This compound was stable in air for many months.

m.p. 128-131 °C

^{1}H NMR ($CDCl_3$, 200 MHz): δ(ppm)= 7.7-7.55 (m, 6H), 7.45-7.35 (m, 9H), 1.01 (s, 9H), 0.19 (s, 6H)

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ(ppm)= 135.3, 134.5, 129.4, 128.3, 115.6, 107.7, 26.1, 16.6, -4.5

^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ(ppm)= -8.9

IR (KBr) υ(cm^{-1})= 3060 m, 3050 m, 3020 w, 2995 w, 2940 st, 2920 st, 2880 st, 2850 st, 2140-2000 w, 1960 w, 1885 w, 1820 w, 1765 w, 1665 w, 1480 w, 1465 m, 1455 m, 1425 st, 1380 w, 1355 w, 1300 w, 1240 st, 1180 w, 1083 st, 830 st, 817 st, 805 st, 765 st, 725 st, 715 st, 685 st, 660 m, 450 st.

MS (EI, m/z reported for ^{74}Ge isotope): 444 (M^+, 14), 429 (8), 387 (100), 367 (6), 305 (14), 228 (26), 221 (77), 197 (45), 159 (79), 151 (80), 135 (91), 105 (23), 77 (48).

HRMS: (M^+ reported for ^{74}Ge isotope) mass observed: 444.1340, mass calculated: 444.1329

4.4.5) [Tris(dimethylamino)silyl](trimethylsilyl)acetylene

$(Me_2N)_3Si\text{-}C{\equiv}C\text{-}SiMe_3$

The lithium salt of (trimethylsilyl)acetylide (21.3 mmol) in tetrahydrofuran (THF; 15 ml) prepared as shown previously was added at -78°C to a solution of tris(dimethylamino)chlorosilane (95% from Aldrich; 4.5 ml, 21.2 mmol) in THF (10 ml). The reaction was stirred at -78°C 30 minutes and at room temperature overnight.

Then the solvent was removed by distillation and the residue was distilled at 71-73 °C/7 mm Hg to give 4.09 g of this new compound (15.9 mmols, 75% of yield). The product must be handled in nitrogen atmosphere.

^{1}H NMR ($CDCl_3$, 200 MHz): δ(ppm)= 2.48 (s, 18H), 0.17 (s, 9H)

^{13}C NMR ($CDCl_3$, 62.9 MHz): δ(ppm)= 112.4, 109.6, 36.8, -0.05

^{29}Si NMR ($CDCl_3$, 49.63 MHz): δ(ppm)= -19.4, -41.7

IR (neat) υ(cm^{-1})= 2970 st, 2890 st, 2865 st, 2840 st, 2795 st, 1485 m, 1465 m, 1450 m, 1410 w, 1295 st, 1250 st, 1180 st, 1145 m, 1070 m, 990 st, 855 st, 845 st, 770 st, 720 st, 620 w.

MS (EI, m/z): 257 (M^+, 79), 242 (7), 214 (42), 213 (100), 199 (30), 170 (26), 169 (22), 73 (15).

HRMS: mass observed: 257.1753, mass calculated: 257.1744

4.4.6) [Bis(dimethylamino)methylsilyl](trimethylsilyl)acetylene

$(Me_2N)_2MeSi\text{-}C{\equiv}C\text{-}SiMe_3$

Synthesis of $(Me_2N)_2MeSi\text{-}C{\equiv}C\text{-}SiMe_3$ was done with the same procedure for $(Me_2N)_3Si\text{-}C{\equiv}C\text{-}SiMe_3$. The lithium salt of the trimethylsilylacetylide (12.2 mmol) in tetrahydrofuran (THF; 15 ml) was added to bis(dimethylamino)methylchlorosilane (95% from Aldrich; 2.160g, 12.31 mmols) in THF (10 ml). The compound was obtained (2.215g, 79%) after distillation at 90-92 °C/22 mm Hg.

^{1}H NMR ($CDCl_3$, 200 MHz): δ(ppm)= 2.48 (s, 12H), 0.16 (s, 12H)

^{13}C NMR ($CDCl_3$, 62.9 MHz): δ(ppm)= 113.0, 110.4, 37.2, -0.12, -3.05

^{29}Si NMR ($CDCl_3$, 49.63 MHz): δ(ppm)= -19.2, -25.7

IR (neat) υ(cm^{-1})= 2970 st, 2890 st, 2870 st, 2845 st, 2795 st, 1480 w, 1450 m, 1410 w, 1290 st, 1255 st, 1175 st, 1070 w, 985 st, 855 st, 840 st, 795 st, 755 st, 735 st, 695 w, 680 w.

MS (EI, m/z): 228 (M^+, 78), 213 (50), 185 (49), 184 (100), 183 (21), 170 (51), 155 (9), 141 (23), 117 (16), 73 (37).

HRMS: mass observed: 228.1473, mass calculated: 228.1478

4.4.7) Synthesis of (trichlorosilyl)(trimethylsilyl)acetylene[104] and tetrakis(trimethylsilylacetylide)silane[118,119]

Cl_3Si-C≡C-$SiMe_3$ and (Me_3Si-C≡C-)$_4$Si

The synthesis of these two compounds was not done according to the literature procedures[104,118] and will be described here. Moreover, some physical characterizations of Cl_3Si-C≡C-$SiMe_3$ have not been reported[104] and will be given here.

The lithium salt of (trimethylsilyl)acetylide (70.8 mmol) in tetrahydrofuran (THF; 40 ml) was added slowly over 30 minutes at 0°C to an excess of silicon tetrachloride ($SiCl_4$; 65ml, 8 eq.) in dichloromethane (CH_2Cl_2; 200ml) and stirred over 18 hours. Then the solvent was removed by simple distillation and the residue was distilled at 55°C/15 mm Hg to give 3.5 g of Cl_3Si-C≡C-$SiMe_3$ (15.1 mmols, 21 % yield). Afterwards, the residue was washed with water, extracted with ether and recrystallized several times in hexane to give 3 g of (Me_3Si-C≡C-)$_4$Si (7.1 mmols, 41 % yield).

Cl_3Si-C≡C-$SiMe_3$[104]

b.p.: 55 °C at 15 mm Hg; literature: 71 °C at 25 mm Hg

^{1}H NMR ($CDCl_3$, 200 MHz): δ(ppm)= 0.25 (s)

^{13}C NMR ($CDCl_3$, 62.9 MHz): δ(ppm)= 120.6, 102.3, -0.6

^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ(ppm)= -15.1, -33.9

IR (neat) υ(cm^{-1})= 2955 st, 2890 w, 2095 m, 1400 w, 1240 st, 1080 w, 830 st, 790 st, 750 st, 690 m, 585 st, 500 m.

MS (CI + CH_4, m/z): 232 (M^+, 7), 215 (100),195 (63).

HRMS: (M^+ reported for ^{74}Ge isotope) mass observed for M^+- CH_3: 214.9082, mass calculated for M^+- CH_3: 214.9076

(Me_3Si-C≡C-)$_4$Si[118,119]

m.p.: 154-159 °C (from hexane); literature: 160 °C (from petroleum ether)[118] or 161 °C[119]

^{1}H NMR ($CDCl_3$, 200 MHz): δ(ppm)= 0.21 (s); literature (C_6D_6)[119]: 0.05

^{13}C NMR ($CDCl_3$, 62.9 MHz): δ(ppm)= 117.2, 104.2, -0.3; literature (C_6D_6)[119]: 120.3, 104.1, -0.86

^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ(ppm)= -17.5, -101.6; literature (C_6D_6)[119]: -17.0, -100.1

IR (CH_2Cl_2) υ(cm^{-1})= 2965 h, 2900 m, 2010 m, 1950 w, 1875 w, 1400 m, 1250 st, 900-720 st, 700 st, 480 st, 290 st.

MS (EI, m/z): 416 (M^+, 21), 401 (34), 343 (12), 328 (11), 313 (100), 231 (29), 179 (32), 155 (56)

HRMS: mass observed: 416.1663, mass calculated: 416.1669

The synthesis of the other metalated (trimethylsilyl)acetylide compounds were performed with some modification from the procedures reported in the literature. The synthesis were done by the reaction of lithium salt of (trimethylsilyl)acetylide (Me_3Si-C≡C^-Li^+, 1.1 equivalent) with the appropriate silyl, germyl, or stannyl chloride compounds in tetrahydrofuran or ether[117].

4.4.8) (Trimethylstannyl)(trimethylsilyl)acetylene[103]

Me_3Sn-C≡C-$SiMe_3$

Yield: 71 %; literature: 68 %

b.p.: ≈25 °C at 1 mm Hg; literature: ≈25 °C at 1 mm Hg

^{1}H NMR ($CDCl_3$, 200 MHz): δ(ppm)= 0.28 (s, 9H), 0.16 (s, 9H)

^{13}C NMR ($CDCl_3$, 62.9 MHz): δ(ppm)= 117.6, 113.2, 0.5, -7.4

^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ(ppm)= -20.9

^{119}Sn NMR ($CDCl_3$, 93.28 MHz): δ(ppm)= -73.6

IR (neat) υ(cm^{-1})= 2965 st, 2920 st, 2905 st, 2370 w, 2075 w, 1450 m, 1405 m, 1305 w, 1245 st, 1190 w, 830 st, 750 st, 690 st.

MS (EI, m/z reported for ^{119}Sn isotope): 247 (M^+- CH_3, 100), 217 (12), 185 (6)

HRMS: (M^+ reported for ^{119}Sn isotope) mass observed for M^+- CH_3: 246.9984, mass calculated for M^+- CH_3: 246.9965

4.4.9) (Tri-*n*-butylstannyl)(trimethylsilyl)acetylene[120]

Bu_3Sn-C≡C-$SiMe_3$

Yield: 90 %; literature: 91 %

b.p.: 134-137 °C at 8-9 mm Hg; literature: 89 °C at 0.27 mm Hg

^{1}H NMR ($CDCl_3$, 200 MHz): δ(ppm)= 1.67-1.45 (m, 8H), 1.45-1.2 (m, 8H), 1.0-0.9 (d-d, 8H), 0.9 (t, 12H), 0.16 (s, 9H); literature (CCl_4): δ(ppm)= 2.3-0.4 (m, 27H), 0.14 (s, 9H)

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ(ppm)= 118.9, 113.1, 29.0, 27.0, 13.7, 11.3, 0.4

^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ(ppm)= -21.2

^{119}Sn NMR ($CDCl_3$, 93.28 MHz): δ(ppm)= -71.0

IR (neat) $\upsilon(cm^{-1})$= 2950 st, 2920 st, 2865 st, 2845 st, 2065 w, 1945 w, 1845 w, 1450 st, 1410 m, 1370 m, 1335 w, 1285 w, 1240 st, 1170 w, 1130 w, 1065 m, 950 w, 845 st, 830 st, 750 st, 685 st, 590 m.

MS (CI + CH_4, m/z reported for ^{119}Sn isotope): 373 (M^+- CH_3, 24), 331 (100), 291 (89), 269 (14), 235 (17), 177 (6), 97 (5), 83 (24), 73 (32)

4.4.10) (Triphenylstannyl)(trimethylsilyl)acetylene[121]

Ph_3Sn-C≡C-$SiMe_3$

Yield: 92 %; literature: 61 %

m.p.: 73-74 °C; literature: 74-76 °C

^{1}H NMR ($CDCl_3$, 200 MHz): δ(ppm)= 7.75-7.65 (m, 6H), 7.5-7.4 (m, 9H), 0.3 (s, 9H)

^{13}C NMR ($CDCl_3$, 62.9 MHz): δ(ppm)= 139.9, 136.7, 129.5, 129.2, 121.4, 108.7, 0.17

^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ(ppm)= -19.5

^{119}Sn NMR ($CDCl_3$, 93.28 MHz): δ(ppm)= -175.4

MS (EI, m/z reported for ^{119}Sn isotope): 448 (M^+, 3), 433 (5), 371 (39), 341 (4), 294 (3), 274 (35), 221 (27), 197 (37), 159 (50), 135 (32), 120 (100), 97 (18)

HRMS: (M^+ reported for ^{119}Sn isotope) mass observed: 448.0677, mass calculated: 448.0669

4.4.11) (Trimethylgermyl)(trimethylsilyl)acetylene[122]

$Me_3Ge\text{-}C\equiv C\text{-}SiMe_3$

Yield: 70 %; literature: 68 %

b.p.: 65 °C at 55 mm Hg; literature: 150-151 °C at 750 mm Hg

m.p.: 32-33°C

^{1}**H NMR** ($CDCl_3$, 200 MHz): δ(ppm)= 0.35 (s, 9H), 0.16 (s, 9H)

^{13}**C NMR** ($CDCl_3$, 62.9 MHz): δ(ppm)= 114.1, 112.1, 0.1, -0.1

^{29}**Si NMR** ($CDCl_3$, 49.69 MHz): δ(ppm)= -20.2

MS (EI, m/z, reported for ^{74}Ge isotope): 216 (M^+, 2), 201 (100), 120 (56), 118 (59), 97 (19)

4.4.12) (*t*-Butyldimethylsilyl)(trimethylsilyl)acetylene[123]

$t\text{-}BuMe_2Si\text{-}C\equiv C\text{-}SiMe_3$

Yield: 74 %

b.p.: 45-55 °C at 8-9 mm Hg

^{1}H NMR ($CDCl_3$, 200 MHz): δ(ppm)= 0.93 (s, 9H), 0.16 (s, 9H), 0.09 (s, 6H)

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ(ppm)= 114.4, 112,2, 26.3, 16.7, 0.2, -4.4

^{29}**Si NMR** ($CDCl_3$, 49.69 MHz): δ(ppm)= -19.6, -9.6

IR (neat) υ(cm^{-1})= 2960 st, 2940 st, 2900 st, 2860 st, 1460 m, 1405 m, 1385 w, 1360 m, 1250 st, 1000 m, 850 st, 840 st, 820 st, 810 st, 770 st, 755 st, 690 m, 670 m.

MS (EI, m/z): 212 (M^+, 2), 197 (7), 155 (100), 125 (4), 97 (4), 83 (5), 73 (14)

HRMS: mass observed: 212.1415, mass calculated: 212.1417

4.4.13) (Triphenylsilyl)(trimethylsilyl)acetylene[121]

$Ph_3Si\text{-}C{\equiv}C\text{-}SiMe_3$

Yield: 55 %; literature: 73 %

m.p.: 70-71 °C; literature: 42-44 °C

^{1}H NMR ($CDCl_3$, 200 MHz): δ(ppm)= 7.7-7.6 (m, 6H), 7.5-7.3 (m, 9H), 0.27 (s, 9H)

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ(ppm)= 135.5, 133.4, 129.9, 127.9, 119.5, 108.1, -0.13

^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ(ppm)= -18.4, -30.9

IR (CCl_4) υ(cm^{-1})= 3050 m, 3030 m, 3000 m, 2955 m, 2870 w, 1955 w, 1880 w, 1820 w, 1770 w, 1530 w, 1475 w, 1420 m, 1245 m, 1100 m, 830 st, 760 st, 690 st.

4.4.14) (Chlorodimethylsilyl)(trimethylsilyl)acetylene[124]

$ClMe_2Si\text{-}C{\equiv}C\text{-}SiMe_3$

Yield: 57 %; literature: 60 %

b.p.: 50-55 °C at ≈15 mm Hg; literature: 48-50 °C at 12 mm Hg

^{1}H NMR ($CDCl_3$, 200 MHz): δ(ppm)= 0.57 (s, 6H), 0.20 (s, 9H)

^{13}C NMR ($CDCl_3$, 62.9 MHz): δ(ppm)= 117.0, 108.6, 4.0, -0.1

^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ(ppm)= -2.1, -17.9

IR (neat) υ(cm^{-1})= 2960 m, 2900 m, 2100 w, 1405 w, 1250 m, 1050 w, 830 st, 815 st, 785 st, 775 st, 750 st.

HRMS: mass observed for $M^+\text{-}CH_3$: 175.0129; mass calculated for $M^+\text{-}CH_3$: 175.0166

4.4.15) Tetrakis(trimethylsilylacetylide)stannane[118]

$(Me_3Si\text{-}C\equiv C\text{-})_4Sn$

Yield: 73 %; literature: 35 %

m.p.: 170-172 °C (from petroleum ether or hexane); literature: decomposition at 140 ° (from petroleum ether)

^{1}H NMR ($CDCl_3$, 200 MHz): δ(ppm)= 0.21 (s)

^{13}C NMR ($CDCl_3$, 62.9 MHz): δ(ppm)= 119.5, 103.2, -0.3

^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ(ppm)= -18.1

^{119}Sn NMR ($CDCl_3$, 93.28 MHz): δ(ppm)= -384.5

IR (KBr) υ(cm^{-1})= 2960 st, 2900 m, 2090 w, 2010 w, 1950 w, 1865 w, 1405 m, 1310 m, 1250 st, 840 st, 755 st, 695 st, 605 m.

MS (EI, m/z reported for ^{119}Sn isotope): 508 (M^+, 15), 493 (17), 405 (16), 314 (72), 247 (83), 217 (35), 179 (80), 165 (86), 119 (30), 97 (100), 73 (79)

HRMS: (M^+ reported for ^{119}Sn isotope) mass observed: 508.0915, mass calculated: 508.0916

4.4.16) Tetrakis(trimethylsilylacetylide)germane[118]

$(Me_3Si\text{-}C{\equiv}C\text{-})_4Ge$

Yield: 94 %; literature: 95 %[118a], 58 %[118b]

m.p.: 175-176 °C (from petroleum ether); literature: 160 °C[118a] (from petroleum ether), 176 °C[118b]

^{1}H NMR ($CDCl_3$, 200 MHz): δ(ppm)= 0.21 (s)

^{13}C NMR ($CDCl_3$, 62.9 MHz): δ(ppm)= 114.0, 102.1, -0.3

^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ(ppm)= -17.7

^{73}Ge NMR ($CDCl_3$, 8.73 MHz): δ(ppm)= -188.5 (line width of 125 Hz)

IR (KBr) υ(cm^{-1})= 2970 st, 2900 m, 2105 w, 2000 w, 1955 w, 1870 w, 1450 w, 1410 m, 1315 w, 1255 st, 850 st, 760 st, 820 st, 405 m, 305 m, 300 st.

MS (EI, m/z reported for ^{74}Ge isotope): 447 (41), 389 (18), 359 (25), 253 (10), 229 (12), 201 (53), 155 (18), 119 (100), 97 (32), 73 (95)

HRMS: (M^+ reported for ^{74}Ge isotope) mass observed for M^++ 1: 461.1032; mass calculated for M^++ 1: 461.1028

4.4.17) (Dimethylmethoxysilyl)(trimethylsilyl)acetylene[125]

$Me_2(MeO)Si\text{-}C\equiv C\text{-}SiMe_3$

Yield: 95 %; literature: 56 %

b.p.: 53-55 °C at ≈67-70 mm Hg; literature: 70-71 °C at 25 mm Hg

^{1}H NMR ($CDCl_3$, 200 MHz): δ(ppm)= 3.48 (s, 3H), 0.23 (s, 6H), 0.17 (s, 9H)

^{13}C NMR ($CDCl_3$, 50.32 MHz): δ(ppm)= 114.4, 110.5, 50.6, -0.1, -0.2

^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ(ppm)= -8.4, -18.8

IR (neat) υ(cm^{-1})= 2960 st, 2900 m, 2838 m, 2100 w, 1450 w, 1400 w, 1252 st, 1185 w, 1090 st, 830 st, 790 st, 755 st, 695 w.

MS (EI, m/z): 171 (M^+- CH_3, 100), 155 (5), 141 (57)

HRMS: mass observed for M^+- CH_3: 171.0665; mass calculated for M^+- CH_3: 171.0661

4.4.18) (Methyldimethoxysilyl)(trimethylsilyl)acetylene[125]

$Me(MeO)_2Si\text{-}C\equiv C\text{-}SiMe_3$

Yield: 93 %; literature: 48 %

b.p.: 75-80 °C at ≈35 mm Hg; literature: 72-73 °C at 16 mm Hg

^{1}H NMR ($CDCl_3$, 200 MHz): δ(ppm)= 3.51 (s, 6H), 0.18 (s, 3H), 0.15 (s, 9H)

^{13}C NMR ($CDCl_3$, 62.9 MHz): δ(ppm)= 114.0, 106.5, 50.3, -0.6, -3.5

^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ(ppm)= -18.2, -32.7

IR (neat) υ(cm^{-1})= 2970 st, 2910 st, 2805 m, 2105 w, 1455 w, 1410 w, 1250 st, 1185 m, 1080 st, 840 st, 810 st, 785 st, 760 m, 695 w.

MS (EI, m/z): 187 (M^+-CH_3, 100), 171 (4), 157 (54), 141 (5), 127 (15), 86 (8), 83 (6), 73 (13)

HRMS: mass observed for M^+- CH_3: 187.0613; mass calculated for M^+- CH_3: 187.0611

4.5 Kinetic Experimental Procedure

All reactions have been carried out with 0.5 ml of 0.05M solution of the acetylene compound (0.025 mmol) in chloroform-*d* ($CDCl_3$) in an NMR tube 5 mm. The reactions were followed by NMR spectroscopy on Bruker AC-200 (200 MHz) and WM-500 (500 MHz) spectrometers. The reaction rates were measured on Bruker AC-200 (200 MHz) at room temperature (the temperature was not recorded, but it was supposed to be maintained around 23°C) and the time was recorded at the end of each spectrum of four scans. A kinetic program provided by Bruker AC-200 software was used for the fast reactions.

In the case of the stannyl (trimethylsilyl)acetylene compounds (Table 3-1), the reactions were initiated by the addition of 10 µl (0.025 mmol) of 2.5 M solution of the carboxylic acid in $CDCl_3$ to 0.5 ml of a 0.05 M solution of compound in a NMR tube. The adjustment of the NMR spectrometer required an average of 90 seconds, afterwards the spectra were recorded. In a special case, for the fast reaction between the (tri-*n*-butylstannyl)(trimethylsilyl)acetylene with $Cl_2CHCOOH$, the spectra were recorded after 50 seconds without adjusment of the "shim" of the NMR spectrometer and by taking only one scan for each spectrum.

The reactions of (trimethylgermyl)(trimethylsilyl)acetylene with trifluoroacetic acid (CF_3COOH) were started by the addition of 10 µl of CF_3COOH solution at different concentrations in $CDCl_3$ to 0.5 ml of a 0.05M solution of the compound in a NMR tube. However, for the high concentration of CF_3COOH solution with the (trimethylgermyl)(trimethylsilyl)acetylene as well as the bis(trimethylsilyl)acetylene and the (trimethylgermyl)(trimethylsilyl)acetylene, the reactions were started by the addition of 0.10 ml of CF_3COOH solution at different concentrations in $CDCl_3$ to 0.4 ml (0.025 mmol) of a 0.0625 M solution of the compound in a NMR tube.

For all studies with the methanesulfonic acid (CH_3SO_3H), the reactions were started by the addition of 0.10 ml of CH_3SO_3H solution at different concentrations (saturated solution) in $CDCl_3$ to 0.4 ml (0.025 mmol) of a 0.0625 M solution of the compound in a NMR tube. Due to the poor solubility of CH_3SO_3H in $CDCl_3$, the concentration of the acid in the NMR tube was checked with the spectra recorded by the proton signals intensities of the methyl groups.

The triflic acid (CF_3SO_3H) was used neat. Thus the reactions were started by the addition of 2.2 μl (0.025 mmol) of CF_3SO_3H to 0.5 ml of a 0.05 M solution of the compound in a NMR tube.

The degree of completion of the reaction was measured from the change of the relative intensity of the proton signal of the methyl substituent (singlet) for each silyl, germyl and stannyl groups. The relative intensity was best evaluated by the manual measurement of the peak height. The reactions are of second order and the data were treated with a least-square fit to a straight line using computer programs (GraphPAP InPlot and Quattro,Borland). The standard deviations calculated were generally less than 5% of the slops. The error on the rate constants was estimated by a systematic 5% error in addition to the standard deviation.

One of the experiments involving the reaction of $Me_3Si\text{-}C{\equiv}C\text{-}SiMe_3$ with 0.0725M of CH_3SO_3H (Table A.2-15) was discarded in the evaluation of the rate constant (Graph 3-5) due to an experimental error. A volume larger than 0.1 ml of saturated acid solution (≈0.35 M) was added into the NMR tube. This dilution reduced both $Me_3Si\text{-}C{\equiv}C\text{-}SiMe_3$ concentration and the reaction rate. The rate constant observed (k_{obs}= 0.365×10^{-3} $M^{-1}s^{-1}$) did not fit in a straight line with the other rate constants observed for this series of experiments (Table A.2-15, Table A.2-16 and Table A.2-17).

APPENDIX 1

A.1.1) X-ray Structure Determination of the Tetrekis(trimethylsilyl)germane

Crystal Data

Empirical Formula	C_{20} H_{36} Ge Si_4
Crystal System	Orthorhombic
Space Group	Pnma
Unit Cell Dimensions	a = 10.189(3) Å
	b = 17.827(6) Å
	c = 15.830(6) Å
Volume	2875.4(17) $Å^3$
Z	4
Formula Weight	461.4
Density(calc.)	1.066 Mg/m^3
Absorption Coefficient	1.234 mm^{-1}
F(000)	976

Data Collection

Diffractometer Used	Nicolet R3
Radiation	MoKα (λ = 0.71069 Å)
Temperature (K)	183
Monochromator	Highly oriented graphite crystal
2θ Range	3.0 to 55.0°
Scan Type	$2\theta-\theta$
Scan Speed	Variable; 3.91 to 29.30°/min. in 2θ
Scan Range (θ)	2.00° plus Kα-separation
Background Measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time
Standard Reflections	2 measured every 48 reflections
Index Ranges	$-10 \leq h \leq 10$, $-10 \leq k \leq 19$ $-17 \leq \ell \leq 17$
Reflections Collected	4329
Independent Reflections	1948 (R_{int} = 1.78%)
Observed Reflections	1487 ($F > 5.0\sigma(F)$)
Absorption Correction	N/A

Solution and Refinement

System Used	Siemens SHELXTL PLUS (VMS)
Solution	Direct Methods
Refinement Method	Full-Matrix Least-Squares
Quantity Minimized	$\sum w(F_o-F_c)^2$
Absolute Structure	N/A
Extinction Correction	$\chi = 0.00051(5)$, where $F^* = F\ [\ 1 + 0.002\chi F^2/\sin(2\theta)\ ]^{-1/4}$
Hydrogen Atoms	Riding model, common isotropic U
Weighting Scheme	$w^{-1} = \sigma^2(F) + 0.0001F^2$
Number of Parameters Refined	148
Final R Indices (obs. data)	R = 3.83 %, wR = 3.92 %
R Indices (all data)	R = 5.55 %, wR = 4.69 %
Goodness-of-Fit	1.39
Largest and Mean Δ/σ	0.022, 0.001
Data-to-Parameter Ratio	10.0:1
Largest Difference Peak	0.47 eÅ^{-3}
Largest Difference Hole	-0.56 eÅ^{-3}

Table A.1-1: Atomic coordinates (x10^4) and equivalent isotropic displacement coefficients ($Å^2$x10^3)

	x	y	z	U(eq)
Ge(1)	4874(1)	2500	-35(1)	27(1)
Si(2)	5560(2)	2500	-3131(1)	42(1)
Si(3)	8933(2)	2500	1671(1)	42(1)
Si(4)	2803(1)	4909(1)	722(1)	54(1)
C(1)	5173(5)	2500	-1212(4)	31(2)
C(2)	5338(5)	2500	-1970(4)	33(2)
C(3)	6479(5)	2500	569(4)	31(2)
C(4)	7457(6)	2500	996(4)	34(2)
C(5)	3948(3)	3383(2)	260(3)	30(1)
C(6)	3458(3)	3976(2)	441(3)	35(1)
C(21)	3901(8)	2500	-3598(6)	104(5)
C(22)	6499(5)	3354(3)	-3420(3)	64(2)
C(31)	10397(6)	2500	967(5)	70(3)
C(32)	8862(5)	3355(3)	2336(3)	67(2)
C(41)	4013(6)	5387(3)	1376(4)	77(2)
C(42)	1271(6)	4767(3)	1330(7)	139(5)
C(43)	2529(6)	5429(3)	-278(4)	95(3)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Table A.1-2: Bond lengths (Å)

Ge(1)-C(1)	1.889 (7)	Ge(1)-C(3)	1.894 (6)
Ge(1)-C(5)	1.893 (4)	Ge(1)-C(5A)	1.893 (4)
Si(2)-C(2)	1.851 (7)	Si(2)-C(21)	1.844 (9)
Si(2)-C(22)	1.855 (5)	Si(2)-C(22A)	1.855 (5)
Si(3)-C(4)	1.844 (6)	Si(3)-C(31)	1.862 (7)
Si(3)-C(32)	1.853 (5)	Si(3)-C(32A)	1.853 (5)
Si(4)-C(6)	1.847 (4)	Si(4)-C(41)	1.821 (6)
Si(4)-C(42)	1.852 (8)	Si(4)-C(43)	1.856 (7)
C(1)-C(2)	1.212 (9)	C(3)-C(4)	1.205 (8)
C(5)-C(6)	1.204 (5)		

Table A.1-3: Bond angles (°)

C(1)-Ge(1)-C(3)	111.0(2)	C(1)-Ge(1)-C(5)	108.9(1)
C(3)-Ge(1)-C(5)	107.8(1)	C(1)-Ge(1)-C(5A)	108.9(1)
C(3)-Ge(1)-C(5A)	107.8(1)	C(5)-Ge(1)-C(5A)	112.5(2)
C(2)-Si(2)-C(21)	106.6(3)	C(2)-Si(2)-C(22)	107.9(2)
C(21)-Si(2)-C(22)	112.0(2)	C(2)-Si(2)-C(22A)	107.9(2)
C(21)-Si(2)-C(22A)	112.0(2)	C(22)-Si(2)-C(22A)	110.2(3)
C(4)-Si(3)-C(31)	107.8(3)	C(4)-Si(3)-C(32)	107.2(2)
C(31)-Si(3)-C(32)	111.8(2)	C(4)-Si(3)-C(32A)	107.2(2)
C(31)-Si(3)-C(32A)	111.8(2)	C(32)-Si(3)-C(32A)	110.6(3)
C(6)-Si(4)-C(41)	108.3(2)	C(6)-Si(4)-C(42)	107.9(2)
C(41)-Si(4)-C(42)	109.8(4)	C(6)-Si(4)-C(43)	107.4(2)
C(41)-Si(4)-C(43)	110.7(3)	C(42)-Si(4)-C(43)	112.6(3)
Ge(1)-C(1)-C(2)	178.7(5)	Si(2)-C(2)-C(1)	179.0(5)
Ge(1)-C(3)-C(4)	176.2(5)	Si(3)-C(4)-C(3)	178.8(6)
Ge(1)-C(5)-C(6)	174.5(3)	Si(4)-C(6)-C(5)	176.7(3)

Table A.1-4: Anisotropic displacement coefficients ($\mathrm{\mathring{A}}^2 \times 10^3$)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ge(1)	32(1)	21(1)	27(1)	0	-1(1)	0
Si(2)	37(1)	61(1)	29(1)	0	6(1)	0
Si(3)	39(1)	58(1)	30(1)	0	-5(1)	0
Si(4)	47(1)	24(1)	90(1)	6(1)	14(1)	1(1)
C(1)	38(3)	21(3)	34(5)	0	-3(3)	0
C(2)	28(3)	35(3)	34(5)	0	0(3)	0
C(3)	34(3)	26(3)	34(4)	0	3(3)	0
C(4)	39(3)	28(3)	36(4)	0	3(3)	0
C(5)	32(2)	26(2)	31(3)	-5(2)	-6(2)	5(2)
C(6)	30(2)	29(2)	46(3)	0(2)	-1(2)	3(2)
C(21)	57(5)	216(11)	39(5)	0	4(5)	0
C(22)	78(4)	64(3)	51(4)	4(3)	18(3)	12(3)
C(31)	42(4)	111(7)	57(6)	0	-2(4)	0
C(32)	79(3)	72(3)	50(4)	-20(3)	-4(3)	-15(3)
C(41)	117(5)	39(3)	75(5)	-10(3)	14(4)	-16(3)
C(42)	88(5)	51(3)	277(12)	24(3)	103(6)	6(5)
C(43)	102(4)	44(3)	138(7)	10(3)	-35(5)	17(4)

The anisotropic displacement factor exponent takes the form:

$-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12})$

Table A.1-5: H-Atom coordinates ($\times10^4$) and isotropic displacement coefficients ($\text{Å}^2\times10^3$)

	x	y	z	U
H(21A)	3457	2950	-3427	114(5)
H(21B)	4007	2500	-4153	114(5)
H(22A)	7382	3335	-3209	114(5)
H(22B)	6506	3284	-4021	114(5)
H(22C)	6118	3832	-3287	114(5)
H(31A)	10400	2951	635	114(5)
H(31B)	11183	2500	1300	114(5)
H(32A)	8706	3787	1989	114(5)
H(32B)	8146	3293	2724	114(5)
H(32C)	9663	3422	2646	114(5)
H(41A)	4095	5105	1890	114(5)
H(41B)	4854	5421	1106	114(5)
H(41C)	3697	5882	1503	114(5)
H(42A)	1332	4428	1800	114(5)
H(42B)	895	5232	1516	114(5)
H(42C)	725	4550	900	114(5)
H(43A)	3355	5550	-536	114(5)
H(43B)	2024	5122	-656	114(5)
H(43C)	2057	5882	-159	114(5)

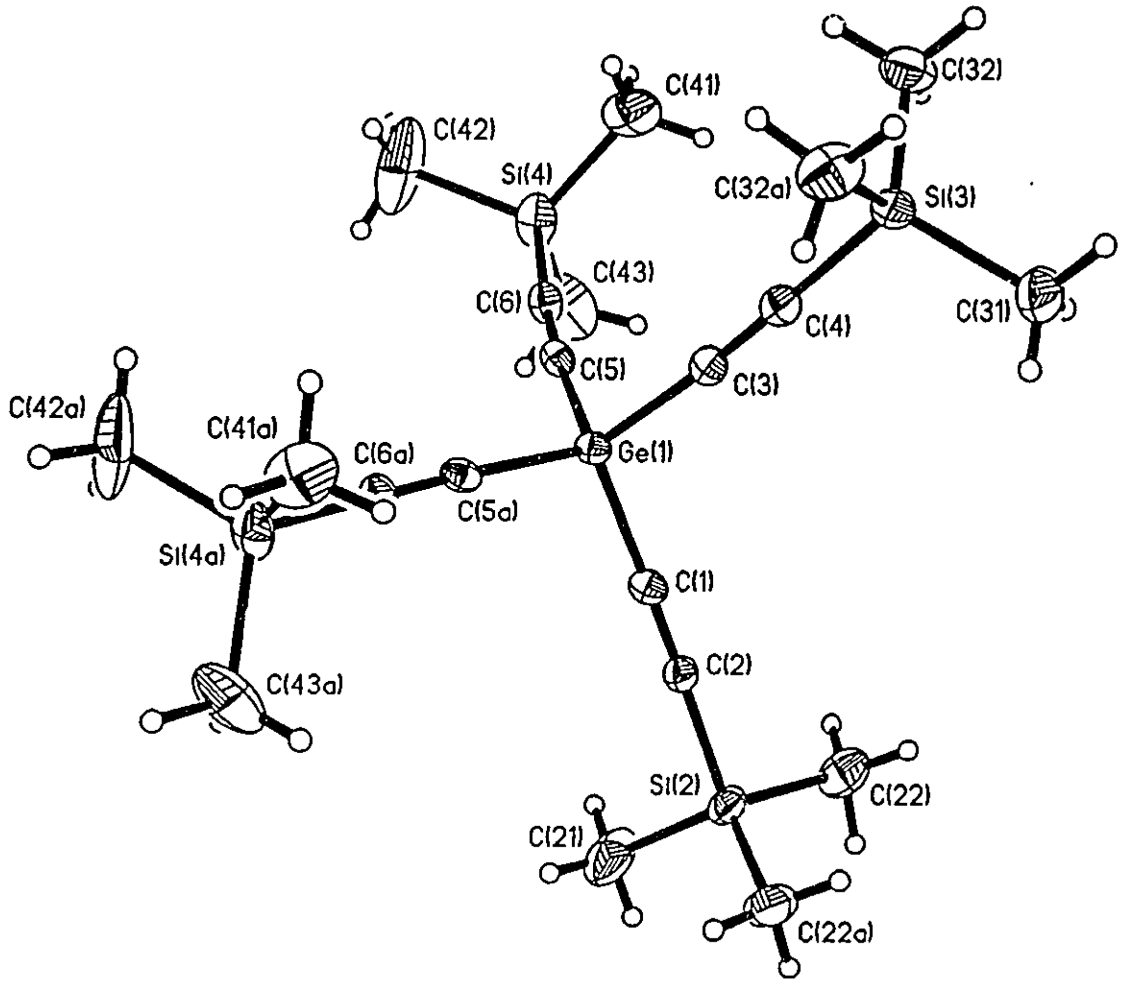


Figure A-1: X-ray crystal structure of $(Me_3Si\text{-}C{\equiv}C\text{-})_4Ge$

A.1.2) X-ray Structure Determination of the Tetrekis(trimethylsilyl)stannane

Crystal Data

Empirical Formula	$C_{20} H_{36} Si_4 Sn$
Crystal System	Orthorhombic
Space Group	Pnma
Unit Cell Dimensions	$\underline{a}$ = 10.465(2) Å
	$\underline{b}$ = 18.317(4) Å
	$\underline{c}$ = 16.156(4) Å
Volume	3096.9(12) $Å^3$
Z	4
Formula Weight	507.5
Density(calc.)	1.089 Mg/m^3
Absorption Coefficient	0.982 mm^{-1}
F(000)	1048

Data Collection

Diffractometer Used	Nicolet R3
Radiation	MoKα (λ = 0.71069 Å)
Temperature (K)	298
Monochromator	Highly oriented graphite crystal
2θ Range	3.0 to 45.0°
Scan Type	$2\theta-\theta$
Scan Speed	Variable; 5.86 to 29.30°/min. in 2θ
Scan Range (ω)	2.00° plus Kα-separation
Background Measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time
Standard Reflections	2 measured every 48 reflections
Index Ranges	$-4 \le h \le 11$, $-19 \le k \le 19$ $0 \le \ell \le 17$
Reflections Collected	4699
Independent Reflections	2109 (R_{int} = 1.22%)
Observed Reflections	1488 ($F > 5.0\sigma(F)$)
Absorption Correction	N/A

Solution and Refinement

System Used	Siemens SHELXTL PLUS (VMS)
Solution	Direct Methods
Refinement Method	Full-Matrix Least-Squares
Quantity Minimized	$\sum w(F_o - F_c)^2$
Absolute Structure	N/A
Extinction Correction	χ = 0.00131(13), where $F^* = F\ [\ 1 + 0.002\chi F^2/\sin(2\theta)\ ]^{-1/4}$
Hydrogen Atoms	Riding model, common isotropic U
Weighting Scheme	$w^{-1} = \sigma^2(F) + 0.0001F^2$
Number of Parameters Refined	144
Final R Indices (obs. data)	R = 2.94 %, wR = 3.65 %
R Indices (all data)	R = 4.89 %, wR = 4.47 %
Goodness-of-Fit	1.61
Largest and Mean Δ/σ	0.384, 0.030
Data-to-Parameter Ratio	10.3:1
Largest Difference Peak	0.29 eÅ^{-3}
Largest Difference Hole	-0.27 eÅ^{-3}

Table A.1-6: Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$)

	x	y	z	U(eq)
Sn(1)	4867(1)	2500	-12(1)	56(1)
Si(2)	5515(2)	2500	-3149(1)	86(1)
Si(3)	9009(2)	2500	1659(1)	94(1)
Si(4)	2798(2)	4919(1)	772(2)	121(1)
C(1)	5185(5)	2500	-1280(4)	65(2)
C(2)	5333(6)	2500	-2011(4)	71(3)
C(3)	6571(6)	2500	626(4)	67(3)
C(4)	7543(6)	2500	1013(4)	69(2)
C(5)	3886(4)	3435(3)	303(3)	67(2)
C(6)	3425(5)	4013(3)	487(3)	78(2)
C(21)	3890(8)	2500	-3569(5)	208(9)
C(22)	6458(7)	3317(4)	-3429(4)	151(4)
C(31)	10397(7)	2500	934(5)	146(6)
C(32)	8953(7)	3332(4)	2300(4)	160(4)
C(41)	4039(10)	5387(5)	1354(5)	188(5)
C(42)	1362(12)	4799(6)	1345(10)	301(9)
C(43)	2571(10)	5434(6)	-191(6)	217(6)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Table A.1-7: Bond lengths (Å)

Sn(1)-C(1)	2.076 (6)	Sn(1)-C(3)	2.060 (6)
Sn(1)-C(5)	2.060 (5)	Sn(1)-C(5A)	2.060 (5)
Si(2)-C(2)	1.849 (6)	Si(2)-C(21)	1.831 (8)
Si(2)-C(22)	1.848 (8)	Si(2)-C(22A)	1.848 (8)
Si(3)-C(4)	1.855 (7)	Si(3)-C(31)	1.866 (8)
Si(3)-C(32)	1.844 (7)	Si(3)-C(32A)	1.844 (7)
Si(4)-C(6)	1.842 (6)	Si(4)-C(41)	1.818 (10)
Si(4)-C(42)	1.779 (13)	Si(4)-C(43)	1.834 (10)
C(1)-C(2)	1.190 (9)	C(3)-C(4)	1.194 (9)
C(5)-C(6)	1.202 (7)		

Table A.1-8: Bond angles (°)

C(1)-Sn(1)-C(3)	110.8(2)	C(1)-Sn(1)-C(5)	108.9(1)
C(3)-Sn(1)-C(5)	107.9(1)	C(1)-Sn(1)-C(5A)	108.9(1)
C(3)-Sn(1)-C(5A)	107.9(1)	C(5)-Sn(1)-C(5A)	112.4(3)
C(2)-Si(2)-C(21)	105.8(3)	C(2)-Si(2)-C(22)	107.3(2)
C(21)-Si(2)-C(22)	113.9(3)	C(2)-Si(2)-C(22A)	107.3(2)
C(21)-Si(2)-C(22A)	113.9(3)	C(22)-Si(2)-C(22A)	108.1(5)
C(4)-Si(3)-C(31)	106.9(3)	C(4)-Si(3)-C(32)	106.8(3)
C(31)-Si(3)-C(32)	112.2(3)	C(4)-Si(3)-C(32A)	106.8(3)
C(31)-Si(3)-C(32A)	112.2(3)	C(32)-Si(3)-C(32A)	111.5(4)
C(6)-Si(4)-C(41)	107.4(4)	C(6)-Si(4)-C(42)	108.6(4)
C(41)-Si(4)-C(42)	113.1(6)	C(6)-Si(4)-C(43)	107.3(4)
C(41)-Si(4)-C(43)	106.8(4)	C(42)-Si(4)-C(43)	113.3(6)
Sn(1)-C(1)-C(2)	178.3(5)	Si(2)-C(2)-C(1)	178.4(6)
Sn(1)-C(3)-C(4)	178.4(5)	Si(3)-C(4)-C(3)	177.4(6)
Sn(1)-C(5)-C(6)	173.8(4)	Si(4)-C(6)-C(5)	177.2(4)

Table A.1-9: Anisotropic displacement coefficients ($\mathring{A}^2 \times 10^3$)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn(1)	70(1)	52(1)	46(1)	0	-2(1)	0
Si(2)	88(1)	121(2)	48(1)	0	10(1)	0
Si(3)	82(1)	142(2)	57(1)	0	-13(1)	0
Si(4)	129(1)	59(1)	174(2)	20(1)	37(1)	0(1)
C(1)	75(4)	69(5)	52(4)	0	7(3)	0
C(2)	74(4)	79(6)	61(4)	0	3(3)	0
C(3)	74(4)	67(5)	61(4)	0	-9(3)	0
C(4)	80(4)	68(5)	59(4)	0	3(3)	0
C(5)	78(3)	63(4)	60(3)	6(3)	0(2)	1(2)
C(6)	81(3)	67(4)	87(4)	-2(3)	0(3)	9(3)
C(21)	97(7)	461(24)	68(6)	0	-9(5)	0
C(22)	181(7)	161(8)	109(5)	-23(6)	47(4)	29(5)
C(31)	76(5)	263(15)	98(6)	0	12(5)	0
C(32)	168(6)	206(9)	105(5)	-40(6)	-12(5)	-62(5)
C(41)	260(11)	108(7)	196(9)	-32(8)	48(8)	-52(7)
C(42)	255(13)	121(7)	526(22)	54(8)	261(14)	34(11)
C(43)	239(11)	115(8)	297(13)	48(8)	-8(10)	84(9)

The anisotropic displacement factor exponent takes the form:

$-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$

Table A.1-10: H-Atom coordinates ($\times 10^4$) and isotropic displacement coefficients ($Å^2 \times 10^3$)

	x	y	z	U
H(21A)	3987	2500	-4160	237(10)
H(21C)	3428	2928	-3402	237(10)
H(22A)	6624	3363	-4011	237(10)
H(22B)	5911	3707	-3252	237(10)
H(22C)	7249	3339	-3129	237(10)
H(31A)	11169	2500	1256	237(10)
H(31C)	10374	2928	591	237(10)
H(32A)	9718	3412	2616	237(10)
H(32B)	8735	3770	2006	237(10)
H(32C)	8267	3204	2667	237(10)
H(41A)	3756	5886	1371	237(10)
H(41B)	3880	5161	1880	237(10)
H(41C)	4938	5373	1236	237(10)
H(42A)	926	5260	1343	237(10)
H(42B)	796	4424	1150	237(10)
H(42C)	1632	4686	1899	237(10)
H(43A)	2485	5952	-264	237(10)
H(43B)	3118	5241	-615	237(10)
H(43C)	1746	5209	-227	237(10)

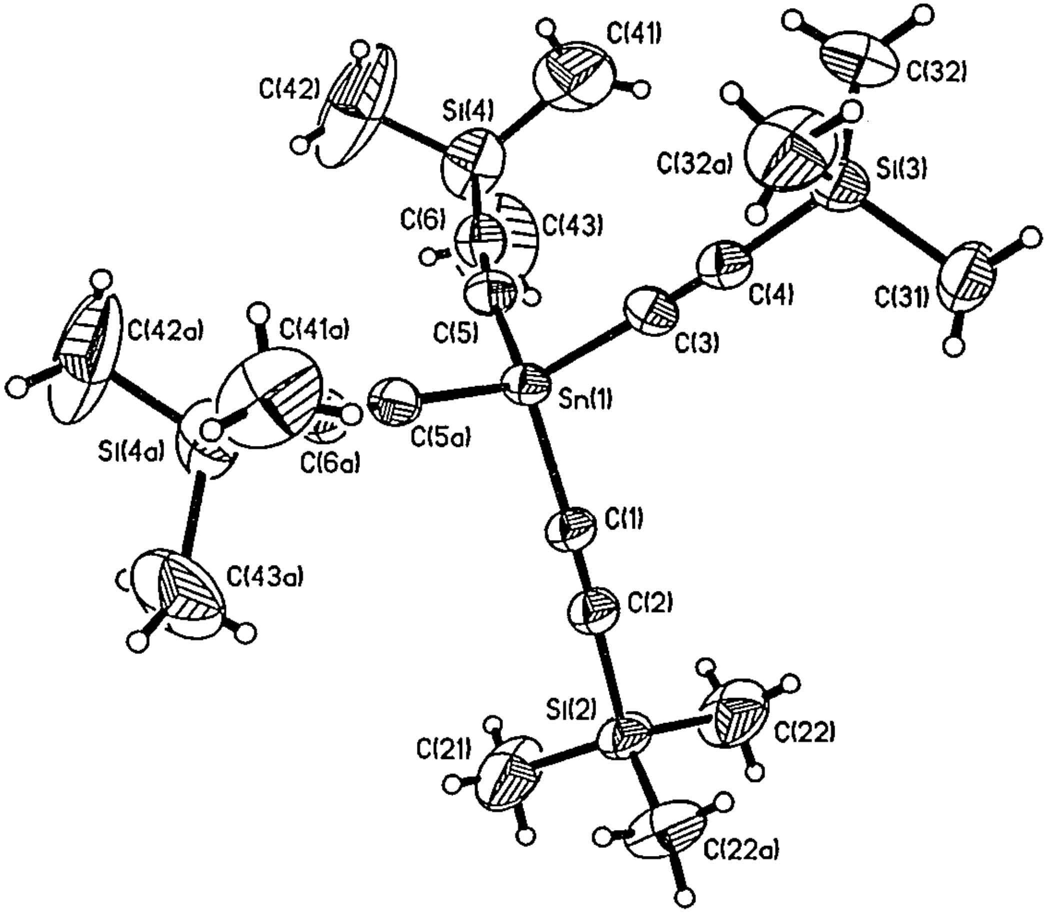


Figure A-2: X-ray crystal structure of $(Me_3Si\text{-}C{\equiv}C\text{-})_4Sn$

APPENDIX 2

Table A.2-1:
$Me_3Si\text{-}C\equiv C\text{-}SnMe_3$ 0.05M + $ClCH_2COOH$ 0.05M in $CDCl_3$

Experiment # 1
$k_{obs} = 1.82 \times 10^{-2}\ M^{-1}s^{-1}$
$\sigma = \pm\ 0.02 \times 10^{-2}$
$r^2 = .9970$
$r = .9985$

Experiment # 2
$k_{obs} = 2.18 \times 10^{-2}\ M^{-1}s^{-1}$
$\sigma = \pm\ 0.05 \times 10^{-2}$
$r^2 = .9908$
$r = .9954$

time (s)	NMR int.	time (s)	NMR int.
0	1	0	1
158	0.87	80	0.92
270	0.79	112	0.90
411	0.72	164	0.86
454	0.71	228	0.85
576	0.66	390	0.73
680	0.61	466	0.69
745	0.6	549	0.66
847	0.57	630	0.63
975	0.53	714	0.60
1116	0.51	782	0.58
1213	0.48	850	0.55
1431	0.44	964	0.52
1684	0.40	1127	0.48
1942	0.36	1339	0.42
2140	0.34	1769	0.37
2738	0.28	2006	0.33
2936	0.26	2340	0.29
3360	0.24	2806	0.25
4890	0.19	3518	0.20
		4164	0.1

Table A.2-2:
$Me_3Si\text{-}C{\equiv}C\text{-}SnMe_3$ 0.05M + $ClCH_2COOD$ 0.05M in $CDCl_3$

Experiment # 1	Experiment # 2
$k_{obs} = 0.80 \times 10^{-2}\ M^{-1}s^{-1}$	$k_{obs} = 0.67 \times 10^{-2}\ M^{-1}s^{-1}$
$\sigma = \pm\ 0.02 \times 10^{-2}$	$\sigma = \pm\ 0.01 \times 10^{-2}$
$r^2 = .9916$	$r^2 = .9938$
$r = .9958$	$r = .9969$

time (s)	NMR int.	time (s)	NMR int.
0	1	0	1
208	0.92	96	0.96
472	0.84	226	0.93
595	0.81	382	0.89
720	0.77	543	0.84
1004	0.71	718	0.81
1278	0.66	780	0.79
1547	0.61	1079	0.73
1657	0.59	1508	0.65
1810	0.57	2200	0.57
2193	0.54	2491	0.53
2423	0.50	2791	0.48
2648	0.48	2920	0.47
2923	0.45	3217	0.45
3294	0.42	3556	0.44
3793	0.40	4240	0.40
4308	0.39	4955	0.37
		6140	0.34
		7020	0.31
		12120	0.20

Table A.2-3:
n-Bu_3Sn-C≡C-$SiMe_3$ 0.05M + $ClCH_2COOH$ 0.05M in $CDCl_3$

<u>Experiment # 1</u>
k_{obs}= 0.73 × 10^{-2} $M^{-1}s^{-1}$
σ= ± 0.01 × 10^{-2}
r^2= .9943
r= .9972

<u>Experiment # 2</u>
k_{obs}= 0.64 × 10^{-2} $M^{-1}s^{-1}$
σ= ± 0.01 × 10^{-2}
r^2= .9936
r= .9968

time (s)	NMR int.	time (s)	NMR int.
0	1	0	1
120	0.94	125	0.94
250	0.906	319	0.90
430	0.86	624	0.80
579	0.82	809	0.794
792	0.78	996	0.76
1000	0.75	1184	0.746
1254	0.71	1478	0.71
1465	0.685	1670	0.69
1780	0.64	1910	0.665
2125	0.59	2672	0.54
2447	0.56	2948	0.53
2799	0.52	3420	0.497
3101	0.50	3813	0.46
3457	0.46	4449	0.44
3865	0.42	4866	0.416
4156	0.41	6180	0.31
4518	0.39	8580	0.26
5260	0.33	11400	0.208
6106	0.32		
6940	0.27		
8040	0.246		
8980	0.22		
12060	0.18		
13860	0.17		

Table A.2-4:
n-Bu_3Sn-C≡C-$SiMe_3$ 0.05M + $Cl_2CHCOOH$ 0.05M in $CDCl_3$

k_{obs}= 0.65 $M^{-1}s^{-1}$
σ= ± 0.05
r^2= .9642
r= .9820

time (s)	NMR int.
0	1
55	0.359
66	0.336
74	0.268
84	0.246
106	0.221
115	0.202
132	0.195

Table A.2-5:
Ph_3Sn-C≡C-$SiMe_3$ 0.05M + $Cl_2CHCOOH$ 0.05M in $CDCl_3$

k_{obs}= 0.38 × 10^{-2} $M^{-1}s^{-1}$
σ= ± 0.01 × 10^{-2}
r^2= .9896
r= .9948

time (s)	NMR int.
0	1
120	0.959
540	0.904
1980	0.753
3060	0.671
4080	0.591
5160	0.516
5580	0.505
8220	0.397
9780	0.37
11100	0.333
13560	0.291
15120	0.28
18960	0.204
21600	0.191

Table A.2-6:

$Ph_3Sn\text{-}C{\equiv}C\text{-}SiMe_3$ 0.05M + CCl_3COOH 0.05M in $CDCl_3$

Experiment # 1
k_{obs}= 0.183 $M^{-1}s^{-1}$
$\sigma = \pm 0.004$
r^2= .9950
r= .9975

Experiment # 2
k_{obs}= 0.204 $M^{-1}s^{-1}$
$\sigma = \pm 0.008$
r^2= .9851
r= .9925

time (s)	NMR int.	time (s)	NMR int.
0	1	0	1
101	0.50	99	0.525
118	0.455	115	0.48
139	0.42	132	0.43
158	0.39	151	0.39
175	0.375	170	0.37
192	0.356	188	0.35
209	0.344	226	0.32
221	0.327	244	0.308
260	0.30	265	0.28
290	0.275	305	0.255
325	0.253	338	0.22
348	0.0.24	397	0.20
450	0.20	480	0.157

Table A.2-7:

Experiment # 3
k_{obs}= 0.162 $M^{-1}s^{-1}$
$\sigma = \pm 0.004$
r^2= .9939
r= .9970

time (s)	NMR int.
0	1
90	0.582
115	0.525
140	0.474
165	0.432
215	0.373
315	0.273
365	0.237
440	0.22
565	0.185

Table A.2-8:

Ph_3Sn-C≡C-$SiMe_3$ 0.05M + CF_3COOH 0.05M in $CDCl_3$

k_{obs}= 0.57 $M^{-1}s^{-1}$
σ= ± 0.02
r^2= .9946
r= .9973

time (s)	NMR int.
0	1
94	0.29
111	0.26
128	0.235
144	0.22
176	0.18
360	0.08
458	0.07

Table A.2-9:

Me_3Ge-C≡C-$SiMe_3$ 0.05M + CF_3COOH in $CDCl_3$

[CF_3COOH] 0.05M
k_{obs}= 0.78 × 10^{-3} $M^{-1}s^{-1}$
σ= ± 0.06 × 10^{-3}
r^2= .9545
r= .9770

time (s)	NMR int.
0	1
2040	0.89
2820	0.85
3840	0.80
6000	0.78
11700	0.66
14400	0.63
17100	0.62
21600	0.56

Table A.2-10:

[CF$_3$COOH] 0.15M
k_{obs}= 2.9 × 10^{-3} $M^{-1}s^{-1}$
σ= ± 0.1 × 10^{-3}
r^2= .9885
r= .9942

time (s)	NMR int.
0	1
480	0.75
840	0.65
1740	0.45
2400	0.38
2760	0.32
3840	0.24
4620	0.19
4860	0.16
5880	0.13
6840	0.11

[CF$_3$COOH] 0.315M
k_{obs}= 5.60 × 10^{-3} $M^{-1}s^{-1}$
σ= ± 0.06 × 10^{-3}
r^2= .9990
r= .9995

time (s)	NMR int.
0	1
266	0.63
303	0.59
340	0.56
377	0.525
413	0.50
450	0.47
525	0.425
572	0.39
598	0.37
636	0.345

Table A.2-11:

[CF$_3$COOH] 0.41M
k_{obs}= 7.67 × 10^{-3} $M^{-1}s^{-1}$
σ= ± 0.09 × 10^{-3}
r^2= .9983
r= .9992

time (s)	NMR int.
0	1
146	0.641
184	0.56
222	0.491
261	0.437
305	0.385
337	0.355
380	0.311
417	0.283
454	0.256
524	0.222
598	0.174
672	0.146
710	0.126
788	0.102

[CF$_3$COOH] 0.5M
k_{obs}= 9.2 × 10^{-3} $M^{-1}s^{-1}$
σ= ± 0.1 × 10^{-3}
r^2= .9993
r= .9997

time (s)	NMR int.
0	1
128	0.555
195	0.427
325	0.237
370	0.194
410	0.168
443	0.148
512	0.114

Table A.2-12:

$[CF_3COOH]$ 0.5M
k_{obs}= 9.9 × 10^{-3} $M^{-1}s^{-1}$
σ= ± 0.2 × 10^{-3}
r^2= .9923
r= .9962

$[CF_3COOH]$ 0.5M
k_{obs}= 9.8 × 10^{-3} $M^{-1}s^{-1}$
σ= ± 0.1 × 10^{-3}
r^2= .9981
r= .9991

time (s)	NMR int.	time (s)	NMR int.
0	1	0	1
129	0.468	133	0.511
153	0.407	152	0.469
186	0.404	170	0.427
211	0.364	190	0.39
243	0.29	209	0.36
272	0.268	228	0.33
300	0.238	246	0.305
328	0.207	281	0.267
356	0.182	318	0.24
408	0.143	332	0.212
464	0.114	353	0.201
521	0.092	389	0.165
579	0.072	425	0.14
635	0.059	464	0.123
		501	0.105
		535	0.085
		570	0.074
		626	0.O6

Table A.2-13:

Me_3Si-C≡C-$SiMe_3$ 0.05M + CF_3COOH in $CDCl_3$

[CF_3COOH] 0.65M
k_{obs}= 1.83 × 10^{-5} $M^{-1}s^{-1}$
σ= ± 0.06 × 10^{-5}
r^2= .9887
r= .9943

[CF_3COOH] 0.8M
k_{obs}= 3.55 × 10^{-5} $M^{-1}s^{-1}$
σ= ± 0.07 × 10^{-5}
r^2= .9953
r= .9976

time (s)	NMR int.	time (s)	NMR int.
0	1	0	1
3600	0.943	1200	0.973
6900	0.913	3360	0.913
15840	0.814	7380	0.823
19140	0.783	12240	0.731
22680	0.742	15180	0.669
25200	0.745	16980	0.642
26800	0.727	19440	0.603
31800	0.687	21000	0.567
38280	0.642	23760	0.523
44100	0.616	28800	0.443
		32400	0.406
		36000	0.368
		38400	0.325

Table A.2-14:

$[CF_3COOH]$ 1.05M	$[CF_3COOH]$ 1.30M
$k_{obs} = 3.79 \times 10^{-5}\ M^{-1}s^{-1}$	$k_{obs} = 4.68 \times 10^{-5}\ M^{-1}s^{-1}$
$\sigma = \pm 0.08 \times 10^{-5}$	$\sigma = \pm 0.06 \times 10^{-5}$
$r^2 = .9935$	$r^2 = .9977$
$r = .9967$	$r = .9988$

time (s)	NMR int.	time (s)	NMR int.
0	1	0	1
300	0.99	240	0.98
1740	0.919	1620	0.893
3540	0.828	2640	0.836
5880	0.735	4560	0.744
7380	0.70	7560	0.62
14400	0.542	9540	0.557
16260	0.512	11580	0.491
18420	0.476	13620	0.436
20340	0.451	15780	0.402
22780	0.376	17580	0.344
28020	0.336	20340	0.277
30900	0.309	24060	0.247
35400	0.264	28020	0.19

Table A.2-15:

$Me_3Si\text{-}C{\equiv}C\text{-}SiMe_3$ 0.05M + CH_3SO_3H in $CDCl_3$

[CH_3SO_3H] 0.0725M
$k_{obs} = 0.37 \times 10^{-3}\ M^{-1}s^{-1}$
$\sigma = \pm 0.02 \times 10^{-3}$
$r^2 = .9319$
$r = .9654$

[CH_3SO_3H] 0.09M
$k_{obs} = 1.30 \times 10^{-3}\ M^{-1}s^{-1}$
$\sigma = \pm 0.08 \times 10^{-3}$
$r^2 = .9178$
$r = .9580$

time (s)	NMR int.	time (s)	NMR int.
0	1	0	1
105	0.98	193	0.969
855	0.87	1155	0.75
2040	0.765	1830	0.642
3600	0.64	2310	0.613
5160	0.568	3127	0.554
6600	0.512	3545	0.49
8520	0.453	5838	0.391
11700	0.424	6460	0.39
14580	0.383	7730	0.375
17220	0.345	10200	0.324
19620	0.327	10800	0.302
23820	0.291	12900	0.287
27000	0.276	14400	0.263
32400	0.224	19260	0.205
		23640	0.156
		24360	0.152
		27720	0.15
		31620	0.115

Table A.2-16:

$[CH_3SO_3H]$ 0.12M
k_{obs}= 1.55 × 10^{-3} $M^{-1}s^{-1}$
σ= ± 0.07 × 10^{-3}
r^2= .9674
r= .9838

$[CH_3SO_3H]$ 0.1375M
k_{obs}= 2.16 × 10^{-3} $M^{-1}s^{-1}$
σ= ± 0.09 × 10^{-3}
r^2= .9760
r= .9879

time (s)	NMR int.	time (s)	NMR int.
0	1	0	1
85	0.97	98	0.945
360	0.875	271	0.885
760	0.79	607	0.75
2390	0.51	975	0.68
3140	0.465	1561	0.57
5410	0.34	2214	0.48
6060	0.31	2895	0.41
8340	0.22	3616	0.362
10440	0.205	4750	0.257
12600	0.149	5520	0.226
15000	0.126	6495	0.174
19560	0.087	9420	0.127
21600	0.07	12900	0.07

Table A.2-17:

$[CH_3SO_3H]$ 0.2125M
$k_{obs} = 3.4 \times 10^{-3}\ M^{-1}s^{-1}$
$\sigma = \pm 0.1 \times 10^{-3}$
$r^2 = .9793$
$r = .9896$

time (s)	NMR int.
0	1
129	0.87
172	0.855
300	0.748
500	0.643
712	0.547
900	0.49
1192	0.427
1230	0.35
1630	0.327
1866	0.294
2033	0.255
2273	0.223
2584	0.185
2810	0.16
2955	0.156
3165	0.143
3615	0.119
4230	0.10

$[CH_3SO_3H]$ 0.26M (saturated)
$k_{obs} = 3.3 \times 10^{-3}\ M^{-1}s^{-1}$
$\sigma = \pm 0.1 \times 10^{-3}$
$r^2 = .9652$
$r = .9824$

time (s)	NMR int.
0	1
155	0.829
257	0.735
424	0.627
552	0.564
732	0.487
878	0.445
1098	0.369
1267	0.317
1397	0.293
1542	0.262
1648	0.24
1800	0.228
2016	0.198
2247	0.179
2676	0.144
3147	0.117
3447	0.098

Table A.2-18:

Me$_3$Si-C≡C-SiMe$_2$*t*-Bu 0.05M + CH$_3$SO$_3$H in CDCl$_3$

[CH$_3$SO$_3$H] 0.145M
k_{obs}= 2.8 × 10^{-3} $M^{-1}s^{-1}$
$\sigma = \pm 0.1 \times 10^{-3}$
r^2= .9678
r= .9838

time (s)	NMR int.
0	1
190	0.88
328	0.81
392	0.77
735	0.68
1470	0.55
2020	0.40
2480	0.39
3080	0.32
3540	0.28
4160	0.25
5880	0.18

[CH$_3$SO$_3$H] 0.155M
k_{obs}= 3.05 × 10^{-3} $M^{-1}s^{-1}$
$\sigma = \pm 0.05 \times 10^{-3}$
r^2= .9984
r= .9969

time (s)	NMR int.
0	1
140	0.93
594	0.72
980	0.62
1523	0.48
2298	0.40
2674	0.35
3125	0.28
3540	0.24
3920	0.21
4350	0.18
4980	0.15

Table A.2-19:

[CH$_3$SO$_3$H] 0.175M
k_{obs}= 3.3 × 10^{-3} $M^{-1}s^{-1}$
$\sigma = \pm 0.1 \times 10^{-3}$
r^2= .9710
r= .9859

time (s)	NMR int.
0	1
101	0.93
172	0.88
257	0.83
693	0.68
788	0.63
901	0.57
1080	0.51
1323	0.45
1616	0.40
1931	0.34
1366	0.27
2790	0.25
3720	0.20

[CH$_3$SO$_3$H] 0.3375M (saturated)
k_{obs}= 4.4 × 10^{-3} $M^{-1}s^{-1}$
$\sigma = \pm 0.2 \times 10^{-3}$
r^2= .9876
r= .9938

time (s)	NMR int.
0	1
141	0.76
228	0.65
390	0.52
538	0.44
669	0.38
825	0.32
915	0.30
1286	0.16
1555	0.11
1845	0.10

Table A.2-20:

[CH_3SO_3H] 0.37M (saturated)
$k_{obs} = 4.7 \times 10^{-3}\ M^{-1}s^{-1}$
$\sigma = \pm 0.2 \times 10^{-3}$
$r^2 = .9805$
$r = .9902$

time (s)	NMR int.
0	1
167	0.694
200	0.667
230	0.62
284	0.57
342	0.51
400	0.466
516	0.39
572	0.365
629	0.335
686	0.31
821	0.26
955	0.216
1091	0.18
1222	0.16

[CH_3SO_3H] 0.445M (saturated)
$k_{obs} = 4.8 \times 10^{-3}\ M^{-1}s^{-1}$
$\sigma = \pm 0.2 \times 10^{-3}$
$r^2 = .9557$
$r = .9776$

time (s)	NMR int.
0	1
181	0.62
198	0.59
215	0.57
248	0.53
282	0.49
316	0.46
350	0.43
400	0.40
433	0.37
467	0.345
501	0.32
577	0.28
627	0.26
753	0.20
928	0.157
1240	0.11

Table A.2-21:

$Me_3Si\text{-}C{\equiv}C\text{-}SiPh_3$ 0.05M + CH_3SO_3H in $CDCl_3$

[CH_3SO_3H] 0.1425M
$k_{obs} = 0.79 \times 10^{-4}\ M^{-1}s^{-1}$
$\sigma = \pm 0.02 \times 10^{-4}$
$r^2 = .9962$
$r = .9981$

time (s)	NMR int.
0	1
46800	0.616
53580	0.593
60420	0.546
73020	0.477
81600	0.432

[CH_3SO_3H] 0.15M
$k_{obs} = 0.76 \times 10^{-4}\ M^{-1}s^{-1}$
$\sigma = \pm 0.06 \times 10^{-4}$
$r^2 = .9706$
$r = .9852$

time (s)	NMR int.
0	1
3600	0.927
12120	0.816
16380	0.765
63900	0.56
72000	0.513
99120	0.346

Table A.2-22:

$[CH_3SO_3H]$ 0.21M
k_{obs}= 1.61 × 10^{-4} $M^{-1}s^{-1}$
σ= ± 0.05 × 10^{-4}
r^2= .9925
r= .9962

time (s)	NMR int.
0	1
615	0.986
3900	0.978
7560	0.744
11400	0.676
16200	0.598
23400	0.488
33000	0.351
41940	0.288

$[CH_3SO_3H]$ 0.40M (saturated)
k_{obs}= 1.80 × 10^{-4} $M^{-1}s^{-1}$
σ= ± 0.04 × 10^{-4}
r^2= .9964
r= .9982

time (s)	NMR int.
0	1
1175	0.929
3600	0.792
8100	0.52
12000	0.412
16620	0.325
18900	0.277
24060	0.19
32520	0.122

Table A.2-23:

$[CH_3SO_3H]$ 0.825M (saturated)
k_{obs}= 2.01 × 10^{-4} $M^{-1}s^{-1}$
σ= ± 0.08 × 10^{-4}
r^2= .9897
r= .9948

time (s)	NMR int.
0	1
1140	0.845
3180	0.56
4380	0.472
5160	0.41
8520	0.214
11040	0.182
13680	0.131
15300	0.082

$[CH_3SO_3H]$ 0.825M (saturated)
k_{obs}= 1.90 × 10^{-4} $M^{-1}s^{-1}$
σ= ± 0.04 × 10^{-4}
r^2= .9970
r= .9985

time (s)	NMR int.
0	1
600	0.915
2580	0.636
3780	0.521
6300	0.40
9000	0.233
11520	0.17
13800	0.131
16200	0.088

Table A.2-24:

$Ph_3Ge\text{-}C\equiv C\text{-}SiMe_3$ 0.05M + CH_3SO_3H in $CDCl_3$

$[CH_3SO_3H]$ 0.1325M
$k_{obs} = 8.4 \times 10^{-3}\ M^{-1}s^{-1}$
$\sigma = \pm\ 0.5 \times 10^{-3}$
$r^2 = .9459$
$r = .9726$

time (s)	NMR int.
0	1
160	0.745
324	0.574
527	0.476
711	0.398
790	0.375
940	0.317
1038	0.313
1261	0.262
1482	0.22
1699	0.193
1998	0.172
2263	0.149
2880	0.103
3480	0.074

$[CH_3SO_3H]$ 0.325M (saturation)
$k_{obs} = 22.5 \times 10^{-3}\ M^{-1}s^{-1}$
$\sigma = \pm\ 0.3 \times 10^{-3}$
$r^2 = .9987$
$r = .9994$

time (s)	NMR int.
0	1
142	0.394
163	0.333
184	0.284
204	0.25
226	0.216
267	0.159
325	0.118
367	0.09

Table A.2-25:

Ph_3Ge-C≡C-$SiMe_3$ 0.05M + CF_3COOH in $CDCl_3$

[CF_3COOH] 0.50M
$k_{obs} = 7.3 \times 10^{-5}\ M^{-1}s^{-1}$
$\sigma = \pm 0.3 \times 10^{-5}$
$r^2 = .9799$
$r = .9899$

time (s)	NMR int.
0	1
1740	0.96
2160	0.91
4080	0.792
6000	0.787
9240	0.678
10800	0.647
14400	0.576
17220	0.527
21000	0.487
24300	0.439
29100	0.4063
32940	0.336
36000	0.242
40200	0.26

APPENDIX 3

The normal behavior for an organic reaction that goes through an ionic intermediate is that the rate of reaction increases with increasing dielectric constant of the medium[13,111]. Thus the rate of reaction for an Ad_E2-E2 mechanism is increased by addition of an ionic salt (positive salt effect).

It is known that the rate of addition of a protic electrophile depends strongly on the acidity of the medium[111]. The salt effect described herein refer only to the hydrogen ion activity of the organic medium ($CDCl_3$)[126]. Since this parameter, as well as the pKa of the acids in chloroform-*d* solution are unknown, we used the concentration of the acid.

Therefore, the second-order rate constant observed is described by:

$k_{obs} = k \times a_{H+}$

or if $a_{H+} \approx \delta[\text{acid}]$

$k_{obs} \cong k \times \delta[\text{acid}]$

where k is the second-order rate contant of the reaction and δ is a value depending on the acid used in $CDCl_3$ solution (or the pK). If δ is constant in the range of acid concentration used, the plot of k_{obs} versus [acid] is linear with δk as the slop and 0 as intercept. By extrapolation, we get the k_{obs} of the reaction of the alkyne (0.05M) with an acid concentration of 0.05M.

The constant δ has the unit M^{-1}, then by the following operation:

$k_{obs} \times [Alk]/[Akl] \cong k \times \delta[acid] \times [Alk]/[Akl]$

$k_{obs} \cong k \times \epsilon[acid]/[Akl]$

where $\epsilon = \delta/[acetylene] = \delta[0.05M]$

and ϵ is a constant without unit and reflects the ionic strenght of the medium from the acid and depends on the pk of the acid in $CDCl_3$ solution.

With the plot of k_{obs} versus the [acid]/[Akl] ratio, we get the k_{obs} for the reaction between an alkyne and an acid concentration of 0.05M in $CDCl_3$ solution, from a [acid]/[Akl] ratio of one or from the slop ϵk.

In this study, we assumed that the comparison of the rate contant observed for a stoichiometric reaction of 0.05M in $CDCl_3$ between different alkynes with the same acid (the same pk and ϵ) minimizes the error.

REFERENCES

1) For a review see, P. J. Stang, Z. Rappoport, M. Hanack and L. R. Subramanian, "Vinyl Cations", Academic Press, New York (1979).

2) S. Winstein, E. Grunward, R. E. Buckles and C. Hanson, J. Am. Chem. Soc., 70, 816 (1948) and references therein.

3) L. Radom, P. C. Hariharan, J. A. Pople and P. von R. Schleyer, J. Am. Chem. Soc., 95, 6531 (1973) and references therein.

4) C. A. Grob and G. Csek, Helv. Chim. Acta, 47, 194 (1964).

5) Z. Rappoport, Acc. Chem. Res., 9, 265 (1976).

6) M. Hanack, Acc. Chem. Res., 9, 364 (1976).

7) M. Hanack, Pure and Appl. Chem., 56, 1819 (1984).

8) S. Kobayashi, T. Kitamura, H. Taniguchi and W. Schnabel, Chem. Lett., 1117 (1983).

9) H.-U. Siel and E.-W. Koch, J. Org. Chem., 49, 575 (1984).

10) H. Mayr, R. Schneider, D. Wilhelm and P. von R. Schleyer, J. Org. Chem., 46, 5336 (1981).

11) S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Leevin and W. G. Mallard, J. Phys. Chem. Ref. Data, Vol. 17, Suppl. 1 (1988).

12) Y. Apeloig, P. von R. Schleyer and J. A. Pople, J. Org. Chem., 42, 3004 (1977).

13) E. S. Amis and J. F. Hinton, "Solvent Effects on Chemical Phenomena", Vol. 1, Academic Press (1973).

14) G. Melloni, G. Modena and U. Tonellato, Acc. Chem. Res., 14, 227 (1981) and references therein.

15) Y. Apeloig, J. B. Collins, D. Cremer, T. Bally, E. Haselbach, J. A. Pople, J. Chandrasekhar and P. von R. Schleyer, J. Org. Chem., 45, 3496 (1980).

16) J. Weber, M. Yoshimine, and A. D. McLean, J. Chem. Phys., 64, 4159 (1976).

17) Y. Apeloig and D. Arad, J. Am. Chem. Soc., 107, 5285 (1985) and references therein.

18) R. Sustmann, J. E. Williams Jr., M. J. S. Dewar, L. C. Allen and P. von R. Schleyer, J. Am. Chem. Soc., 91, 5350 (1969); A. C. Hopkins, K. Yates and I. G. Csizmadia, J. Phys. Chem., 55, 3835 (1971).

19) For a review on electrophilic addition to allenes see: W. Smadja, Chem. Rev., 83, 263 (1983).

20) R. H. Summerville and P. von R. Schleyer, J. Am. Chem. Soc., 96, 1100 (1974).

21) For a review see: a) W. S. Johnson, Angew. Chem., Int. Ed. Engl., 15, 9 (1976); b) M. B. Groen and F. J. Zeelen, Recl. Trav. Chim. Pays-Bas, 105, 465-487 (1986).

22) W. S. Johnson, B. Frei, A. S. Gopalan, J. Org. Chem., 46, 1513 (1981); W. S. Johnson, R. S. Brinkmeyer, V. M. Kapoor and T. M. Yarnell, J. Am. Chem. Soc., 99, 8341 (1977).

23) W. N. Speckamp and H. Hiemstra, Tetrahedron, 41, 4367 (1985); W. J. Klaver, H. Hiemstra and W. N. Speckamp, Tetrahedron, 44, 6729 (1988).

24) L. D. M. Lolkema, H. Hiemstra, H. Mooiweer and W. N. Speckamp, Tetrahedron Lett., 6365 (1988).

25) F. P. J. T. Rutjes, H. Hiemstra, H. Mooiweer and W. N. Speckamp, Tetrahedron Lett., 6975 (1988).

26) P. J. Stang, M. Hanack and L. R. Subramanian, Synthesis, 82 (1982).

27) W. D. Pfeifer, C. A. Bahn, P. von R. Schleyer, S. Bocher, C. E. Harding, K. Hummel, M. Hanack and P. J. Stang, J. Am. Chem. Soc., 91, 1513 (1971).

28) R. J. Hargrove and P. J. Stang, Tetrahedron 32, 37 (1976).

29) I. Harder and M. Hanack, Chem. Ber., 118, 2974 (1985).

30) H. Mayr and F. Shütz, Tetrahedron Lett., 925 (1981).

31) Z. Rappoport and A. Gal, J. Chem. Soc. Perkin II, 301 (1973).

32) C. A. Grob and R. S. Spaar, Helv. Chim. Acta, 53, 2119 (1970).

33) M. Hanack, T. Bässel, W. Eymann, W. E. Heyd and R. Koop, J. Am. Chem. Soc., 96, 6686 (1974).

34) M. D. Schiavelli, T. C. Germroth and J. W. Stubbs, J. Org. Chem., 41, 681 (1976).

35) For a review on vinylidene metal complexes see: M. I. Bruce and A. G. Swinger, Adv. Org. Chem., 22, 59 (1983).

36) L. I. Zarharkin and V. V. Kobak, J. Organomet. Chem., 246, C65 (1983); D. F. Marten, J. Chem. Soc., Chem. Commun., 341 (1980).

37) D. Bauer, P. Härter and E. Herdtweck, J. Chem. Soc., Chem. Commun., 829 (1991); A. Davison and J. P. Selegue, J. Am. Chem. Soc., 102, 2455 (1980); T. S. Abram and W. E. Watts, J. Chem. Soc., Perkin I, 1522, 1527 (1977).

38) N. M. Kostic and R. F. Fenske, Organomet., 1, 974 (1982).

39) D. Kaufman, R. Kupper and T. Neal, J. Org. Chem., 44, 3076 (1979).

40) M. I. Bruce, C. Dean, D. N. Duffy, M. G. Humphrey and G. A. Kousantonis, J. Organomet. Chem., 295, C40 (1985).

41) M. I. Bruce, G. A. Kousantonis and M. J. Liddell, J. Organomet. Chem., 320, 217 (1980); M. I. Bruce and R. C. Wallis, Aust. J. Chem., 32, 1471 (1979).

42) N. E. Kolobova, V. Skripkin, T. V. Rozantseva, Y. T. Struchkov and G. Aleksandrov, J. Organometal. Chem., 218, 351 (1981).

43) H. C. Clark and L. E. Manzer, J. Organomet. Chem., 47, C17 (1973).

44) R. A. Bell and M. H. Chisholm, Inorg. Chem., 16, 68 (1977) and references therein.

45) K. Oguro, M. Wada and R. Okawara, J. Organomet. Chem., 159, 417 (1978); *ibid.* J. Chem. Soc., Chem. Commun., 899 (1975).

46) For reviews see a) J. B. Lambert, Tetrahedron, 46, 2677 (1990); b) A. R. Bassindale and P. G. Taylor, *Activating and Directing Effects of Silicon,* in "The Chemistry of Organic Silicon Compounds", Chapter 14, Ed. S. Patai and Z. Rappoport, John Wiley (1989).

47) For a review see: E. W. Colvin, "Silicon in Organic Synthesis", Butterworths, London (1981).

48) J. A. Soderquist and A. Hassner, Tetrahedron Lett., 1899 (1988).

49) V. J. Shiner Jr., M. W. Ensinger and R. D. Rutkowske, J. Am. Chem. Soc., 109, 804 (1987); W. Kirmse and F. Söllenböhmer, J. Am. Chem. Soc., 111, 4127 (1989).

50) A. C. Hopkinson and M. H. Lien, J. Org. Chem., 46, 998 (1981).

51) C. G. Pitt, J. Organomet. Chem., 61, 49 (1973).

52) Y. Apeloig and A. Stanger, J. Am. Chem. Soc., 107, 2806 (1985).

53) S. G. Wierschke, J. Chandrasekhar and W. L. Jorgensen, J. Am. Chem. Soc., 107, 1496 (1985).

54) X. Li and J. A. Stone, J. Am. Chem. Soc., 111, 5586 (1989); Y. Apeloig and A. Stanger, J. Am. Chem. Soc., 109, 272 (1987).

55) D. Hajdasz and R. Squires, J. Chem. Soc., Chem. Commun., 1212 (1983).

56) J. A. Pople, Y. Apeloig and P. von R. Schleyer, Chem. Phys. Lett., 85, 489 (1985).

57) M. D. Schiavelli, D. M. Jung and A. K. Vaden, J. Org. Chem., 46, 92 (1981).

58) Y. Apeloig and A. Stanger, J. Org. Chem., 47, 1462 (1982); see also corrections in J. Org. Chem., 48, 5413 (1983).

59) L. H. Sommer and F. C. Whitmore, J. Am. Chem. Soc., 68, 485 (1946); L. H. Sommer, E. Dorfman, G. M. Goldberg and F. C. Whitmore, J. Am. Chem. Soc., 68, 488 (1946).

60) A. J. Bourne and A. W. P. Jarvie, J. Organomet. Chem., 24, 335 (1970); A. W. P. Jarvie, A. Holt and J. Thompson, J. Chem. Soc. B, 746 (1970).

61) M. A. Cook, C. Eaborn and D. R. M. Walton, J. Organomet. Chem., 24, 301 (1970).

62) T. G. Taylor, W. Hanstein, H. J. Berwin, N. A. Clinton and R. S. Brown, J. Am. Chem. Soc., 93, 5715 (1971); T. G. Traylor, Pure and Appl. Chem., 30, 599 (1972).

63) a) S. J. Hannon and T. G. Traylor, J. Org. Chem., 46, 3645 (1981) and references therein; b) T. G. Traylor and G. S. Koermer, J. Org. Chem., 46, 3651 (1981) and references therein.

64) J. B. Lambert, G.-t. Wang and D. H. Teramura, J. Org. Chem., 53, 5422 (1988) and references therein; J. B. Lambert and G.-t. Wang, Tetrahedron Lett., 2551 (1988).

65) J. B. Lambert, G.-t. Wang, R. B. Finzel and D. H. Teramura, J. Am. Chem. Soc., 109, 7838 (1987).

66) J. B. Lambert and E. C. Chelius, J. Am. Chem. Soc., 112, 8120 (1990).

67) G.-t. Wang, D. Li, E. C. Chelius and J. B. Lambert, J. Chem. Soc., Perkin Trans. 2, 331, (1990); J. B. Lambert and G.-t. Wang, J. Phys. Org. Chem., 1, 169 (1988).

68) P. Deslongchamps, "Stereoelectronic Effects in Organic Chemistry", Organic Chemistry series; Vol. 1, Pergamon Press (1983).

69) M. R. Ibrahim and W. L. Jorgensen, J. Am. Chem. Soc., 111, 819 (1989).

70) Y. Apeloig, P. von R. Schleyer and J. A. Pople, J. Am. Chem. Soc., 99, 5901 (1977); see also J. C. White, R. J. Cave and E. R. Davidson, J. Am. Chem. Soc., 110, 6308 (1988).

71) F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 4th Ed., John Wiley (1980).

72) K. Ohwada, Polyhedron, 2, 423 (1983) and references therein.

73) A. J. Smith, W. Adcock and W. Kitching, J. Am. Chem. Soc., 92, 6140 (1970).

74) T. G. Traylor, H. J. Berwin, J. Jerkunica and M. L. Hall, Pure Appl. Chem., 30, 599 (1972).

75) For a revised set of σ^+_Y see: D. D. Davis, J. Organomet. Chem., 206, 21 (1981); D. Davis and H. M. Jacocks III, J. Organomet. Chem., 206, 33 (1981).

76) W. F. Reynolds, G. K. Hamer and A. R. Bassindale, J. Chem. Soc., Perkin II, 971 (1977).

77) J. M. Jerkunica and T. G. Traylor, J. Am. Chem. Soc., 93, 6278 (1971).

78) I. Fleming, "Frontier Orbitals and Organic Chemical Reactions", John Wiley (1982).

79) H. G. Kuivila and J. A. Verdone, Tetrahedron Lett., 119 (1964).

80) M. A. Brook and A. Neuy, J. Org. Chem., 55, 3609 (1990); M. A. Brook, M. A. Hadi and A. Neuy, J. Chem. Soc., Chem. Commun., 957 (1989).

81) Weifeng Yu, The Role of Ligands on Silicon, M. Sc. dissertation, McMaster University, Hamilton, Canada (1991).

82) H. Mayr and G. Hagen, J. Chem. Soc., Chem. Commun., 91 (1989).

83) G. Hagen and H. Mayr, J. Am. Chem. Soc., 113, 4954 (1991).

84) R. W. Bott, C. Eaborn, and D. R. M. Walton, J. Organomet. Chem., 1, 420 (1964); R. W. Bott, C. Eaborn and D. R. M. Walton, J. Chem. Soc., 384 (1965).

85) J. C. Cochran and H. G. Kuivila, Organometallics, 1, 97 (1982); H. G. Kuivila and J. C. Cochran, J. Am. Chem. Soc., 89, 7152 (1967).

86) J. A. Verdone, J. A. Mangravite, N. M. Mangravite, N. M. Scarpa and H. G. Kuivila, J. Am. Chem. Soc., 97, 843 (1975).

87) J. C. Cochran, S. C. Bayer, J. T. Bilbo, M. S. Brown, L. B. Colen, F. J. Gaspirini, D. W. Goldsmith, M. D. Jamin, K. A. Nealy, C. T. Resnick, G. J. Schwartz, W. M. Short, K. R. Skarda, J. P. Sping and W. L. Strauss, Organometallics, 1, 586 (1982).

88) J. P. Pillot, B. Bennetau, J. D. Dunoguès et B. Calas, Tetrahedron Lett., 22, 3401 (1981); P. Bourgeois et G. Méreault, J. Organomet. Chem., 39, C44 (1972).

89) L. G. Kozar, R. D. Clark and C. H. Heathcock, J. Org. Chem., 42, 1386 (1977).

90) D. Schinzer, Synthesis, 263 (1988) and references therein; J. Pornet, D. Damour et L. Miginiac, J. Organomet. Chem., 319, 333 (1987) and references therein; S. Prasad and L. S. Liebeskind, Tetrahedron Lett., 4253 (1988).

91) R. L. Danheiser, E. J. Stoner, H. Koyama, D. S. Yamashita and C. A. Klade, J. Am. Chem. Soc., 111, 4407 (1989) and reference therein; I. Fleming, Pure & Appl. Chem., 62, 1879 (1990).

92) R. L. Danheiser, D. J. Carini, D. M. Fink and A. Basak, Tetrahedron, 39, 935 (1983).

93) T. Hayashi, Y. Okamoto and M. Kumada, Tetrahedron Lett., 807 (1983).

94) R. L. Danheiser, D. J. Carini and C. A. Kwasigroch, J. Org. Chem., 51, 3870 (1986).

95) R. M. Williams, D. J. Aldous and S. C. Aldous, J. Chem. Soc., Perkin Trans. I, 171 (1990).

96) M. D. Bachi, N. Bar-Ner, C. M. Crittell, P. J. Stang and B. L. Williamson, J. Org. Chem., 56, 3912 (1991) and references therein; P. J. Stang, B. W. Surber, Z.-C. Chen, K. A. Roberts and A. G. Anderson, J. Am. Chem. Soc., 109, 228 (1987).

97) T. Kitamura and P. J. Stang, J. Org. Chem., 53, 4105 (1988) and reference therein.

98) P. J. Stang, A. M. Arif and C. M. Crittell, Angew. Chem., Int. Ed. Engl., 29, 287 (1990) and references therein.

99) J.-i. Haruta, K. Nishi, S. Matsuda, Y. Tamura and Y. Kita, J. Org. Chem., 55, 4853 (1990).

100) G. Guillerm, F. Meganem et M. Lequan, J. Orrganomet. Chem., 67, 43 (1974); G. Mérault, P. Bourgeois et J. Donoguès, C. R. Acad. Sc. Paris, 274 C, 1857 (1972); J.-C. Masson, M. Le Quan et P. Cadiot, Bull. Soc. Chim. Fr., 777 (1967); M. Le Quan et P. Cadiot, Bull. Soc. Chim. Fr., 6, 145 (1965).

101) M. Le Quan et P. Cadiot, Bull. Soc. Chim. Fr., 5, 35 (1965).

102) W. E. Davidsohn and M. C. Henry, Chem. Rev., 67, 73 (1967).

103) W. Findeiss, W. E. Davidsohn and M. C. Henry, J. Organomet. Chem., 9, 435 (1967).

104) O. G. Yarosh, L.V. Zhilitzkaya, T. D. Burnashova and M. G. Voronkov, Metalloorg. Khim., 2, 515 (1989).

105) K. Ruitenberg, H. Westmijze, H. Kleijn and P. Vermeer, J. Organomet. Chem., 277, 227 (1984); K. Ruitenberg and P. Vermeer, Tetrahedron Lett. 3019 (1984); E. Keinan and M. Peretz, J. Org. Chem. 48, 5302 (1983).

106) G. A. Razuvaev, A. N. Egorochkin, S. E. Skobeleva, V. A. Kuznetsov, M. A. Lopatin, A. Petrov, V. S. Zavgorodny, E. T. Bogoradovsky, J. Organomet. Chem., 222, 55 (1981).

107) M. Rumeau, Ann. Chim., 2, 131 (1973).

108) For studies on *cis*-bending of alkynes see: K. Kamieńska-Trela, H. Ilcewicz, M. Rospenk and M. Pajdowska, J. Chem. Research (S), 122 (1987); W. F. Maier, G. C. Lau and A. B. McEven, J. Am. Chem. Soc., 107, 4724 (1985).

109) A. D. Allen, Y. Chiang, A. J. Kresge and T. T. Tidwell, J. Org. Chem., 47, 775 (1982) and references therein.

110) D. S. Noyce and M. D. Schiavelli, J. Am. Chem. Soc., 90, 1020 (1968); *ibid.* 90, 1023 (1968).

111) T. H. Lowry and K. S. Richardson, "Mechanism and Theory in Organic Chemistry", Third Edition (1987), Chapter 2.

112) P. Baekelmans, M. Gielen, P. Malfroid and J. Nasielski, Bull. Soc. Chim. Belges, 77, 85 (1968).

113) S. N. Tandura, M. G. Voronkov and N. V. Alekseev, Top. Curr. Chem., 131, 99 (1986).

114) For a review on pentacoordinated structures see: R. R. Holmes, Prog. Inorg. Chem., Vol. 32, 119 (1984).

115) B. J. Helmer, R. West, R. J. P. Corriu, M. Poirier, G. Royo and de Saxce, J. Organomet. Chem., 251, 295 (1983); R. J. P. Corriu and J. C. Young, *Hypervalent Silicon Compounds* in "The Chemistry of Organic Silicon Compounds", Ed. S. Patai and Z. Rappoport, Wiley (1989) p. 1242 and references therein.

116) L. Brandsma and H. D. Verkruijsse, "Synthesis of Acetylenes, Allenes and Cumulenes", Study in Organic Chemistry, Vol. 8, Elsevier, p. 55 (1981).

117) N. J. Fitzmaurice, R. Jackson and P. Perlmutter, J. Organomet. Chem., 285, 375 (1985).

118) a) N. V. Komarov, O. G. Yarosh, J. Gen. Chem. USSR (Engl. Transl.) 37, 260 (1967); b) M. F. Shostakovskii, N. V. Komarov and O. G. Yarosh, Bull. Acad. Sci. URSS Div. Chem. Sci., 2458 (1967).

119) H. Schmidbaur, J. Ebenhöch und G. Müller, Z. Naturforsch, 43b, 49 (1988).

120) M. W. Logue and K. J. Tendy, J. Org. Chem., 47, 2259 (1982).

121) C. S. Kraihanzel and M. L. Losee, J. Organomet. Chem., 10, 427 (1967).

122) V. F. Mironov and A. L. Kravchenko, Bull. Acad. Sci. URSS, Div. Chem. Sci. (Engl. Transl.) 1026 (1965).

123) R. J. Schmitt, J. C. Bottaro, R. Malhotra and C. D. Bedford, J. Org. Chem., 52,2294 (1987).

124) G. Fritz und N. Z. Szczepanski, Anorg. Allg. Chem., 44, 367 (1969).

125) O. G. Yarosh, N. V. Komarov and M. G. Voronkov, Bull. Acad. Sci. URSS Div. Chem. Sci. (Engl. Transl.), 1633 (1973).

126) J. Benitez, M. del Mar Graciani, C. D. Hubbard and F. Sanchez-Burgos, J. Solut. Chem., 19, 19 (1990).