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THE DIRECT DETECTION OF GERMENES IN SOLUTION:
THE PHOTOCHEMISTRY OF 1,1-DIPHENYLGERMETANE, ARYLGERMASILANES, AND ARYLDIGERMANES

By

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A Thesis
Submitted to the School of Graduate Studies
in Partial Fulfillment of the Requirements
for the Degree
Doctor of Philosophy

McMaster University

GERMANIUM-CARBON DOUBLY-BONDED COMPOUNDS

DOCTOR OF PHILOSOPHY (1999) McMaster University
(Chemistry) Hamilton, Ontario

TITLE: The Direct Detection of Germenes in Solution: The Photochemistry of 1,1-Diphenylgermetane, Aryldisilanes, and Aryldigermanes.

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NUMBER OF PAGES: xiv, 124

Abstract

"Silenes" and "germenes" are molecules containing Si=C and Ge=C double bonds, respectively. Unlike their all-carbon analogues, they are normally highly reactive (only a few stable derivatives of each type are known), and are involved as intermediates in the thermal and photochemical reactions of a wide variety of organosilicon and organogermanium compounds. Some of the reactions which involve the intermediacy of these species will be reviewed, as will some of the recent efforts to characterize transient silenes and germenes and investigate the mechanisms of their more common reactions.

The first part of this thesis focuses on the generation and characterization of a germanium-carbon doubly bonded species in solution. Direct irradiation of 1,1-diphenylgermetane in hexane solution in the presence or absence of aliphatic alcohols leads to products consistent with the formation of 1,1-diphenylgermene as the primary photochemical product. Nanosecond laser flash photolysis of the germetane in hexane, acetonitrile and tetrahydrofuran gives rise to the formation of a transient, assignable to the germene on the basis of its second order decay kinetics, UV spectrum (λ_{max} = 325-nm), and the fact that its lifetime is shortened by the addition of alcohols and acetic acid. Absolute rate constants for reaction of 1,1-diphenylgermene with a variety of nucleophiles (aliphatic alcohols, acetic acid, the *O*-deuterated isotopomers, and acetone) have been determined in three solvents (hexane, acetonitrile, and THF), using the germetane as the precursor. The kinetics and mechanisms of these germene trapping reactions are discussed and compared to those of silenes.

The mechanism of silene and germene dimerization reactions was investigated using 1,1-diphenylsilacyclobutane and 1,1-diphenylgermetane as precursors to 1,1-diphenylsilene and 1,1-diphenylgermene respectively. 1,1,3,3-Tetraphenyl-1,3-disilacyclobutane, -1,3-digermacyclobutane, and 1,3-germasilacyclobutane have been synthesized by direct photolysis of hexane solutions of 1,1-diphenylsilacyclobutane, 1,1-diphenylgermetane, and a 1:1 mixture of the two. The molecular structures of the three compounds have been determined by single crystal X-ray crystallography. Direct photolysis of the dimetallacyclobutanes in the presence of methanol yields the corresponding alkoxymetallanes from trapping of 1,1-diphenylsilene and/or 1,1-diphenylgermene in all three cases. The quantum yield for photocycloreversion of the digermacyclobutane is roughly 25% that of 1,1-diphenylgermacyclobutane, but about five times higher than that for the silagermacyclobutane and about fifteen times higher than that for the disilacyclobutane. This variation in photocycloreversion quantum yield throughout the series of dimetallacyclobutanes is rationalized in terms of the chemistry of the 1,4-biradicaloid intermediates formed by initial, excited state M-C bond cleavage in the three compounds.

The photochemistry of 1,1,1-trimethyl-2,2,2-triphenylgermasilane ($Ph_3GeSiMe_3$), 2,2,2-trimethyl-1,1,1-triphenylgermasilane ($Ph_3SiGeMe_3$), and 1,1,1-trimethyl-2,2,2-triphenyldigermane ($Ph_3GeGeMe_3$) has been studied in hydrocarbon solution by steady state and laser flash photolysis methods. The results are compared to previously reported data for the homologous disilane $Ph_3SiSiMe_3$, whose photolysis under similar conditions results in the exclusive formation of a 1,3,5-(1-sila)hexatriene resulting from

photochemical [1,3]-trialkylsilyl migration into one of the aromatic rings. In contrast, complex mixtures of products are formed upon photolysis of the three germanium-containing homologues in the presence of 2,3-dimethyl-1,3-butadiene and/or chloroform. In each case the major products are derived from dimethyl- or diphenylgermylene extrusion and M-M' bond homolysis. However, products derived from 1,3,5-(1-metalla)hexatriene intermediates are also observed as minor products. While the product studies indicate that germylenes are the major products of photolysis, only triphenylsilyl-/germyl radicals and the 1,3,5-(1-metalla)hexatrienes can be detected by laser flash photolysis. The (1-metalla)hexatrienes have been identified on the basis of their time-resolved UV absorption spectra and absolute rate constants for reaction with various silene/germene trapping agents. These studies provide the first quantitative indication of the fundamental differences in the reactivity of Si=C and Ge=C double bonds in solution.

ACKNOWLEDGEMENTS

There are a number of people who played important roles during the course of this thesis and to whom I owe a great deal of gratitude:

First of all, I would like to state that it has truly been an honour and a pleasure to work under the supervision of Professor William J. Leigh (Willie). Willie is an inspirational leader who is dedicated to attaining scientific excellence through creativity and hard work. He prides himself on being available to his students and is always ready to offer assistance which has allowed me to mature as a scientist and as a person over the past five years. It was a twist of fate that gave me the opportunity to enter Willie's lab many years ago and it is without hesitation that I say that I would not have had it any other way; Willie is a true mentor and a good friend.

I would like to thank the members of my supervisory committee, Professor Michael J. McGlinchey, Professor Françoise M. Winnik, and the late Professor John Yarwood, who offered their insights during the committee meetings and thesis.

A special thanks needs to be extended to the various staff members of the department without whom things would not run as smoothly as they do. Brian Sayer and Dr. Don Hughes of the NMR facility, Dr. Richard Smith of the Mass Spec facility, George Timmins for training, Michael Palme of the Glassblower shop, and Mike Malott the computer geek all require mention.

It is not a secret that ABB 467 is a special place to work and the part that makes it special are the people that work there. I would like to thank my coworkers (past and present): Dr. Johnathon Lewis, Dr. Al Postigo, Dr. Christine Bradaric, Dr. Rabah

Boukerrhoub, Dr. Corrina Kerst, Bruce Cook, Ed Lathioor, and Tracy Morkin. I will never forget all of the friends that I have made within the department over the years.

I would like to thank my family (Mom, Dad, David, and Lisa) for their support and understanding over the years. You guys mean the world to me and I am lucky to have a family who is as loving as all of you.

Finally, thanks to the love of my life, Tracey. You have been a pillar of strength for me over the years and it has been your love and support that has carried me through. I share this success with you and I look forward to our future together.

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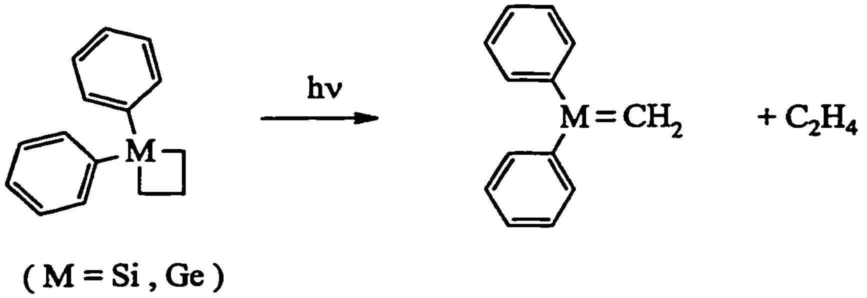
CHAPTER 1

INTRODUCTION

1.1 - Overview

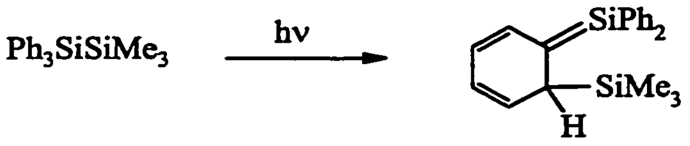
This thesis will begin with a review of the chemistry of the Si=C bond in silene reactive intermediates, focusing on 1,1-diphenylsilene. Subsequently, there will be a discussion of the photochemistry of aryldisilanes and mechanistic investigations on the reactivity of (1-sila)hexatrienes with alcohols and carbonyl compounds. The Introduction will conclude with a review of the photochemistry of arylgermasilanes and aryldigermanes, and a preliminary assessment of the validity of previously published work in this area.

There are numerous studies on the generation and chemistry of silicon-carbon double bonds. On the contrary, very little is known about the mechanistic aspects of germene reactivity. Therefore, one of the main goals of this research was to generate and characterize a germanium-carbon doubly-bonded species in solution. This goal was achieved through the synthesis of 1,1-diphenylgermetane in the expectation that this compound, under photolytic conditions, will afford 1,1-diphenylgermene as the primary photoproduct (eqn. 1). This represents the first study of the photochemistry of a germetane derivative, and the first quantitative study of the kinetics and mechanisms of germene reactions. Our results allow a direct comparison to be made between the chemical reactivity of the Si=C and Ge=C double bonds.



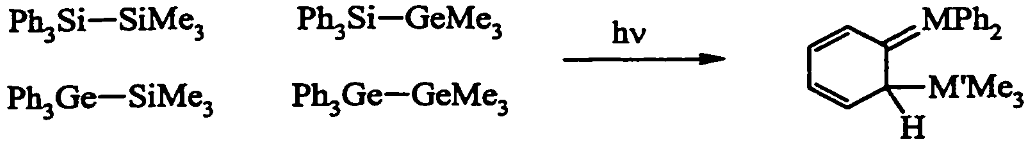
[1]

Aryldisilanes have found extensive use as photochemical precursors to silene reactive intermediates, whose reactivity can be studied using nanosecond laser flash photolysis techniques. Photolysis of aryldisilanes in non-polar solvents leads to predominant [1.3]-silyl migration, resulting in the formation of a 1,3,5-(1-sila)hexatriene (eqn. 2).



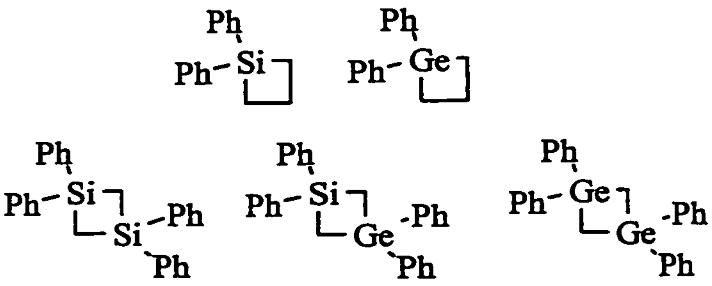
[2]

In an attempt to discover whether this behaviour also extends to germasilanes and digermanes, the photochemistry of a homologous series of compounds of the type $Ph_3MM'Me_3$ has been studied (eqn. 3). This work provides a second opportunity to quantitatively define the reactivity of Ge=C bonds and to compare their behaviour to the analogous silenes.



[3]

Finally, the 1,3-dimetallacyclobutanes derived from homo- and cross-[2+2] cycloaddition of 1,1-diphenylsilene and 1,1-diphenylgermene have been synthesized, and their photochemistry in solution has been studied by steady state and laser flash photolysis techniques. This is the first study to be reported of the photochemical behaviour of germanium-containing 1,3-dimetallacyclobutanes.



1.2 - Reactive Intermediates

It is already known, or at least strongly suspected, that the silicon- and germanium-carbon double bonded species we are interested in studying are very reactive compounds and will hence possess lifetimes much shorter than one second in solution at ambient temperatures.[1,2] They classify as "reactive intermediates" which implies a substance that cannot be isolated and characterized under ambient conditions. The most common method for identifying a transient reaction intermediate is through the use of chemical traps to form stable, isolable compounds whose structures are consistent with bimolecular reaction of the trap with the suspected intermediate. An alternative method involves time-resolved spectroscopic detection of transient chemical species, which allow the determination of one or more of their spectral properties, their lifetimes under various conditions, and absolute rate constants for their reactions. These include the measurement of reaction rates, activation parameters, the effects of substituents, solvents and isotopic substitution on rate, and acid-base catalysis.

Over the years, there has been considerable interest in the chemistry of Group 14 reactive intermediates such as divalent species (carbenes, silylenes, germylenes, and stannylenes)[3-14], radical species ($R_3M\bullet$ where M=C,Si,Ge,Sn)[15-26], cations (R_3M+ where M=C,Si)[27,28], dimetallenes ($R_2M=MR_2$ where M=Si, Ge)[2,14,29-33], and metal-carbon doubly bonded species ($R_2M=CR_2$ where M=Si, Ge)[1,2]. There are a number of photochemical precursors that can be used to generate these reactive intermediates under mild conditions in solution, which allows for the direct examination of their properties by time-resolved techniques and the investigation of the reactivity by using chemical trapping experiments.

1.3 - Silenes and Germenes

1.3.1 Prelude

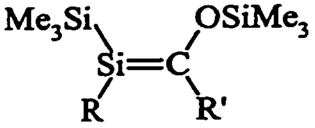
Studies comparing the reactivity of homologous series of group IV reactive intermediates have so far been limited to the study of divalent species (R_2M:) and radicals $R_3M\bullet$). The main goal of this thesis is to provide the first quantitative comparison of the reactivity of silicon-carbon and germanium-carbon double bonds. Silicon-carbon double bonds (silenes) have received considerable attention over the last 30 years, and in recent years a number of kinetic studies have been reported on many of their characteristic reactions.[1,34,35] Many of the mechanisms of these reactions are now fairly well understood, as is the manner in which substituents at Si and C affect the reactivity of Si=C bonds.[36,37]

Much less is known about the Ge=C double bond, although germenes have been postulated as reactive intermediates in a number of organogermanium reactions,[2] and several stable derivatives have been synthesized.[33] While, in general, germenes appear to behave in similar fashion to silenes in their reactivity; no absolute kinetic data have ever been reported and the mechanisms of their reactions are not well understood.

1.3.2 - Stable Silenes and Germenes

A number of stable silenes and germenes have been reported. These compounds owe their stability to the steric bulk of the substituents on the M=C bond, and to their ability to reduce the natural polarity of the M=C bond.[36] A couple of examples of stable M=C containing compounds are shown below.[38,39]

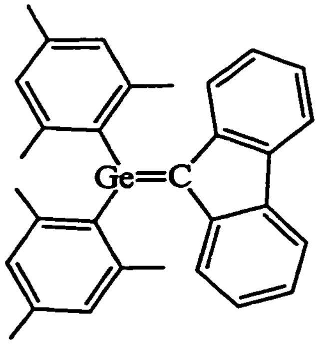
Brook



R = -SiMe$_3$
R'= adamantyl

1

Satgé



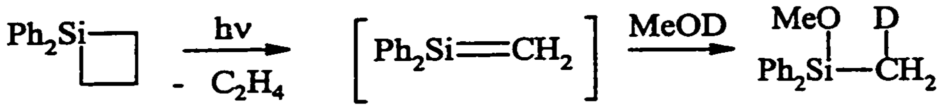
2

A.G. Brook and coworkers[38] synthesized the first stable silene (1) and characterized it by X-ray crystallography. The term "stable" refers to the compound's propensity towards dimerization. Silene **1** does not undergo a dimerization reaction in solution. However, **1** exhibits rapid reactivity towards nucleophiles and therefore the persistence of these compounds is in fact controlled by the presence of oxygen or other nucleophiles. According to the calculations by Apeloig and coworkers, this silene owes its stability to the resonance (π) donor substituent (Me_3SiO-) at carbon and the π-acceptor (Me_3Si-) at silicon, combined with the steric effects of the other two substituents.[36]

Satgé and coworkers[39] have synthesized, isolated, and characterized the stable germene (**2**). This germene owes its stability primarily to the steric hindrance caused by the bulky mesityl substituents.[33]

1.3.3 - Transient Silenes

Silenes which lack sterically bulky substituents fall in the category of ***transient*** species. The existence of these reactive intermediates has been inferred in various reactions from the isolation of stable molecules consistent with some characteristic trapping reactions of the species. For example, the photolysis of 1,1-diphenylsilacyclobutane (**3**) in the presence of MeOD leads to the formation of alkoxysilane (**5**), which is consistent with trapping of 1,1-diphenylsilene (**4**) by addition of the alcohol across the Si=C bond (eqn. 4).[1]



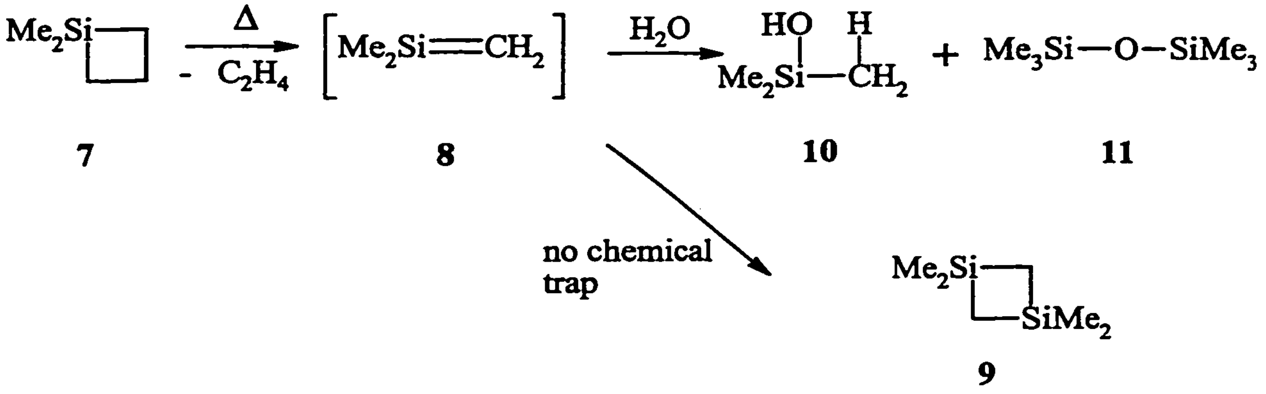
[4]

3 **4** **5**

A number of methods for generating silenes are described in the literature, including dehydrohalogenation reactions,[40] thermal and photochemical cycloreversion and sigmatropic rearrangements,[41-49] and carbene rearrangements.[50] The formation of silenes by photochemical [2+2]-cycloreversion of silacyclobutanes and [1,3]-sigmatropic rearrangement of aryldisilanes will be discussed in detail in the following sections.

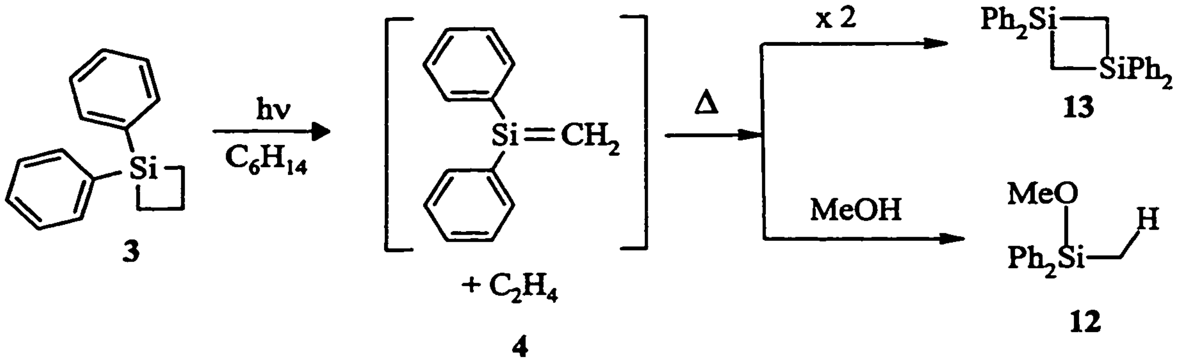
1.3.4 - The Generation of Silenes from 1-Silacyclobutanes

The very first report of the formation of a silene was published in 1967 by Gusel'nikov and Flowers, who isolated products consistent with the formation of 1,1-dimethylsilene (**8**) from pyrolysis of 1,1-dimethylsilacyclobutane (**7**).[4] Pyrolysis of **7** at >600°C afforded 1,1,3,3-tetramethyl-1,3-disilacyclobutane (**9**), the product of head-to-tail [2+2] dimerization of **8**. Pyrolysis of **7** in the presence of H_2O yielded silanol (**10**) and hexamethyldisiloxane (**11**), (eqn. 5) the products expected from reaction of **8** with water.



[5]

Sommer and coworkers later reported that silacyclobutanes also yield silenes by photochemical [2+2] cycloreversion.[51] Thus, photolysis of 1,1-diphenylsilacyclobutane (**3**) in the presence of MeOD yielded methoxymethyldiphenylsilane (**5**) in > 95% chemical yield (eqn. 6), consistent with the formation of 1,1-diphenylsilene as a primary product of photolysis. Subsequent work by Jutzi and Langer showed that photolysis of **3** in the absence of nucleophiles affords the head-to-tail dimer, 1,1,3,3-tetraphenyl-1,3-disilacyclobutane (**13**) in high chemical yield (eqn. 6).



[6]

1.3.5 - The Direct Detection of 1,1-Diphenylsilene in Solution

Laser flash photolysis of **3** in hydrocarbon or acetonitrile solution gives rise to a transient species which decays with 2nd order kinetics, exhibits a UV absorption maximum at 325 nm, and reacts rapidly with aliphatic alcohols, acetone, and acetic acid.[34,52] This evidence led to the assignment of this species to 1,1-diphenylsilene(**4**).

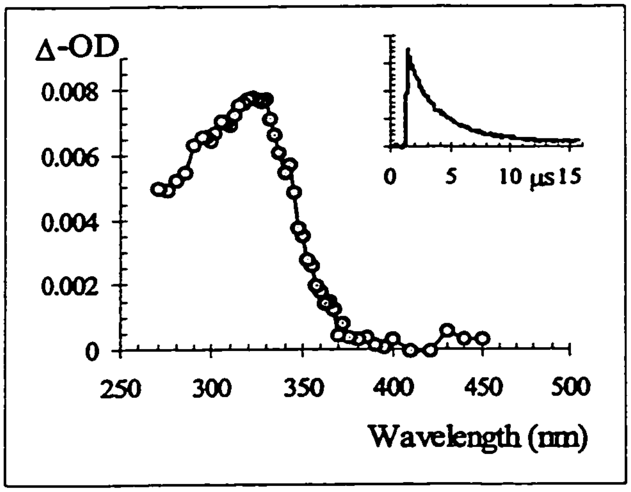


Figure 1.1 - Transient UV absorption spectrum of 1,1-diphenylsilene (**4**), from nanosecond laser flash photolysis of air-saturated solutions of **3** (0.0075 M) in hexane. The spectrum shown was recorded 0.5-1.0 μs after the laser pulse. The insert shows a typical decay trace recorded at a monitoring wavelength of 325 nm.[34]

Absolute rate constants for the reaction of 1,1-diphenylsilene **4** with a variety of chemical traps are summarized in Table 1.1.

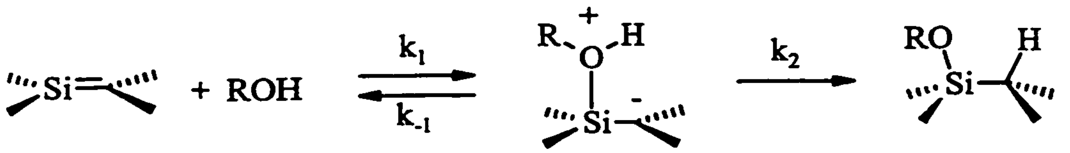
Table 1.1 - Absolute rate constants and deuterium kinetic isotope effects for reaction of 1,1-diphenylsilene (**4**) with water, aliphatic alcohols, and acetic acid (ROH) in air-saturated acetonitrile solution at 23.5 ± 0.3 °C.[34]

ROH	k_q / 10^9 $M^{-1}s^{-1}$	k_H / k_D
H_2O	0.76 ± 0.09	1.4 ± 0.2
MeOH	1.5 ± 0.1	1.5 ± 0.1
EtOH	1.0 ± 0.1	1.8 ± 0.2
^{i}PrOH	0.72 ± 0.05	*b*
^{t}BuOH	0.41 ± 0.02	2.2 ± 0.3
HOAc	1.23 ± 0.07	1.1 ± 0.1

Determined by nanosecond laser (248-nm) flash photolysis. Errors are quoted as twice the standard deviation, from linear least squares analysis of decay rate - concentration data according to $k_{decay} = k_d^o + k_q[Q]$

b. Not determined.

1,1-Diphenylsilene reacts with water, alcohols, and acetic acid with rate constants which are within an order of magnitude of the diffusion-controlled limit. As might thus be expected, the rate constants show little sensitivity to nucleophilicity or acidity within this series of compounds. Deuterium kinetic isotope effects on the order of k_{ROH}/k_{ROD} = 1.5-2.2 are observed for the alcohols; these are small but clearly primary effects, indicating that proton transfer is involved in the rate-determining step for reaction. The results are compatible with the mechanism shown in equation 7.[34] Additional evidence in support of this mechanism has been obtained from the Arrhenius parameters for the reaction of alcohols with diphenylsilene.[35,53]

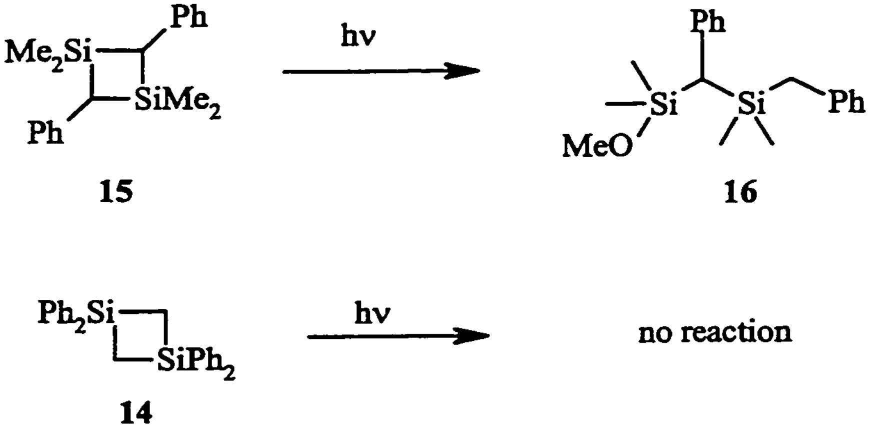


[7]

1.3.6 - Thermolysis/Photolysis of 1,3-Disilacyclobutanes

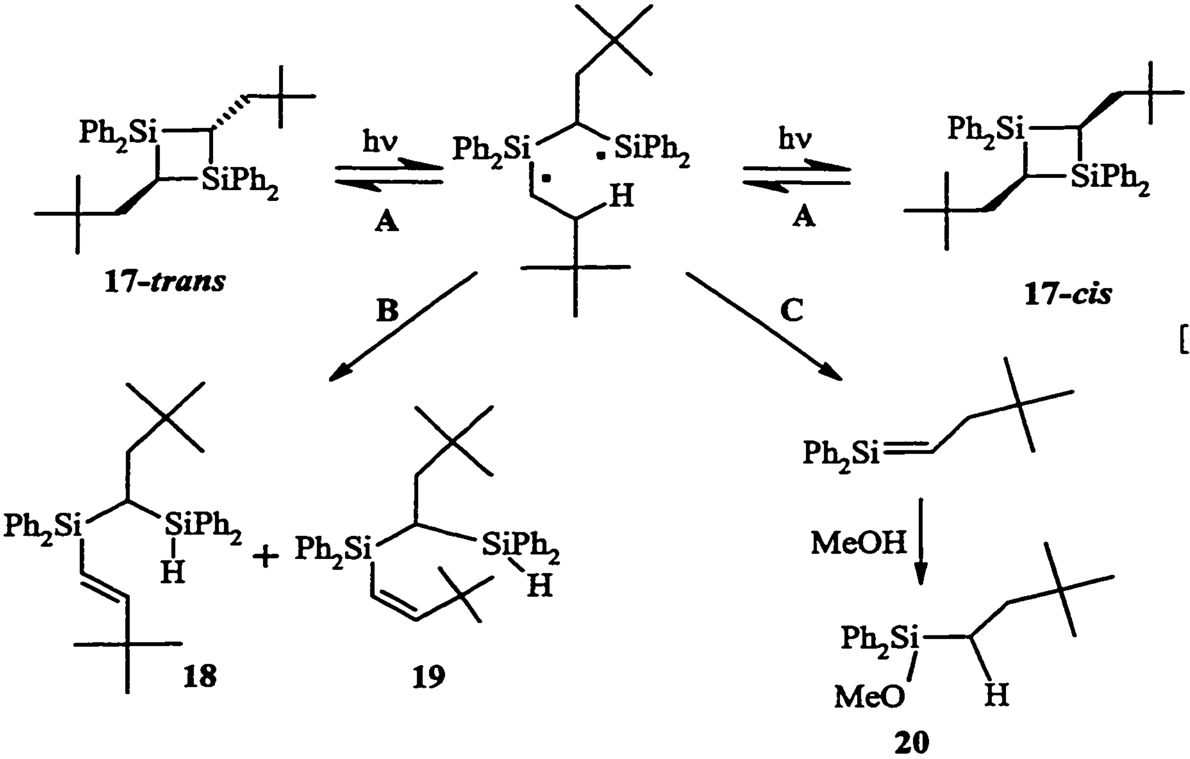
1,3-Disilacyclobutanes that have been studied in the literature do not appear to be prone to [2+2] cycloreversion under thermolytic conditions. For example, thermal reaction of 1,1,3,3-tetramethyl-1,3-disilacyclobutane occurs at 150°C higher than 1,1-dimethylsilacyclobutane and affords a complex mixture of products due to the rupture of silicon-carbon bonds of both the four membered ring and methyl groups. Crossover experiments have shown that equilibration between the disilacyclobutane and the silene does not occur.[54] 1,1,3,3-Tetramethyl-1,3-digermacyclobutane proved to be stable under conditions used for the thermal decomposition of 1,1-dimethyl-1-germacyclobutane.[54]

There have been few studies reported of the photochemistry of 1,3-disilacyclobutanes.[55-57] Jutzi and coworkers investigated the photochemistry of 1,1,3,3-tetraphenyl-1,3-disilacyclobutane (**14**) and 1,1,3,3-tetramethyl-2,4-diphenyl-1,3-disilacyclobutane (**15**) in the presence of methanol. The latter compound afforded **16** as the only isolated product, which was suggested to be consistent with the formation of a 1,4-biradicaloid intermediate. 1,1,3,3-Tetraphenyl-1,3-disilacyclobutane (**14**) was reported to be photoinert (eqn. 8).



[8]

These results prompted an investigation of the photochemistry of **cis-** and **trans-**1,1,3,3-tetraphenyl-2,4-dineopentyl-1,3-disilacyclobutane (**17-*cis*** and **17-*trans***). Photolysis of these compounds in methanolic hydrocarbon solution afforded products which were proposed to arise via reaction of a 1,4-biradical intermediate by radical recombination resulting in **cis-trans** isomerization, intramolecular hydrogen abstraction to yield **18** and **19**, or 2-3 bond cleavage to yield a pair of silenic intermediates which are trapped by methanol to form alkoxysilane **20** (eqn. 9).[55]



[9]

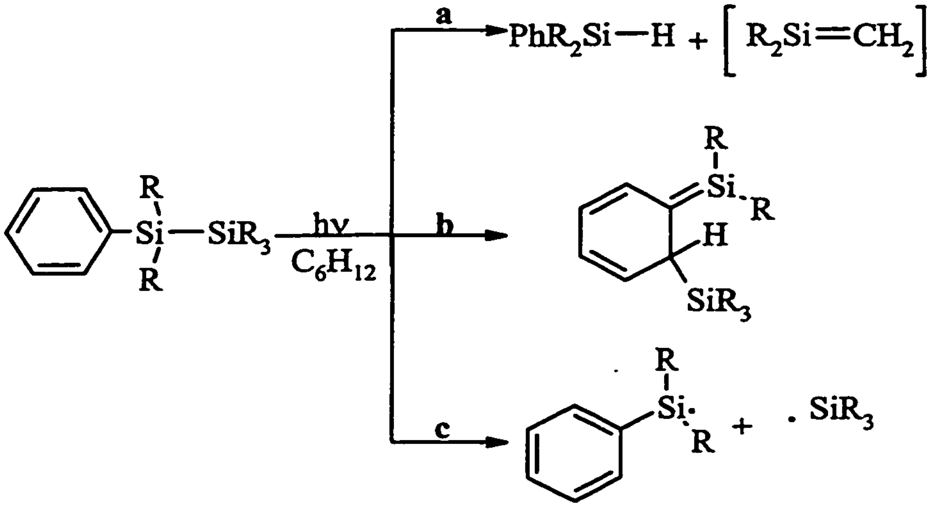
Photolysis of the 1,3-disilacyclobutanes gives rise to a singlet 1,4-biradical intermediate which then undergoes three competing reactions. The fact that ring closure is apparently the most rapid of these processes provides an explanation for the lack of reactivity exhibited by tetraphenyldisilacyclobutane **14**.[55] 1,3-Disilacyclobutanes appear to have a relatively low propensity towards photochemically initiated [2+2]-cycloreversions. This is illustrated by the product distribution observed during steady state photolyses performed on **17** or **14**. Products consistent with the formation of a silenic intermediate are formed in low yields or not at all.

1.4 - Aryldisilane Photochemistry

1.4.1 - Introduction

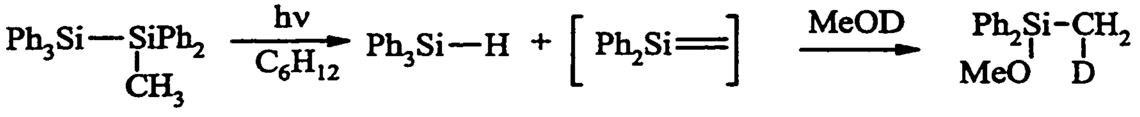
The photochemistry of aryldisilanes has been the subject of a number of investigations over the past 25 years.[41,46,47,58,59] Depending on the substitution pattern, direct photolysis of aryldisilanes results in the formation of three distinct types of transient intermediates: (1-sila)hexatrienes via formal [1,3]-silyl migration into the phenyl ring, simpler silenes by formal dehydrosilylation, and free silyl radicals resulting from Si-Si bond homolysis.[60] Examination of the product distributions obtained from the photolysis of various disilanes shows that the preferred reaction pathway is dependent on the degree and type of aryl/alkyl substitution at silicon. Efficient dehydrosilylation (path a) occurs when one of the substituents on silicon is a methyl group and the second silicon bears one or more sterically bulky substituents. The [1,3]-silyl migration pathway (path b) is favoured by a low degree of steric bulk at the migrating silicon. Silicon-silicon bond homolysis (silyl radical formation, path c) is favoured when both silicons bear sterically bulky substituents and by polar solvents (Scheme 1.1).[60]

Scheme 1.1 - The Photochemistry of Aryldisilanes



1.4.2 - The Steady State Photolysis of Aryldisilanes

In the first study of the photochemistry of an aryldisilane, Sommer and coworkers reported that the photolysis of methylpentaphenyldisilane (**21**) in the presence of methanol-O*d* led to the formation of triphenylsilane (**22**) and methoxy(methyl-d)-diphenylsilane (**23**).[61] The latter was attributed to nucleophilic trapping of 1,1-diphenylsilene (**4**) by the deuterated alcohol (eqn. 10).

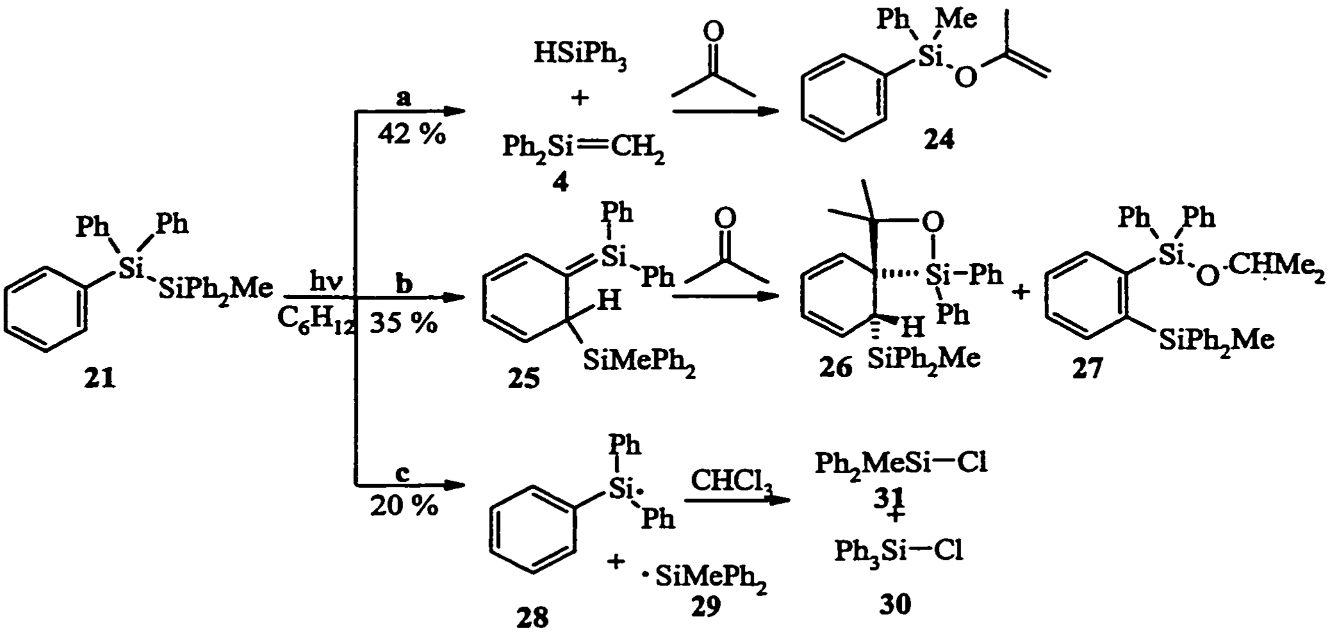


$$\mathrm{Ph_3Si{-}\underset{CH_3}{SiPh_2}} \xrightarrow[C_6H_{12}]{h\nu} \mathrm{Ph_3Si{-}H} + \left[\mathrm{Ph_2Si{=}}\right] \xrightarrow{\mathrm{MeOD}} \mathrm{\underset{MeO}{Ph_2Si}{-}\underset{D}{CH_2}} \qquad [10]$$

21 **22** **4** **23**

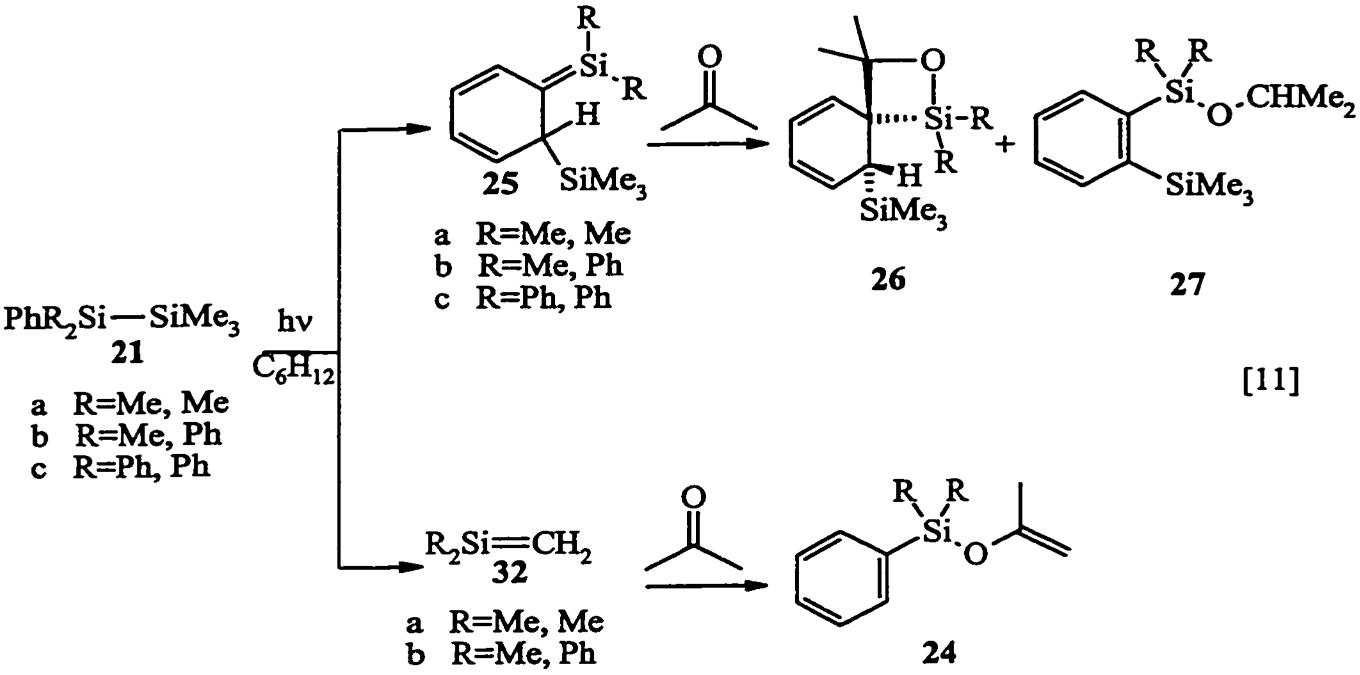
The photochemistry reported for **21** is unusual compared to that of other aryldisilanes which were studied subsequently. These studies show that (1-sila)-hexatriene formation usually dominates the photochemistry of these compounds. Leigh and Sluggett reinvestigated the photochemistry of **21** and found it to be much more complex than was originally reported by Boudjouk and Sommer. For example, photolysis of the compound in the presence of acetone and chloroform as silene and silyl radical traps, respectively, leads to the products shown in scheme 1.2.

Scheme 1.2 - Photochemistry of Methylpentaphenyldisilane



Photolysis of **21** leads to reaction by all three reaction pathways. Silyl enol ether **24** (path a) is derived from the reaction of acetone with 1,1-diphenylsilene (**4**) while 1,2-siloxetane **26** and silyl ether **27** are due to reaction of acetone with (1-sila)hexatriene **25** (path b). Chlorosilanes **30** and **31** are formed by chlorine atom abstraction by silyl radicals **28** and **29**, respectively, the result of Si-Si bond homolysis.

The characterization of (1,3,5)-1-silahexatrienes has been accomplished through a variety of trapping experiments with alcohols,[44] alkenes,[43] alkynes,[45] dienes,[42] and carbonyl compounds[62] as silene traps. The photochemistry of three aryldisilanes, $PhRR'SiSiMe_3$ **21a-c** (R,R' = methyl, phenyl) has been studied by both steady state and laser flash photolysis techniques.[47] Photolysis of hydrocarbon solutions of these compounds leads to the formation of a transient 1,3,5-(1-sila)hexatriene (**25a-c**) reactive intermediate as the major product in each case. In the cases of **21a,b**, the simple silenes **32a,b** are also formed in low yields, presumably due to a dehydrosilylation reaction (eqn. 11).

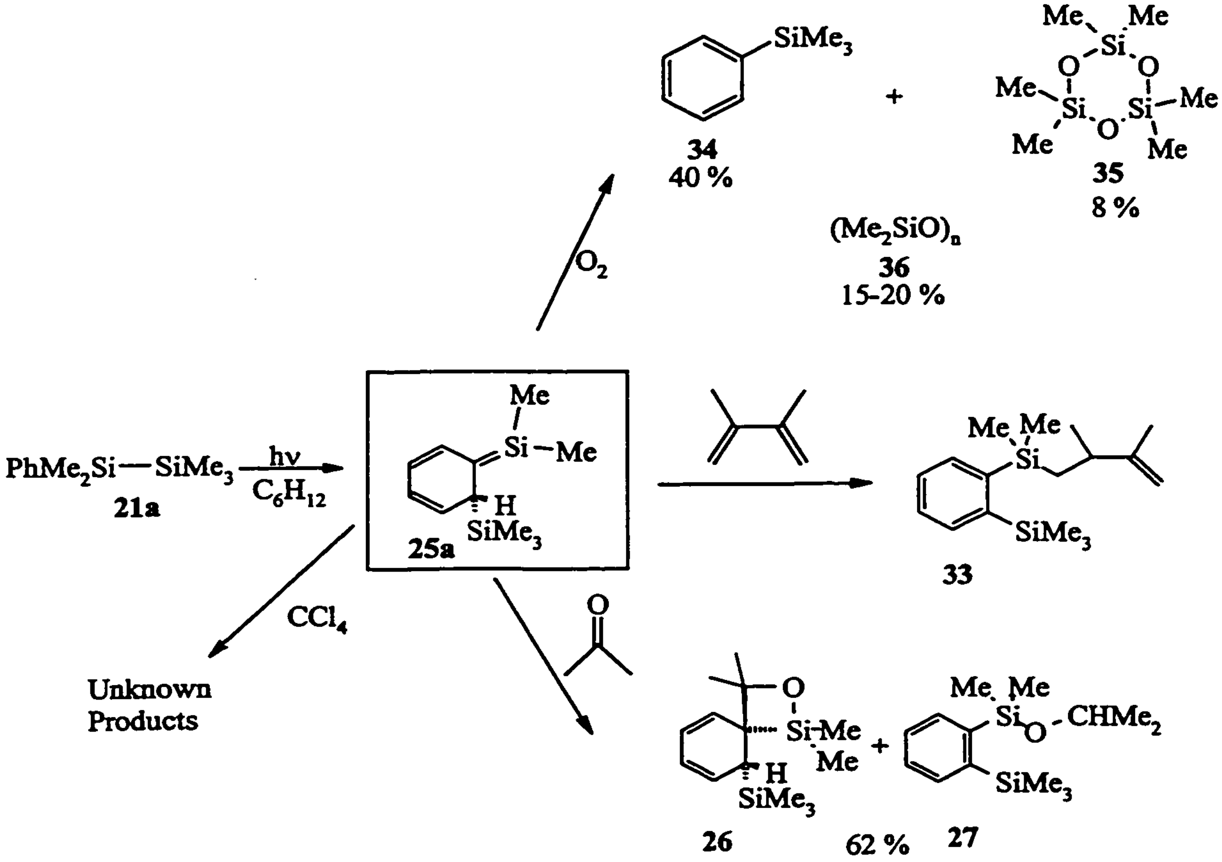


[11]

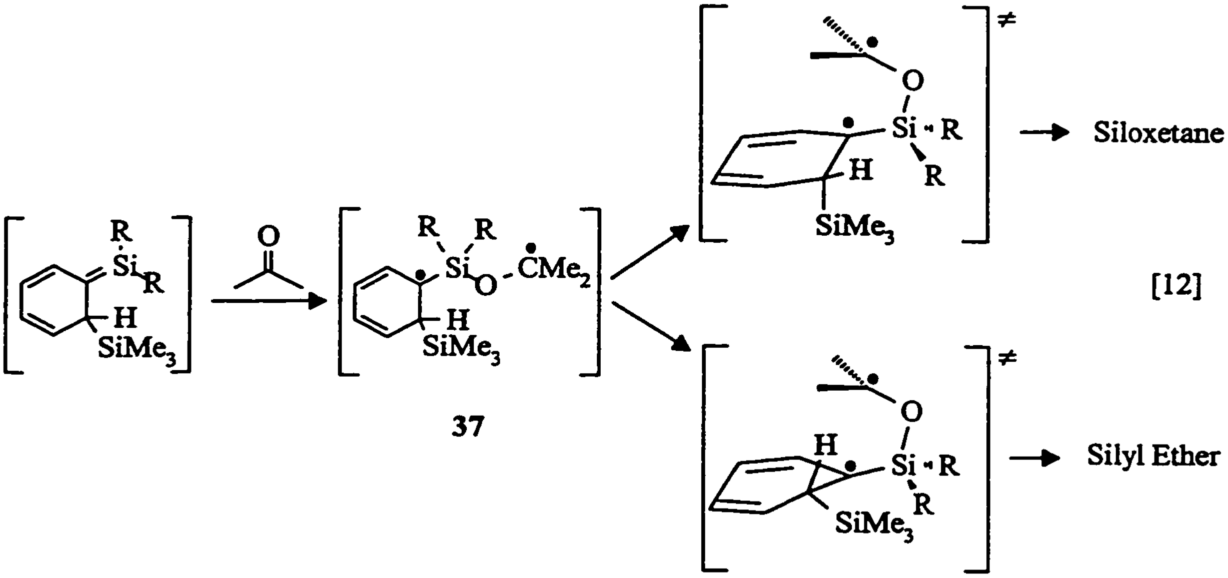
The intermediacy of **25a-c** and **32a,b** in the photolysis of these compounds is strongly suggested by the products of steady state photolysis in the presence of acetone. For example, **26** and **27** are products of acetone trapping of the (1-sila)hexatriene (**25**) while silyl enol ether (**24**) is the product of acetone trapping of the simpler silenes. Trimethylsilane is also formed in comparable yields to **32**. No deuterium is incorporated in this compound when **21** is photolysed in deuterated solvents; thus trimethylsilane is formed as a co-product of 32 and is not derived from hydrogen abstraction from solvent by free trimethylsilyl radicals.

The products of reaction of 1,3,5-(1-sila)hexatriene derived from **21a** (**25a**) with acetone, 2,3-dimethyl-1,3-butadiene, methanol, O_2, and CCl_4 are shown in Scheme 1.3.[47]

Scheme 1.3 - The Reactivity of (1-Sila)hexatriene 25a with Various Reagents

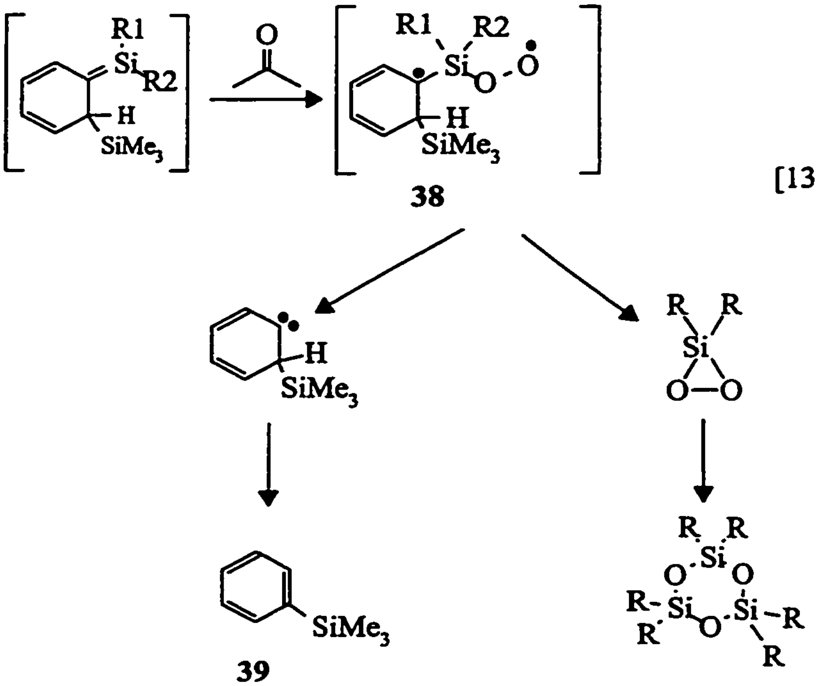


The reactions of **25a** with acetone and 2,3-dimethyl-1,3-butadiene are considerably more complex than others have previously reported.[62,63] When acetone is used as a chemical trap, the two major products were the 1,2-siloxetane (**26a**) and the silyl ether (**27a**). The types of products observed in this reaction suggest that the reaction proceeds in stepwise fashion and involves a biradical (or zwitterionic) intermediate. The reaction of the (1-sila)hexatriene with acetone can be described as involving initial attack at trivalent silicon by the carbonyl oxygen to yield biradical intermediate 37 (eqn. 12). This intermediate undergoes coupling and H-migration to yield siloxetane and silyl ether, respectively.[47] It was speculated that the relative yields of siloxetane and silyl ether are dictated by differential steric effects in the transition states for formation of the two products. Hydrogen abstraction in the biradical (leading to silyl ether) requires that the allylic hydrogen be in the pseudoaxial position, which necessitates that the trimethylsilyl group in the intermediate occupy the pseudoequatorial site. Increasing the steric bulk of the substituents on the adjacent silicon would clearly be expected to force the trimethylsilyl group into the pseudoaxial position and thus favour the formation of the 1,2-siloxetane adduct.[47] The isolation of the 1,2-siloxetanes and silyl ethers was accomplished by Toltl and Leigh but will not be discussed here.[64]



The product mixture obtained from steady state experiments using 2,3-dimethyl-1,3-butadiene suggests that this reaction also proceeds in stepwise fashion. The major product is the formal ene adduct, **33**, accompanied by small amounts of isomeric compounds which arise presumably from competing cyclization of the biradical intermediate.[47]

The products of photolysis of aryldisilanes in the presence of oxygen have been reported by Leigh & Sluggett.[47] The reaction formally involves loss of RR'Si: to yield phenyltrimethylsilane, but it appears that the reaction does not proceed via this simple mechanism. NLFP experiments show that oxygen reacts rapidly with the (1-sila)hexatriene intermediate but does not affect its initial yield. Therefore, the plausible most mechanism for this reaction involves one or more intermediates which arise from initial attack of O_2 on the (1-sila)hexatriene. The mechanism for reaction of both acetone and DMB with the silene is postulated to proceed via stepwise processes. On this basis, the oxygen reaction is presumed to proceed via a biradical intermediate, which is also consistent with the fact that (1-sila)hexatrienes exhibit considerably higher reactivity towards oxygen than do simpler silenes such as 1,1-diphenylsilene (**4**). Biradical **38** would be expected to be strongly stabilized by conjugation of one of the radical centers with the cyclohexadienyl moiety. Polar solvents have no effect on the absolute rate constant for the reaction of (1-sila)hexatriene with O_2, adding more evidence consistent with the involvement of a nonpolar reactive intermediate. The final products are most likely derived from the loss of the corresponding dioxasilirane to yield a cyclohexadienyl-carbene intermediate which rearranges to form phenyltrimethylsilane **39**. The dioxasilirane is thought to yield dimethylsilanone upon thermal decomposition which than leads to the formation of the $(R_2SiO)_n$ oligomers (eqn. 13).[47]



[13]

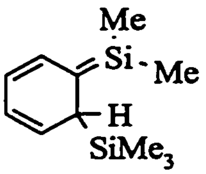
1.4.3 - The Photophysics/Photochemistry of Aryldisilanes

The photochemistry and photophysics of aryldisilanes have been widely studied.[65-67] Steady state[68] and time-resolved fluorescence emission results[69] indicate that the intramolecular $2p\pi^* \rightarrow 3d\pi^*$ charge transfer of phenyldisilane occurs very rapidly (<10ps). At room temperature, the $^1(2p\pi^* \rightarrow 3d\pi^*)$ CT state mainly gives the 425 nm transient with a rise time of 30 ps. This 425 nm transient is assigned to the (1-sila)hexatriene arising from direct [1,3]-silyl migration in a singlet $(p\pi^* \rightarrow d\pi^*)$ charge transfer state of the aryldisilane.[69] Sakurai and co-workers disagree with this $(p\pi^* \rightarrow d\pi^*)$ assignment.[70] They have assigned the phenyldisilane CT state to the orthogonal intramolecular charge transfer $(\sigma,\pi^*)^1$ excited state on the basis of substituent and solvent effects. Their data indicate that the dual fluorescence of a number of aryldisilanes and related compounds are characterized by the existence of the polar low-energy $(\sigma,\pi^*)^1$ ICT state in which donor σ and acceptor π orbitals are favourably orthogonal (OICT). Although there is controversy over which charge transfer state preceeds the 1,3-silyl migration, the fact still remains that simple silenes and (1-sila)-hexatrienes are derived from rearrangements in the disilane lowest excited singlet state and are the major products in hydrocarbon solvents.[46,63]

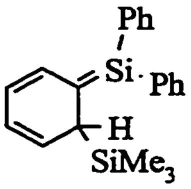
The role of the triplet state in direct aryldisilane photolyses has been established by Sluggett and Leigh.[49] The relative yields of silene- and radical-derived products is strongly dependent on solvent polarity. Since intersystem crossing (ISC) in aryldisilanes is known to be enhanced in polar media,[69] the results imply that silenes and silyl radical reactive intermediates arise from excited states of different multiplicities. Silenes are derived from the excited singlet state of the aryldisilane while silyl free radicals are triplet-derived and are the major products in polar solvents such as acetonitrile. These conclusions have been verified using triplet sensitization and quenching experiments.[49]

1.4.4 - The Direct Detection of (1-Sila)hexatrienes by Laser Flash Photolysis

Nanosecond laser flash photolysis of deoxygenated solutions of $PhMe_2SiSiMe_3$ (**21a**), $Ph_2MeSiSiMe_3$ (**21b**), and $Ph_3SiSiMe_3$ (**21c**) affords strongly absorbing transients which decay with mixed first and second order kinetics in hexane and pseudo-first-order kinetics in acetonitrile (MeCN).[47] The transient absorption spectra obtained from laser flash photolysis experiments of **21a,c** are shown in Figure 1.2. The position of the absorption maximum shifts to longer wavelengths with increasing phenyl substitution at silicon. For example, λ_{max} = 425 nm in (1-sila)hexatriene **25a**, λ_{max} = 460 nm in **25b** and λ_{max} = 490 nm **25c**.



25a



25c

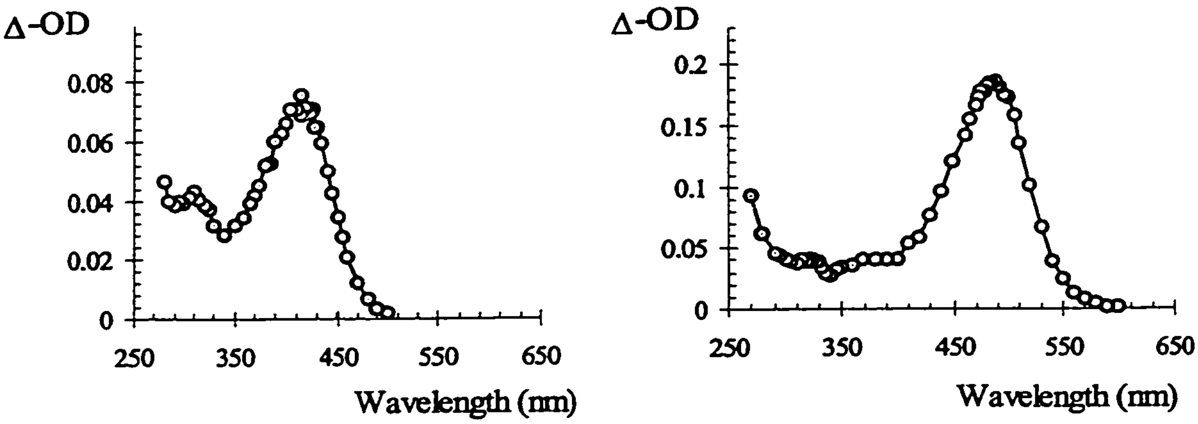
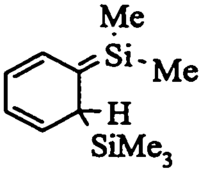
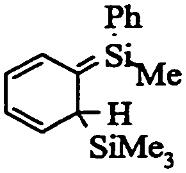
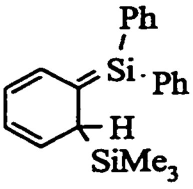
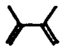


Figure 1.2 - Transient UV absorption spectra of the (1-sila)hexatrienes produced from the photolysis of $PhMe_2SiSiMe_3$ (**21a**) and $Ph_3SiSiMe_3$ (**21c**), from nanosecond laser flash photolysis of nitrogen-saturated solutions in hexane. The spectra shown were recorded 0.5-1.0 μs after the laser pulse.[47]

Absolute rate constants (k_q) for reaction of **25a-c** in hexane and MeCN with acetone, DMB, O_2, and CCl_4 are listed in Table 1.4.[47] These rate constants were obtained from experiments in which the transient decay rate constant was measured in the presence of varying concentrations of the trap (Q). The slope of a plot of k_{decay} vs. [Q] is equal to k_q (eqn 14).[47]

$$k_{decay} = k_0 + k_q[Q] \qquad [14]$$

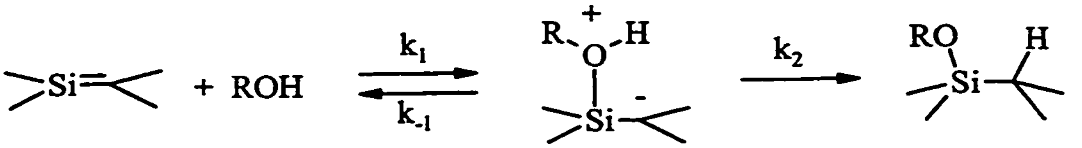
Table 1.2 - Absolute Rate Constants (Units of 10^8 $M^{-1}s^{-1}$) for the Reaction of (1-Sila)hexatrienes **25a-c** with Various Reagents

Quencher	Solvent	 **25a**	 **25b**	 **25c**
acetone	OCT	45.0 ± 0.6	15.8 ± 0.6	5.42 ± 0.05
	MeCN	7.7 ± 0.2	3.1 ± 0.2	1.5 ± 0.1
	OCT	1.28 ± 0.03	0.68 ± 0.01	0.30 ± 0.01
	THF	0.09 ± 0.01	0.07 ± 0.01	-
Oxygen	OCT	6.9 ± 0.2	3.5 ± 0.1	1.9 ± 0.2
	MeCN	8.5 ± 0.8	4.8 ± 0.6	2.6 ± 0.5
CCl_4	OCT	4.4 ± 0.1	1.6 ± 0.1	1.1 ± 0.1
	MeCN	6.4 ± 0.2	3.8 ± 0.1	-

Errors are quoted as ± 2σ. Data from reference 47.

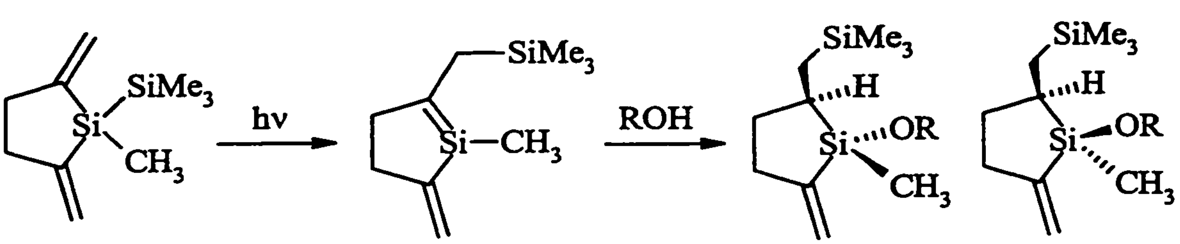
1.4.5 - The Addition of Alcohols to Transient Silenes

One of the most common trapping reactions used to show the presence of a silenic intermediate involves the addition of alcohol across the double bond. Wiberg proposed a multistep mechanism initiated by formation of a silene-alcohol complex, which proceeds to product by migration of the proton from oxygen to carbon (eqn. 15).[27]


[15]

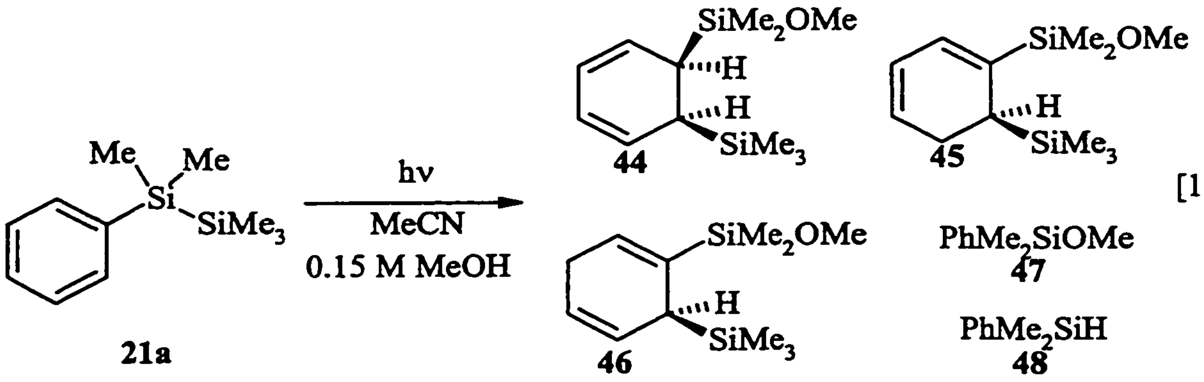
At the time, the experimental evidence in support of this mechanism consisted mainly of the fact that silenes form complexes with ethers.[71] It is also supported by the fact that the relative rates of addition of a series of alcohols to a stable silene are roughly proportional to the nucleophilicity of the alcohol and inversely proportional to acidity.[27]

Kira and coworkers expanded on this mechanism with the results of a study investigating the stereochemistry of alcohol addition to a cyclic transient silene.[5] The silene (**41**) was generated by photolysis of vinyldisilane **40**, which induces a 1,3-silyl migration to one of the exocyclic vinyl groups. Photolysis of the disilane in the presence of various aliphatic alcohols led to the formation of two stereoisomeric alkoxysilanes, corresponding to *syn* (**42**) and *anti* (**43**) addition of ROH to the Si=C bond (eqn. 16). In the case of MeOH addition, the yield of the *anti*-adduct increases with increasing alcohol concentration. This led the authors to propose that product formation occurs by two kinetically distinct pathways, one involving one molecule of ROH and the other involving two. This mechanism is essentially an expanded version of that proposed earlier by Wiberg.


[16]

40 **41** **42** **43**

Additional evidence for the mechanism shown in equation 12 was provided by a kinetic and product study on the addition of alcohols to (1-sila)hexatriene **25a** (eqn. 17). Steady state photolysis of disilane **21a** in methanolic acetonitrile affords the [1,2]-, [1,4]-, and [1,6]-addition products of the alcohol to the silatriene. While a number of other groups have described the successful isolation and characterization of [1,4]- and [1,6]-alcohol adducts **45** and **46**, the report by Leigh and Sluggett is the first to describe the identification of the elusive [1,2]- adduct **44**. Their results showed that the relative yields of the three methanol adducts vary with both the solvent and the concentration of the alcohol, with the [1,2]-adduct being formed in significant yields only at very low alcohol concentrations.[48]

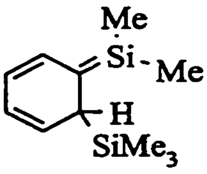


[17]

Nanosecond laser flash photolysis studies of the quenching of (1-sila)hexatrienes **25a-c** by aliphatic alcohols in acetonitrile gave rise to nonlinear plots of k_{decay} versus [ROH]. Analysis of the data according to the quadratic expression shown in eqn 18 showed that two mechanistic pathways are involved in the reaction of these silenes with MeOH over the concentration range studied, one which is 1st order in [ROH] and one which is 2nd order. Substitution of MeOD for MeOH reduced the 1st order component, indicating that H-transfer is rate-determining. Quenching by CF_3CH_2OH, a much more weakly nucleophilic and more highly acidic alcohol than MeOH, gave rise to a linear dependence of k_{decay} on [ROH]. The list of rate constants are summarized in Table 1.3 below.[48]

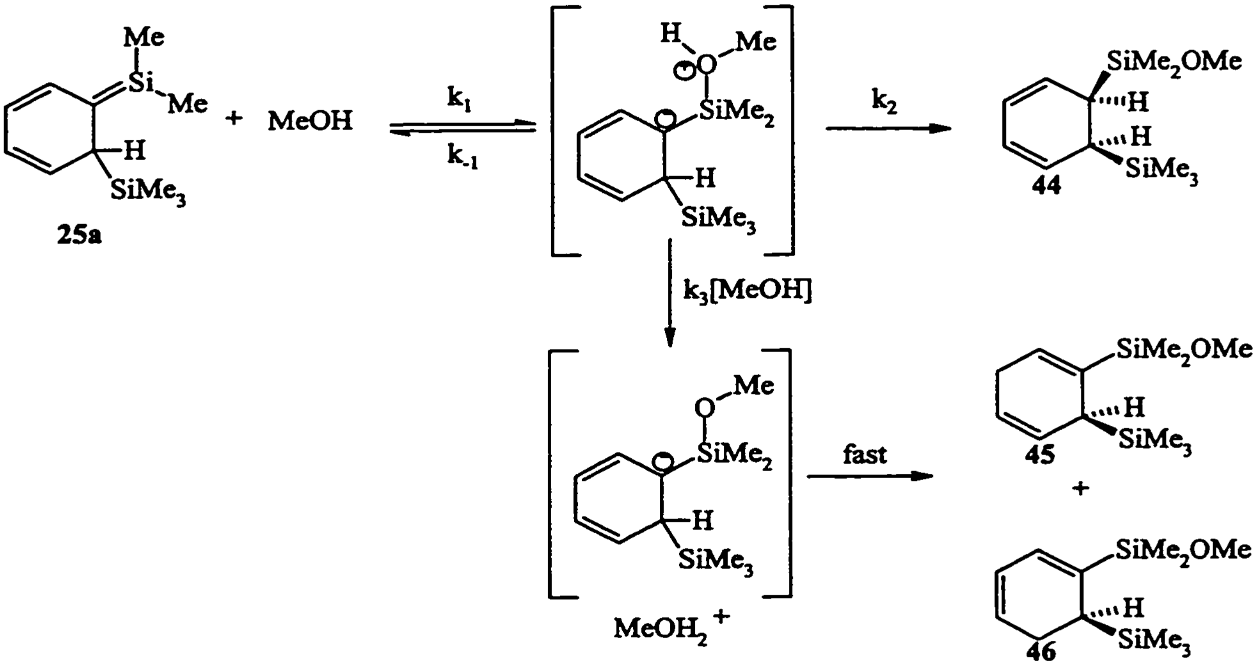
$$k_{decay} = k_0 + k_q[Q] + k_q^{(2)}[Q]^2 \qquad [18]$$

Table 1.3 - Absolute rate constants for the reaction of (1-sila)hexatriene **25a** with various reagents in dry acetonitrile at 21°C. [48]

Quencher		 **25a**
MeOH	k_q / 10^8 $M^{-1}s^{-1}$	2.3 ± 0.7
	k_q (2)/ 10^8 $M^{-1}s^{-1}$	49 ± 10
MeOD	k_q / 10^8 $M^{-1}s^{-1}$	1.2 ± 0.2
	k_q (2)/ 10^8 $M^{-1}s^{-1}$	51 ± 4
CF_3CH_2OH	k_q / 10^8 $M^{-1}s^{-1}$	0.236 ± 0.004

Errors are quoted as ± 2σ.

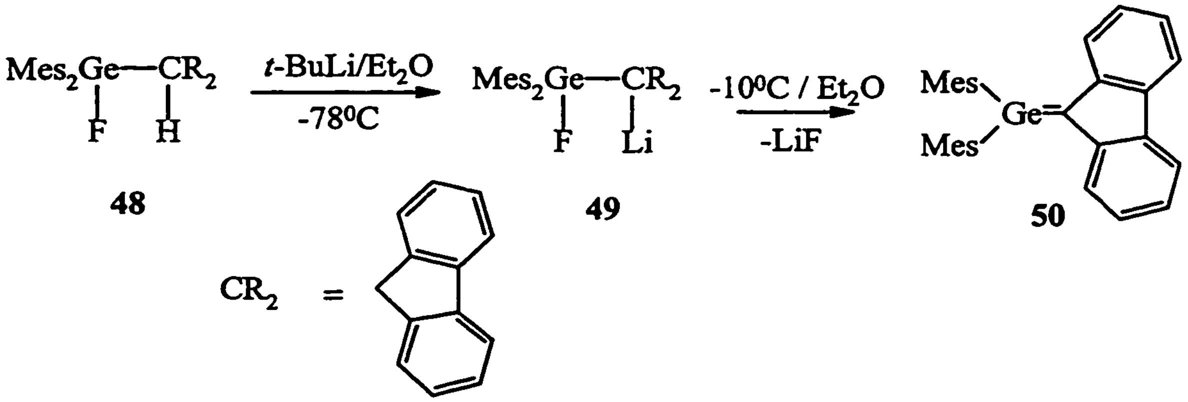
Scheme 1.4 - Mechanism for the Reaction of 1,3,5-(1-sila)hexatriene 25a with Methanol



The results are consistent with the mechanism shown in scheme 1.5. The initial step involves reversible formation of a silatriene-alcohol complex, followed by competing intracomplex and extracomplex proton transfer. The proton transfer steps are rate-determining when the alcohol is only weakly acidic, while complex formation is rate-determining for acidic alcohols. The [1,2]-adduct is the main product of intracomplex proton transfer since it predominates at very low methanol concentrations. Conversely, the extracomplex proton transfer reaction most likely proceeds by a general base catalysis mechanism involving deprotonation of the complex by alcohol, followed by rapid protonation. The general base catalysis pathway results in the formation of the [1,4]- and [1,6]-adducts and predominates at very high alcohol concentrations.[48]

1.5 - Germanium-Carbon Double Bonds

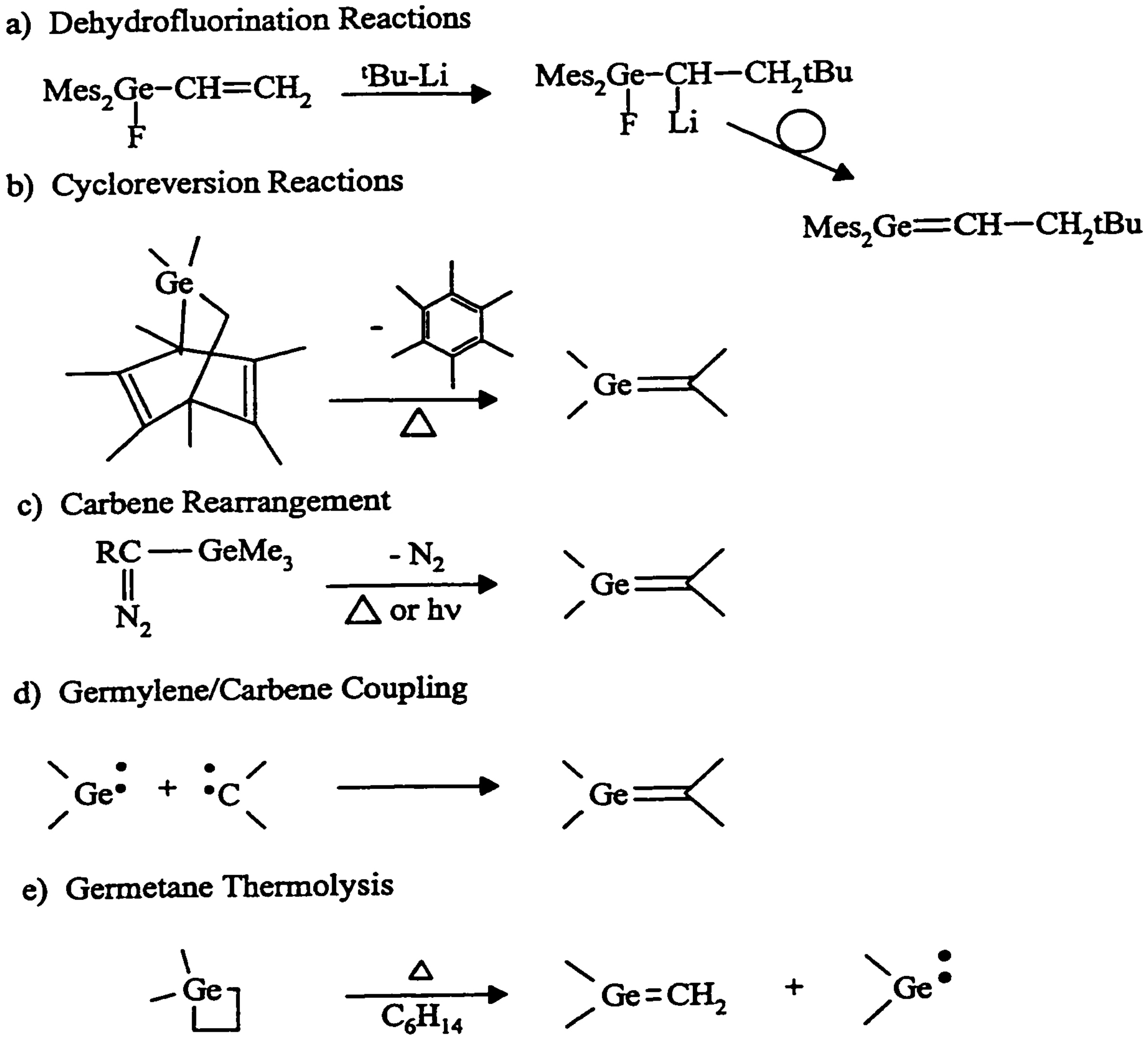
Several stable germenes have been isolated and characterized by X-ray crystallography.[33,40] To date, numerous crystal structures of compounds containing trivalent germanium have been reported, allowing for some structural information to be obtained. The geometry observed at the germanium atom is trigonal planar and the length of the germanium-carbon double bond is about 2.0 Å. Although many synthetic routes have been employed for generating germenes, the most common method involves the dehydrofluorination of an organofluorogermane. For example, treatment of **48** with *tert*-butyllithium in ether leads to the formation of the lithium salt **49**, which eliminates LiF at -10°C to yield the crystalline germene **50** (eqn. 19).[2]



[19]

Many of the same reactions used to generate transient silenes have been adapted for germene synthesis.[2] Scheme 1.6 shows, in generic form, the five such methods that have been studied. These include a) dehydrofluorination reactions, b) the thermal extrusion of hexamethylbenzene from a germylbarrelene compound, c) the photolysis or thermolysis of substituted trimethylgermyldiazomethanes, d) the direct reaction of a germylene and a carbene generated *in situ*, and e) thermolysis of dimethylgermetane. In all cases, the formation of germenes in these reactions has been inferred on the basis of the products observed in the presence (or absence) of various trapping agents (water, alcohols, dienes, carbonyl compounds, etc.).[2]

Scheme 1.5 - Synthetic Routes to Transient Germenes



a) Dehydrofluorination Reactions

b) Cycloreversion Reactions

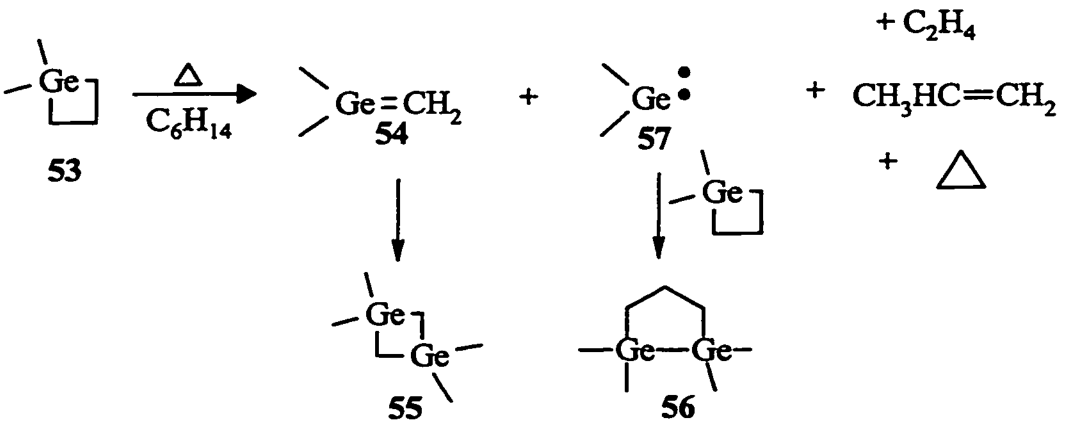
c) Carbene Rearrangement

d) Germylene/Carbene Coupling

e) Germetane Thermolysis

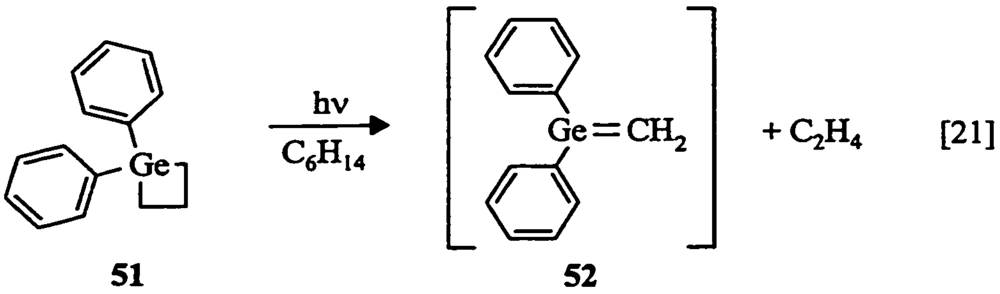
The gas-phase unimolecular thermal decomposition of 1,1-dimethylgermetane (**53**) (eqn. 20), has been studied.[72] The major product, 1,1,3,3-tetramethyl-1,3-digermetane (**55**), has been explained as arising from dimerization of 1,1-dimethylgermene (**54**). Other products observed as well are cyclopropane, propene, and

1,1,2,2-digermacyclopentane (**56**). Adduct **56** is apparently formed by the insertion of dimethylgermylene (**57**) into the strained germanium-carbon bond of dimethylgermetane. The photochemistry of germetanes has not been previously studied.



[20]

Both silacyclobutanes and germacyclobutanes undergo thermal cycloreversion to yield the corresponding M=C compounds and ethylene. As mentioned earlier, the same process occurs photochemically with silacyclobutanes. Whether or not germacyclobutanes behave similarly is not known, but it is reasonable to expect that they should. Given the utility of **3** as a photochemical precursor to **4** for study by LFP methods, we proposed to investigate the photochemistry of **51** in the hopes that it would yield $Ph_2Ge{=}CH_2$ under conditions where it could be studied similarly (eqn. 21). This would provide the opportunity to study the kinetics and mechanisms of Ge=C reactions in a quantitative way, and provide a basis for direct comparison to the chemistry of Si=C bonds.



[21]

1.6 - Photochemistry of Arylgermasilanes and Aryldigermanes

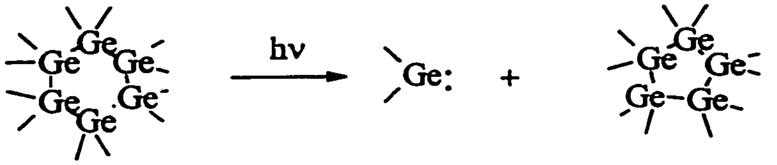
1.6.1 - Introduction

In general, the photolysis of aryldisilanes leads to the formation of three distinct types of reactive intermediates, a) a silene generated by dehydrosilylation (loss of H-SiR_3), b) a silene by a formal [1,3]-silyl migration into an aromatic ring, and c) silyl radicals derived from Si-Si bond homolysis. Both of the silene reaction pathways are singlet-derived; silyl free radical formation results from the triplet state of the disilane, and can be made to predominate either by enhancing intersystem crossing through adjustment of the solvent polarity[47] or by slowing down the singlet-derived reaction pathways by attaching sterically bulky substituents.[60]

Interestingly, the homologous reactive intermediates have also been observed upon the photolysis of arylgermasilanes and aryldigermanes. However, there are very few studies reported which compare the photochemistry of disilanes, germasilanes, and digermanes in a systematic way. The various reports which do exist suggest that the replacement of one or both silicons in a disilane with germanium drastically changes the distribution of the reactive intermediates produced and enhances the yields of free radicals. Photolysis of arylgermasilanes and aryldigermanes presents another potential opportunity for the study of germene reactivity in solution with a set of compounds for which the all-silicon analogues have already been well studied.

1.6.2 - The Generation of Germylenes From Polygermanes and Germasilanes

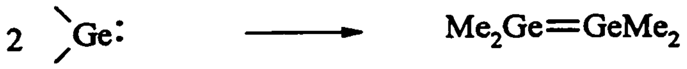
The photochemistry of polygermanes has been the subject of a number of investigations studying divalent germanium compounds, germylenes. Mochida and coworkers studied the photochemistry of dodecamethylcyclohexagermane (**58**), and found products consistent with extrusion of Me_2Ge: as the major reaction (eqn. 22).[73]



[22]

58 **57** **59**

Flash photolysis of **58** afforded a transient absorption centered around 450 nm which decayed with second-order kinetics and was assigned to dimethylgermylene (**57**). The transient absorption spectrum taken 2 μs after photoexcitation showed no signal remaining at 450 nm but instead displayed a sharp absorption centered at 370 nm. The 370 nm transient was tentatively assigned to tetramethyldigermene (**60**), formed by dimerization of **57** (eqn. 23). This species was formed in a second-order process whose kinetics were the same as those of the disappearance of **57**.



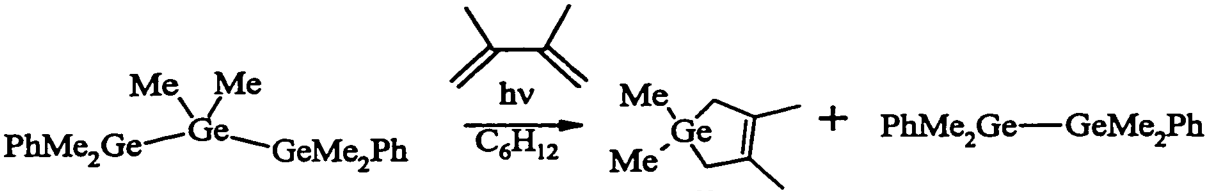
[23]

57 **60**

450 nm 370 nm

The rate constants for bimolecular reaction of **57** with a variety of different quenchers were determined, and the corresponding products from each reaction were isolated from steady state photolysis experiments. Most interestingly, **57** does not react with alcohols; this contrasts the behaviour of dimethylsilylene which reacts rapidly with methanol by O-H insertion ($k_q \sim 10^8$ $M^{-1}s^{-1}$).[6,12] A summary of the absolute rate constants for the reaction of dimethylgermylene with various reagents can be found in Table 1.4.

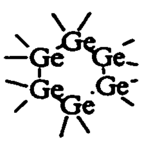
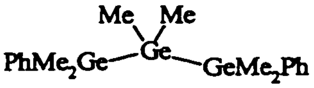
Similarly, steady state photolysis of $(PhMe_2Ge)_2GeMe_2$ (**65**) in the presence of 2,3-dimethyl-1,3-butadiene affords mainly germacyclopentene (**62**) and 1,3-diphenyl-1,1,2,2-tetramethyldigermane (**66**) (eqn. 24) consistent with the extrusion of dimethylgermylene as the major reaction pathway.



65 **62** **66** [24]

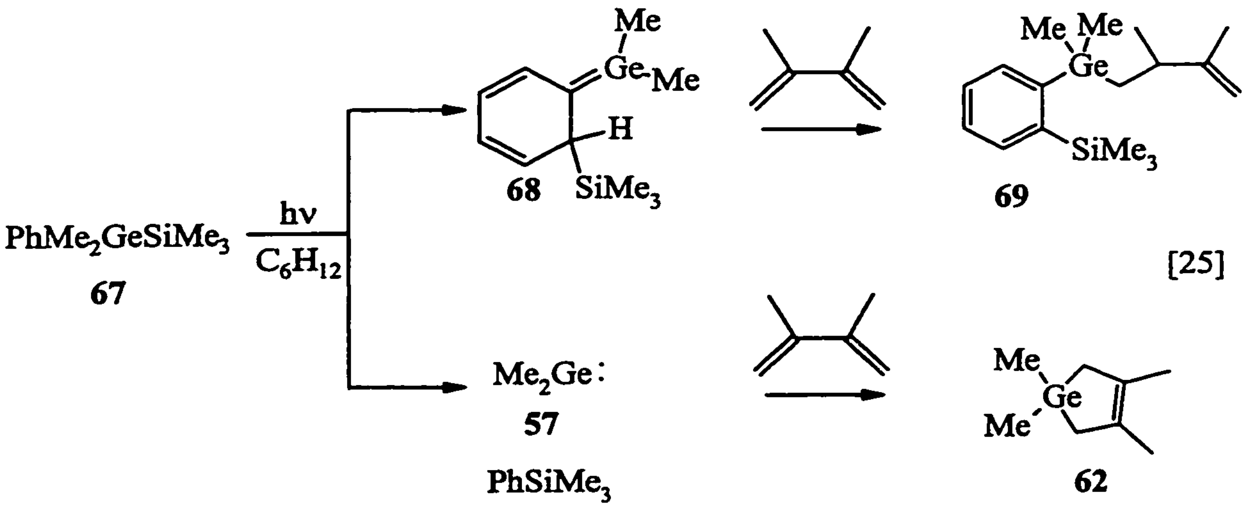
Laser flash photolysis of **65** gave rise to a transient which decayed with second-order kinetics and displayed λ_{max}= 420 nm. Based on its reactivity with DMB, CCl_4, and ethanol, the transient was identified as dimethylgermylene (Table 1.4).[74]

Table 1.4 - Comparison of absolute rate constants for reactions of species assigned to dimethylgermylene, generated from different precursors

	 **58**	 $\mathrm{PhMe_2Ge{-}\overset{Me\ \ Me}{Ge}{-}GeMe_2Ph}$ **65**	$\mathrm{PhMe_2Ge{-}SiMe_3}$ **67**
Substrate	**k_2 / $M^{-1}s^{-1}$**	**k_2 / $M^{-1}s^{-1}$**	**k_2 / $M^{-1}s^{-1}$**
O_2	9.7×10^8	-	2×10^9
CCl_4	4.9×10^8	quenched	3.1×10^8
2,3-dimethylbutadiene	2.2×10^7	2.4×10^7	1.7×10^7
MeOH	no reaction	no reaction	1.9×10^4
Et_3Si-H	-	4.2×10^6	$< 10^4$
Reference	73	74	83

A third compound which gives high yields of Me_2Ge: upon photolysis is germasilane **67**, and laser flash photolysis experiments have also been interpreted in terms of Me_2Ge: being the major transient observed.[83] Photolysis of this compound in the presence of DMB affords **62** (65%) and **69** (35%), indicative of the formation of Me_2Ge: and (1-germa)hexatriene **68**, respectively (eqn. 25). Again, flash photolysis of this compound gave rise to a transient absorbing at 425 nm, which reacted with O_2, CCl_4, DMB, and MeOH at measurable rates. Some of these rate constants agree reasonably well with those determined using other precursors, but others (particularly that with

MeOH) do not. Absolute rate constants for reaction of "dimethylgermylene", determined by flash photolysis with **58**, **65**, and **67** as precursors, are summarized in Table 1.4.

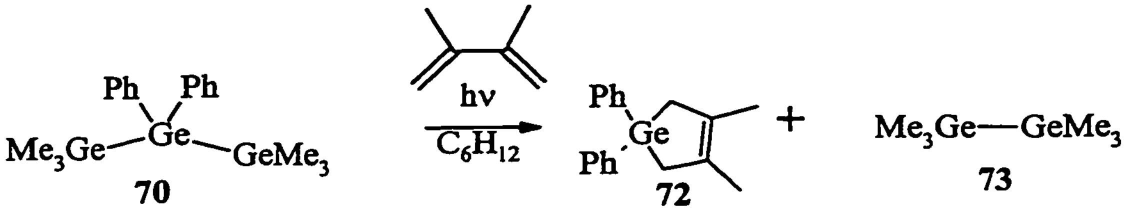


[25]

Product studies indicate that the formation of 1,3,5-[1-germa]hexatriene **68** is observed in significant yields (35%), yet the possible assignment of the 425 nm transient from **67** to this species was not considered. Given the discrepancies in kinetics shown in Table 1.4, it seemed likely to us that this might be the correct assignment.

1.6.3 - Laser Flash Photolysis Studies of "Diphenylgermylene"

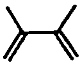
The photolysis of aryltrigermane (Me$_3$Ge)$_2$GePh$_2$, (**70**) in the presence of 2,3-dimethyl-1,3-butadiene affords products consistent with the extrusion of diphenylgermylene (**71**) as the major reaction pathway (eqn. 26).[74] Photoadduct **72** is derived from the reaction of diphenylgermylene with DMB, while the co-product of the extrusion is hexamethyldigermane (**73**). Laser flash photolysis of this compound gave rise to an absorption with λ_{max} = 460 nm which was assigned to Ph$_2$Ge: on the basis of its reactivity and the fact that the spectrum is similar to that reported for Ph$_2$Si:.[75]

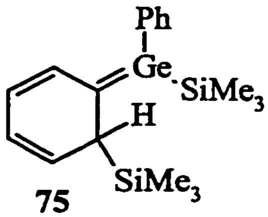


[26]

Gaspar and coworkers also set out to investigate the reactivity of diphenylgermylene in solution, using *bis*-trimethylsilyldiphenylgermane (**74**) as photochemical precursor to diphenylgermylene.[66] Surprisingly, no product studies were performed with this compound. Laser flash photolysis also showed the formation of a transient with λ_{max} = 460 nm, but absolute rate constants for reaction of the species with DMB and hydrosilane do not agree well with those reported by Mochida and coworkers using **70** as precursor. Table 1.5 summarizes the kinetic data reported in these two studies. Again, alternate transient assignments (for example, the germatriene species **75** and **76**) were not considered (eqn. 27).[66,74]

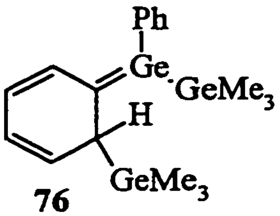
Table 1.5 - Absolute rate constants for reaction of "Diphenylgermylene", generated from two different precursors

Trapping Agent	$(Me_3Ge)_2GePh_2$ **70**	$(Me_3Si)_2GePh_2$ **74**
O_2	-	1.02×10^8
$EtMe_2SiH$	6.6×10^5	1.01×10^4
	7.2×10^5	2.75×10^4
MeOH	no reaction	no reaction
$(CH_3)_2CHCH_2Br$	-	6.36×10^5
Reference	74	66



75

460 nm



76

460 nm

[27]

Mochida and co-workers have also investigated the photochemistry of aryldigermanes as potential sources of germylenes.[76] The digermane $Ph_3GeGeMe_3$ undergoes predominant Ge-Ge bond homolysis to afford a pair of germyl radicals in high chemical yield. These radicals were trapped with CCl_4 to give the corresponding chlorogermanes in quantitative yields (eqn. 28). Other products observed in the absence of quenchers include Me_3GeH, Ph_3GeH, and Ph_3GeMe, and their presence indicates that other reaction pathways may be involved here. In any event, products of trapping of the 1,3,5-(1-germa)hexatriene analogue of **25c** (pp. 13-30) were not reported.[76] Photolysis of $PhMe_2GeGeMe_3$ in hydrocarbon solution afforded an intractable mixture of products which consisted mainly of hydrogermanes and digermanes as the major products.

$$Ph_3GeGeMe_3 \xrightarrow{h\nu} Ph_3Ge^{\cdot} + {}^{\cdot}GeMe_3 \xrightarrow{CCl_4} Ph_3Ge{-}Cl + Me_3Ge{-}Cl \qquad [28]$$

77

Laser flash photolysis of digermane **77** yielded a transient whose absorption spectrum was consistent with the formation of a pair of germyl radicals as the major reaction pathway. However, NLFP experiments performed on $PhMe_2GeGeMe_3$ (**77**) afforded a transient spectrum with 2 absorption bands with different decay kinetics; one centered at 330 nm and the other at 425 nm. Absolute rate constants for the reaction of the transient at 425 nm with oxygen ($1.7 \times 10^9\ M^{-1}s^{-1}$), DMB ($2.1 \times 10^7\ M^{-1}s^{-1}$), and ethanol (no reaction) were determined, on the basis of which the authors assigned it to dimethylgermylene.[77]

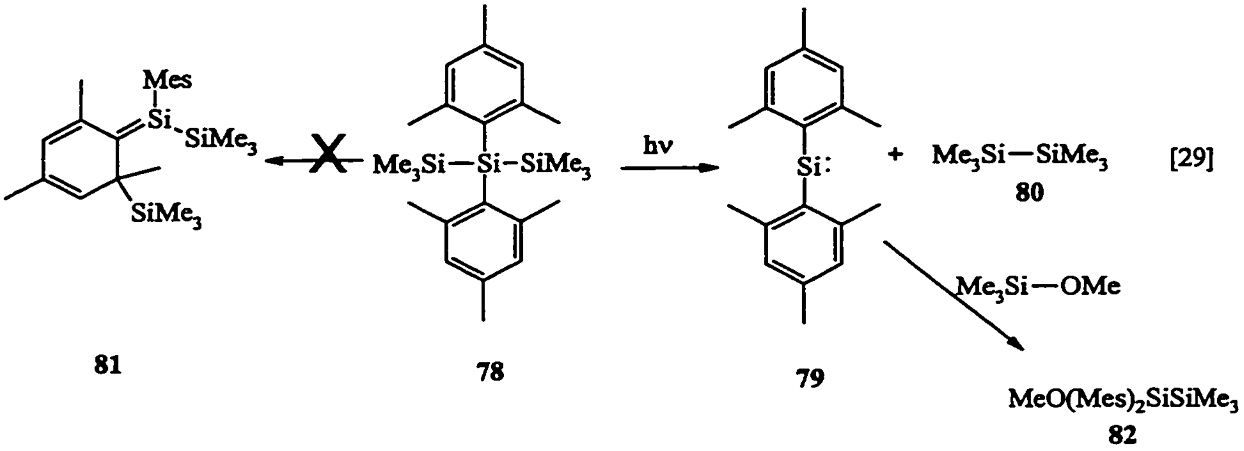
1.6.4 - Laser Flash Photolysis Studies of "Germylenes"

In view of the fact that there are numerous discrepancies in the germylene literature, a more reliable germylene precursor is necessary. The inherent problem with using arylgermasilanes and aryldigermanes as photochemical precursors to germlyenes is that they are not "clean" germylene sources. There exists the possibility that laser flash photolysis experiments are analyzing a transient derived from a [1,3]-silyl or [1,3]-germyl migration into one of the phenyl rings to yield the (1-metalla)hexatriene intermediate.

It is therefore necessary to find a photochemical precursor of germylenes where the migration pathway leading to silenes/germenes is blocked. The substitution of phenyl for mesityl groups in trisilanes affords silylene intermediates in hight yields under photolytic conditions.[8] The ortho and para methyl groups of 2,2-dimesityl-1,1,1,3,3,3-hexamethyltrisilane appear to block the [1,3]-silyl migration pathway and instead yield dimesitylsilylene as the only photoproduct. The study of dimesitylsilylene and comparing its reactivity to dimesitylgermylene is a reliable way of comparing the reactivity of a homologous series of Group IV divalent species.

1.6.5 - Characterization of Dimesitylsilylene

Conlin, Scaiano and coworkers synthesized 2,2-dimesitylhexamethyltrisilane (**78**) in the anticipation that it would afford dimesitylsilylene (**79**) and hexamethyldisilane (**80**) upon photolysis (eqn. 29).[8] As was previously mentioned, the mesityl substituent is extremely useful because the methyl groups in the ortho and para positions on the phenyl ring block the formal 1,3-silyl migration pathway which would normally lead to the silahexatriene intermediate (**81**). Steady state photolysis of **78** in the presence of methoxytrimethylsilane (**82**) yields methoxydimesityl-2,2,2-trimethyldisilane (**82**) as the primary photoproduct. This product is presumably derived from the insertion of dimesitylsilylene (**79**) into the Si-O bond of the alkoxysilane quencher.



[29]

NLFP experiments on trisilane **78** yield a transient that has an absorption maximum centered around 580 nm. The rate constants for the bimolecular reaction of this transient with some common silylene traps is summarized in Table 1.6.[6,8] On the basis of its absorption maximum and chemical reactivity, the transient has been identified as dimesitylsilylene.

Table 1.6 - Absolute rate constants for the reaction of dimesitylsilylene with some common silylene traps

Substrate	k_2 / $M^{-1}s^{-1}$
triethylsilane	7.9 X 10^7
acetone	2.5 X 10^{10}
2,3-dimethylbutadiene	8.8 X 10^6
oxygen	3.2 X 10^7

1.6.6 - Characterization of Dimesitylgermylene using NLFP Techniques

Laser flash photolysis (NLFP) of a solution of *bis*(trimethylsilyl)dimesitylgermane (**83**) resulted in the production of two transient absorptions; one centered around 550 nm range which was assigned as dimesitylgermylene (**84**) and the other at 405 nm identified as tetramesityldigermene (**85**).[84] Transient UV absorption spectra are shown in Figure 1.3.

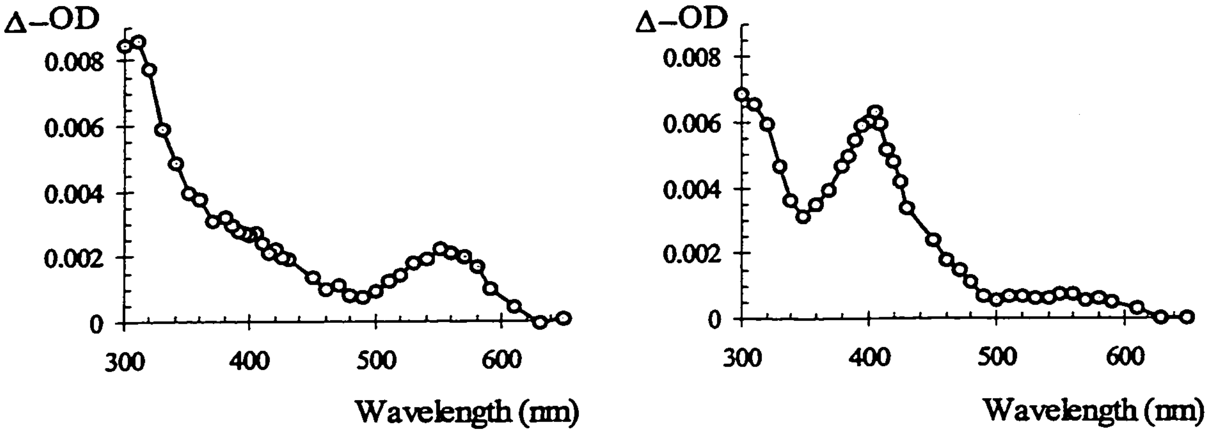


Figure 1.3 - Transient UV absorption spectra, from nanosecond laser flash photolysis of **84**. The spectrum on the left was recorded 0.1-0.6 μs after the laser pulse, while the spectrum on the right was recorded over the last 10% of the monitored time window.

$$(Me_3Si)_2Ge(mes)_2 \xrightarrow[C_6H_{14}]{h\nu} Si_2Me_6 + [(mes)_2Ge:] \longrightarrow (mes)_2Ge{=}Ge(mes)_2 \qquad [30]$$

83 **84** **85**

Similar experiments with hexane solutions of hexamesitylcyclotrigermane (**86**) afforded transient absorptions which occurred in the same spectral ranges but were stronger in intensity. Again, they could be assigned as dimesitylgermylene **84** and tetramesityldigermene **85** (Figure 1.4).

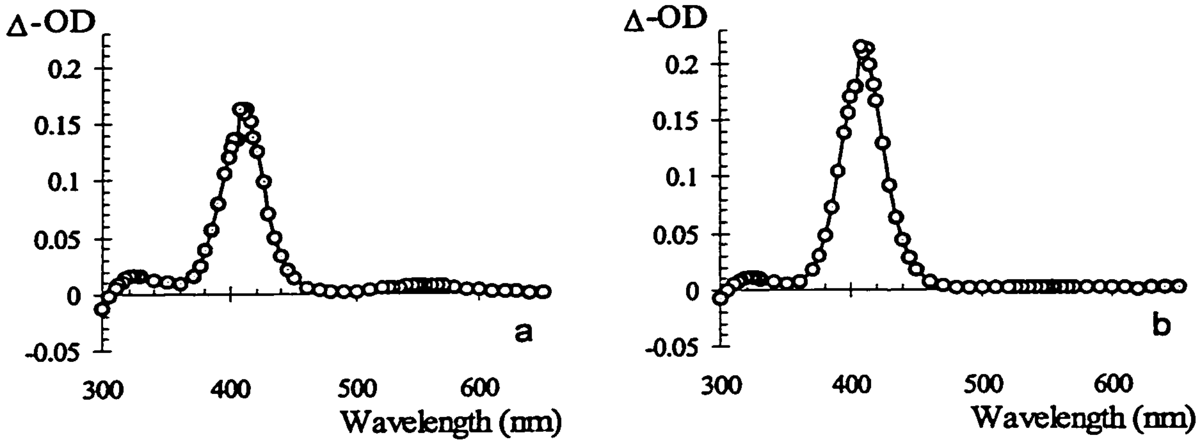
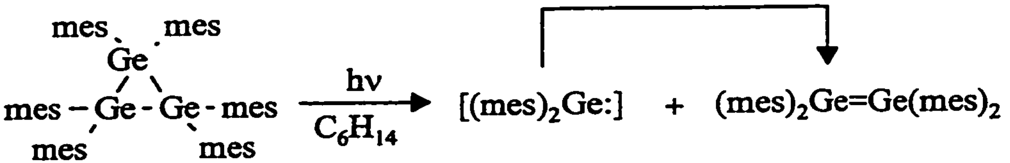


Figure 1.4 - Transient UV absorption spectra, from nanosecond laser flash photolysis of **86** under the same conditions as in Figure 1.4. Spectrum (a) was recorded 0.1-0.8 μs after the laser pulse, while spectrum (b) was recorded over the last 10% of the monitored time window.



86 **84** **85** [31]

NLFP experiments on **86** in the presence of oxygen affords rate constants of (7.3 ± 0.8) X 10^6 and (2.3 ± 0.4) X 10^5 $M^{-1}s^{-1}$ for the reaction with oxygen with germylene **84** and digermene **85**, respectively. Quenching rate constants were also determined for the reaction of **84** with triethylsilane (k_q = 1.1 X 10^5 $M^{-1}s^{-1}$) and 1-bromohexane (k_q = 5.4 X 10^6 $M^{-1}s^{-1}$). Addition of up to 1.5 M ethanol to a hexane solution of **86** had no effect on lifetimes of either species, allowing estimation of an upper limit k ~ 10^4 $M^{-1}s^{-1}$ for the rate constant.

1.6.7 - Summary

The studies investigating the reactivities of dimesitylsilylene and dimesitylgermylene are extremely useful. Absolute rate constants for the reactivity of these transients with a variety of chemical traps allow for a direct comparison of their reactivities under similar conditions. Also, the use of mesityl substituents simplifies the photochemistry of these precursors. Upon photolysis, these compounds yield silylenes/germylenes as the only primary transient photoproduct. Products derived from the formation of silenic or germenic reactive intermediates are not observed which increases the confidence the authors have in assigning the transient observed in laser flash photolysis experiments as the silylene or germylene. These results afford several potentially relevant pieces of information comparing the reactivities of silylenes and germylenes, and allow a fairly systematic comparison of at least one aspect of the reactivity of divalent Group IV species as a function of the heteroatom.

1.7 - Objectives of this Work

Originally, the objective of this work was to explore the photochemical behaviour of $Ph_3SiGeMe_3$, $Ph_3GeSiMe_3$, $Ph_3GeGeMe_3$, ($Ph_3SiSiMe_3$ analogues) where either one or both of the silicons of the original disilane are replaced by germanium. It was anticipated that the photolysis of arylgermasilanes/aryldigermanes may cause the [1,3-metalla] migration that is observed in disilane photochemistry and therefore result in a new reactive intermediate, a germanium-carbon doubly bonded hexatriene. In light of the discrepancies that appear in the literature on the reactivity of germylenes, another reason for studying this series of compounds is to clear up what may be numerous errors that currently exist in the literature. If indeed conjugated germenes and silenes are produced in addition to Ph_2Ge: or Me_2Ge:, their absorptions should be shifted to longer wavelengths; away from where germylenes should appear.

In order to properly characterize a germenic reactive intermediate, the detection of a simple germene using 1,1-diphenylgermetane as a photochemical precursor required exploration. The photolysis of this compound was expected to afford 1,1-diphenylgermene and its transient absorption spectrum and reactivity with a variety of chemical traps could be measured. This would be the first example of the direct detection of a germanium-carbon doubly bonded species. The knowledge gained from these experiments could then be used to help figure out the more complicated photochemistry of arylgermasilanes and aryldisgermanes.

The mechanism for the addition of nucleophiles to 1,1-diphenylsilene has been thoroughly investigated and the conclusion is that the mechanism proceeds via a 2-step process where the initial step is fast, *reversible* formation of a σ-bonded silene-alcohol complex followed by rate-determining proton transfer. This work represents the first investigation into the mechanism of nucleophile additions to germenes using time-resolved methods. The reaction of silenes in the absence of chemical traps has been shown to take place in either a head-to-head or head-to-tail fashion. 1,1-Diphenylsilene undergoes head-to tail dimerization to afford 1,1,2,2-tetraphenyl-1,3-disilacyclobutane and this product has been shown to be photochemically inert. This work investigates the dimerization of 1,1-diphenylgermene and the photochemical behaviour of the resulting 1,3-digermacyclobutane in solution. These results will allow some mechanistic comparisons to be made involving the synthesis and photochemical behaviour of 1,3-dimetallocyclobutanes.

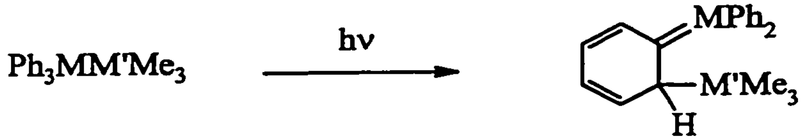
In any event, it is anticipated that the photochemistry of germasilanes, digermanes, arylgermetanes, 1,3-dimetallocyclobutanes will yield novel germanium divalent and trivalent reactive intermediates. These studies will use a combination of product and time-resolved spectroscopic studies to allow detailed comparisons of the reactivities of homologous silenes and germenes under identical conditions. Furthermore, the investigation into the photochemistry of disilanes, germasilanes, and digermanes may also aid in clarifying the transient assignments currently found in the literature.

CHAPTER 2

2.1 - RESULTS - THE DIRECT DETECTION AND REACTIVITY OF 1,1-DIPHENYLGERMENE

2.1.1 - Introduction

The reactivity of silenes generated from silacyclobutanes or aryldisilanes has been an intensely investigated subject in our laboratory. Although various germanium-carbon doubly bonded species have been reported in the literature, there have been no kinetic or mechanistic studies of Ge=C reactivity.[2] It was our intention to study the photochemistry of a homologous series of aryldimetallanes, $Ph_3SiSiMe_3$, $Ph_3SiGeMe_3$, $Ph_3GeSiMe_3$, and $Ph_3GeGeMe_3$, with the goal of detecting the 1,3,5-(1-metalla)hexatrienes resulting from formal [1,3]-metalla migration into one of the aryl rings. This would also be the first systematic comparative study of the reactivity of Si=C and Ge=C bonds, using these compounds as precursors (eqn. 32).

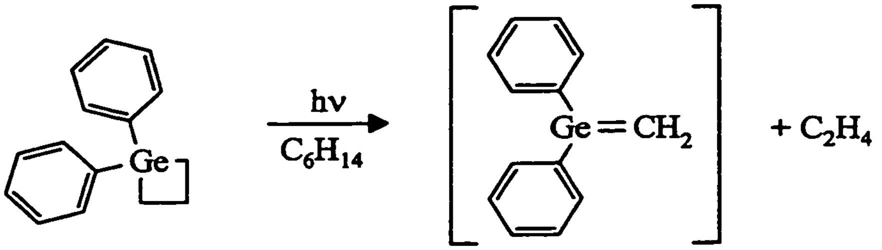


[32]

a. M = M' = Si
b. M = Si, M' = Ge
c. M = Ge, M' = Si
d. M = M' = Ge

The characterization of a (1-germa)hexatriene resulting from the photolysis of arylgermasilanes is difficult due to the complex nature of the germasilane photochemistry. This is compounded by the fact that there were no kinetic data in the literature for the reactions of transient germenes, at the time we began our work. A clean photochemical source of a simple germenic intermediate was therefore required in order to lay the groundwork for transient assignments in more complex situations, and to provide a basis for comparisons to silenes of homologous structures.

On the basis of our previous work with 1,1-diphenylsilacyclobutane, an efficient photochemical precursor of the transient 1,1-diphenylsilene, we identified 1,1-diphenylgermetane (**51**) as the most reasonable choice of a precursor of a transient germene whose silicon analogue had been studied in great detail by earlier workers in our group (eqn. 33).

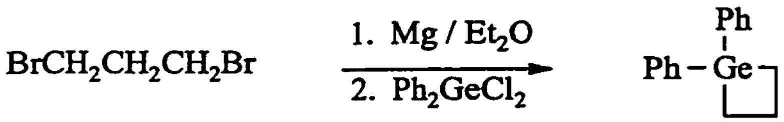


[33]

51 **52**

2.1.2 - Synthesis of 1,1-Diphenylgermetane

The synthesis of 1,1-diphenylgermetane (**51**) was accomplished using a modification of a procedure previously reported by Bickelhaupt and coworkers.[78] Thus, reaction of 1,3-dibromopropane with a ~10-molar excess of ground magnesium followed by addition of diphenylgermanium dichloride afforded 1,1-diphenylgermetane (**51**) in 91% yield (eqn. 34). Column chromatography was used to purify the compound to >99% purity and **51** was identified on the basis of spectroscopic and analytical data (See Experimental Section 5.4.1).

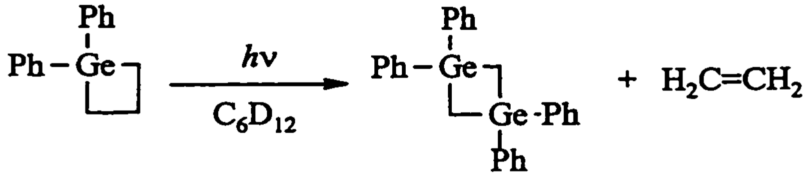


51

[34]

2.1.3 - Steady State Photolysis of 1,1-Diphenylgermetane

Steady state photolysis of a 0.01 M solution of **51** in cyclohexane-d_{12} led to the disappearance of the starting material and the formation of several new signals in the ^{1}H NMR spectrum of the crude reaction mixture: a singlet at δ= 5.3 ppm assignable to ethylene, a second singlet at δ= 1.62 ppm, and several new peaks in the aromatic region. Column chromatography of large scale photolyses allowed for the isolation of a single compound, which was identified as 1,1,3,3-tetraphenyl-1,3-digermetane (**87**) on the basis of spectroscopic, analytical, and X-ray crystallographic data (eqn. 35). Photolysis of less pure samples of **51** (purity < 95%) under similar conditions led to the formation of ethylene, digermetane **87**, and significant amounts of a polymeric material which was not identified. Gel permeation chromatography allowed the molecular weight of this material to be estimated as $M_n = 3400$.

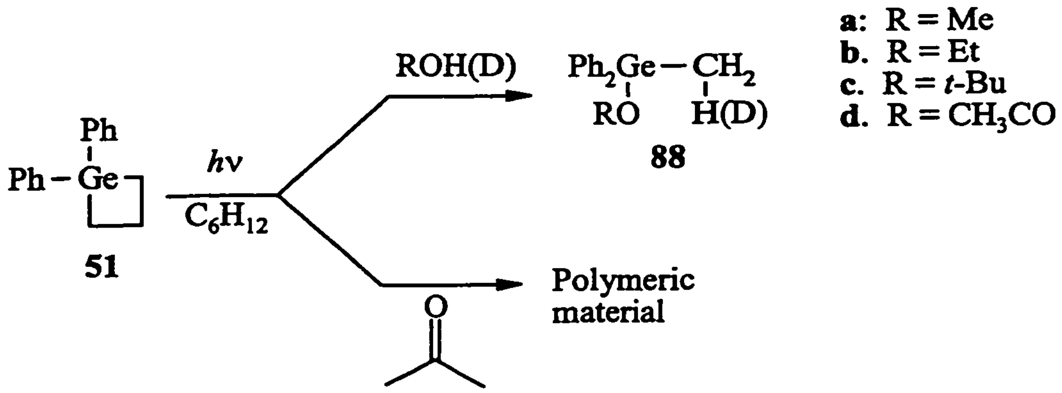


51 **87**

[35]

2.1.4 - Steady State Trapping of 1,1-Diphenylgermene with Alcohols

Photolysis of a hexane solution containing **51** (0.03 M) and methanol, ethanol, or *t*-butanol (0.5 M) also led in each case to the formation of ethylene and a single product as shown by ^{1}H NMR and GC analysis. The product observed in the absence of alcohols, digermetane **87**, was not formed in detectable yields in these experiments. These products were identified as the corresponding alkoxymethyldiphenylgermanes **88a-c** (eqn. 36), after isolation by semi-preparative gas chromatography from larger scale photolyses of deoxygenated solutions of **51** in the neat alcohols, and/or by comparison to authentic samples prepared by reaction of the appropriate alcohol with methyldiphenylgermanium chloride.[79] The NMR spectra of each of these compounds exhibits a singlet at $\delta \sim 0.74$ due to the Ge-Me group. This resonance changes to a triplet upon photolysis in the presence of methanol-O*d* indicating the presence of a Ge-CH_2D group (eqn. 34). Photolysis of a solution of **51** in cyclohexane-d_{12} containing acetic acid led to the formation of a product whose nmr spectrum was consistent with acetoxygermane **88d** (eqn. 36), but the compound decomposed during attempts to isolate it by semi-preparative GC. Photolysis of a 0.03 M solution of **51** in cyclohexane-d_{12} containing 0.07 M acetone led to the formation of polymeric material and ethylene; no other products were detectable after ~20% conversion of **51**. Experiments in which methanolic hexane solutions of **51** were photolysed simultaneously with similar solutions of 1,1-diphenylsilacyclobutane (**3**) ($\Phi = 0.21 \pm 0.04^{34}$) indicated that the quantum yield for consumption of the germetane is also 0.21 ± 0.03.



[36]

2.1.5 - Nanosecond Laser Flash Photolysis Studies on 1,1-Diphenylgermetane

Nanosecond laser flash photolysis (NLFP) of nitrogen-saturated 4.4 X 10^{-3} M solutions of **51** in hexane, acetonitrile or tetrahydrofuran (THF), with the pulses from a KrF Excimer laser (248-nm), gave rise to readily detectable transient absorptions in the 300-360 nm spectral range, which decayed over several tens of microseconds with predominant second order kinetics. The transient absorption spectrum, measured in point-by-point fashion 0.5-1.0 μs after the laser pulse, showed an absorption band with a maximum at 325-nm in all three solvents. The spectrum obtained using hexane as solvent is shown in Figure 2.1. The lifetime of the transient is insensitive to the presence of oxygen or 1,3-octadiene (indicating that it is not a triplet species), but is shortened upon addition of aliphatic alcohols or acetic acid to the solution. On the basis of these observations, the transient is assigned to 1,1-diphenylgermene (**52**).

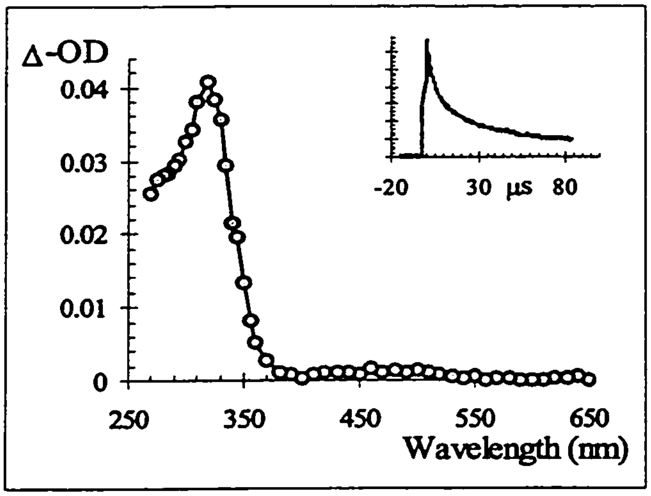


Figure 2.1 - UV absorption spectra of 1,1-diphenylgermene (**52**), from nanosecond laser flash photolysis of air-saturated solutions of **51** (0.0045 M) in hexane. The spectrum shown was recorded 0.5-1.0 μs after the laser pulse. The insert shows the decay trace recorded at a monitoring wavelength of 325 nm.

2.1.6 - Reactivity of 1,1-Diphenylgermene With Alcohols and Acetic Acid

The addition of MeOH, EtOH, 2-PrOH, or *t*-BuOH (0.005-0.02 M) caused the decay of germene **52** to proceed with clean pseudo-first order kinetics, and the lifetime of the transient varied linearly with alcohol concentration (Figure 2.2).

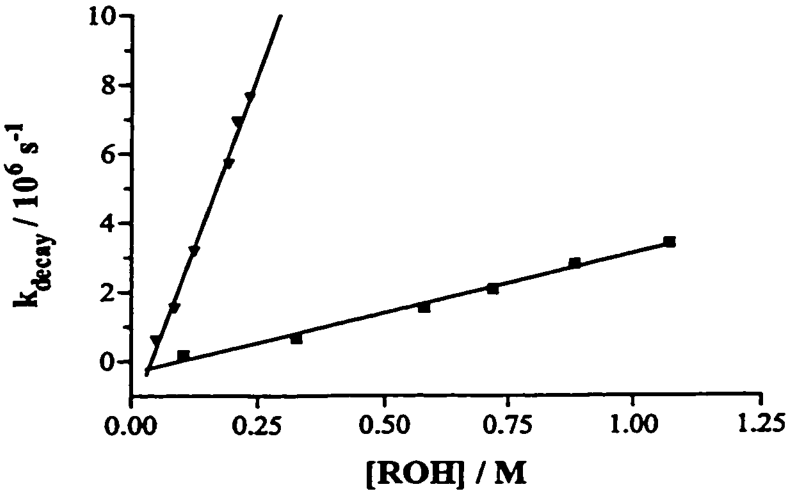


Figure 2.2 - Plots of the pseudo-first-order rate constants for decay (k_{decay}) of diphenylgermene (**52**) in the presence of methanol (-▼-) and t-butanol (-■-) in air-saturated hexane at 23°C

Linear least-squares analysis of the data according to Equation 14 gave fits with acceptable correlation coefficients, but the intercepts were found to be negative. The rate constants determined from the slopes of the plots are summarized in Table 2.1. Rate constants were also determined for reaction with MeOD and *t*-BuOD, and the results are expressed in Table 2.1 as k_H/k_D-values. Plots of k_{decay} *vs.* [Q] for acetic acid and acetic acid-*d* exhibited excellent linear correlations and positive y-intercepts. Reaction of 1,1-diphenylgermene with acetone was found to be too slow to be measurable with our system, and only an upper limit for the quenching rate constant could be determined (from the lifetime of **52** in the presence of 0.23 M acetone). The rate constants obtained in all of these experiments are listed in Table 2.1.

$$k_{decay} = k_d^o + k_q[Q] \qquad [14]$$

Table 2.1 - Absolute rate constants for reaction of 1,1-diphenylgermene (**52**) with alcohols, acetic acid, and acetone in air-saturated hexane solution at 23 °C.[a]

Quencher	Rate Constant (k_q X 10^{-8} M s)	k_H / k_D
MeOH	3.6 ± 0.4	1.3 ± 0.4
EtOH	2.5 ± 0.2	*b*
i-PrOH	1.6 ± 0.2	*b*
t-BuOH	0.35 ± 0.03	1.9 ± 0.3
acetic acid	16 ± 2	0.9 ± 0.2
acetone	< 0.004 ± 0.001	*b*

a. From the slopes of plots of k_{decay} vs. [Q] (eqn. 14). Errors are quoted as ± 2σ.

b. Not determined.

The addition of aliphatic alcohols and acetic acid to acetonitrile solutions of 1,1-diphenylgermetane also resulted in the shortening of the lifetime of germene **52**. Upon addition of methanol or *t*-butanol, plots of k_{decay} *versus* [ROH] exhibited strong positive curvature over the ranges of alcohol concentration studied. Analysis of these plots showed that they fit well to the square of the alcohol concentration ($r^2 > 0.99$) according to Eqn. 38. Fitting these data to a polynomial expression containing both 1st and 2nd order terms in [ROH] (eqn. 18) resulted in 1st-order coefficients identical to zero within two standard deviations. Figure 2.3 shows representative plots of k_{decay} *versus* [ROH], for quenching of germene **52** by MeOH and *t*-BuOH in MeCN solution.

$$k_{decay} = k_d^{o} + k_{2q}[Q]^2 \qquad [38]$$

$$k_{decay} = k_d^{o} + k_q[Q] + k_{2q}[Q]^2 \qquad [18]$$

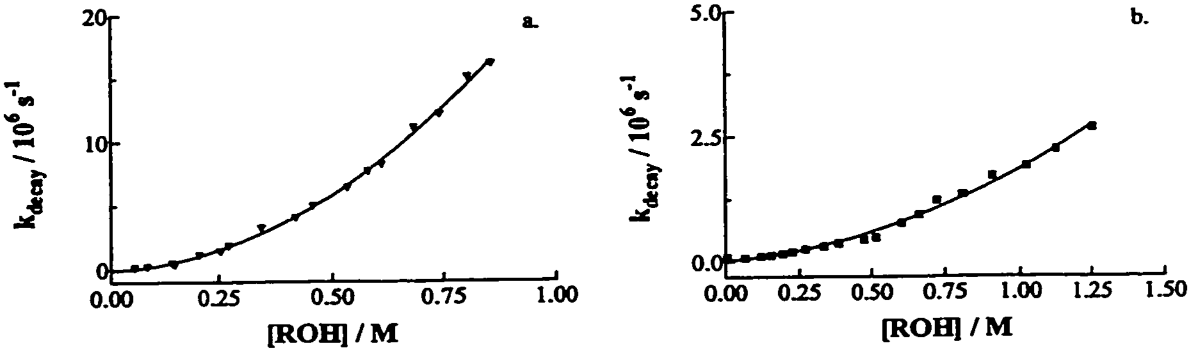


Figure 2.3 - Plots of the pseudo-first-order rate constants for decay (k_{decay}) of diphenylgermene (**52**) in the presence of a) methanol (-▼-) and b) t-butanol (-■-) in air-saturated acetonitrile at 23°C.

Table 2.2 - Absolute rate constants for reaction of 1,1-diphenylgermene (**52**) with MeOH, *t*-BuOH and HOAc in air-saturated acetonitrile and tetrahydrofuran solution at 23 °C.[a]

Quencher		MeOH	*t*-BuOH	HOAc[b]
MeCN	k_q / 10^7 $M^{-1}s^{-1}$	0.03 ± 0.2 [c]	0.04 ± 0.3 [c]	77 ± 4
	k_{2q} / 10^7 $M^{-2}s^{-1}$	2.2 ± 0.2	0.14 ± 0.02	-
THF	k_q / 10^7 $M^{-1}s^{-1}$	0.5 ± 0.2	0.06 ± 0.03	18 ± 1
	k_{2q} / 10^7 $M^{-2}s^{-1}$	1.4 ± 0.4	0.13 ± 0.03	-

a. From polynomial least-squares fitting of k_{decay} vs. [Q] data according to Eqn. 18. Errors are quoted as ± 2σ.

b. k_{decay} varies linearly with [HOAc] according to Eqn. 14.

c. Indistinguishable from zero within experimental error.

The use of THF as a solvent also caused the plots of k_{decay} *versus* [MeOH] to be curved. Fitting the data to Eqn. 18 afforded non-zero values for both the 1st and 2nd order terms in [ROH]. Figure 2.4 shows a representative plot of this type for quenching of **52** in THF at 23 °C. Plots of k_{decay} *vs.* [HOAc] for quenching of the germene by acetic acid in both acetonitrile and THF solution were linear, with positive intercepts. The second- and third-order rate constants (k_q and k_{2q}, respectively) obtained from the experiments in MeCN and THF solution are collected in Table 2.2.

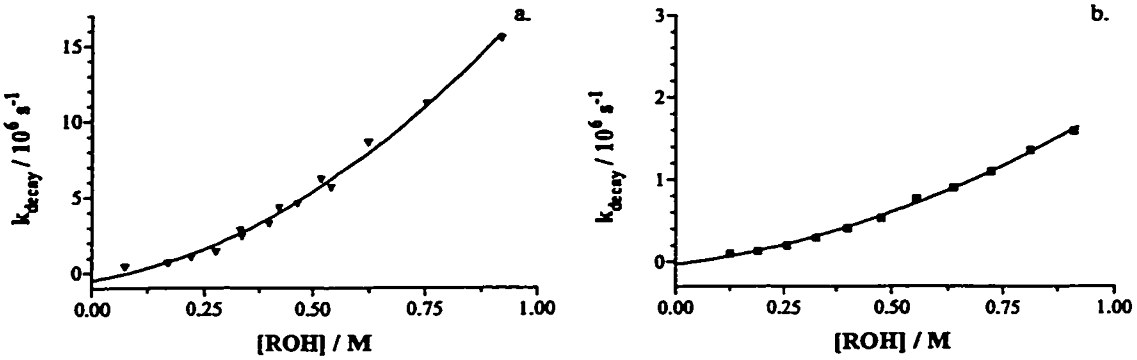


Figure 2.4 - Plots of the pseudo-first-order rate constants for decay (k_{decay}) of diphenylgermene (52) in the presence of a) methanol (-▼-) and b) t-butanol (-■-) in THF at 23^{0}C.

2.2 - RESULTS - THE MOLECULAR STRUCTURES AND PHOTOCHEMISTRY OF THE 1,3-DIMETALLACYCLOBUTANES DERIVED FROM THE CYCLOADDITION OF 1,1-DIPHENYLSILENE AND 1,1-DIPHENYLGERMENE

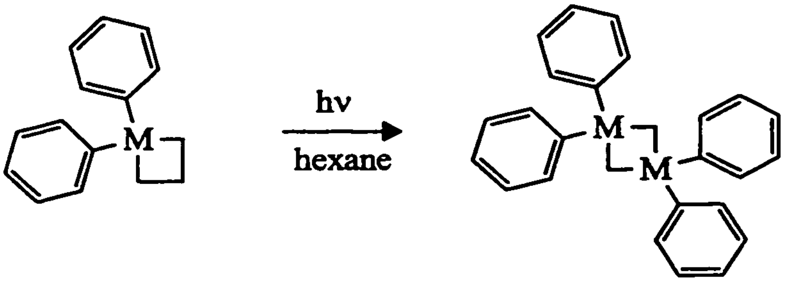
2.2.1 - Introduction

One of the best known and most general reactions of transient silenes is the formation of disilacyclobutanes by head-to-tail or head-to-head [2+2]-dimerization.[1,29] The most commonly observed regiochemistry is head-to-tail, while head-to-head dimerization has only been observed with electronically-stabilized silenes. In these cases, the polarity of the Si=C bond is reduced due to the electronic effects of substituents at silicon (*e.g.*, trialkylsilyl) and carbon (*e.g.*, alkyl, aryl, or alkoxy). Although they have been much less extensively studied, transient germenes are also known to dimerize to yield 1,3- or 1,2-digermacyclobutane derivatives.[2,72]

In this study, three dimetallacyclobutanes have been synthesized; the head-to-tail dimerization products of 1,1-diphenylsilene and 1,1-diphenylgermene, and the crossed cycloaddition product resulting from the reaction of **4** and **52**. These three compounds were isolated and fully characterized, and to our knowledge, this is the first example of a silene-germene cross-cycloaddition product. This study investigates the dimerization mechanism of silenes and germenes and will also allow for a systematic comparison of the photochemistry of 1,3-dimetallocyclobutanes where the Group 14 element is changed from silicon to germanium.

2.2.2 - Synthesis of Silene and Germene Homodimers

Steady-state photolysis of deoxygenated, 0.01 M solutions of 1,1-diphenylsilacyclobutane(**3**) or 1,1-diphenylgermetane(**51**) in cyclohexane or cyclohexane-d_{12} led to the gradual disappearance of the metallacyclobutanes, and the subsequent formation of a new peak in the NMR. The ^{1}H NMR spectrum of the crude product mixture after 10-50% conversion of **3** and **51** showed a prominent resonance at $\delta = 1.12$ ppm, and 1.62 ppm respectively along with aromatic signals in the range 7.2-7.6 ppm (20 ^{1}H). The isolated product obtained from the photolysis of 1,1-diphenylsilacyclobutane displayed spectroscopic and analytical properties identical to those already published for 1,1,3,3-tetraphenyl-1,3-disilacyclobutane(**13**).[57] The identification of the photoadduct derived from the photolysis of **51** was accomplished using spectroscopic data along with comparisons to trends in the spectroscopic data for **3** and **51**. The compilation of this information allowed the product to be tentatively assigned as 1,1,3,3-tetraphenyl-1,3-digermetane(**87**) (eqn. 40).



[40]

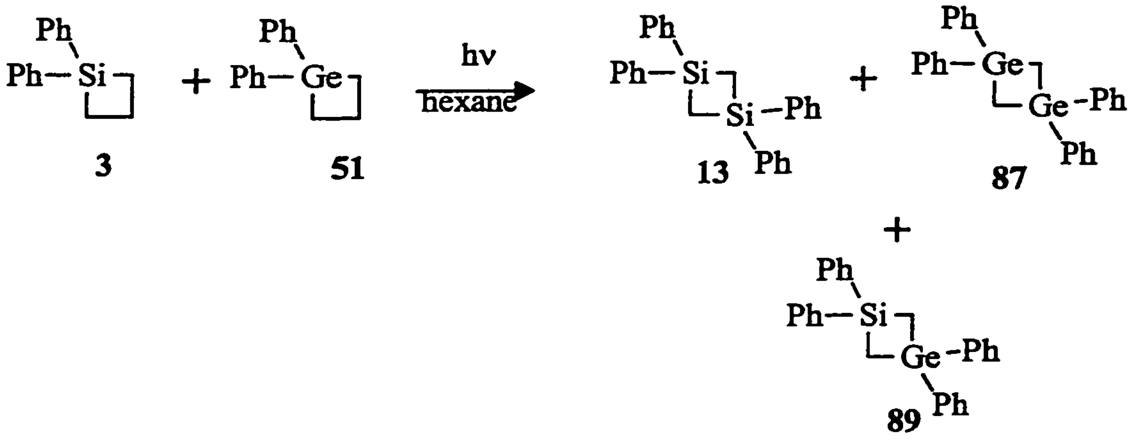
3 = Si
51 = Ge

13 = Si
87 = Ge

Isolation of the dimers was accomplished by radial chromatography, and the products were recrystallized from pentane as colourless crystals.

2.2.3 - Synthesis of Cross Cycloaddition Product 89 (1,1,3,3-Tetraphenyl-3-germa-1-silacyclobutane)

Photolysis of an equimolar mixture of 1,1-diphenylsilacyclobutane (3) and 1,1-diphenylgermetane (51) in deoxygenated cyclohexane-d_{12} solution afforded 3 products. Two of the products were identified as 1,1,3,3-tetraphenyl-1,3-digermetane (87) and 1,1,3,3-tetraphenyl-1,3-disilacyclobutane (13) based on GC/MS and ^{1}H NMR data obtained from the crude photolysis mixture. The ^{1}H NMR spectrum of the crude photolysis mixture showed a new signal growing in at δ=1.37 ppm which was between the signals observed for the disila- (1.12 ppm) and the digermacyclobutane (1.62 ppm). This new photoadduct also displayed a GC retention time which was slightly longer than the retention time for the silene dimer and yet slightly shorter than the retention time of the germene dimer. GC/MS analysis of the product mixture showed that this new product has a molecular ion of m/z = 434 and contains a single germanium atom. These data are consistent with the product being the crossed cycloadduct, 1,1,3,3-tetraphenyl-3-germa-1-silacyclobutane(89) (eqn. 41). The ratio of **13**:**87**:**89** was found to be 1:3:2 based on GC and ^{1}H NMR peak integrations at long photolysis times and ~40% conversion. GC analysis of crude photolysis mixtures at ~15% conversion of **3** and ~35% conversion of **51** revealed that the product mixture consisted of a **13**:**87**:**89** ratio of 1.0:2.1:4.8.

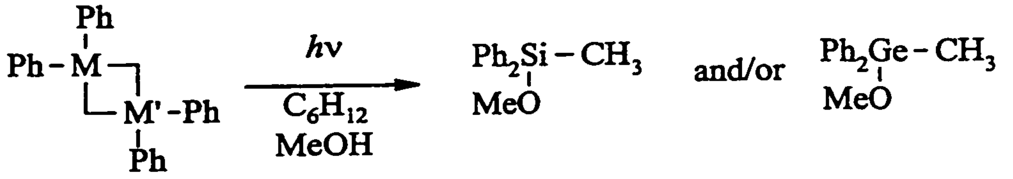


[41]

The isolation of crossed cycloadduct **89** was accomplished using reverse-phase HPLC techniques using MeCN:water mixtures as the eluting solvent and the product was recrystallized from pentane as colourless crystals.

2.2.4 - Photolysis of 1,3-Dimetallacyclobutanes

Steady state irradiation of deoxygenated solutions of **13,87,89** in cyclohexane or cyclohexane-d_{12} containing 0.5 M methanol led to the formation of methoxymethyldiphenylsilane (**14**) and/or methoxymethyldiphenylgermane (**88**), indicative of the formation of **4** and/or **52** as the initially formed products (eqn. 42). Qualitatively, the photolysis of digermacyclobutane **87** appeared to be roughly ten times more efficient than that of **89**, and at least 20 times more efficient than that of disilacyclobutane **13**. The photolyses of **87** and **89** were clean, producing only the methoxysilane and/or -germane within the limits of our GC detection method. In the case of **13**, on the other hand, the material balance was poor (~10%), and GC/MS analysis indicated the co-formation of 1,1'-bicyclohexyl in the early stages of the photolysis. This product is presumably derived from cyclohexyl radicals, further evidence of which was revealed by the additional formation of cyclohexanol and cyclohexanone in less completely deoxygenated solutions. These products are not formed in detectable yields in the photolyses of the other two compounds.



[42]

13 - M=M'=Si
89 - M=Si, M'=Ge
87 - M=M'=Ge

14

88

2.2.5 - Quantum Yield Determinations

Quantum yields for formation of **14** and/or **88** from photolysis of 1,1-diphenylgermacyclobutane (**51**) and the three dimetallacyclobutanes were determined by merry-go-round photolysis of deoxygenated 0.01 M solutions in cyclohexane containing 0.5 M methanol, using similar solutions containing 1,1-diphenylsilacyclobutane (**3**; Φ_{14} = 0.21 ± 0.02[34]) as the actinometer. These experiments afforded values of Φ_{14} = 0.007 ± 0.003 from disilacyclobutane **3a**, Φ_{88} = 0.22 ± 0.02 and 0.11 ± 0.02 from the mono- and digermacyclobutanes **51** and **87**, respectively, and Φ_{14+88} = 0.04 ± 0.01 from germasilacyclobutane **89**.

2.2.6 - NLFP of 1,1,3,3-Tetraphenyl-1,3-Disilacyclobutane and 1,1,3,3-Tetraphenyl-1,3-Digermetane

Nanosecond laser flash photolysis (NLFP) of nitrogen-saturated 2 X 10^{-3} M solutions of digermetane **87** in hexane gave rise to a transient that displayed almost identical spectral and kinetic behaviour to 1,1-diphenylgermene.[80] Figure 2.5 compares the transient absorption spectra obtained from optically matched solutions of **51** and **87**.

The germene signal generated from **51** is approximately twice as intense than in the case for 1,3-digermatane **87**. This is consistent with the relative quantum yields for the formation of the alkoxygermane product, from the same two compounds, determined by steady state photolysis in the presence of methanol.

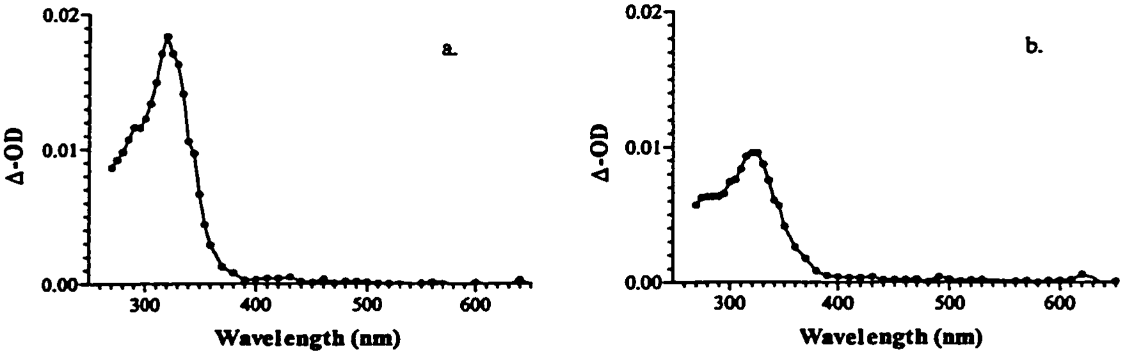


Figure 2.5 - Time-resolved UV absorption spectrum of a) 1,1-diphenylgermetane(**51**) compared to the spectrum of an optically matched solution of b) 1,1,3,3-tetraphenyl-1,3-digermetane(**87**) in air-saturated hexane solution at 23 °C.

Nanosecond laser flash photolysis (NLFP) of nitrogen-saturated 2.0 X 10^{-3} M solutions of **13** in hexane did NOT give rise to transient absorptions in the 300-380 nm range attributable to the silenic intermediate. Interestingly, flash photolysis of this compound did yield a transient which exhibited an absorption spectrum consisting of a single broad band centered at 540 ± 20 nm. This transient was found to have a lifetime of <15 ns (inferred from the fact that the transient seemed to follow the laser pulse). While it can be noted that the general appearance of the spectrum shows marked similarities to those of arylsilyl monoradicals,[77] we have not yet been able to identify the species giving rise to these absorptions conclusively.

2.3 - RESULTS - THE PHOTOCHEMISTRY OF GROUP 14 1,1,1-TRIMETHYL-2,2,2-TRIPHENYLDIMETALLANES ($PH_3MM'ME_3$; M, M' = SI, GE)

2.3.1 - Introduction

The photochemistry of aryldisilanes has been extensively investigated over the past 25 years.[81] There are three distinct types of reactive intermediates that are formed during the photolysis of this class of compounds. The yield of each type of intermediate is dependent on the degree of aryl substitution and on solvent. The most notable example of this complex reaction pathway is demonstrated by the photochemistry of methyl-pentaphenyldisilane. Irradiation of this compound yields two types of silenes; a silahexatriene via formal [1,3]-$SiPh_2Me$ migration and a simple silene from dehydrosilylation (loss of H-$SiPh_3$), and a pair of silyl radicals derived from Si-Si bond homolysis.[46] For this particular aryldisilane, the formation of the (1-sila)hexatriene is a minor pathway. However, there are many other examples where this photoproduct is the major pathway of the photoreaction.[42-47,49] The formation of both the silahexatriene and simple silene occur from the excited singlet state of the disilane while silyl free radicals have been shown to result from the triplet state.[49] The yield of free radicals can be altered by enhancing the rate of intersystem crossing through the use of polar solvents and by attaching sterically bulky substituents to the silicon atoms.

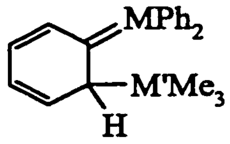
The photochemistry of tri- and higher oligosilanes usually affords a silylene as the major reactive intermediate. Silylene extrusion is a relatively minor photochemical reaction pathway in aryldisilanes, except in specific cases.[82]

In solution, arylgermasilanes and -digermanes exhibit all three of the photoreaction pathways shown by aryldisilanes.[76,77,83] However, the few compounds of this type that have actually been studied show little selectivity when compared to analogous disilanes, and the photochemistry is strongly dominated by free radical chemistry. In contrast to disilane photochemistry, irradiation of both germasilanes and digermanes results in germylene extrusion.[66,74,83,84]

Laser flash photolysis studies of aryldisilanes have been extremely fruitful in providing information on the reactions of transient silenes with various reagents such as alcohols, ketones and aldehydes, carboxylic acids, dienes, and oxygen.[46-49,64,85] In this section, we report the results of a study investigating the photochemistry of the trimethyltriphenylgermasilane derivatives **93a,b** and 1,1,1-trimethyl-2,2,2-triphenyldigermane (**93c**) by steady state and laser flash photolysis techniques.

$Ph_3MM'Me_3$

24c. M = M' = Si
93a. M = Si, M' = Ge
93b. M = Ge, M' = Si
93c. M = M' = Ge



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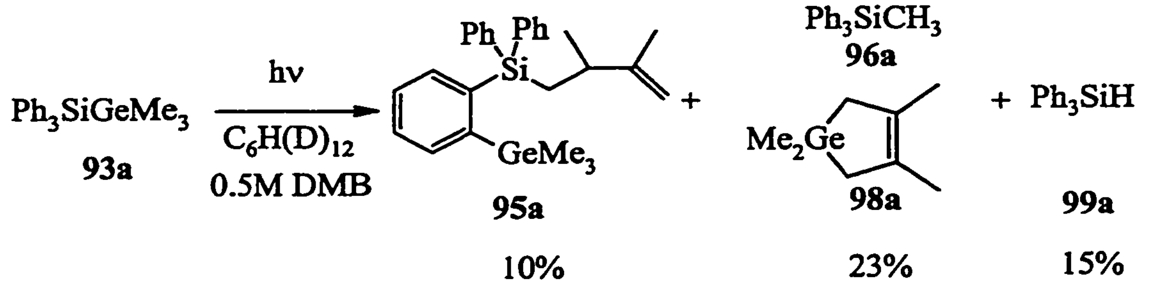
The objective was to systematically investigate the changes induced in the photochemistry of **24c** as a result of replacement of first one and then both of the silicon atoms with germanium. In addition, it was hoped that new silenic and germenic intermediates could be detected: namely the corresponding (1-metalla)hexatriene reactive intermediates **94a-c**. The reactivity of these homologous silatrienes and germatrienes towards various nucleophiles could be investigated. Digermane **93c** has been studied previously, and was reported to give high yields of germyl-radicals upon photolysis in solution.[76].

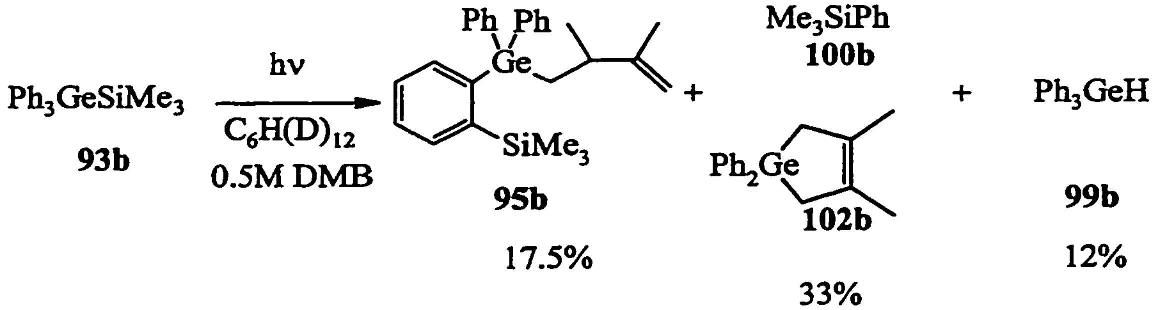
2.3.2 - Steady State Photolysis of Arylgermasilanes and Aryldigermanes

2.3.2a - 2,3-Dimethyl-1,3- butadiene Trapping Experiments

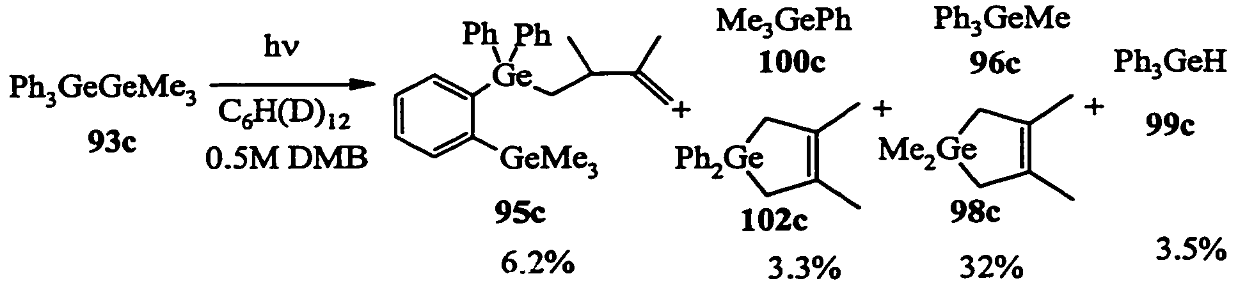
Steady state photolysis (254 nm) of deoxygenated solutions of **93a-c** (0.05 M) in cyclohexane or cyclohexane-d_{12} containing 0.5 M 2,3-dimethyl-1,3-butadiene (DMB) afforded the products shown in Eqns. 43-45. The majority of products are known compounds, and were identified by GC/MS and ^{1}H NMR analysis of the crude photolysis mixtures. The identities of Ph_3SiMe, Me_3SiPh, Me_3GePh, Ph_3GeMe, Ph_3Si-H, Ph_3Ge-H, and photoadducts **98a,c**, **102b,c** were determined by comparing the spectroscopic data for these compounds to analogous data from authentic samples. Compound **95b** was identified after isolation from larger scale photolyses, and exhibited ^{1}H NMR data similar to 1-(trimethylsilyl)-2-((2,3-dimethyl-1-buten-4-yl)diphenylsilyl)benzene (**32**).[47] The mass spectrum of **95b** was similar to the fragmentation pattern exhibited by 1-(trimethylsilyl)-2-((2,3-dimethyl-1-buten-4-yl)dimethylgerma)benzene (**68**).[83] Compounds **95a,c**, formed from germasilane **93a** and digermane **93c**, respectively, were observed in extremely low yields. These compounds could not be isolated but were tentatively identified as **95a,c** by comparison of their mass spectrum (obtained by GC/MS) to that of **95b**. Product yields were determined by GC and are the averages of data obtained at various conversions between 10 and 50% of starting material. The photolysis mixtures each contained several other products which could not be rigorously identified; they were each formed in individual yields of <5% as estimated by GC. Comparison of the mass spectra of **99a-c** obtained from photolyses in C_6H_{12} and C_6D_{12} indicated that no deuterium was incorporated in this product in the latter solvent.



[43]



[44]



[45]

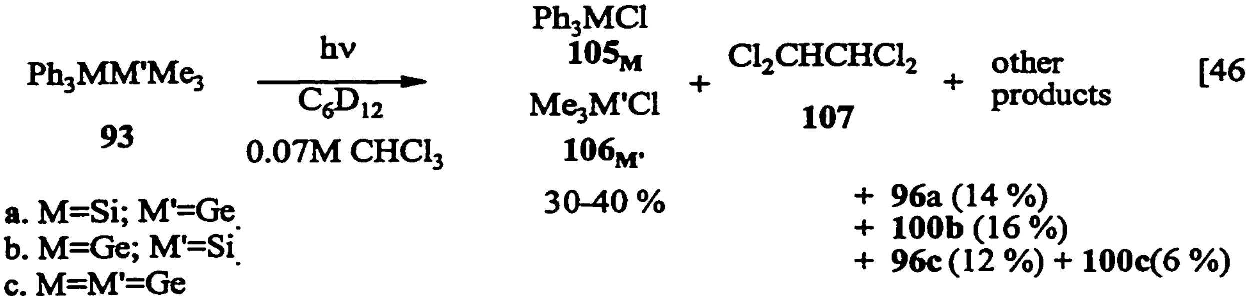
2.3.2b - 1-Decanol Trapping Experiments

Photolysis of **93a-c** as deoxygenated cyclohexane solutions containing 0.1 M n-decanol afforded 1-trimethylsiloxy- or 1-trimethylgermoxydecane (**103$_{Si}$** and **103$_{Ge}$**, respectively) along with the germylene extrusion co-product, **96a** and **100b**, and Ph$_3$Si-H or Ph$_3$Ge-H, respectively. The yields of **103** were similar to those of **99a-c** in each case. Authentic samples of **103$_M$** were synthesized by reacting a 1:1 mixture of 1-decanol with chlorotrimethylsilane or trimethylgermanium chloride in dichloromethane in the presence of an equimolar amount of imidazole.

$Me_2Ge{=}CH_2$ **104a** $Me_2Si{=}CH_2$ **104b** $Me_3MO{-}C_{10}H_{21}$ **103_M**

2.3.2c -Chloroform Trapping Experiments

Steady state photolysis (254 nm) of deoxygenated cyclohexane-d_{12} solutions of 0.05 M **93a-c** containing 0.07 M $CHCl_3$ and 0.002 M CH_2Cl_2 as an internal NMR integration standard afforded chlorotriphenylsilane or triphenylgermanium chloride (**105_{Si}** **105_{Ge}**; detected by GC), chlorotrimethylsilane or trimethylgermanium chloride (**106_{Si}** **106_{Ge}**; detected by NMR), and 1,1,2,2-tetrachloroethane (**107**), which were identified by comparisons to corresponding data obtained on authentic samples (eqn. 46). The yields of these products were determined relative to reacted starting material by GC and NMR analysis of the crude photolysis mixtures at several conversions between 10 and 50%, and were ~30% from **93a** and ~40% from **93b,c**. Several other products were also detected by GC and NMR, but were not identified owing to their low yields.



$$\underset{\mathbf{93}}{Ph_3MM'Me_3} \xrightarrow[C_6D_{12}\;\; 0.07M\ CHCl_3]{h\nu} \begin{matrix} Ph_3MCl \\ \mathbf{105_M} \\ Me_3M'Cl \\ \mathbf{106_{M'}} \\ 30\text{–}40\ \% \end{matrix} + \underset{\mathbf{107}}{Cl_2CHCHCl_2} + \begin{matrix}\text{other} \\ \text{products}\end{matrix} \qquad [46]$$

a. M=Si; M'=Ge
b. M=Ge; M'=Si
c. M=M'=Ge

+ **96a** (14 %)
+ **100b** (16 %)
+ **96c** (12 %) + **100c**(6 %)

2.3.3 - NLFP Experiments on Arylgermasilanes and Aryldigermanes

Nanosecond laser flash photolysis experiments were carried out with continuously flowing, deoxygenated hexane solutions of **93a-c** (5×10^{-4} M), using a KrF excimer laser as excitation source (248 nm, ~20 ns pulses, ~120 mJ). Strong transient absorptions were observed throughout the 280-600 nm monitoring range in all cases, but were particularly prominent in the 300-340 nm and 420-550 nm ranges. For **93a,b**, the short wavelength transient absorptions decayed with mixed pseudo-first and second order kinetics and apparent lifetimes in excess of 10-μs, while the long wavelength absorptions decayed with clean pseudo-first order kinetics and lifetimes in the 1-2 μs range. Figure 2.6 shows transient absorption spectra recorded for **93a** and **93b**.

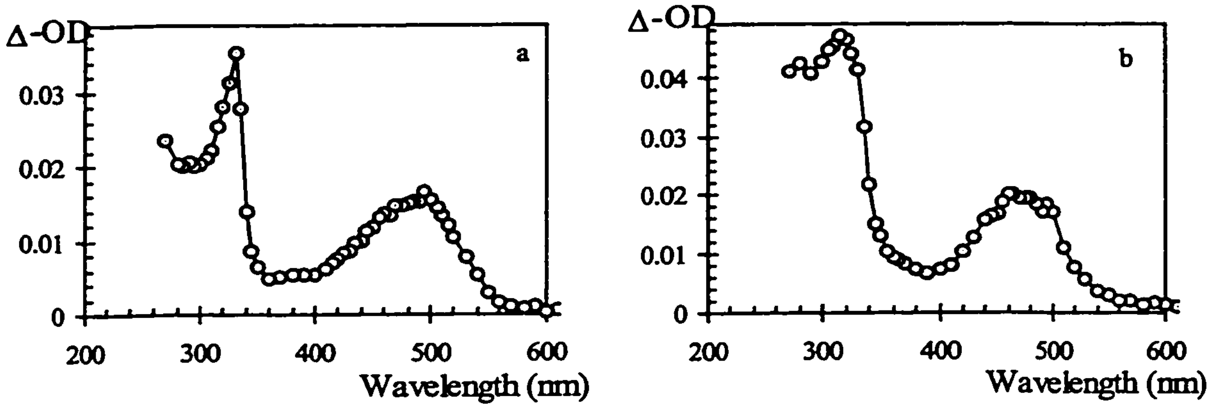


Figure 2.6 - Time-resolved UV absorption spectra recorded with deoxygenated 5.0 x 10^{-4} M solutions of a) $Ph_3SiGeMe_3$ (**93a**) and b) $Ph_3GeSiMe_3$ (**93b**) in hexane at 23 °C, 0.2-1.0 μs after 248-nm pulsed laser excitation.

<u>2.3.4 - Absolute Rate Constants for Reaction of the 480 nm Transient with Various Reagents</u>

Addition of methanol (MeOH), DMB, acetone, acetic acid, carbon tetrachloride or oxygen to the solutions of **93a** resulted in an increase in the pseudo-first order rate constant for decay of the long-wavelength transient absorption. Plots of k_{decay} *versus* concentration of added reagent were curvilinear for methanol, but fit acceptably to the second order polynomial expression shown in Eqn. 18, where k_d^o is the decay rate constant in the absence of methanol, and k_{MeOH} and k_{2MeOH} are the first and second order coefficients in [MeOH]. Similar plots for the other reagents were rectilinear, and were analyzed according to Eqn. 14. Of these six reagents, only oxygen and carbon tetrachloride affected the lifetime of the transient absorption at 330-nm as well as that at longer wavelengths. In contrast, addition of chloroform to the solution resulted in a shortening of the lifetime of the 330-nm transient ($k_q = (1.7 \pm 0.2) \times 10^8$ $M^{-1}s^{-1}$), but had no effect on that of the long wavelength transient absorption within the concentration range examined ($[CHCl_3] < 0.02$ M).

$$k_{decay} = k_d^{o} + k_{MeOH}[MeOH] + k_{2MeOH}[MeOH]^2 \qquad [18]$$

$$k_{decay} = k_d^{o} + k_q[Q] \qquad [14]$$

The lifetime of the 480-490 nm transient absorption from photolysis of trimethylsilyltriphenylgermane (**93b**) was also quenched upon addition of DMB, HOAc, acetone, carbon tetrachloride or oxygen to the solution, but with the exception of the halocarbon, quenching was much less effective than with the analogous transient from **93a**. The decay rate constants varied in direct proportion to concentration of added reagent in each case. Again, addition of up to ~0.06 M chloroform had no effect on the lifetime of the long wavelength absorption but quenched that at 330-nm. Addition of up to 1.7 M MeOH had no discernible effect on the lifetimes at either monitoring wavelength.

2.3.5 - NLFP Experiments on Aryldigermane 93c

The transient absorption spectrum recorded by flash photolysis of a deoxygenated hexane solution of **93c** showed similarities to those from the other two compounds

(Figure 2.7), but the long wavelength absorption band was significantly less intense than the short wavelength band at 300-340 nm. Still, transient decays recorded at 330 nm and at 480 nm showed the same marked differences in lifetime to those shown in Figure 2.6 for **93a,b**, indicating that two different transient species are being observed. As with **93b**, addition of 0.065 M chloroform to the solution shortens the lifetime of the 330 nm transient to < 25 ns but has little effect on that of the 480 nm transient ($\tau \sim 2.5$ μs). This allows isolation of the spectrum due to the long wavelength-absorbing species, as shown in Figure 2.7.

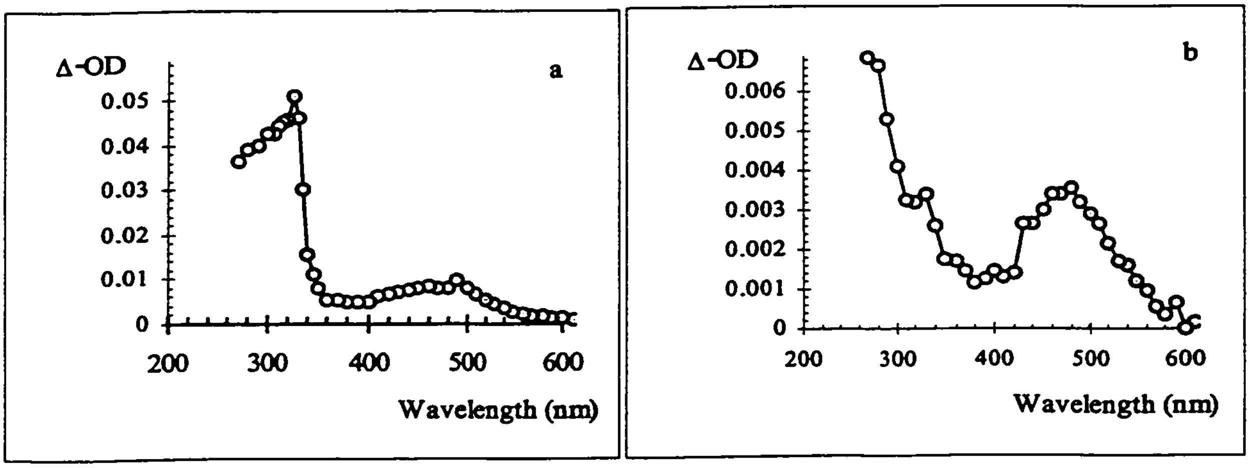
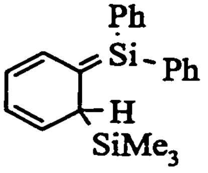
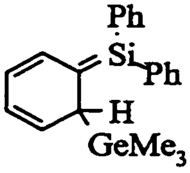
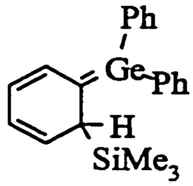
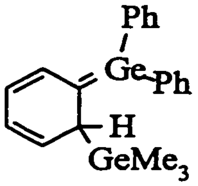


Figure 2.7 - Time-resolved UV absorption spectra recorded with deoxygenated 5.0 x 10^{-4} M solutions of $Ph_3GeGeMe_3$ (**93c**) at 23 °C, in (a) hexane and (b) hexane containing 0.07 M chloroform. The spectra were recorded 0.2-1.0 μs after 248-nm pulsed laser excitation.

Addition of DMB, carbon tetrachloride or oxygen to the chloroform/hexane solutions resulted in shortening of the lifetime of this transient, and the transient decay rate varied linearly with concentration. Quenching by HOAc and MeOH was not investigated in this case.

Table 2.3 summarizes the absolute rate constants for quenching of the 480-490 nm transient absorptions from flash photolysis of **93a-c** by the six quenchers studied, along with the analogous data for quenching of the transient 1-silahexatriene (**25c**) derived from **24c** in the same solvent.[47,48]

Table 2.3 - Absolute rate constants (in units of 10^8 $M^{-1}s^{-1}$) for quenching of transient 1-metallahexatrienes (**25c,93a-c**) by 2,3-dimethyl-1,3-butadiene (DMB), acetone, acetic acid, methanol, oxygen, carbon tetrachloride, and triethylsilane and in hexane solution at 23 °C.[a]

Quencher				
DMB	0.30 ± 0.01	0.34 ± 0.03	0.030 ± 0.003	0.027 ± 0.002
acetone	5.42 ± 0.05	5.68 ± 0.05	0.0021 ± 0.0005	*b*
acetic acid	3.69 ± 0.48	2.21 ± 0.20	0.0039 ± 0.0005	*b*
MeOH	(1.1 ± 0.4) + (64 ± 12)[MeOH]	(1.5 ± 0.6) + (58 ± 13)[MeOH]	< 0.001[c]	*b*
O_2	1.9 ± 0.2	1.62 ± 0.10	0.961 ± 0.045	0.96 ± 0.05
CCl_4	1.1 ± 0.1	1.2 ± 0.1	0.29 ± 0.03	0.35 ± 0.03
$HSiEt_3$	< 0.0001	< 0.0004[d]	< 0.0004[d]	< 0.0004[d]

a. From polynomial least squares fitting of k_{decay} vs. [Q] data according to Eqns. 14 or 18. Errors are quoted as ± 2σ.

b. not determined.

c. addition of up to 1.7 M MeOH had no effect on the lifetime in deoxygenated solution.

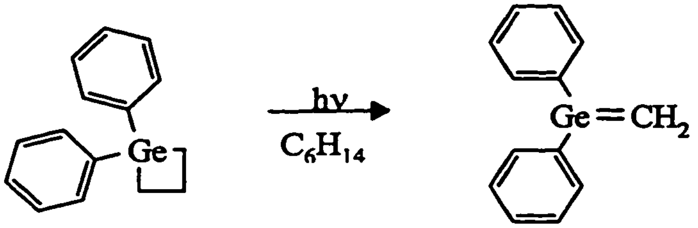
d. addition of up to 4 M $HSiEt_3$ had no effect on the lifetime in deoxygenated solution.

CHAPTER 3

DISCUSSION

3.1 - The Characterization of 1,1-Diphenylgermene From 1,1-Diphenylgermetane

The products obtained from the photolysis of 1,1-diphenylgermetane (**51**) in the absence of chemical traps (dimer **87**) or in the presence of aliphatic alcohols (alkoxygermanes **88a-d**) are all consistent with the transient intermediate being 1,1-diphenylgermene (**52**) (eqn. 47). The behaviour of **51** is almost exactly analogous to that previously reported for 1,1-diphenylsilacyclobutane.[34,52,53,57] It is therefore not difficult to conclusively assign the transient obtained from the photolysis of **51** as 1,1-diphenylgermene because these common reactivity trends exhibited by silenes and germenes are well known.[2,40]



51 **52** [47]

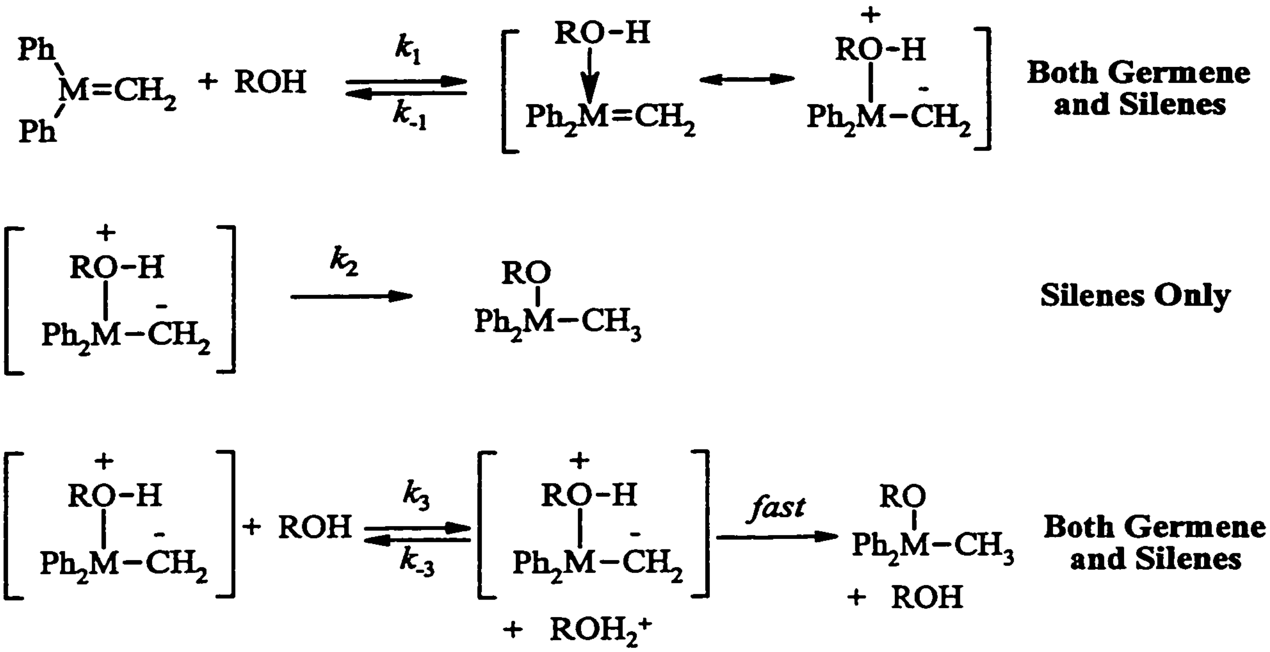
The quantum yield for the formation of alkoxygermane **88a** from **51** was determined to be the same as its silicon analog **3** (0.21).[34] The initial intensities of the transient absorptions resulting from laser irradiation of solutions of **51** and **3** were similar and did not vary as a function of oxygen or diene quenching. This indicated that the silene and germene are formed with similar quantum yields, most likely directly from the lowest excited singlet state of the precursors. Thus, the photochemical behavior of 1,1-diphenylgermetane (**51**) is identical in almost every respect to that of its silicon analog **3**, at least with respect to 1,1-diphenylmetallaene formation.

The kinetic behavior of the 325-nm transient observed in laser flash photolysis experiments is also consistent with its assignment as 1,1-diphenylgermene. In hexane solution, the absorption due to **52** decays with predominant second order kinetics in hexane solution which is indicative of dimerization. After a certain concentration of either aliphatic alcohols or acetic acid is added, the decay proceeds with pseudo-first order kinetics. The UV spectrum is indistinguishable from that of 1,1-diphenylsilene (**4**).[52] Similarly to **4**, the absorption maximum and overall span of the absorption band do not differ in hexane and acetonitrile, but there is a difference in the spectra recorded in THF. For germene **52**, there is a slight broadening of the spectrum in THF solution which may result from weak complexation with the solvent. This solvent effect is extremely subtle when compared to that on the spectrum of the silicon homologue, whose absorption spectrum broadens significantly under the same conditions.[34]

In hexane solution, the lifetime of 1,1-diphenylgermene shortens upon addition of aliphatic alcohols and acetic acid, but the concentration of alcohol required to cause a significant reduction in lifetime is an order of magnitude greater than those previously reported for silene **4**.[34] Because of alcohol oligomerization in hexane,[86] mechanistic interpretations of the absolute rate constants measured for **52** in hexane are not possible. However, they do allow a qualitative comparison of the reactivities of germene **52** and silene **4** to be made. The relative reactivity is as follows: HOAc > MeOH > EtOH > 2-PrOH > *t*-BuOH.

Plots of k_{decay} versus alcohol concentration in acetonitrile suggest that the mechanism for the reaction of 1,1-diphenylgermene with alcohols differs significantly from that of 1,1-diphenylsilene over a similar alcohol concentration range. The reaction of 1,1-diphenylsilene with alcohols is initiated by fast, reversible nucleophilic attack at silicon to form a zwitterionic complex, which collapses to alkoxysilane by two competing proton-transfer pathways - one intramolecular, and one which involves a second molecule of alcohol (Scheme 3.1).[5,34,48] The kinetic data, obtained for the reaction of the silene with alcohols indicates that the intermolecular proton transfer pathway is not involved during the reaction over the concentration ranges studied.[34]

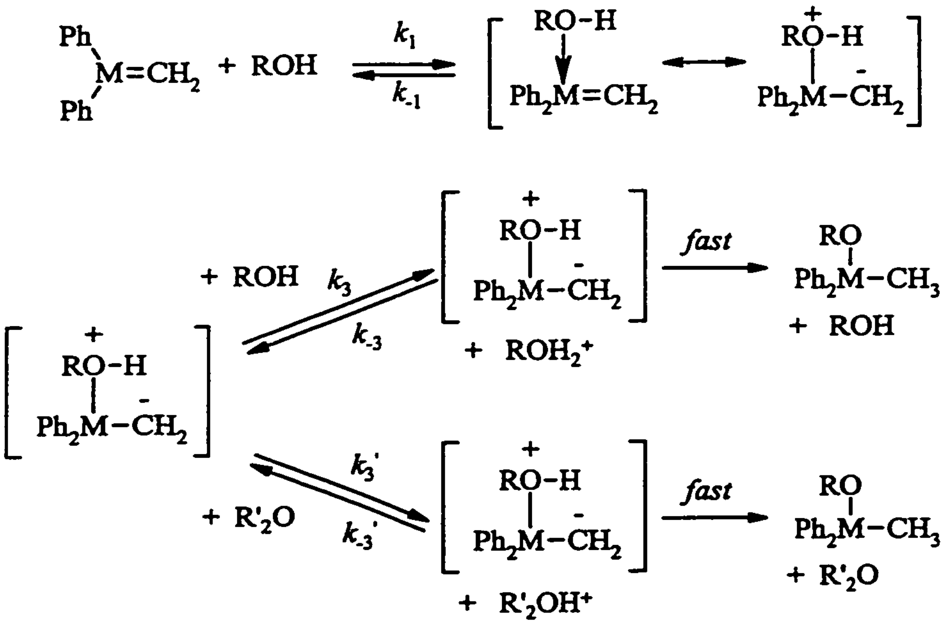
Scheme 3.1 - Reaction of Germenes/Silenes with Alcohols



On the contrary, the kinetic data for the reaction of diphenylgermene with methanol indicate that there is no contribution from the intramolecular proton transfer pathway, even at very low alcohol concentrations. However, this is not the first example of a reaction mechanism where the zwitterionic complex collapses with the aid of a second molecule of alcohol. This was first proposed in order to explain a dependence of alkoxysilane *syn* and *anti* product distribution on bulk alcohol concentration in the reaction of a transient cyclic silene with aliphatic alcohols.[5] Other examples of such behavior have been reported for other transient silenes as well.[34,48] Curvilinear quenching plots are observed in the reaction of 1,3,5-(1-sila)hexatrienes with water and alcohols, where the intracomplex proton transfer is relatively slow.[48,49] For these cases, the intracomplex proton transfer is slow enough that there is a quadratic dependence of the pseudo-first order rate constant for silene decay on alcohol concentration.[46,48] In the case of 1,1-diphenylsilene however, proton transfer by the intramolecular route is so fast that quenching plots exhibit only a first order dependence of k_{decay} on alcohol concentration in both acetonitrile and hexane solution.[34,53]

The kinetic data for reaction of germene **52** with aliphatic alcohols are indeed consistent with a mechanism where the proton transfer leading to conversion of the intermediate complex to alkoxygermane proceeds entirely by the general base catalysed routes shown in Scheme 3.2.

Scheme 3.2 - General Base Catalysis with Alcohols or Solvent



The base required for this step can either be the solvent (*e.g.*, THF) or a second molecule of alcohol, and the two can be expected to compete for deprotonation of the complex according to their relative basicities and concentrations. If deprotonation by the solvent is important, then this should lead to a first order dependence on alcohol concentration. In the absence of a sufficiently basic solvent, deprotonation by a second molecule of ROH should result in a second order dependence on [ROH]. Application of the equilibrium assumption for the germene-alcohol complex leads to the expression shown in Equation 52 for the pseudo-first order rate constant for decay of **52** in the presence of alcohol, where k_1, k_{-1}, k_3 and k_3' are defined in Scheme 3.2. THF is significantly less basic than MeOH in non-aqueous solvents;[87] thus, k_{decay} is predicted to vary with [ROH] according to Eqn. 18 in THF, with $k_q = (k_1/k_{-1})k_3'[\text{THF}]$ and $k_{2q} = (k_1/k_{-1})k_3$. In weakly basic solvents such as MeCN or hexane (where $k_3' << k_3$), this expression collapses to Eqn. 38.

$$k_{\text{decay}} = k_d^{\circ} + k_q[\text{Q}] + k_{2q}[\text{Q}]^2 \qquad [18]$$

$$k_{\text{decay}} = k_d^{\circ} + k_{2q}[\text{Q}]^2 \qquad [38]$$

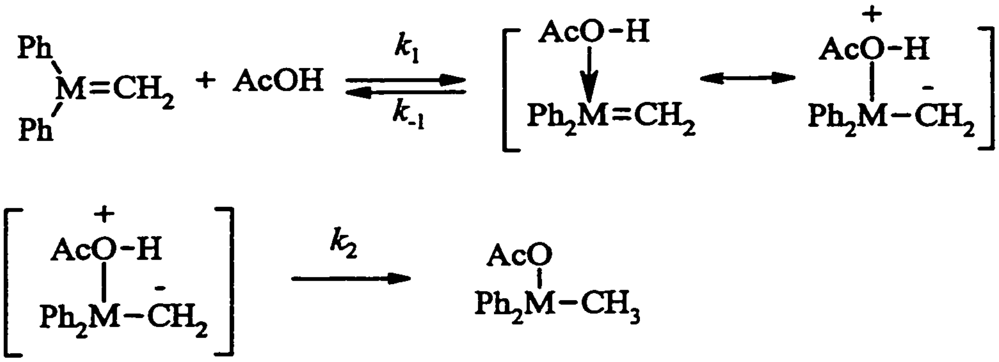
$$k_{\text{decay}} = k_d^{\circ} + \frac{k_1[\text{ROH}]}{k_{-1}}(k_3'[\text{THF}] + k_3[\text{ROH}]) \qquad [52]$$

The curved quenching plots obtained when **52** is quenched by MeOH and *t*-BuOH in THF and MeCN afford results that fit the proposed mechanism extremely well. In MeCN, attempts to fit the data to a polynomial second order equation affords a second order rate constant that is equal to zero, within experimental error. In THF solution, the second order rate coefficient k_q yields $(k_1/k_{-1})k_3' = (4 \pm 2) \times 10^5\ \text{M}^{-2}\text{s}^{-1}$, which corresponds to the reaction pathway involving deprotonation of the complex by the solvent. This is a factor of ~35 lower than that involving deprotonation by a second molecule of alcohol, which is consistent with the difference between the acid dissociation constants of protonated THF (pK_a 1.1) and MeOH_2^+ (pK_a 2.36) in acetonitrile solution.[87]

While the plots of k_{decay} vs. [ROH] in hexane solution are linear within experimental error, these numbers can only be used as a qualitative indicator of germene reactivity. Mechanistic conclusions cannot be drawn in these cases because the least-squares analyses of the data yield significantly negative intercepts, indicating that the quenching kinetics are inadequately described by the equation $k_{\text{decay}} = k_d^{\circ} + k_q[\text{Q}]$. Because of the slow reactivity of the germene with aliphatic alcohols, the concentration range required to obtain pseudo-first-order conditions needs to be relatively high (near 0.5 M). At these alcohol concentrations in hexane, both methanol and *t*-butanol are substantially oligomerized.[86] The plot of k_{decay} *versus* bulk ROH concentration should afford a line with an intense negative curvature due to a steady decrease in effective free alcohol concentration. This negative curvature coupled with the quadratic positive curvature proposed by the mechanism in Scheme 3.1 could effectively lead to a plot where the opposite curvatures cancel one another yielding a relatively straight line. A quantitative treatment of the hexane data, taking alcohol oligomerization effects into account, is difficult to carry out without considerably more data than we have collected.

The ^{1}H nmr spectra of crude product mixtures from photolysis of **51** in the presence of HOAc suggest that reaction of **52** with the carboxylic acid proceeds with the same regiochemistry as the reaction with alcohols, yielding methyldiphenylgermanium acetate (**88d**). Unfortunately, the acetoxygermane proved to be too labile to be isolated. Acetic acid quenching of 1,1-diphenylgermene proceeds rapidly with strict overall second order kinetics in all three solvents. The plots of k_{decay} vs. [HOAc] are linear and assuming that the reaction of this germene with acetic acid proceeds via the same 2-step mechanism, then the linearity implies that the intramolecular proton transfer occurs far more rapidly than in the case of aliphatic alcohols.

Scheme 3.3 - Reaction of Germenes/Silenes with Acetic Acid



This would be expected on the basis of the substantially greater acidity of the carboxylic acid, as well as the fact that proton transfer can proceed via a six-membered transition state if complexation occurs at the carbonyl oxygen. In hexane solution, quenching is rapid enough that a rate constant could be determined at acetic acid concentrations below that at which dimerization of the acid starts to become significant.[88]

However, this particular reaction has not been studied in sufficient detail to allow us to rule out other mechanisms. A mechanism involving initial protonation of the Ge=C bond is particularly difficult to rule out. The substantially greater reactivity of **52** toward HOAc compared to MeOH actually makes this a reasonable possibility (**4** exhibits similar reactivities toward the two reagents[34,89]), and we are continuing to investigate this idea.

Theoretical studies on the reaction of nucleophiles with silenes and germenes have already appeared in the literature. Nagase and coworkers have reported ab initio theoretical calculations on the addition of water to silene ($H_2Si{=}CH_2$) and germene ($H_2Ge{=}CH_2$).[90] These calculations predict a mechanism involving initial complexation followed by proton transfer from oxygen to carbon, for both species. The proton transfer occurs via a four-membered transition state in both cases. The calculated barriers to proton transfer within the complexes are similar, suggesting that germene and silene should show similar reactivities toward nucleophilic addition. However, although the data is consistent with the initial formation of a complex, all of our NLFP experiments illustrate a 'sluggish' reactivity trend for the reaction of germene **52** with nucleophiles when compared to silene **4**. In acetonitrile, **52** requires a second molecule of alcohol to cause the collapse of the complex to product which is a behaviour not observed with **4**. This difference in reactivity is most likely due to the complexation being significantly weaker with germenes than with silenes, resulting in a lower degree of charge transfer from oxygen to the α-carbon. This would be consistent with the observed differences in the UV absorption spectra of **52** and **4** in tetrahydrofuran solution. The spectrum of **4** is broadened considerably and slightly red-shifted in THF compared to MeCN,[34] while the spectrum of **52** in THF shows at most a very slight broadening compared to that in MeCN. These results indicate that the silene is solvated significantly more strongly than the germene by the ether solvent.

Carbonyl compounds are common chemical traps for both stable and transient silenes and germenes where the reaction leads to 1,2-metallaoxetane or enol ether products.[1,2,40] The reaction between acetone (and other aliphatic ketones) and transient silenes affords silyl enol ethers and/or siloxetane derivatives, some examples of which have been discussed in Section 1.4.[1,29] The rate constants, at least for enol ether formation, are typically quite fast; for example, **4** reacts with acetone with a rate constant $k \sim 3 \times 10^8$ $M^{-1}s^{-1}$ in hexane at 23°C.[52] Our lab has already investigated the mechanistic aspects of the silene/acetone reaction and have reported that this reaction is also initiated by complex formation.[91]

Surprisingly, no reaction between germene **52** and acetone could be detected by steady state or flash photolysis methods. This may be the result of germene **52** reacting in the same manner, forming a very weak complex in the initial stage of the mechanism. However, this weak complex would result in very little charge development on the germenic carbon and therefore not contain enough negative charge to cause the proton transfer.

3.2 - Synthesis and Photochemistry of Silene and Germene Dimers

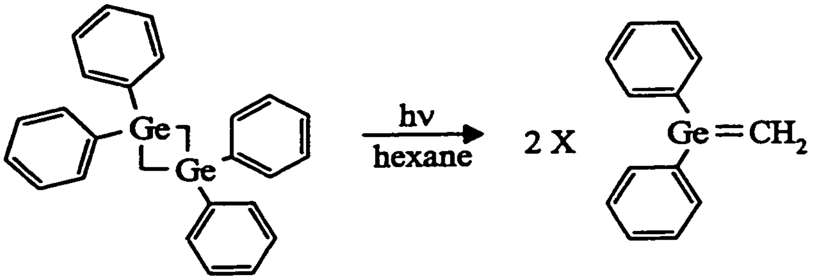
The homo-[2+2] cycloadducts of diphenylsilene and diphenylgermene were isolated and identified as 1,1,3,3-tetraphenyl-1,3-disilacyclobutane and 1,1,3,3-tetraphenyl-1,3-digermacyclobutane respectively. This was not surprising since this type of dimerization reaction is common for silenes/germenes under conditions where all nucleophiles have been scrupulously removed. Because of the ease with which the dimerization process took place in both cases, it seemed reasonable to propose that cross-cycloaddition to yield 1,1,3,3-tetraphenyl-3-germa-1-silacyclobutane might occur if the silene and germene could be generated together in solution. Indeed, cross-cycloadduct **89** was synthesized by photolyzing an equimolar mixture of 1,1-diphenylsilacyclobutane and 1,1-diphenylgermetane in hydrocarbon solution. The resulting product mixture consisted of dimers **13** and **87** along with the mixed cycloadduct **89** in a ratio of **13**:**89**:**87** = 1:5:2 when the reaction was monitored at low conversions. This ratio changes constantly during the course of the photolysis which implies that one or more of the resulting cycloadducts are themselves photoactive. As the photolysis progresses, the three cycloadducts increase in concentration and ultimately reach a point where they are also absorbing light. Prolonged photolysis of the mixture results in an eventual product ratio of **13**:**89**:**87** = 1:3:2. However, it has been previously reported that 1,3-disilacyclobutanes are relatively inert and therefore the change in cycloadduct ratio is presumably due to the photochemistry of one or both of the germanium-containing dimetallacyclobutanes.

The isolation of cross cycloadduct **89** from this mixture proved to be difficult by using conventional column or semi-preparative gas chromatography. The compound was successfully isolated in pure form by reverse phase high performance liquid chromatography.

The isolation of all three cycloadducts allowed the photochemistry of each compound to be studied individually under steady state conditions. Surprisingly, the photolysis of **13** under steady state conditions did afford the alkoxysilane product in low yields. This product is presumably due to the inefficient cycloreversion process of the dimer to two silenic units. Accompanying the formation of alkoxysilane was the obvious appearance of bicyclohexyl, cyclohexanol and cyclohexanone which is something that we have not seen during the photolysis of any of the other compounds. The three products are derived from the dimerization and oxidation of cyclohexyl radicals, which presumably result from hydrogen abstraction from the cyclohexane solvent by a radical or biradical intermediate. These products are not formed in detectable yields in the photolyses of the other two compounds. It is not yet clear how cyclohexyl radicals are formed in this case, but their formation would be consistent with the involvement of a radical or biradical intermediate which is formed in higher steady state concentrations in the photolysis of **13** than in those of the other two compounds.

The steady state irradiation of **87** or **89** in the presence of methanol afforded the alkoxygermane or alkoxysilane product as the only detectable products. Quantum yield determinations show that the digermetane undergoes photolysis at least 5 times more efficiently than the crossed cycloadduct, and more than 15 times more efficiently than the 1,3-disilacyclobutane analogue **13**.

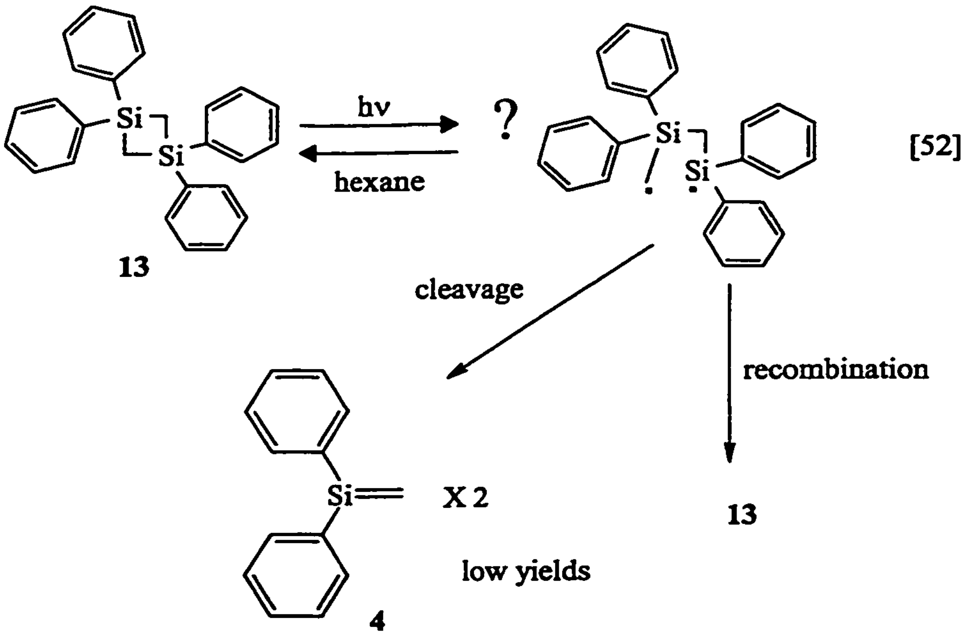
Laser flash photolysis of optically matched solutions of 1,1-diphenylgermetane and 1,1,3,3-tetraphenyl-1,3-digermetane afforded transients with identical UV spectra and kinetic behaviour, consistent with their assignment as 1,1-diphenylgermene. The relative optical densities (Figure 2.6) are in excellent qualitative agreement with the relative quantum yields determined using steady state techniques. The intensity of the signal from **51** is approximately 1.5 times that from **87**. Thus, both NLFP and steady state experiments show that 1,3-digermetane **87** undergoes [2+2] photocycloreversion to afford two molecules of 1,1-diphenylgermene (eqn. 51).



87 **52**

[51]

On the other hand, silene dimer **13** does not give rise to a transient absorption identifiable as 1,1-diphenylsilene. The quantum yield for silene formation is extremely low ($\Phi = 0.007$), so this result is not surprising. NLFP experiments performed on **13** afforded a transient whose decay followed the laser pulse, which meant that quenching studies could not be performed. The resulting transient absorption spectrum consisted of two bands; a sharp one centered around 400 nm and a very broad band between 430-580 nm. This spectrum resembles the 2-band absorption spectrum of the methyldiphenylsilyl radical[47] but in this case, the spectrum is blue shifted by about 70 nm. Thus, it is possible that the transient might be the 1,4-biradical resulting from cleavage of an Si-C bond within the 4-membered ring.[55] Efforts are currently underway to investigate this problem.



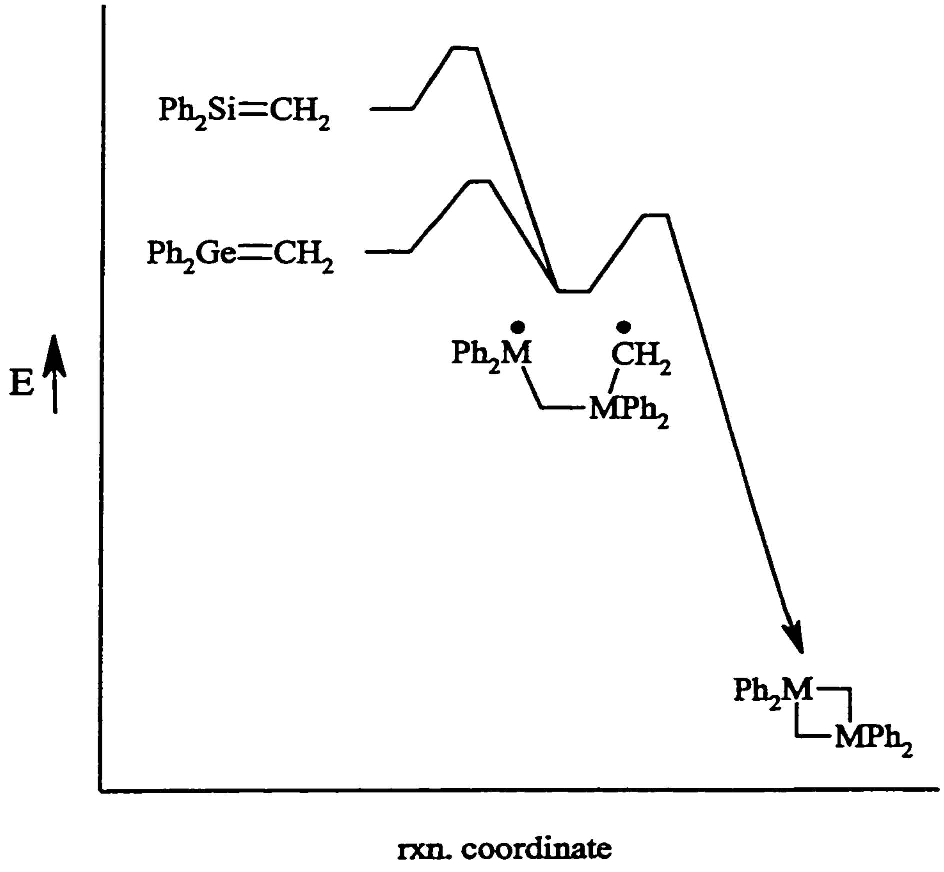
[52]

The fact that photolysis of silene dimer **13** yields **4** in extremely low yields is not unexpected because studies investigating the photochemistry of other 1,3-disilacyclobutanes have yielded similar results.[55]

The photocycloreversion process of disilacyclobutanes has been shown to involve a multistep mechanism which includes the formation of a 1,4-biradical intermediate.[55] In this type of mechanism, the overall efficiency of silene/germene formation from the three 1,3-dimetallacyclobutanes is dependent on two factors; a) the efficiency of biradical formation as opposed to other non productive photochemical processes and b) the efficiency of biradical cleavage as opposed to recoupling to starting material. The observed differences in the quantum yields for the formation of silenes/germenes must be a function of the factors that effect biradical formation and biradical cleavage. Although these data are still in the preliminary stages, it is not unreasonable to think that the initial rate of biradical formation is not the controlling factor in this process. Irradiation of diphenylsilacyclobutane affords diphenylsilene with good efficiency while the formation of the same silene from the disilyl analog is relatively inefficient. However, it seems unlikely that photophysics would be the dominant contributor to these differences; there is no reason to suspect that the rate of excited state ring cleavage (k_{BIR}) should be much different in **13** than in the monosilyl analog **3**, for which the overall quantum yield for formation of **4** is 20-30 times higher, nor that the rates of any of the possible non-productive modes of excited state decay (fluorescence, internal conversion) should vary much within the series.

The 1,4-biradicals, on the other hand, would clearly be expected to differ significantly in their propensities toward cleavage vs. coupling, because this will depend on the relative thermodynamic stabilities of the biradicals and the corresponding M=C compounds which they yield upon cleavage. Figure 3.4 illustrates a representation of a reaction coordinate diagram for the dimerization reaction of silenes and germenes. Our experimental results show that germenes react sluggishly with alcohols and acetone and this is most likely due to its thermodynamic stability. Therefore, the photochemistry of 1,3-dimetallacyclobutanes is presumed to afford a 1,4-biradical which then can either cleave to form a pair of doubly bonded species or couple to regenrate the precursor. The 1,4-biradicals would be expected to differ significantly in their propensities toward cleavage vs. coupling, because this will depend on the relative thermodynamic stabilities of the biradicals and the corresponding M=C compounds which they yield upon cleavage. Since the germene has been shown to be more thermodynamically stable when compared to the silene with regards to their reaction with nucleophiles, then it would be expected that the biradical cleavage should be faster for the digermyl biradical than for the disilyl homologue.

Scheme 3.4 - Reaction Coordinate Diagram for the Dimerization Reaction of Silenes/Germenes

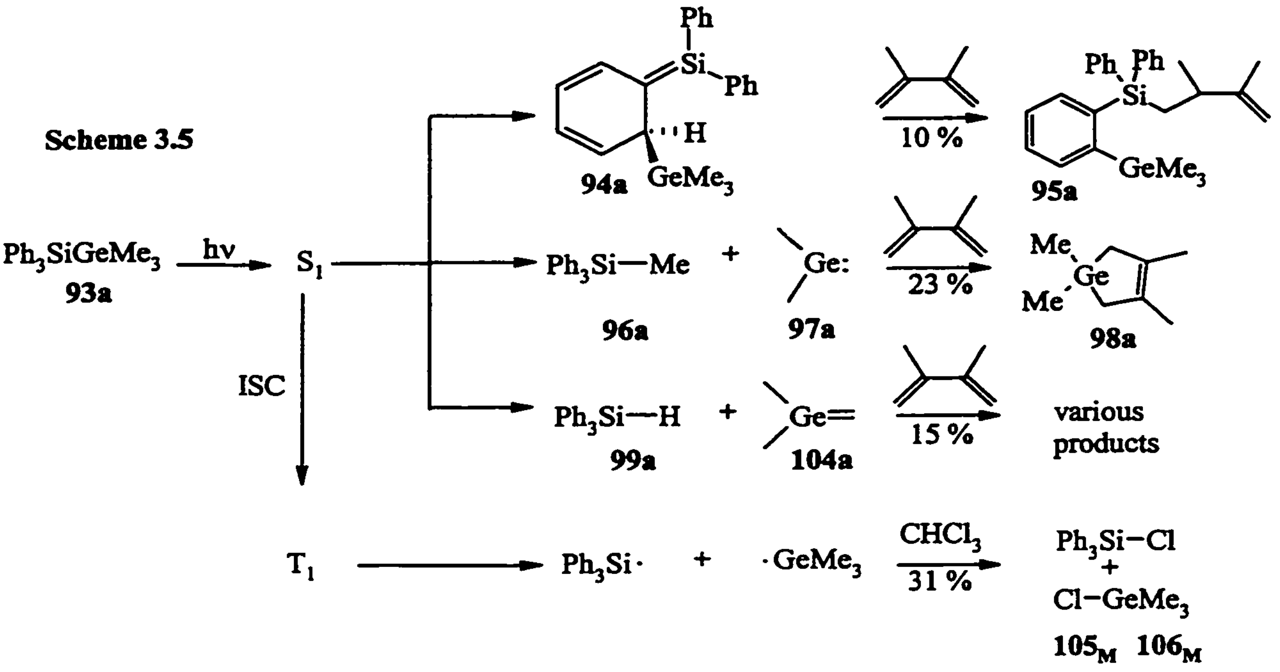


3.3 - The Photochemistry of Germasilanes and Digermanes

The photochemistry of 1,1,1-trimethyl-2,2,2-triphenyldisilane has been thoroughly studied in our laboratory.[47] A combination of steady state and nanosecond laser flash photolysis studies have illustrated that the major product of photolysis (> 95%) of this compound in hydrocarbon solvents is the 1,3,5-(1-sila)hexatriene derived from formal 1,3-silyl migration. NLFP experiments have shown that the (1-sila)hexatriene intermediate has an absorption maximum centered around 490 nm, and exhibits appreciable reactivity with a variety of known silene chemical traps. It also reacts rapidly with several reagents that do not normally react with transient silenes at detectable rates (eg. O_2, CCl_4, 2,3-dimethyl-1,3-butadiene). This reactivity is summarized in Table 2.3.1.

Photolysis of a hydrocarbon solution of $Ph_3SiGeMe_3$ in the presence of 2,3-dimethyl-1,3-butadiene affords a much more complex mixture of products than the disilane. The yield of radical-derived products is significantly lower in the presence of diene, which suggests that they are derived from Si-Ge bond homolysis in the lowest triplet state. This enhanced triplet state reactivity compared to the disilane is presumably due to a heavy-atom effect on the intersystem crossing efficiency. The other reactive intermediates formed arise from to direct excited singlet state reaction.

Scheme 3.5

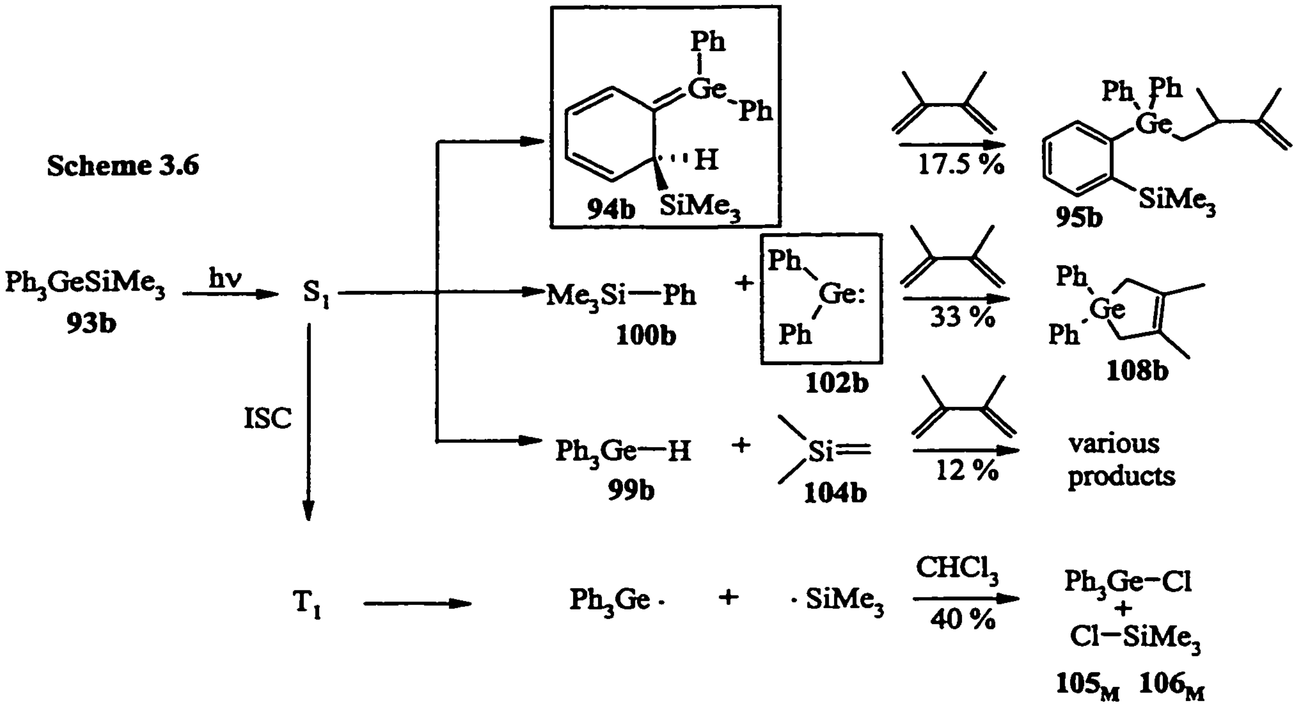


Scheme 3.5 summarizes the various products formed upon photolysis of $Ph_3SiGeMe_3$ (**93a**) in the presence of DMB and $CHCl_3$. The lowest excited singlet state of the germasilane reacts via three competitive pathways to form reactive intermediates which are then trapped by DMB: [1,3]-$GeMe_3$ migration to yield the (1-sila)hexatriene

species **94a**, dehydrogermylation to yield Ph_3SiH (**99a**) and $Me_2Ge{=}CH_2$ (**104a**) and extrusion of dimethylgermylene (**97a**) with the concomitant formation of Ph_3SiCH_3 (**96a**). Germylene extrusion is the major singlet reaction pathway. As described in the Introduction (Section 1.3), photolysis of aryldisilanes (*e.g.*, $Ph_3SiSiMe_3$) generally does not lead to the analogous process. Dehydrosilylation, though it is frequently observed in aryldisilane photochemistry depending on substituents, does not occur in significant yields with the homologous disilane **24**. In the germasilanes and digermane **93a-c**, dehydrosilylation/dehydrogermylation is a minor reaction pathway which dominates only slightly over [1,3]-M'Me_3 migration.

The photolysis of a hydrocarbon solution of $Ph_3GeSiMe_3$ (**93b**) in the presence of DMB and chloroform also afforded a complex mixture of products, analogous to the behaviour of $Ph_3SiGeMe_3$. (Scheme 3.6)

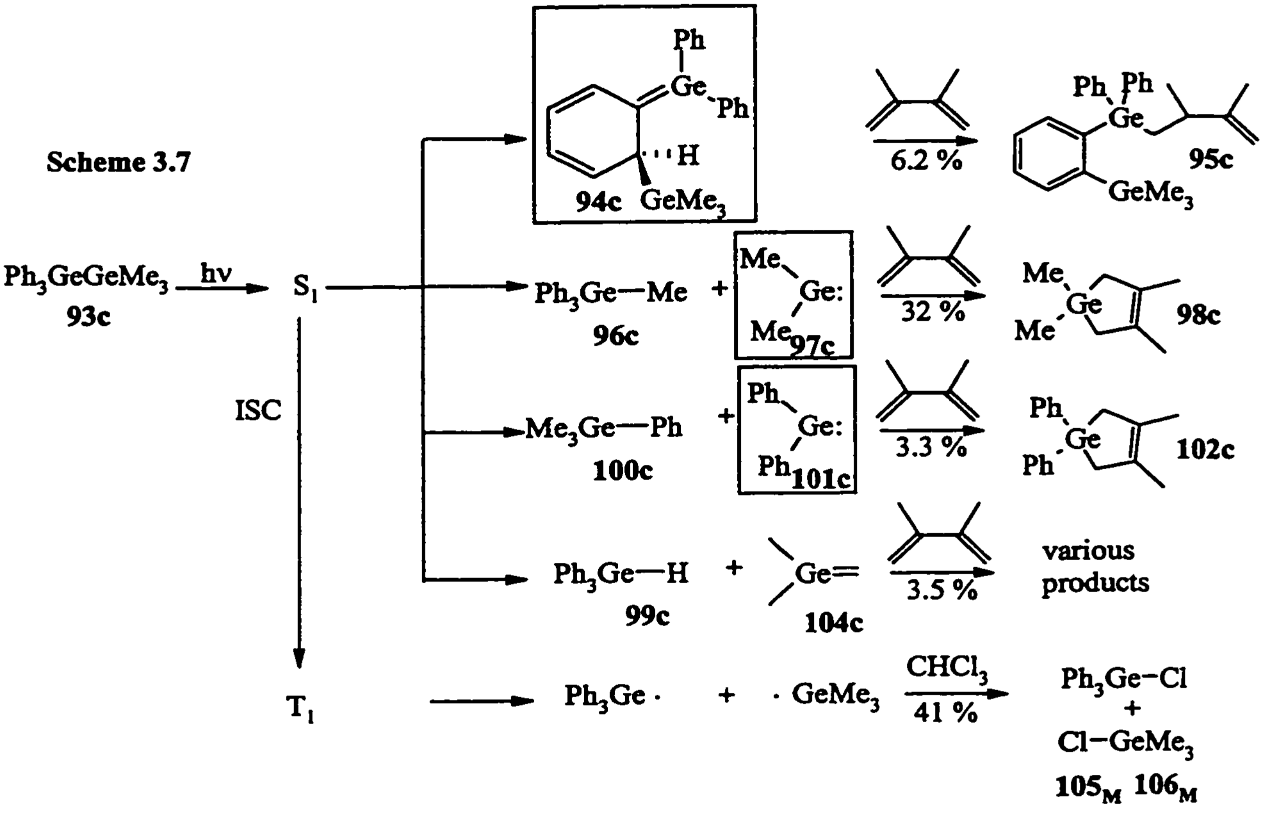
Scheme 3.6



The product distributions are similar for the two germasilane derivatives **93a** and **93b**. Two similarities in the photochemistry of **93a** and **93b** are particularly noteworthy. First, the major reaction pathway is the extrusion of a germylene transient intermediate in both cases. Secondly, the identification of **95b** as a product of **93b** during the photolysis allows one to infer the presence of a germanium-carbon doubly-bonded transient intermediate generated from a [1,3]-silyl migration pathway.

Mochida and coworkers have reported that photolysis of $Ph_3GeGeMe_3$ (**93c**) leads only to the formation of $Ph_3Ge\bullet$ and $Me_3Ge\bullet$.[76] In contrast, we find a complex mixture of products which is directly analogous to those formed from the photolysis of **93a,b** (scheme 3.7).

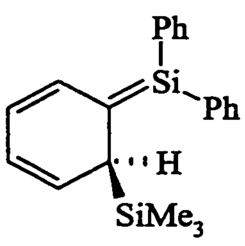
Scheme 3.7



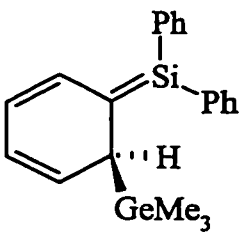
In this case, the extrusion of dimethylgermylene is the major reaction pathway while the generation of diphenylgermylene is also detected but only in very low yields. Again, the formation of Ph_3GeH suggests that dehydrogermylation occurs in low yields. GC/MS analysis provided evidence for the formation of a product consistent with DMB trapping of a (1-germa)hexatriene resulting from [1,3]-trimethylgermyl migration into one of the phenyl rings.

Laser flash photolysis of $Ph_3SiGeMe_3$ (**93a**) afforded a transient absorption spectrum comprised of contributions from two different transients; a sharp absorption band centered at 330 nm (τ~1-2 μs) and a second broad absorption centered at 480 nm (τ~10μs). The lifetime of the 330 nm transient was unaffected by addition of MeOH ($\leq$ 0.04 M), HOAc ($\leq$ 0.01 M), or acetone ($\leq$ 0.05 M), but was shortened significantly in the presence of $CHCl_3$, CCl_4, DMB, and O_2. This behaviour suggests the transient to be due to $Ph_3Si\bullet$.[77]

The 480 nm transient from **93a** exhibits a UV spectrum which is nearly identical to the spectrum of the 1,3,5-(1-sila)hexatriene derived from photolysis of $Ph_3SiSiMe_3$ under similar conditions.[47] In this case, all of the quenchers noted above except $CHCl_3$ had a significant effect on the lifetime, allowing bimolecular quenching rate constants to be obtained. These data are consistent with the assignment of this transient to germa-hexatriene **94a** (eqn. 53). The similarity between the two transient absorption spectra is not surprising because the two silahexatriene intermediates only differ by the substitution at the 7 position of the triene.



25a



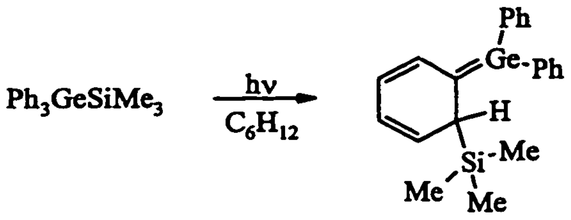
94a

[53]

An obvious alternative assignment to this transient would be Me_2Ge: since a) the 1-germa-3-cyclopentene adduct presumably derived from the reaction of dimethylgermylene with DMB is the major product from steady state photolysis and b) dimethylgermylene has been reported to have an absorption maximum in the 420-450 nm range. However, silatrienes **25a** and **94a** both have absorption maxima centered around 480 nm which is well above the values published for dimethylgermylene.[76,92,93] Furthermore, the absolute rate constants for the reaction of silatrienes **25a** and **94a** show that the two display identical reactivity with six different chemical traps. Our results indicate a relatively high reactivity of this transient with methanol (with a quadratic dependence of k_{decay} on alcohol concentration) and a very low reactivity with EtSi-H ($< 10^4\ M^{-1}s^{-1}$). On the contrary, dimethylgermylene has been reported to be unreactive toward methanol ($< 10^4\ M^{-1}s^{-1}$) and markedly reactive with triethylsilane ($10^6\ M^{-1}s^{-1}$).[74]

Laser flash photolysis of $Ph_3GeSiMe_3$ (**93b**) afforded a transient whose absorption spectrum was almost identical to that obtained from the photolysis of $Ph_3SiGeMe_3$. The sharp absorption at 330 nm was assigned as triphenylgermyl radicals based on its spectral properties and its reactivity.[77] The lifetime of this transient was also shortened by the presence of carbon tetrachloride, oxygen, and DMB in the solution while the addition of methanol (up to 1.7 M) had no discernible effect on the lifetime.

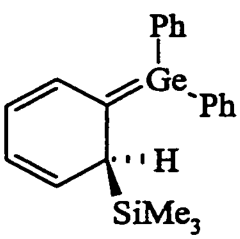
However, the transient with the absorption centered around 480 nm displays reactivity that is quite different from that of the 480 nm transient from **93a**. In this case, the reactivity with all chemical traps is at least one order of magnitude slower. The most striking difference in reactivity is observed in the case of methanol where the addition of 1.7 M methanol had no effect on the lifetime of the transient. On the basis of this information and the following arguments, the 480 nm transient from **93b** can be assigned as 1,3,5-(1-germa)hexatriene (**94b**) (eqn. 54).



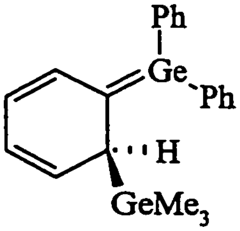
[54]

93b **94b**

Nanosecond laser flash photolysis of aryldigermane **93c** yielded a transient absorption spectrum consistent with the formation of triphenylgermyl radicals (λ_{max} = 330 nm). However, upon addition of 0.065 M $CHCl_3$ to the solution, the lifetime of the radical absorption was reduced to < 100 ns, revealing a weak absorption (τ= 4 μs) centered around 480 nm. Absolute rate constants for the reaction of this transient with DMB and oxygen illustrated that it had almost identical reactivity to that described earlier for the 1,3,5-(1-germa)hexatriene (**94b**) derived from the photolysis of germasilane **93b**. Thus, this transient can be assigned with reasonable certainty to germahexatriene **94c**.



94b



94c

Our study of 1,1-diphenylgermene and 1,1-diphenylsilene shows that germenes and silenes of identical structure (other than the identity of M in the M=C bond) exhibit nearly identical UV absorption spectra.[34,93] This study also shows that germenes exhibit a 10 to 1000 fold decrease in reactivity toward nucleophiles, compared to silenes of analogous structure. These same similarities and differences are seen for the long wavelength transients observed in flash photolysis experiments with **93a** and **93b,c**. Even toward reagents which do not exhibit significant reactivity toward simple silenes such as $Ph_2Si=CH_2$ (eg O_2, CCl_4, DMB), the transients from **93b,c** are 2-10 times less reactive than those from **93a** and **25**. All of our data are thus consistent with a (1-germa)hexatriene assignment for the long wavelength transients observed in flash photolysis experiments with **93b** and **93c**.

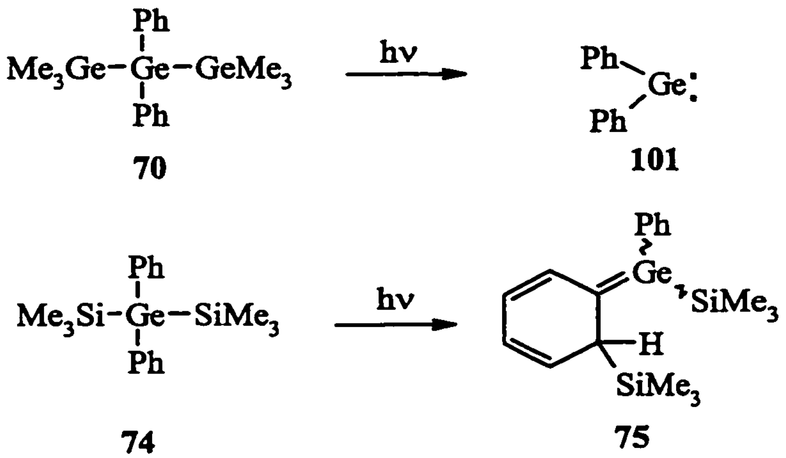
On the other hand, these assignments are not consistent with those reported by other workers who have examined the photochemistry of similar compounds by laser flash photolysis. Thus, our conclusions suggest that at least some of this work requires re-evaluation. These studies are all concerned with the characterization of the reactivity of germylene reactive intermediates. A summary of the work done in this area is summarized in Table 3.1.

Table 3.1 - UV absorption maxima and quenching rate constants for transients assigned to dimethyl-, methylphenyl-, or diphenylgermylene in cyclohexane solution.[a]

Germylene	Precursor	λ_{max} (nm)	k_{DMB} / 10^7 $M^{-1}s^{-1}$	k_{CCl4} / 10^8 $M^{-1}s^{-1}$	k_{O2} / 10^9 $M^{-1}s^{-1}$	k_{ET3SiH} / 10^6 $M^{-1}s^{-1}$	Ref.
Me_2Ge:	$(Me_2Ge)_6$	450	2.2	4.9	0.97	*b*	73
	$(PhMe_2Ge)_2GeMe_2$	420	2.4	*b*	*b*	4.2	74
	$PhMe_2GeSiMe_3$	430	4.1	*b*	2.1	*b*	77
	$PhMe_2GeSiMe_3$	425	1.7	3.2	2	< 0.01	83
	$PhMe_2GeGeMe_3$	430	2.1	*b*	1.7	*b*	77
MePhGe:	$(Me_3Ge)_2GeMePh$	440	0.22	0.65	-	4.1	74
	$Ph_2MeGeGeMePh_2$	450[c]	0.45	*b*	0.23	*b*	76
Ph_2Ge:	$(Me_3Ge)_2GePh_2$	450	0.072	1.5	*b*	0.66	74
	$(Me_3Si)_2GePh_2$	440	0.0028	*b*	0.10	0.01	66
	$Ph_3GeGePh_3$	470[c]	0.10	*b*	0.18	*b*	76

a. Measured by laser flash photolysis. Errors were generally reported to be in the 5-10% range.
b. Not reported.
c. Solvent: THF.

Studies of diphenylgermylene have been conducted using *bis*-trimethylsilyl-diphenylgermane (**74**) and hexamethyl-2,2-diphenyltrigermane (**70**) as precursors. It is not unreasonable, in either case, to assign the observed transient as diphenylgermylene since the major product of steady state photolysis is the adduct resulting from reaction of diphenylgermylene with 2,3-dimethyl-1,3-butadiene. Laser flash photolysis studies have shown dimethylgermylene to have a λ_{max} ranging between 420-450 nm. The general reactivity patterns displayed by the transients resulting from these compounds differ significantly with regard to their reactivity with triethylsilane and DMB. For example, the transient formed from **70** reacts with triethylsilane and DMB with rate constants over an order of magnitude larger than that from **74**, in the same solvent at nearly the same temperature. On the basis of these reactivity patterns, we think it likely that the transient formed from the trigermane was correctly assigned to Ph_2Ge:, while the transient from germasilane (**74**) is probably something else. We believe that a more likely assignment for the latter is the (1-germa)hexatriene derivative **75** (eqn. 55). This assignment was not considered in the original work but makes sense because of the reactivity displayed by the transient towards aliphatic alcohols and triethylsilane.[66,74]

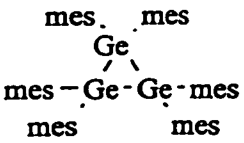


[55]

The one reported transient spectroscopic study of diarylgermylene reactivity over which there can be little controversy is that on Mes_2Ge:, which was generated by laser flash photolysis of two different precursors, **83** and **86**.[84] It should be noted that disilylgermane **83** is a very clean source of the germylene, since formation of a (1-germa)hexatriene species by 1,3-trimethylgermyl migration is blocked by the ortho-methyl groups of the mesityl rings.

$(Me_3Si)_2Ge(mes)_2$

83



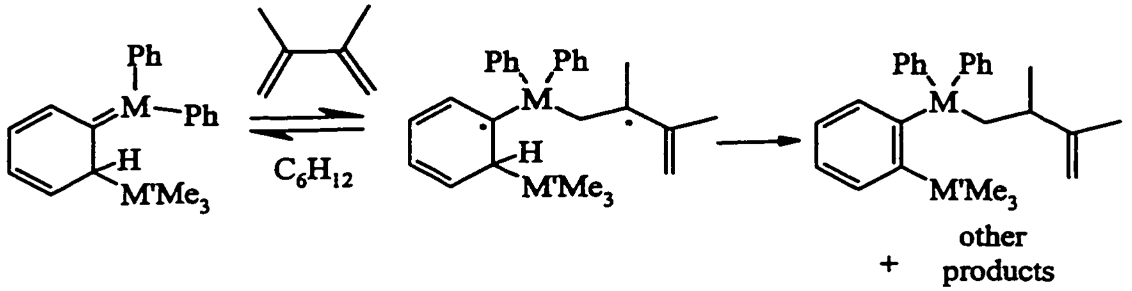
86

Flash photolysis of this compound gave rise to a very weak transient with λ_{max} = 550 nm which was assigned to the germylene. The germylene absorption decayed with 2nd order kinetics to yield a new species with λ_{max} = 405 nm, which was assigned to the known $Mes_2Ge{=}GeMes_2$.[94] The same two species were obtained upon flash photolysis of **86**. With this compound, digermene formation occurs over two timescales; it is formed both in the initial photochemical event (i.e. during the laser pulse) and over a longer timescale due to dimerization of the germylene. The latter process follows similar second-order kinetics to those of the decay of the germylene, and disappears when reagents are added to trap the germylene. One feature of this study which was actually not discussed in the paper is that it allows an estimate to be made of the extinction coefficient of the germylene absorption relative to that of the digermene, since the two species are initially formed in a 1:1 ratio. The reported transient absorption spectrum recorded immediately after the laser pulse affords $\varepsilon^{max}{}_{Ge=Ge}/\varepsilon^{max}{}_{Ge:} = 33 \pm 1$. The digermene is a stable one, and its extinction coefficient has been estimated to be $\varepsilon^{max}{}_{Ge=Ge} \sim 20{,}000$.[95] This is a upper limit which affords a rough estimate of $\varepsilon^{max}{}_{Ge:} \leq 600$ for the extinction coefficient of the germylene at its absorption maximum.

The ε of the germylene at its absorption maximum is thus relatively small. This is because the absorption is due to a n,π*transition, which is both orbital overlap and orbital symmetry forbidden.[96] The ε_{max} value for the germylene is ~ 33 times than that for the digermene because the latter's absorption is due to a π,π* absorption. In general, we can thus expect that germylenes will be difficult to detect by UV spectroscopic methods, particularly when a strongly absorbing co-product, with absorptions in a similar region, is also formed. Almost all of the silagermanes, disilylgermanes, digermanes, and trigermanes used by other workers as germylene precursors yield (1-metalla)hexatriene or radical species in significant yields. Although the germylene is the major product in all cases, its extinction coefficient is likely to be so small that it is hidden by the absorptions due to the radicals and the hexatriene intermediates.

The mechanism for alcohol additions to silahexatrienes has been shown to involve reversible formation of a silene-alcohol complex, followed by competing intra- and extracomplex proton transfer to yield the ultimate addition product(s). The extracomplex proton transfer process appears to proceed via a general base catalysis mechanism in which a second molecule of alcohol (or the solvent) deprotonates the complex in the rate determining step. The intra-/extracomplex rate ratios indicate that intracomplex proton transfer is substantially slower than the extracomplex process, which has been attributed to special stabilization of the silene-alcohol complex by the cyclohexadienyl-substituent at the silenic carbon.[47] On the contrary, the germahexatrienes show at least a 1000-fold decrease in reactivity towards the same nucleophilic chemical traps (acetone, acetic acid, and aliphatic alcohols). Actually, the addition of up to 1.7 M methanol had no detectable effect whatsoever on the lifetime of the transient we have identified as the germahexatriene. This lack of reactivity toward MeOH is consistent with the differences in the reactivity of $Ph_2Ge=CH_2$ and $Ph_2Si=CH_2$ toward alcohols.

The reaction of **25a** with DMB proceeds via ene-addition, although there is at least one other addition product which is formed in yields which are too low to allow isolation.[47] The photolysis of germasilane **93a** in the presence of DMB also affords the ene-addition product (**95a**) along with significant amounts of an additional isomeric product. The corresponding behaviour is almost identical to that exhibited by the disilane analog. This additional product is not formed in the photolyses of germasilane **93b** and digermane **93c**, in spite of the fact that they both yield products consistent with ene addition of DMB to the corresponding germahexatriene (eqn. 56). It is thought that the reaction of dienes with 1,3,5-(1-sila)hexatrienes and 1,3,5-(1-germa)hexatrienes proceeds via non-concerted reaction pathway via a biradical intermediate. The enhanced reactivity of the metallahexatrienes compared to simpler silenes/germenes with DMB is presumably due to greater resonance stabilization of the biradical intermediate, owing to the presence of the cyclohexadienyl substituent on the silenic/germenic carbon as well as an additional driving force (aromatization) in the collapse of the biradical to product.



[56]

Both oxygen and CCl_4 exhibit considerably higher reactivity with 1,3,5-(1-sila)-hexatrienes and 1,3,5-(1-germa)hexatrienes than they do with simpler metallenes. These reactions probably proceed by radical-like mechanisms. In the case of oxygen, the reaction most likely goes through a triplet biradical intermediate.[47] The reaction of the metallahexatrienes with CCl_4 is possibly initiated by electron transfer, based on the fact that CCl_4 is ~ 100 times more reactive than $CHCl_3$, in keeping with the reduction potentials of these two halocarbons.[97] However, the mechanistic details of this reaction are also difficult to determine because CCl_4 has been shown to quench the excited singlet state of aryldisilanes. This occurs through an electron transfer which results in Si-Si bond cleavage and the subsequent formation of a pair of chlorosilanes.

CHAPTER 4

CONCLUSIONS

4.1 - Conclusions

The transient 1,1-diphenylgermene (**52**) can be generated and detected in solution by laser flash photolysis of 1,1-diphenylgermetane (**51**). The UV spectrum of **52** is almost identical to that of its silene analog, 1,1-diphenylsilene (**4**). Germene **52** undergoes head-to-tail [2+2]-dimerization in hexane solution, or can be trapped by aliphatic alcohols as the corresponding alkoxymethyldiphenylgermanes. This behaviour is almost exactly analogous to the chemistry of 1,1-diphenylsilene. However, NLFP experiments show that there are significant differences in silene and germene reactivity. Germenes react 10-1000 times slower compared to their silicon analogues. Kinetic evidence suggests that the reaction of germene **52** with aliphatic alcohols proceeds by a mechanism involving the initial formation of a germene-alcohol complex, as is the case with alcohol additions to silenes. Silene-alcohol complexes collapse to product by rapid intramolecular proton transfer, as well as by an intermolecular general base-catalysed process which usually becomes important only at relatively high alcohol concentrations. In contrast, proton transfer in 1,1-diphenylgermene-alcohol complexes appears to proceed only by the general base-catalysed pathway. This involves a second molecule of alcohol in hexane or acetonitrile. In more basic solvents like THF, the solvent itself can also participate in the proton transfer.

1,1-Diphenylsilene (4) and 1,1-diphenylgermene (**52**) dimerize to yield 1,1,3,3-tetraphenyl-1,3-disilacyclobutane and 1,1,3,3-tetraphenyl-1,3-digermacyclobutane respectively. The generation of both silene **4** and germene **52** from photolysis of a 1:1 mixture of the metallacyclobutane precursors together in solution afforded a -1-sila-3-germacyclobutane as one of the primary photoproducts. This is the first example of a reaction between a silene and a germene.

Although disilacyclobutane **13** has been previously reported to be photochemically inert in solution,[57] it was found that it does undergo cycloreversion to the silene upon photolysis in solution in the presence of methanol, although extremely inefficiently. The quantum yield for photocycloreversion is 4-5 times higher in the homologous 1-sila-3-germacyclobutane (**89**), and 20-30 times higher in 1,3-digermacyclobutane **87**. These significant differences in quantum yield are most likely due to differences in the reactivity of the corresponding 1,4-biradicaloid intermediates toward cleavage relative to reclosure to the starting materials. This is believed to be a reflection of the relative thermodynamic stabilities of the silene and germene, which is also reflected in their relative reactivities toward nucleophiles such as alcohols, amines, carboxylic acids, and ketones.

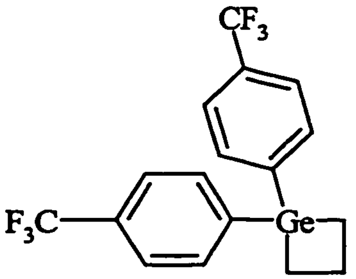
The photochemistry of germasilanes and digermanes is far more complex than that of the corresponding disilane analogue. Steady state experiments show that germylene extrusion is the major reaction pathway in every case. Product studies also reveal that other singlet state reactions include dehydrosilylation/dehydrogermylation reactions and formal 1,3-silyl-/germyl migration to form a (1-metalla)hexatriene intermediate. Bond homolysis is a triplet reaction and occurs in high yields presumably due to a heavy-atom effect on intersystem crossing. However, NLFP experiments do not confirm the presence of the germylene as the major product. Instead, the (1-metalla)-hexatriene absorption is observed during the experiments and the reactivity of this transient has been studied. It appears that even though the germylene is formed in the highest yield, the extinction coefficient of this transient is quite small when compared to that of the (1-metalla)hexatriene.

Kinetic studies of the (1-metalla)hexatrienes derived from $Ph_3SiGeMe_3$, $Ph_3GeSiMe_3$, and $Ph_3GeGeMe_3$ show there to be profound differences in the reactivity of the Si=C and Ge=C bonds in these compounds. The (1-sila)hexatriene derivatives **99a** (from **98a**) and **25a** (from disilane **24a**) are roughly three orders of magnitude more reactive than the germanium analogs **99b,c** toward methanol, acetic acid and acetone. These differences are also observed in the simpler M=C derivatives **4** and **52**. One subtle difference observed is that the germahexatriene did not appear to react with methanol at appreciable rates.

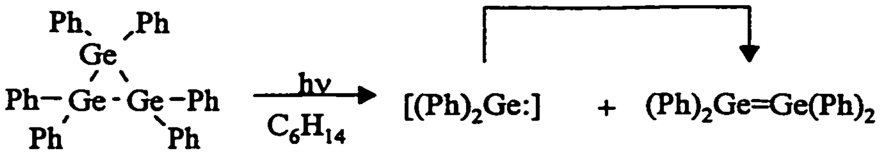
On the other hand, the reactivities of silahexatrienes and germahexatrienes toward the diene, oxygen and carbon tetrachloride are much less dependent on the identity of the Group IV heteroatom than is the case with nucleophilic quenchers. These three reagents do not react with silene **4**, from which it can be concluded that their unusually high reactivity toward the sila-/germahexatrienes is due to the unique structure of the (1-metalla)hexatriene system, which enhances reactivity (compared to simpler metallene systems) via biradical or biradicaloid mechanisms.

4.2 - Future Work

Arylsilacyclobutanes were used in the study of 1,1-diarylsilenes because they are a versatile class of compounds that are readily synthesized with a wide variety of substituents at silicon. Para substituents on the phenyl groups did not change the photochemistry of the precursor. These substituents did, however, have a significant and mechanistically informative effect on the reactivity of the resulting silene. The reactivity of 1,1-diphenylgermene with nucleophiles is rather sluggish. It is reasonable to expect that adding electron-withdrawing substituents to the para position of the phenyl groups may enhance the resulting germene's reactivity. The increase in reactivity may accelerate the intramolecular proton transfer to the point where the reaction between 1,1-diarylgermene and methanol affords a linear quenching plot. Studies on temperature dependence could then be performed to further enhance our knowledge on the mechanistic aspects of the reactivity of Ge=C bonds with various nucleophiles.



To date, a clean source of diphenylgermylene has not been described in the literature. The use of trigermanes or germasilanes raises questions about the possibility of competing pathways involving silenic or germenic intermediates. However, the use of hexaphenylcyclotrigermane may prove to be an excellent germylene precursor and would allow for continued study of the detection and reactivity of diphenylgermylene.



Our studies of the silagermanes **93a,b** and digermane **93c** have revealed several problems in the literature on germylene reactivity in solution. In the case of Me_2Ge:, only one study can likely be considered reliable,[73] and the same is true of Ph_2Ge:.[74] Neither of these two studies provide any more than a glimpse of the fundamental behaviour of germylene reactive intermediates in solution. Our work shows that aryl-substituted oligosilagermanes and oligogermanes yield silenes or germenes, which absorb rather strongly in similar regions of the spectrum. Other precursors to transient germylenes, which do not possess this photochemical diversity must be employed for the reliable definition of germylene reactivity.

CHAPTER 5

EXPERIMENTAL

5.1 - General

^{1}H and ^{13}C NMR spectra were recorded on Bruker AC200, AC300, or DRX500 NMR spectrometers in deuterated chloroform or cyclohexane-d_{12} solutions and are reported in parts per million downfield from tetramethylsilane using residual solvent resonances as the internal standard. ^{29}Si NMR were recorded on the DRX500. Ultraviolet absorption spectra were recorded on Hewlett-Packard HP8451 or Perkin-Elmer Lambda 9 spectrometers. Low resolution mass spectra and GC/MS analyses were determined using a Hewlett-Packard 5890 gas chromatograph equipped with a HP-5971A mass selective detector and a DB-5 fused silica capillary column (30m x 0.25mm; Chromatographic Specialties, Inc.). High resolution desorption electron impact (DEI) and chemical ionization (CI) mass spectra and exact masses were recorded on a VGH ZAB-E mass spectrometer. Exact masses employed a mass of 12.000000 for carbon-12. Infrared spectra were recorded on a BioRad FTS-40 FTIR spectrometer and are reported in wavenumbers (cm^{-1}). Elemental analyses were performed by Galbraith Laboratories Inc. or Guelph Chemical Laboratories. Melting points were determined using a Mettler FP82 hot stage (controlled by a Mettler FP80 central processor) mounted on an Olympus BH-2 microscope and are uncorrected.

Analytical gas chromatographic analyses were carried out using a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector, a Hewlett-Packard 3396A recording integrator, conventional heated splitless injector, and a DB-1 fused silica capillary column (15-m X 0.20-mm; Chromatographic Specialties, Inc.). Semi-preparative GC separations employed a Varian 3300 gas chromatograph equipped with a thermal conductivity detector, and a stainless steel OV-101 packed column (6 ft. X ¼ in; Chromatographic Specialties). Radial chromatographic separations employed a Chromatotron® (Harrison Research, Inc.), 2- or 4-mm silica gel 60 thick-layer plates, and hexane / ethyl acetate mixtures as eluant.

5.2 - Commercial Reagents and Solvents

Acetonitrile (Caledon Reagent) was refluxed over calcium hydride (Fisher) for several days and distilled under dry nitrogen. Hexane (Caledon Reagent) was stirred for several days over concentrated sulfuric acid, washed several times with water, once with saturated aqueous sodium bicarbonate, dried over anhydrous sodium sulfate, and distilled from sodium. Tetrahydrofuran (BDH Omnisolv) was refluxed for several days over sodium under nitrogen and distilled. Methanol, 2-propanol, *t*-butanol (HPLC grade), acetone (HPLC grade), acetic acid, acetic acid-d_1, triethylsilane (Aldrich), 1,3-octadiene, and 1,3-dibromopropane were used as received from Aldrich Chemical Co. Absolute ethanol was predried with calcium hydride, distilled from magnesium under nitrogen, and stored over 3Å molecular sieves. Benzene (Caledon) was distilled from sodium. Carbon tetrachloride (Caledon), chloroform (Caledon), diethylether (Caledon) were used as received. Deuterated materials were used as received from Cambridge Isotope Labs. Diphenylgermanium dichloride was used as received from Gelest, Inc.

5.3 - Nanosecond Laser Flash Photolysis

Nanosecond laser flash photolysis experiments employed the pulses (248 nm; ca.16 ns; 70-120 mJ) from a Lumonics 510 excimer laser filled with F_2/Kr/He mixtures or a Lambda-Physik laser containing the same gas mixtures (70-165 mJ), and a microcomputer-controlled detection system. The system incorporates a brass sample holder whose temperature is controlled to within 0.1°C by a VWR 1166 constant temperature circulating bath. Solutions were prepared at concentrations such that the absorbance at the excitation wavelength (248 nm) was ca. 0.7 (4.4×10^{-3} M), and were flowed continuously through a 3 x 7 mm Suprasil flow cell connected to a calibrated 100 mL reservoir. The solutions were deoxygenated continuously with a stream of dry nitrogen. Oxygen quenching studies were carried out using a Matheson 600 gas proportioner to regulate the composition of oxygen/nitrogen mixtures which were bubbled continuously through the solution contained in the reservoir. The concentrations of oxygen in oxygen-saturated hexane, acetonitrile, and tetrahydrofuran, are 0.015 M, 0.0085 M, 0.010 M, respectively.[98] Solution temperatures were measured with a Teflon-coated copper/constantan thermocouple which was inserted directly into the flow cell. Quenchers were added directly to the reservoir by microlitre syringe as aliquots of standard solutions. Rate constants were calculated by linear least-squares analysis of decay rate-concentration data (6-15 points, depending on whether the plots were linear or curved) which spanned at least 1 order of magnitude in the transient decay rate. Errors are quoted as twice the standard deviation obtained from the least squares analysis in each case.

5.4 - Preparation and Characterization of Compounds

5.4.1 - The Direct Detection of 1,1-Diphenylgermene in Solution

1,1-Diphenylgermetane (**51**) was prepared by placing freshly ground magnesium turnings (45g, 1.85 g-atom) and anhydrous ether (300 mL) in a flame dried 2-neck 500 mL round bottom flask fitted with a condenser and addition funnel. A solution of 1,3-dibromopropane (26.0g, 0.129 mol) in anhydrous ether (40 mL) was added dropwise with vigorous stirring over a period of 4 hours, and then left to stir overnight at room temperature. Diphenylgermanium dichloride (5.50 g, 0.0185 mol) was then added rapidly with a syringe and the mixture went white in colour for about 5 seconds and then returned to its original gray colour. The mixture was left to stir for at least 8 hours (overnight). The reaction mixture was decanted into a large flask, placed in an ice bath, and slowly and carefully quenched with saturated aqueous ammonium chloride (200mL). The organic layer was separated and washed sequentially with water, 5% sodium bicarbonate, and water, and then dried with anhydrous magnesium sulfate. The solvent was removed on the rotary evaporator to yield a slightly yellow oil. Purification was accomplished using silica gel column chromatography with hexane as the eluting solvent, affording the product as a colorless oil (4.58 g, 0.0168 mol, 91%) in >99% purity. It was identified as 1,1-diphenylgermetane (**51**) on the basis of the following spectroscopic data: ^{1}H NMR, δ = 1.96 (t, 4H), 2.40 (m, 2H), 7.37-7.41 (m, 6H), 7.56-7.61 (m, 4H); ^{13}C NMR, δ = 20.45, 21.46, 128.29, 129.07, 134.01, 138.81; IR (neat), 3067.2 (s), 2926.3 (s), 1952.6 (w), 1817.1 (w), 1483.1 (m), 1430.5 (s), 1303.5 (m), 1262.0 (w), 1182.0 (w), 1091.1 (s), 843.2

(s), 788.7 (s); MS (EI), *m/z* (I) = 270 (5), 242 (5), 227 (7), 151 (8), 84 (20); [NH$_3$ CI], m/z (I) = 288(95), 269 (15), 244 (8), 210 (100), 181 (10), 162 (10), 137 (12), 113 (13), 78 (45), 52 (82); Exact mass, Calcd. for $C_{15}H_{16}Ge$, 270.0464; found 270.0470. Anal. Calcd for $C_{15}H_{16}Ge$: C, 67.01, H, 6.00. Found C, 67.07, H, 6.05.

Authentic samples of **88a** and **88c** were prepared using the reaction of methyldiphenylgermanium chloride and the appropriate alcohol. Methyldiphenylgermanium chloride was synthesized as follows. Methyldiphenylgermane (1.75 g, 7.2 mmol) was synthesized using a literature procedure[99] and was dissolved in carbon tetrachloride (25 mL) in a 100 mL round-bottom flask. Chlorine gas was bubbled through the solution until it assumed a slightly yellow tinge. The chlorine gas source was removed, and the solution was irradiated with a sun lamp for eight minutes. Removal of the solvent by vacuum distillation afforded a slightly yellow oil, which was identified as methyldiphenylgermanium chloride (1.97g, 7.1 mmol, 99%) on the basis of the following spectroscopic data: ^{1}H NMR, δ = 0.99 (s, 3H), 7.26-7.30 (m, 6H), 7.50-7.55 (m, 4H); ^{13}C NMR, δ = 1.91, 128.84, 130.41, 133.72, 137.76; IR (neat oil), 3070.8 (m), 2914.0 (w), 2861.2 (w), 1958.9 (w), 1883.9 (w), 1818.6 (w), 1484.9 (m), 1433.1 (s), 1334.9 (m), 1245.0 (m), 1094.1 (s), 1066.7 (m), 1026.6 (m), 802.5 (s), 735.0 (s), 696.9 (s); MS (EI), *m/z* (I) = 278 (20), 263 (90), 243 (35), 201 (10), 151 (20), 117 (25), 91 (7), 77 (25); Exact mass, Calcd. for $C_{13}H_{13}GeCl$, 277.9917; found 277.9914.

Methoxy- and *t*-butoxymethyldiphenylgermane (**88a,c**) were synthesized by reaction of methyldiphenylgermanium chloride with methanol and *t*-butanol, respectively, in dry benzene in the presence of triethylamine. For example, methyldiphenylgermanium chloride (0.25g, 0.9 mmol) and dry methanol (0.1151g, 3.6 mmol) were placed in benzene (10 mL) and stirred at room temperature. Triethylamine (0.3636g, 3.6 mmol) was added rapidly to the stirred solution, causing the immediate formation of a white precipitate. The reaction mixture was stirred under reflux for 24 hours (72 hours for *t*-butanol), cooled and filtered, and then concentrated to ca. 1 mL by vacuum distillation. GC analysis of the crude reaction mixture indicated the conversion of the chloro- to alkoxygermane to be quantitative in both cases. The alkoxygermanes were isolated from the crude reaction mixtures by semi-preparative gas chromatography.

Methoxymethyldiphenylgermane (88a). ^{1}H NMR, $\delta = 0.71$ (s, 3H), 3.44 (s, 3H), 7.10-7.35 (m, 6H), 7.42-7.61 (m, 4H); ^{13}C NMR, $\delta = -3.67$, 52.76, 128.57, 129.90, 134.35, 137.61; IR (neat oil), 3069.9 (m), 2955.3 (m), 2925.9 (s), 2816.8(m), 1962.9 (w), 1884.4 (w), 1829.2 (w), 1484.9 (m), 1431.8 (s), 1376.3 (m), 1185.8 (w), 1095.3 (s), 1052.7 (s), 998.6 (m), 847.7 (m), 790.9 (m); MS (EI), *m/z* (I) = 274 (6), 259 (100), 229 (60), 167 (20), 151 (50), 89 (20), 77 (10); Analysis, Calcd. for $C_{14}H_{16}GeO$: C 61.62%, H 5.91%; Found: C 61.95%, H 5.88%.

***t*-Butoxymethyldiphenylgermane (88c).** ^{1}H NMR, $\delta = 0.80$ (s, 3H), 1.18 (s, 9H), 7.22-7.25 (m, 6H), 7.47-7.51 (m, 4H); ^{13}C NMR, $\delta = 0.55$, 33.03, 73.17, 128.40, 129.55, 134.26, 140.40; IR (neat oil), 3071.5 (m), 2973.5 (s), 2886.3 (w), 2857.5 (w), 1950.3 (w), 1882.6 (w), 1817.3 (w), 1431.9 (s), 1361.5 (s), 1240.3 (m), 1192.4 (s), 1095.1 (s), 970.8 (s), 851.7 (w), 613.0 (m); MS (EI), *m/z* (I) = 301 (30), 243 (100), 223 (10), 183 (7), 151 (25), 125 (3), 91 (15), 77 (15), 43 (40); Exact mass, Calcd. for (M-15) $C_{16}H_{19}GeO$, 297.0678; found 297.0669.

Preparative irradiations of **51** employed a Rayonet Photochemical Reactor (Southern New England Ultraviolet Co.) equipped with 8-10 RPR-2537 lamps. For the synthesis of digermetane **87**, a solution of **51** (0.25 g, 0.9 mmol) in hexane (15 mL) was dexoygenated for 15 minutes by bubbling argon through the solution in a quartz photolysis tube sealed with a rubber septum, and irradiated for 8 hours. The solvent was removed on the rotary evaporator to yield a slightly yellow oil whose NMR spectrum (in $CDCl_3$) consisted of **51** and **87** in a 3:2 ratio. The dimer was isolated by radial chromatography using hexane as the eluting solvent. After elution of starting material (**51**, 0.15 g), the solvent was changed to 10% dichloromethane in hexane. The product was collected as a colourless oil (0.08 g, 0.16 mmol, 91% yield based on recovered **51**) which crystallized upon addition of a small amount of pentane and cooling to -10 °C. A second recrystallization from pentane afforded the compound as colorless needles (m.p. 120-121 °C) which were identified as 1,1,3,3-tetraphenyl-1,3-digermetane (**87**) on the basis of the following spectroscopic data:

1,1,3,3-tetraphenyl-1,3-digermetane (87) ^1H NMR, $\delta = 1.62$ (s, 4H), 7.31-7.36 (m, 12H), 7.50-7.56 (m, 8H); ^{13}C NMR, $\delta = 7.71$, 128.22, 128.96, 133.67, 139.53; IR (neat), 3070.2 (m), 2955.3 (m), 2926.2 (m), 1952.5 (w), 1879.7 (w), 1814.8 (w), 1484.6 (m), 1431.4 (s), 1373.7 (m), 1354.4 (m), 1091.8 (s), 954.6 (m), 908.9 (s); MS, *m/e* (I) = 482 (10), 406 (15), 391 (50), 305 (100), 271 (5), 243 (40), 227 (40), 151 (50); Exact mass, Calcd. for $C_{26}H_{24}Ge_2$, 484.0261; found 484.0302. Anal. Calcd for $C_{26}H_{24}Ge_2$: C, 64.84, H, 5.02. Found C, 64.64, H, 5.06.

Solutions of **51** (0.1g, 3.66 X 10^{-4} mol) in hexane (15-mL) containing 1.0 M of MeOH, MeOD, EtOH, or *t*-BuOH were placed in quartz tubes, sealed with a rubber septum, deoxygenated with a stream of dry argon, and then photolysed for one hour. Monitoring the course of the photolyses by GC revealed the formation of a single detectable product in all cases. The solvent was removed on the rotary evaporator to yield colorless oils containing product and small amounts of residual **51**. The products were isolated by semi-preparative GC. Those from photolysis with MeOH and *t*-BuOH were identical to the authentic samples of **88a** and **88c**. Products obtained from the photolysis with MeOD and EtOH were identified as **88a-*d*** and **88b**, respectively, on the basis of the following spectroscopic data:

Methoxy(methyl-*d*)diphenylgermane (88a-*d*) ^{1}H NMR, δ = 0.69 (t, 2H), 3.44 (s, 3H), 7.27-7.35 (m, 6H), 7.46-7.61 (m, 4H); ^{13}C NMR, δ = -4.30, -3.92, -3.54, 52.77, 128.77, 129.90, 134.34, 137.59; IR (neat oil), 3069.1 (m), 2926.6 (m), 2854.1 (m), 1960.2 (w), 1889.6 (w), 1824.6 (w), 1486.1 (m), 1431.3 (s), 1157.6 (m), 1094.9 (s), 844.7 (s), 734.2 (s); MS (EI), *m/z* (I) = 275 (5), 259 (100), 244 (20), 229 (70), 168 (20), 151 (60), 125 (30), 105 (15), 77 (10).

Ethoxymethyldiphenylgermane (88b) ^{1}H NMR, δ = 0.71 (s, 3H), 1.12 (t, 3H), 3.62 (q, 2H), 7.24-7.31 (m, 6H), 7.47-7.51 (m, 4H); ^{13}C NMR, δ = -3.12, 19.59, 60.74, 128.54, 129.84, 134.77, 138.07; IR (neat oil), 3069.4 (m), 2966.4 (m), 2872.7 (m), 1960.8 (w), 1885.1 (w), 1824.9 (w), 1484.8 (m), 1431.5 (s), 1383.3 (m), 1241.5 (w), 1095.7 (s), 1061.1 (s), 1026.6 (w), 848.6 (m), 788.9 (m); MS (EI), *m/z* (I) = 288 (5), 273 (50), 243 (70), 229 (100), 165 (20), 151 (80), 123 (15), 77(20); Exact mass, Calcd. for $C_{15}H_{18}GeO$, 288.0581; found 288.0569.

NMR scale photolyses were carried out in quartz NMR tubes, using ~0.1M solutions of **51** in cyclohexane-d_{12}. The solutions also contained 1.0 M of MeOH, EtOH, *t*-BuOH or HOAc in order to perform chemical trapping experiments. These experiments gave comparable results to those described above; in addition, the formation of ethylene appeared in the NMR in the form of a singlet at 5.30 ppm, which was verified by the addition of a small amount of an authentic sample to one of the photolysis mixtures. Acetone trapping experiments were carried out using a 0.03M solution of **51** containing 0.07M dry acetone and led only to the formation of a polymer characterized by a singlet at 0.19 ppm and broad resonances in the aromatic region.

5.4.2 - The Photochemistry of 1,3-Dimetallacyclobutanes

Synthesis of 1,1,3,3-Tetraphenyl-1,3-digermetane and 1,1,3,3-tetraphenyl-1,3-disilacyclobutane

Preparative irradiations of **3**,**51** employed a Rayonet Photochemical Reactor (Southern New England Ultraviolet Co.) equipped with 8-10 RPR-2537 lamps. Solutions of the metallacyclobutanes (0.25 g) were dissolved in hexane (15 mL), sealed in a quartz photolysis tube with a rubber septum, deoxygenated with dry argon, and irradiated to 20-50% conversion of starting material (6-10 hours). The dimers (**13**,**87**) were separated from residual starting material by radial chromatography, and recrystallized from pentane. Their melting points (**13**, m.p. 135-136 °C; **87**, m.p. 120-121 °C) and spectroscopic data matched the previously reported data in both cases.[57,80] The following spectroscopic data for **13** have not been reported previously:

1,1,3,3-tetraphenyl-1,3-disilacyclobutane(13) ^{1}H NMR, δ = 1.10 (s, 4H), 7.31-7.36 (m, 12H), 7.50-7.56 (m, 8H); ^{13}C NMR, δ = 0.85, 127.88, 129.42, 134.29, 137.37; IR (neat), 3065.7 (m), 3018.0 (m), 2999.5 (m), 2924.2 (m), 1428.0 (s), 1375.6 (m), 1344.4 (m), 1262.6 (m), 1110.4 (s), 1064.9 (s), 1024.7 (s), 936.6 (m); MS, *m/e* (I) = 392 (5), 377 (7), 314 (40), 301 (40), 257 (20), 237 (20), 223 (20), 181 (30), 157 (25),105 (100), 91 (10),79 (10); HRMS, Calcd. for $C_{26}H_{24}Si_2$, 392.1408; found 392.1416.

1,1,3,3-Tetraphenyl-(1-sila-3-germa)cyclobutane (89) was prepared by photolysis of a deoxygenated solution of **3** (0.24 g, 1.07 mmol) and **51** (0.27 g, 1.0 mmol) in hexane (20 mL), under similar conditions to those described above. The solution was photolysed for 8 hours at which time GC analysis revealed that the reaction had undergone about ~40% conversion of the two starting materials. Radial chromatography of the crude reaction mixture after evaporation of the residual solvent allowed separation of the starting materials (**3**,**51**) from the three dimetallacyclobutanes, which eluted together and were isolated as a mixture. The three compounds were successfully separated by reverse phase HPLC, after which **89** was recrystallized from pentane to yield colorless prisms (m.p. 98-99 °C). The compound exhibited the following spectroscopic and analytical data:

1,1,3,3-Tetraphenyl-(1-sila-3-germa)cyclobutane (89) ^{1}H NMR, δ = 1.35 (s, 4H), 7.31-7.36 (m, 12H), 7.50-7.56 (m, 8H); ^{13}C NMR, δ = 3.85, 127.86, 128.22, 128.99, 129.37, 133.72, 134.19, 137.82, 138.97; IR (neat), 3070.2 (m), 2965.5 (m), 2858.3 (m), 1464.1 (m), 1425.8 (m), 1382.1 (m), 1259.1 (m), 1112.2 (s), 1069.8 (s), 1022.5 (s), 846.7 (w); MS, *m/e* (I) = 438 (5), 423 (5), 360 (35), 347 (50), 259 (100), 226 (10), 209 (10), 195

(15), 181 (15), 151 (15), 105 (20), 91 (10),79 (5); HRMS, Calcd. for $C_{26}H_{24}SiGe$, 438.0834; found 438.0859.

Reversed phase HPLC separations were carried out using a Hewlett Packard 1090 liquid chromatograph equipped with a diode-array UV detector and a 5 micron Vydac reversed phase column (25 cm X 4.6 mm i.d., Separations Group, Heseria, CA). The HPLC was operated with a column temperature of 40^{0}C, a flow rate of 1.0 mL/min. and at a monitoring wavelength range of 250-274 nm. The separation employed a gradient elution with water-acetonitrile mixtures (30% water → 81% water at 16 min. → 90% water at 20 min.). Under these conditions, *ca.* 1-mg samples of a mixture of the three dimetallacyclobutanes could be separated cleanly into the three components.

Quantum Yield Determination

A typical quantum yield experiment employs the use of 1,1-diphenylsilacyclobutane as a secondary actinometer (Φ=0.21[34]). Quartz photolysis tubes containing 0.1 M of either **3**,**51**,**13**,**87**, or **89** and 1.0 M methanol in hexane were deoxygenated for 20 minutes by bubbling argon through the solutions. The photolysis employed a merry-go-round apparatus which ensured equal distribution of light to each of the samples. The disappearance of starting material and the formation of alkoxysilane/alkoxygermane products **14** or **88** were monitored by GC or NMR using decane and dichloromethane as internal standards, respectively. A plot of product formation versus time yielded a straight line, in each case, whose slope relative to that for 1,1-diphenylsilacyclobutane, corresponded to the quantum yield of the compound.

Steady State Photolysis of 1,3-Dimetallacyclobutanes (13,87, and 89)

NMR scale photolyses were carried out in quartz NMR tubes, using ~0.1M solutions of **13**, **87**, or **89** in cyclohexane-d_{12} containing 1.0 M of MeOH. The experiment using digermetane **87** gave comparable results to those described above for the photolysis of 1,1-diphenylgermetane. A single product was formed whose ^{1}H NMR and mass spectral properties were identical to those already described for methyldiphenylmethoxygermane (**88**). Photolysis of disilacyclobutane (**13**) under similar conditions afforded 3 products as detected by GC/MS analysis of crude photolysate mixtures. One of the products displayed spectral properties identical to methyldiphenylmethoxysilane (**14**) while the other two products were identified as cyclohexanone and bicyclohexyl based on GC co-injection with authentic samples.

5.4.3 - Germasilane and Digermane Photochemistry

A solution of either **93a-c** (0.1g, 3.66 X 10^{-4} mol) in hexane (15-mL) containing 0.5 M of 2,3-dimethyl-1,3-butadiene was placed in a quartz tube, sealed with a rubber septum, deoxygenated with a stream of dry argon, and then photolysed for one hour. Periodic monitoring of the course of the photolysis by GC revealed the formation of many detectable products. Triphenylmethylsilane, triphenylsilane, trimethylphenylsilane, triphenylmethylgermane, triphenylgermane, trimethylphenylgermane, were characterized by GC coinjection with authentic samples obtained from Aldrich Inc. The solvent was removed on the rotary evaporator to yield a colourless oil containing products and small amounts of residual starting material. Photoadducts **98a** and **102b,c** exhibited ^{1}H NMR and mass spectral data that were identical to those already appearing in the literature.[83] Product **95b** was isolated by semi-preparative GC and was identified on the basis of the ^{1}H NMR and mass spectral data. Compounds **95a,c** were identified on the basis of the GC/MS data listed below:

1-(trimethylgermyl)-2-((2,3-dimethyl-1-buten-4-yl)diphenylsilyl)benzene (95a) MS (EI), *m/z* (I) = 460 (1), 445 (4), 377 (20), 367 (15), 341 (15), 299 (15), 259 (50), 222 (100), 197 (50), 181 (50), 135 (25), 105 (25).

1-(trimethylsilyl)-2-((2,3-dimethyl-1-buten-4-yl)diphenylgermyl)benzene (95b) ^{1}H NMR, δ = 0.02 (s, 9H), 0.92 (d, 3H), 1.13 (s, H), 1.23 (m, H), 1.64 (s, 3H), 4.59 (m, 2H), 7.32-7.35 (m, 6H), 7.47-7.51 (m, 4H); MS *m/z* (I) = 460 (5), 445 (1), 377 (100), 362 (5), 347 (5), 299 (30), 243 (20), 227 (30), 195 (20), 181 (20), 151 (40), 135 (35), 105 (10), 73 (20); Exact mass, Calcd. for (M-82) $C_{21}H_{23}GeSi$, 373.0811; found 373.0793.

1-(trimethylgermyl)-2-((2,3-dimethyl-1-buten-4-yl)diphenylgermyl)benzene (95c) MS (EI), *m/z* (I) = 489 (1), 421 (100), 407 (10), 389 (10), 343 (25), 310 (20), 268 (20), 243, (50), 227 (50), 181 (50), 151 (80), 119 (25), 91 (20).

A solution of either **93a-c** (0.1g, 3.66 X 10^{-4} mol) in hexane (15-mL) containing 0.07 M of $CHCl_3$ and 0.003 M CH_2Cl_2 (NMR integration standard) was placed in a quartz tube, sealed with a rubber septum, deoxygenated with a stream of dry argon, and then photolysed for 15 minutes. Periodic monitoring of the course of the photolysis by ^{1}H NMR revealed the formation of chlorotrimethylsilane/trimethylgermanium chloride, Ph_3MMe or $PhMMe_3$, (where M=Si or Ge) and $Cl_2HC\text{-}CHCl_2$ as the only detectable products.

In similar fashion, a solution of either **93a-c** (0.1g, 3.66 X 10^{-4} mol) in hexane (15-mL) containing 0.5 M of 1-decanol was placed in a quartz tube and deoxygenated with a stream of dry argon, and then photolysed for 15 minutes. Periodic monitoring of the course of the photolysis by GC revealed the formation of 1-trimethylsiloxydecane-/1-trimethylgermoxydecane, along with other products. Authentic samples of **104**$_{M}$ and **104**$_{M'}$ were synthesized in the following manner: 1-decanol (0.25 mL, 1.3 mmol) and imidazole (0.08 g, 1.2 mmol) were stirred in 20 mL of CH_2Cl_2 at room temperature. Chlorotrimethylsilane (0.13 g, 1.2 mmol) or trimethylgermanium chloride (0.18 g, 1.2 mmol) was added rapidly causing the instantaneous formation of a white precipitate. The solution was filtered and the solvent evaporated using a stream of nitrogen. The products were isolated by semi-preparative GC. Compounds **104**$_{M}$ and **104**$_{M'}$ were identified on the basis of the spectroscopic data listed below:

1-Trimethylgermoxydecane (104$_{M}$**)** MS (EI), *m/z* (I) = 276 (5), 261 (10), 231 (5), 203 (5), 189 (5), 173 (7), 149 (75), 119 (100), 105 (30), 89 (30), 75 (5).

1-Trimethylsiloxydecane (104$_{M'}$**)** MS (EI), *m/z* (I) = 230 (5), 215 (100), 199 (5), 187 (5), 157 (10), 143 (10), 129 (10), 115 (20), 103 (30), 75 (75), 73 (50).

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