Silenes: novel synthetic reagents for olefin functionalisation

Russell Jon Griffiths

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Silenes: Novel Synthetic Reagents for Olefin Functionalisation

Russell Jon Griffiths, B.Sc. (Hons)
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DECLARATION

The work contained in this thesis was carried out in the Department of Chemistry, University of Durham or GlaxoWellcome, Medicines Research Centre, Gunnels Wood Road, Stevenage, Herts. between October 1996 and September 1999. All the work is my own, unless otherwise indicated. It has not previously been submitted for a degree at this or any other university.

PAPERS PUBLISHED

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Finally I would like to thank GlaxoWellcome for funding this work, and Dr. Malcolm Berry for his help and advice over the past three years.

Abbreviations

Ac	: acetyl
b.p.	: boiling point
Bu	: butyl
CI	: chemical ionisation
d	: doublet
de	: diastereomeric excess
DEPT	: distortionless enhancement by polarisation transfer
DMAP	: 4-dimethylaminopyridine
DMPU	: 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone
ee	: enantiomeric excess
EI	: electron impact
Et	: ethyl
FAB	: fast atom bombardment
GC	: gas chromatography
GC-MS	: gas chromatography – mass spectrometry
Hal	: halogen
HOMO	: highest occupied molecular orbital
HMDS	: hexamethyldisilazide
HMPA	: hexamethylphosphoric triamide
HRMS	: high resolution mass spectrometry
IR	: infra red
LUMO	: lowest unoccupied molecular orbital
M	: multiplet
Me	: methyl
Mes	: mesityl
mcpba	: 3-chloroperbenzoic acid
m.p.	: melting point
MS	: mass spectrometry
NMR	: nuclear magnetic resonance
Ph	: phenyl
q	: quartet
s	: singlet

t	: triplet
TBAF	: *tert*-butylammonium fluoride
TBDMS	: *tert*-butyldimethylsilyl
Tf	: trifluoromethanesulfonyl
THF	: tetrahydrofuran
tlc	: thin layer chromatography
TMS	: trimethylsilyl
Tol	: tolyl (4-methylphenyl)

ABSTRACT

Silenes: Novel Synthetic Reagents for Olefin Functionalisation

Russell Jon Griffiths

Ph.D. 2000

Silenes, compounds containing silicon-carbon double bonds, have been subject to much theoretical interest over the past 25 years. However, despite their high reactivity, to date there have been no reports of the attempted use of silenes as synthetic reagents.

Silenes have been formed by the thermolysis of acyltris(trimethylsilyl)silanes, which have been found to react with dienes to give Diels-Alder cycloadducts in good yield. Further to this, it has been found that silene dimers, formed by the photolysis of acyltris(trimethylsilyl)silanes, have been found to revert to give silenes at much lower temperatures. These dimers have been found to be excellent low-temperature silene sources.

The reactions of acyltris(trimethylsilyl)silanes with silyl Lewis acids have been found to give novel products in excellent yield, via a series of migration reactions. These migrations are believed to involve the formation of a silyl cation or "silylenium" ion intermediate. Furthermore, the reaction with trimethylsilyl triflate is believed to proceed via the formation of a silene intermediate, the existence of which has been supported by trapping with methanol.

Finally, the oxidation of silene cycloadducts has been attempted, using established conditions. The first series of silene cycloadducts obtained were found to be unreactive towards oxidation. However, the reaction of a silene, formed by a Peterson elimination process, with dienes has been found to give a cycloadduct as a single diastereoisomer. It has been shown that this cycloadduct can be oxidised, following established protocols, to give either a homoallylic alcohol or 1,5-diol in reasonable overall yield. This result provides evidence for the utility of silenes as reagents for functionalising dienes.

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Chapter 1

Introduction

1.1 Introduction

This thesis details work studying the chemistry of silenes, compounds containing silicon-carbon double bonds. The study of multiply bonded silicon species has grown enormously since the existence of silenes was established 30 years ago. Despite a variety of methods available to form silenes and their potent reactivity, their potential use as reagents in synthetic organic chemistry has so far not been investigated. Several excellent reviews on the chemistry of silenes have been published previously.[1,2] This section will deal with the most important aspects of the synthesis and reactions of silenes.

The most common methods for the formation of silenes are the 1,3-sigmatropic rearrangements of acylpolysilanes and a variety of 1,2 elimination reactions. These methods are accompanied by a variety of less-well explored routes. The most popular methods are outlined below.

1.2 Comparison of Carbon and Silicon

Carbon and silicon are both Group IV, tetravalent elements. However, they exhibit many differences in their chemistry.[3] This can be best illustrated by considering the various bond energy/bond lengths of carbon and silicon to a variety of elements, (Table 1.1):[4]

	Bond Energy, kJmol^{-1}	Bond Length, Å
Si-C	318	1.89
Si=C	490	[1.72]
Si-O	531	1.63
Si-Cl	471	2.05
Si-F	808	1.60
C-C	334	1.54
C=C	620	1.32
C-O	340	1.41
C-Cl	335	1.78
C-F	452	1.39

Table 1.1

As can be seen from the table 1.1, the silicon-carbon bond is over 20% longer than the carbon-carbon bond. Conversely however, silicon forms much stronger bonds to heteroatoms, such as O, F and Cl than carbon, and much of the chemistry utilising silicon makes use of this. Indeed, the silicon-fluorine bond is one of the strongest single bonds known.

A major aspect of organic chemistry is that carbon readily forms multiple bonds with itself or other elements, notably oxygen and nitrogen. However, Si=Si double bonds are comparatively rare, and Si=C compounds, the subject of this project, are also infrequently reported in the literature. This can be explained by considering the difference in the strengths of the bonds in alkenes and silenes. The 3p orbitals on silicon are larger and more diffuse than the 2p orbitals of carbon. As the overlap of orbitals is strongly affected by the wavefunction in the overlap region, the denser 2p orbitals have a much stronger overlap region than the 3p orbitals, leading to a much stronger double bond for carbon than silicon. This can also be explained by considering the sheer difference in bond length, Si-Si and Si-C bonds being much longer than C-C, C-O and C-N bonds.

1.3 Historical Aspects

1.3.1 Discovery of silenes

Attempts were made to form compounds containing silicon-carbon double bonds for many years, without any success.[5] Kipping, during his pioneering research into organosilicon chemistry, attempted to form silenes by the dehydration of $EtPrSi(OH)CH_2Ph$ (1)[6] and $Ph(c\text{-}C_6H_{11})_2SiOH$ (2), without success, eventually reaching the conclusion that "substances containing a Si=C bond are probably incapable of existence".[7] However, in 1967, Gusel'nikov and Flowers made a landmark discovery in silene chemistry. They observed that the pyrolysis of silacyclobutane (3) gave the disilacyclobutane (4). They rationalized this observation by postulating that the silacyclobutane underwent a retro [2+2] cycloaddition to give ethene and silene (5), which then dimerized to give (4), Figure 1.1.[8,9]

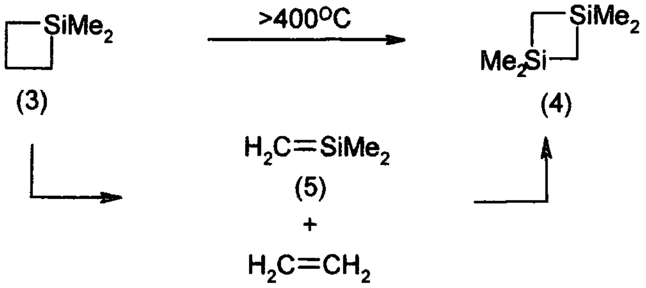


Figure 1.1

In 1976, two groups established firm experimental evidence of the existence of silenes. Chapman and co-workers discovered that the photolysis of (trimethylsilyl)-diazomethane (6) or (trimethylsilyl)diazirine (7) in an argon matrix at 8K formed 1,1,2-trimethylsilene (9), (Figure 1.2).[10] Shechter and co-workers, using the same methodology, recorded the IR spectrum of this silene.[11] It was found to exist only at very low temperatures; above 45K it dimerized to give the head-to-tail dimer (10), Figure 1.2.

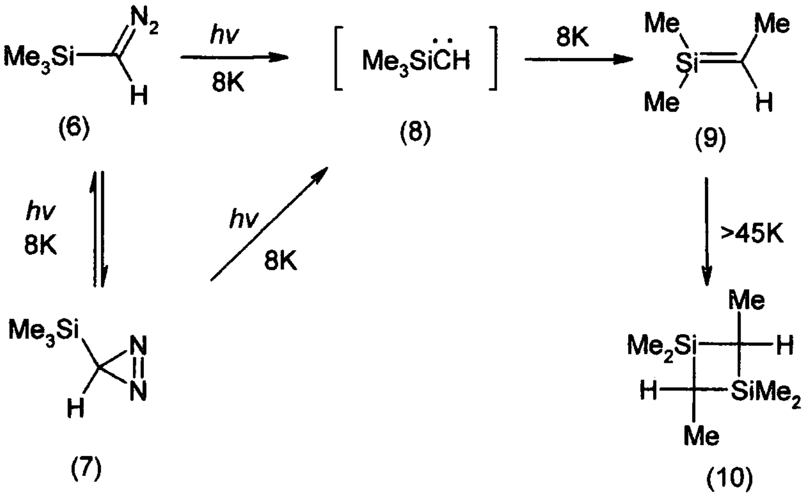
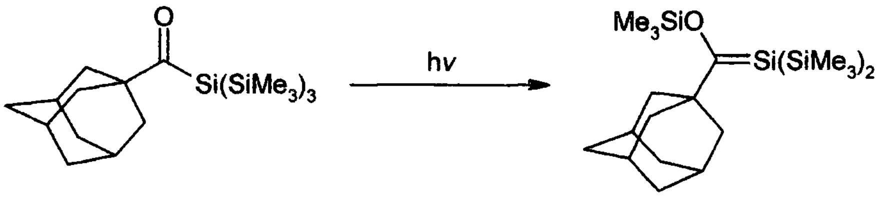


Figure 1.2

The next challenge lay with the synthesis of a stable, directly observable silene species. It appeared that such a silene would have to be sufficiently bulky as to prevent dimerization taking place. This was finally achieved in 1981 by Brook and co-workers, who found that the photolysis of the adamantyl-substituted acylsilane (11) gave the product silene (12), Figure 1.3.[12]

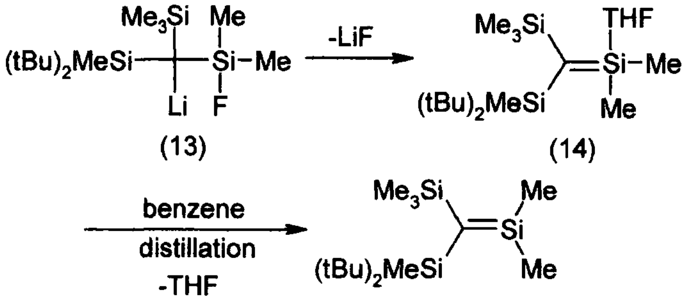


(11) (12)

Figure 1.3

This silene was found to be stable, crystalline solid under argon at room temperature, however in the presence of air the silene decomposed rapidly.

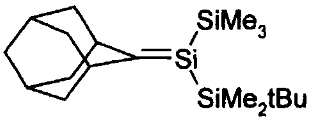
Subsequent to this discovery, further syntheses of stable silenes have been achieved using different methodology. The first of these was achieved by Wiberg and co-workers, who formed the stable silene (15) via the thermal elimination of LiF from (13), Figure 1.4.[13]



(13) (14) (15)

Figure 1.4

More recently, Apeloig and co-workers have achieved the synthesis of a third stable silene (16), Figure 1.5.[14]



(16)

Figure 1.5

At about the same time as the discovery of stable silenes, compounds containing silicon-silicon double bonds known as disilenes were discovered, by West and co-workers.[15] Disilenes, like silenes are generally unstable high-energy systems. The chemistry of disilenes has been reviewed previously,[1] and further discussion is beyond the scope of this report.

1.3.2 Structural Aspects

Early *ab initio* calculations for the parent silene $H_2Si=CH_2$ indicated a Si-C bond length of 1.69-1.71 Å.[16] The first experimental evidence for the Si-C double bond length came in 1980 from a gas-phase electron diffraction study of $Me_2Si=CH_2$.[17] However, the bond length observed, 1.832 Å, is considerably longer than that predicted thereotically, and has now been discounted.[16]

The isolation of stable, crystalline silenes allowed the determination of the silene carbon-silicon bond length by x-ray crystallography. These results are summarized below, Table 1.2.

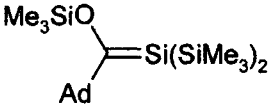
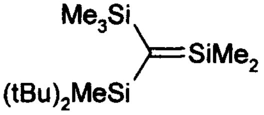
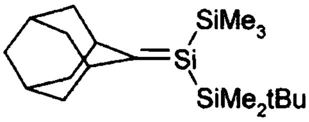
Silene	Bond length, Å	Ref
 (12)	1.764	12
 (15)	1.702	13
 (16)	1.741	14

Table 1.2

The X-ray crystal structures of the above silenes indicate that the silenes are basically planar, with both Si and C atoms approximately sp^2-hybridized. In addition, the barrier to rotation around the silene is large enough to prevent any observation of rotation on the NMR timescale. The silene formed by Wiberg and co-workers (15), was initially formed as an adduct with THF (14), Figure 1.4.[18] The carbon-silicon bond length in this THF solvate was unsuprisingly found to be much longer, at 1.75 Å, than the uncomplexed silene. Similar silenes coordinated to triethylamine or fluoride ions also exhibit similar behaviour.[19,20]

The value for the silicon-carbon double bond length is somewhat longer for the "Brook" silene (12) than that predicted from the calculations performed for the parent silene. This has been attribututed both to the effect of the trimethylsilyloxy substituent, and the bulk of the substituents causing a twisting of the silene by 16° in the crystal lattice, leading to a reduction of planarity and lengthening of the silicon-carbon bond. Theoretical calculations suggest that the bond strengths of silenes are largely unaffected by such twist angles.[21] However, the bond length obtained for silene (15) is very similar to that predicted by theory.

1.3.3. Spectroscopic study of silenes

The ^{29}Si NMR chemical shifts of the sp^2 hybridized silicon of the silene occur at a higher chemical shift than $SiMe_4$, and are generally over a very wide range of approximately 40-150 ppm. The chemical shift appears to be heavily dependent on the nature of the substituents on the silene.

Brook has utilized the relatively deshielded ^{29}Si signal of the sp^2- hybridized silicon atom as further evidence for the intermediacy of silenes in the photolysis of acyltris(trimethylsilyl)silanes and silene dimer reversion reactions.[22]

1.4. Formation of silenes

1.4.1. Introduction

Since the initial discovery of the formation of silenes in pyrolysis reactions, a number of syntheses have been discovered. There are now several very different methods for the formation of silenes. Many of these processes involve a high-energy pathway, either through extreme temperature or by photolytic generation. However, there are some notable routes to silenes at much lower temperatures. The most commonly encountered methods are described below.

1.4.2. Pyrolytic Methods

As mentioned previously, the first evidence for the existence of silenes was found from the pyrolysis of a silacyclobutane (3).[8] It has been found that this cycloreversion can also be initiated photochemically, to form the same silene (5).[23] Mechanistic evidence suggests that the formation of silene (5) is a singlet process, whereas the presence of xenon and benzene promotes the triplet pathway to form silylene (17) and cyclopropane, Figure 1.6.[24]

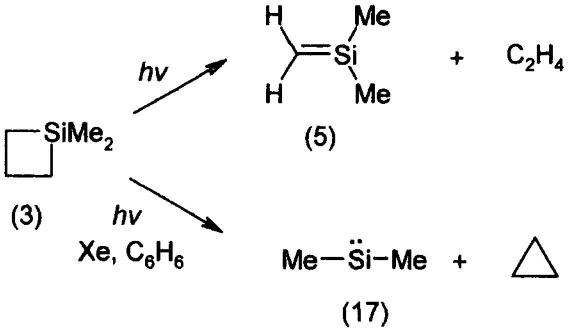


Figure 1.6

Subsequently, a variety of pyrolytic methods have been used to form transient silenes. These usually involve retro-Diels-Alder or retro-ene processes. Examples of the more common reactions are described below.

The gas-phase pyrolysis of silabicyclo[2.2.2]octadiene (18) has been used to produce the parent silene, $H_2C{=}SiH_2$ (19), Figure 1.7.[25,26]

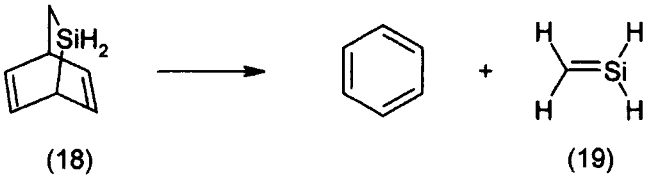


Figure 1.7

In a similar fashion, silanorbornene (20) was found to undergo a retro-Diels-Alder reaction at high temperatures to give the silene (21), which dimerized to give the head-to-tail dimer (22), Figure 1.8.[27]

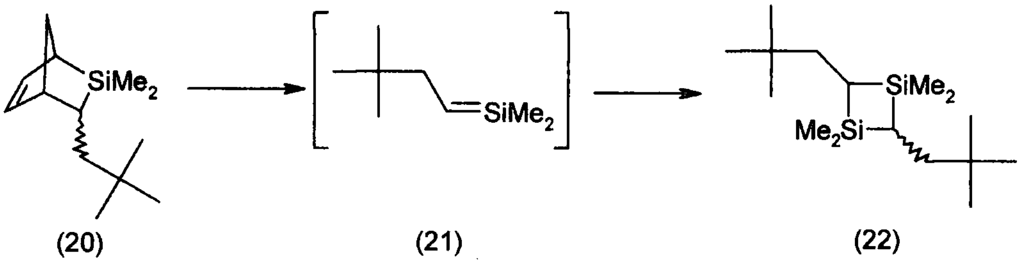


Figure 1.8

Allyltrimethylsilane was found to undergo a retro-ene reaction at very high temperatures to give dimethylsilene (5). Evidence for this was provided by deuterium labelling experiments. As expected, the silene was found to spontaneously dimerize to give dimer (4), or react with 2,3-dimethylbutadiene to give the [4+2] adduct (24), Figure 1.9.[28]

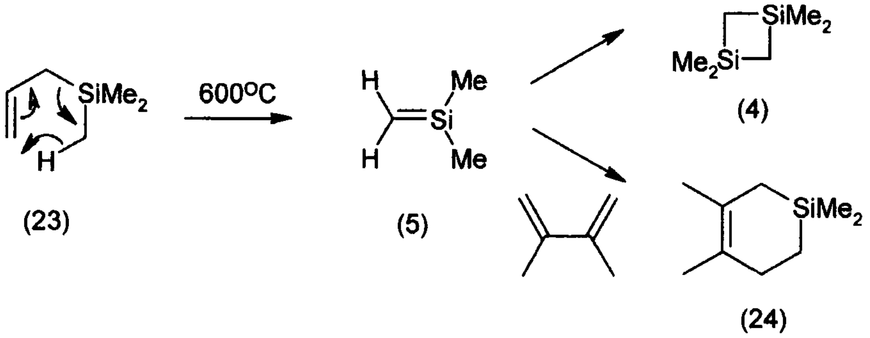


Figure 1.9

The synthetic utility of such methods is limited due to the high temperatures and small scales involved. However, Wiberg and coworkers have discovered a low temperature route to silenes via [4+2] and [2+2] cycloreversions of preformed silene adducts (25) and (28) to form $Me_2Si{=}C(SiMe_3)_2$ (26), Figure 1.10.[29]

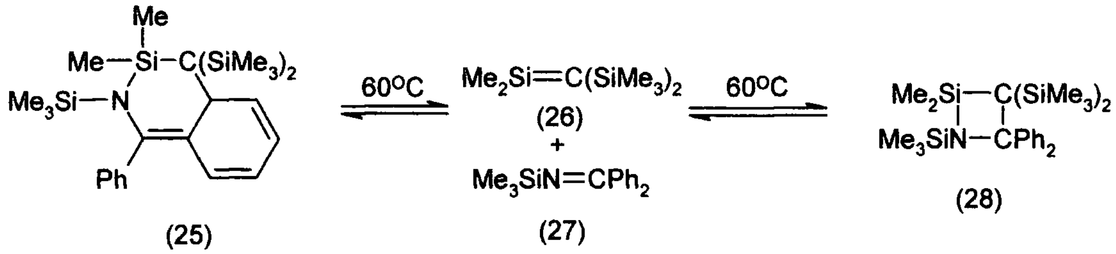


Figure 1.10

1.4.3. 1,2-Migrations

One of the earliest methods for generating silenes was from the photolysis of disilyl-substituted diazocarbonyl compounds (29), a reaction discovered by Ando and co-workers. The reaction proceeds via the formation of an intermediate carbene species (30), which then rearranges to give the silene (31), Figure 1.11.[30,31]

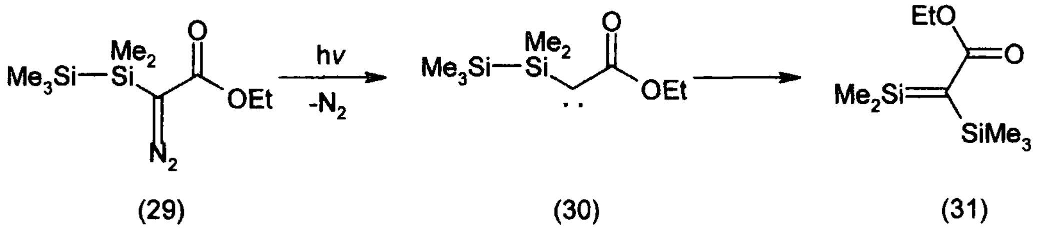


Figure 1.11

Maas and co-workers have studied this reaction further, and have found that these silenes undergo unusual transformations depending on the nature of the acyl subtituent. Bulky substituents such as adamantyl (31a) and *tert*-butyl (31b) led to an intramolecular [2+2] reaction to siloxetenes (32a) and (32b) respectively. As the steric bulk of the substituent decreases the acylsilene tends to undergo an unusual dimerization reaction, Figure 1.12.[31]

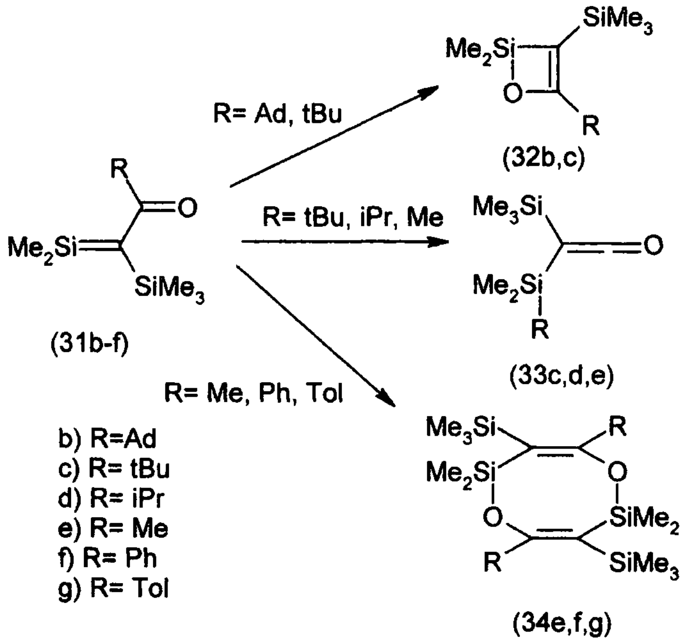


Figure 1.12

The photolysis of bis(trimethylsilyl)diazomethane (35) has been found to produce a silene (36), via a similar migration pathway. In the absence of any trapping agent, the intermediate silene was found to dimerize to give dimer (37), whereas the addition of methanol led to the formation of silyl ether (38), Figure 1.13.[32]

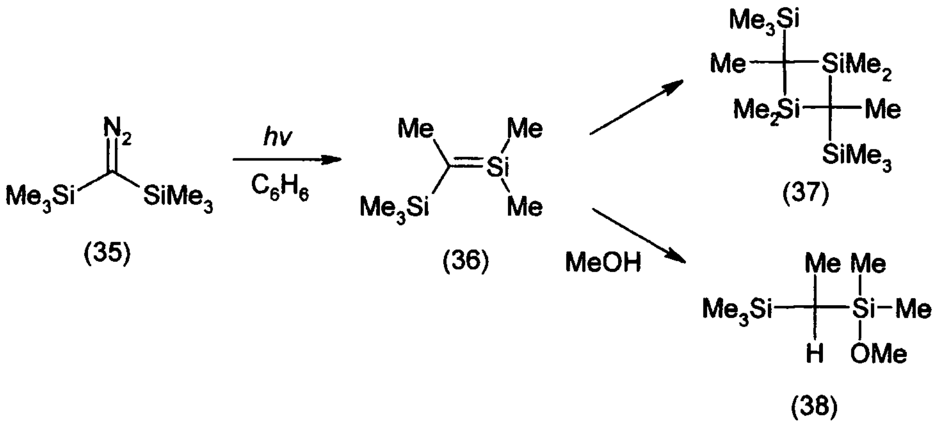


Figure 1.13

As a further example, Ando and co-workers have used a similar process to form a conjugated silene (41), Figure 1.14.[33]

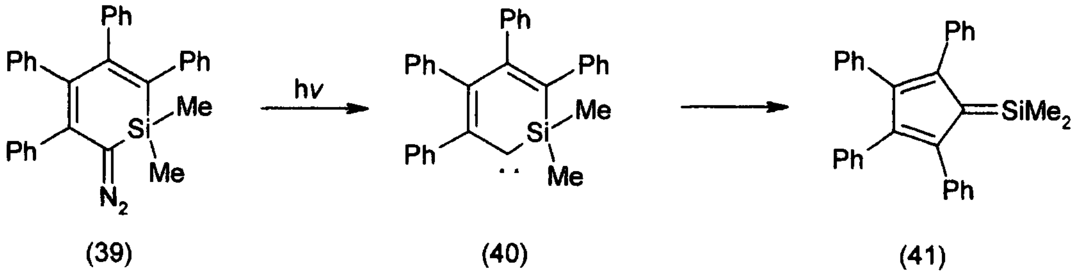


Figure 1.14

1.4.4 Electrocyclic Ring Opening

In addition to the photochemical methods outlined previously, another less common photochemical method involves the irradiation of silacyclobutene (42) which opens to give silabutadiene (43). This conjugated silene was found to react with acetone to give the cyclic product (44), Figure 1.15.[34, 35]

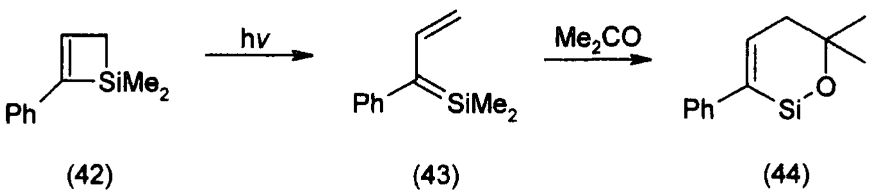


Figure 1.15

1.4.5 1,3-Sigmatropic Rearrangments

One of the most widely reported and versatile syntheses of silenes is the photochemical 1,3-sigmatropic rearrangment of acyltris(trimethylsilyl)silanes (11), first reported by Brook in 1976, Figure 1.16.[36]

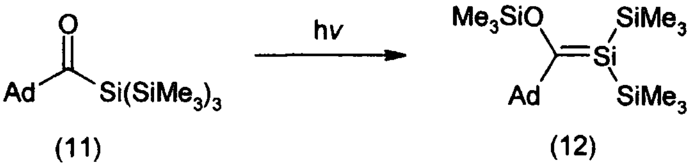


Figure 1.16

It was using this methodology that Brook produced the first stable silene (12), using a bulky adamantyl substituent (R= Ad) to prevent dimerization.[12] The principal feature of this reaction is that it generates a silene with a trimethylsilyloxy substituent on the carbon atom.

It was subsequently found that the rearrangement can also be performed thermally. Brook and co-workers discovered that by heating trimethylacetyltris(trimethylsilyl)silane (45) at 170°C in the presence of 1-phenylpropyne or alcohols gave the expected trapping products (47) and (48), Figure 1.17.[37]

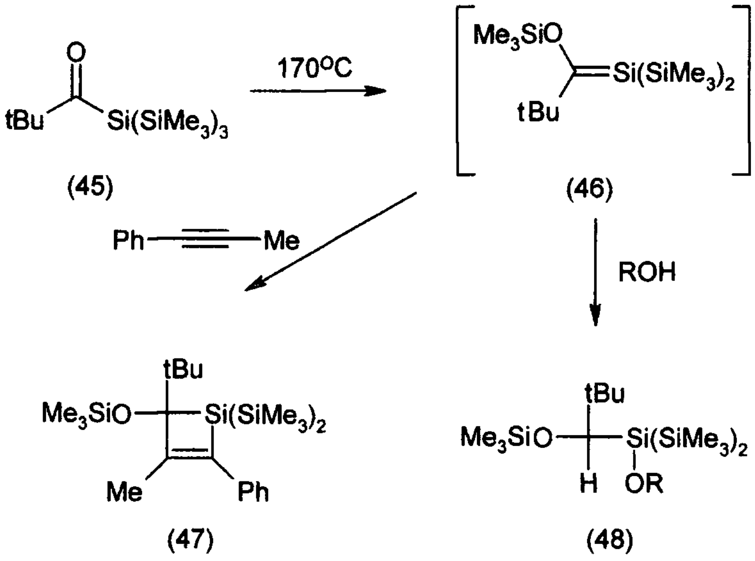


Figure 1.17

Brook has shown that the replacement of the trimethylsilyl substituents with alkyl or aryl groups generally leads to the reduction in stability of the silenes formed. For example, the photolysis of acylsilane (49) initially forms the silene (50), which undergoes a series of complex rearrangements to give a new silene (51), which dimerized to give a head-to-tail dimer (52). Altenatively, addition of methanol gave the expected methanol adducts (53) and (54) of the two silenes. Evidently the considerable bulk of the substituents around this silene was unable to prevent dimerization in this case, Figure 1.18.[38]

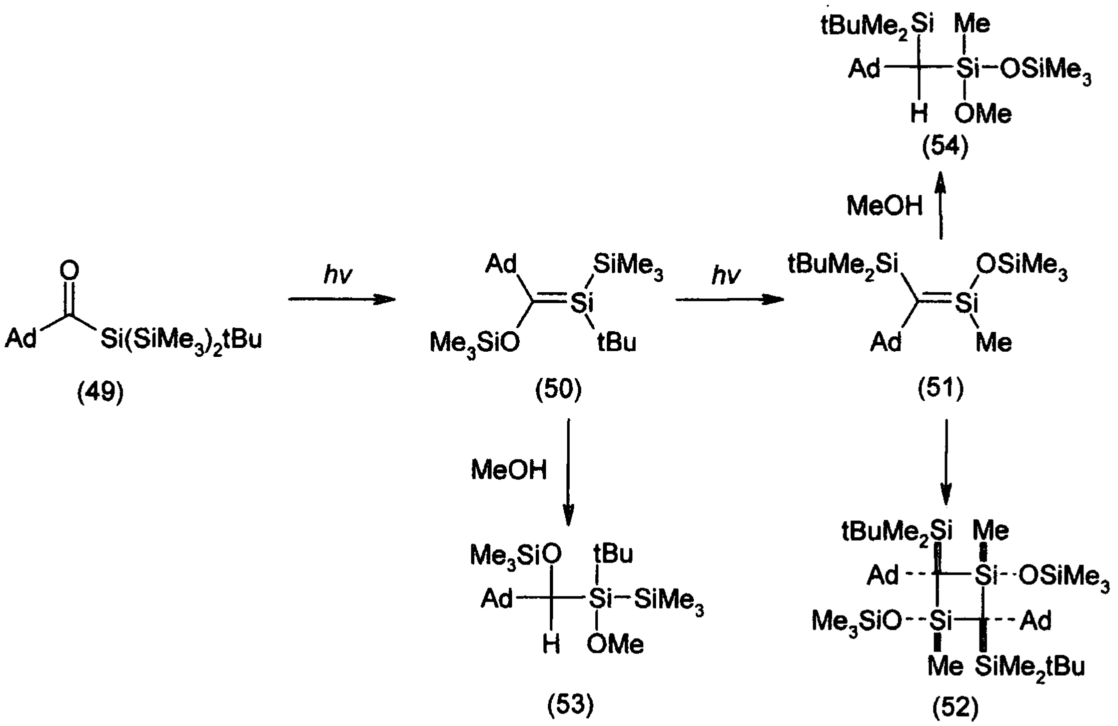


Figure 1.18

1,3 sigmatropic rearrangements to form silenes (56) have also been observed in the photolysis of disilanes (55). The existence of silene intermediates was supported by trapping experiments with methanol and deuteromethanol, Figure 1.19.[39]

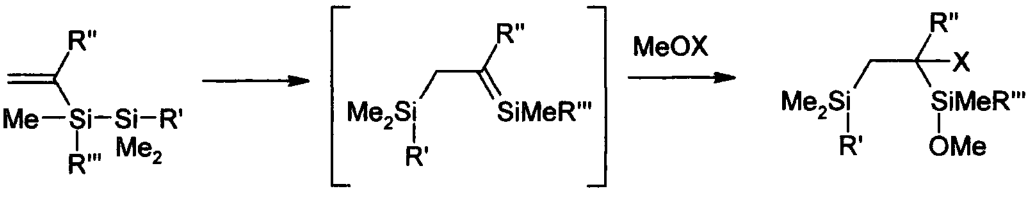


Figure 1.19

1.4.6 Thermal 1,2 eliminations

A number of 1,2-elimination reactions to form silenes have been reported. Generally they involve the thermal elimination of a lithium halide. This methodology has been studied by Wiberg and co-workers.[40] As mentioned above this has also been utilized to generate the stable silene (14), Figure 1.20.

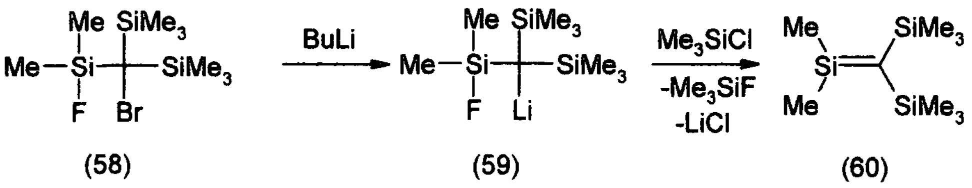


Figure 1.20

It is believed such elimination reactions proceed via the formation of a dipolar intermediate (60), Figure 1.21.[41]

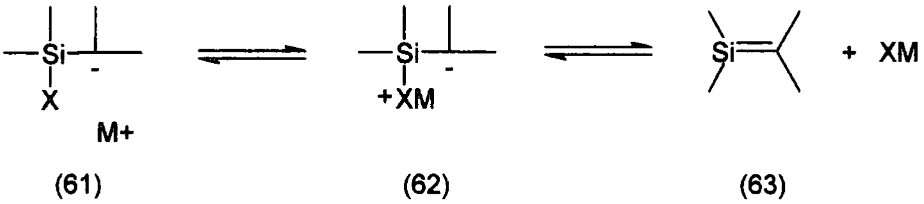


Figure 1.21

Jones and co-workers observed that the addition of *t*-BuLi to vinylsilane (62) led to the formation of the lithiated intermediate (63), which underwent elimination as before to give the neopentyl-substituted silene (64), Figure 1.21.[42]

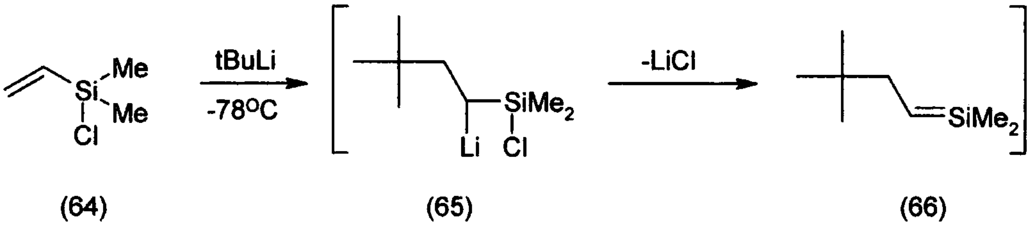


Figure 1.21

The reaction initially involves a Michael-type addition to the vinylsilane, giving the α-lithiochlorosilane. Presumably the bulk of the t-BuLi prevents substitution or metallation at the silicon centre. This reaction has been more extensively studied by

Auner and coworkers, who have formed a number of silenes by varying the substituents of the silicon atom.[1] The restriction of this reaction is that only silenes bearing neopentyl substituents can be formed, a function of the necessity of using t-BuLi to form the silene.

Recently, Couret and co-workers have formed the stable silene, dimesityl-neopentylsilene (71) in almost quantitative yield, by reacting t-BuLi with dimesitylvinylfluorosilane (69) in a similar manner to that illustrated above, Figure 1.23.[43]

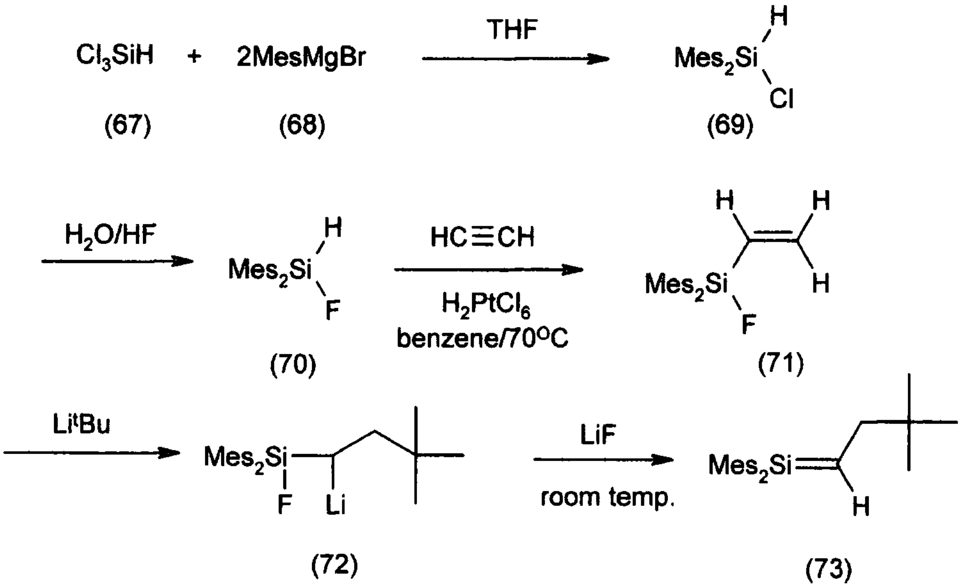


Figure 1.23

1.4.7 Modified Peterson Elimination

The Peterson reaction, effectively the silicon equivalent of the Wittig reaction, has proved to be a useful method of forming carbon –carbon double bonds. The process has been adapted to form silenes. Oehme and co-workers have reacted silyllithium species (74) with carbonyl compounds. The intermediate formed (75) undergoes a spontaneous elimination to form silene (76), Figure 1.24.[44]

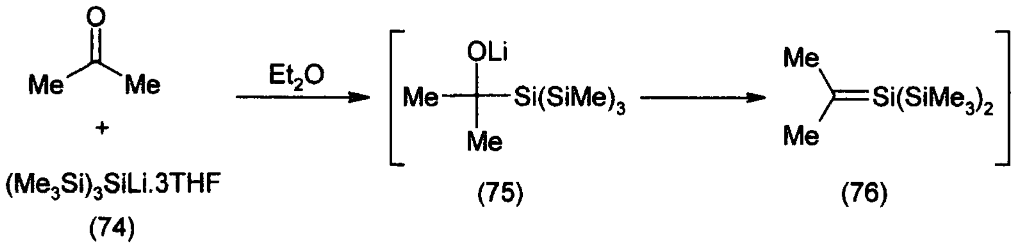


Figure 1.24

The main problem found with this reaction was that the silyllithium reagent adds to carbonyls and spontaneously undergo elimination, thereby not allowing the investigation of the effect of changing the base. Additionally, it was found that aromatic aldehydes and ketones could not be used,as it was found that these did not undergo nucleophilic attack by the silyllithium species at the carbonyl carbon. Both of these problems were overcome by the use of the silyl Grignard reagent (75), the more stable magnesium alkoxide allowing the isolation of the intermediate silyl alcohol. This silyl-Grignard reagent was easily prepared by addition of silyllithium (72) to magnesium bromide, Figure 1.25.[45]

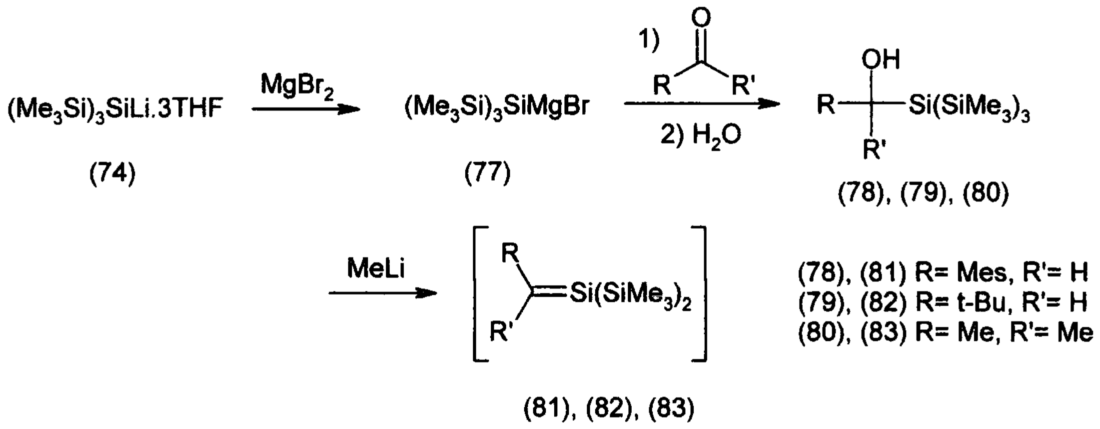


Figure 1.25

This type of reaction has been utilized recently by Apeloig and co-workers to produce a family of adamantyl-substituted silenes.[46] As mentioned previously in Section 1.3.2, this method proved successful in producing a new type of stable silene (16), Figure 1.25.[14]

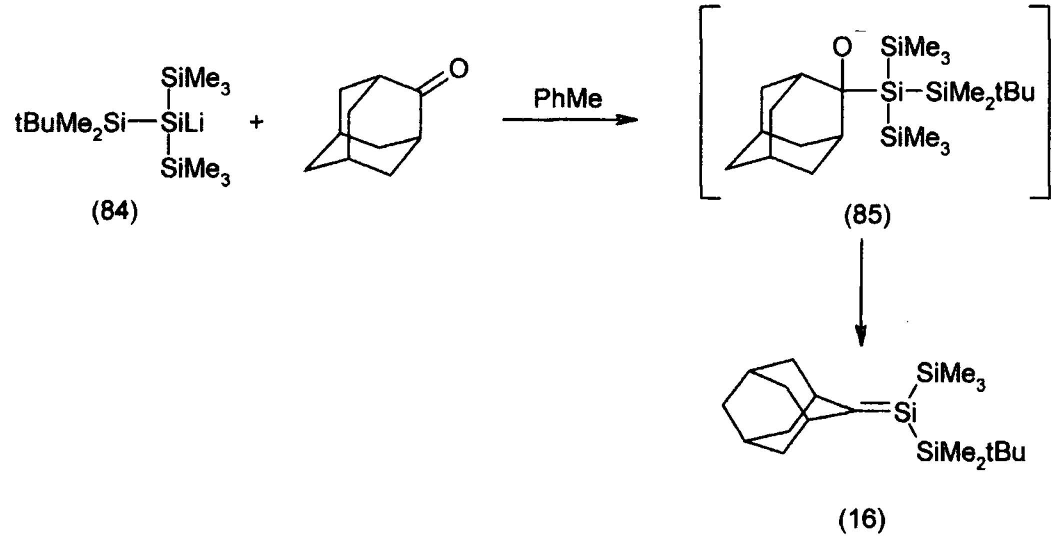


Figure 1.25

Ishikawa has reported another Peterson formation of silenes by the addition of methyllithium to acyltris(trimethylsilyl)silanes (86) and (87), giving an alkoxide intermediate which then undergoes a Peterson-type elimination, Figure 1.26.[47]

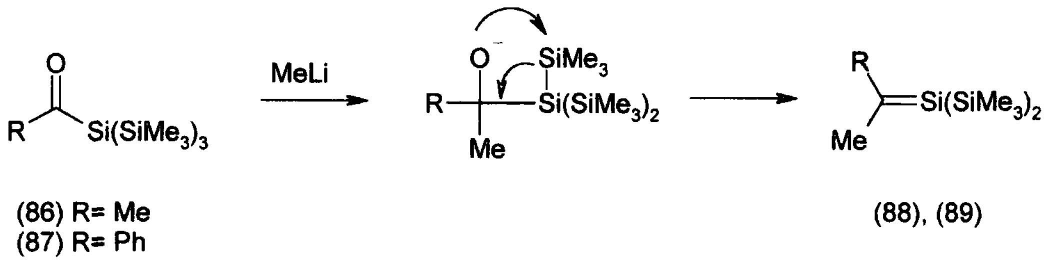
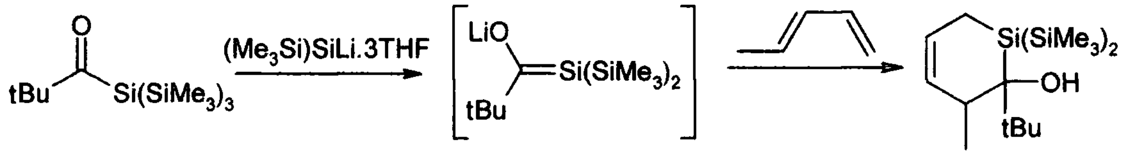


Figure 1.26

Interestingly, when trimethylacetyltris(trimethylsilyl)silane was used no silene formation was observed.

Recently, Ishikawa, Ohshita and co-workers have prepared "lithium silenoates", effectively a "silene enolate", from acyltris(trimethylsilyl)silanes, [48,49] and have demonstrated their reactivity with a number of dienes, forming only one regioisomer (91) in the example below with (45) and 1,3-pentadiene, Figure 1.27.[50]

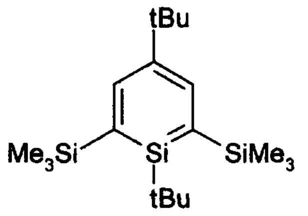


(45) (90) (91)

Figure 1.27

1.4.8 Formation of sila-aromatic compounds

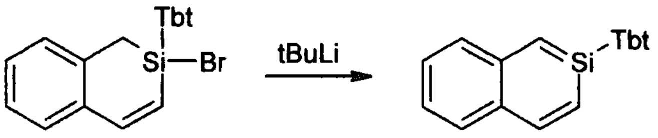
Accompaning the discovery of sp^2-hybridized silicon species is the research into the formation of silaromatic compounds. For many years sila-aromatic compounds could only be synthesized as transient species in pyrolysis and photolysis reactions. Even the bulky silabenzene derivative (92) was found to have limited stability at -100°C, Figure 1.28.[51]



(92)

Figure 1.28

A breakthrough discovery in the chemistry of silaaromatic compounds was made by Tokitoh and co-workers, who found that cyclic silane (93) bearing a 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) protecting group underwent elimination of HBr, to form the stable 2-Tbt-2-silanaphthalene (94), Figure 1.29.[52]



(93) (94)

Figure 1.29

Theoretical calculations for 2-silanaphthalene suggest that sila-aromatics are true aromatic compounds.[53, 54] Sila-aromatic compounds have been found to undergo much of the same chemistry as silenes. This has been comprehesively reviewed before.[1]

1.5 Reactions of Silenes

1.5.1 Introduction

Silenes, being highly reactive species, undergo a number of reactions, from spontaneous fragmentation to a variety of cycloaddition reactions with alkenes and dienes.

1.5.2 Silene rearrangement and fragmentation reactions

In general, most of the silenes formed by the photolysis of acylsilanes undergo dimerization and/or cycloaddition reactions. However, replacement of either or both of the trimethylsilyl substituents on the sp^2 hybridized silicon atom leads to these silenes undergoing rearrangement reactions to give different silene species. Brook and coworkers found that the acylsilane (49) underwent photolysis to initially give the expected silene (50), which then underwent a photochemical rearrangement to give the head-to-tail dimer (52) of a new silene, Figure 1.30.[55]

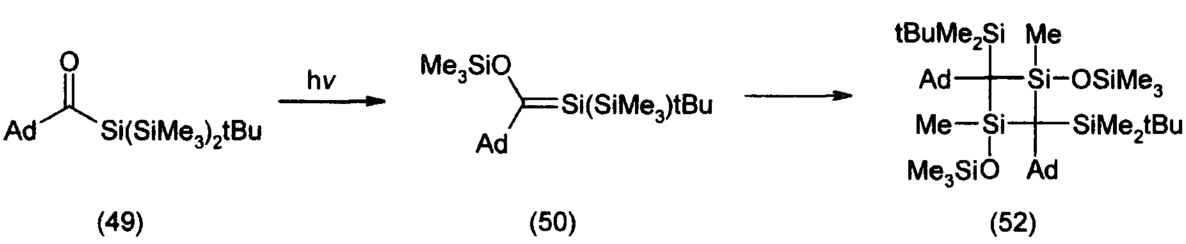


Figure 1.30

The following mechanism has been reported to explain the formation of this new silene, involving the initial isomerization to a silylene species (95), followed by subsequent isomerization reactions to give a new silene (51), which dimerizes to give the observed product, Figure 1.31.[55]

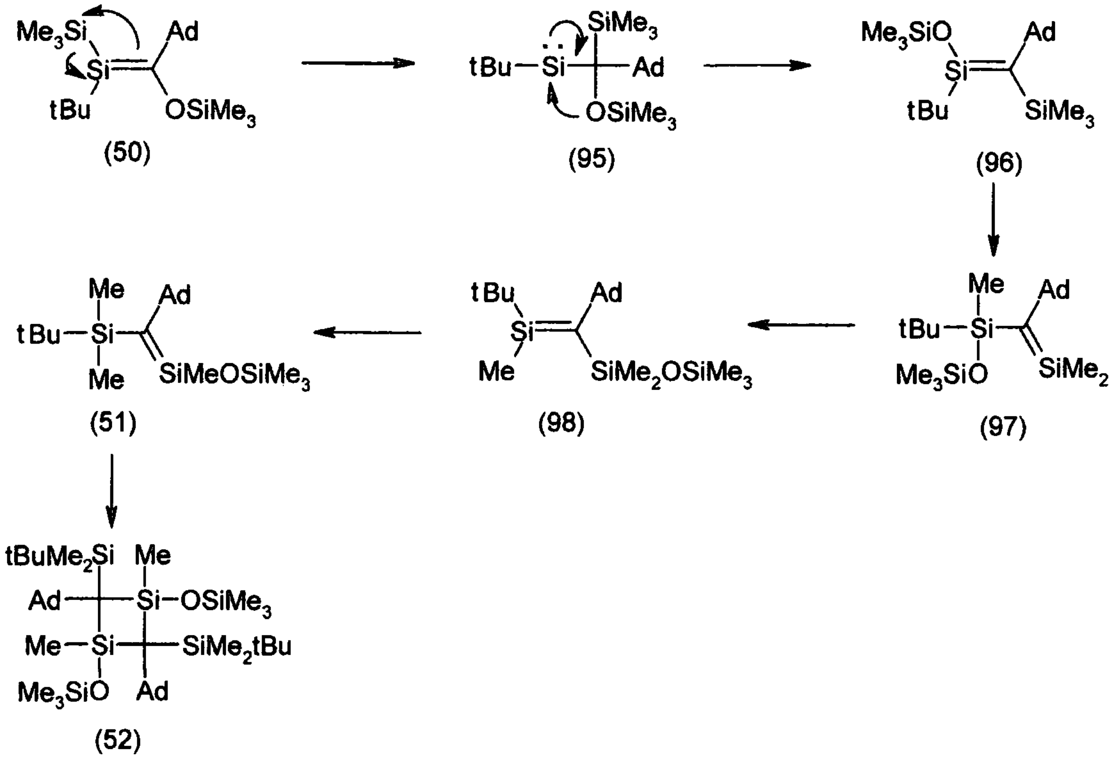


Figure 1.31

1.5.3 Reactions with Nucleophiles

Silenes themselves are very potent Lewis acids, and readily undergo attack with a variety of nucleophiles. The products of the reaction of silenes with alcohols are often used to provide evidence for the existence of transient silene species. Some of the more common reactions are illustrated below, Figure 1.32.[1]

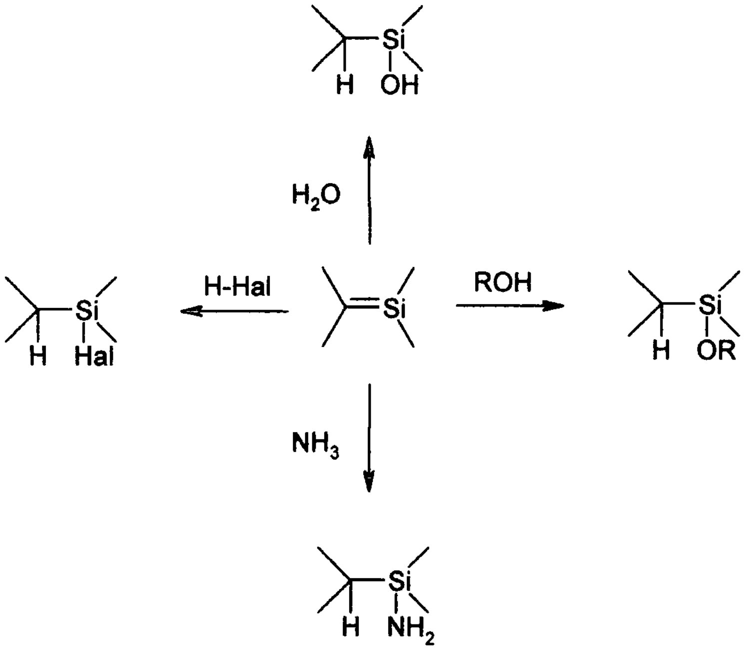


Figure 1.32

Brook and co-workers have studied the reaction of stable silenes with Grignard reagents.[56] These reactions were performed both with preformed silene, and in a co-photolysis reaction with the acylsilane and the Grignard reagent. It was found that a complex series of addition and rearrangement reactions took place, Figure 1.33.

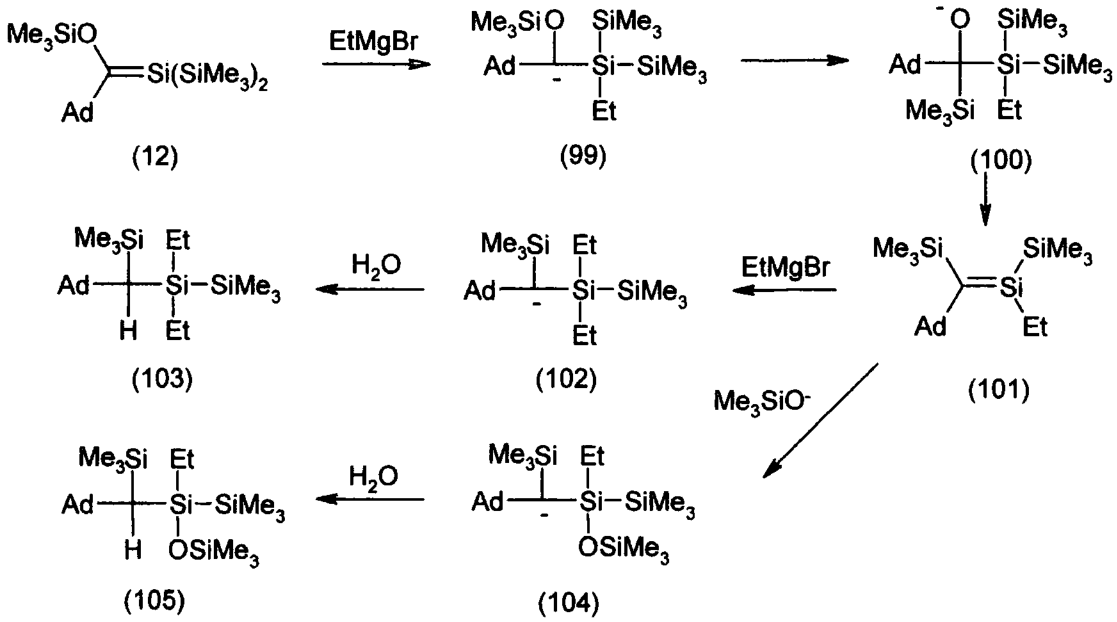


Figure 1.33

Initial nucleophilic attack by the Grignard reagent at the silicon end of the silene is followed by a reverse-Brook rearrangement to give the alkoxide intermediate (100). A Peterson elimination, similar to that observed by Oehme, leads to the formation of the silene species (101). This then reacts, either with an excess of the Grignard reagent, or with the eliminated trimethylsilanoate ion, to give the products (103) or (105) indicated.

1.6 Cycloaddition Reactions

1.6.1 Introduction

One of the common methods used to trap transient silene species is to form such silenes in the presence of dienes, resulting in the formation of cycloaddition products. Generally [4+2] cycloadducts are obtained, however [2+2] and "ene" type reactions can compete, Figure 1.34.

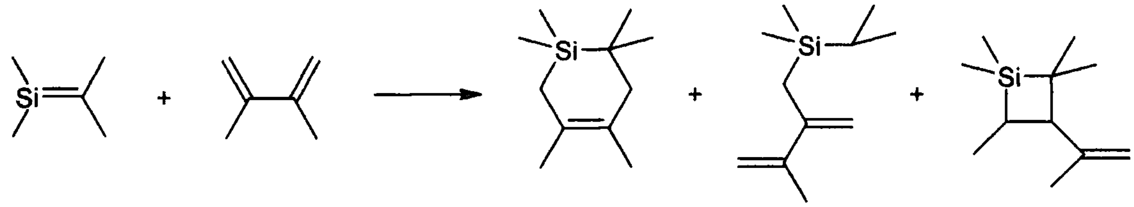


Figure 1.34

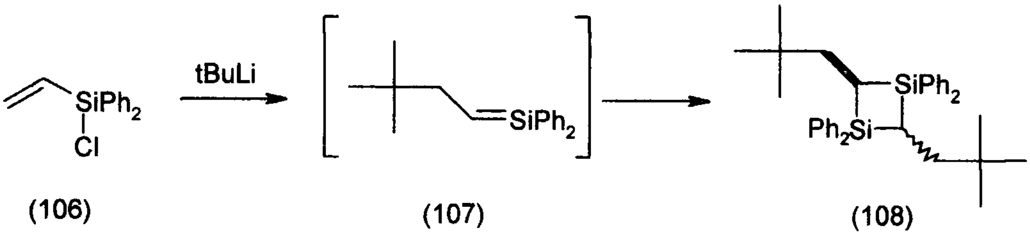
1.6.2 Silene Dimerization

1.6.2.1 Introduction

An interesting form of [2+2] cycloaddition reaction for silenes is dimerization. In the absence of other reagents, silenes tend to form dimers, either in a head-to-head or head-to-tail fashion, depending on the structure of the silene concerned. The mechanism of silene dimerization has been a subject of some debate.[1] A concerted 2_S+2_S cycloaddition is forbidden by the Woodward-Hoffman rules.[57] However, it is believed that the strong polarization of the silicon-carbon double bond leads to a relaxation of these rules.[2] As has been mentioned previously, dimerization can be supressed using bulky substituents, in some case leading to the formation of stable silenes.

1.6.2.2 Head-to-tail dimerization

The most common form of dimerization reaction for silenes is the formation of head-to-tail dimers. Auner has observed such dimers in the formation of silenes by the addition of t-BuLi to vinylsilanes, Figure 1.35.



(106) (107) (108)

Figure 1.35

1.6.2.3 Head-to-head dimerization

The formation of head-to-head dimers is a less common, but very important dimerization process. The polarization of the carbon-silicon bond, Si^+-C^-, would imply that the mechanism of the reaction almost certainly proceeds in a stepwise manner. Evidence for this is provided by the observation of radical intermediates during their formation.

Head-to-head dimerisation has been observed by Brook with the photolysis of trimethylacetyltris(trimethylsilyl)silane (45). Interestingly, the silene formed is stable enough to be observed in equilibrium with its dimer by NMR spectroscopy. The silene was observed for 2 weeks, slowly reverting to the parent acylsilane.[37] The crystal structure of the dimer indicated a very long carbon-carbon bond length between the ring carbons of 1.66 Å, Figure 1.36.[58]

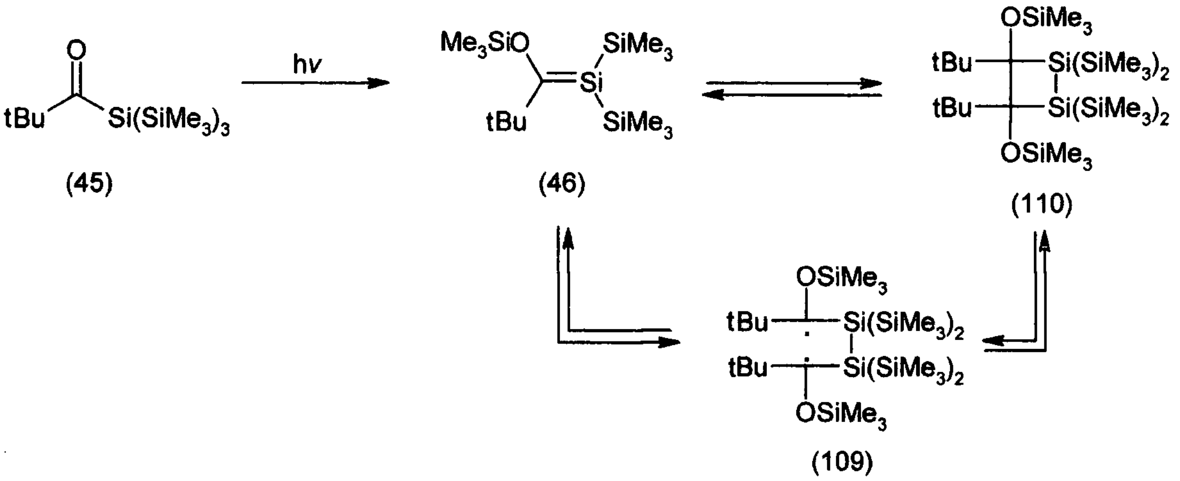


Figure 1.36

The existence of the diradical intermediate (109) is supported by the existence of an ESR signal, both from the photolysis solution and when the dimer was dissolved; this signal was absent for the solid dimer. However, attempts to trap the diradical intermediate failed.

A related form of dimerization is the formation of a “linear” dimer, which is believed to be formed via a similar 1,4-diradical intermediate (112). The presence of hydrogen atoms in the “allylic” position relative to the silene, leads to hydrogen abstraction, to give the linear disilane (113), Figure 1.37.[59]

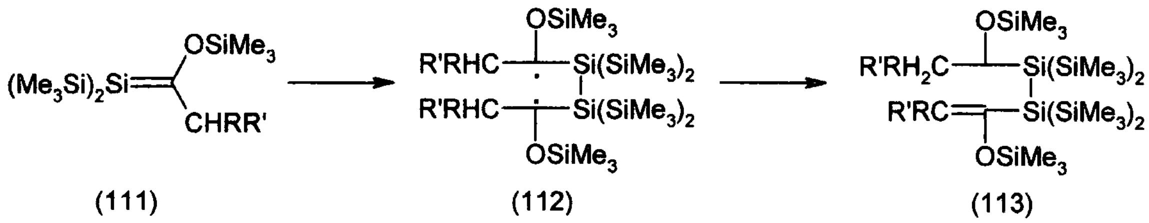
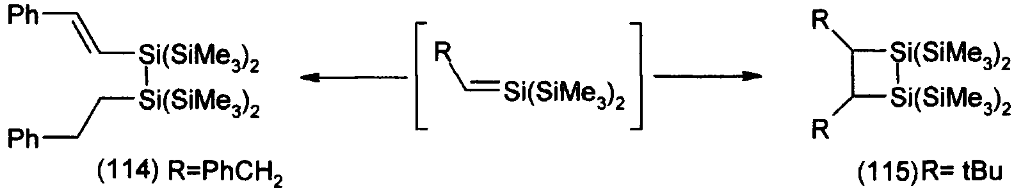


Figure 1.37

Oehme and co-workers have also reported the formation of head-to-head and linear dimers of silenes formed by the modified Peterson reaction described above, Figure 1.38.[45]

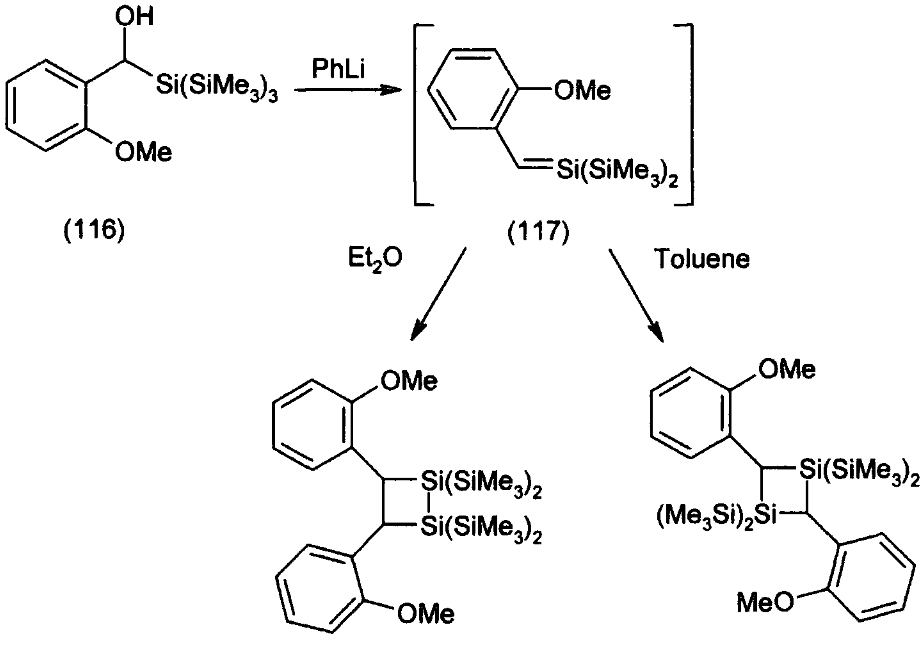


(114) R=PhCH$_2$ (115)R= tBu

Figure 1.38

As in Figure 1.37, the presence of protons in the alpha position ("allylic" protons) leads to the formation of the linear dimer, supporting the hypothesis that the intermediate in such dimerization reactions is indeed a diradical species.

Interestingly, in a recent paper Oehme has found that the regiospecificity of the dimerization of silene (117) depended critically on the nature of the solvent. In ether, head-to-head dimerization was observed, while in toluene a head-to-tail dimer was formed, Figure 1.39.[60] It is believed that in toluene, an intermolecular donor-acceptor interaction occurs between the methoxy- group and the electrophilic silicon of a neighbouring silene, to give the head-to-tail dimer (119). In the case of ether, the solvent competes with this intermolecular interaction to give the head-to-head dimer (118).



(116) (117) (118) (119)

Figure 1.39

Dimers of this type have also been observed by Ishikawa and co-workers when forming silenes from acyltris(trimethylsilyl)silanes with methyllithium. They found that acetyltris(trimethylsilyl)silane gave exclusively the "linear" dimer expected, due to the presence of "alpha" protons. However, benzoyltris(trimethylsilyl)silane gave a mixture of the "linear" and head-to-head dimer, which was found to undergo isomerization to the "linear" dimer upon thermolysis, Figure 1.40.[47]

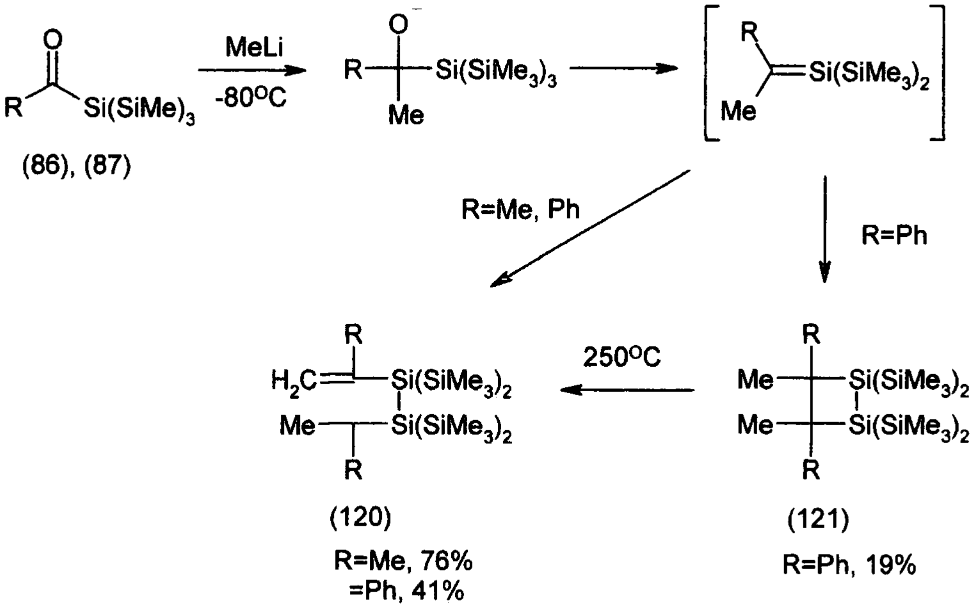


Figure 1.40

1.6.3 [2+2] Cycloaddition reactions

Auner has reported that neopentyl silenes bearing chloro- or trimethylsilyloxy-substituents (formed from the reaction of the corresponding vinylsilanes with tBuLi) on the silicon end of the silene show a large preference to undergo [2+2] cycloadditions with dienes. This is in marked contrast to similar silenes bearing alkyl substituents, which generally give [4+2] adducts, Figure 1.41.[61]

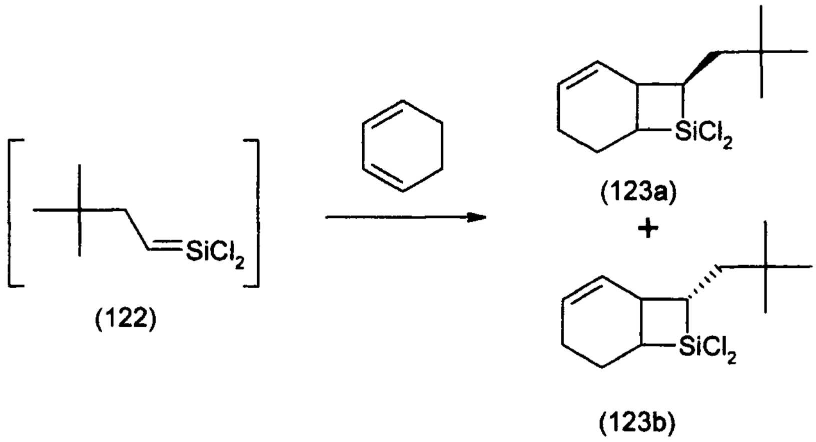


Figure 1.41

This observation has been rationalized due the increased polarisation of the Si=C double bond by electronegative substituents, leading to the formation of the dipolar intermediate (124). This reacts in a stepwise manner with 1,3-cyclohexadiene to give the intermediate (125), Figure 1.42.[61]

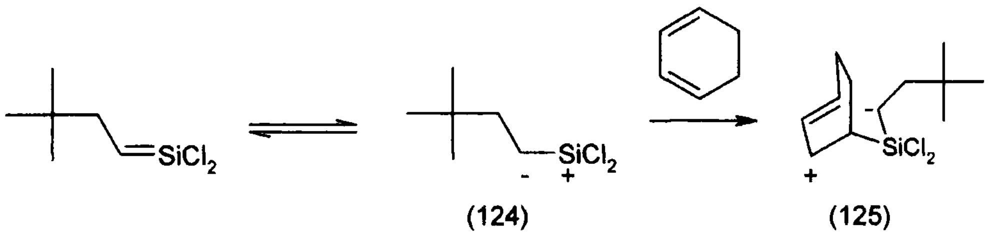


Figure 1.42

1,2-Siloxetanes have been formed by the reaction of silenes with carbonyl compounds. These cyclic species are often unstable, and undergo cycloreversion to give alkenes and a silanone (the silanone is not directly observed as it readily reacts with itself to form oligomers), Figure 1.43.[62]

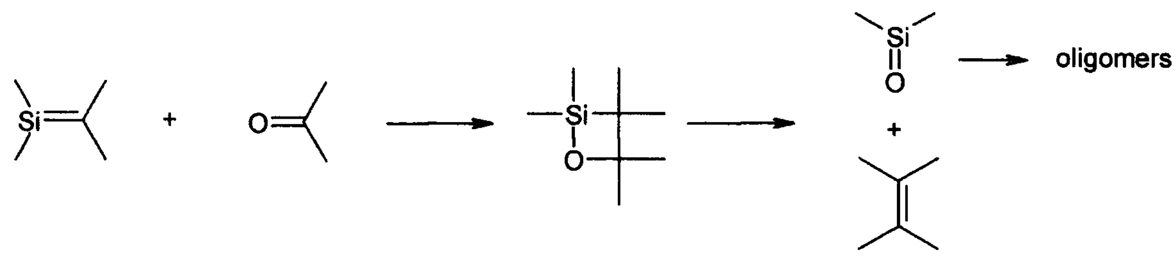


Figure 1.43

Brook has also obtained siloxetanes from the photolysis of acyltris(trimethylsilyl)silanes in the presence of a variety of carbonyl compounds, Figure 1.44.[63]

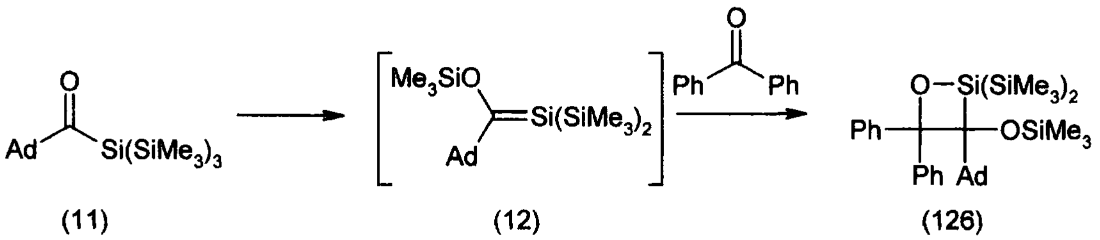


Figure 1.44

The same products were obtained both on co-photolysis and if the carbonyl compound was added to a solution of preformed silene. It is believed that these "thermal" reactions with carbonyl compounds proceed by the initial attack of the lone pair of electrons on the carbonyl oxygen on the silicon atom. This renders the reaction non-pericyclic, and is therefore not in contravention of the Woodward-Hoffman rules.[63]

1.6.4 [4+2] Cycloadditions

One of the most common reactions of both stable and transient silenes is the [4+2] cycloaddition with dienes. As mentioned previously, these reactions are sometimes accompanied by both "ene" and [2+2] reactions.

Wiberg and co-workers have demonstrated that the [4+2] cycloaddition of isoprene or (*E*)-1,3-pentadiene with $Me_2Si{=}C(SiMe_3)_2$ (60), leads to products demonstrating high regioselectivity, forming primarily the "*meta*" isomer, i.e. placing the diene substituent "*meta*" to silicon, Figure 1.45.[64]

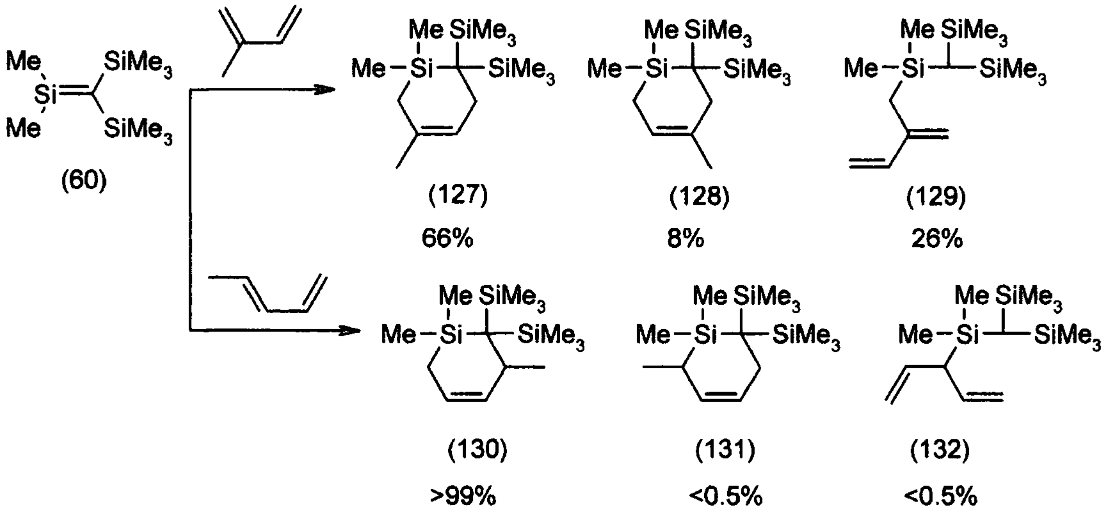


Figure 1.45

The observed regioselectivity of the Diels-Alder reaction is as predicted from frontier orbital theory. The largest coefficient of the LUMO on the silene resides on silicon,[65] interacting with the largest coefficient of the HOMO on the diene in the expected manner, Figure 1.46.[66]

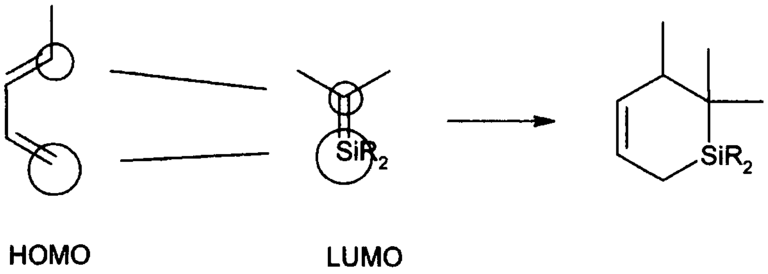


Figure 1.46

Additionally, Wiberg has observed that with (*E*,*E*)-2,4-hexadiene mainly the [4+2] cycloadduct is obtained, however with (*E*,*Z*)-2,4-hexadiene the ene adduct is the major product. This is due to the increased steric interactions between the silene and the (*E*,*Z*) diene in the Diels-Alder transition state, leading to the preferential formation of the more open ene product. As would be expected for a concerted cycloaddition, the [4+2] reactions proceed with retention of relative stereochemistry, Figure 1.47.[67]

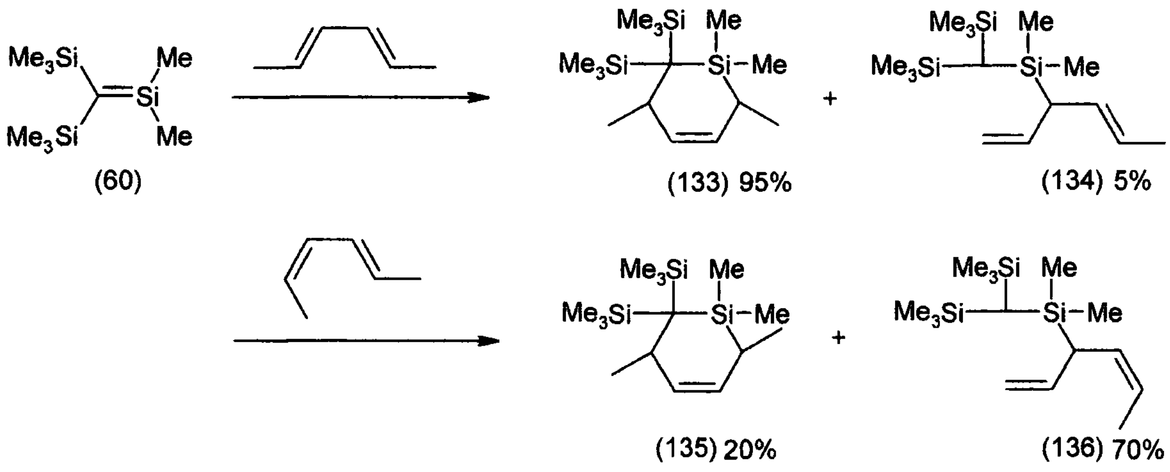


Figure 1.47

Auner and co-workers have reported that the diphenyl-substituted neopentyl silene (111) undergoes [4+2] reactions with dienes. With 2,3-dimethylbutadiene and isoprene "ene" products are also formed; with isoprene a mixture of regioisomers are formed, along with [2+2] cycloadducts. With cyclohexadiene and cyclopentadiene low yields of the [4+2] adducts are formed, with large amounts of the head-to-tail silene dimers being isolated. This is presumably due to the increased steric interactions in the transition states for these cycloadditions, Figure 1.48.[68]

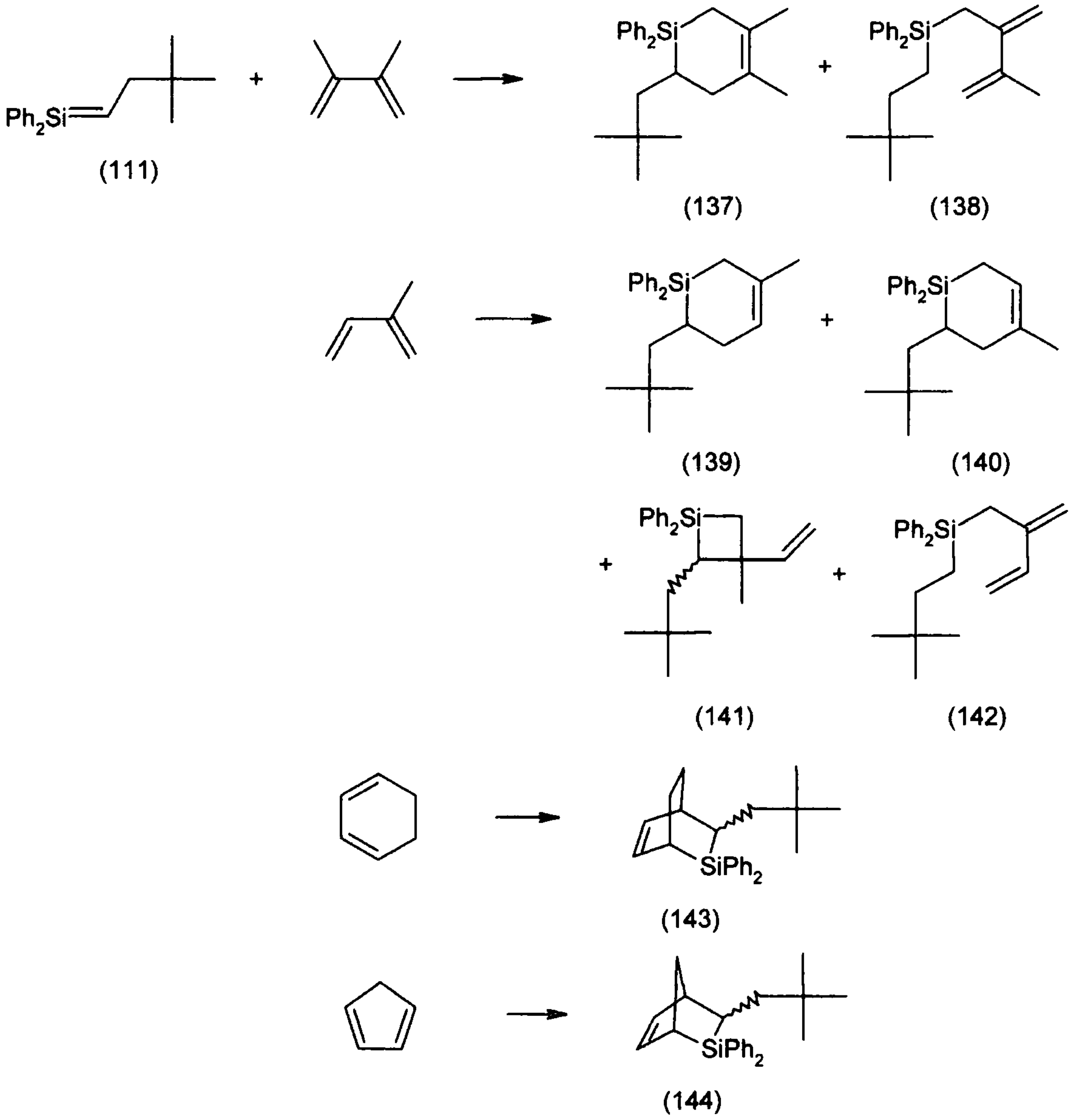
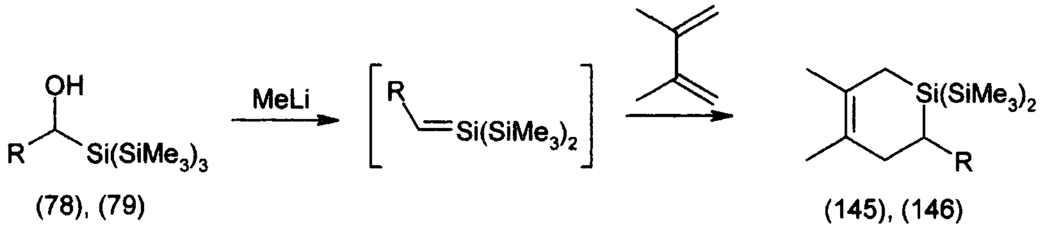


Figure 1.48

Oehme has shown that silenes formed by a Peterson-type elimination can be trapped using 2,3-dimethylbutadiene to give [4+2] cycloadducts exclusively, Figure 1.49.[45]



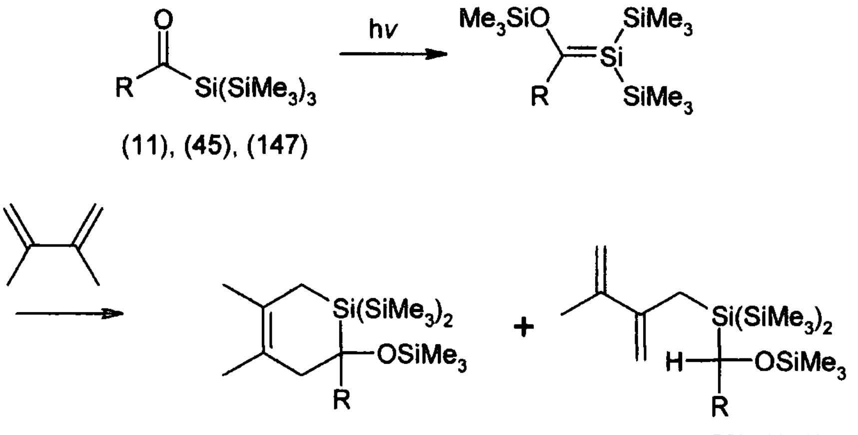
(78), (79)

(145), (146)

(78), (145) R= Mes
(79), (146) R= t-Bu

Figure 1.49

The reactions of stable silenes have been investigated in detail by Brook. It has been found that stable silenes usually react with dienes at room temperature, either by co-photolysis of the acyltris(trimethylsilyl)silane in the presence of diene, or by addition of diene to a preprepared solution of the silene, to give Diels-Alder products, however the competing "ene" reaction products are also found in many cases, Figure 1.50.[69]



(11), (45), (147)

(148), (149), (150)

(151), (152), (153)

(11), (148), (151) R= adamantyl
(45), (149), (152) R= tBu
(147), (150), (153) R= Mes

Figure 1.50

Brook also discovered that the reaction of silene (11) with butadiene led predominantly to give the [2+2] cycloadduct. Attempts to trap any radical intermediates by the addition of Bu3SnH failed, suggesting the reaction is proceeding via a concerted process, Figure 1.51.[69]

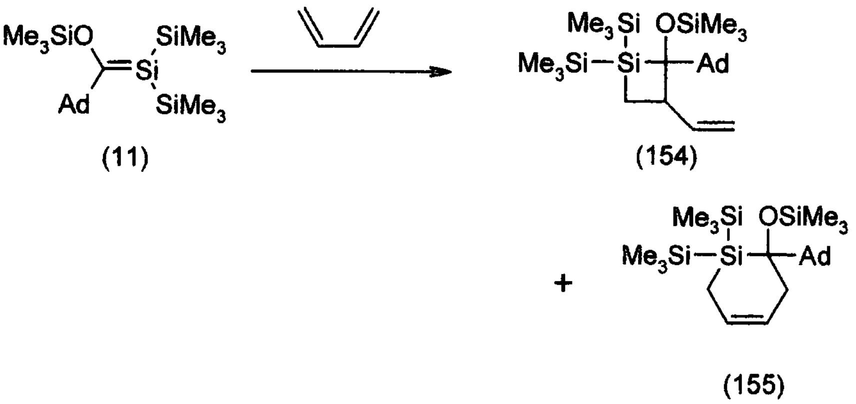

(11)
(154)
(155)

Figure 1.51

Recently, within our group it has been demonstrated that the thermolysis of benzoyltris(trimethylsilyl)silane (87) in the presence of dienes gave Diels-Alder adducts in excellent yield, Figure 1.52. These results are summarized in Table 1.3.[70]

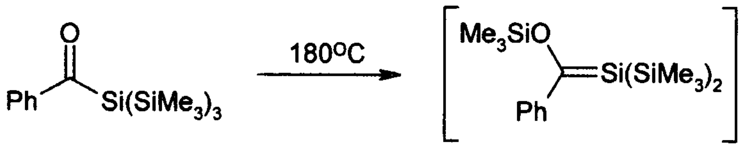

(87)

Figure 1.52

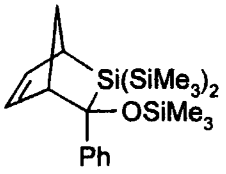
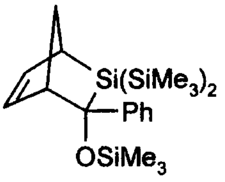
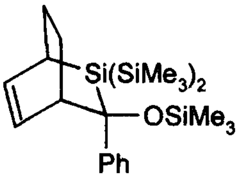
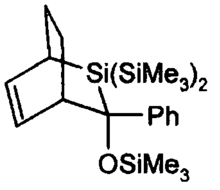
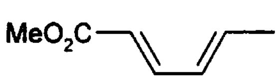
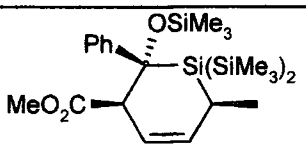
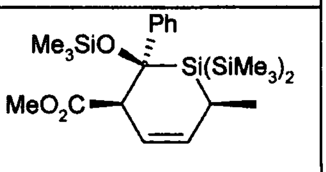
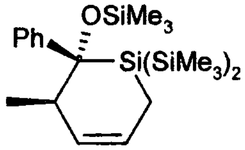
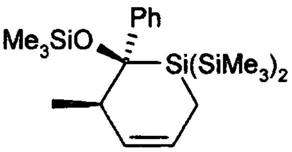
Diene	Conditions	Products
	Toluene 175°C 91%	 (156a) 75:25 (156b)
	Toluene 180°C 64%	 (157a) 75:25 (157b)
	Toluene 180°C 57%	 (158a) 89:11 (158b)
 (83)	Toluene 180°C 62%	 (159a) 85:15 (159b)

Table 1.3

In the case of the reaction with (*E*)-1,3-pentadiene, a single regioisomer is obtained, and in all cases, moderate diastereoselectivity is observed.

Ohshita and co-workers have recently demonstrated that "lithium silenoates", generated from acyltris(trimethylsilyl)silanes and tris(trimethylsilyl)lithium react with butadiene, (*E*)-1,3-pentadiene and isoprene, to give [4+2] cycloadducts. In addition, the reaction with (*E*)-1,3-pentadiene and isoprene gave the products as single regioisomers. No [2+2] or "ene" products were observed. Figure 1.53.

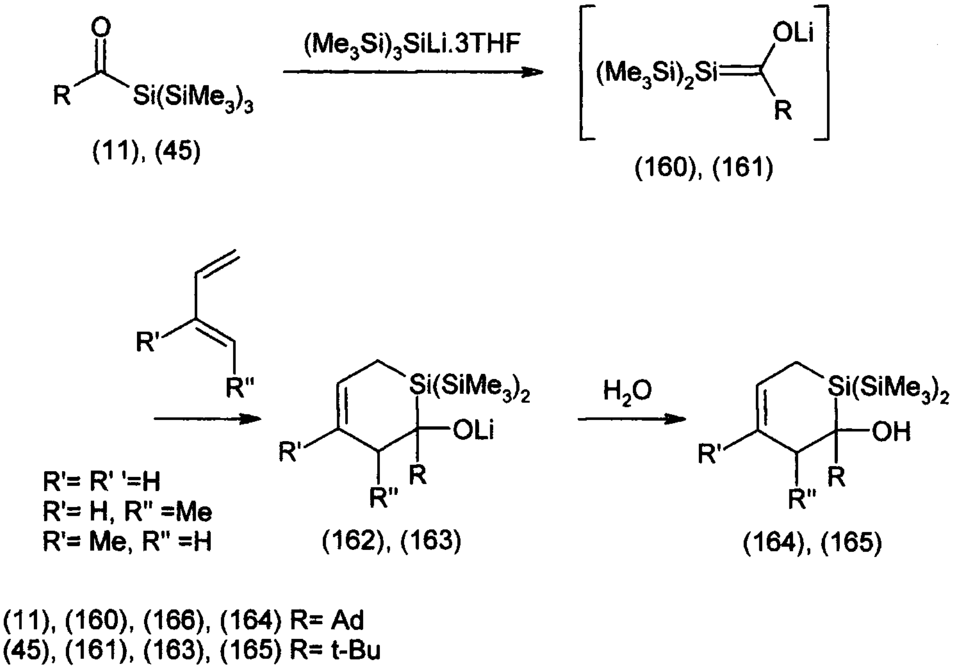


Figure 1.53

The intermediate lithium alkoxides were found to undergo Peterson elimination to give cyclic silenes, which in the presence of excess diene were themselves trapped to form interesting fused ring systems, Figure 1.54.

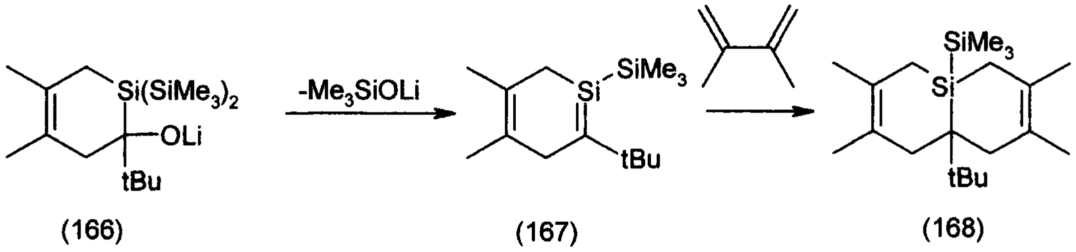


Figure 1.54

1.7 Introduction to Proposed Work

Although the chemistry of silenes has received quite a large amount of study, the reactions of silenes have mainly focused on the trapping of silene intermediates to provide evidence for their existence. To date silenes have not been investigated as potentially useful synthetic reagents. Their high reactivity toward dienes appears to indicate that these species could be used as reagents to introduce functionality to a diene. Elaboration of these cycloadducts using known procedures for oxidising silicon-carbon bonds (discussed in Chapter 4) could lead to a *cis*-stereospecific 1,4 addition across a diene. This process is currently difficult to achieve with the reagents available to the organic chemist, Figure 1.55.

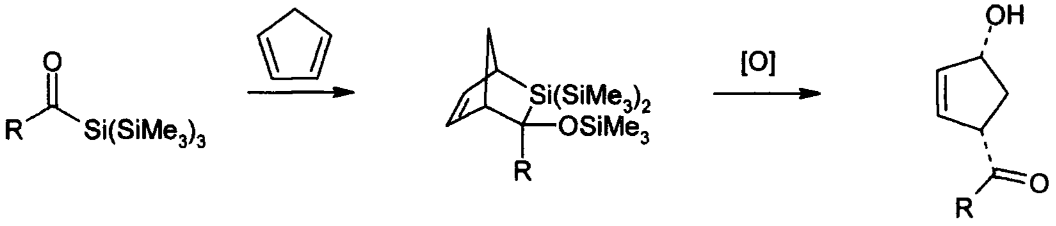
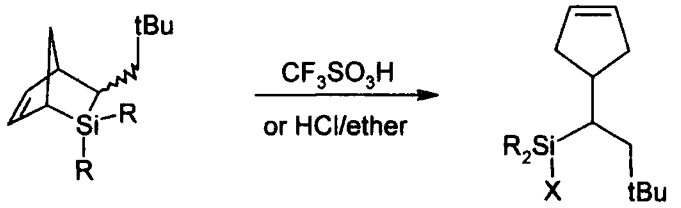


Figure 1.55

Auner has produced the only report (so far) of the subsequent elaboration of a Diels-Alder product formed from the reaction of a silene with a diene. He found that the reaction of 2-silanorbornenes (173)-(175) with triflic acid led to the formation of substituted cyclopentenes, Figure 1.56.[71]



(169), (170), (171)

(169) R= Cl
(170) R= OMe
(171) R= Me

(172), (173), (174)

(172) R=Cl, X=OTf
(173) R=OMe, X=Cl
(174) R=Me, X=Cl

Figure 1.56

In order to fully exploit this, the initial goal was to explore the general diastereoselectivity of the silene cycloadditions, obtained by the thermolysis of acyltris(trimethylsilyl)silanes; this work is detailed in Chapter 2. In Chapter 3, approaches to alternative methods for silene generation are explored. Finally, in Chapter 4 the oxidation of the silene cycloadducts is detailed.

Chapter 2

Thermolysis Reactions

2. Results and Discussion

2.1 Introduction

At the beginning of this work, we required a simple method of forming silenes, allowing us to concentrate on the reactivity of silenes towards dienes. As illustrated previously, a widely reported method is that of Brook, namely the photolysis of acyltris(trimethylsilyl)silanes. Further to this work, previous studies in our group indicated that that silenes could also be formed by thermolysis of these acylsilanes, and in the presence of dienes formed [4+2] cycloadducts exclusively and in excellent yield. Additionally, moderate diastereoselectivities were also observed. The work described in this chapter describes further studies in this area, studying the effect changing the substituent on the acylsilane has on the subsequent silene cycloaddition.

2.2 Synthesis of acyltris(trimethylsilyl)silanes

The initial work in the project involved the synthesis of acyltris(trimethylsilyl)silanes. This was achieved by utilising the method of Gilman[72], initially forming tris(trimethylsilyl)silyllithium from tetrakis(trimethylsilyl)silane[73] and methyllithium, (Figure 2.1).

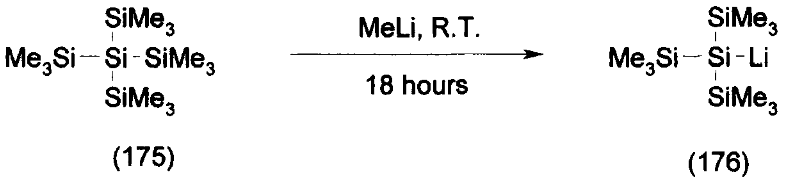


Figure 2.1

Tetrakis(trimethylsilyl)silane is treated with an equimolar amount of MeLi at room temperature. The progress of reaction is monitored using ^{1}H NMR using C_6D_6 as the solvent. Over approx. 18 hours there is a disappearance of the signal at 0.20ppm due to tetrakis(trimethylsilyl)silane, and an appearance of a signal at 0.36ppm due to the formation of the metallated tris(trimethylsilyl)silyllithium species. After cooling to -78°C, the yellow solution is added via cannula to a solution of the appropriate acid chloride, also at -78°C. The resulting solution is then stirred for 4 hours in the dark (the acyltris(trimethylsilyl)silanes are noted as being light sensitive). Workup, followed by purification by flash column chromatography gives the pure acyltris(trimethylsilyl)silane. Table 2.1 below details the different acylsilanes produced.

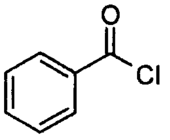
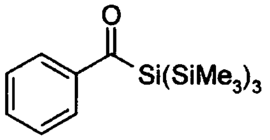
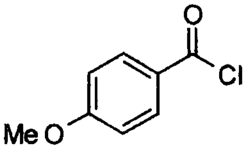
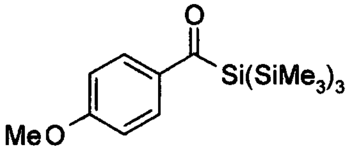
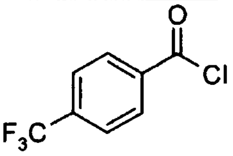
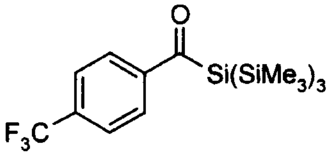
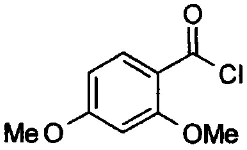
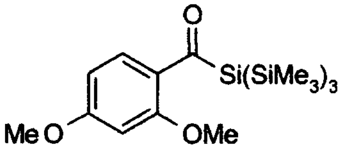
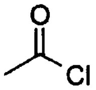
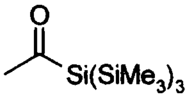
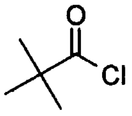
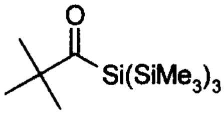
Acid chloride	Acyltris(trimethylsilyl)-silane	Yield, %
 (177)	 (87)	77
 (178)	 (179)	66
 (180)	 (181)	94
 (182)	 (183)	77
 (184)	 (86)	76
 (185)	 (45)	52

Table 2.1

The ^{13}C NMR of such compounds reveals that the carbonyl carbon is strongly deshielded with respect to carbon analogues, the resonance occurring in the region of 230-247 ppm. This is a general feature of all acylsilanes, relative to their carbon analogues.[74] This effect has been ascribed by Brook to "electronegativity" effects,[75] however this appears counter-intuitive as silyl groups attached to carbon usually give rise to low-frequency chemical shifts, due to silicon being more electropositive than carbon. Another explanation is that electron release from the silicon atom leads to the polarization of the carbonyl group, Figure 2.2.[62]

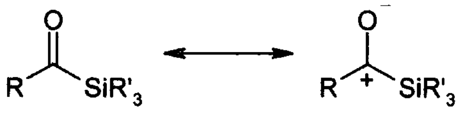


Figure 2.2

However, the interaction of the d-orbitals of silicon with the π-orbital of the carbonyl system is another possible explanation. Additionally, acylsilanes bearing aryl substituents are shifted to a lesser degree, compared to alkyl-substituted acylsilanes. This has been explained by contribution of resonance structures which reduce the amount of positive charge on the carbonyl carbon, Figure 2.3.[76]

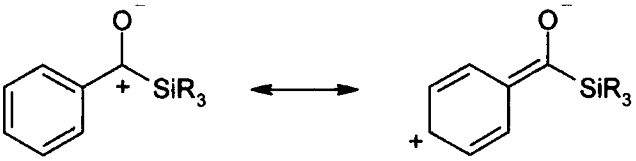


Figure 2.3

The effect of silicon attached to a carbonyl system also leads to lower-frequency carbonyl stretching vibrations (1607-1645cm^{-1}) compared to similar ketones (1675-1712cm^{-1}). The table below gives the ^{13}C NMR shift of the carbonyl carbon, and the C=O stretch for the acyltris(trimethylsilylsilanes), Table 4.2.

Acylsilane	^{13}C NMR shift for carbonyl carbon, ppm	C=O stretching vibration, cm^{-1}
87	234.26	1607
179	232.98	1608
181	236.50	1619
183	237.81	1606
86	244.00	1626
45	248.50	1619

Table 2.2

From Table 2.2 above it can be seen that the carbonyl carbon in alkyltris(trimethylsilyl)silanes is more deshielded than in aryltris(trimethylsilyl)silanes. This is in agreement with the observations made by Brook. The observed C=O stretching frequencies are also in good agreement with those observed previously.[77] The mass spectra of the acylsilanes usually show M^+ and/or MH^+ peaks, and some characteristic fragmentation patterns, however peaks of higher mass are also sometimes observed. This is possibly due to isomerization/dimerization and subsequent fragmentation occurring within the mass spectrometer.

The 4-methoxy- (179) and 4-trifluoromethyl- (181) acyltris(trimethylsilyl)silanes were produced to investigate the effect of electron-donating and withdrawing groups on the diastereoselectivity. Attempts to form the strongly electron-withdrawing 4-nitrobenzoyltris(trimethylsilyl)silane proved futile. Addition of the silyllithium to a solution of 4-nitrobenzoyl chloride led to the formation of a thick red-coloured mixture; after workup no product was isolated on flash column chromatography, and the characteristic high-frequency carbonyl carbon is not observed by ^{13}C NMR. 2,4-dimethoxybenzoyltris(trimethylsilyl)silane (183) was subsequently produced to investigate the effect of a highly electron-rich substituent on the silene, however it must be noted that steric influences of an *ortho*-OMe substituent may cause any difference in diastereoselectivity observed.

The major problem encountered was the widely varying yields of the product acylsilanes obtained, often ranging from poor (~30%) to excellent (>90%). This problem appears to be associated with the method of generation of the tris(trimethylsilyl)silyllithium. Brook has experienced similar problems with this method, and attributed this to possible side reactions occurring. It is, however, possible to form pure $(Me_3Si)_3SiLi.3THF$ as a crystalline solid (in the absence of air), and this appears to be a much better silylating agent, with excellent yields being usually reported.[78].

2.3 Thermolysis of acyltris(trimethylsilyl)silanes with dienes

2.3.1 Introduction

As stated in the introduction, the initial aim of the project was to develop the work initiated within the group into the study of the diastereoselectivity of the [4+2] cycloaddition of (trimethylsilyloxy)silenes with dienes. The effect of electron-donating and withdrawing groups on both the silene and diene were to be investigated. Three dienes were chosen, (*E*)-1,3-pentadiene, cyclopentadiene and dimethyl (*E,E*)-2,4-hexadienoate (186), Figure 2.4.

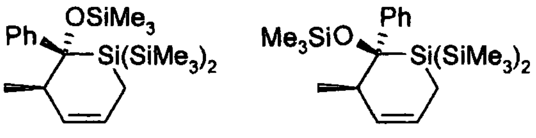
(186)

(*E*)-1,3-pentadiene cyclopentadiene dimethyl (*E,E*)-2,4-hexadienoate

Figure 2.4

Cyclopentadiene was chosen to eliminate the possibility of regioisomers, also the rigidity of its structure prohibits the formation of "ene" products. Dimethyl (*E,E*)-2,4-hexadienoate (186) was chosen as a symmetrical electron deficient diene, and (*E*)-1,3-pentadiene was chosen to investigate the regioselectivity of the Diels-Alder reaction with the silenes.

Previous work within the group indicated that, when heated at ~180°C, benzoyltris(trimethylsilyl)silane reacts with (*E*)-1,3-pentadiene to give the Diels-Alder adduct as a single regioisomer, with reasonable diastereoselectivity forming predominantly the *cis* isomer (with respect to the phenyl substituent), Figure 2.5.[70]



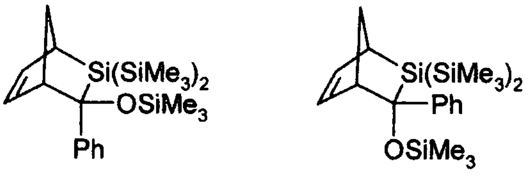
(159a) (159b)

cis 85:15 *trans*

Figure 2.5

The regiochemical control has been rationalized as being due to the $HOMO_{diene}$-$LUMO_{silene}$ interaction, with the largest orbital coefficient of the silene LUMO being located on silicon. However, from a model calculation it appears there is a possibility that there is little energy difference between $HOMO_{diene}$-$LUMO_{silene}$ and $HOMO_{silene}$-$LUMO_{diene}$.[79]

With cyclopentadiene, preference for the formation of the *endo* isomer (with respect to the phenyl substituent) was observed, Figure 2.6.



(160a) (160b)

endo-Ph 75:25 *exo*-Ph

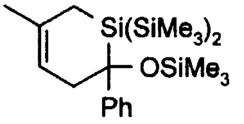
Figure 2.6

This result appears at first hand puzzling, as normally the bulky group (in this case phenyl) would normally occupy the less-hindered *exo* position. With cyclopentadiene it could be argued that interactions between the substituent and the CH_2 bridge of the bicyclic system leads to the *endo* isomer being favoured. It is unlikely that this is a thermodynamically-controlled reaction, as this would form the thermodynamically more favourable *exo* isomer, also once formed, the retro Diels-Alder reaction occurs generally at very high temperatures (>600°C). It is perhaps possible that there is some form of secondary-orbital overlap between the diene and the phenyl group of the silene, stabilising the *endo* transition state.

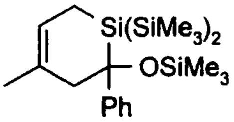
In the work described below, all thermolysis reactions were undertaken using similar conditions. A solution of acyltris(trimethylsilyl)silane and diene (2x excess) in benzene or toluene in a Carius tube, were thoroughly degassed using the freeze-pump-thaw technique, using a minimum of three cycles. Once degassed, the tube was sealed, and heated for 4 hours at 180°C. The resulting mixture was then concentrated, and purified by flash column chromatography.

2.3.2 Trapping with isoprene

Thermolysis of benzoyltris(trimethylsilyl)silane (87) with isoprene gave a ~1:1 mixture of regioisomers (187) and (188), after purification by flash column chromatography, Figure 2.7.



(187)



(188)

Figure 2.7

Wiberg has observed better regiocontrol in the reaction of a different silene with isoprene,[64] (see Figure 1.45), however in that case a significant amount of "ene" product (26% yield) is also observed. It is possible that the high temperatures involved with the thermolysis reaction led to the reduction in regiocontrol.

2.3.3 Trapping with (*E*)-1,3-pentadiene

The formation of the Diels-Alder adduct with (*E*)-1,3-pentadiene can most easily be detected from the presence of a pair of doublets, one for each diastereoisomer, around 1ppm in the ^1H NMR spectrum, corresponding to the protons on the methyl group on the ring. The diastereoselectivity of the reaction is thus easy to assess by comparing the relative intensities of the two doublets. Table 4.3 below shows the products obtained, along with the apparent diastereoselectivity observed.

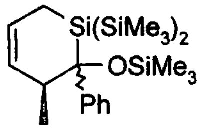
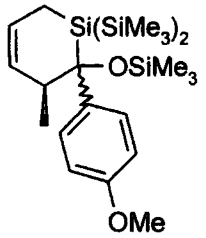
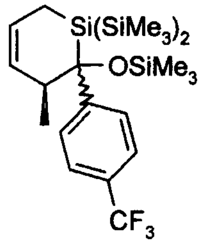
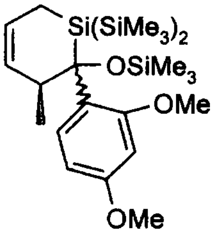
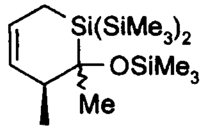
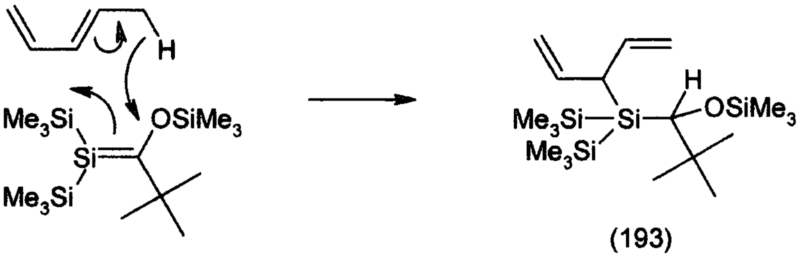
Acylsilane	Product	Yield, %	Diastereoselectivity, *cis*:*trans*
87	 (159a,b)	64	2:1
179	 (189a,b)	80	3:2
181	 (190a,b)	46	4:1
183	 (191a,b)	(80)	~1:1
86	 (192a,b)	20	2:1

Table 2.3

The above results appear to be consistent with those observations made previously within the group. However, the thermolysis of trimethylacetyltris(trimethylsilyl)silane with (*E*)-1,3-pentadiene does not appear to give, at first inspection, the same product. It appears to have possibly undergone both [4+2] and “ene” reactions, given the complexity of the ^{1}H NMR spectrum of the purified product, Figure 2.8.



(193)

Figure 2.8

Brook has observed the “ene” reaction with the thermolysis of trimethylacetyltris(trimethylsilyl)silane in the presence of isoprene,[37] so this is perhaps not a surprising result. However, lack of time precluded further evaluation of this reaction.

2.3.4 Trapping with Cyclopentadiene

Freshly distilled cyclopentadiene was used for all thermolysis reactions. The table below summarizes the products and diastereoselectivites obtained, Table 2.4.

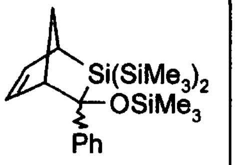
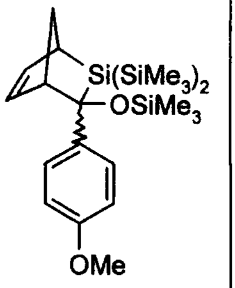
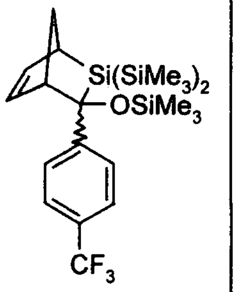
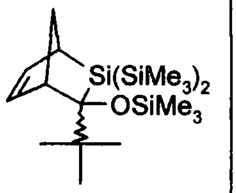
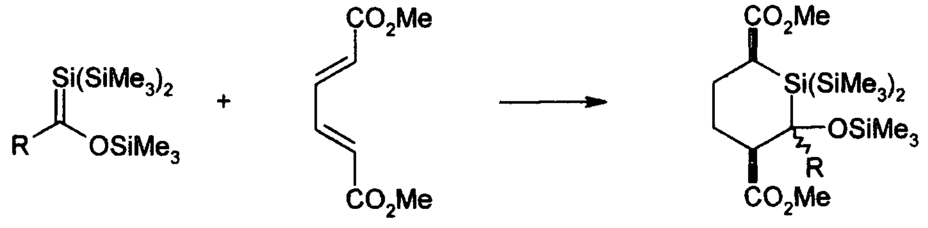
Acylsilane	Product	Yield, %	Diastereoselectivity; endo:exo
87	 (194a,b)	91	3:1
179	 (195a,b)	68	2.5:1
181	 (196a,b)	85	4:1
45	 (197a,b)	70	6:1

Table 2.4

Generally, the yields with cyclopentadiene are greater than those with (*E*)-1,3-pentadiene. Also the 4-CF_3-substituted acylsilane gives slightly higher *endo*:*exo* ratios than those found for benzoyltris(trimethylsilyl)silane and 4-(methoxy)benzoyltris(trimethylsilyl)silane. Trimethylacetyltris(trimethylsilyl)silane appears to demonstrate much higher diastereoselectivities with cyclopentadiene. The diastereoselectivities were deduced by comparison of the ^{1}H NMR spectra with that for (194a,b), for which a crystal structure has been obtained previously within the group.[70]

2.3.5 Trapping with dimethyl (*E,E*)-2,4-hexadienoate

Initially, it was conceived that dimethyl (*E,E*)-2,4-hexadienoate would react with silenes in a [4+2] manner, Figure 2.7.



(186)

Figure 2.7

However, on inspection of the ^{1}H NMR spectra for the reactions performed, it became clear that the coupling patterns observed in no way correlated with the structure. It is possible that the two other reactions could have occurred, either a heteroatom-[4+2] reaction, or a [2+2] cycloaddition, Figure 2.8.

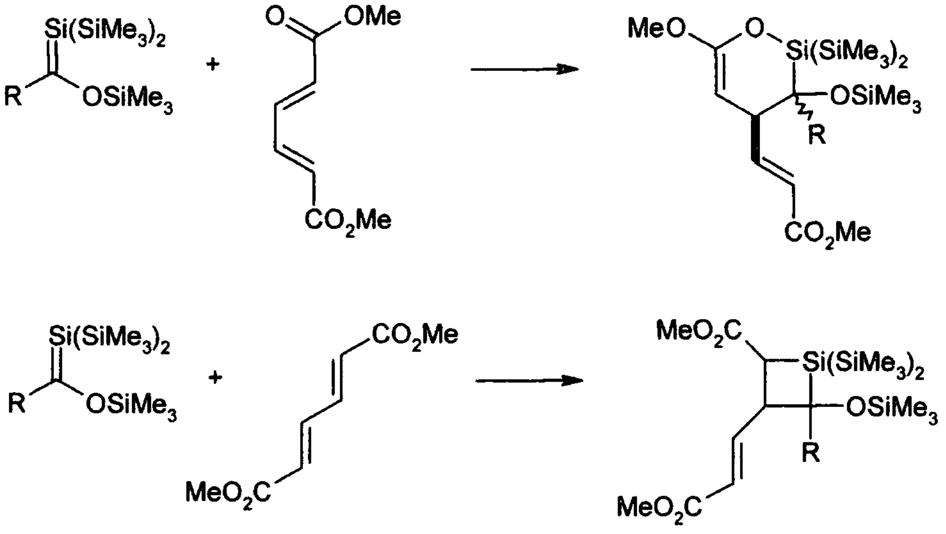


Figure 2.8

Both the ^{13}C NMR and the IR spectra of these adducts provide evidence of the presence of an α,β-unsaturated ester system within the molecule. However, the ^{1}H NMR only contains 2 vinyl protons, ruling out the hetero-Diels-Alder product. ^{1}H COSY experiments on two of the adducts obtained (R=tBu, pMeOC_6H_4-) provide evidence that supports the formation of the [2+2] adduct. A model of the initially proposed [4+2] adduct appears to show that the structure is considerably sterically crowded in any conformation. This may well explain why this product is not detected.

The most interesting observation is that these [2+2] cycloadducts are formed as single stereoisomers, from several possible isomers, no other isomeric material being detected. A coupling constant of J=~15Hz for the α,β-unsaturated system indicate that the stereochemistry is maintained. Table 2.5 below summarizes the products and yields obtained.

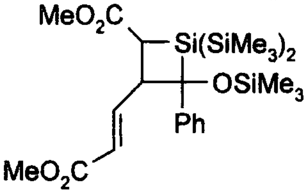
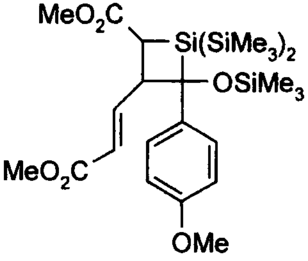
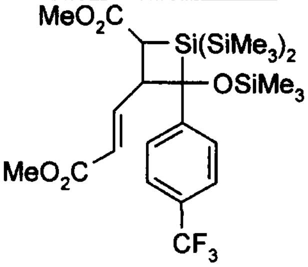
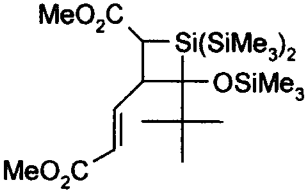
Acylsilane	Product	Yield, %
87	 (198)	67
179	 (199)	49
181	 (200)	49
45	 (201)	20

Table 2.5

2.3.6 Conclusions

It appears from the data presented above that there is little effect upon varying the substituents on the silene on the diastereoselectivity of the cycloaddition reactions. Brook has reported that 4-methoxyphenyl and C_6F_5- substituents have little or no effect on the stability of the silenes generated, compared with the parent benzoyltris(trimethylsilyl)silane.[80] The slight variations in observed diastereoselectivity could be due to the secondary orbital interaction mentioned above, with substituents affecting the π-system of the phenyl group such that the interaction is increased when the substituent is CF_3, and decreased when the substituent is OMe. Also, the high temperatures used in the reaction may lead to a small difference in activation energy between the transition states for the *endo* and *exo* products.

The results of the thermolysis reactions with diene diester (186) appear to give predominantly a single isomer of the [2+2] isomer. This is an interesting result, as trimethylsilyloxy-substituted silenes almost exclusively undergo [4+2] reactions with substituted dienes.

2.4 Acylbisphenyl(trimethylsilyl)silanes

2.4.1 Introduction

In the light of our work focusing on the oxidation of the adducts obtained from the [4+2] reaction of silenes with dienes (see Chapter 4), we wished to form silenes bearing phenyl substituents on the silicon atom. Following our established thermolysis protocol, this required the synthesis of acylbisphenyl(trimethylsilyl)silanes. The synthesis of such acylsilanes has been described by Brook, using a similar protocol to that used for the synthesis of acytris(trimethylsilyl)silanes described above, Figure 2.9.[81]

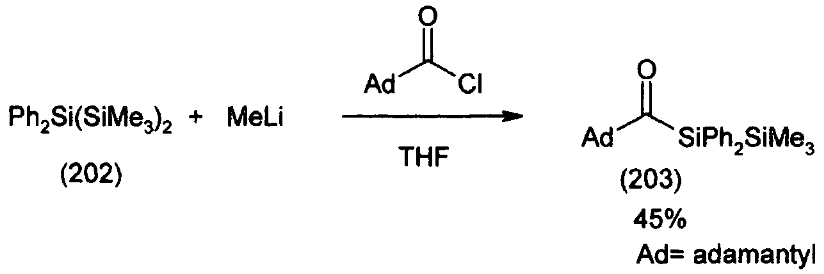


Figure 2.9

2,2-Diphenyl-1,1,1,3,3,3-hexamethyltrisilane (202) was prepared by the Grignard reaction of trimethylsilyl chloride and dichlorodiphenylsilane (204), Figure 2.10.[82]

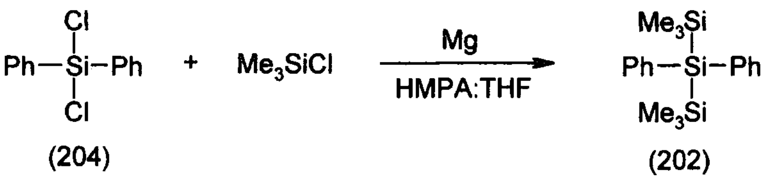


Figure 2.10

The original procedure used HMPA as solvent. The potential health risks associated with this solvent led us to investigate safer alternatives. DMPU used in place of HMPA led to the formation of the product in low yield. In our hands, the use of a 1:1 mixture of HMPA:THF was found to give the best yield.

Treatment of trisilane (202) with methyllithium, followed by addition of this mixture to benzoyl chloride gave benzoylbisphenyl(trimethylsilyl)silane (205), Figure 2.11

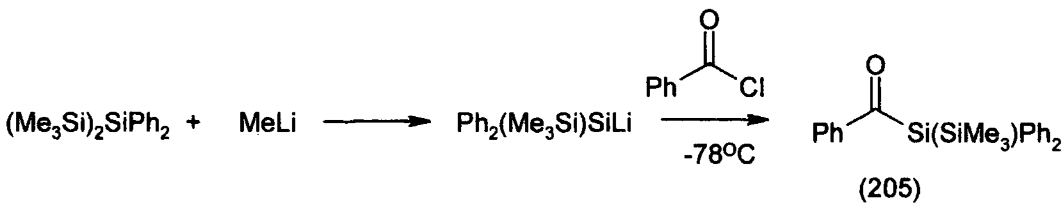


Figure 2.11

2.4.2 Thermolysis of benzoylbisphenyl(trimethylsilyl)silane

Benzoylbisphenyl(trimethylsilyl)silane (205) was thermolysed in the presence of (*E*)-1,3-pentadiene as described previously. Unfortunately, no product silacycle was isolated, with only polymeric material apparently present, Figure 2.12.

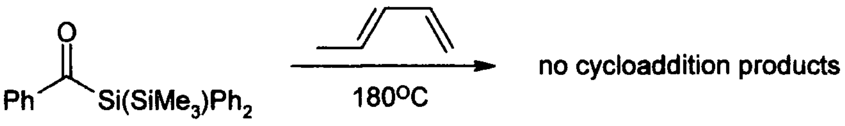
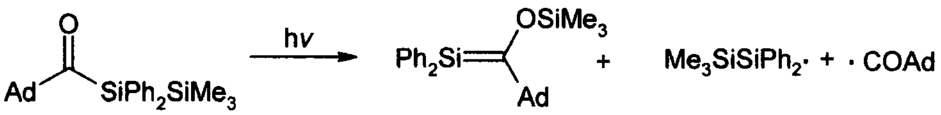


Figure 2.12

Attempts using shorter reaction times and lower temperatures appeared not to be successful either.

Brook has indicated that these silenes are less stable than their bis(trimethylsilyl) substituted analogues. The photolysis of adamantyl-substituted acylsilane (203) led to the formation of expected silene (206), accompanied with radicals (207) and (208), formed by a Norrish type 1 cleavage, Figure 2.13.[81]



(203) (206) (207) (208)

Figure 2.13

It appears likely, therefore, that the lower stability of these silenes is leading to the lack of success of the thermolysis reaction.

2.5 Conclusions

Overall, electron-donating and withdrawing substituents appear to have a small effect on the diastereoselectivity of the Diels-Alder reactions observed above. The apparent formation of the [2+2] adduct with the diene diester (190) is an interesting and unusual result. The major problem with the thermolysis route remains the use of sealed tube equipment, limiting the scale and the nature of the substrates used. It also appears that this method is only applicable to acyltris(trimethylsilyl)silanes, as the thermolysis of the bisphenyl-substituted acylsilane (205) was wholly unsuccessful.

In addition, the further elaboration of the silacycles formed by oxidising out the ring silicon (as discussed in Chapter 1), the main thrust of the project, led us to investigate alternative methods of forming silenes, allowing us to vary the substituents on the silicon atom.

Chapter 3

Alternative Methods of Silene Formation

3.1 Introduction

The previous chapter illustrated the formation of silenes from acyltris(trimethylsilyl)silanes using thermolysis. The problems with this technique are twofold:

1) The high temperatures involved (~180°C) necessitate the use of specialist sealed apparatus, leading to potential problems with scaling up the reaction.
2) The high temperatures involved may lead to the low diastereoselectivity observed.

We therefore wished to pursue a different route to silenes at lower temperatures. This would eliminate the need for sealed glass tubes (Carius tubes) or "bomb" equipment, which are thick-walled metal reaction vessels. In addition, lower temperatures may lead to an increase in the diastereoselectivity of the cycloaddition reactions, by increasing the relative difference in the transition state energies for the *endo* and *exo* transition states.

One solution to the problem appeared to be the use of head-to-head silene dimers as silene precursors. Brook has indicated that these dimers, formed from the photolysis of acyltris(trimethylsilyl)silanes, undergo thermal cycloreversion to give silenes at much lower temperatures than that required by the thermolysis of acyltris(trimethylsilyl)silanes, Figure 3.1

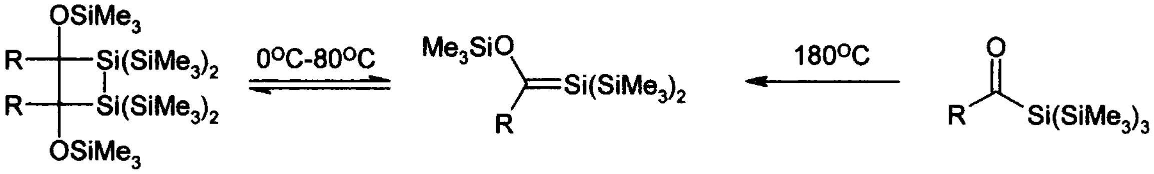


Figure 3.1

When R= tBu it was found that the dimer and silene exist in equilibrium in solution, while when R= Ph the reduction in steric bulk led to a more stable dimer which reverted on gentle heating (60°C-80°C). These temperatures are much lower than those for the direct thermolysis of acyltris(trimethylsilyl)silanes.

3.2 Formation of Silene dimers

3.2.1 Introduction

The generation of dimers required the use of photolysis equipment. Initially a 1kW mercury arc lamp was used. A solution of benzoyltris(trimethylsilyl)silane in cyclohexane, degassed by passing a stream of argon through the solution for 30 minutes, was irradiated for 20 minutes. During this time, the intense yellow colour of the acylsilane solution diminished significantly. Removal of the solvent followed by purification by column chromatography gave the silene dimer in a moderate yield. The yield of dimer was lower than that obtained previously.[37] This was most likely because the power of the lamp used was far greater than that used before. In addition the heat generated by the lamp led to significant heating of the reaction solution. In an attempt to circumvent this latter issue, a reaction vessel equipped with a water-cooled insertion probe was used. This reduced the temperature of the solution, alas the yield did not improve significantly, Figure 3.2

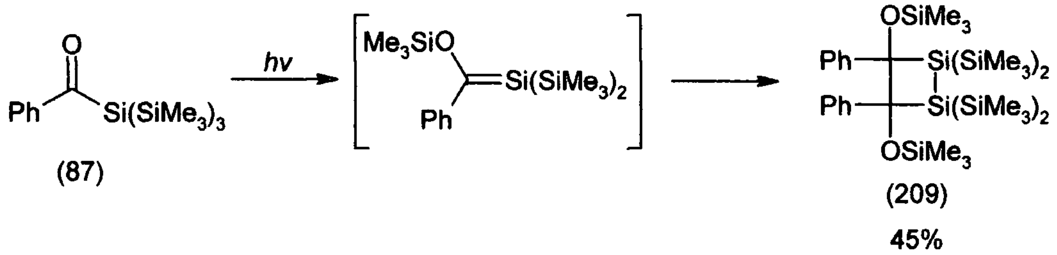


Figure 3.2

With the silene dimer in hand, the next step was to investigate the thermal cycloreversion to give the parent silene. Silene dimer (209) was dissolved in THF, in the presence of a twofold excess of (*E*)-1,3-pentadiene. The mixture was heated in a rotaflow tube at 70°C for 18 hours. Concentration gave a colourless oil, whose ^1H NMR spectrum contained signals due to both silene dimer and the [4+2] Diels-Alder adduct produced by the earlier thermolysis reaction. In this case, however, a slight increase in diastereoselectivity, from 2:1 to 3:1 favouring the *cis* diastereoisomer (159a) was observed. We had postulated that a decrease in reaction temperature could lead to an increase in diastereoselectivity, however the observed increase is disappointingly small.

Work in other areas, principally in the oxidation of the Diels-Alder adducts, led us to investigate different silene dimer species as silene precursors. This is discussed in the following section.

3.2.2 Alternative silene dimers

During our work on the oxidation of Diels-Alder adducts of silenes, we wished to form silenes bearing phenyl substituents on the silicon atom. This would allow us to use a variety of electrophilic reagents to displace the phenyl group, Figure 3.3.

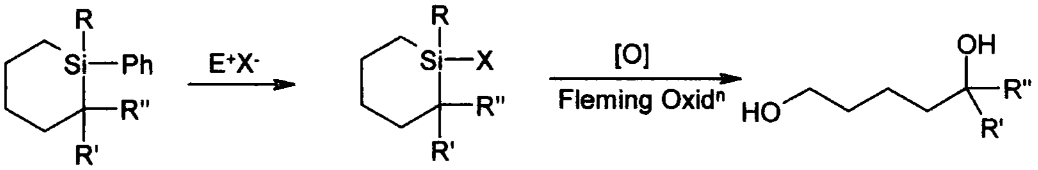


Figure 3.3

Brook has described the synthesis of alkyl and aryl-substituted acylbis(trimethylsilyl)silanes. These are formed in an analogous manner to acyltris(trimethylsilyl)silanes by coupling phenylbis(trimethylsilyl)silyllithium and an acid chloride, Figure 3.4.[83]

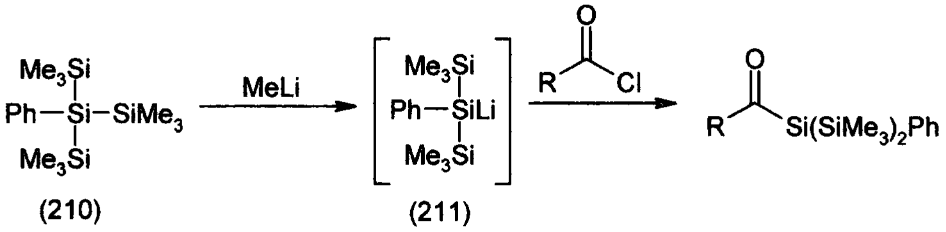


Figure 3.4

He went on to show that these acylsilanes undergo photochemical rearrangements to give silenes, Figure 3.5.[83]

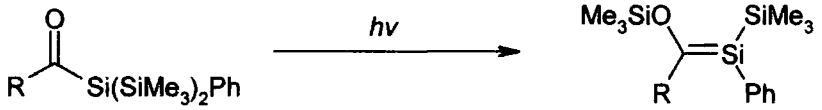


Figure 3.5

Some of these silenes subsequently undergo complex rearrangements, however one example was found to give the head-to-head silene dimer in almost quantitative yield, Figure 3.6.

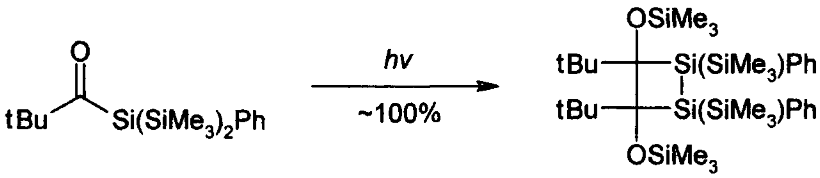

(212) (213)

Figure 3.6

Furthermore, this dimer was found to react with ethanol at room temperature, to give products associated with the nucleophilic reaction of alcohols with the parent silene, Figure 3.7.

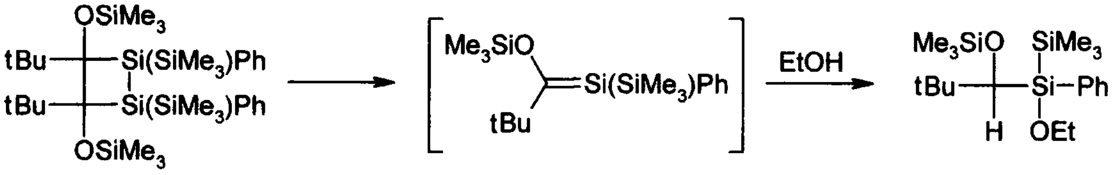

(213) (214) (215)

Figure 3.7

However, no other experiments that would support the formation of an intermediate silene, such as reactions with dienes, have been performed. This is perhaps surprising, as it is possible to imagine the alcohol reacting directly with the dimer to give the observed product. If the silene was indeed formed from the dimer, this result appeared initially to overcome two of the problems we had encountered so far in the synthesis of silenes, namely low-temperature silene formation and the formation of silenes bearing phenyl substituents on silicon. We therefore embarked on the formation of these acylbis(trimethylsilyl)phenylsilanes, and the subsequent photolysis reaction.

3.2.3 Formation of acylbis(trimethylsilyl)phenylsilanes

In order to produce the acylbis(trimethylsilyl)phenylsilanes required for subsequent photolysis, it was necessary to produce phenyltris(trimethylsilyl)silane. Brook has produced this compound in two steps from tris(trimethylsilyl)silane, firstly reacting this with bromobutane to give the intermediate bromosilane, using a procedure used by Gilman.[84] This was followed by the addition of phenylmagnesium bromide, Figure 3.8.

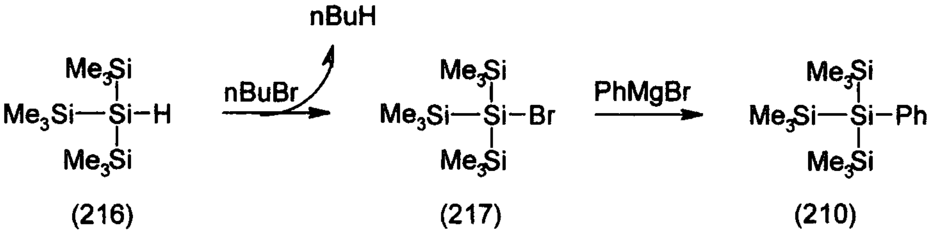


Figure 3.8

Due to the expense of commercially available tris(trimethylsilyl)silane, this was formed through the reaction of tetrakis(trimethylsilyl)silane with MeLi, followed by aqueous workup and distillation, using the procedure of Gilman and co-workers.[85] It was then found that it was possible to form phenyltris(trimethylsilyl)silane in a "one pot" procedure, without the need to isolate and purify the intermediate bromosilane. The reaction sequence could be followed easily by GC analysis. It was found that after standard extractive workup that the "crude" material, a pale brown semisolid, was ~90-95% pure by GC analysis, and could be used in the subsequent step quite satisfactorily without further purification. However, yields in further reactions could be increased slightly by purifying the phenyltris(trimethylsilyl)silane by filtration though a short pad of silica, with petrol as the elutant. This gave the phenyltris(trimethylsilyl)silane as a colourless, waxy solid.

With the phenyltris(trimethylsilyl)silane in hand, the precursor acylbis(trimethylsilyl)phenylsilanes were synthesized using a procedure modified from that used by Brook and co-workers.[83] They initially formed the silyllithium species in THF, followed by the replacement of this solvent with hexane, with subsequent addition to an ice-cooled solution of the acid chloride in hexane. However, in our hands it was found that the whole sequence could be performed more efficiently in THF throughout, to give the product acylsilane in excellent yields, Figure 3.9.

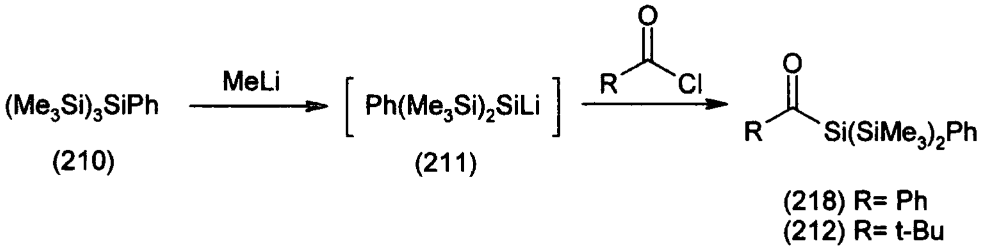


Figure 3.9

However, it proved impossible to form the acetyl derivative using this methodology. It seemed likely that the presence of enolizable protons on the carbon atom α- to the carbonyl could be causing the problem in this case. As an alternative route, it can be envisaged that, like ketones, acyl silanes could be formed by the oxidation of a suitably substituted secondary alcohol to give the acylsilane, Figure 3.10.

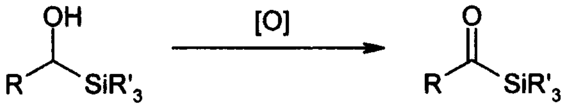


Figure 3.10

Oehme and co-workers have generated such silyl alcohols by the addition of silyl-Grignard reagents to aldehydes, the silyl-Grignard reagents being formed by the transmetallation of the pre-formed silyllithium reagent with $MgBr_2$ Figure 3.11.[45]

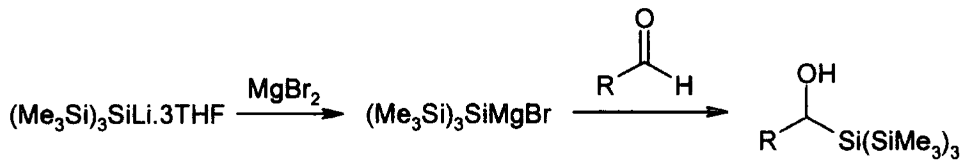


Figure 3.11

In our hands it was found unnecessary to isolate the intermediate silyllithium species. A solution of phenyltris(trimethylsilyl)silane in THF was reacted with an equimolar amount of methyllithium. After 18 hours the THF was removed under reduced pressure, and replaced with an equal volume of dry ether. This solution was then added via cannula to a suspension of $MgBr_2$ in ether. After stirring for 1 hour, this mixture was cooled to -78°C, whereupon the aldehyde (in twofold excess) was added dropwise. The mixture was stirred at -78°C for a further 18 hours. Acid workup, followed by flash column chromatography gave the desired silyl alcohol (220) or (221), Figure 3.12.

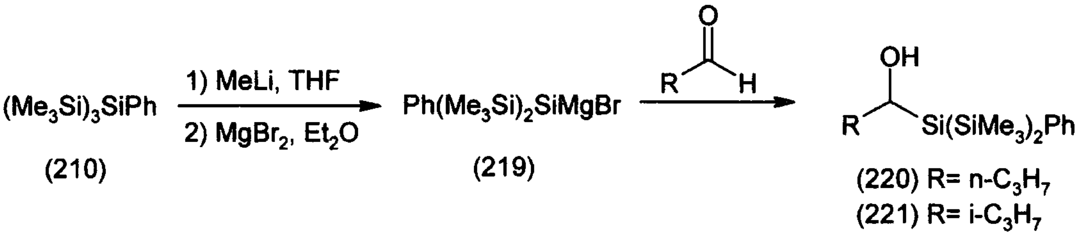


Figure 3.12

Initial attempts to carry out the oxidation involved the use of PCC on alumina. However, this led to the complete decomposition of the starting material. However, reaction of the silyl alcohols under standard Swern conditions (oxalyl chloride, DMSO and triethylamine) gave the desired acylsilanes in excellent yields, Figure 3.13.

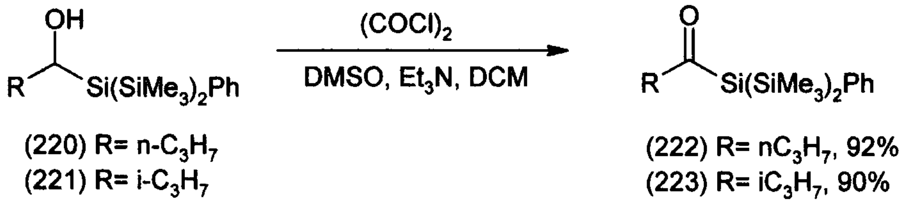


Figure 3.13

3.2.4 Photolysis of acylbis(trimethylsilyl)phenylsilanes

With the acylbis(trimethylsilyl)phenylsilanes in hand, the next stage was to attempt the photochemical formation of the corresponding silene species. This stage of the work was carried out at GlaxoWellcome's Medicines Research Centre in Stevenage. Amongst the photochemical equipment available was a Photochemical Reactors Ltd. 125W medium-pressure Hg lamp, which was similar in description to that used by Brook in his experiments. The equipment is made up of a reaction vessel, inside which was fitted a water-cooled jacket which surrounded the lamp itself. A nitrogen inlet was provided to allow degassing of the solution prior to, and agitation during, photolysis. A schematic diagram of the lamp apparatus is provided below, Figure 3.14.

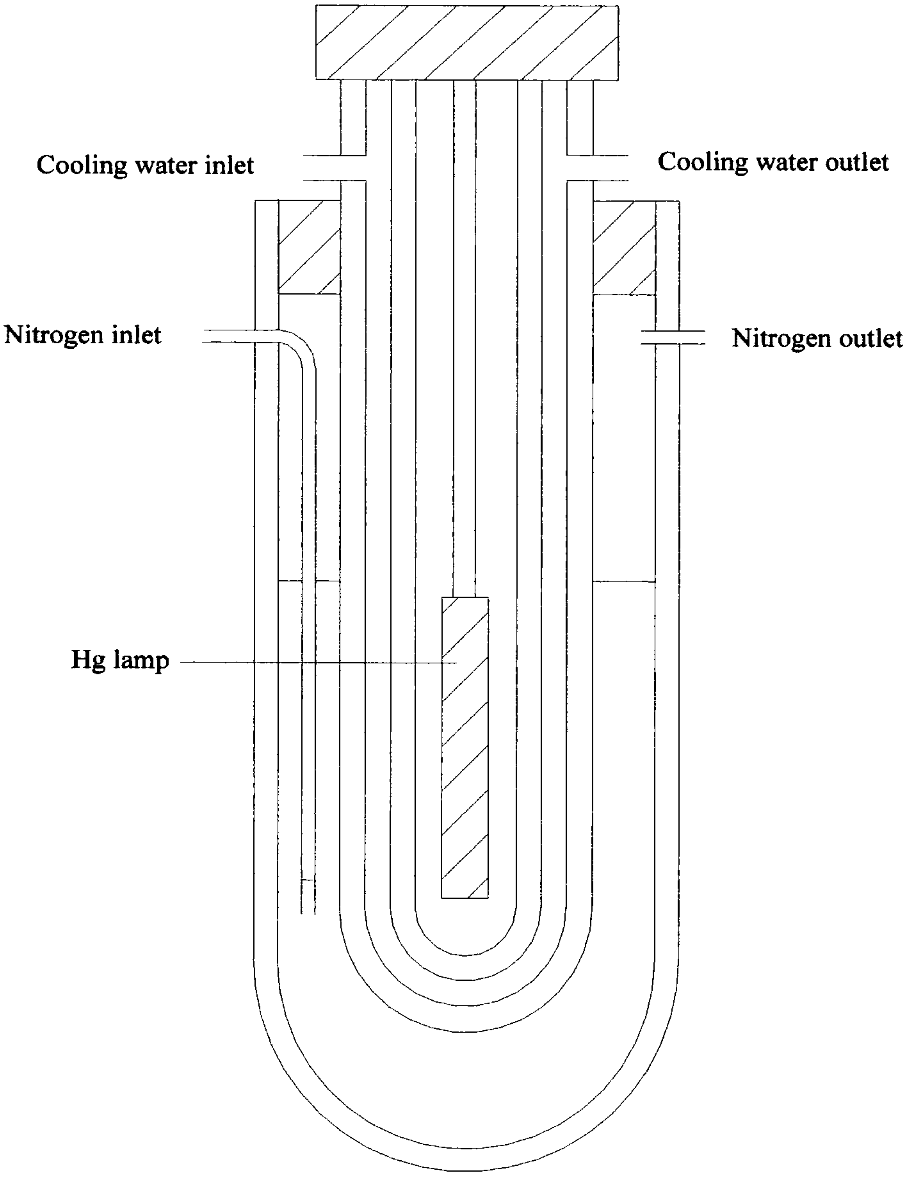


Figure 3.14

Initially work focused on the photolysis of trimethylacetylbis(trimethylsilyl)phenylsilane (212). Brook indicated that, on an NMR tube scale, this acylsilane underwent photolysis to give "an essentially quantitative yield" of head-to-head silene dimer (213), Figure 3.15.[83]

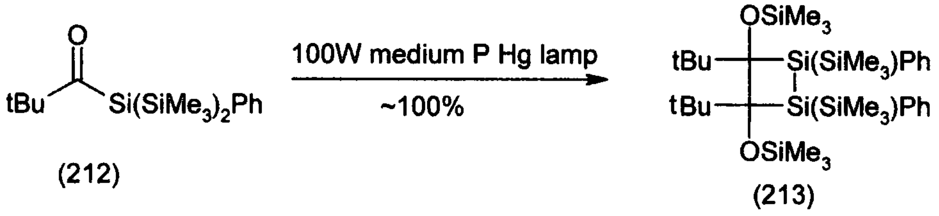


Figure 3.15

In our hands, it was found that photolysis of acylsilane (212) over a 30-40 minute period led to complete consumption of the acylsilane, as evidenced by thin-layer chromatography. Concentration of the cyclohexane solution led to a white solid precipitating out of the solution. It was found that this solid was the silene dimer, and simple filtration gave the product as essentially pure (by ^{1}H NMR).

However, on returning to Durham it was found impossible to reproduce this reaction at all, using a 100W medium-pressure Hg lamp available in the department. At this point we gained access to the 125W lamp used at GlaxoWellcome. Measurement of the outputs of both these lamps indicated that the spectral output of the lamp available in Durham, Figure 3.16a was different to that used at GlaxoWellcome, Figure 3.16b.

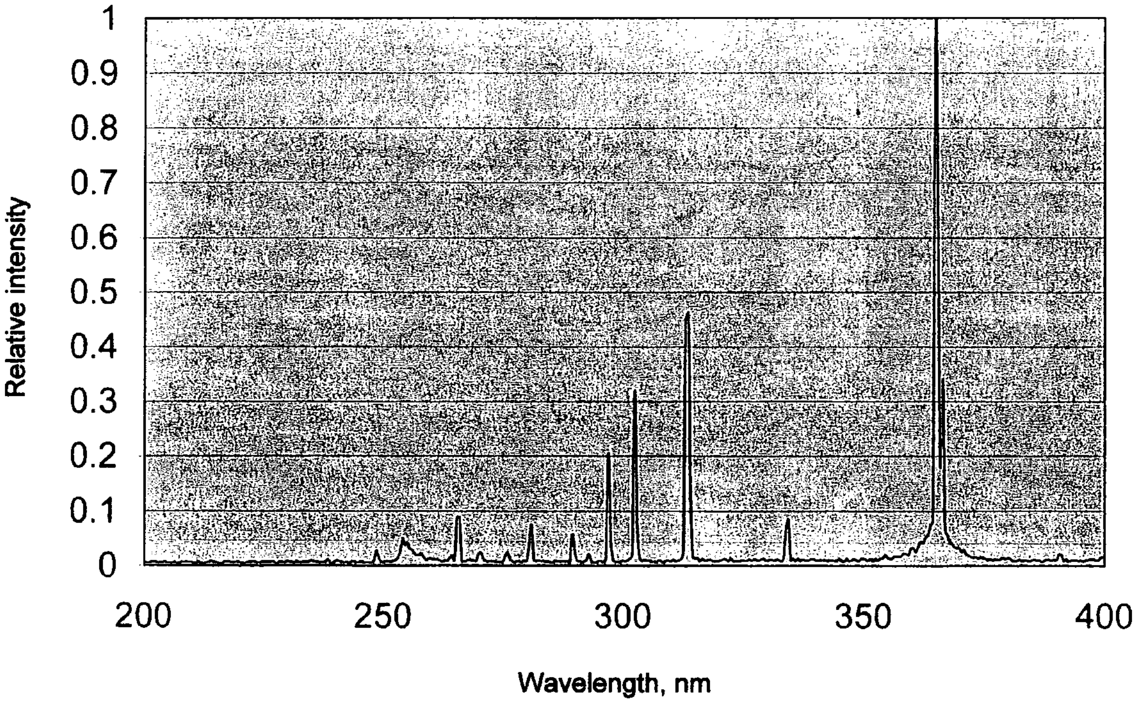


Figure 3.16a

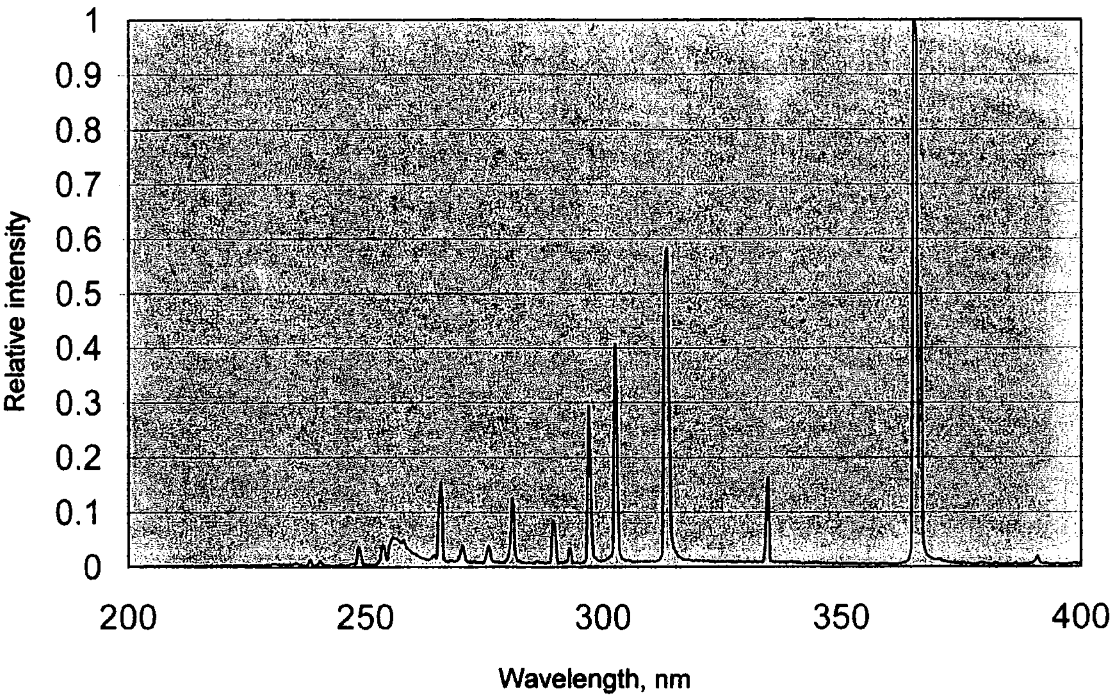


Figure 3.16b

The output of each lamp was focused onto the entrance slit of a 320mm focal length monochromator (ISA Triax 320), both entrance and exit slits were adjusted to give a band pass of approx. 2nm focal width. The transmitted light was detected by a photomultiplier (Mamamatsu R928) operating in photon counting mode. Spectra were recorded by scanning the monochromator from 200-400 nm in 1nm steps, recording the count rate at 1 nm intervals. The control of the monochromator and data acquisition were performed by a PC using "Labview" software.

The main difference between the "Durham" and "Glaxo" mercury lamps is the sharp reduction in intensity of the 253.7 nm line of the "Glaxo" lamp. The diminished intensity is due to a phenomenon known as "inversion", where self-absorption occurs due to a higher concentration of cool mercury atoms near the lamp walls. This is a very common feature of medium-pressure lamps. This difference in the emission profile indicated that the lamp used at Durham was of a lower mercury pressure, and this appeared to be a likely cause of the problems we were encountering.

Initially, using the 125W lamp in Durham proved no more successful, even when using the same solvent (Fisher). This was very surprising and frustrating, given the success of the reaction at GlaxoWellcome. At this stage, it appeared that the only difference could be the cooling water running around the lamp. At GlaxoWellcome this water was recycled, and treated to prevent formation of diseases, whereas mains water was used in Durham.

Various metal salts can be used as filters in photochemical reactions, the most popular being $CuSO_4$. Use of a ~0.5M solution of $CuSO_4$ as the cooling liquid round the lamp resulted in vastly improving the reaction, giving yields of the silene dimer (213) comparable to those obtained previously. It appears that the additive in the cooling water used previously was indeed absorbing some of the higher energy UV radiation emitted by the lamp.

Extensions to other systems were then explored. The photolysis of phenylbis(trimethylsilyl)phenylsilane (218) led to the formation of the expected dimer (224) in very small yield, accompanied by large amounts of decomposed material, Figure 3.17.

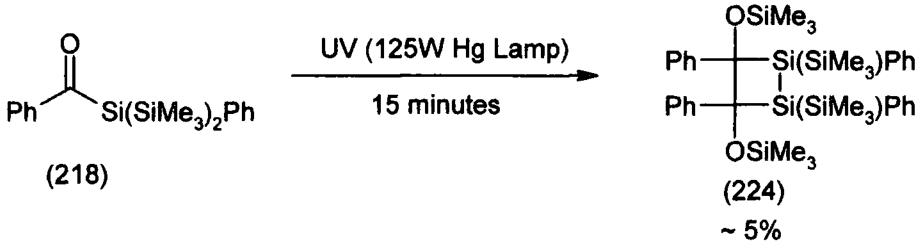


Figure 3.17

Photolysis of the alkyl-substituted acylbis(trimethylsilyl)phenylsilanes (222) and (223), under the same conditions used before, led to the decomposition of the starting acylsilanes, with no dimers being detected.

It appears that the photochemical formation of the silene is critically dependent on the nature of the substituent. It is unclear whether photolysis of the acylsilanes above led directly to decomposition, or whether the product silene or silene dimer were themselves decomposed by the UV radiation. It is perhaps not surprising that some of these photochemical reactions appear to give difficulties, given that some silenes are known to undergo further photochemical transformations. It is possible that the use of different wavelengths of UV radiation and/or the use of different filter media could improve this reaction, however, lack of time meant that no work could be carried out in this area.

3.2.5 Silene dimer reversion-Formation of silene cycloadducts

With the silene dimer (213) in hand, the next stage was to investigate the cycloreversion of the dimer in the presence of dienes. A solution of dimer (213) was stirred at room temperature in the presence of a twofold excess of (*E*)-1,3-pentadiene. After 10-12 hours, tlc showed the consumption of the starting material, and the appearance of a new spot, with a slightly higher R_f. Concentration, followed by purification by flash column chromatography, gave the Diels-Alder cycloadduct (225) in good yield, Figure 3.18.

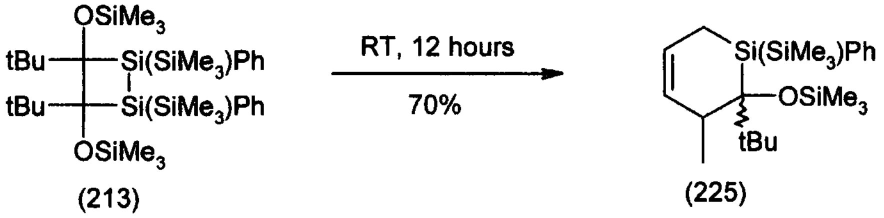


Figure 3.18

Repeating the reaction in the presence of 1,3-cyclohexadiene led to the formation of the bicyclic adduct (226) in a similar yield, Figure 3.19.

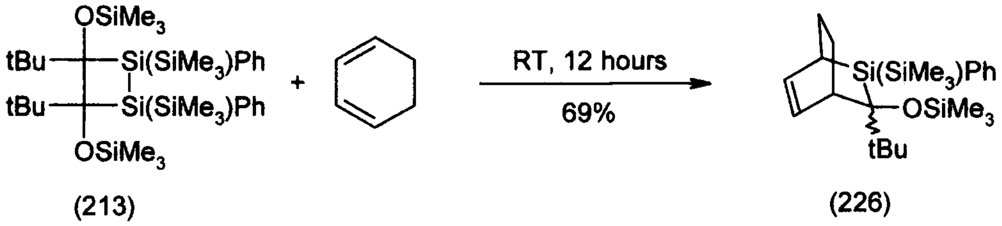


Figure 3.19

In both cases, only the [4+2] cycloadduct was formed in excellent yield. However, both of these adducts appear to have been formed as 1:1 diastereomeric mixtures. Overall, though, we have found that silene dimers can be used as stable silene precursors.

The attempts to oxidize these adducts is discussed in Chapter 4.

3.3. Lewis acid reactions with Acyltris(trimethylsilyl)silanes

3.3.1 Introduction

An appealing but, before this work started, unexplored method of forming silenes was potentially by using trimethylsilyl-based Lewis acids (for example TMSOTf). We proposed that they may react with acyltris(trimethylsilyl)silanes, initially by coordination at the carbonyl oxygen, followed by elimination to give the silene, Figure 3.20.

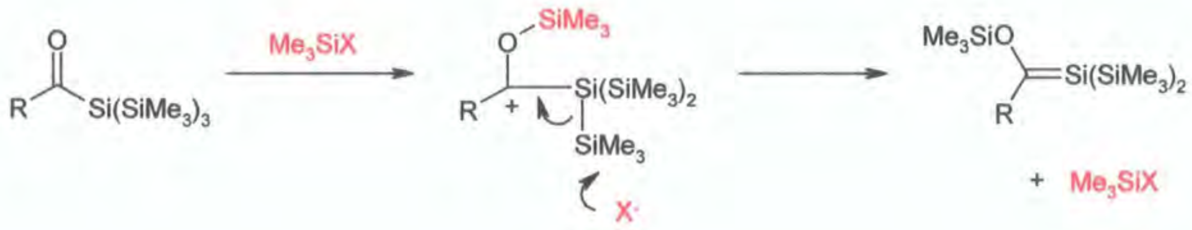


Figure 3.20

The main feature of this hypothesis is that the TMSX species would be regenerated, thus allowing catalytic amounts of the Lewis acid to be used.

3.3 2. Reaction of benzoyltris(trimethylsilyl)silane with TMSOTf

The first experiment attempted was the addition of trimethylsilyltriflate (TMSOTf) to a solution of benzoyltris(trismethylsilyl)silane in dichloromethane. (*E*)-1,3-Pentadiene was also present to trap any silene formed. If either a stoichiometric or a catalytic amount of TMSOTf was added, a complex mixture of products was obtained, containing a large amount of polymerized diene. The reaction was then carried out in the absence of diene, with a view to isolate a silene dimer, if silenes were indeed being formed. However, no dimeric species were isolated, the product that was isolated was a new species, with a molecular mass of 442, Figure 3.21.

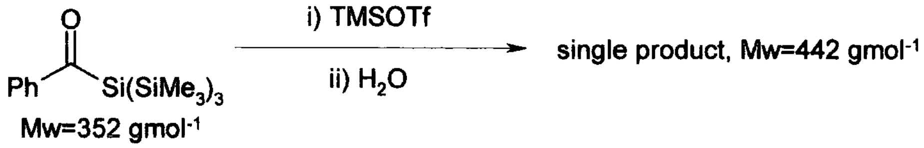


Figure 3.21

The gain in mass over the starting acylsilane of 90 gmol^{-1} appeared to indicate a gain of trimethylsilanol (Me_3SiOH). HRMS also supported this observation, indicating a molecular formula of $C_{19}H_{42}O_2Si_5$. However, at this stage the absolute structure of the product could not be deduced from the analytical data obtained.

3.3.3. Reaction of benzoyltris(trimethylsilyl)silane with $TMSNTf_2$

Recently Ghosez and co-workers have indicated that trimethylsiyl bistriflamide ($TMSNTF_2$) is a more potent Lewis acid than TMSOTf. Additionally, it was reported that this reagent does not cause the diene polymerisation observed with TMSOTf, Figure 3.22.[86]

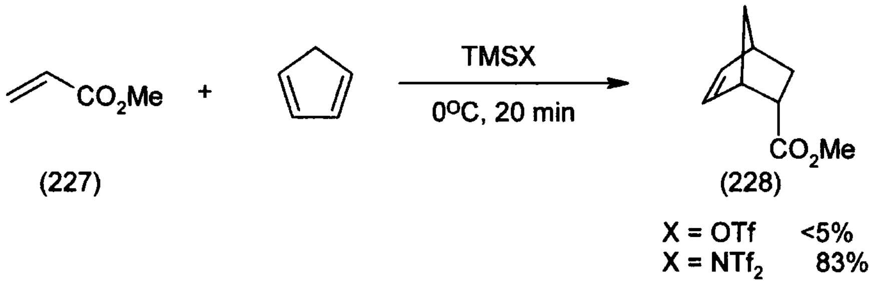


Figure 3.22

$TMSNTf_2$ (230) is easily made by stirring allyltrimethylsilane and bis(trifluoromethylsulfonyl)imide (229), followed by distillation, Figure 3.23. However, Robertson and co-workers have found that this reagent can be generated *in situ* at much lower temperatures.[87]

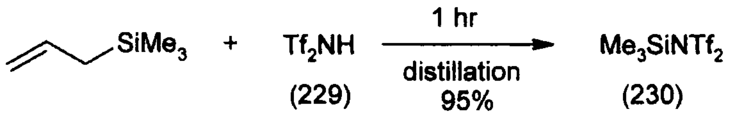


Figure 3.23

However, the use of TMSNTf$_2$ in place of TMSOTf in the reaction with benzoyltris(trimethylsilyl)silane and (*E*)-1,3-pentadiene at –78°C again resulted in rapid diene degradation. Indeed, adding TMSNTf$_2$ to a solution of the diene alone led to the instantaneous formation of a black polymeric material.

The reaction of an equimolar amount TMSNTf$_2$ with benzoyltris(trimethylsilyl)silane in dichloromethane at -78°C in the absence of diene, initially gave a deep red solution. After 18 hours, aqueous workup and flash column chromatography gave a colourless solid. Again, mass spectrometry indicated a molecular ion of 442 gmol^{-1}, indicating a product isomeric with that obtained from the TMSOTf reaction. This was supported by elemental analysis however this product was more polar, having a smaller R$_f$ value by tlc. In addition, IR spectroscopy indicated the presence of an OH group, absent in the TMSOTf product. ^{29}Si NMR spectroscopy indicated 5 distinct signals. Again, it was impossible to deduce a structure from the analysis we had available. Fortunately, in this case the product was highly crystalline, and recrystallisation from ethanol gave crystals suitable for X-ray diffraction. This revealed the structure of the adduct to be silanol (231), Figure 3.25.

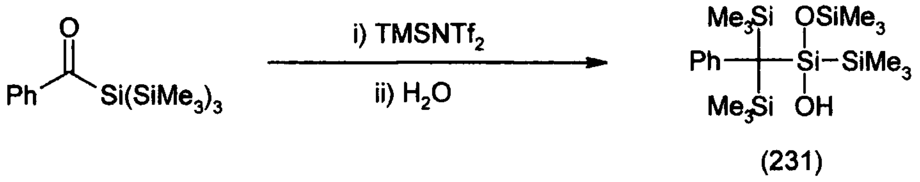


Figure 3.24

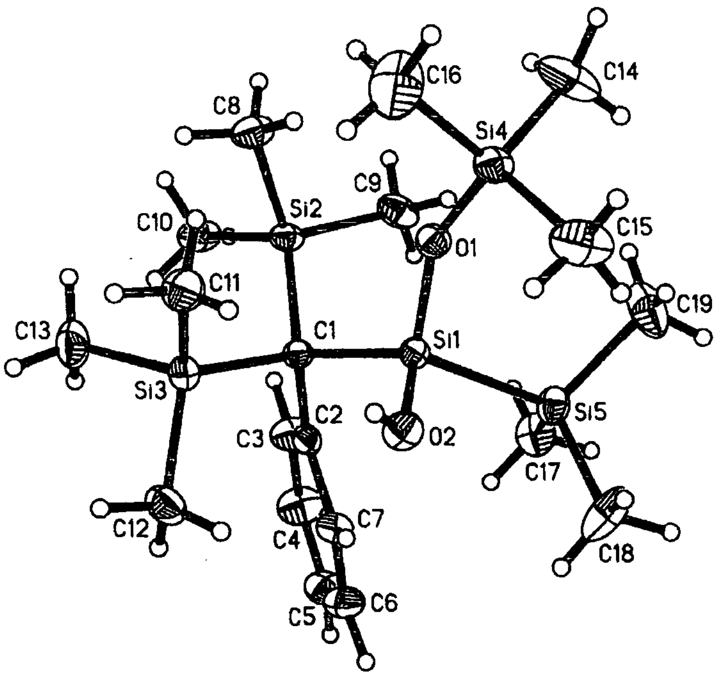


Figure 3.25

At first this product was surprising, as it was evident that some complex series of rearrangement reactions must have taken place to produce this product from benzoyltris(trimethylsilyl)silane.

To test the generality of this process a series of acyltris(trimethylsilyl)silanes were used. All except the trimethylacetyltris(trimethylsilyl)silane, which did not react at all, reacted in an analogous manner, although with 4-methoxybenzoyltris(trimethylsilyl)silane the reaction appeared to proceed in the same manner, except the product decomposed upon attempted isolation. Again, in all cases 5 signals were observed in the ^{29}Si NMR, Figure 3.27. A second confirmatory X-ray crystal structure was obtained for the 4-trifluoromethylphenyl adduct, Figure 3.26. The results are summarized below, Table 3.1.

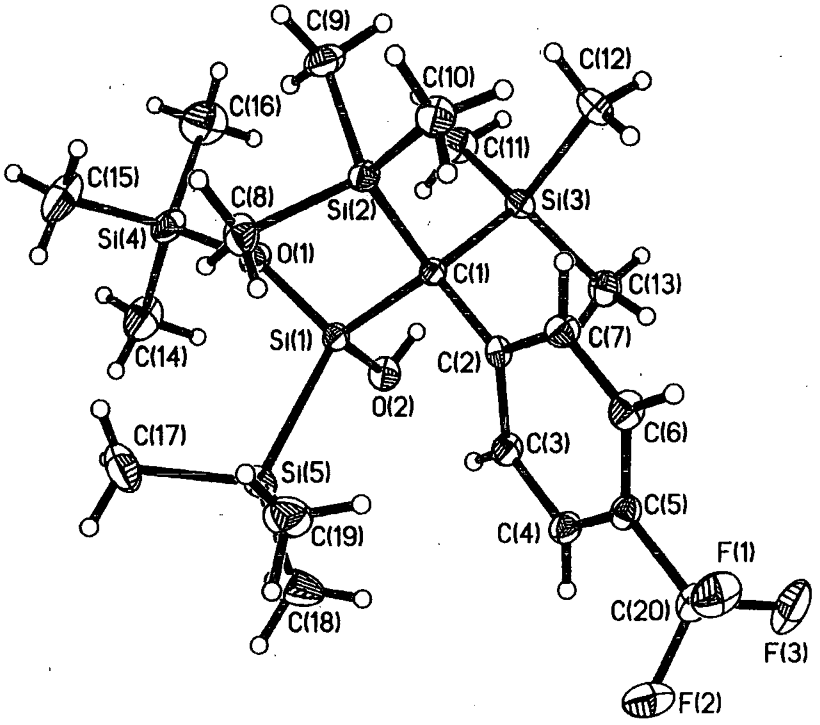

C(9)
C(10)
C(12)
C(16)
C(11)
C(15)
C(8)
Si(2)
Si(3)
Si(4)
O(1)
C(1)
C(13)
C(7)
Si(1)
C(2)
C(14)
O(2)
C(6)
C(17)
C(3)
Si(5)
C(5)
C(4)
C(19)
F(1)
C(20)
F(3)
C(18)
F(2)

Figure 3.26

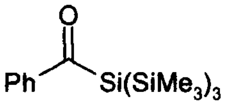
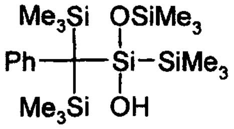
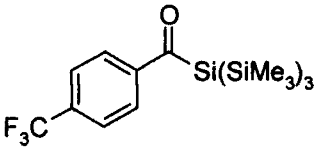
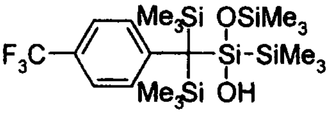
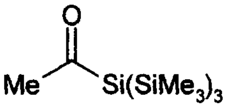
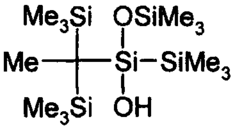
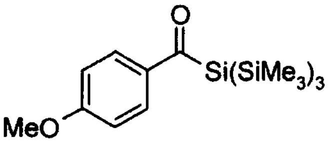
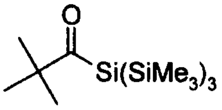
Acylsilane	Product	Yield, %
 (87)	 (231)	93
 (181)	 (232)	82
 (86)	 (233)	77
 (179)	decomposed	--
 (45)	No reaction	--

Table 3.1

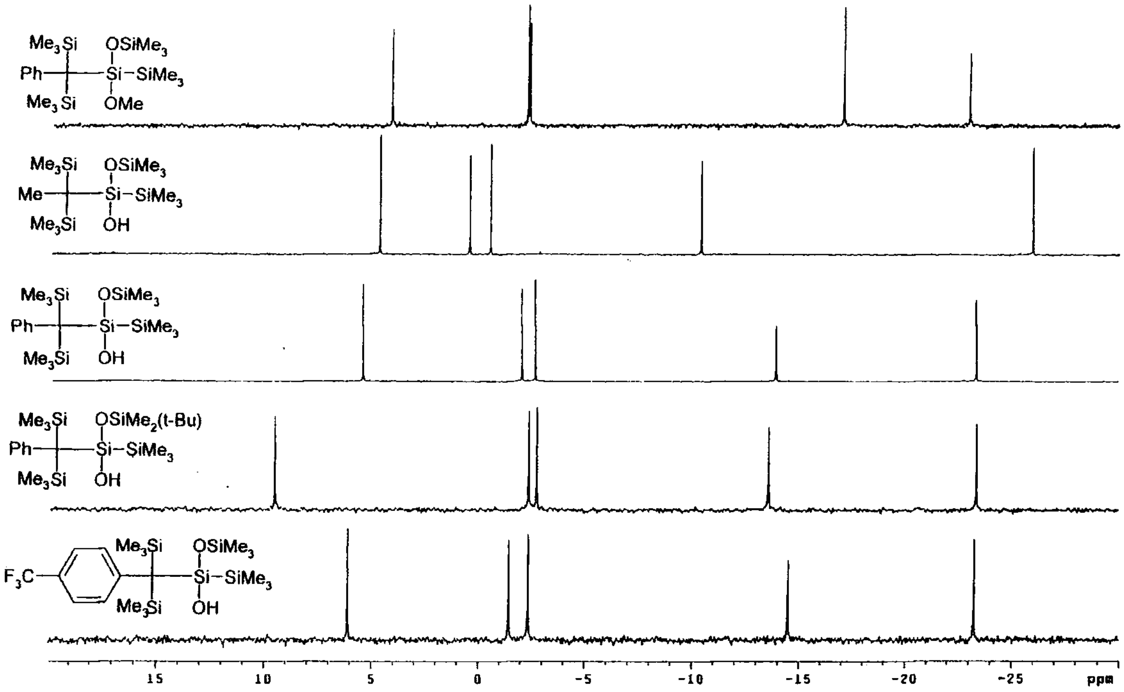


Figure 3.27

To account for the observed products we propose the following mechanism, Figure 3.28. Initial coordination of the carbonyl oxygen to the Lewis acid leads to an oxacarbenium ion intermediate (234). This cation is stabilized by three β-trimethylsilyl groups and the aryl or methyl substituent, either by conjugative or hyperconjugative effects respectively. In the case of trimethylacetyltris(trimethylsilyl)silane, the t-Bu group offers no stabilising effect, and so the cation is never formed. In the next step a 1,2-migration of a Me_3Si group from silicon to carbon occurs to give (235). This is followed by the 1,2-migration of the Me_3SiO group in the opposite direction to give (237). A final 1,2-migration of a Me_3Si group produces a silylenium ion intermediate (238). This then reacts with water on workup to give the observed silanols. The absolute order of events is unclear, and either a stepwise or concerted series of reactions can be envisaged, Figure 3.28.[88]

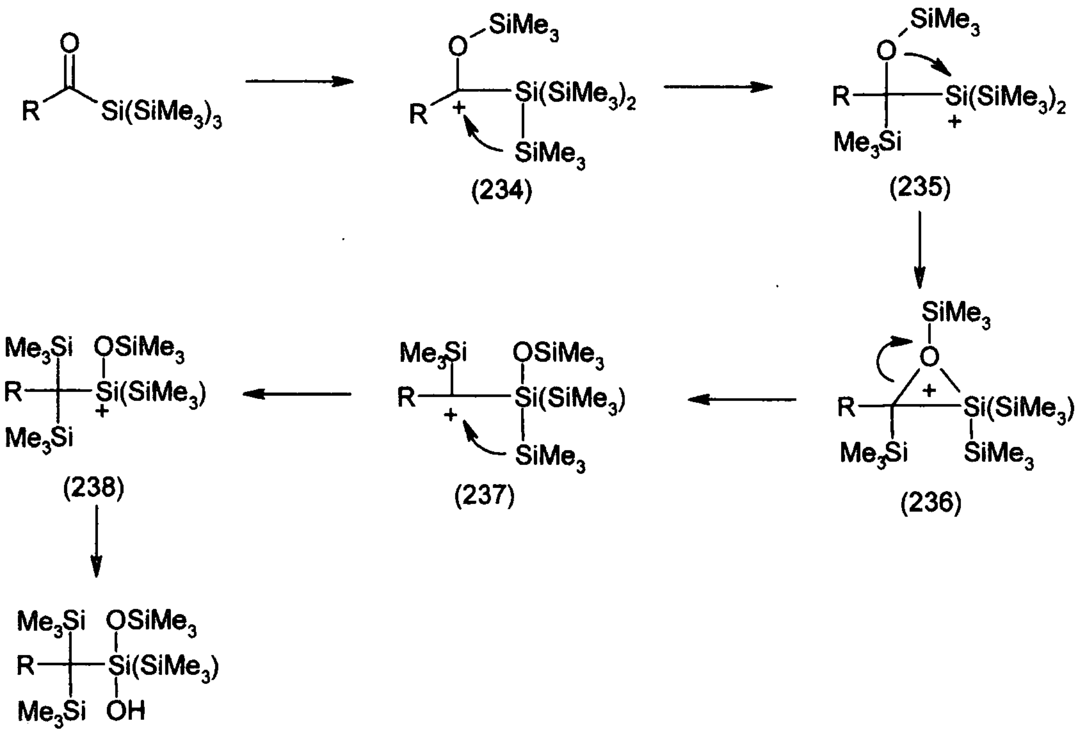


Figure 3.28

The use of a sub stoichiometric amount of TMSNTf$_2$ led to the formation of the rearrangement product in a yield consistent with the evidence that the TMSNTf$_2$ was acting as a stoichiometric reagent. Further to this, the use of *tert*-butyldimethylsilylbistriflamide, TBDMSNTf$_2$ (239) led to the incorporation of the TBDMS group at the silyloxy position (240), Figure 3.29.

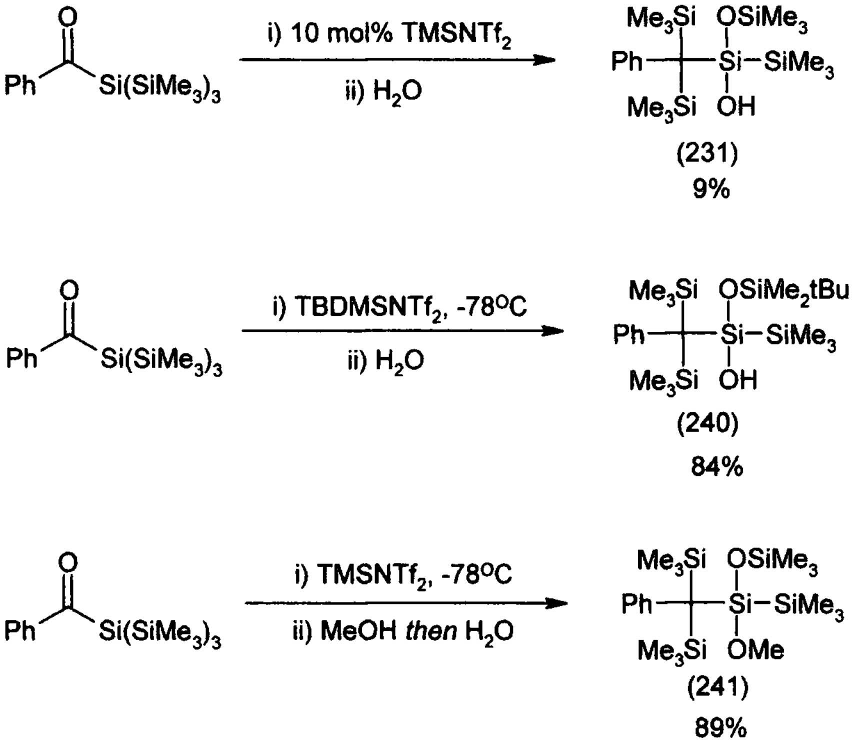
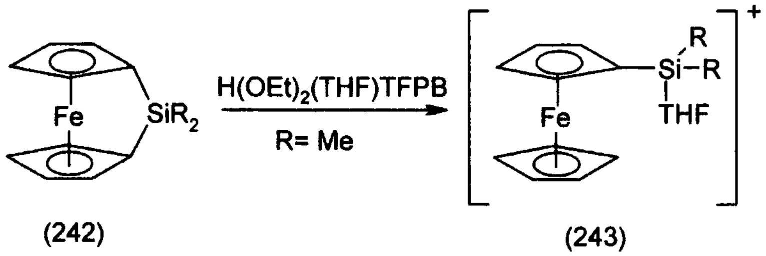


Figure 3.29

The addition of methanol before the usual aqueous workup gave, as a final product, the silyl ether (241), supporting our hypothesis that a "silylenium ion" is formed as the final intermediate in the reaction, Figure 3.29. The existence of silylenium ions, the silicon equivalent of carbocations, has been a subject of much debate.[89] The ability of substituents to stabilize a positive charge on silicon via conjugative or hyperconjugative effects is diminished due to the increased bond lengths than those for carbon.[90] However, several recent reports indicate that silylenium ions do indeed exist. Lambert and co-workers have formed isolated $[(Mes)_3Si]^+$ ions in the presence of the tetrakis(pentafluorophenyl)borate anion.[91] Additionally, Manners and co-workers have formed ferrocenyl-substituted silylenium ions (243) in the presence of a non-coordinating anion, Figure 3.30.[92]



TFPB = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate

Figure 3.30

Oehme and co-workers have proposed silylenium ion intermediate (246) in the reaction of silyl alcohols with acids, Figure 3.31.[93]

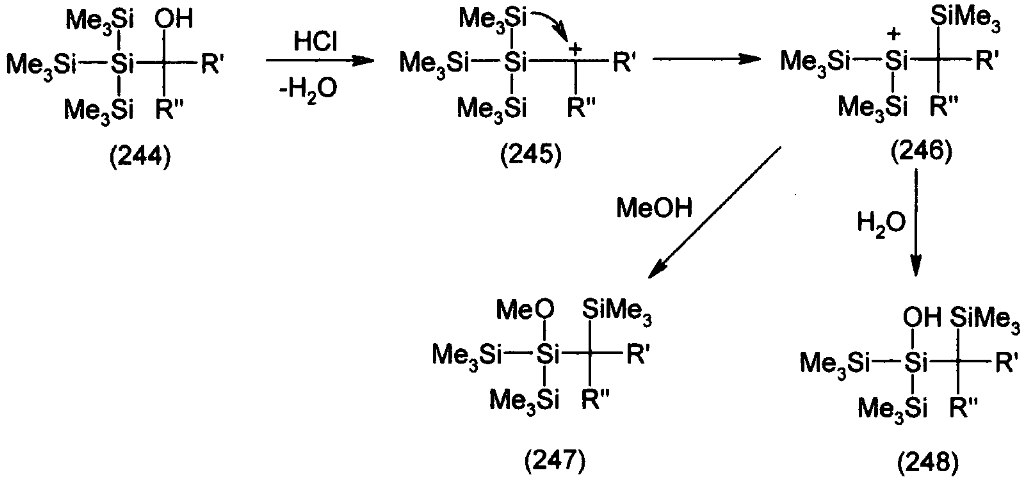


Figure 3.31

A related process has been observed by Brook in the reaction of acyltris(trimethylsilyl)silanes with titanium tetrachloride ($TiCl_4$), Figure 3.32.[94]

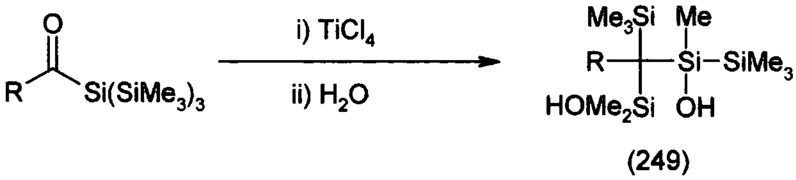


Figure 3.32

The reported mechanism for this reaction is similar to the mechanism that is proposed for the reaction with $TMSNTf_2$. However in this case a 1,3-methyl shift from one of the trimethylsilyl groups to the silylenium ion also occurs, Figure 3.33.

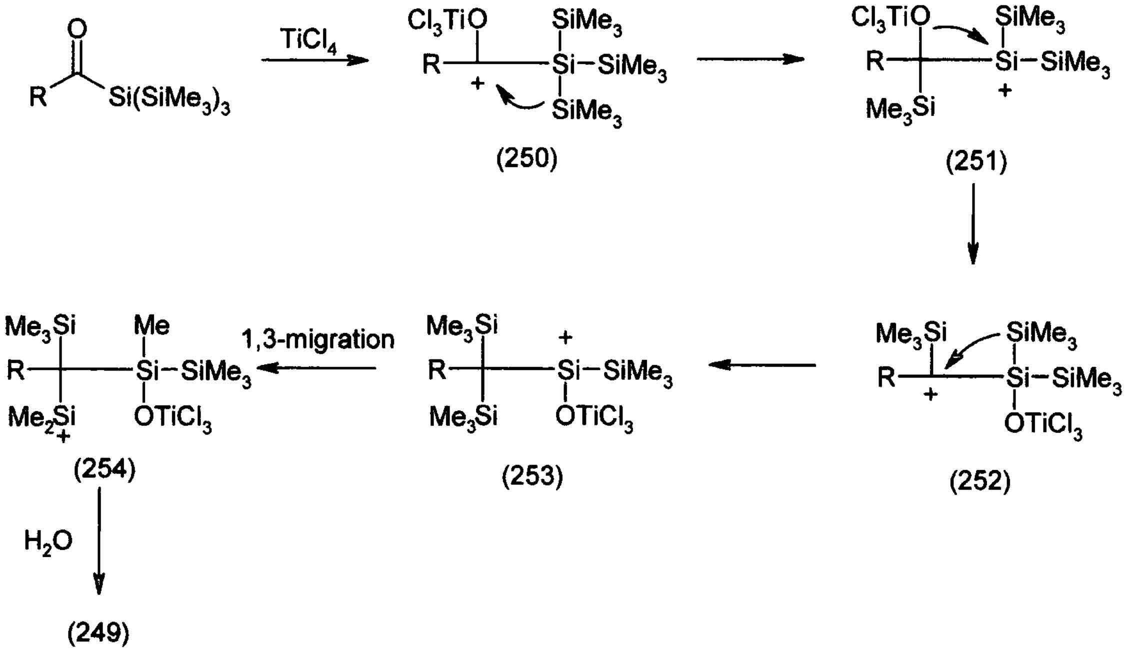


Figure 3.33

The ready formation of these rearrangement products, with their α, β-hydroxysilane functionality, led us to speculate that treatment with base may lead to a Peterson-type elimination taking place to give a silene, Figure 3.34.

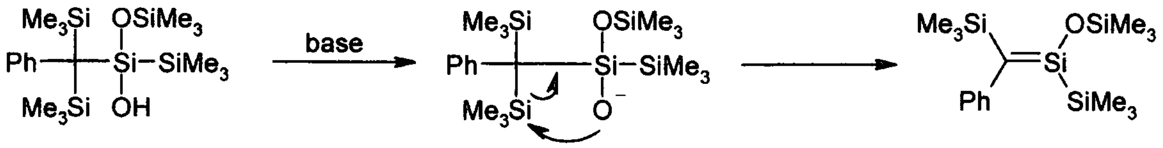


Figure 3.34

This type of reaction has been utilized by Oehme in his synthesis of silenes.[45] On first inspection however, the reaction appeared unlikely as the formation of the strong Si-O bond, the driving force of the Peterson reaction, is competing with the breaking of another Si-O bond. In fact, treatment of the silanol (231) with methyllithium in ether led to the formation of product (257), with no evidence of silenes or silene dimers being formed, Figure 3.35.

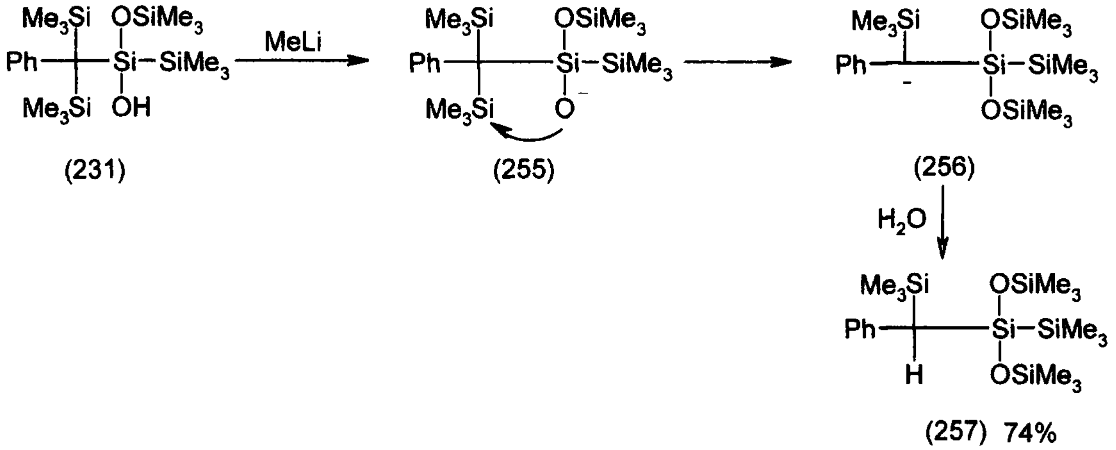


Figure 3.35

[H-C] Heteronuclear correlation NMR experiments provided evidence that the single resonance at 1.60 ppm was indeed due to the isolated benzylic proton, the observation of this signal was complicated by residual H_2O in the deuterochloroform solvent.

Anionic intermediates of the type in Figure 3.35 have been postulated as an intermediate in the Peterson reaction.[95] The 1,3 migration of trimethylsilyl groups from silicon to oxygen was first observed by Brook with the reaction of tris(trimethylsilyl)silylethanol with K/Na alloy, Figure 3.36.[96]

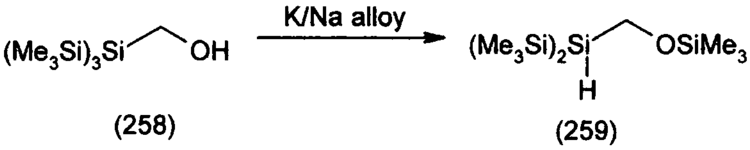


Figure 3.36

A similar reaction has also been observed by Oehme, where again a Si-O bond would have to be broken. Treatment of (260) with NaH was found to give the bis-silyl ether species (263), Figure 3.36.[97]

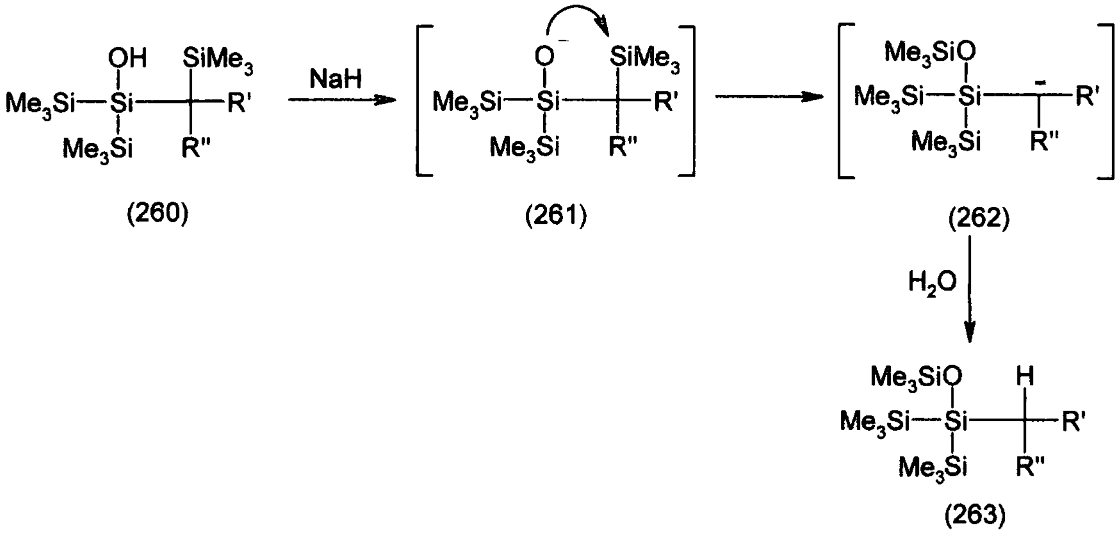


Figure 3.36

The Peterson reaction is also known to occur under acidic conditions.[95] The silanol X was also exposed to a variety of acids (HBF_4, HF/pyr) to attempt to promote this reaction. However, in all cases the silanol was recovered unreacted. Again, it appears that it is impossible to induce a Peterson-type elimination from this substrate.

The bis-silyl ether (257) obtained from the reaction of silanol (231) with methyllithium appeared to be identical to the product obtained from the reaction of TMSOTf with benzoyltris(trimethylsilyl)silane described earlier. This product exhibited an identical ^1H NMR spectrum, an identical retention time on GC, and identical fragmentation pattern on EI mass spectrometry, Figure 3.37.

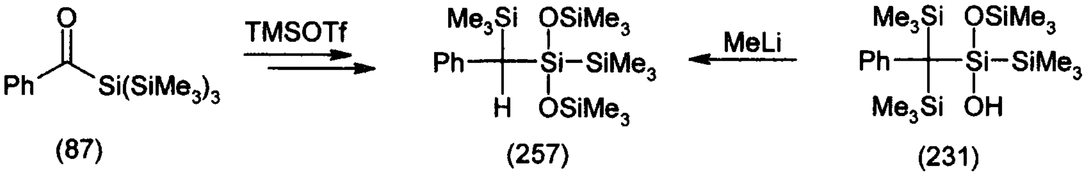


Figure 3.37

Initially this observation appeared surprising, as it looked as though an even more complex rearrangement had taken place than with $TMSNTf_2$.

The reaction was investigated in greater detail. It was found that quenching the reaction after 4 hours led to the isolation of both the product (257) and the silanol product (231) obtained from the $TMSNTf_2$ reaction, Figure 3.38.

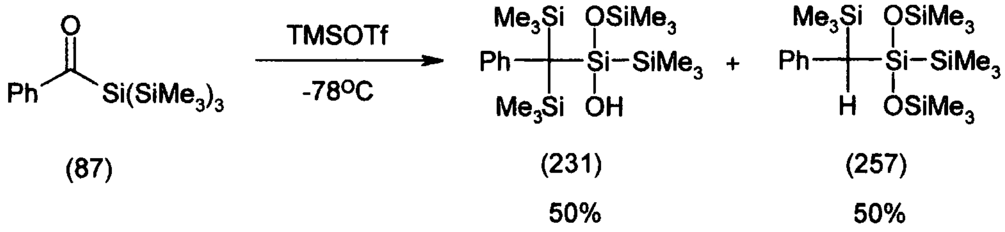


Figure 3.38

This appeared to indicate that the intermediate (236) was common to reactions using both $TMSNTf_2$ and TMSOTf. In addition, larger scale reactions allowed the detection of the alternative regioisomer (264), formed by the reverse addition of trimethylsilanol to the silene species, Figure 3.39. Evidence for this structure is provided by Si satellites in the ^1H NMR spectrum.

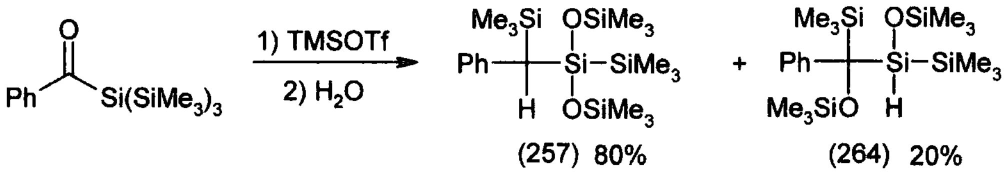


Figure 3.39

At this stage we proposed the following unified mechanism. Initial coordination of the trimethylsilyl Lewis acid to the carbonyl oxygen gives the carbocation (267). There follows a series of 1,2-migrations to give the silyl cation intermediate (268). With $TMSNTf_2$, the reaction stops at this stage, and the intermediate is intercepted on workup to give either the silanol (231) (aqueous conditions) or the methyl ether (241) (methanol workup). However, with TMSOTf, it is postulated that the triflate anion is a strong enough nucleophile to cause an E1-like elimination process to generate silene (267), regenerating TMSOTf in the process. Aqueous workup leads to the trapping of this silene, which is then silylated by the TMSOTf present to give the observed product (257), Figure 3.40.

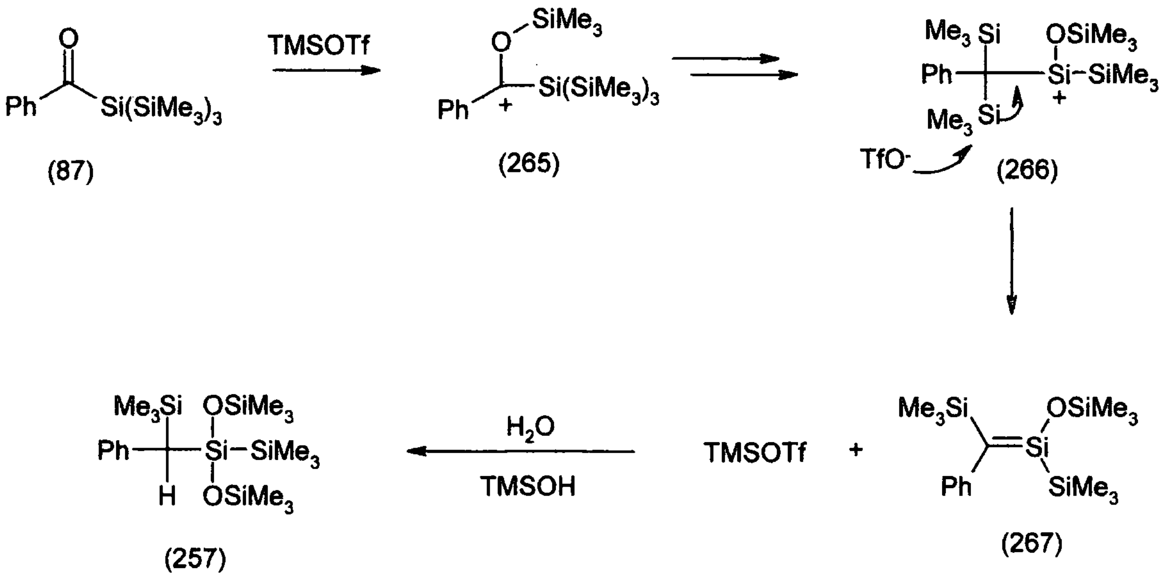


Figure 3.40

In order to test this hypothesis, the reaction with TMSOTf was repeated, but methanol was added before the standard aqueous workup. In this case the methyl ether (268) was isolated, which is the expected product for the reaction of a silene such as (267) with an alcohol, Figure 3.41.

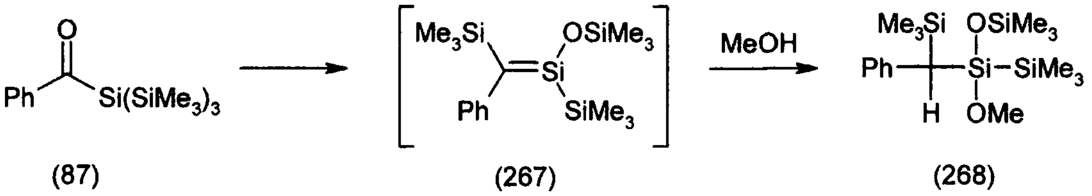


Figure 3.41

This reaction supported our hypothesis that a silene was indeed being formed in the TMSOTf reaction. Our attentions then returned to the trapping of this postulated silene with dienes. It was hoped that a substoichiometic amount of TMSOTf could be used to perform the reaction, and that this might lead to a reduction in the level of diene degradation observed previously. However, the use of 0.1 and 0.5 equivalents of TMSOTf led to a large decrease in the rate of the reaction, and caused a similar level of diene polymerisation. In any case, no products attributable to the cycloaddition reaction of the silene with the diene were isolated.[98]

3.3.4. Conclusion

The reaction of trimethylsilyl Lewis acids with acyltris(trimethylsilyl)silanes leads to the formation of novel, heavily silylated products due to an interesting series of migration reactions. As initially proposed, the use of TMSOTf appears to give a silene species, albeit not the silene which was originally proposed. However, all attempts to trap this silene as its Diels-Alder adduct have proved unsuccessful so far. Time constraints and the pressure of working on other aspects of the project meant that further work in this area remains incomplete. However, it has to be emphasized that this is a novel method for forming silenes, and given that low temperature routes to silenes are few in number, is an interesting development worthy of further investigation.

At this stage in the project, it appeared that we ideally required silenes bearing phenyl substituents on the sp^2-hybridized silicon, which undergo [4+2] cycloaddition reactions with dienes.

3.4 Modified Peterson Reaction

3.4.1 Introduction

During our investigation into the photolysis of acylbis(trimethylsilyl)phenylsilanes, a couple of silyl alcohols were formed as synthetic intermediates. Oehme and co-workers have used similar silyl alcohols to form silenes via a modified Peterson elimination, some of which have undergone [4+2] cycloaddition reactions with 2,3-dimethylbutadiene Figure 3.42.[45]

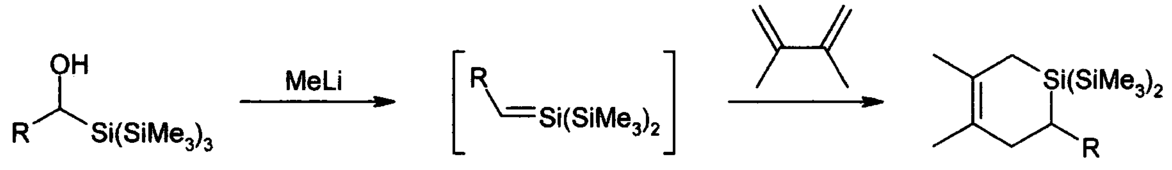


Figure 3.42

At about the same time, our investigations into the oxidation of the silacycles obtained by the reaction of silenes with dienes had proved unsuccessful. It appeared that the trimethylsilyloxy- substituted silenes we were forming through thermolysis or silene dimer cycloreversion were incompatible with the oxidation methodology used so far. It appeared that we required a simpler silene species, ideally bearing a phenyl substituent on silicon. Jones and Auner have formed neopentyl-substituted silenes bearing a variety of substituents on silicon, however the Diels-Alder reactions of such silenes are often low-yielding, with considerable amounts of ene and [2+2] products also being formed. However, Oehme's rather limited investigations looked to hold far more promise, with a high yield for the single Diels-Alder reaction that has been reported. Therefore on first inspection, the silyl alcohols obtained appeared to be ideal silene precursors, Figure 3.43.

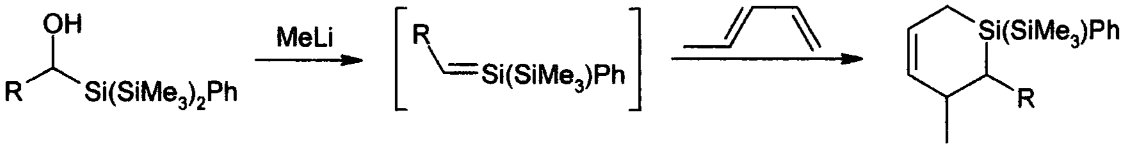


Figure 3.43

3.4.2 Formation of silene cycloadducts

Initially, following the same process as Oehme, methyllithium was added to a solution of the silyl alcohol in the presence of (*E*)-1,3-pentadiene at -78°C. This solution was allowed to warm to -20°C, and stirred for 6 hours. In the case of the n-butyl substituted silyl alcohol (220), the alcohol was recovered intact. The reaction was allowed to warm to room temperature over an 18 hour period, alas to no effect. However, in the case of the isopropyl-substituted silyl alcohol (221), when reaction times were extended to 18 hours, a 65% yield of a product that was attributable to the [4+2] Diels-Alder adduct. Further spectroscopic data supported the proposed structure. However, the most interesting fact appeared to be that the Diels-Alder adduct was formed as a single diastereoisomer. NOESY NMR experiments proved inconclusive in determining the relative stereochemistry of the silacycle, Figure 3.44.

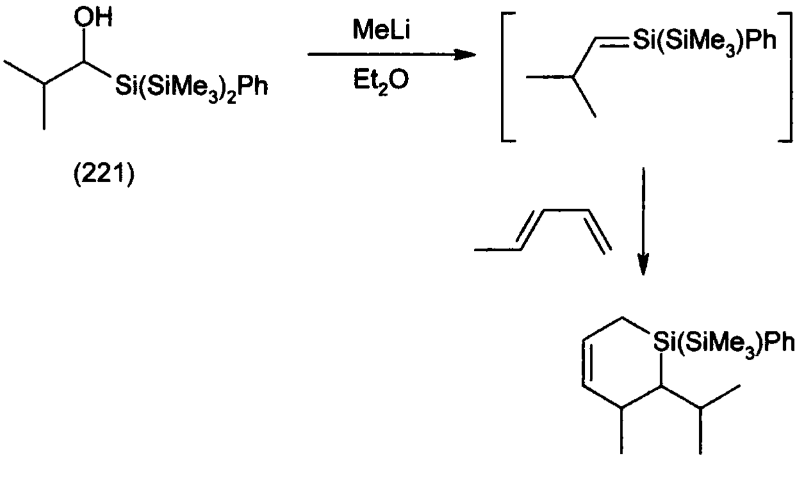


Figure 3.44

The generality of this process was investigated by using different dienes. The use of isoprene appeared to also give the [4+2] adduct, however this product proved to be unstable in the deuterochloroform solution used for the NMR measurements. The use of both cyclopentadiene and cyclohexadiene led to the formation of a product identified as a silene dimer species, Figure 3.45.

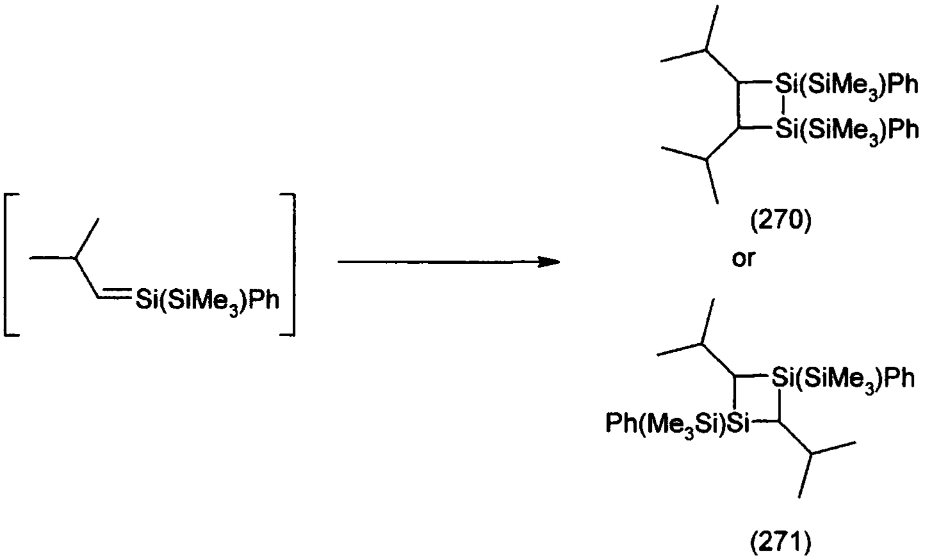


Figure 3.45

In order to confirm that the silene dimer was formed without any interaction with the diene added, silyl alcohol (221) was reacted with MeLi in the absence of any trapping agent, which gave the same dimeric species. The simplicity of the ^1H NMR spectrum suggested that a [2+2] had been formed. Oehme has indicated that the formation of these types of silenes in the absence of trapping agents can lead to the formation of head-to-head dimers. However silenes bearing α-protons tend to form linear dimers, due to a disproportionation reaction in the diradical intermediate, Figure 3.46.[45]

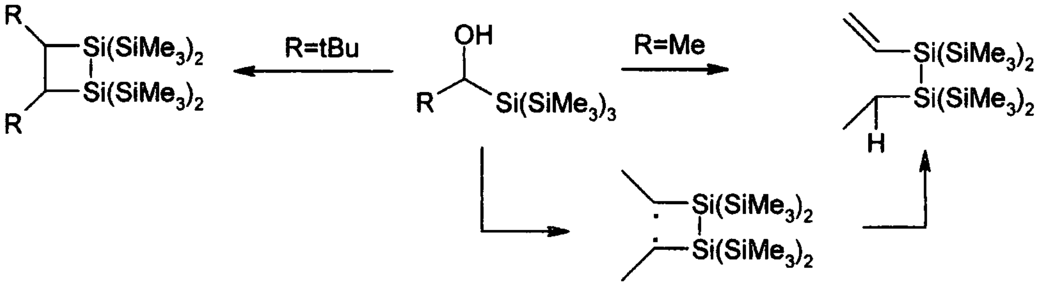


Figure 3.46

It has been noted by Auner that neopentyl-substituted silenes, generated under similar reaction conditions, react very poorly with cyclopentadiene and cyclohexadiene, and give silene dimers as the major products, Figure 3.47.[68]

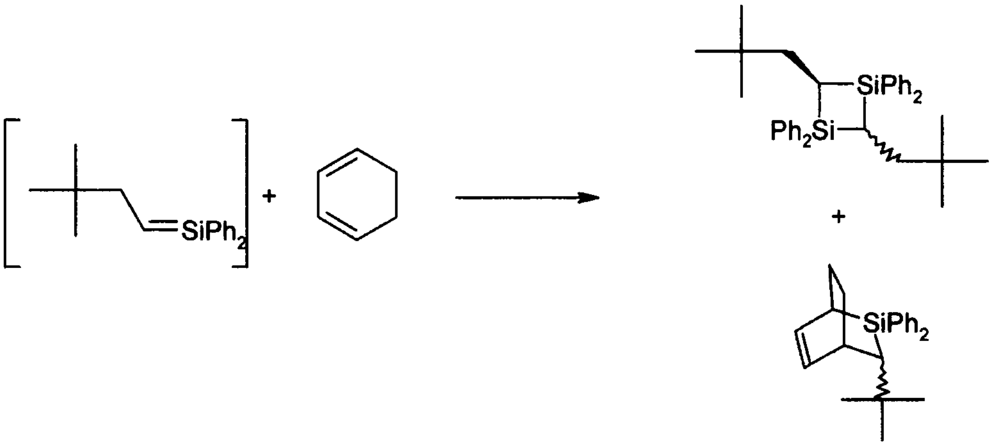


Figure 3.47

This observation has been attributed to increased steric interactions in the bicyclic transition state for the [4+2] Diels-Alder reaction. The silene, itself being a very reactive species, then preferentially reacts with itself to give a head-to-tail silene dimer. Under these reaction conditions, there is no possibility of dimer cycloreversion, therefore the dimer is the main product isolated from the reaction. It appears that the "Oehme" type silenes generated in this case exhibit a similar level of reactivity towards cyclic dienes.

3.4.3 Alternative bases

In order to optimize the Peterson elimination reaction, different bases were used in place of MeLi (nBuLi, LiHMDS). However, in both cases the silyl ether (272) was the only product isolated, Figure 3.48.

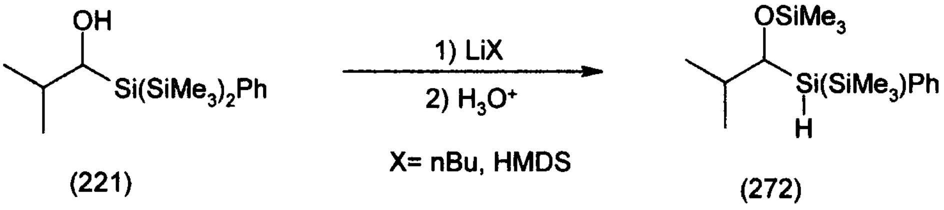


Figure 3.48

It appears that with nBuLi or LiHMDS the intermediate silyl anion does not undergo the elimination reaction to form the silene

3.5 Conclusion

The formation of silyl alcohols as precursors to acylsilanes led us to investigate the modified Peterson reaction, as pioneered by Oehme, as a route to silenes. Our preliminary results indicate that, for at least one silyl alcohol (221), the process leads to the exclusive formation of [4+2] cycloadducts in good yield, as single regioisomers, with excellent diastereoselectivity. Preliminary investigations indicate that, although acyclic dienes react to give [4+2] cycloadducts exclusively, cyclic dienes do not react, presumably due to steric interactions in the transition state inhibiting the Diels-Alder cycloaddition.

Chapter 4

The Oxidation of Organosilicon Compounds

4. The Oxidation of Organosilicon Compounds

4.1 Introduction

The oxidation of organosilicon compounds is now a well known and powerful synthetic technique. The oxidation of organosilicon compounds was discovered by Tamao, and the synthetic utility of the reaction was elaborated further by Fleming. This area has been comprehensively reviewed recently.[99,100] This chapter will deal with the main principles, scope and limitations of the reaction.

Organosilicon compounds are generally resistant to standard oxidation procedures used in organic chemistry. In fact, it is their unreactive nature which makes organosilicon groups useful as protecting and/or directing groups in synthetic chemistry. However, under certain conditions organosilicon groups bearing suitable substituents can undergo oxidation. The first example of the oxidative cleavage of silicon-carbon bonds was described over 40 years ago by Buncel and Davies, who discovered that organic substituents on silicon were found to undergo 1,2-migrations from silicon to oxygen, Figure 4.1.[101]

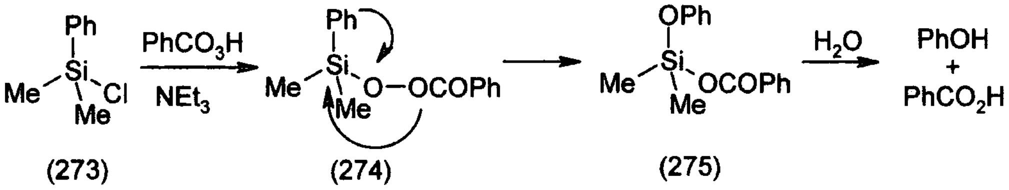


Figure 4.1

However, several years passed until the first general procedures for the oxidation of organosilicon compounds were published by Tamao. These observations are described below.

4.2. Tamao Oxidation

4.2.1 Introduction

Organosilicon compounds are usually resistant to oxidative cleavage, and oxidation reactions can be performed on organosilicon compounds without silicon-carbon bond cleavage. The first reported oxidation was that of hexacoordinated organopentafluorosilicates with mCPBA in DMF, Figure 4.2.[102] Subsequently, Tamao discovered that the process was general for organosilicon species bearing electronegative substituents on silicon, which underwent oxidation with peroxide reagents, Figure 4.2.[103]

$$\mathrm{R_3SiX} \xrightarrow{\mathrm{mCPBA,\ KHF_2}} \mathrm{ROH}$$

Figure 4.2

Initially mCPBA was used as the oxidant, however further refinement of the process led to the use of the cheaper and more readily available hydrogen peroxide. In addition to the oxidising agent, base (usually $KHCO_3$) is required to promote the nucleophilic attack of the peroxy-species at the silicon centre.

4.2.2 Mechanism

The mechanism of this process has been studied in some detail.[99] In the first instance the organosilicon species undergoes nucleophilic attack, to generate a pentavalent intermediate. In the next step, an alkyl group undergoes a migration reminiscent of a 1,2 Bayer-Villiger-type process, from silicon to oxygen, Figure 4.3.

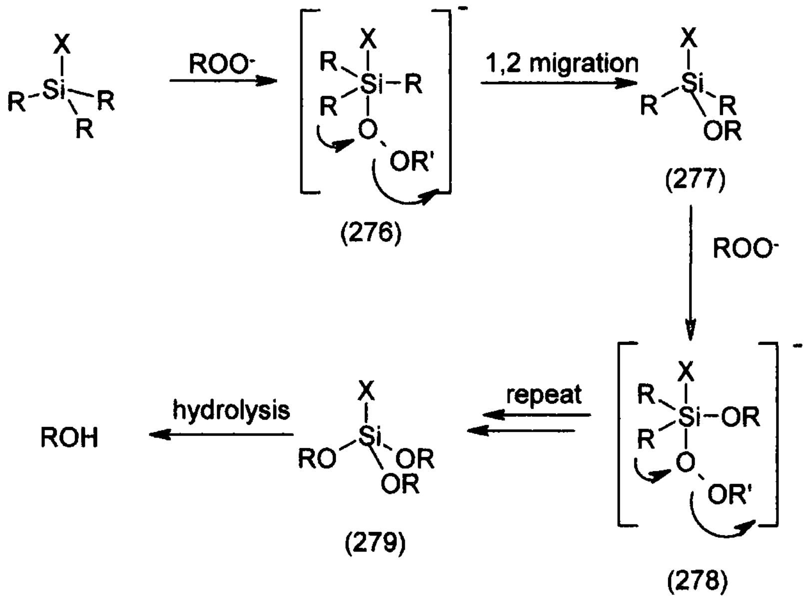


Figure 4.3

However, Tamao has proposed a mechanism which proceeds via the formation of a hexacoordinate silicon species (281), Figure 4.4.[104]

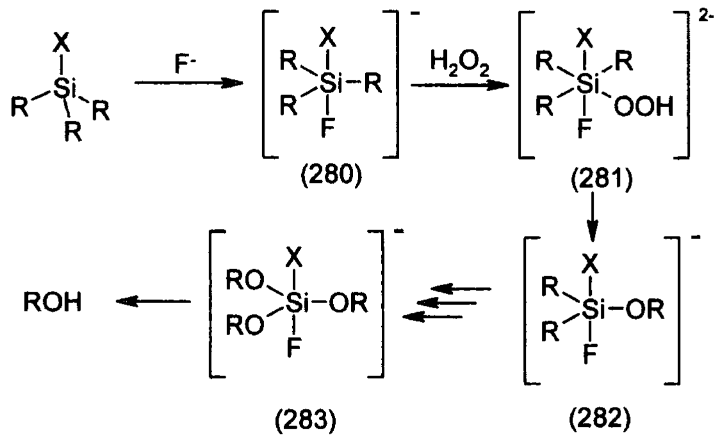


Figure 4.4

However, it is unclear whether this or the previous mechanism is the more realistic description of the reaction, as no detailed kinetic studies have yet been performed.

This process is in many ways similar to the oxidation of organoboranes, in that the nucleophilic attack by the peroxy species is followed by a 1,2-Bayer-Villiger type migration. However, boranes are much more easily oxidized due to the vacant *p*-orbital, whereas with silicon an electron-withdrawing substituent is required to allow a peroxy species to react.

The formation of intermediate silyl ethers and silanols during the course of the reaction is supported by the work of Knölker and co-workers. They found that methoxysilane (285a) and silanol (285b) were isolated during the oxidation of fluorosilane (284) under standard Tamao conditions, Figure 4.5.[105]

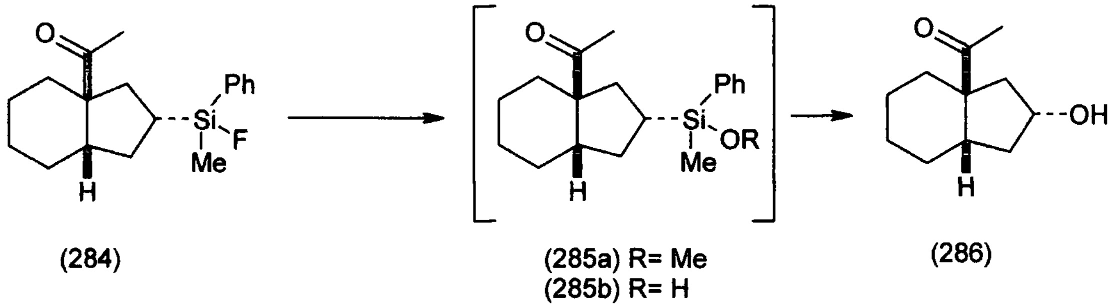
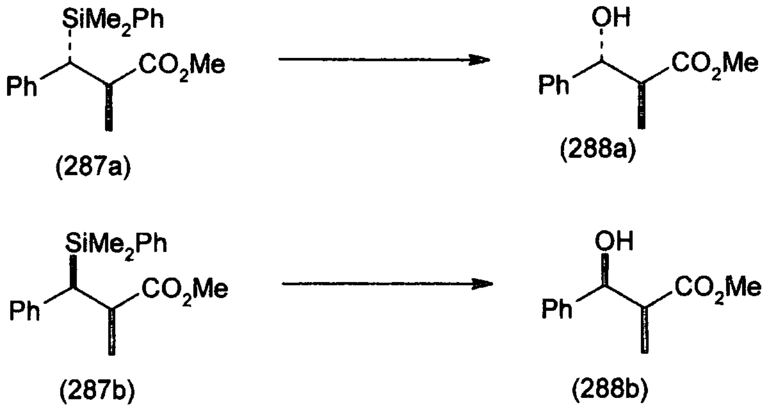


Figure 4.5

The first organosilanes oxidized by Tamao carried halogen substitutents. However, in subsequent work it was discovered that other electronegative substituents could also promote the oxidation reaction

One of the main points to note is that the reaction proceeds to give *retention* of configuration at the carbon centre. This is due to the fact that the alkyl group migrates with a pair of electrons, thus retaining configuration.[106] An example of this has been demonstrated by Fleming by the oxidation β-silylesters (287a,b) of known relative configurations to the corresponding β-hydroxyesters (288a,b), Figure 4.6.[107]



(287a) (288a)

(287b) (288b)

Conditions: 1) $HBF_4.OEt_2$ 2) mCPBA, NEt_3

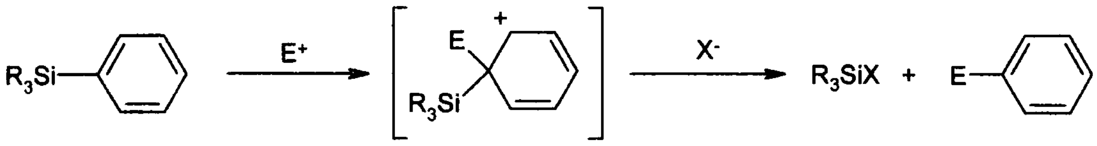
Figure 4.6

4.3 Fleming Oxidation

4.3.1 Introduction

The main problem associated with the Tamao oxidation is that organosilicon compounds bearing electronegative substituents, especially chlorine and bromine, are generally very reactive species, making them difficult to handle. However, Fleming devised an elegant two-step oxidation process using far more stable aryl-substituted organosilanes, which can be easily converted to oxidizable intermediates.[108]

The Fleming oxidation involves two steps: protodesilylation followed by oxidation. This procedure relies on an observation by Eaborn and co-workers, who found that aryl-silicon bonds are selectively cleaved in the presence of alkyl-silicon bonds using electrophilic reagents, Figure 4.7.[109]



(289) (290) (291)

Figure 4.7

In the first step the electrophile attacks at the *ipso* position on the aromatic, to generate a β-carbocation stabilized by silicon (290). This stabilising effect occurs due to (σ-p)π hyperconjugation between vacant p orbitals on the β-carbocation and the σ-orbital of the silicon-carbon bond, Figure 4.8.[110]

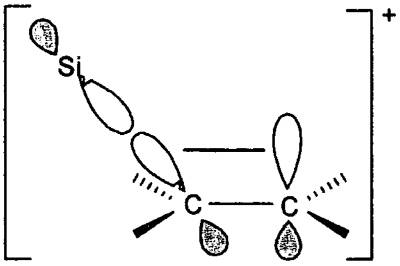


Figure 4.8

Fleming's initial investigations centred on the use of HCl as the electrophile, with at least a threefold excess of mCPBA as the oxidising agent, to ensure that complete migration of all the alkyl substituents on silicon occurs, Figure 4.9.[107]

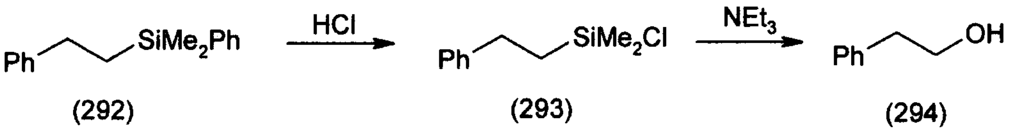
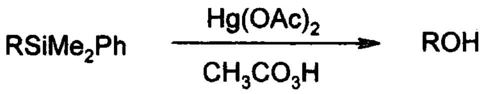


Figure 4.9

However, it was subsequently found that the protodesilylation could be performed by $HBF_4.OEt_2$. This had the advantage of giving a silyl fluoride, which was easier to handle than the silyl chloride intermediates, and could be partially purified by washing with aqueous base during workup. It has been found subsequently that trifluroborane-acetic acid complex[107] ($BF_3.2AcOH$) or trifluoroacetic acid[111] often give higher yields in the protodesilylation step.

The use of the electrophilic species above used a two-step procedure as the initial electrophilic reaction using an acidic species is incompatible with the subsequent Tamao oxidation, which occurs under basic conditions. Subsequently it was found that the reaction could be performed sequentially using $Hg(OAc)_2$ (based on an earlier observation[112]) or Br_2 as the electrophile, followed by the addition of peracetic acid. This allowed the transformation to be performed as a "one-pot" procedure, Figure 4.10.[107]



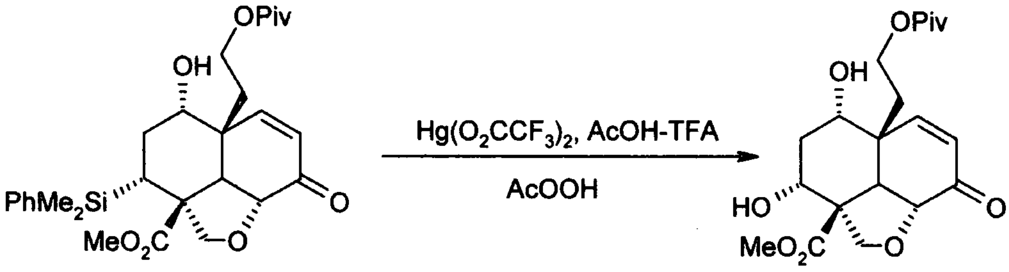
$$\mathrm{RSiMe_2Ph} \xrightarrow[\mathrm{CH_3CO_3H}]{\mathrm{Hg(OAc)_2}} \mathrm{ROH}$$

Figure 4.10

Fleming has described the phenyldimethylsilyl substituent as a "masked hydroxy group", as opposed to a protected hydroxy group, as the effect of the the silyl group to reacting centres nearby is much different to that of a hydroxy or protected hydroxy group.

4.3.2 Modified Fleming Oxidations

The problems which arise from the Fleming oxidation are usually due to the strong electrophilic conditions required to perform the protodesilylation reaction. Additionally, some very hindered organosilanes have been found to be totally unreactive toward oxidation. Ley and co-workers found during approaches the total synthesis of azadirachtin that $Hg(OAc)_2$ reacts only slowly with the relatively hindered arylsilane (295), $Hg(TFA)_2$ in an acetic acid/TFA mixture gave rapid protodesilylation, which followed by standard Fleming oxidation conditions of peracetic acid gave the desired oxidation product (296), Figure 4.11.[113]



(295)

(296)

Figure 4.11

Another alternative is to use an allyl group on silicon, as these groups can be more easily displaced than aromatic substituents, Figure 4.12.[114]

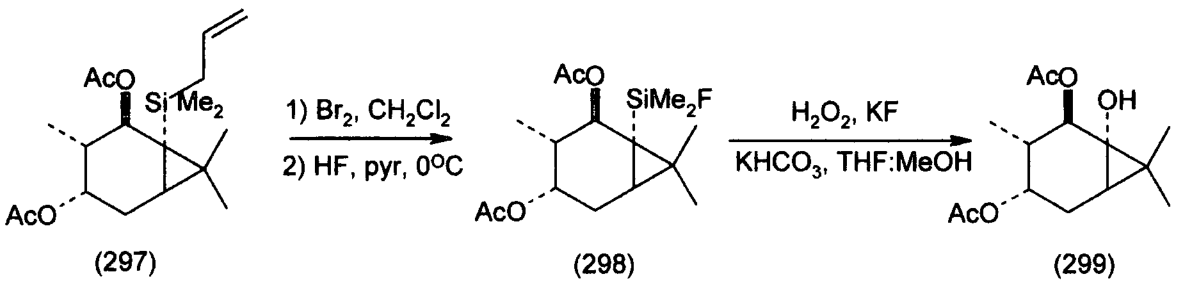


Figure 4.12

Landais and co-wokers have demonstrated the use of the dimethyl(1-phenylthio)cyclopropylsilyl group as an oxidizable silyl group, through the initial oxidation to the sulfoxide (301), followed by a sila-Pummerer rearrangment and Tamao oxidation, Figure 4.13.[115]

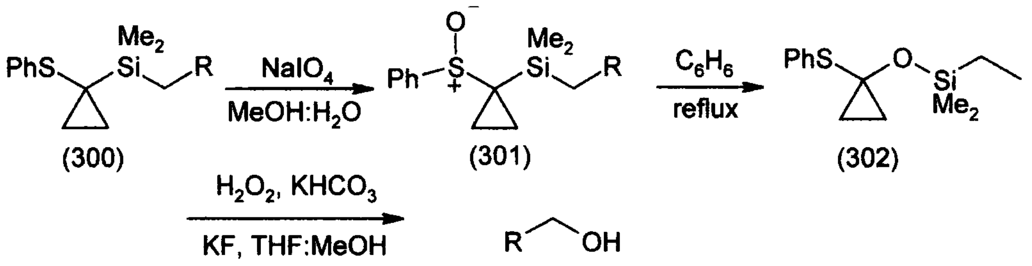


Figure 4.13

Recently, the 2-pyridyl silyl group has been used as an oxidizable group. Interestingly, however, it was found that this group could be oxidized using just the standard "Tamao" reagents, without the need of an initial electrophilic displacement step, Figure 4.14.[116]

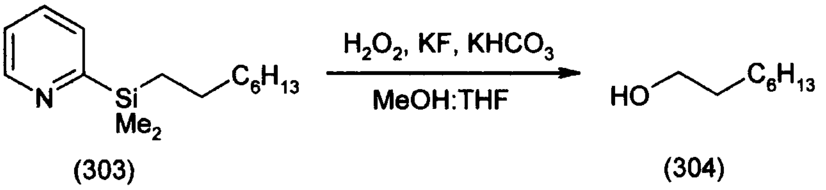
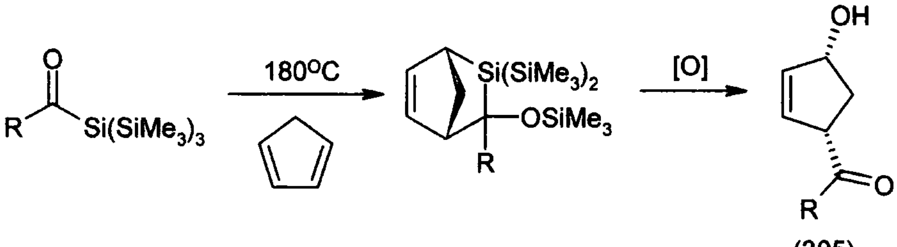


Figure 4.14

4.4 Oxidation of silene cycloadducts

4.4.1 Introduction

Our work initially focused on the oxidation of the silacyles obtained by the thermolysis of acyltris(trimethylsilyl)silanes with dienes, described in Chapter 2. In theory this reaction sequence should lead to the formation of the keto-alcohol (305), Figure 4.15.



(305)

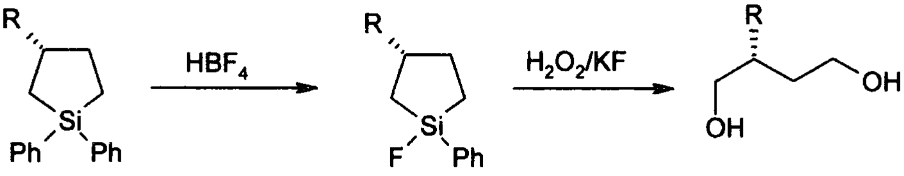
Figure 4.15

The overall transformation is the 1,4-functionalisation of the diene, with complete control (*cis*) over the relative stereochemistry. This type of reaction is very difficult to perform using the standard techniques available in organic chemistry.

The Diels-Alder reaction of a silene with a diene gives a cyclic allylsilane as its product. Allylsilanes are known to be problematic in the oxidation reaction, due to epoxidation etc., so the initial step would be to reduce the double bond.

4.4.2 Oxidation of cyclic organosilanes

The oxidation of cyclic organosilanes provides a convenient route to a variety dihydroxylated compounds. These reactions have been reviewed previously.[117] The oxidation of diphenylsilacyclopentanes, via Fleming-type displacement of a phenyl substituent from silicon using HBF_4, leads to the formation of 1,4-diols, Figure 4.16.[118]



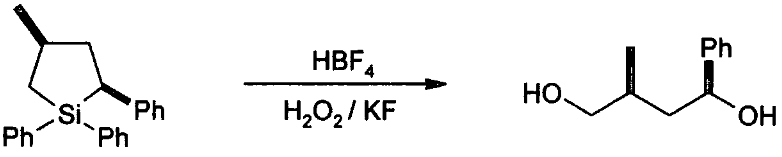
(306) R=Me, 38% ee
(307) R=Ph, 60% ee

(308), (309)

(310), (311)

Figure 4.16

Additionally, diastereomerically pure silacycle (312) underwent oxidation to the diol (313) with retention of relative stereochemistry, as expected from the proposed mechanism (section 4.2.2), Figure 4.17.[119]



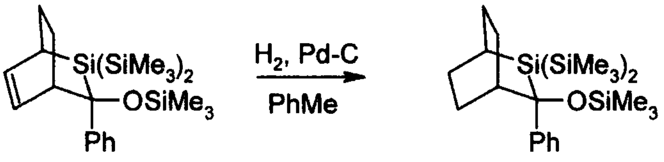
(312)

(313)

Figure 4.17

4.4.3 Attempted oxidation of the adducts obtained by thermolysis

The initial substrate chosen was the bicyclic silacycle (314), as reduction of the double bond gives silacycle (315), which renders the structure symmetrical, and removes the problem of obtaining diastereoisomers in subsequent reactions. This reduction could be easily performed by hydrogenation using 10% Pd-C catalyst, Figure 4.18.



(314)

(315)

Figure 4.18

Under standard Tamao conditions, we found that the silacycle (315) was unreactive, with only unchanged silacycle obtained from the reaction mixture. This is unsurprising, as there are no reports of disilanes having been oxidized by this method in the literature. This led us to attempt the use of methods which are known to oxidize disilyl groups. These reactions generally occur under much more severe conditions.

Krohn and co-workers have found the disilane group $Me_3Si(Me_2Si)$- to be oxidizable in the synthesis of rabelomycin (318), using $AlCl_3$ to cleave the Si-Si bond and KF/H_2O_2 to oxidize the resultant silanol (317), Figure 4.19.[120]

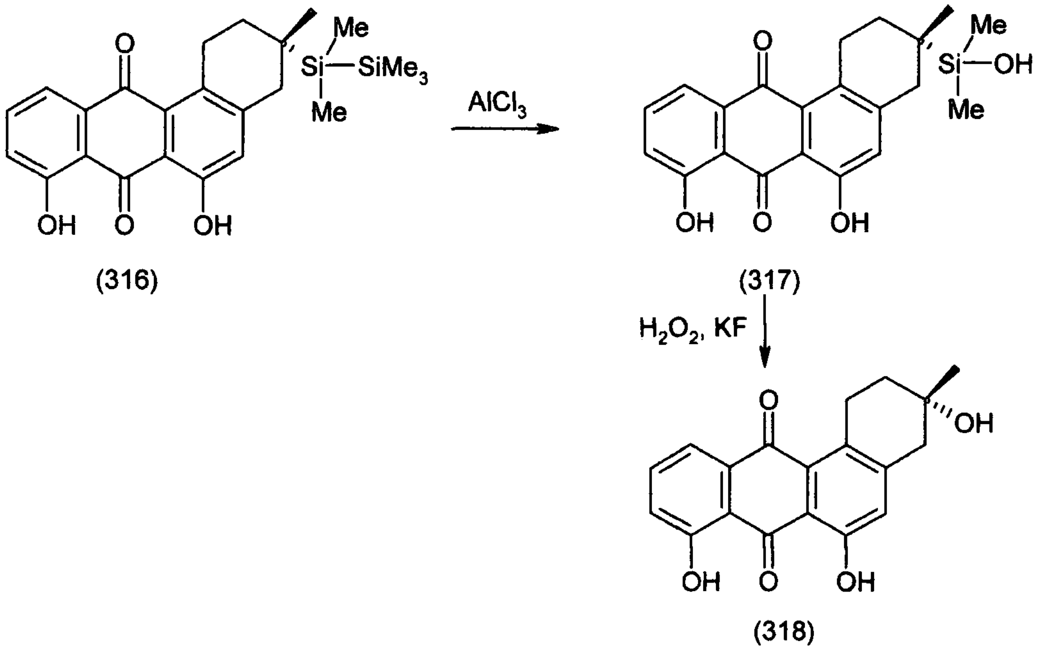
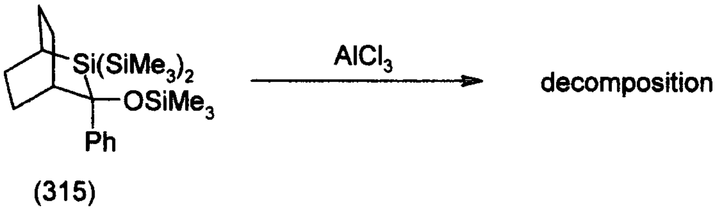


Figure 4.19

It is unclear by which mechanism the Si-Si bond is cleaved by $AlCl_3$, and Krohn offers no precedent or explanation.

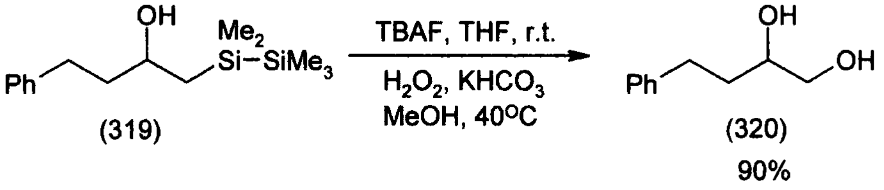
In our hands, treatment of the silacycle (315) with a stoichiometric amount of $AlCl_3$ immediately gave rise to an increase in temperature, and a dark red-brown solution. Workup of the reaction mixture gave multiple decomposition products, Figure 4.20.



(315)

Figure 4.20

Ito and co-workers have found the disilanyl group can be oxidized using TBAF, followed by standard Tamao-type conditions, Figure 4.21.[121]



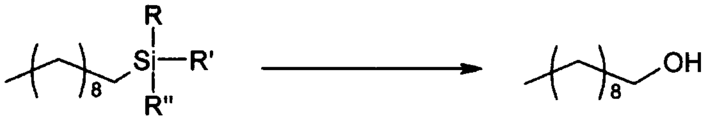
(319)

(320)
90%

Figure 4.21

However, the same reaction conditions applied to adduct (315) led to complete decomposition, with neither the starting silacyle or product being obtained.

A more versatile oxidation method has been developed by Woerpel and co-workers, involving the use of strongly basic conditions. In fact, even the trimethylsilyl group (322) has been found to undergo oxidation under these conditions, albeit in relatively low yield. This is remarkable, given that all previous oxidations (as outlined above) have involved either an electronegative or labile group on silicon, Figure 4.22.[122]



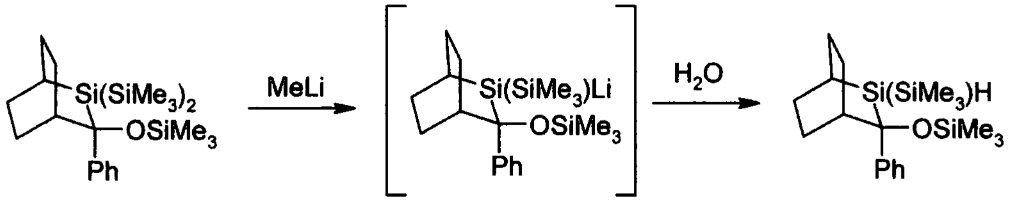
(321) R=R'=Me, R''=Ph, conditions: tBuOOH, KH, NMP, 70°C,
yield= 82%

(322) R=R'=R''=Me, conditions: t-BuOOH, KH, 1:1:2 THF/toluene/NMP, 120°C
yield= 37%

Figure 4.22

Silacycle (315) was reacted under the conditions outlined by Woerpel for the oxidation of the trimethylsilyl substituent. However, this led to complete decomposition of the starting material, with no product isolated. This is not surprising, considering the strongly basic conditions under which the reaction is performed.

As has been demonstrated previously with the formation of tris(trimethylsilyl)silyllithium, MeLi is known to cleave Si-Si bonds. If successful, aqueous workup of the silyllithium should give silane (324), Figure 4.23.



(315) (323) (324)

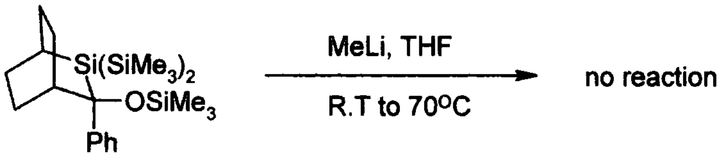
Figure 4.23

Silanes have been shown to easily undergo oxidation under standard Tamao conditions, Figure 4.24.[123]

$$\mathrm{RSiMe_2H} \xrightarrow[\mathrm{MeOH/THF}]{\mathrm{H_2O_2,\ KHCO_3}} \mathrm{ROH}$$

Figure 4.24

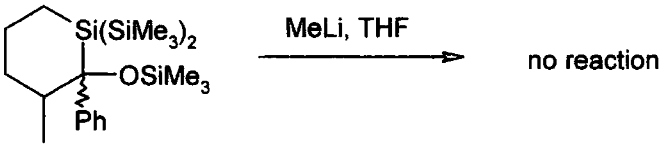
However, surprisingly no reaction was observed when MeLi was added to a solution of silacycle (315) in THF at room temperature. Repeating this reaction in refluxing THF was no more successful, Figure 4.25.



(315)

Figure 4.25

Initially it was felt that either steric interactions were preventing the approach of the nucleophile, or that the rigidity of the bicyclic structure was preventing the formation of the silyl anion. However, use of the monocyclic adduct (325) instead also led to isolation of unchanged starting material only, Figure 4.26.



(325)

Figure 4.26

It appeared at this stage that the oxidation of the silacycles above was proving to be very difficult.[124] It appeared that we required adducts bearing more easily displaceable groups on silicon. The most obvious choice would be a phenyl group, as this would allow the use of the chemistry Fleming has developed, which is described above. Chapter 3 described the synthesis of such adducts from their corresponding silenes. The attempts to oxidize the adducts obtained is described below.

4.4.4 Attempted Oxidation of cycloadducts obtained by dimer reversion

As described previously, we had found that the silene dimer (213), formed by the photolysis of acysilane (212), underwent facile cycloreversion in the presence of dienes, to give cycloadducts in excellent yield, Figure 4.27.

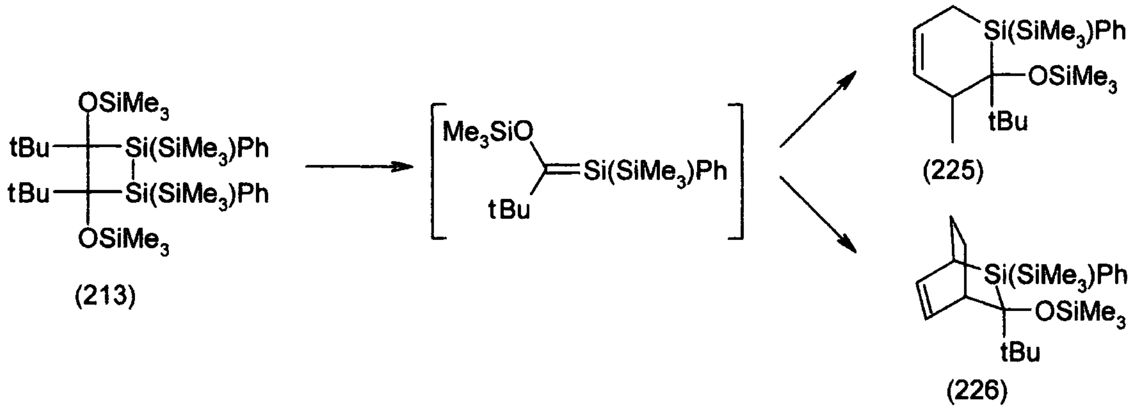


Figure 4.27

With these cycloadducts in hand, the next stage was to attempt the oxidation. Again, the double bonds in the silacycles were reduced using H_2 and 10% Pd-C catalyst, to give the reduced silacycles in excellent yield. In the case of the monocyclic adduct (227), ethyl acetate was used, as the use of ethanol as the reaction solvent led to excess decomposition of the starting material, Figure 4.28.

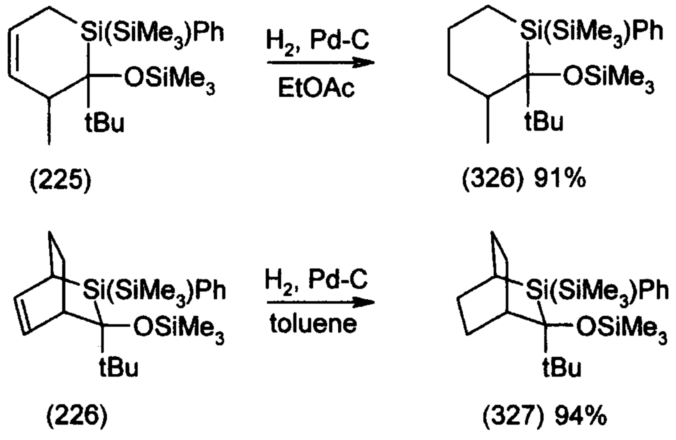


Figure 4.28

Unfortunately silacycle (327) was found to decompose under the standard Fleming "one-pot" reaction conditions,[107] with no evidence for the formation of oxidation products, Figure 4.29.

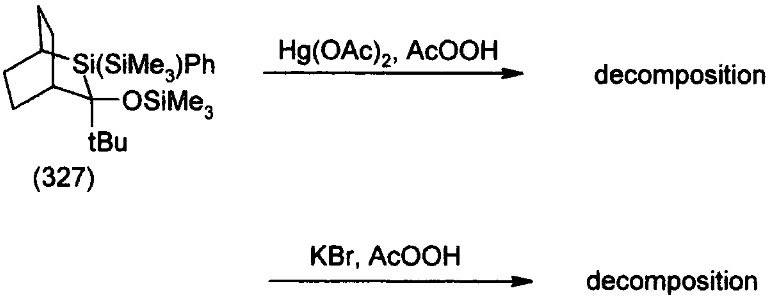


Figure 4.29

The lack of success in oxidising these adducts under standard Fleming conditions led to the investigation described below.

4.4.5 Birch reduction of phenylsilacycles

The problems encountered with the attempted oxidation of the phenyl-substituted silacycles prompted the investigation of alternative, more easily displaced groups. Allyl substituents on silicon are known to react with electrophiles to generate, in the first instance, a carbocation β- to silicon, Figure 4.30.[125]

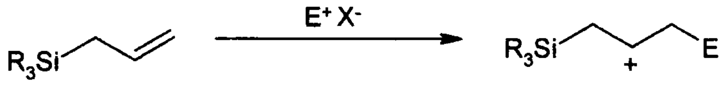


Figure 4.30

However, the presence of an allyl group when generating a silene species would almost certainly lead to the silene reacting either with itself, or the precursor acylsilane. It was therefore necessary to introduce an allyl group *after* the formation and trapping of the silene. Taber has demonstrated that allylsilanes can be generated from arylsilanes using lithium in liquid ammonia (Birch reduction), Figure 4.31.[126]

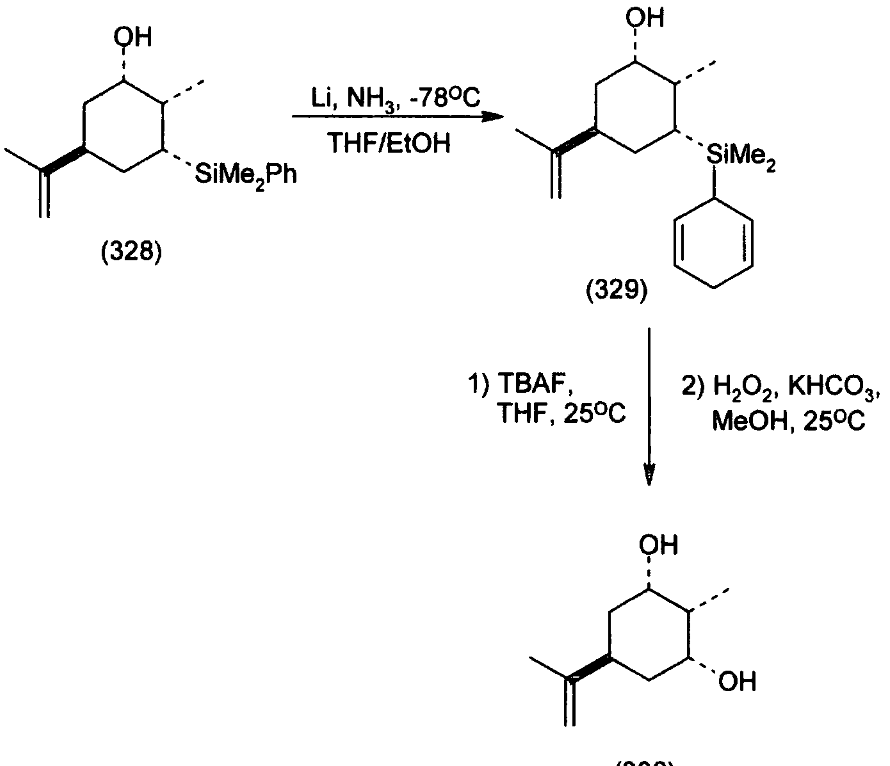


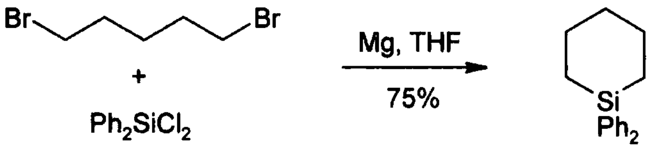
Figure 4.31

Silacycle (327) was reacted using the same conditions described by Taber. Addition of lithium to the solution of the substrate gave an intense blue colour, which disappeared quickly. Addition of further amounts of lithium metal gave the same result. Initially, using the amount of lithium indicated by Taber, only unreacted starting material was recovered. However, doubling the amount of lithium used gave a new product. The mass spectrum of the product obtained indicated a molecular ion mass of 422, whereas the product expected should have a mass of 420. This appeared to indicate that overreduction had taken place, Accurate mass measurements gave a molecular formula of $C_{23}H_{46}OSi_3$, again supporting the idea that overreduction has taken place. Repeatability of this reaction also appeared to be a problem, with either unreacted starting material or the "overreduced" product being obtained each time. These problems, coupled with time restrictions meant that further research was abandoned.

At this stage, it was becoming clear that the oxidation of the silacycle adducts obtained from the reaction of the "Brook" silenes with dienes was proving to be far more difficult than first envisaged. The simple bis(trimethylsilyl)-substituted silacycles proved to be unreactive under a variety of conditions, and the phenyl substituted silacycles, which should have been amenable to Fleming-type oxidations proved to be equally troublesome. It was at this point we decided that the best course of action would be to form a more simple, less substituted silene. Hopefully this would give an easier product on which to investigate.

4.4.6 A Model Study – Oxidation of 1,1-diphenylsilacyclohexane

In order to assertain the feasibility of oxidising simple silacycles , we first looked at 1,1-diphenylsilacyclohexane (331) as a suitable model compound to study. This compound can be obtained easily and in large scale by the double-Grignard reaction of 1,5-dibromopentane with dichlorodiphenylsilane, Figure 4.32.[127]



(331)

Figure 4.32

The next stage was to perform the electrophilic displacement of the phenyl substituent. Knölker and co-workers have found that diphenyl-substituted silanes undergo selective monoprotodesilylation with 2.2 equivalents of $BF_3.2AcOH$, Figure 4.33.[105]

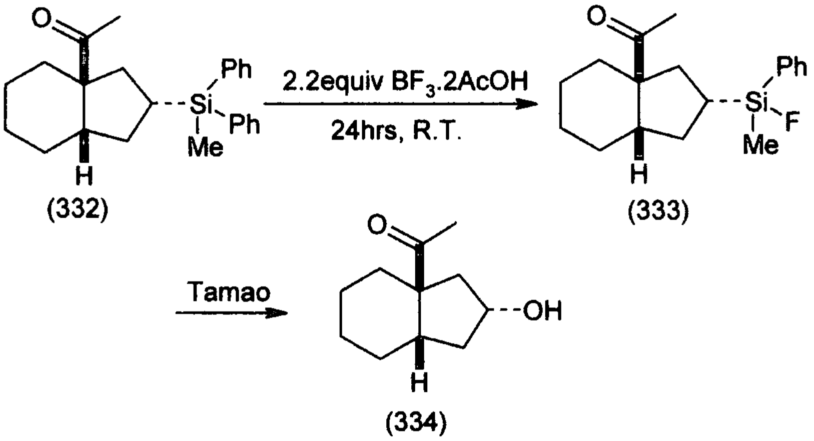
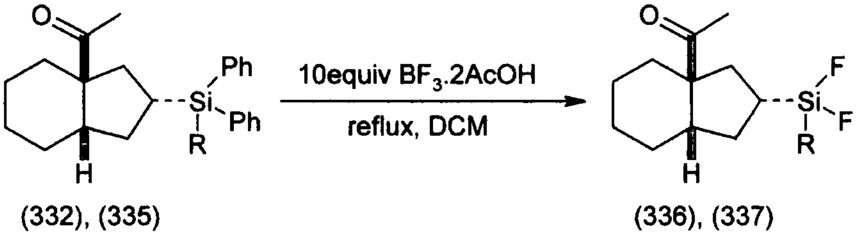


Figure 4.33

In order to attempt to optimize the subsequent oxidation, Knölker found that both phenyl substituents are displaced if a larger excess of BF_3.2AcOH at higher temperatures is used, Figure 4.34.[128]



(336) R= Me, 20hrs, 89%
(337) R= t-Bu, 14days, 92%

Figure 4.34

The reaction was performed as described by Knölker. The crude material (338), obtained in essentially quantitative yield, appeared very clean, with a single ^{19}F NMR signal at –178.58ppm, and a single peak in the GC. As in the acyclic cases studied by Knölker, the reaction appeared to selectively displace only one of the phenyl groups from the silicon atom, as evidenced by the ^{1}H NMR which indicated that the relative intensity of the aromatic proton resonances had decreased by exactly half, Figure 4.35.

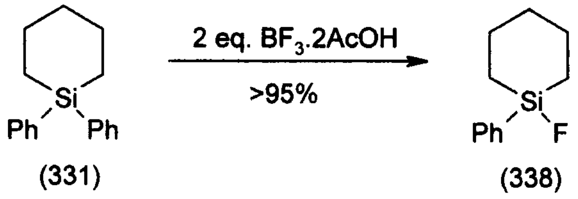


Figure 4.35

With this fluorosilacycle (338) in hand, the next stage was to perform the oxidation. The fluorosilacycle was reacted under standard Tamao conditions. GCMS of the crude material after workup indicated the presence of phenol, which suggested the reaction had been successful. The high water solubility of 1,5-pentanediol proved a problem. This was easily overcome by the addition of acetic anhydride, DMAP and pyridine to the reaction mixture prior to workup, followed by distillation, which led to the isolation of the diacetyl ester of 1,5-pentanediol, Figure 4.36.

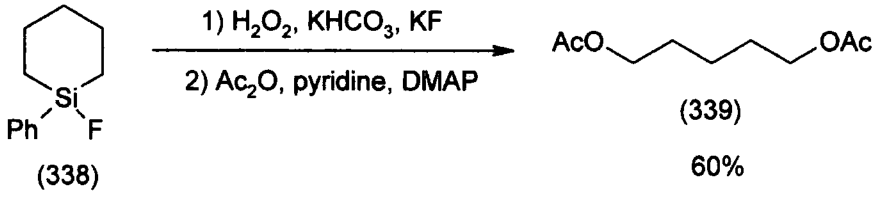
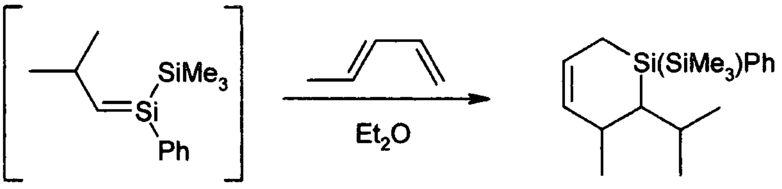


Figure 4.36

The success of this model study led us to believe that the most likely route to performing the overall silene cycloaddition/oxidation sequence lay with the use of silenes bearing phenyl substituents. It was this observation which led to the investigation of the chemistry of acylbis(trimethylsilyl)phenylsilanes, notably the formation and cycloreversion of their silenes, as described in Chapter 3.

4.4.7 Oxidation of silene cycloadducts obtained from "Oehme" silenes

Coincidentally, as part of the work described in Chapter 3, we were forming silyl alcohols bearing phenyl substituents on silicon, as precursors to acylsilanes. Silyl alcohols similar to these have been used by Oehme to generate simple silene species. As has already been described in Chapter 3, reaction of silyl alcohol (221) with MeLi produced a silene, which was trapped in the presence of (*E*)-1,3-pentadiene, to form a Diels-Alder cycloadduct (271) as a single (>95%) diastereoisomer, Figure 4.37.



(269)

Figure 4.37

Additionally, if the oxidation reaction proved successful, we felt that the resultant diol could be converted to a crystalline derivative, allowing the determination of the relative stereochemistry of the initial silene cycloadduct.

With this silacycle in hand, the next step was to reduce the double bond of the allylsilane generated. The optimum conditions found were 10% Pd on carbon with toluene as solvent, for ~4-6 hours, which gave a yield of the reduced silacycle (340) of 80%. It was found that the use of ethanol or ethyl acetate as solvent led to the rapid decomposition of the silacycle, with only small amounts of the desired product being obtained. Eventually we found that the use of toluene as the solvent led to the reduction occurring in 4-6 hours, with negligible decomposition taking place.

The reduction completed, the next stage was the electrophilic displacement of the phenyl group. The use of $BF_3.2AcOH$ would hopefully give the fluorosilane as intermediate, and the use of the two-step procedure, which is a similar reaction used in the model study described above, would allow us to determine whether any problems caused were due to the initial displacement or the subsequent oxidation.

Initially, small scale (~10mg) reactions were perfomed on NMR tube scale in $CDCl_3$. Two equivalents of $BF_3.2AcOH$ was added to a solution of the silacycle, and the solution was monitored by ^1H and ^{19}F nmr spectroscopy. Initially we found that the reaction was very sluggish at room temperature, however increasing the temperature to 70°C led to an apparent reaction, a ^{19}F nmr signal appearing at −187.4ppm, and the disappearance of the aromatic signals in the 1H nmr, to be replaced by a singlet at 7.30 ppm, which we assigned to be due to benzene being formed as the reaction progressed.

Despite the increased temperature, the reaction required 20 hours to achieve complete reaction.

With this evidence, a preparative scale reaction was performed. In this instance, $CHCl_3$ was used as solvent. After heating the reaction mixture to reflux for 20 hours, workup with saturated $NaHCO_3$ solution, followed by extraction and concentration gave the crude fluorosilane (341), Figure 4.38.

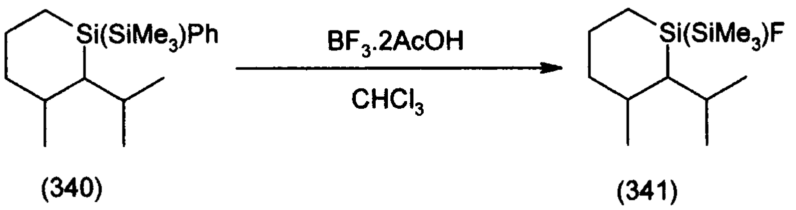


Figure 4.38

The next step was the oxidation reaction. The fluorosilane (341) was reacted with H_2O_2, KF, $KHCO_3$ in a MeOH:THF solvent and refluxed for 18 hours. Workup followed by flash column chromatography gave the desired diol (342) in reasonable overall yield of 60%, given the small scale of the reaction, Figure 4.39.

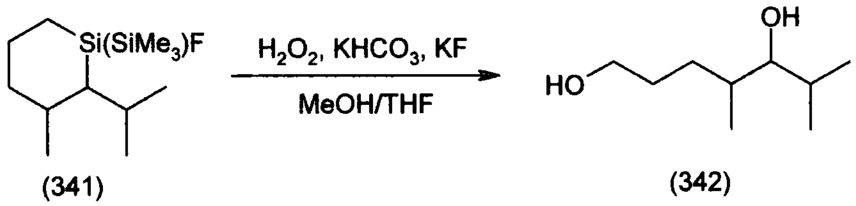


Figure 4.39

This observation was a major breakthrough, as it indicated that the overall reaction sequence was a viable method for functionalising dienes.

Suitable functionalisation of this diol could render a crystalline derivative, which could give evidence of the relative orientation of the substituents in the diol, and from this the relative stereochemistry of silacycle (269). 4-Nitrobenzoyl esters of alcohols are known to be crystalline in many cases. Reaction of the diol (342) with 4-nitrobenzoyl chloride in the presence of DMAP and triethylamine gave, after flash column chromatography (elutant: 10% ethyl acetate:petrol) a colourless solid. The ^1H NMR spectrum of this material supported the formation of the dinitrobenzoyl ester (343), Figure 4.40.

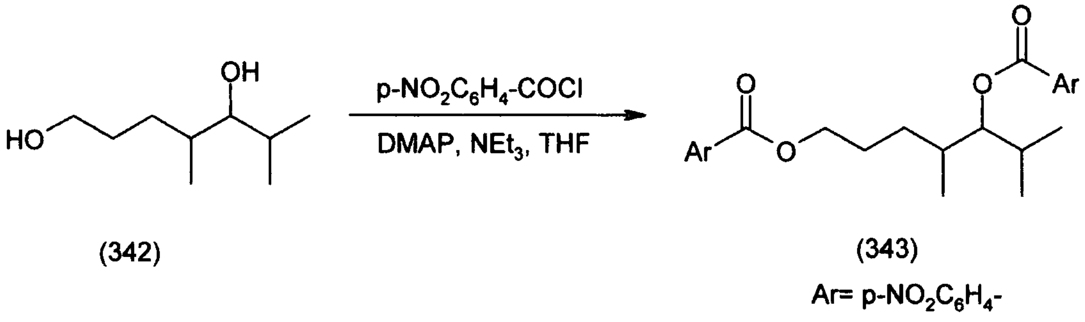


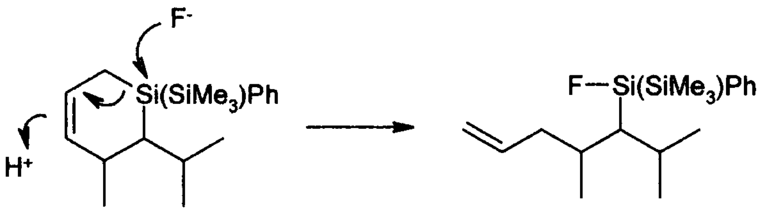
Figure 4.40

Attempts were made to crystallize this material from a diethyl ether/petrol solvent mixture, however the small amount of material available (~20mg) made this task very difficult.

Unfortunately, lack of time prevented any further examples being attempted.

4.4.8 Oxidation of unreduced silacycle (269)

Following the observation that silacyle (340) could be oxidized to give the diol (342), the idea occurred that the unreduced silacycle (269), should react with an electrophile as an allylsilane, to give the intermediate (344), Figure 4.41.

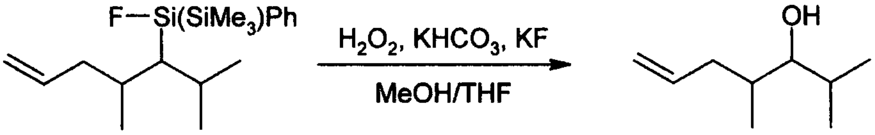


(344)

Figure 4.41

Reaction of the silacycle (271) with $BF_3.2AcOH$ led to the exclusive formation of the predicted fluorosilane (344), with no displacement of the phenyl group detected. The reaction unsurprisingly occurring much more rapidly (1-2 hours) than when reacting with the phenyl group.

Oxidation of the crude fluorosilane (344) led to the formation of an unsaturated alcohol. The ^1H NMR spectrum of the isolated material was consistent with the homoallyl alcohol (345) expected, compared to literature data for this compound.[129,130] Evidently the double bond is not affected in this reaction, Figure 4.42.



(344) (345)

Figure 4.42

The simplicity of the spectrum obtained indicated that the alcohol is formed as a single diastereoisomer. However the small scale of the reaction, and the lack of time precluded the determination of the relative stereochemistry in this alcohol, and any further study of this reaction.

4.5 Conclusions and Future Work

The silacycles formed by both thermolysis and dimer reversion of acylpolysilanes proved impossible to oxidize with the conditions described above. This is not to say that future investigation would be equally unsuccessful. Silene dimer cycloreversion is probably the easiest method of forming silenes currently available. Hopefully, further work will allow the development of a suitable oxidation protocol for the silene cycloadducts obtained through dimer reversion.

The silacycles produced by the conditions described by Oehme proved to be far more successful. Developing the work performed previously, we have found that silenes bearing phenyl substituents could be formed, and to give cycloadducts in reasonable yield. This reaction and the subsequent oxidation appear, given the high level of diastereoselectivity observed in the initial silene cycloaddition, to be a viable method for forming diasteromerically pure diols and homoallylic alcohols. Further work in this area would be to determine the generality of the cycloaddition reaction with different dienes and silenes. Potential also exists for the investigation of the cycloreversion of dimers formed in this Peterson elimination, Figure 4.43.

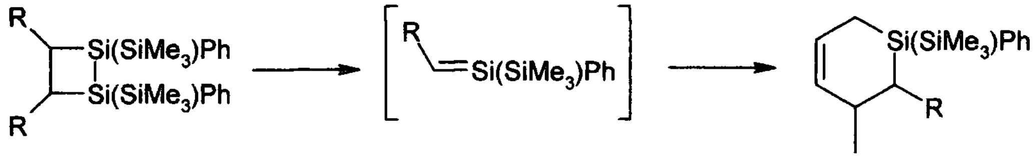


Figure 4.43

This would eliminate the low temperature Peterson elimination, and may overcome the difficulties encountered using cyclic dienes.

Chapter 5

Experimental Detail

5. Experimental Detail

5.1 Introduction

All reactions were carried out under an atmosphere of dry nitrogen or argon in pre-dried glassware.

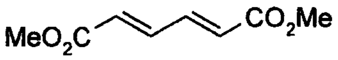
Unless otherwise stated, nuclear magnetic resonance (NMR) spectra were obtained on Varian Gemini 200 (^{1}H at 199.975 MHz, ^{13}C at 50.289 MHz), Varian VXR-200 (^{1}H at 200.057 MHz), Varian Mercury-200 (^{1}H at 199.991 MHz, ^{13}C at 50.288 MHz, ^{19}F at 188.179 MHz), Bruker AC-250 (^{1}H at 250.133 MHz, ^{13}C at 62.257 MHz, ^{19}F at 235.3 MHz), Bruker AM-250 (^{1}H 250.133 MHz, ^{13}C at 62.896 MHz), Varian Unity-300 (^{1}H at 299.908 MHz, ^{13}C at 75.412 MHz), Varian VXR-400(S) (^{1}H at 399.952 MHz, ^{13}C at 100.577 MHz), Bruker AMX-500 (^{1}H at 500.137 MHz, ^{13}C at 125.771 MHz) and Varian Inova-500 (^{1}H at 499.779 MHz, ^{13}C at 125.669 MHz, ^{29}Si at 99.293 MHz) spectrometers, with deuterochloroform as solvent (residual $CHCl_3$: $\delta(^1H)$= 7.26, $\delta(^{13}C)$= 77.0) and are recorded in ppm (δ units). Signal splitting patterns are described as singlet (s), doublet (d), triplet (t), quartet (q) or multiplet. Infrared (IR) spectra were recorded on a Perkin-Elmer FT-IR 1720X or 1600 spectrometer. Low resolution mass spectra were recorded on a VG Analytical 7070E and VG Autospec Organic Mass Spectrometers, and gas chromatography-mass spectra (GC-MS) were recorded using a Hewlett-Packard 5890 Series II gas chromatograph, equipped with a 25m SE30 column, connected to a VG Mass Lab Trio 1000. High resolution mass spectra were performed by the EPSRC service at the University of Swansea and on a VG Autospec Organic Mass Spectrometer. Reactions were followed by thin-layer chromatography (tlc). Flash column chromatography was performed according to the method[131] of Still *et al* using silica gel (60-240 mesh). Melting points were determined using Gallenkamp melting point apparatus and are uncorrected.

All solvents were distilled prior to use following standard protocols.[132] Petroleum ethers refer to the fraction boiling in the 40-60°C range unless otherwise stated. Solvents were dried from the following reagents under a nitrogen atmosphere: hexane and benzene (calcium hydride), THF and diethyl ether (sodium benzophenone ketyl), methanol (sodium methoxide) and ethanol (sodium ethoxide). All other reagents were used as supplied, unless otherwise stated.

Unless otherwise stated, photochemical reactions were performed using a Photochemical Reactors Ltd. 125W medium pressure mercury lamp. All photochemical reaction mixtures were thoroughly degassed by passage of nitrogen through for at least 30 minutes prior to reaction.

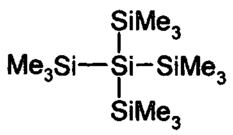
5.2 Experimental Detail

Dimethyl (*E,E*)-2,4-hexadienoate (186)



(*E,E*)-2,4-Hexadienoic acid (1.12 g, 7.9 mmol) was dissolved in a mixture of THF:water (3:1, 50 ml). An ethereal solution of diazomethane was produced[133] by the addition of N-methyl-N-nitroso-*p*-toluenesulfonamide (6.75 g, 31 mmol) in ether (50 ml) and ethanol (~2 ml) to a solution of potassium hydroxide (2 g) in ethanol (10 ml) and water (3 ml) which was heated to 65°C. The solution of diazomethane was added to the acid solution until the yellow colour persisted. The resultant mixture was then extracted with ether (3x10 ml), the organic extracts were combined and dried over $MgSO_4$. Concentration gave the crude product. Recrystallisation from ethyl acetate gave the title compound as a white crystalline solid (1.10 g, 82%); m.p. 156-157°C (lit:[134] 158.5°C). ν_{max} (KBr disc) 3066, 3046, 3002, 2950, 2856, 2010, 1834, 1716, 1609, 1436, 1313 cm^{-1}. δ_H (250MHz) 7.33 (2H, d, J=11.7 Hz, -C$\underline{\mathbf{H}}$=CH-CO_2CH_3), 6.21 (2H, dd, J=11.7, 3.1Hz, -CH=C$\underline{\mathbf{H}}$-CO_2CH_3), 3.79 (6H, s, -$CO_2C\underline{\mathbf{H}}_3$); δ_C (63MHz) 166.20, 140.90, 127.79, 51.61; MS (EI^+) m/z 170 (M^+, 12%), 155 (M^+-CH_3, 3%), 139 (M^+-2CH_3,), 139 (24%), 123.94 (9%), 112 (6%), 111 (100%), 79 (15).

Tetrakis(trimethylsilyl)silane (175)[73]



$$Si(SiMe_3)_4$$

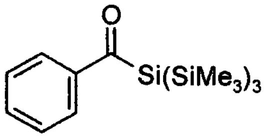
An aliquot (10 ml) of a solution of silicon tetrachloride (15.29 g, 90 mmol) in THF (75 ml) was added to a mixture of chlorotrimethylsilane (46.0 g, 423 mmol), and lithium ribbon (7.5 g, 1071 mmol) in THF (100 ml). The solution was stirred for 3 hours, after which the remaining silicon tetrachloride solution was added dropwise. The mixture was stirred for 18 hours. The mixture was then filtered through a celite pad to remove unreacted lithium and lithium salts. Dilute HCl (3 M, 150 ml) was then added to the filtrate. The organic layer was separated, and the aqueous layer extracted with diethyl ether (3x50 ml). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Recrystallisation of the semisolid residue from acetone yielded the title compound as a white crystalline solid (15.32 g, 53.2%). Sublimes at 254°C (lit:[73] 256-260°C).

ν_{max} ($CHCl_3$) 3019, 2949, 2893, 1522, 1423, 1395, 1256, 1245, 1225, 1207 cm^{-1}. δ_H (250MHz) 0.20; δ_C (63MHz) 2.63; MS (EI^+) m/z 320 (M^+, 10%), 305 (M^+-CH_3, 9%), 232 (M^+-CH_3-TMS, 48%), 173 (16), 158 (15), 73 (100).

General Procedure for the formation of Acyltris(trimethylsilyl)silanes[37]

Methyllithium (1.6 M solution in ether) was added to a solution of tetrakis(trimethylsilyl)silane (0.23 M, 1 equiv.) in THF. After approximately 18 hours ^1H NMR showed the complete disappearance of the signal for tetrakis(trimethylsilyl)silane, and the appearance at 0.32ppm of the signal for tris(trimethylsilyl)silyllithium. The yellow solution was then cooled to -78°C and added dropwise via cannula to a cooled (-78°C) solution of acyl chloride (0.46 M, 2 equivs.) THF,over a 2 hour period. After stirring for 4 hours at -78°C, dilute HCl (3 M, 100 ml) was added. The organic layer was separated, and the aqueous layer extracted with diethyl ether. The combined organic layers were dried over $MgSO_4$. The mixture was then filtered, and the solvents removed via rotary evaporation. Flash column chromatography yielded the pure acyltris(trimethylsilyl)silane.

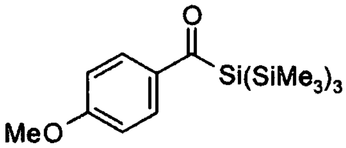
Benzoyltris(trimethylsilyl)silane (87)[37]



Tris(trimethylsilyl)silyllithium (generated from (175) (2.52 g, 7.89 mmol) and methyllithium (4.93 ml, 7.89 mmol) in THF (30 ml)) was combined with benzoyl chloride (2.22 g, 15.8 mmol) to afford, after workup and flash column chromatography (2% ether:petrol) the title compound (2.15 g, 77%) as a yellow oil.

ν_{max} (thin film) 3062, 2949, 2893, 2360, 2341, 1737, 1607, 1593, 1575, 1445, 1399, 1308, 1245, 1200, 1167cm^{-1}. δ_H (200MHz) 7.7-7.3 (5H, m, $\underline{\mathbf{Ar}}$), 0.25 (27H, s, 3xSi(C$\underline{H}_3$)$_3$); δ_C (126MHz) 234.26, 144.09, 133.35, 128.48, 127.52, 1.26; MS (EI$^+$) m/z 352 (M$^+$, 1%), 279 (M$^+$-Si(CH$_3$)$_3$, 5%), 135 (14), 73 (100).

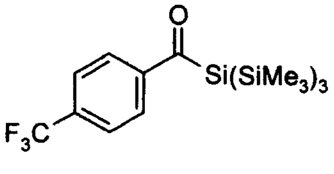
4-Methoxybenzoyltris(trimethylsilyl)silane (179)[80]



Tris(trimethylsilyl)silyllithium (generated from (175) (2.52 g, 7.89 mmol) and methyllithium (4.93 ml, 7.89 mmol) in THF (30 ml)) was combined with 4-methoxybenzoyl chloride (2.78 g, 16.3 mmol) to afford, after workup and flash column chromatography (10% ether:petrol) the title compound (1.86 g, 62%) as a yellow oil. ν_{max} (thin film) 3004, 2953, 2895, 2839, 2360, 2341, 1691, 1608, 1586, 1569, 1505, 1463, 1552, 1399, 1307, 1259, 1209, 1159 cm^{-1}; δ_H (400MHz) 7.73 (2H, d, J=8.7Hz), 6.92 (2H,d, J=8.7Hz), 3.67 (3H, s, OC$\underline{H}_3$), 0.25 (27H, Si(C$\underline{H}_3$)$_3$); δ_C (126MHz) 232.98, 163.16, 137.61, 129.97, 113.28, 55.42, 1.528; MS (EI) m/z 383 (MH$^+$, 4%), 367 (M$^+$-CH$_3$, 15%), 311 (MH$^+$-SiMe$_3$), 279 (40), 221 (12), 209 (41) 152 (100), 147 (61), 135

(100), 92 (40), 73 (100); MS (CI) m/z 383 (MH$^+$, 6%), 209 (19), 170 (17), 152 (27), 137 (32), 90 (42).

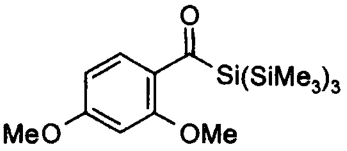
4-Trifluoromethylbenzoyltris(trimethylsilyl)silane (181)



Tris(trimethylsilyl)silyllithium (generated from (175) (2.50 g, 7.82 mmol) and methyllithium (4.89 ml, 7.82 mmol) in THF (30 ml)) was combined with 4-(trifluoromethyl)benzoyl chloride (3.25 g, 15.6 mmol) to afford, after workup and flash column chromatography (2% ether:petrol) the title compound (3.11 g, 94%) as a yellow oil.

ν_{max} (thin film) 3063, 2956, 2896, 1933, 1800, 1730, 1619, 1605, 1580, 1505, 1405, 1327, 1249 cm^{-1}; δ_H (200MHz) 7.80 (2H, d, J= 8.4Hz)-7.72 (2H, d, J= 8.4Hz), 0.23 (27H, s, 3xSi(C$\underline{H}_3$)$_3$; δ_C (126MHz) 236.50, 145.88, 133.28 (q, $^2J_{C\text{-}F}$=32.7Hz, $\underline{C}$-CF$_3$), 127.02, 125.11 (q, $^3J_{C\text{-}F}$= 3.8Hz, $\underline{C}$-C-CF$_3$) , 123.34 (q, $^1J_{C\text{-}F}$=272.9Hz, $\underline{C}$F$_3$), 1.20; δ_F (235MHz) -63.28; MS (EI$^+$) m/z 405 (M$^+$-CH$_3$), 281 (60), 207 (36), 190 (35), 173 (62), 147 (66), 73 (100).

2,4-(Dimethoxy)benzoyltris(trimethylsilyl)silane (183)



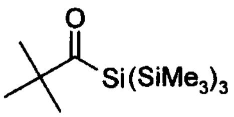
Tris(trimethylsilyl)silyllithium (generated from (175) (2.06 g, 6.44 mmol) and methyllithium (4.93 ml, 7.89 mmol) in THF (30 ml)) was combined with 2,4-

(dimethoxy)benzoyl chloride (2.56 g, 12.79 mmol) to afford, after workup and flash column chromatography (2% ether:petrol) the title compound (0.91 g, 35%) as a yellow oil. ν_{max} (thin film) 2955, 2893, 2837, 2361, 2340, 1606, 1497, 1464, 1439, 1412, 1307, 1284, 1258, 1245, 1159 cm^{-1}; δ_H (250MHz) 7.20-7.10 (1H, m, $\underline{\mathbf{Ar}}$), 6.5-6.3 (2H, m, $\underline{\mathbf{Ar}}$), 3.83 (3H, s, -OC$\underline{\mathbf{H}}_3$), 3.78 (3H, s, -OC$\underline{\mathbf{H}}_3$), 0.19 (27H, s, -Si(Si(C$\underline{\mathbf{H}}_3$)$_3$)); δ_C (63MHz) 237.81, 162.43, 157.35, 131.38, 129.92, 103.59, 98.56, 56.51, 1.27; MS (EI$^+$) m/z 413 (MH$^+$, 15%), 398 (MH$^+$-CH$_3$, 15%), 339 (M$^+$-Si(CH$_3$)$_3$, 11%) 309 (31), 281 (24), 239 (36), 191 (60), 165 (100%), 149 (63), 131 (58), 73 (100).

Acetyltris(trimethylsilyl)silane (86)[37]

Tris(trimethylsilyl)silyllithium (generated from (175) (2.11 g, 6.58 mmol) and methyllithium (4.11 ml, 6.58 mmol) in THF (30 ml)) was combined with acetyl chloride (1.03 g, 13.16 mmol), to afford, after workup and flash column chromatography (eluting: petrol) the title compound (1.18 g, 76%) as a colourless semisolid.
ν_{max} (CHCl$_3$) 3019, 2959, 2867, 2360, 2340, 1740, 1626, 1251, 1225 cm^{-1}; δ_H (200MHz) 2.29 (3H, s, -C$\underline{\mathbf{H}}_3$), 0.24 (27H, s, -SiC$\underline{\mathbf{H}}_3$); δ_C (CDCl$_3$) 244.03, 42.11, 1.00.

Trimethylacetyltris(trimethylsilyl)silane (45)[37]



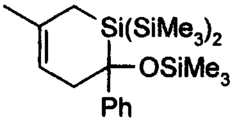
Tris(trimethylsilyl)silyllithium (generated from (175) (2.59 g, 8.09 mmol) and methyllithium (5.06 ml, 8.09 mmol) in THF (30 ml)) was combined with trimethylacetyl chloride (1.95 g, 16.18 mmol) to afford, after workup and flash column chromatography (2% ether:petrol) the title compound (1.40 g, 52%) as a colourless crystalline solid. M.p. 181-182°C dec.

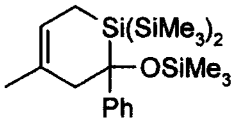
ν_{max} ($CHCl_3$) 3020, 2963, 2896, 1709, 1619, 1522, 1247, 1225 cm^{-1}; δ_H (250MHz) 1.02 (s, 9H, $C(O)C(C\underline{H}_3)_3$), 0.23 (s, 27H, $3x(Si(C\underline{H}_3)_3)$; δ_C (63MHz) 248.5, 49.5, 24.7, 1.61 MS (EI$^+$) m/z 317 (M^+-CH_3, 16%), 275 (M^+-$C(CH_3)_3$, 5%), 259 (M^+-$Si(CH_3)_3$, 22%), 205 (11),191 (10), 173 (100), 159 (19), 147 (55), 131 (31), 117 (21), 73 (100); (CI) m/z 317 (M^+-CH_3, 13%), 191 (9), 90 (13).

General procedure for the thermolysis of acyltris(trimethylsilyl)silanes in the presence of dienes

A solution of the appropriate polysilane (0.28M) and diene (2x excess) in benzene or toluene was placed in a Carius tube, and thoroughly degassed using the freeze-pump-thaw technique (minimum 3 cycles). The tube was then sealed, and heated at 180°C for 4 hours. Removal of the solvent by rotary evaporation, followed by flash column chromatography gave the Diels-Alder adduct as a mixture of regio- and/or diastereoisomers.

1,1-Bistrimethylsilyl-2-phenyl-2-(trimethylsilyloxy)-4-methylsilacyclohex-4-ene (187); 1,1-Bistrimethylsilyl-2-phenyl-2-(trimethylsilyloxy)-5-methylsilacyclohex-4-ene (188)

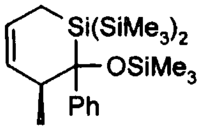




A solution of benzoyltris(trimethylsilyl)silane (1.11 g, 3.15 mmol) and isoprene (0.43 g, 6.30 mmol) in benzene (10 ml) was heated at 180°C for 4 hours in a sealed tube. Flash column chromatography (eluting: petrol) gave the title compounds as a white solid as a

(1:1) mixture of regioisomers, (0.81 g, 61%). M.p. 113-114°C. [Found (CI): MH$^+$, 421.2235; $C_{21}H_{40}Si_4O$ requires *M*, 421.2234]; ν_{max} (CHCl$_3$) 3019, 2955, 2894, 1597, 1488, 1443, 1400, 1248 cm^{-1}; δ_H (CDCl$_3$) 7.45-6.90 (10H, m, **Ar**), 6.75-5.65 (1H, m, -(Me)C=C**H**-, (188)), 5.45-5.35 (1H, m, -(Me)C=C**H**-,(187)), 2.95-2.50 (2H, m, -Si-C(OTMS)(Ph)-C**H**$_2$-), 1.79 (3H, s, -HC=C(C**H**$_3$)-(188)), 1.70 (3H, s, -HC=C(C**H**$_3$)-(187)), 1.65-1.15 (2H, m, -Si-C**H**$_2$-C=), 0.11 (9H, s, Si(C**H**$_3$)$_3$), 0.02 (9H, s, Si(C**H**$_3$)$_3$), 0.01(7) (9H, s, Si(C**H**$_3$)$_3$), -0.08 (9H, s, Si(C**H**$_3$)$_3$), -0.18 (9H, s, Si(C**H**$_3$)$_3$), -0.25 (9H, s, Si(C**H**$_3$)$_3$); δ_C (63MHz) 149.89, 135.41, 134.25, 127.79, 125.32, 125.07, 124.59, 121.60, 46.27, 40.50, 30.87, 27.60, 25.30, 13.80, 7.90, 2.89, 0.07, -0.49; MS (EI$^+$) m/z 421 (MH$^+$, 3%), 405 (M$^+$-CH$_3$, 93%), 347 (M$^+$-Si(CH$_3$)$_3$, 100%), 332 (61), 317 (10), 293 (36), 273 (55), 259 (64), 245 (63), 209 (65), 199 (77), 191 (100), 157 (41), 147 (100), 135 (100), 133 (100), 129 (40), 73 (100); (CI) 421 (MH$^+$, 2%), 348 (18%), 331 (67), 90 (64).

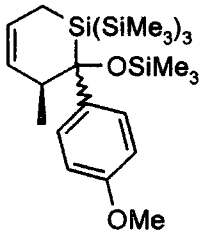
1,1-Bistrimethylsilyl-2-phenyl-2-(trimethylsilyloxy)-3-methyl-silacyclohex-4-ene (159a,b)



A solution of benzoyltris(trimethylsilyl)silane (0.57 g, 1.62 mmol) and (*E*)-1,3-pentadiene (0.21 g, 3.23 mmol) in benzene (5 ml) was heated at 180°C in a sealed tube for 4 hours. Flash column chromatography (eluting: petrol) gave the title compound as a mixture of diastereoisomers (0.44 g, 64%, 2:1 *cis*:*trans*). M.p. 173-174°C

ν_{max} (CHCl$_3$) 3155, 2998, 2953, 2895, 1793, 1639, 1599, 1471, 1389, 1251 cm^{-1}; δ_H (250MHz) 7.32-7.03 (10H, m, **Ar**), 5.93-5.85 (1H, m, =C**H**-CH(Me)-, trans), 5.56-5.43 (1H, m, -C**H**=CH-CH(Me)-, cis), 3.20-3.10 (1H, m, =CH-C**H**(Me)-, trans), 3.10-2.95 (1H, =CH-C**H**(Me)-, cis) 1.80-1.23 (2H, m, =CH-C**H**$_2$-Si-), 1.04 (3H, d, J=7.4Hz, =CH-CH(C**H**$_3$)-, trans), 0.95 (3H, d, J=7.2Hz, =CH-CH(C**H**$_3$)-, cis), 0.18 (9H, s, -OSi(C**H**$_3$)$_2$, cis), 0.17 (9H, s, -Si(C**H**$_3$)$_2$, cis), 0.07 (9H, s, -OSi(C**H**$_3$)$_2$, trans), 0.03 (9H, s, -Si(C**H**$_3$)$_2$, trans), -0.02 (9H, s, -Si(C$\underline{H}_3$)$_2$, cis), -0.32 (9H, s, -Si(C$\underline{H}_3$)$_2$, cis); δ_C (50MHz) 148.10, 146.00, 136.98, 134.44, 127.95, 127.65, 126.61, 125.89, 125.37, 125.00, 80.98, 79.11, 43.17, 40.19, 16.57, 16.19, 9.21, 8.44, 3.76, 3.50, 0.71, 0.24, -0.97; MS (EI$^+$) m/z 420 (M$^+$, 3%), 405 (M$^+$-CH$_3$, 1%), 347 (M$^+$-SiMe$_3$, 37%) 332 (13%) 331 (M$^+$-OSiMe$_3$, 7%), 317 (17), 307 (19), 259 (21), 245 (100), 231 (12), 209 (18), 205 (41), 199 (61), 191 (31), 157 (31), 147 (100), 133 (61), 117 (41), 73 (100).

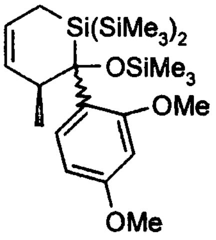
1,1-Bistrimethylsilyl-2-(4-methoxyphenyl)-2-(trimethylsilyloxy)-3-methyl-silacyclohex-4-ene (189a,b)



A solution of 4-methoxybenzoyltris(trimethylsilyl)silane (0.47 g, 1.24 mmol) and (*E*)-1,3-pentadiene (0.17 g, 2.48 mmol) in benzene (5 ml) was heated at 180°C in a sealed tube for 4 hours. Flash column chromatography (eluting: 5% ether: petrol) gave the title compound as a mixture of diastereoisomers (0.443 g, 80%, 3:2 *cis*:*trans*).

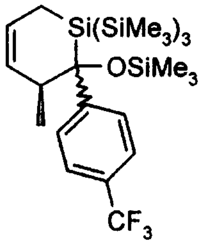
ν_{max} (thin film) 2997, 2951, 2894, 2833, 1608, 1508, 1463, 1441, 1391, 1291, 1250, 1179, 1068, 836 cm^{-1} ; δ_H (400MHz) 7.30-7.18 (4H, m, Ar), 6.90-6.75 (4H, m, Ar), 6.0-5.85 (1H, m, =C$\underline{H}$-CH(Me)-, trans), 5.6-5.4 (1H,m, -C$\underline{H}$=CH-CH(Me)-, cis), 3.81 (3H, s, -OMe, trans), 3.80 (3H, s, -OMe, cis), 3.20-3.10, (1H, m, =CH-C$\underline{H}$(Me)-, trans), 3.10-3.00 (1H, m, =CH-C$\underline{H}$(Me)-), 1.85-1.2 (2H, m, allylic) 1.08 (1H, d, J=7.2Hz, =CH-CH(C$\underline{H}_3$), trans), 0.97 (1H, d, J=7.2Hz, =CH-CH(C$\underline{H}_3$), cis), 0.20 (9H, s, OSi(C$\underline{H}_3$)$_3$, cis), 0.18 (9H, s, -Si(C$\underline{H}_3$)$_3$, cis), 0.08 (9H, s, -OSi(C$\underline{H}_3$)$_3$, trans), 0.04 (9H, s, -Si(C$\underline{H}_3$)$_3$, trans), -0.07 (9H, Si(C$\underline{H}_3$)$_3$, trans), -0.25 (9H, Si(C$\underline{H}_3$)$_3$, cis) ; δ_C (63 MHz) 157.20, 157.17, 140.46, 138.39, 136.91, 134.46, 126.79, 126.63, 126.53, 125.88, 113.23, 113.00, 80.44, 78.82, 55.25, 55.22, 43.18, 40.31, 16.53, 16.13, 9.15, 8.50, 3.63, 3.40, 0.61, 0.23, 0.15, -0.03, -0.88; MS (EI$^+$) m/z 450 (M$^+$, 7%), 435 (M$^+$-CH$_3$, 9), 377 (M$^+$-Si(CH$_3$)$_3$, 12%), 275 (100), 205 (13), 165 (16), 147 (24), 73 (84).

Thermolysis of 2,4-(Dimethoxy)benzoyltris(trimethylsilyl)silane in the presence of (*E*)-1,3-pentadiene; formation of 1,1-Bistrimethylsilyl-2-(2,4-bismethoxyphenyl)-2-(trimethylsilyloxy)-3-methyl-silacyclohex-4-ene (191a,b)



A solution of 2,4-bis(methoxy)benzoyltris(trimethylsilyl)silane (0.25 g, 0.61 mmol) and (*E*)-1,3-pentadiene (0.08 g, 1.22 mmol) in benzene (3 ml) was heated at 180°C in a sealed tube for 4 hours. Concentration, followed by flash column chromatography (eluting: 2% ether: petrol) gave the [4+2] adduct as a mixture of diastereoisomers (0.443 g, 80%, ~1:1 *cis:trans*) (^{1}H NMR) along with several inseparable components. MS (CI) 481 (MH$^+$, 100%), 408 (MH$^+$-Si(CH$_3$)$_3$, 4%), 392 (MH$^+$-OSi(CH$_3$)$_3$, 31%).

1-Bistrimethylsilyl-2-(4-trifluoromethyl)phenyl-2-trimethylsilyloxy-3-methylsilacyclohex-4-ene (190a,b)



A solution of 4-trifluoromethylbenzoyltris(trimethylsilyl)silane (0.52 g, 1.23 mmol) and (*E*)-1,3-pentadiene (0.16 g, 2.42 mmol) in benzene (5 ml) was heated at 180°C in a sealed tube for 4 hours. Concentration, followed by flash column chromatography (eluting: petrol) gave the title compound as a mixture of diastereoisomers (0.27 g, 46%, 4:1 *cis*:*trans*). M.p. 98-100°C.

ν_{max} (KBr disc) 2998, 2955, 2895, 1614, 1408, 1329, 1243, 1161, 1119, 1079, 1069, 835 cm^{-1}; δ_H (250MHz) 7.60-7.20 (4H, m, $\underline{\mathbf{Ar}}$), 6.00-5.80 (1H, m, vinylic), 5.50-5.20 (1H, m, vinylic), 3.20-3.10 (1H, m, allylic, $\underline{\text{trans}}$), 3.10-3.00 (1H, m, allylic, $\underline{\text{cis}}$),1.80-1.30 (2H, m, allylic), 1.03 (3H, d, J=7.4Hz, $=CH-CH(C\underline{\mathbf{H}}_3)-C$), 0.97 (3H, d, J=7.2Hz, $=CH-CH(C\underline{\mathbf{H}}_3)-C$, $\underline{\text{cis}}$) 0.21, 0.12, -0.01 (9H each, $Si(C\underline{\mathbf{H}}_3)_3$); $\delta^{19}F$ (235MHz) -62.52; MS (EI^+) m/z 487 (M^+-1, 2%), 415 ($M^+-Si(SiMe_3)_3$, 17%), 400 (17), 384 (12), 322 (16), 312 (30), 306 (14), 262 (37), 205 (24), 191 (20), 147 (28), 141 (10), 131 (13), 117 (12), 73 (100).

Repeated flash column chromatography (eluting: petrol) gave the *cis* diastereoisomer as the only product.

δ_H (300 MHz) 7.51 (2H, d, J=8.4 Hz, $\underline{\mathbf{Ar}}$), 7.46 (2H, d, J=8.4 Hz, $\underline{\mathbf{Ar}}$), 5.95 (1H, m, $CH=C\underline{\mathbf{H}}CH(CH_3)$)), 5.58 (1H, m, $C\underline{\mathbf{H}}=CHCH(CH_3)$)), 3.10 (1H, m, $=CH-C\underline{\mathbf{H}}(CH_3)$)), 1.40 (2H, m, $Si-C\underline{\mathbf{H}}_2-CH=CH$), 0.98 (3H, d, J=7.2 Hz, $=CH-CH(C\underline{\mathbf{H}}_3)-C$), 0.22 (9H, s, $OSi(C\underline{\mathbf{H}}_3)_3$), 0.20 (9H, s, $Si(C\underline{\mathbf{H}}_3)_3$), -0.30 (9H, s, $Si(C\underline{\mathbf{H}}_3)_3$); δ_C (75 MHz) 150.59, 136.82, 127.06 (q, $^2J_{C-F}$=31.95 Hz $F_3C-\underline{C}$), 126.02, 125.32, 124.60 (q, $^3J_{C-F}$=3.75 Hz, $F_3C-CH-\underline{C}H$), 124.49 (q, $^1J_{C-F}$=269.93 Hz, $\underline{C}F_3$), 122.69, 119.10, 79.09, 42.97, 16.52, 8.26, 3.45, 0.66, -1.10.

All other data identical with that obtained for the mixture.

Thermolysis of trimethylacetyltris(trimethylsilyl)silane with (*E*)-1,3-pentadiene

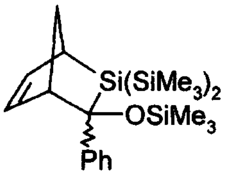
A solution of trimethylacetyltris(trimethylsilyl)silane (0.13 g, 0.40 mmol) and (*E*)-1,3-pentadiene (0.05 g, 0.80 mmol) in benzene (2 ml) was heated at 180°C in a sealed tube for 4 hours. Concentration, followed by flash column chromatography (eluting: petrol) gave a complex mixture of [4+2] and ene products as a colorlesss oil (0.08 g). δ_H (250MHz) 6.0-5.0 (vinylic), 3.2 (m), 2.8-2.5 (m), 1.68 (d) 1.5-0.5 (m), 0.30-0.05 (several singlets, $Si(C\underline{\mathbf{H}}_3)_3$)

Thermolysis of acetyltris(trimethylsilyl)silane with (*E*)-1,3,-pentadiene (192a, b)

A solution of acetyltris(trimethylsilyl)silane (0.21 g, 0.72 mmol) and (*E*)-1,3-pentadiene (0.10 g, 1.44 mmol) in benzene (2 ml) was heated at 180°C in a sealed tube for 4 hours. Concentration, followed by flash column chromatography (eluting: petrol) gave the title compound as a mixture of diastereoisomers (0.053 g, 21%, 2:1 *cis*:*trans*), along with other inseparable components.

δ_H (200MHz) 5.80-5.20 (2H, m, vinylic), 2.60-2.50 (1H, m, allylic), 2.26-2.20 (1H, m, allylic), 1.70-1.10 (2H, m, allylic), 1.53 (3H, s, -CH(Me)-C(OTMS)(C**H**$_3$)-Si, trans), 1.34 (3H, s, , -CH(Me)-C(OTMS)(C**H**$_3$)-Si, cis), 1.09 (3H, d, J=6.8Hz, =CH-CH(C**H**$_3$)-C, trans), 1.00 (3H, d, J=7.2Hz, =CH-CH(C**H**$_3$)-C, cis), 0.16—0.13 (5 singlets, Si(C**H**$_3$)$_3$) δ_C (100MHz) 135.00, 125.78, 45.62, 43.48, 30.70, 23.34, 16.48, 14.92, 8.86, 7.98, 3.54, 0.38, 0.23; MS (EI$^+$) m/z 285 (M$^+$-Si(CH$_3$)$_3$, 7%), 269 (M$^+$-OSi(CH$_3$)$_3$, 18%), 207 (61), 197 (14), 191 (17), 183 (29), 157 (17), 147 (72), 133 (58), 117 (24), 73 (100).

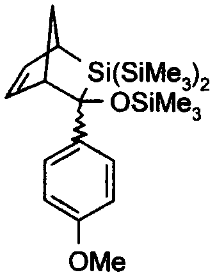
2,2-Bis(trimethylsilyl)-3-phenyl-3-trimethylsilyloxy-2-silabicyclo[2.2.1]hept-5-ene (194a, b)



A solution of benzoyltris(trimethylsilyl)silane (0.50 g, 1.42 mmol) and cyclopentadiene (0.19 g, 2.84 mmol) in benzene (5 ml) was heated at 180°C in a sealed tube for 4 hours. Kugelrohr distillation (oven temp. 225°C/ 0.1 mbar) gave the title compound as a mixture of diastereoisomers (0.433 g, 68%, 3:1 *endo*:*exo*). M.p. 88-89°C

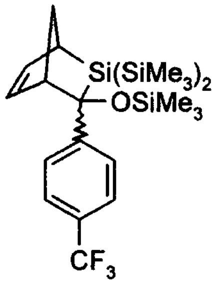
ν_{max} (CHCl$_3$) 3050, 2948, 2878, 1599, 1500, 1250, 1169, 1041, 1021, 838 cm^{-1}; δ_H (400 MHz) 7.40-7.05 (10H, m, **Ar**), 6.32 (1H, dd, J=5.40, 3.30 Hz, 5-**H**, exo), 6.11 (1H, dd, J=5.40, 3.30 Hz, 5-**H**, endo), 5.86 (1H, dd, J=5.40, 3.30 Hz, 6-**H**, exo), 5.77 (1H, dd, J=5.40, 3.30 Hz, 6-**H**, endo), 3.40 (1H, m, 4-**H**, exo), 3.30 (1H, m, 4-**H**, endo), 2.45 (1H, m, 7-**H**H, exo), 2.35 (3H, m, 7-**HH**, endo and 7-H**H**, exo), 2.02 (1H, m, 1-**H**, endo), 1.95 (1H, m, 1-**H**, exo), 0.28 (9H, s, OSi(C**H**$_3$)$_3$, endo), 0.21 (9H, s, OSi(C**H**$_3$)$_3$, exo), -0.16 (9H, s, SiSi(C**H**$_3$)$_3$, exo), -0.18 (9H, s, SiSi(C**H**$_3$)$_3$, endo), -0.28 (9H, s, SiSi(C**H**$_3$)$_3$, endo), -0.29 (9H, s, SiSi(C**H**$_3$)$_3$, exo); δ_C (100 MHz) 148.11, 146.46, 140.37, 139.07, 129.89, 129.51, 127.84, 127.75, 126.10, 125.66, 87.07, 84.45, 51.54, 50.66, 45.44, 44.56, 34.15, 30.86, 2.44, 0.89, 0.06, -0.33, -0.59; MS (EI$^+$) m/z 418 (M$^+$, 2%), 403 (M-Me, 1), 345 (M-SiMe$_3$, 16), 337 (50), 329 (M-OSiMe$_3$, 1), 263 (13), 249 (17), 205 (15), 191 (15), 175 (17), 147 (42), 135 (21), 117 (21), 73 (100).

2,2-Bis(trimethylsilyl)-3-[4'-methoxyphenyl]-3-trimethylsilyloxy-2-silabicyclo[2.2.1]hept-5-ene (195a, b)



A solution of 4-methoxybenzoyltris(trimethylsilyl)silane (0.54 g, 1.42 mmol) and cyclopentadiene (0.19 g, 2.84 mmol) in benzene (5 ml) was heated at 180°C in a sealed tube for 4 hours. Flash column chromatography (eluting: petrol) gave the title compound as a mixture of diastereoisomers (0.433 g, 68%, 2.5:1 *endo*:*exo*). [Found (EI$^+$): M$^+$, 448.2113; $C_{22}H_{40}O_2Si_4$ requires *M*, 448.2105]; ν_{max} (thin film) 3048, 2953, 2894, 1608, 1509, 1249, 1177, 1042, 1021, 838 cm^{-1}; δ_H (200MHz) 7.21 (2H, d, J=7.6Hz, **Ar**, exo), 7.17 (2H, d, J=7.6Hz, **Ar**, endo), 6.81 (2H, d, J=7.6Hz, **Ar**, exo), 6.75 (2H, d, J=7.6Hz, **Ar**, endo) 6.40-6.30 (1H, dd, J=5.4Hz, 3.0Hz, 5-**H**, exo), 6.20-6.10 (1H, dd, J=5.4Hz, 3.0Hz, vinylic, 5-**H**, endo), 5.95-5.85 (1H, dd, J=5.4Hz, 3.0Hz, 6-**H**, exo), 5.85-5.75 (1H, dd, J=5.4Hz, 3.0Hz, 6-**H**, endo), 3.87 (3H, s, -OC**H**$_3$, exo), 3.85 (3H, s, -OC**H**$_3$, endo) 3.37 (1H, m, 4-**H**, exo), 3.25 (1H, m, 4-**H**, endo), 2.40 (1H, m, 7-HH, exo), 2.35 (3H, m, 7-HH exo + 7-HH endo), 1.98 (1H, m, 1-H, endo), 1.90 (1H, m, 1-H, exo), 0.26 (9H, s, -OSi(CH_3)$_3$, endo), 0.16 (9H, s, -OSi(CH_3)$_3$, exo), -0.14 (9H, s, -Si(CH_3)$_3$, exo), -0.16 (9H, Si(CH_3)$_3$, endo)-0.26 (9H, s, -Si(CH_3)$_3$, endo), -0.27 (9H, s, Si(CH_3)$_3$, exo); δ_C (50 MHz) 157.86, 140.18, 138.86, 133.52, 132.21, 131.34, 130.97, 129.73, 129.50, 113.16, 112.98, 87.50, 86.45, 55.31, 55.25, 51.85, 50.89, 45.30, 44.58, 34.22, 33.4, 30.96, 2.55, 2.46, 0.94, 0.14, -0.13, -0.37; MS (EI^+) m/z 448 (M^+, 1%), 367 (3), 279 (10), 263 (5), 209 (20), 191 (8), 135 (5), 73 (100).

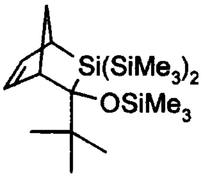
2,2-Bistrimethylsilyl-3-[4'-(trifluoromethyl)phenyl]-3-trimethylsilyloxy-2-silabicyclo[2.2.1]hept-5-ene (196a, b)



A solution of 4-trifluoromethylbenzoyltris(trimethylsilyl)silane (0.49 g. 1.17 mmol) and cyclopentadiene (0.15 g, 2.34 mmol) in benzene (5 ml) was heated at 180°C in a sealed tube for 4 hours. Flash column chromatography (eluting: petrol) gave the title compound as a mixture of diastereoisomers (0.486g, 85%, 4:1 *endo*:*exo*).

ν_{max} 3062, 2955, 2896, 1926, 1794, 1614, 1445, 1406, 1326, 1250, 1168 cm^{-1}; δ_H (250MHz) 7.51 (2H, d, J=8.2Hz, Ar, endo), 7.40 (2H, d, J=8.2Hz, Ar, endo), 7.35 (2H, d, J= 8.2Hz, Ar, exo), 7.27 (2H, d, J= 8.2Hz, Ar, exo), 6.30 (1H, dd, J= 8.3Hz, 3.6Hz, 5-H, exo), 6.15 (1H, dd, J= 8.3Hz, 3.6Hz, 5-H, endo), 5.94 (1H, dd, J= 8.3Hz, 3.2Hz, 6-H, exo), 5.79 (1H, dd, J= 8.3Hz, 3.2Hz, 6-H, endo), 3.31 (1H, m, 4-H, exo), 3.05 (1H, m, 4-H, endo), 2.35 (4H, m, 7-HH, exo + 7-HH, endo), 2.05 (1H, m, 1-H, endo), 2.01 (1H, m, 1-H, exo), 0.32 (9H, s, -Si(CH_3)$_3$, endo), 0.14 (9H, s, -Si(CH_3)$_3$, exo), -0.07 (9H, s, -Si(CH_3)$_3$, exo), -0.16 (9H, s, -Si(CH_3)$_3$, endo), -0.30 (9H, s, -Si(CH_3)$_3$, endo); δ_C (63MHz) 152.85, 151.14, 141.03, 139.39, 129.54 (q, J=32.4Hz, C-CF_3, exo), 128.20 (q, J=32.4 Hz, C-CF_3, endo), 125.80(q, j=3.6Hz, C-C-CF_3, exo) 124.72 (q, J=3.7 Hz, C-C-CF_3, endo), 124.24 (q, J=272.3 Hz, CF_3, endo) 123.80 (q, J= 272.4Hz, CF_3, exo), 86.82 (C-OSiMe$_3$, endo), 84.51(C-OSiMe$_3$, exo), 51.53, 50.93, 45.62, 44.79, 34.21, 30.95, 2.5, 2.14, 0.86, 0.03, -0.36, -0.61; δ^{19}F (235MHz) -62.69; MS (EI$^+$) m/z 486 (M$^+$, 1%), 467 (M$^+$-F, 3%), 413 (M$^+$-SiMe$_3$, 10%), 405 (23), 280 (10), 255 (7), 203 (21), 191 (23), 151 (11), 147 (39), 117 (20),73 (100); (CI) m/z 487 (MH$^+$, 2%), 466 (MH$^+$-F, 3%), 405 (24), 397 (30), 203 (57), 191 (12), 147 (20), 117 (11), 90 (58), 73 (100).

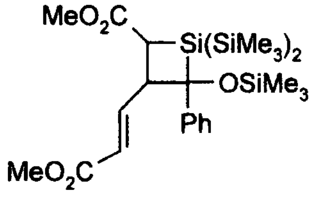
2,2-Bistrimethylsilyl-3-*tert*-butyl-3-trimethylsilyloxy-2-silabicyclo[2.2.1]hept-5-ene (197a, b)



A solution of trimethylacetyltris(trimethylsilyl)silane (0.47 g, 1.41 mmol) and cyclopentadiene (0.19 g, 2.82 mmol) in benzene (5 ml) was heated at 180°C for 4 hours in a sealed tube. Flash column chromatography (eluting: petrol) gave the title compound as a mixture of diastereoisomers (0.39 g, 70%, 6:1 *endo*:*exo*).

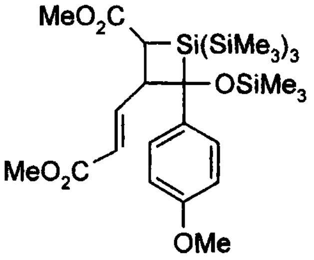
ν_{max} (thin film) 3051, 2945, 2887, 1621, 1500, 1212, 1153, 1042, 1021, 822 cm^{-1}; δ_H (250MHz) 6.31 (1H, dd, J=5.3, 3.2Hz, 5-**H**, exo), 6.09 (1H, dd, J=5.4, 3.2Hz, 5-**H**, endo), 5.90 (1H, dd, J=5.3, 3.2 Hz, 6-**H**, exo), 5.65 (1H, dd, J=5.4, 3.2Hz, 6-**H**, endo), 2.89 (1H, m, 4-**H**, exo), 2.77 (1H, m, 4-**H**, endo), 2.35-2.18 (4H, m, 7-**HH** exo and 7-**HH** endo); 2.90-2.80 (1H, m, 1 allylic H), 1.06 (3H, s, -C(C**H**$_3$)$_3$, exo), 0.99 (3H, s, -C(C**H**$_3$)$_3$, endo), 0.22, 0.21, 0.19, 0.17, 0.15, 0.14 (9H each, -Si(C**H**$_3$)$_3$; δ_C (100MHz) 138.77, 129.36, 100.14, 52.12, 47.69, 38.43, 31.24, 30.42, 4.68, 2.08, 1.53; MS (EI$^+$) m/z 400 (M$^+$, 1%), 385 (M$^+$-CH$_3$, 1%), 73 (100).

1,1-Bistrimethylsilyl-4-carbomethoxy-3-(2'-carbomethoxyeth-1'-en-1'yl)-2-phenyl-2-(trimethylsilyloxy)silacyclobutane (198)



A solution of benzoyltris(trimethylsilyl)silane (0.25 g, 0.71 mmol) and dimethyl (*E,E*)-2,4-hexadienoate (0.24 g, 1.42 mmol) in benzene (3 ml) was heated at 180°C for 4 hours. Concentration, followed by flash column chromatography (eluting: 10% ether:petrol) gave the title compound as a colourless semisolid material (0.25 g, 67%). [Found (CI): MH$^+$, 523.2188; $C_{24}H_{43}Si_4O_5$ requires *M*, 523.2187]; ν_{max} ($CHCl_3$) 3024, 2953, 2896, 1717, 1645, 1598, 1490, 1439, 1375, 1339, 1251, 1197 cm^{-1}; δ_H (250MHz) 7.40-7.10 (5H, **Ar**), 6.32 (1H, dd, J=15.6, 10.4Hz, MeO$_2$C-CH=C**H**-CH-), 6.04 (1H, d, J=15.4Hz, MeO$_2$C-C**H**=CH-CH-), 3.76(3H, s, OC**H**$_3$), 3.70 (3H, s, OC**H**$_3$), 2.53 (1H, dd, J=10.4, 4.7Hz, =CH-C**H**-CH-CO$_2$Me), 2.38 (1H, d, J=4.7Hz, =CH-CH-C**H**-CO$_2$Me), 0.20 (9H, s, Si(C**H**$_3$)$_3$), 0.03 (9H, s, Si(C**H**$_3$)$_3$, -0.10 (9H, s, Si(C**H**$_3$)$_3$); δ_C (126MHz) 172.23, 166.15, 148.25, 139.69, 131.06, 128.23, 126.06, 120.66, 83.23, 55.80, 51.89, 36.65, 35.76, 2.16, 0.00, -0.20; MS (EI$^+$) m/z 523 (MH$^+$, 1%), 507 (M$^+$-15, 14%), 449 (M$^+$-Si(SiMe$_3$)$_3$, 100%), 433 (M$^+$-OSi(SiMe$_3$)$_3$,2%) 417 (24), 387 (4), 377 (5), 359 (18), 343 (24), 285 (12), 237 (10), 228 (13), 221 (98), 211 (40), 191 (37), 163 (24), 147 (28), 117 (92), 89 (27), 73 (100); (CI) m/z 540 ([M+NH$_4$]$^+$, 12%), 523 (MH$^+$, 12%), 449 (M$^+$-Si(SiMe$_3$)$_3$, 17%), 433 (M$^+$-OSi(SiMe$_3$)$_3$, 100%) 278 (4), 221 (5), 180 (6) 151 (3), 90 (31), 73 (100).

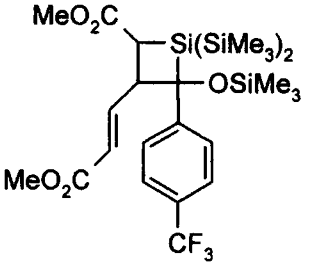
1,1-Bistrimethylsilyl-4-carbomethoxy-3-(2'-carbomethoxyeth-1'-en-1'yl)-2-(4'-methoxyphenyl)-2-(trimethylsilyloxy)silacyclobutane (199)



A solution of 4-methoxybenzoyltris(trimethylsilyl)silane (0.44 g, 1.14 mmol) and dimethyl (*E,E*)-2,4-hexadienoate (0.39 g, 2.29 mmol) in benzene (5 ml) was heated at180°C for 4 hours. Concentration, followed by flash column chromatography (eluting: 15% ether:petrol) gave the title compound as a colourless semisolid material (0.31 g, 49%).

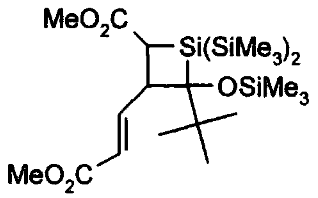
ν_{max} (CHCl$_3$) 2999, 2953, 2897, 2838, 1718, 1645, 1608, 1509, 1440, 1348, 1249, 1175cm^{-1}; δ_H (250MHz) 7.04 (2H, d, J=8.6Hz, **Ar**), 6.78 (2H, d, J=8.6Hz, **Ar**), 6.31 (1H, dd, J=15.3, 10.4Hz, -C**H**=CH-CO$_2$Me), 6.01 (1H, d, J=15.3Hz, -CH=C**H**-CO$_2$Me), 3.77 (3H, s, Ar-OC**H**$_3$), 3.72 (3H, s, -CO$_2$C**H**$_3$), 3.68 (3H, s, -CO$_2$C**H**$_3$), 2.51 (1H, dd, J=10.4, 4.7Hz, -C**H**-CH=CH-CO$_2$CH$_3$),2.31 (1H, d, J=4.7Hz), 0.17 (9H, s, OSi(C**H**$_3$)$_3$, 0.03, -0.11 (9H each, -Si-(Si(C**H**$_3$)$_3$)$_2$; δ_C (63MHz) 172.29, 166.36, 157.99, 148.62, 132.06, 131.68, 120.71, 113.67, 81.53, 55.32, 52.02, 51.44, 35.91, 34.75, 2.33, 0.12, -0.81; MS (CI) m/z 553 (MH$^+$, 1%), 463 (M-OSiMe$_3$, 3%), 280 (8), 192 (5), 90 (100).

1,1-Bistrimethylsilyl-4-carbomethoxy-3-(2'-carbomethoxyeth-1'-en-1'yl)-2-(4'-trifluorophenyl)-2-(trimethylsilyloxy)silacyclobutane (200)



A solution of 4-(trifluoromethyl)benzoyltris(trimethylsilyl)silane (0.48 g, 1.14 mmol) and dimethyl (*E,E*)-2,4-hexadienoate (0.39 g, 2.29 mmol) in benzene (5 ml) was heated at 180°C for 4 hours. Concentration, followed by flash column chromatography (eluting: 15% ether:petrol) gave the title compound as a colourless semisolid (0.31 g, 49%). [Found (CI): MH^+, 591.2061; $C_{25}H_{42}O_5Si_4F_3$ requires *M*, 591.2061]; ν_{max} ($CHCl_3$) 3018, 2953, 2897, 1719, 1647, 1615, 1441, 1405, 1325, 1252, 1167, 1130, 1051 cm^{-1}; δ_H (400MHz) 7.50 (2H, d, J=8.0Hz, **Ar**), 7.20 (2H, d, J=8.0Hz, **Ar**), 6.17 (1H, dd, J=15.6Hz, 10.4Hz, -CH=C**H**-CH), 6.04 (1H, d, J= 15.6Hz, MeO_2C-C**H**=), 3.74, 3.69 (2x3H, s, $CO_2C\mathbf{H}_3$), 2.55 (1H, dd, J= 10.4Hz, 4.4Hz, CH-C**H**-CH=CH-), 2.35 (1H, d, J= 4.4Hz, CH-C**H**-CO_2Me) 0.19 (9H, s, $OSi(C\mathbf{H}_3)_3$), 0.03, -0.18 (2x9H, s, Si-$Si(C\mathbf{H}_3)_3$; δ_F (235MHz) -62.8; δ_C (100 MHz) 172.31, 166.15, 147.32, 144.60, 131.43, 128.64 (q, $^2J_{C\text{-}F}$= 32.25 Hz, Ar, F_3C-**C**), 125.50 (q, $^3J_{C\text{-}F}$= 3.8 Hz, F_3C-CH-**C**H-), 124.36 (q, $^1J_{C\text{-}F}$= 270.2 Hz, F_3**C**-), 121.53, 82.53, 52.29, 51.55, 35.53, 35.20, 2.22, 0.15, 0.08; MS (CI) m/z 591 (MH^+, 43%), 517 (M^+-$SiMe_3$, 37%), 501 (MH^+-$OSiMe_3$).

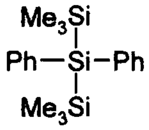
1,1-Bistrimethylsilyl-4-carbomethoxy-3-(2'-carbomethoxyeth-1'-en-1'yl)-2-(*tert*-butyl)-2-(trimethylsilyloxy)silacyclobutane (201)



A solution of trimethylacetyltris(trimethylsilylsilane) (0.18 g, 0.54 mmol) and dimethyl (*E,E*)-2,4-hexadienoate (0.19 g, 1.09 mmol) in benzene (2 ml) was heated in a sealed tube at 180°C for 4 hours. Concentration, followed by flash column chromatography (eluting: 10% ether:petrol) gave the title compound as a colourless semisolid (0.05 g, 20%).

ν_{max} ($CHCl_3$) 3021, 2953, 2899, 1709, 1643, 1437, 1252, 1084, 1031, 841 cm^{-1}; δ_H (400MHz) 7.10 (1H, dd, J=15.2Hz, J=10.3Hz, MeO_2C-CH=C**H**-CH-), 6.02 (1H, d, J=15.2Hz, MeO$_2$C-CH=CH-), 3.74 (3H, s, -CO$_2$CH$_3$), 3.65 (3H, s, -CO$_2$CH$_3$), 2.35 (1H, dd, J=10.3Hz, 4.8Hz, MeO$_2$C-CH-CH-CH=), 1.09 (9H, s, -C(CH$_3$)$_3$), 1.01 (1H, d, J=4.8Hz, MeO$_2$C-CH-CH-CH=) 0.15 (9H, s, -OSi(CH$_3$)$_3$), 0.13 (9H, s, -Si(CH$_3$)$_3$) 0.12 (9H, s, -Si(CH$_3$)$_3$); δ_C (100MHz) 172.78, 166.59, 148.17, 121.94, 78.40, 51.92, 51.49, 38.11, 34.78, 33.11, 31.26, 3.27, 0.72, 0.56; MS (CI) m/z 503 (MH$^+$, 7%), 413 (M-OSiMe$_3$, 24%), 333 (5), 280 (26), 258 (18), 226 (7), 209 (11), 192 (6), 90 (100).

2,2-Diphenyl-1,1,1,3,3,3-hexamethyltrisilane (202)[82]

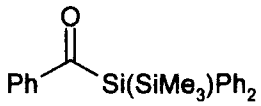


$Ph_2Si(SiMe_3)_2$

A mixture of chlorotrimethylsilane (14.96 g, 137.2 mmol) and dichlorodiphenylsilane (17.36 g, 68.62 mmol) was added to a stirred suspension of magnesium turnings in THF/HMPA (1:1, 100 ml), so as to maintain a gentle reflux. The mixture was then heated to reflux for a further 12 hours. Saturated NH$_4$Cl solution (100 ml) was then carefully added. The organic layer was separated, and the aqueous layer extracted with ether (3x40 ml). The combined organic extracts were dried over MgSO$_4$, filtered and concentrated. Distillation gave the title compound as a colourless oil (11.90 g, 53%). b.p. 140°C/1 mbar (lit[82] 147-148°C/2 mbar).

ν_{max} (thin film) 3021, 2948, 2885, 1420, 1216, 1201, 1196, 914, 842 cm^{-1}; δ_H (300MHz) 7.55-7.28 (10H, m, **Ar**), 0.19 (18H, s, Si(CH$_3$)$_3$; δ_C (75MHz) 135.93, 133.97, 128.12, 127.81, -0.50; MS (EI) m/z 328 (M$^+$, 33%), 313 (M-CH$_3$, 10%), 255 (M-Si(CH$_3$)$_3$, 100%).

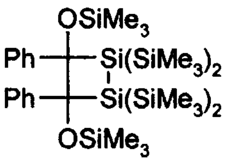
Benzoyldiphenyltrimethylsilylsilane (205)



Methyllithium (1.6 M solution in diethyl ether, 6.33 ml, 10.08 mmol) was added to a solution of diphenylbis(trimethylsilyl)silane (3.02 g, 9.21 mmol) in THF (30 ml). After 18 hours the solution was added via cannula to a solution of benzoyl chloride (2.61 g, 18.65 mmol) in THF (30 ml) at -78°C. The mixture was stirred at -78°C for 6 hours. 3M HCl was then added (50 ml). The aqueous layer was separated, and extracted with diethyl ether (3x50 ml). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated. Flash column chromatography (eluting: 2% diethyl ether: petrol) gave the title compound as a colourless oil (1.79 g, 54%).

ν_{max} (thin film) 3067, 3050, 2955, 2894, 1608, 1574, 1428, 1246, 1207, 839 cm^{-1}; δ_H (300 MHz) 7.80-7.30 (15H, m, Ar), 0.22 (9H, s, $Si(CH_3)_3$); δ_C (50 MHz) 232.76, 142.22, 135.81, 134.11, 129.40, 128.33, 128.19, 128.10, 127.74, -1.21; MS (EI) m/z 360 (M^+, 5%), 345 (M^+-Me, 22), 287 (M^+-$SiMe_3$, 25), 105 (67), 73 (100).

3,4-Diphenyl-3,4-bis(trimethylsilyloxy)-1,1,2,2-tetrakis(trimethylsilyl)-1,2-disilacyclobutane (209)[37]



A solution of benzoyltris(trimethylsilyl)silane (0.49 g, 1.38 mmol) in cyclohexane (50 ml) was irradiated for approx. 2 hours using a 1kW mercury lamp. Concentration gave the crude product. Flash column chromatography (eluting: petrol) gave the title compound as a white crystalline solid (0.21 g, 43%); m.p. 148°C (lit.[37] 149-150°C).

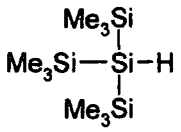
ν_{max} (KBr disc) 3050, 2956, 2893, 1597, 1489, 1442, 1402, 1250 cm^{-1}; δ_H (200MHz) 7.70-7.58 (5H, m, Ar), 7.40-7.20 (5H, m, Ar), 0.41 (18H, s, $2xOSi(CH_3)_3$, 0.07 (18H, s, 2xSi(C$\underline{\mathrm{H}}_3$)$_3$, -0.26 (18H, s, 2xSi(C$\underline{\mathrm{H}}_3$)$_3$); δ_C (63MHz) 158.28, 144.92, 132.74, 127.08, 98.69,3.530, 3.074, 2.868; MS (EI) m/z 355(13%), 353 (monomer MH$^+$), 281 (24), 221 (63), 205 (36), 191 (20), 147 (100), 131 (64), 73 (100); (CI) 592 (12%), 356 (12), 353 (11), 282 (18), 264 (16), 221 (44), 207 (16), 191 (13), 164 (20), 148 (65), 131 (33), 117 (16), 90 (90), 73 (100).

Thermolysis of silene dimer (209) in the presence of (*E*)-1,3-pentadiene[37]

A solution of 3,4-diphenyl-3,4-bis(trimethylsilyloxy)-1,1,2,2-tetrakis-(trimethylsilyl)-1,2-disilacyclobutane (0.09 g, 0.13 mmol) and (*E*)-1,3-pentadiene (0.07 g, 1.04 mmol) in THF (2 ml) was heated at 70°C for 24 hours. Concentration, followed by flash column chromatography (eluting: petrol), gave a complex mixture of dimer (117) and cycloadduct (84a,b) as a colourless solid (40 mg).

δ_H (200MHz) 7.40-7.05 (5H, m, $\underline{\mathrm{Ar}}$), 6.00-5.45 (2H, m, vinylic), 3.20-3.00 (1H, m, allylic), 1.6-1.2 (2H, m, allylic), 1.04 (3H, d, =CH-CH(C$\underline{\mathrm{H}}_3$)-C-, $\underline{\mathrm{exo}}$), 0.95 (3H, d, =CH-C(C$\underline{\mathrm{H}}_3$)-C-, $\underline{\mathrm{endo}}$), 0.5- -0.4 (several singlets, -Si(C$\underline{\mathrm{H}}_3$)$_3$); GCMS (EI) 405 (M$^+$-CH$_3$, 0.5%), 347 (M$^+$-Si(Me$_3$)$_3$, 259 (4), 245 (27), 205 (12), 199 (7), 147 (20), 135 (11), 117 (10), 73 (100).

Tris(trimethylsilyl)silane (216)[85]

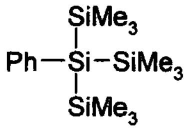


$(\mathrm{Me_3Si})_3\mathrm{Si{-}H}$

Methyllithium (1.6 M solution in diethyl ether, 31.25 ml, 50 mmol) was added to a solution of tetrakis(trimethylsilyl)silane (15.36 g, 48.0 mmol) in THF (150 ml). The solution was stirred at room temperature for 18 hours. The solution was then poured into 0.1M hydrochloric acid. The aqueous layer was extracted with diethyl ether (3x60ml). The combined organic layers were dried over MgSO$_4$, filtered and concentrated. Distillation gave the title compound as a colourless oil (9.89 g, 81%), b.p. 80°C/ 8 mbar (lit. 80-83°C/ 10 mbar[85]).

ν_{max} (thin film) 2951, 2894, 1441, 1399, 1245, 1061, 837 cm^{-1}; δ_H (300MHz) 2.15 (1H, s, $\mathrm{Si\underline{H}}$), 0.19 (27H, s, $\mathrm{3xSi(C\underline{H}_3)_3}$); MS (EI) m/z 248 ($M^+$, 12%), 233($M-CH_3$, 13%), 174, 175 ($M-SiMe_3$, 42%), 159 (58), 129 (25), 115 (22), 73 (100).

Phenyltris(trimethylsilyl)silane (210)[83]

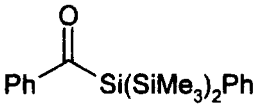


$\mathrm{Ph{-}Si(SiMe_3)_3}$

A mixture of tris(trimethylsilyl)silane (37.08 g, 149.1 mmol) and 1-bromobutane (82.22 g, 600.0 mmol) were heated at 100°C for 24 hours. GC-MS confirmed the formation of bromotris(trimethylsilyl)silane.[84] Phenylmagnesium bromide (1 M solution in THF, 300 ml, 300 mmol) was then added. The mixture was strirred for 5 hours. Saturated ammonium chloride solution (50 ml) was then added. The aqueous layer was extracted with diethyl ether (3x30 ml), the combined organic extracts were then dried over $MgSO_4$, filtered and concentrated. Flash column chromatography (eluting: petrol) gave the title compound as a waxy colourless solid (43.60 g , 90%) ,m.p. 88-89°C (lit:[135] 88-90°C).

ν_{max} ($CHCl_3$) 3019, 2951, 2896, 1430, 1250, 1224, 1206, 929, 842 cm^{-1}; δ_H (400MHz) 7.50-7.20 (5H, m, aromatic), 0.23 (27H, s, 3x $\mathrm{Si(C\underline{H}_3)_3}$; δ_C (63 MHz) 136.57, 135.53, 127.68, 127.31, 1.17; MS (EI^+) m/z 324 (M^+, 32%), 309 ($M-CH_3$, 18%), 251 ($M-SiMe_3$, 20%), 191 (40), 174 (100), 159 (62), 135 (90), 73 (96).

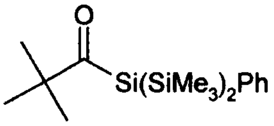
Benzoylbis(trimethylsilyl)phenylsilane (218)



Methyllithium (1.6 M solution in diethyl ether, 9.7 ml, 15.52 mmol) was added to a solution of phenyltris(trimethylsilyl)silane (5.16 g, 15.94 mmol) in THF (40 ml). After 18 hours the solution was added via cannula to a solution of benzoyl chloride (2.24g, 15.94mmol) in THF (40 ml) at -78°C. The mixture was stirred at -78°C for 6 hours. 3M HCl was then added (50 ml). The aqueous layer was separated, and extracted with diethyl ether (3x30 ml). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated. Flash column chromatography (eluting: 2% diethyl ether:petrol) gave the title compound as a yellow oil (2.75 g, 50%).

ν_{max} (thin film) 3066, 2953, 2893 1739, 1720, 1700, 1605, 1573, 1400, 1314, 1247, 1202, 1171, 1110, 1065, 838 cm^{-1}; δ_H (300 MHz) 7.75-7.30 (10H, m, Ar), 0.23 (18H, s, Si(C**H**$_3$)$_3$; δ_C (100 MHz) 235.39, 142.65, 135.77, 134.91, 132.60, 128.52, 128.37, 128.26, 128.17, 0.42; MS (ES) m/z 357 (M+1, 20%), 279 (M-Ph, 100%).

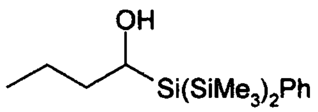
Trimethylacetylbis(trimethylsilyl)phenylsilane (212)[83]



Methyllithium (1.6 M solution in diethyl ether, 28.7 ml, 45.9 mmol) was added to a solution of phenyltris(trimethylsilyl)silane (14.85 g, 45.83 mmol) in THF (120 ml). After 18 hours the yellow silyllithium solution was added via cannula to a solution of trimethylacetylchloride (5.52 g, 45.80 mmol) in THF (100 ml) at -78°C. The mixture was stirred at -78°C for 6 hours, and then was allowed to warm to room temperature. 3M HCl was then added (50 ml). The aqueous layer was separated, and extracted with diethyl ether (3x50 ml). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated. Flash column chromatography (eluting: 2% diethyl ether:petrol) gave the title compound as a colourless oil (12.57 g, 82%).

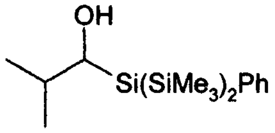
ν_{max} (thin film) 3069, 2957, 2897, 2868, 1729, 1703, 1619, 1475, 1428, 1361, 1246, 1063, 943, 837 cm^{-1}; δ_H (200MHz) 7.64-7.30 (5H, m, **Ar**), 0.95 (9H, s, -C(CH$_3$)$_3$), 0.25 (18H, s, Si(CH$_3$)$_3$); δ_C (125MHz) 249.55, 136.87, 135.38, 128.76, 128.10, 50.27, 25.01, 0.33; MS (EI) 279 (M$^+$-C(CH$_3$)$_3$, 25%), 265 (M$^+$-Si(CH$_3$)$_3$, 3), 251 (M$^+$-C(O)tBu, 100), 209 (26), 193 (32), 177 (22), 73 (67).

1,1,1,3,3,3-Hexamethyl-2-phenyl-2-(1'-hydroxybutyl)trisilane (220)



Methylithium (1.6 M solution in diethyl ether, 6 ml, 9.70 mmol) was added to a solution of phenyltris(trimethylsilyl)silane (3.14 g, 9.70 mmol) in THF (30 ml). The solution was stirred for 18 hours. The mixture was then concentrated. The solid silyllithium was dissolved in diethyl ether (40 ml). The solution was then added via cannula to a solution of MgBr$_2$ (1.81 g, 9.85 mmol) in diethyl ether. The solution was stirred for 60 minutes. The solution was then cooled to -78°C. Butyraldehyde (1.40 g, 19.4 mmol) was then added dropwise. The mixture was stirred for 12 hours. Saturated NH$_4$Cl solution was then added (50 ml). The aqueous layer was separated and extracted with ether (3x30 ml). The organic layers were combined, dried over MgSO$_4$ and concentrated. Flash column chromatography (gradient elution: petrol/5% diethyl ether: petrol/10% diethyl ether: petrol) gave the title compound as a colourless oil (2.35 g, 74%).[Found: C, 59.24%; H, 10.00%; required for $C_{16}H_{32}OSi_3$: C, 59.19%; H, 9.93%]; ν_{max} (thin film) 3472 (b, OH), 3067, 2955, 2894, 2833, 1426, 1244, 1095, 836 cm^{-1}; δ_H (400MHz) 7.55-7.30 (5H, m, **Ar**), 4.06 (1H, m, CH$_2$C**H**(OH)Si), 1.75 (1H, broad, O**H**), 1.70-1.30 (4H, m, CH(OH)C**H$_2$**C**H$_2$**CH$_3$) 0.93 (3H, t, J=7.2 Hz, CH$_2$C**H$_3$**), 0.23, 0.21 (2x9H, s, Si(Si(CH$_3$)$_3$)$_2$, diastereotopic); δ_C (100MHz) 135.67, 135.38, 128.19, 127.94, 65.42, 38.81, 20.46, 13.79, 0.29, 0.16; MS (CI) m/z 342 ([M+NH$_4$]$^+$, 8%), 324 (M$^+$, 39%), 268 (100), 246 (14).

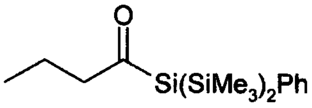
1,1,1,3,3,3-Hexamethyl-2-phenyl-2-(1'-hydroxy-2'-methylpropyl)trisilane (221)



Methylithium (1.6 M solution in diethyl ether, 10.35 ml, 16.56 mmol) was added to a solution of phenyltris(trimethylsilyl)silane (5.37 g, 16.57 mmol) in THF (30 ml). The solution was stirred for 18 hours. The solvent was then removed. The solid silyllithium was dissolved in diethyl ether (30 ml). The solution was then added via cannula to a solution of $MgBr_2$ (3.13 g, 17.01 mmol) in diethyl ether. The solution was stirred for 60 minutes. The solution was then cooled to -78°C. Isobutyraldehyde (2.39 g, 33.14 mmol) was then added dropwise. The mixture was stirred for 12 hours. Saturated NH_4Cl solution was then added (50 ml). The aqueous layer was separated and extracted with ether (3x30 ml). The organic layers were combined, dried over $MgSO_4$ and concentrated. Flash column chromatography (gradient elution: petrol/5% diethyl ether: petrol/10% diethyl ether: petrol) gave the title compound as a colourless oil (3.65 g, 69%).

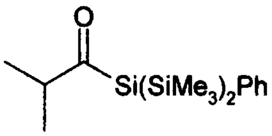
ν_{max} (thin film) 3457 (broad, OH), 2955, 2893, 1716, 1245, 836 cm^{-1}; δ_H (300 MHz) 7.60-7.25 (5H, m, **Ar**), 3.80 (1H, d, J=7.2 Hz, CH-C**H**(OH)-Si), 1.96 (1H, m, $(H_3C)_2C\mathbf{H}$-CH(OH)), 0.99, 0.88 (2x3H, d, J=6.6 Hz, diastereotopic CH($C\mathbf{H}_3)_3$), 0.24, 0.20 (2x9H, s, diastereotopic Si($C\mathbf{H}_3)_3$); δ_C (75 MHz) 136.45, 135.63, 128.06, 127.85, 72.45, 34.62, 21.17, 19.86, 0.49, 0.31; MS (CI) m/z 342 (M+NH_4, 43%), 324 (M^+, 100%), 309 (M-CH_3, 19%).

Butanoylbis(trimethylsilyl)phenylsilane (222)



Dimethylsulfoxide (0.31 g, 3.91 mmol) was added to a stirred solution of oxalyl chloride (0.30 g, 2.37 mmol) in DCM at -78°C, and the resultant solution stirred at this temperature for 10 minutes. The solution of silylalcohol (220) (0.51 g, 1.56 mmol) in dichloromethane was added dropwise, and the reaction was stirred at -78°C for a further 20 minutes. Triethylamine (1.08 ml, 7.8 mmol) was then added, and the reaction was allowed to attain ambient temperature. The reaction mixture was then diluted with ether (20 ml) and washed with dilute hydrochloric acid (2x10 ml) and saturated $NaHCO_3$ solution (10 ml). After back extraction of the aqueous washings with ether (15 ml), the combined organic layers were dried over $MgSO_4$, filtered and concentrated. Flash column chromatography (eluting: 5% ether:petrol) gave the title compound as a colourless oil (0.50 g, 95%). [Found: C, 59.30%; H, 9.36%; Calc. for $C_{16}H_{30}OSi_3$ C, 59.56%; H, 9.37%]; ν_{max} (thin film) 3068, 3051, 2958, 2894, 1631, 1427, 1399, 1246, 1095, 837 cm^{-1}; δ_H (400MHz) 7.60-7.30 (5H, m, $\underline{Ar}$), 2.58 (2H, t, J=7.2Hz, $CH_3CH_2C\underline{H}_2C(O)$), 1.51 (2H, tq, $CH_3C\underline{H}_2CH_2C(O)$), 0.83 (3H, t, J=7.2Hz, $C\underline{H}_3CH_2CH_2C(O)$), 0.24 (18H, s, $Si(C\underline{H}_3)_3$; δ_C (100 MHz) 246.67, 136.04, 133.46, 128.64, 128.13, 54.22, 15.78, 13.84, 0.24; MS (CI) m/z 323 (MH^+, 11%),

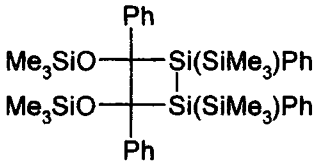
2-Methylpropanoylbis(trimethylsilyl)phenylsilane (223)



Dimethylsulfoxide (1.20 g, 15.33 mmol) was added to a stirred solution of oxalyl chloride (1.17 g, 9.20 mmol) in DCM at -78°C, and the resultant solution stirred at this temperature for 10 minutes. The solution of silylalcohol (221) (1.99 g, 6.14 mmol) in dichloromethane was added dropwise, and the reaction was stirred at -78°C for a further 20 minutes. Triethylamine (4.26 ml, 30.7 mmol) was then added, and the reaction was allowed to attain ambient temperature. The reaction mixture was then diluted with ether (50 ml) and washed with dilute hydrochloric acid (2x15 ml) and saturated $NaHCO_3$ solution (15 ml). After back extraction of the aqueous washings with ether (20 ml), the combined organic layers were dried over $MgSO_4$, filtered and concentrated. Flash column chromatography (eluting: 5% ether:petrol) gave the title compound as a colourless oil (1.98 g, 93%).

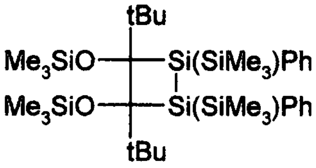
ν_{max} (thin film) 3067, 2962, 2894, 2870, 1728, 1627, 1465, 1427, 1400, 1377, 1245, 1095, 971, 836 cm^{-1}; δ_H (200 MHz) 7.60-7.30 (5H, m, **Ar**), 2.95 (1H, septet, J=6.8 Hz, C**H**$(CH_3)_2$), 0.89 (6H, d, J=6.8 Hz, CH(C**H**$_3$)$_2$), 0.24 (18H, s, **Ar**); δ_C (50 MHz) 249.94, 136.16, 135.61, 128.69, 128.17, 46.77, 16.51, 0.13; MS (CI) m/z 323 (MH^+, 23%), 307 (M-CH_3, 8), 249 (M-$SiMe_3$, 22), 209 (37), 193 (63), 135 (100).

3,4-Diphenyl-3,4-bis(trimethylsilyloxy)-1,2-bis(trimethylsilyl)-1,2-diphenyl-1,2-disilacyclobutane (224)



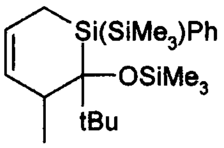
A solution of benzoylphenylbis(trimethylsilyl)silane (1.00 g, 2.80 mmol) was dissolved in cyclohexane (150 ml). This solution was then degassed by the passage of a steady flow of nitrogen for 30 minutes. The mixture was then irradiated for 45 minutes. The solution was then concentrated. Flash column chromatography (eluting: hexane) gave the title compound as a white solid, (0.04 g, 5%); m.p. 165-166°C dec. [Found: C, 62.75%; H, 7.73%; $C_{38}H_{56}O_2Si_6$ requires C, 63.98%; H, 7.91%]; ν_{max} (KBr disc) 3052, 2957, 2894, 1596, 1488, 1442, 1427, 1249, 1042 cm^{-1}; δ_H (300MHz) 7.80-7.20 (20H, m, **Ar**), -0.01 (18H, s, OSi(C**H**$_3$)$_3$), -0.54 (18H, s, Si-Si(C**H**$_3$)$_3$); δ_C (75MHz) 144.51, 137.33, 136.51, 131.24, 128.19, 127.41, 127.15, 126.72, 95.68, 3.22, 0.39; MS (EI) m/z 712 (M^+, 1%), 639 (M^+-TMS, 2%), 356 (1/2 M^+ [monomer M^+], 100%).

3,4-Bis(*tert*-butyl)-3,4-bis(trimethylsilyloxy)-1,2-bis(trimethylsilyl)-1,2-diphenyl-1,2-disilacyclobutane (213)[83]



A solution of trimethylacetylphenylbis(trimethylsilyl)silane (9.31 g, 27.7 mmol) was dissolved in cyclohexane (150 ml). The solution was then degassed by the passage of a steady flow of nitrogen for 30 minutes. The mixture was then irradiated for 45 minutes. The solution was then concentrated to give a white solid. The solid was removed by filtration and washed with cold cyclohexane, to give the title compound as a white solid. The material was used without further purification. (9.15 g, 98%) m.p. 98-100°C dec.
ν_{max} (CHCl$_3$) 3017, 2957, 2897, 1703, 1614, 1479, 1427, 1362, 1253, 1206, 1060, 931, 841 cm^{-1}; δ_H (300 MHz) 7.70-7.25 (10H, m, **Ar**), 1.20 (18H, bs, C(C**H**$_3$)$_3$), 10.28 (18H, s, OSi(C**H**$_3$)$_3$, 0.13 (18H, s, Si-Si(C**H**$_3$)$_3$; δ_C (63 MHz) 137.72, 137.05, 127.74, 126.94, 108.82, 38.90, 26.93, 5.96, 0.70.

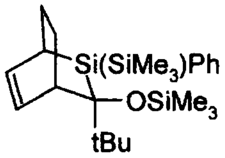
2-(*tert*-Butyl)-3-methyl-1-phenyl-1-trimethylsilyl-2-(trimethylsilyloxy)silacyclohex-4-ene (225)



Silene dimer (213) (2.07 g, 3.08 mmol) and (*E*)-1,3-pentadiene (0.82 g, 12.40 mmol) were dissolved in THF (10 ml). The solution was stirred for 18 hours. Concentration followed by flash column chromatography (eluting: petrol) gave the title compound (a 1:1 mixture of diastereoisomers) as a colourless oil (1.74 g, 70%).
ν_{max} (thin film) 3066, 2953, 1478, 1427, 1359, 1258, 1247, 1127, 1104, 967, 887 836 cm^{-1}; δ_H (300MHz) 7.65-7.30 (10H, m, **Ar**), 6.90-5.30 (4H, m, C**H**=CH and CH=C**H**),

3.28, (1H, m, =CH-C**H**(CH$_3$)), 3.12, 1.70 (2x3H, m, =CHCH(C**H**$_3$)), 1.55-1.22 (2x2H, m, =CHC**H**$_2$), 1.20-1.15 (2x1H, m, =CH-C**H**(CH$_3$)) 1.04, (9H, s, C(C**H**$_3$)$_3$, isomer A), 0.98 (9H, s, C(C**H**$_3$)$_3$, isomer A) 0.11, (9H, s, OSi(C**H**$_3$)$_3$), 0.06 (9H, s, OSi(C**H**$_3$)$_3$), -0.24 (9H, s, Si-Si(C**H**$_3$)$_3$), -0.30 (9H, s, Si-Si(C**H**$_3$)$_3$); δ_C (100MHz) 138.95, 135.08, 134.574, 134.07, 128.41, 128.13, 127.58, 127.48, 124.32, 122.90, 96.17, 92.50, 53.72, 45.16, 38.00, 37.30, 28.20, 28.00 (broad), 18.03, 17.56, 11.53, 10.71, 2.80, 2.31, -0.95, -1.50; MS (EI) m/z 404 (M^+, 1%), 389 (M-CH$_3$, 1%), 347 (M-tBu, 5%), 331 (M-SiMe$_3$, 5%), 321 (21), 283 (16), 263 (58), 209 (89), 193 (100); HRMS Calc. for $C_{22}H_{40}OSi_3$: 404.2387; found: 404.2397.

3-(*tert*-Butyl)-2-phenyl-2-trimethylsilyl-3-trimethylsilyloxy-2-silabicyclo[2.2.2]oct-5-ene (226)



Silene dimer (213) (5.08 g, 7.56mmol) and cyclohexa-1,3-diene (2.42 g, 30.26 mmol) were dissolved in THF (40 ml). The solution was stirred for 18 hours. Concentration followed by flash column chromatography (eluting: petrol) gave the title compound (a 1:1 mixture of diastereoisomers) as a colourless solid (4.37 g, 69%). M.p. 114-115°C. [Found: C, 65.92%; H, 9.67%; required for $C_{23}H_{40}OSi_3$ C, 66.28%; H, 9.67%]; ν_{max} (KBr disc) 3069, 3045, 2982, 2950, 2861, 1476, 1426, 1390, 1261, 1247, 1103, 965, 836 cm^{-1}; δ_H (500MHz) 7.60-7.30 (10H, m, **Ar**), 6.20-6.18 (1H, m, 5-**H**, isomer A), 6.16-6.14 (1H, m, 5-**H**, isomer B), 6.10-6.02 (1H, m, 6-**H**, isomer B), 3.25 (1H, m, 4-**H**, isomer b), 2.85 (1H, m, 4-**H**, isomer A) 2.42 (1H, m, 1-**H**, isomer A), 2.40 (1H, m. 1-**H**, isomer B), 2.02 (2H, m, 7-**H**H and 8-H**H**, isomer B), 1.90 (2H, m, 7-**H**H and 8-H**H**, isomer A), 1.75 (2H, m, 7-H**H** and 8-**H**H, isomer B), 1.65 (2H, m, 7-H**H** and 8-**H**H, isomer A), 1.08 (9H, s, C(C**H**$_3$)$_3$, isomer B), 1.06 (9H, s, C(C**H**$_3$)$_3$, isomer A), -0.02 (9H, s, OSi(C**H**$_3$)$_3$, isomer A), 0.11 (9H, s, OSi(C**H**$_3$)$_3$, isomer B), -0.18 (9H, s, SiSi(C**H**$_3$)$_3$, isomer A), -0.19 (9H, s, SiSi(C**H**$_3$)$_3$, isomer B); δ_C (125MHz) 138.20, 136.10, 132.42, 129.21, 128.03, 122.00, 121.63, 96.80, 90.22, 44.00, 42.10, 39.21, 30.11, 26.95, 21.00, 19.80, 9.80, 3.11, -0.08, -0.20; MS (EI$^+$) m/z 416 (M$^+$, 2%), 401 (M-CH_3, 5), 343 (M-$SiMe_3$, 15), 327 (M-$OSiMe_3$, 10), 73 (100).

Allyl*tert*-butyldimethylsilane

Freshly distilled allyl chloride (7.51 g, 98 mmol) was added over 12 hours via syringe pump to a suspension of magnesium turnings (2.4 g, 100 mmol) in THF (50ml). Tert-butyldimethylsilyl chloride (11.75 g, 78 mmol) in THF (20 ml) was then added. The mixture was allowed to stir for 3 hours. Saturated ammonium chloride solution (50 ml) was then added. The aqueous layer was extracted with ether (3x30 ml), the combined organic layers were dried over $MgSO_4$, filtered and concentrated. Distillation gave the title compound as a colourless oil (8.29 g, 68%), b.p. 30°C/ 44mbar (lit:[136] 65-66°C/ 63mbar).

ν_{max} (thin film) 3074, 2958, 2929, 2892, 2860, 1631, 1472, 1394, 1366, 1252, 1198, 1158, 1044 cm^{-1}; δ_H (400 MHz) 6.80 (1H, m $H_2C{=}C\underline{H}CH_2$), 5.85 (), 1.53 (2H, d, J=7.6 Hz), 0.88 (9H, s, $SiC(C\underline{H}_3)_3$), -0.06 (6H, s, $Si(C\underline{H}_3)_2tBu$; δ_C (63MHz) 135.70, 112.65, 26.54, 20.66, -6.63; MS (EI) m/z 156 (M$^+$, 5%), 115 (M$^+$-allyl, 37), 99 (M$^+$-tBu, 58), 73 (100)

Trimethylsilylbis(trifluoromethanesulfonyl)amide (230)[86]

$\mathrm{Me_3SiNTf_2}$

A mixture of bis(trifluoromethanesulfonyl)imide (0.97 g, 3.43 mmol) and allyltrimethylsilane (0.39 g, 3.43 mmol) were strirred at room temperature for 1 hour. Distillation gave the title compound as a colourless liquid (1.15 g, 95%), b.p. 80°C/1mbar.

δ_H (200 MHz) –0.12; δ_F (188 MHz) –76.03.

tert-Butyldimethylsilylbis(trifluoromethanesulfonyl)amide (239)

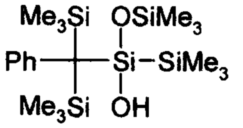
$\mathrm{tBuMe_2SiNTf_2}$

A mixture of allyl*tert*-butyldimethylsilane (0.65 g, 4.18 mmol) and bis(trifluoromethanesulfonyl)imide (1.18 g, 4.18 mmol) were stirred for 1 hour. Distillation gave the title compound as a clear liquid (1.38 g, 80%). B.p. 105°C/ 1 mbar.
δ_H (200MHz) 0.95 (9H, s, $C(C\underline{\mathbf{H}}_3)_3$, -0.15 (6H, s, $Si(C\underline{\mathbf{H}}_3)_2tBu$); δ_F (188MHz)–78.50.

General Procedure for Reaction of Acylpoylsilanes with Silylbistriflamides

A solution of acyltris(trimethylsilyl)silane in dichloromethane (~0.3 M) was cooled to -78°C. Silylbistriflamide (1 eq) was then added. The solution became dark red in colour and was stirred at -78°C for approximately 16 hours when saturated $NaHCO_3$ solution was added. The organic layer was separated, and the aqueous layer extracted with diethyl ether. The combined organic layers were then dried over $MgSO_4$, filtered, and concentrated to give the crude product which was purified as described below.

1-Hydroxy-1-[phenylbis(trimethylsilyl)methyl]-2,2,2-trimethyl-1-trimethylsilyloxydisilane (231)[88]

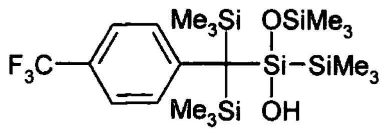


$$\begin{array}{ccc} & Me_3Si & OSiMe_3 \\ Ph- & C & -Si-SiMe_3 \\ & Me_3Si & OH \end{array}$$

A solution of benzoyltris(trimethylsilyl)silane (1.11 g, 3.30 mmol) was treated with trimethylsilylbistriflamide (1.12 g, 3.29 mmol) as described above to give an off white solid. Recrystallisation from ethanol gave the title compound as colourless crystals, (1.35 g, 93%). m.p. 92-93°C; [Found: C, 50.27; H, 9.61; $C_{19}H_{42}O_2Si_5$ requires C, 51.52; H, 9.56%]; ν_{max} (KBr disc) 3629, 3552 (b, -OH), 3055, 1945, 1686, 1593, 1497, 1439, 1403, 1264 1150 cm^{-1}; δ_H (300MHz) 7.52-7.01(5H, m, Ar), 2.20 (1H, s, -OH), 0.23, 0.22, 0.21 (each 9H, s, 2x C-Si(CH_3)$_3$, 1xO-Si(CH_3)$_3$), -0.15 (9H, s, Si-Si(CH_3)$_3$); δ_C (75MHz) 141.5, 131.7, 127.9, 123.8, 28.8, 3.87, 3.86, 2.8, -0.5; δ_{Si} (99 MHz) 5.4, -2.0, -2.7, -13.9, -23.3; MS (EI^+) m/z 442 (14%, M^+), 427 (22, M^+-CH_3), 411 (17), 369 (81, M^+-$SiMe_3$), 353 (46, M^+-$OSiMe_3$), 337 (44), 279 (48), 264 (40), 207 (33), 147 (47), 135 (31), 73 (100).

Crystal data for (231): $C_{19}H_{42}O_2Si_5$,[88] M = 442.98, monoclinic, space group P 2_1/n, *a* = 15.3270(1), *b* = 10.6851(1), *c* = 16.8596(1) Å, β = 105.50(1)°, *U* = 2659.5(9) $Å^3$, *F(000)* = 968, $Z = 4$, $D_C = 1.106$ mg m^{-3}, $\mu = 0.28$ mm^{-1} (Mo-Kα, $\lambda = 0.71073$ Å), T = 120(1)K. 33156 reflections (1.60 = θ = 30.5°) were collected on a Siemens SMART-CCD diffractometer (ω-scan, 0.3°/frame) yielding 7534 unique data (R_{merg} = 0.047). The structure was solved by direct method and refined by full-matrix least squares on F^2 for all data using SHELXL software. All non-hydrogen atoms were refined with anisotropic displacement parameters, H-atoms were located on the difference map and refined isotropically. The H-atom of the OH-group could not be located reliably and was not included in the refinement. Final wR_2 (F^2) = 0.1095 for all data (399 refined parameters), conventional R (F) = 0.0411 for 5539 reflections with I = 2s, GOF = 1.119. The largest peak on the residual map (0.62 a/Å^3) is located on the middle of one of the Si-Si bonds. CCDC 182/1000

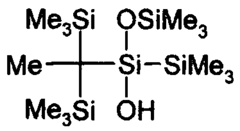
1-Hydroxy-1-[(4'-trifluoromethylphenyl)bis(trimethylsilyl)methyl]-2,2,2-trimethyl-1-trimethylsilyloxydisilane (232)[98]



A solution of 4-trifluoromethylbenzoyltris(trimethylsilyl)silane (0.89 g, 2.12 mmol) was treated with trimethylsilylbistriflamide (0.76 g, 2.15 mmol) as described above to give an off white solid. Recrystallisation from ethanol gave the title compound as colourless crystals, (0.90 g, 82%). m.p. 68-69°C. [Found: C, 46.82; H, 8.38; $C_{20}H_{41}F_3O_2Si_5$ requires C, 47.01; H, 8.09%]; ν_{max} (KBr disc) 3550 (b, OH), 3048, 2933, 2854, 1855, 1550, 1476, 1401, 1245, 1130cm^{-1}; δ_H (250MHz) 7.64-7.43 (4H, m, Ar), 2.20 (1H, bs, -OH), 0.25, 0.22, 0.20 (each 9H, s, 2x C-Si(CH_3)$_3$, 1xO-Si(CH_3)$_3$), -0.14 (9H, s, Si-Si(CH_3)$_3$); δ_C(100 MHz) 146.7, 131.7, 125.8 (q, -CF_3), 29.8, 3.8, 3.6, 2.8, -0.5; δ_F (235MHz) –62.6; δ_{Si} (99 MHz) 6.1, -1.4, -2.3, -14.5, -23.2; MS (EI^+) m/z 510 (M^+, 3.4%), 495 (M^+-CH_3, 2), 437 (M^+-$SiMe_3$, 3), 420 (M^+-$OSiMe_3$, 6), 147 (13), 73 (100), 71 (55).

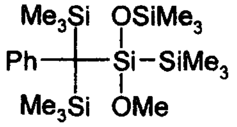
Crystal data for (232): $C_{20}H_{41}F_3O_2Si_5$,[98] M = 510.98, triclinic, space group P -1, a = 10.237(2), b = 10.977(2), c = 13.598(3) Å, α = 100.67(3), β = 109.10(1), γ = 90.40(3) °, U = 1415.2(5) Å^3, F(000) = 548, Z = 2, Dc = 1.199 mg m^{-3}, μ = 0.286 mm^{-1} (Mo-Kα, λ = 0.71073 Å), T = 120(1)K. 15765 reflections (1.62 = θ = 27.48°) were collected on a Bruker SMART-CCD diffractometer (ω-scan, 0.3°/frame) yielding 6471 unique data (R_{merg} = 0.023). The structure was solved by direct methods and refined by full-matrix least squares on F^2 for all data using SHELXL software. All non-hydrogen atoms were refined with anisotropic displacement parameters, H-atoms were placed geometrically and refined with a riding model. Final $wR_2(F^2)$ = 0.0903 and $R(F)$ = 0.0378 for all data (284 refined parameters), GOF = 1.042, residuals min = -0.50 eÅ^{-3} and max = 0.61 eÅ^{-3}.

1-[1',1'-Bis(trimethylsilyl)ethyl]-1-hydroxy-2,2,2-trimethyl-1-trimethylsilyloxydisilane (233)



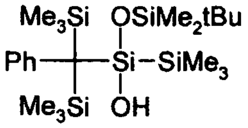
A solution of acetyltris(trimethylsilyl)silane (0.73 g, 2.50 mmol) was treated with trimethylsilylbistriflamide (0.88 g, 2.50 mmol) as described above to give a crude oil. Purification by flash column chromatography (eluting: 5% ethyl acetate:petroleum ether) afforded the title compound as a colourless oil, (0.73 g, 77%). [Found (M+NH$_4$)$^+$, 398.2218. $C_{14}H_{44}O_2NSi_5$ requires M, 398.2218]; ν_{max} (thin film) 3686, 3500 (broad, OH), 2950, 2904, 2864, 1461, 1406, 1254, 1044 cm^{-1}; δ_H (300MHz) 1.95-1.80 (1H, b, -O$\underline{H}$), 1.10 (3H, s, C$\underline{H}_3$) 0.16 (18H, s, 2x C-Si(C$\underline{H}_3$)$_3$), 0.10 (9H, s, 1xO-Si(C$\underline{H}_3$)$_3$), -0.08 (9H, s, Si-Si(C$\underline{H}_3$)$_3$); δ_C (50MHz) 12.5, 6.3, 2.6, 0.9, 0.7, 0.1; δ_{Si} (99 MHz) 4.7, 0.4, -0.5, -10.4, -25.9; MS (EI$^+$) m/z 365 (M$^+$-CH$_3$, 3%), 349 (6), 307 (M$^+$-SiMe$_3$, 17), 217 (35), 147 (14), 73 (100%).

1-Methoxy-1-[phenylbis(trimethylsilyl)methyl]-2,2,2-trimethyl-1-trimethylsilyloxydisilane (241)



A solution of benzoyltris(trimethylsilyl)silane (0.85 g, 2.43 mmol) was treated with trimethylsilylbistriflamide (0.86 g, 2.43 mmol) as described above except that the reaction was quenched by the addition of methanol followed by water. The resultant crude oil was purified by flash column chromatography (eluting: petroleum ether) to afford the title ether as a white solid (0.99 g, 89%). m.p. 207-208°C; [Found: C, 51.43; H, 10.14; $C_{20}H_{44}O_2Si_5$ requires C, 51.56; H, 9.70%]; ν_{max} (KBr disc) 2955, 2899, 2834, 1594, 1497, 1446, 1410, 1255, 1101 cm^{-1}; δ_H (200MHz); 7.56-7.02 (5H, m, $\underline{\mathbf{Ar}}$), 3.64 (3H, s, -$OC\underline{\mathbf{H}}_3$), 0.34, 0.29, 0.26 (each 9H, s, 2x C-$Si(C\underline{\mathbf{H}}_3)_3$, 1xO-$Si(C\underline{\mathbf{H}}_3)_3$), -0.10 (9H, s, Si-$Si(C\underline{\mathbf{H}}_3)_3$); δ_C (50MHz) 141.8, 131.9, 127.8, 123.7, 50.5, 29.0, 4.1, 3.7, 2.9, 0.4; δ_{Si} (99 MHz) 4.1, -2.26, -2.34, -17.0, -22.9; MS (EI^+) m/z 457 (M^+, 4%), 441 (M^+-CH_3, 8), 383 (M^+-$SiMe_3$, 32), 147 (30), 73 (100).

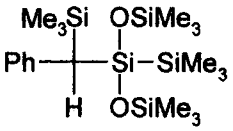
1-Hydroxy-1-[phenylbis(trimethylsilyl)methyl]-2,2,2-trimethyl-1-(*tert*-butyldimethylsilyloxy)disilane (240)



A solution of benzoyltris(trimethylsilyl)silane (1.03 g, 2.94 mmol) was treated with *tert* butyldimethylsilylbistriflamide (1.25 g, 3.16 mmol) as described above to give a crude oil. Purification by flash column chromatography (eluting: 5% ethyl acetate:petroleum ether) yielded the title disilane as a colourless oil, (1.20 g, 84%). [Found: (EI^+) M^+, 484.2465. $C_{22}H_{48}O_2Si_5$ requires *M*, 484.2501]; ν_{max} (thin film) 3674 (s, -OH), 3054, 2955, 2897, 2858, 1593, 1497, 1472, 1361, 1253, 1151 cm^{-1}; δ_H (300MHz) 7.55-7.10

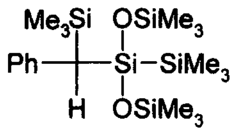
(5H, m, **Ar**), 2.30 (1H, bs, -O**H**), 0.96 (9H, s, -C(C**H**$_3$)$_3$), 0.23, 0.22, (9H each, 2x C-Si(C**H**$_3$)$_3$) 0.18, 0.16 (3H each, -Si(C**H**$_3$)$_2$tBu, diastereotopic), -0.15 (9H, s, Si-Si(C**H**$_3$)$_3$; δ_C (50MHz) 141.7, 131.9, 127.9, 123.9, 29.4, 26.5, 18.8, 4.1, 0.0, -1.3, -1.5; δ_{Si} (99 MHz) 9.5, -2.4, -2.7, -13.5, -23.3; MS (EI$^+$) m/z 484 (M$^+$, 1%), 469 (M$^+$-CH$_3$), 2.5), 424 (M$^+$-tBu, 1.5), 411 (M$^+$-SiMe$_3$, 25), 147 (29), 73 (100%).

1-[Phenyl(trimethylsilyl)methyl]-2,2,2-trimethyl-1,1-bis(trimethylsilyloxy)disilane (257)

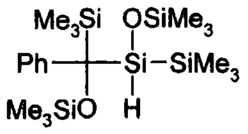


A solution of 1-hydroxy-1-[phenylbis(trimethylsilyl)methyl]-2,2,2-trimethyl-1-trimethylsilyloxydisilane (231) (0.10 g, 0.23 mmol) in diethyl ether (5 ml) was cooled to -78°C. Methyllithium (1.6 M solution in diethyl ether, 0.15 ml, 0.23 mmol) was then added. The solution was allowed to warm to 0°C over 5 hours and then stirred for a further 12 hours at this temperature. Saturated NH$_4$Cl solution was then added, the layers were separated and the aqueous layer extracted with diethyl ether (3x20 ml). The combined organic layers were dried over MgSO$_4$, filtered and concentrated to give the crude product. Flash column chromatography (eluting: petrol) gave the title compound as a white solid, (0.075 g, 74%). m.p. 117-119°C; [Found: C, 51.28; H, 9.66; C$_{19}$H$_{42}$O$_2$Si$_5$ requires C, 51.49; H, 9.56%]; ν_{max} (KBr disc) 2957, 2899, 1598, 1494, 1254, 1201, 1074, 1041 cm^{-1}; δ_H (500MHz) 7.17-7.00 (5H, m, **Ar**), 1.58 (1H, s, Ph(Me$_3$Si)C**H**), 0.15, 0.12 (2x9H, s, 2xOSi(C**H**$_3$)$_3$ diastereotopic), 0.01 (9H, s, CHSi(Si(C**H**$_3$)$_3$)), -0.19 (9H, s, Si-Si(C**H**$_3$)$_3$); δ_C (100MHz) 140.7, 129.7, 128.0, 123.5, 33.8, 2.5, 2.3, -0.1, -1.4; δ_{Si} (99 MHz) 0.2, -0.8, -5.8, -31.7, -32.7; MS (EI$^+$) m/z 442 (M$^+$, 0.5%), 427 (M$^+$-CH$_3$, 3%), 369 (M$^+$-SiMe$_3$, 7%), 279 (40), 265 (12), 191 (29), 147 (19), 73 (100).

Reaction of Benzoyltris(trimethylsilyl)silane 1a with Trimethylsilyl Trifluoromethylsulfonate: 1-[phenyl(trimethylsilyl)methyl]-2,2,2-trimethyl-1,1-bis(trimethylsilyloxy)disilane (257) and 1-[phenyl(trimethylsilyl)(trimethylsilyloxy)methyl]-2,2,2-trimethyl-1-trimethylsilyloxydisilane (264)[98]



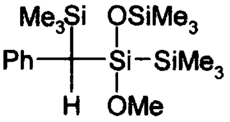
$\mathrm{Ph}-\overset{\mathrm{Me_3Si}}{\underset{\mathrm{H}}{|}}-\overset{\mathrm{OSiMe_3}}{\underset{\mathrm{OSiMe_3}}{\mathrm{Si}}}-\mathrm{SiMe_3}$



$\mathrm{Ph}-\overset{\mathrm{Me_3Si}}{\underset{\mathrm{Me_3SiO}}{|}}-\overset{\mathrm{OSiMe_3}}{\underset{\mathrm{H}}{\mathrm{Si}}}-\mathrm{SiMe_3}$

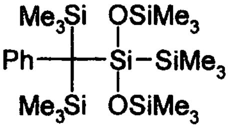
A solution of benzoyltris(trimethylsilyl)silane (87) (1.24 g, 3.52 mmol) in dichloromethane (10 ml) was cooled to -20°C. Trimethylsilyl trifluoromethanesulfonate (3.52 mmol) was then added. The solution was then stirred for approximately 14 hours when saturated $NaHCO_3$ solution was then added. The organic layer was separated, and the aqueous layer extracted with diethyl ether (3x20 ml). The combined organic layers were dried over $MgSO_4$, filtered and concentrated to give the crude product as an orange oil. Purification by flash column chromatography (eluting: petrol) gave the title products (colourless semisolid) as an inseparable mixture, (1.25 g, 2.82 mmol, 80%). Both GC and ^{1}H NMR analyses indicated a value of 81%:19% (257):(264). ν_{max} ($CHCl_3$) 3060, 2957, 2897, 1596, 1494, 1449, 1405, 1252, 1200 cm^{-1} ; δ_H (500MHz) 7.40-6.96 (5H, m, $\underline{\mathrm{Ar}}$, both isomers), 5.26 (1H, s, $\mathrm{Si\underline{H}}$, minor), 1.59 (1H, s, $\mathrm{Ph(Me_3Si)C\underline{H}}$, major), 0.16 (9H, s, $\mathrm{OSi(C\underline{H}_3)_3}$, major & 2x9H, s, $\mathrm{OSi(C\underline{H}_3)_3}$, minor), 0.13 (9H, s, $\mathrm{OSi(C\underline{H}_3)_3}$, major), 0.09 (2x9H, s, $\mathrm{PhC(OSiMe_3)Si(C\underline{H}_3)_3}$ & $\mathrm{Si(SiC\underline{H}_3)_3}$, both minor), 0.01 (9H, s, $\mathrm{PhCHSi(C\underline{H}_3)_3}$, major), -0.18 (9H, s, $\mathrm{Si\text{-}Si(C\underline{H}_3)_3}$); δ_C (125MHz) 141.9, 140.7, 130.9, 129.7, 128.0, 127.6, 123.5, 33.8, 2.5, 2.3, 2.3, 2.0, 1.7, 0.0, -1.4; MS (EI$^+$) major: m/z 442 (M$^+$, 1%), 369 (M$^+$-$Si(CH_3)_3$, 10%), 279 (51), 265 (19), 191 (40), 147 (34), 73 (100); MS (EI$^+$) minor: m/z 442 (M$^+$, 1%), 427 (M$^+$-$SiMe_3$, 8%), 368 (20), 280 (23), 265 (20), 147 (20), 135 (10), 73 (100).

1-[Phenyl(trimethylsilyl)methyl]-2,2,2-trimethyl-1-methoxy-1-trimethylsilyloxydisilane (268)



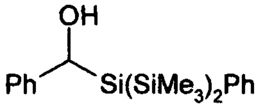
A solution of benzoyltris(trimethylsilyl)silane (87) (0.51 g, 1.46 mmol) in dichloromethane (10 ml) was cooled to -20°C. Trimethylsilyl trifluoromethanesulfonate (1.46 mmol) was then added. The solution was stirred for approximately 14 hrs when methanol was added. After 1 hour saturated $NaHCO_3$ solution was then added. The organic layer was separated, and the aqueous layer extracted with diethyl ether (3x20 ml). The combined organic layers were dried over $MgSO_4$, filtered and concentrated to give the crude product as a dark yellow oil. Purification by flash column chromatography (eluting: petrol) gave the title compound as a colourless oil (0.33 g, 58%). [Found M^+, 384.1792. $C_{17}H_{36}O_2Si_4$ requires *M*, 384.1792]; ν_{max} (thin film) 3020, 2956, 2898, 2835, 1700, 1597, 1493, 1450, 1405, 1287, 1251, 1204 cm^{-1}; δ_H (400MHz) 7.20-7.00 (5H, m, $\underline{Ar}$), 3.52 (3H, s, $-OC\underline{H}_3$), 1.60 (1H, s, $Ph(Me_3Si)C\underline{H}$), 0.16 (9H, s, $OSi(C\underline{H}_3)_3$), 0.01 (9H, s, $PhCHSi(C\underline{H}_3)_3$), -0.17 (9H, s, $Si\text{-}Si(C\underline{H}_3)_3$); δ_C (100 MHz) 140.4, 129.6, 128.1, 123.6, 50.8, 32.7, 2.4, -0.2, -1.0; MS (EI^+) m/z 384 (M^+, 2%), 369 (M^+-CH_3, 22), 311 (M^+-$SiMe_3$, 17), 265 (20), 221 (100), 117 (44), 73 (76).

1-[Phenylbis(trimethylsilyl)methyl]-2,2,2-trimethyl-1,2-bis(trimethylsilyloxy)disilane



Trimethylsilyltrifluoromethanesulfonate (0.06 g, 0.288 mmol) was added to a solution of disilane (231) (0.12 g, 0.28 mmol) in dichloromethane (5 ml) at -78°C. The solution was stirred at this temperature for 18 hours. Saturated $NaHCO_3$ solution was then added (10 ml). The organic layer was then extracted with dichloromethane (3x10 ml). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated. Flash column chromatography (eluting: petrol) gave the title compound as a colourless solid, (0.13 g, 90%) sublimes at 315-320°C. [Found: C, 50.15%; H, 9.89%; $C_{22}H_{50}O_2Si_6$ requires C, 51.29%; H, 9.89%]; ν_{max} (KBr disc) 3057, 2955, 2899, 1594, 1497, 1256, 1151, 1060, 1025, 913, 839 cm^{-1}; δ_H (300MHz) 7.50-6.95 (5H, m, **Ar**), 0.24 (18H, s, OSi(C**H**$_3$)$_3$), 0.21 (18H, s, 2xC-Si(C**H**$_3$)$_3$), -0.18 (9H, s, SiSi(C**H**$_3$)$_3$); δ_C (100 MHz) 141.99, 131.83, 127.70, 123.69, 29.09, 4.28, 3.25, 0.69; MS (EI$^+$) m/z 499 (M$^+$-CH$_3$, 2%), 441 (M$^+$-SiMe$_3$, 20), 191 (8), 147 (27), 135 (8), 73 (100); (CI) m/z 515 (MH$^+$, 100%), 442 (6), 90 (74).

1,1,1,3,3,3-Hexamethyl-2-phenyl-2-(1'-hydroxy-1'-phenylmethyl)trisilane



Methylithium (1.6 M solution in diethyl ether, 10.13 ml, 16.21 mmol) was added to a solution of phenyltris(trimethylsilyl)silane (5.25 g, 16.21 mmol) in THF (40 ml). The solution was stirred for 18 hours. The mixture was then concentrated. The solid silyllithium was dissolved in diethyl ether (50 ml). The solution was then added via cannula to a solution of $MgBr_2$ (3.59 g, 19.50 mmol) in diethyl ether (40 ml). The solution was stirred for 1 hour. The solution was then cooled to -78°C. Benzaldehyde (3.52 g, 33.20 mmol) was then added dropwise. The mixture was stirred for 12 hours. Saturated NH_4Cl solution was then added (50 ml). The aqueous layer was separated and extracted with ether (3x30 ml). The organic layers were washed with saturated sodium metabisulfite solution (3x30 ml). The organic layer was then dried over $MgSO_4$ and concentrated. Flash column chromatography (gradient elution: petrol/ 5% diethyl ether: petrol/10% diethyl ether: petrol) gave the title compound as a colourless waxy solid (3.03 g, 52%). m.p. 61-62°C.

ν_{max} (KBr disc) 3421 (b, OH), 2947, 2891, 1723, 1597, 1492, 1449, 1426, 1260, 1244, 1093, 837 cm^{-1}; δ_H (300 MHz) 7.95-7.10 (10H, m, **Ar**), 5.19 (1H, s, PhC**H**(OH)Si), 1.80 (1H, broad, O**H**), 0.14, 0.10 (2x9H, s, Si(C**H**$_3$)$_3$, diastereotopic); δ_C (100MHz) 136.20, 129.68, 128.48, 128.41, 128.23, 127.92, 125.97, 125.08, 69.70, 0.16, 0.01; MS (CI) m/z 376 ($M+NH_4$, 44%), 358 (M^+, 100), 341 (47), 298 (27), 268 (25).

1-Phenyl-1-trimethylsilyl-2-(prop-2'-yl)-4,5-dimethylsilacyclohex-4-ene

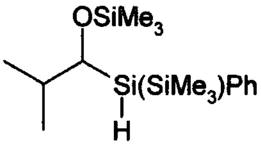
Methyllithium (1.6 M solution in diethyl ether, 0.84 ml, 1.34 mmol) was added to a solution of silyl alcohol (221) (0.45 g, 1.34 mmol) and 2,3-dimethylbutadiene (0.66 g, 8.05 mmol) in diethyl ether (30 ml) at -78°C. The mixture was allowed to warm to -30°C. The mixture was allowed to stir at this temperature for 18 hours. Saturated ammonium chloride solution (20ml) was added. The aqueous layer was extracted with diethyl ether (3x20 ml). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated. Flash column chromatography (eluting: petrol) gave the title compound as a colourless oil, (0.28 g, 65%).

ν_{max} (thin film) 3056, 2990, 2934, 2868, 1434, 1388, 1312, 1230, 1087, 865, 831 cm^{-1}; δ_H (300 MHz) 7.55-7.30 (5H, m, **Ar**), 1.75 (3H, s, ($\underline{H}_3C$)C=C(CH_3), 1.68 (3H, s, =C($C\underline{H}_3$)CH_2Si), 0.15 (9H, s, Si($C\underline{H}_3)_3$); MS (EI) m/z 316 (M^+, 13%), 243 (M^+-$Si(CH_3)_3$, 73%), 201 (7), 187 (62), 161 (51), 135 (36), 121 (31), 105 (26), 73 (100).

1-Phenyl-1-trimethylsilyl-2-(prop-2'-yl)-3-methylsilacyclohex-4-ene (269)

Methyllithium (1.6 M solution in diethyl ether, 0.58 ml, 0.93 mmol) was added to a solution of silyl alcohol (221) (0.30 g, 0.93 mmol) and (*E*)-1,3-pentadiene (0.38 g, 5.58 mmol) in diethyl ether (30 ml) at -78°C. The mixture was allowed to warm to -30°C. The mixture was allowed to stir at this temperature for 18 hours. Saturated ammonium chloride solution (20 ml) was added. The aqueous layer was extracted with diethyl ether (3x20 ml). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated. Flash column chromatography (eluting: petrol) gave the title compound as a colourless oil, (0.19 g, 66%). (Found (EI^+): 302.1889; $C_{18}H_{30}Si_2$ requires *M*, 302.1886); ν_{max} (thin film) 3067, 2997, 2953, 2869, 1461, 1427, 1397, 1365, 1244, 1101, 855, 833 cm^{-1}; δ_H (500MHZ) 7.50-7.30 (5H, m, **Ar**), 5.82 (1H, m, SiCH$_2$C**H**=CH), 5.55 (1H, m, CH$_2$CH=C**H**), 2.36 (1H, m, =CHCH(CH$_3$)C**H**), 2.10 (1H, ds, J=7.0Hz, 3.5 Hz, C**H**(CH$_3$)$_2$), 1.58 (2H, m, =CHC**H**$_2$Si) 1.20 (1H, dd, J=6.0 Hz, 3.5 Hz, C**H**CH(CH$_3$)$_2$) 1.03 (3H, d, J=7.0 Hz, CH(C**H**$_3$)$_2$, diastereotopic), 0.93 (3H, d, J=7.0 Hz, =CHCH(C**H**$_3$)CH), 0.88 (3H, d, J=7.0 Hz, CH(C**H**$_3$)$_2$, diastereotopic), 0.14 (9H, s, Si(C**H**$_3$)$_3$); δ_C (125MHz) 139.40, 137.42, 134.48, 128.18, 127.63, 123.56, 38.19, 32.74, 29.99, 23.53, 22.97, 22.41, 9.72, 0.59; MS (EI) m/z 302 (M^+, 7%), 287 (M^+-CH_3, 2%), 229 (M^+-TMS, 44), 218 (22), 203 (33), 177 (10), 173 (19), 161 (100), 145 (26), 135 (54), 121 (38).

2-Phenyl-1,1,1-trimethyl-2-(1'-trimethylsilyloxy-2'-methylpropyl)disilane (272)



n-Butyllithium (1.5 M solution in hexanes, 0.25 ml, 0.37 mmol) was added to a solution of silyl alcohol (221) (0.12 g, 0.37 mmol) in diethyl ether (30 ml) at -78°C. The solution was allowed to warm to -30°C. The mixture was allowed to stir at this temperature for 12 hours. Saturated ammonium chloride solution (15 ml) was added. The aqueous layer was extracted with diethyl ether (3x20 ml). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated. Flash column chromatography (eluting: petrol) gave the title compound as a colourless oil, (0.08 g, 70%).

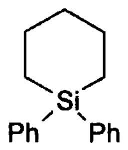
ν_{max} ($CHCl_3$) 3020, 2959, 2100 (Si-H), 929 cm^{-1}; δ_H (500MHz) 7.60-7.28 (5H, m, $\underline{Ar}$), 4.18 (1H, d, J=3.3 Hz, $Si\underline{H}$), 3.82 (1H, dd, J=5, 3.3 Hz), 1.91 (1H, m, $C\underline{H}(CH_3)_2$), 0.97, 0.87 (2x3H, d, J=6.5Hz, $C\underline{H}_3$, diastereotopic), 0.19 (9H, s, $OSi(C\underline{H}_3)_3$, -0.01 $SiSi(C\underline{H}_3)_3$; δ_C (100MHz) 136.01, 134.99, 128.63, 127.69, 72.00, 33.84, 20.81, 19.48, 0.38, -0.69; MS (EI) m/z 309 ($M-CH_3$, 3%), 251 ($M-Si(CH_3)_3$, 5%), 235 ($M-OSi(CH_3)_3$, 5%), 195 (20), 179 (8), 145 (10), 135 (10), 73 (100).

Reaction of Silyl Alcohol (221), MeLi and cyclohexane: formation of Silene Dimer (270)/(271)

Methyllithium (1.6 M solution in diethyl ether, 0.59 ml, 0.94 mmol) was added to a solution of silyl alcohol (221) (0.3032 g, 0.94 mmol) and cyclohexadiene (0.3024 g, 3.78 mmol) in diethyl ether (30ml) at -78°C. The mixture was allowed to warm to -30°C. The mixture was allowed to stir at this temperature for 18 hours. Saturated ammonium chloride solution (20 ml) was added. The aqueous layer was extracted with diethyl ether (3x20 ml). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated. Flash column chromatography (eluting: petrol) gave the silene dimer (275)/(276) as a colourless waxy solid, (0.13 g, 61%). M.p. 114-115°C.

ν_{max} (KBr disc) 2958, 2892, 1654, 1458, 1261, 1095, 1024, 830 cm^{-1}; δ_H (200MHz) 7.70-7.30 (10H, m, $\underline{Ar}$), 2.00 (2H, m, $CHC\underline{H}(CH_3)_2$), 1.15 (2H, bs, $C\underline{H}Si(SiMe_3)Ph$), 0.92, 0.97 (2x6H, d, J=6.4Hz, $CH(C\underline{H}_3)_2$, diastereotopic), 0.08 (18H, s, $2xSi(C\underline{H}_3)_3$); δ_C (75 MHz) 138.00, 134.82, 128.34, 52.72, 27.27, 24.53, -0.64, -2.92; MS (EI) m/z 468 (M^+, 3%), 395 ($M^+-Si(CH_3)_3$, 2), 318 (12),

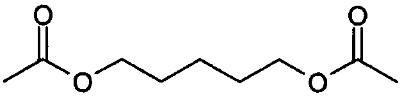
1,1-Diphenylsilacyclohexane (331)[127]



A mixture of 1,5-dibromopentane (19.80 g, 60 mmol) and dichlorodiphenylsilane (15.12 g, 60 mmol) was added dropwise to a stirred suspension of magnesium turnings (3.50 g, 145 mmol) in THF (60 ml) in order to maintain a gentle reflux. The mixture was heated to reflux for a further hour, then stirred at room temperature for 15 hours. Saturated ammonium chloride solution was carefully added. The aqueous layer was then extracted with ether (3x30 ml). The combined organic layers were dried over $MgSO_4$ and concentrated. Distillation gave the title compound (11.19 g, 74%) as a colourless oil, b.p. 118-120°C/0.1 mbar.(lit.[127] 122°C/0.15 mbar).

ν_{max} (thin film) 3067, 2999, 2916, 2851, 1427, 1179, 1113, 987, 908, 775 cm^{-1}; δ_H (300MHz) 7.70-7.30 (10H, m, $\underline{\mathbf{Ar}}$), 1.90-1.80 (4H, m, $SiCH_2C\underline{\mathbf{H}}_2$), 1.70-1.50 (2H, m, $CH_2C\underline{\mathbf{H}}_2CH_2$), 1.30-1.20 (4H, t, J=6.75 Hz, $SiC\underline{\mathbf{H}}_2CH_2$); δ_C (75MHz) 136.73, 134.47, 129.09, 127.83, 29.95, 24.35, 11.56; MS (EI^+) m/z 252 (M^+, 24%), 209 (16), 181 (34), 174 (100), 146 (26).

1,5-Bisacetoxypentane (344)



Method 1

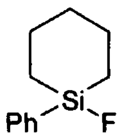
A solution of 1,5-pentanediol (1.75 g, 16.83 mmol) and DMAP (0.02 g, 0.16 mmol) in pyridine (20 ml) was cooled to 0°C. Acetic anhydride (3.50 g, 34.31 mmol) was then added. The solution was allowed to warm to room temperature, and stirred for 4 hours.

Dilute hydrochloric acid (30 ml) and diethyl ether (50 ml) were then added, the aqueous layer was separated and extracted with diethyl ether (3x30 ml). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Kugelrohr distillation (oven temp: 150°C, 10 mbar, lit.[137] 115°C/13 mbar) gave the title compound as a colourless oil, (2.85 g, 90%).

ν_{max} (thin film) 2953, 2872, 1744, 1464, 1367, 1520, 1111, 1040 cm^{-1}; δ_H (300MHz) 4.06 (4H, t, J=6.6Hz, 2x$OC\underline{\mathbf{H}}_2CH_2$), 2.04 (6H, s, 2x$C\underline{\mathbf{H}}_3C(O)$-), 1.65 (4H, m, 2x$OCH_2C\underline{\mathbf{H}}_2CH_2$), 1.42 (2H, m, $CH_2CH_2C\underline{\mathbf{H}}_2CH_2CH_2$); δ_C (75MHz) 171.13, 64.22, 28.22, 22.44, 20.96; MS (CI) m/z 189 (MH^+, 0.5%), 128 (2), 101 (6), 86 (13), 68 (79), 43 (100).

Method 2

Stage 1: Formation of 1-fluoro-1-phenylsilacyclohexane (338)



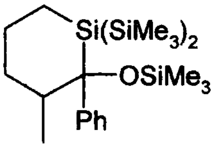
Diphenylsilacyclohexane (336), (2.18 g, 8.64 mmol) was dissolved in dichloromethane (10 ml). Trifluoroborane-acetic acid complex (3.25 g, 17.28 mmol) was added, and the solution was stirred for 18 hours. Saturated $NaHCO_3$ solution was then added. The aqueous layer was extracted with dichloromethane (3x20 ml), dried over $MgSO_4$, filtered and concentrated to give the monofluorophenylsilacyclohexane (1.60 g, 95%). This was used in stage 2 without further purification.

δ_H (300 MHz) 7.70-7.35 (5H, m, <u>**Ar**</u>), 1.95-0.80 (10H, m, remaining H); δ_C (75 MHz) 134.10, 133.34, 130.42, 128.02, 29.44, 23.99, 13.29, 13.11; δ_F (188 MHz) −171.58; MS (EI) m/z 194 (M^+, 13%), 151 (7), 138 (28), 116 (100).

Stage 2

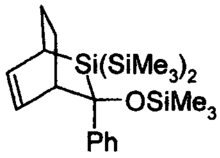
The fluorosilacycle (338) from stage 1 was dissolved in MeOH/THF (1:1 mixture, 20 ml). $KHCO_3$ (3.30 g, 33.0 mmol) and KF (1.91 g, 32.9 mmol) were added. Hydrogen peroxide (27% w/w solution in water, 32 ml, 254 mmol) was then added. The mixture was then heated to 70°C and stirred for 12 hours. The solution was then cooled to 0°C. Pyridine (25 ml), DMAP (0.05 g, 0.41 mmol) and acetic anhydride (1.70 g, 16.67 mmol) were then added. The mixture was allowed to warm to room temperature. Dilute hydrochloric acid (30 ml) and diethyl ether (50 ml) were then added, the aqueous layer was separated and extracted with diethyl ether (3x30 ml). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Kugelrohr distillation (oven temp. 150°C/ 10mbar) gave the diacetyl ester of 1,5-pentanediol as a colourless oil (0.97 g, 60% overall). This material was spectroscopically identical to that prepared above.

1,1-Bistrimethylsilyl-2-phenyl-2-(trimethylsilyloxy)-3-methyl-silacyclohexane (325)



A solution of silacycle (159), (2.11 g, 5.03 mmol), Pd-C (10% Pd, 0.54 g) in ethyl acetate (50 ml) was degassed by repeated evactuation/fill with hydrogen (5 cycles). The mixture was then stirred for 6 hours. Filtration through celite followed by flash column chromatography gave the title compound as a colourless solid (1.95 g, 92%). m.p. 185-186°C. [Found: C, 59.63%; H, 10.15%; Calc. for $C_{20}H_{42}OSi_4$ C, 59.64%; H, 10.01%]; ν_{max} (KBr disc) 3057, 2950, 2900, 2852, 1600, 1491, 1446, 1400, 1254, 1087, 1056, 1008 cm^{-1}; δ_H (500MHz) 7.45-7.00 (5H, m, **Ar**), 2.50 (2H, m, isomer A), 2.10 (2H, m, isomer B), 2.00 (2H, m, iosmer A), 1.75 (2H, m, isomer B), 1.50 (2H, m, isomer B), 1.25 (1H, m, C**H**(CH$_3$), isomer B), 1.10 (1H, m, C**H**(CH$_3$), isomer A), 0.95 (3H, d, J=6.6 Hz, CH(C**H**$_3$), isomer B), 0.90 (3H, d, J=6.6Hz, CH(C**H**$_3$, isomer A), 0.24 (9H, s, OSi(C**H**$_3$)$_3$, isomer A), 0.10 (9H, s, OSi(C**H**$_3$)$_3$, isomer B), 0.09 (9H, s, SiSi(C**H**$_3$)$_3$, isomer B), 0.07 (9H, s, SiSi(C$\underline{H}_3$)$_3$, isomerA), -0.14 (9H, s, SiSi(C$\underline{H}_3$)$_3$, isomer B), -0.22 (9H, s, SiSi(C$\underline{H}_3$)$_3$, isomer A); δ_C (125MHz) 146.22, 127.68, 126.93, 125.60, 108.86, 81.00, 79.80, 41.59, 39.59, 34.85, 33.06, 26.28, 25.98, 22.99, 17.87, 9.19, 8.15, 3.88, 3.45, 1.20, 0.82, 0.60, -0.22; MS (EI) m/z 422 (M^+, 0.5%), 407 (M^+-CH_3, 1), 349 (M^+-$SiMe_3$, 13), 275 (15), 191 (26), 147 (45), 133 (30), 73 (100).

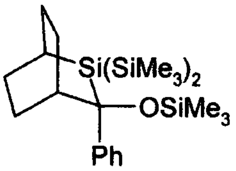
2,2-Bistrimethylsilyl-3-phenyl-3-trimethylsilyloxy-2-silabicyclo[2.2.2]oct-5-ene (314)



Benzoyltris(trimethylsilyl)silane (1.03 g, 2.92 mmol) and cyclohexa-1,3-diene (0.50 g, 6.23 mmol) were dissolved in benzene (10 ml) were degassed by freeze/thaw technique (3 cycles). The tube was then sealed and heated at 180°C for 4 hours. Concentration, followed by flash column chromatography gave the title compound as a colourless solid (0.82 g, 65%).

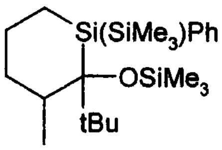
M.p. 204-205°C; [Found (EI^+): M^+, 432.2157; $C_{22}H_{40}OSi_4$ requires *M*, 432.2156]; ν_{max} (KBr disc) 3027, 2949, 2891, 2893, 1598, 1489, 1443, 1248, 1026, 834 cm^{-1}; δ_H (300 MHz) 7.65-7.05 (5H, m, Ar), 6.50 (1H, t, J=8.4 Hz, exo), 6.31 (1H, t, J=8.4 Hz, endo), 6.20 (1H, t, J=8.4 Hz, endo), 6.04 (1H, t, J=8.4 Hz, exo), 3.40 (1H, m, allylic, exo), 3.22 (2H, m, allylic, endo), 2.40 (2H, m, allylic, endo+exo), 2.15-2.00 (4H, m, exo), 1.80-1.40 (4H, m, endo), 0.31 (9H, s, OSi(C$\underline{H}_3$)$_3$, endo), 0.23 (9H, s, OSi(C$\underline{H}_3$)$_3$, exo), -0.18 (9H, s, Si-Si(C$\underline{H}_3$)$_3$, endo), -0.24 (9H, s, Si-Si(C$\underline{H}_3$)$_3$, exo), -0.25 (9H, s, Si-Si(C$\underline{H}_3$)$_3$, exo), -0.37 (9H, s, Si-Si(C$\underline{H}_3$)$_3$, endo); δ_C (75 MHz) 149.05, 145.02, 136.30, 136.01, 131.06, 129.42, 127.89, 127.71, 126.20, 125.94, 83.50, 41.69, 39.50, 24.90, 24.13, 22.81, 22.61, 21.95, 21.86, 2.51, 2.38, 0.69, -0.50, -0.70; MS (EI) m/z 432 (M^+, 21%), 417 (M-CH_3, 3%), 359 (M-$Si(CH_3)_3$, 60%), 337 (52), 263 (32), 191 (17), 147 (32), 73 (100).

2,2-Bistrimethylsilyl-3-phenyl-3-trimethylsilyloxy-2-silabicyclo[2.2.2]octane (315)



Silacycle (314) (0.51 g, 1.16 mmol) was dissolved in ethanol (30 ml). Palladium on carbon (10% Pd, 0.13 g) was then added. The solution was degassed by repeated evacuation (water pump)/filling with hydrogen (4 cycles). The solution was then stirred for 10 hours. The Pd-C was separated by filtration. Concentration, followed by flash column chromatogaphy (eluting: petrol) gave the title compound as a white solid, (0.50 g, 92%) m.p. 193-194°C. [Found: C, 60.37%; H, 10.09%; Calc. for $C_{22}H_{42}OSi_4$ C, 60.76%; H, 9.75%]; ν_{max} (KBr disc) 3055, 2948, 2900, 2852, 1489, 1446, 1397, 1297, 1250, 1082, 1057, 936 cm^{-1}; δ_H (400 MHz) 7.40-7.00 (10H, m, **Ar**), 2.75 (1H, m), 2.55 (1H, m), 2.20-1.40 (17H, m), 1.18 (1H, m), 0.33, 0.32 (2x9H, s, OSi(C**H**$_3$)$_3$), -0.11, -0.22, -0.27, -0.35 (4x9H, s, Si-Si(C**H**$_3$)$_3$); δ_C (100 MHz) 149.55, 146.37, 128.05, 127.79, 126.26, 125.41, 84.19, 79.89, 43.66, 39.09, 34.29, 31.00, 30.69, 25.70, 24.27, 24.10, 23.84, 21.57, 21.22, 2.41, 2.24, 1.88, 1.46, -0.11, -0.19; MS (EI) m/z 434 (M^+, 6%), 419 (M-CH_3, 3%), 361 (M-$SiMe_3$, 54%), 346 (5), 209 (16), 191 (16), 147 (26), 135 (18), 83 (30), 73 (100).

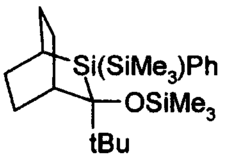
2-(*tert*-Butyl)-3-methyl-1-phenyl-1-trimethylsilyl-2-(trimethylsilyloxy)silacyclohexane (326)



Silacycle (225) (1.01 g, 2.51 mmol) was dissolved in ethyl acetate (15 ml). Palladium on carbon (10% Pd, 0.26 g) was added. The mixture was repeatedly degassed and filled with hydrogen. The mixture was then stirred under a hydrogen atmosphere for 8 hours. The mixture was then filtered through a pad of celite. Concentration, followed by flash column chromatography (eluting: petrol) gave the title compound as a colourless oil (0.93 g, 91%).

ν_{max} (thin film) 3066, 2955, 2900, 1427, 1388, 1357, 1333, 1258, 1247, 1204, 1137, 1095, 1043, 835 cm^{-1}; δ_H (300 MHz) 7.50-7.30 (5H, m, **Ar**), 2.65 (1H, m, -$CH_2C\underline{\mathbf{H}}(CH_3)C$, one diastereoisomer), 2.45 (1H, m, -$CH_2C\underline{\mathbf{H}}(CH_3)C$, other diastereoisomer), 1.80-1.15 (10H, m), 1.12 (9H, s, $C(CH_3)_3$, one diastereoisomer), 0.98 (9H, s, $C(C\underline{\mathbf{H}}_3)_3$, other diastereoisomer), 0.98 (9H, s, $OSi(C\underline{\mathbf{H}}_3)_3$, one diastereoisomer), 0.50 (9H, s, $OSi(C\underline{\mathbf{H}}_3)_3$, other diastereoisomer), -0.25 (9H, s, $SiSi(C\underline{\mathbf{H}}_3)_3$, one diastereoisomer), -0.38 (9H, s, $SiSi(C\underline{\mathbf{H}}_3)_3$, other diastereoisomer); δ_C (50 MHz) 136.99, 136.91, 134.99, 134.65, 128.37, 127.97, 127.50, 127.46, 95.69, 91.76, 52.23, 42.65, 38.00, 37.31, 36.60, 35.45, 28.55, 21.45, 20.10, 14.34, 14.20, 14.34, 14.20, 11.20, 11.07, 2.89, 2.24, -0.84, -1.42; MS (EI) 406 (M^+, 1%), 391 ($M-CH_3$, 1%), 333 ($M-SiMe_3$, 2%), 267 (71), 209 (11), 193 (33), 179 (15), 135 (49), 73 (100).

2-Phenyl-2-trimethylsilyl-3-*tert*-butyl-3-trimethylsilyloxy-2-silabicyclo[2.2.2]octane (327)

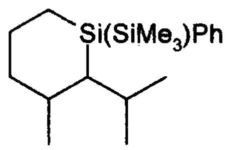


Silacycle (226) (3.45 g, 8.29 mmol) was dissolved in ethanol (100 ml). Palladium hydroxide on carbon (10%Pd ,0.90 g) and ammonium formate (2.09 g, 33.14 mmol) were added. The mixture was then heated to reflux for 2 hours. The mixture was then filtered through a pad of celite. Concentration, followed by flash column chromatography gave the title compound as a colourless solid (3.25 g, 94%), m.p. 122-123°C. [Found (EI^+): 418.2561; Calc. for $C_{23}H_{42}OSi_3$ 418.2543]; ν_{max} (KBr disc) 3069, 2951, 2896, 2851, 1479, 1427, 1389, 1361, 1250, 1099, 1073, 834 cm^{-1}; δ_H (400MHz) 7.50-7.26 (5H, m, **Ar**), 2.15-1.40 (10H, m), 1.14 (9H, s, C(C**H**$_3$)$_3$), 0.03 (9H, s, OSi(C**H**$_3$)$_3$), -0.21 (9H, s, SiSi(C**H**$_3$)$_3$); δ_C (100MHz) 136.68, 135.86, 127.45, 126.99, 88.03, 38.92, 35.39, 28.84, 24.60, 24.48, 22. 65, 21.82, 13.66, 2.76, 0.05; MS (EI$^+$) m/z 418 (M$^+$, 1%), 403 (M-Me, 2), 345 (M-SiMe$_3$, 10), 329 (M-OSiMe$_3$, 3), 315 (6), 287 (3), 268 (36), 253 (43), 209 (26), 195 (82), 179 (40), 135 (61), 73 (100);

Birch reduction of silacycle (327)[126]

Ammonia was condensed, via a primary vessel, into a three-necked round bottom flask, equipped with an acetone/dry ice condenser, at -78°C. Silacycle (332), (0.51 g, 1.21 mmol) was then added. Diethyl ether (10ml) was added to ensure a homogenous solution. Ethanol was then added (2 ml). Lithium metal (0.01 g, 1.43 mmol) was added in small pieces. The solution became dark blue in colour, then returned to a colourless solution, as the lithium metal was added. The mixture was then allowed to warm to room temperature. Water (30 ml) was then added. The mixture was extracted with ethyl acetate (3x30 ml). The combined organic extracts were dried over MgSO$_4$, filtered and concentrated. Flash column chromatography (eluting: petrol) gave a colourless solid (0.41 g, 80%). M.p. 117-118°C. [Found (EI$^+$): 422.2871; C$_{23}$H$_{46}$OSi$_3$ requires *M*, 422.2857]; ν_{max} (KBr disc) 3069, 2951, 2896, 2851, 1479, 1427, 1389, 1361, 1250, 1099, 1073, 834 cm^{-1}; δ_H (300MHz) 6.00-5.90 (2H, m, vinylic, minor), 5.90-5.80 (2H, m, vinylic, major), 2.40-1.40 (m), 1.02 (9H, s, C(C**H**$_3$)$_3$, major), 0.98 (9H, s, C(C**H**$_3$)$_3$, minor), 0.18 (9H, s, OSi(C**H**$_3$)$_3$, minor), 0.13 (9H, s, OSi(C**H**$_3$)$_3$, major), 0.12 (9H, s, Si(C**H**$_3$)$_3$, major), 0.09 (9H, s, Si(C**H**$_3$)$_3$, minor); δ_C (75 MHz) 136.70, 136.40, 134.82, 94.80, 92.20, 89.01, 47.50, 41.82, 38.84, 38.79, 37.89, 35.21, 30.90, 29.44, 28.77, 27.32, 24.68, 22.70, 22.52, 22.04, 14.00, 3.97, 3.33, 0.75; MS (EI$^+$) m/z 422 (M$^+$, 1%), 407 (M$^+$-CH$_3$, 3), 349 (M$^+$-SiMe$_3$, 9), 73 (100).

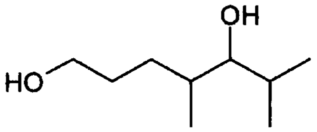
1-Phenyl-1-trimethylsilyl-2-(prop-2'-yl)-3-methylsilacyclohexane (340)



A mixture of silacycle (269), (0.80 g, 2.65 mmol) Pd on carbon (10%Pd, 2.65 g) in toluene was repeatedly evacuated and filled with hydrogen (5 cycles) from a balloon. The mixture was then stirred under a hydrogen atmosphere for 6 hours. The mixture was then filtered through a celite pad. Concentration, followed by flash column chromatography (eluting: petrol) gave the title compound as a colourless oil (0.77 g, 95%).

ν_{max} (thin film) 3067, 2953, 2907, 1453, 1427, 1244, 1099, 853, 833 cm^{-1}; δ_H (300 MHz) 7.60-7.30 (5H, m, **Ar**), 2.15 (1H, m, -C**H**(CH_3)CH_2) 1.00, 0.77 (2x3H, d, J= 7.0 Hz, -CH(C**H**$_3$)$_2$, diastereotopic), 0.95 (3H, d, J=6.4 Hz, CH(C**H**$_3$)-), 0.25 (9H, s, Si(C**H**$_3$)$_3$); δ_C (63 MHz) 140.62, 134.54, 128.11, 127.62, 40.55, 39.01, 34.15, 28.76, 23.60, 23.35, 23.14, 22.58, 12.97, 0.18; MS (EI^+) m/z 304 (M^+, 26%), 289 (M^+-CH_3, 3%), 231 (M^+-Si(CH_3)$_3$, 91%), 187 (12), 175 (31), 161 (52), 153 (27), 147 (32), 121 (100), 73 (63).

Oxidation of silacycle (340); formation of 4,6-dimethylheptane-1,5-diol (342)



Stage 1

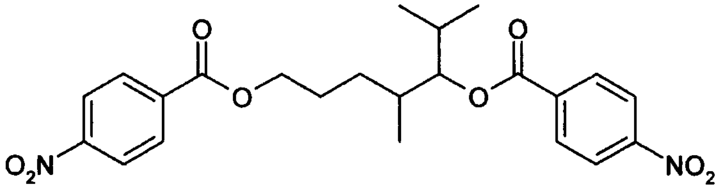
Silacycle (340) (0.16 g, 0.52 mmol) was dissolved in chloroform (5ml). Trifluoroborane-acetic acid complex (0.20 g, 10.40 mmol) was then added. The mixture was heated to reflux and stirred for 18 hours. Saturated $NaHCO_3$ solution was then added. The aqueous layer was extracted with chloroform (3x15 ml). The organic layers were combined, dried over $MgSO_4$, filtered and concentrated to give the crude fluorosilane (0.12 g, 94%). This was used without further purification in stage 2.

δ_F (188MHz) –187.38; MS (EI) m/z 246 (M^+, 12%), 173 (M-$SiMe_3$, 2%), 154 (72), 11 (98), 73 (100).

Stage 2

The crude fluorosilacycle (0.12 g, 0.413 mmol), $KHCO_3$ (0.20 g, 2.0 mmol) and KF (0.12 g, 2.07 mmol) were dissolved in THF:MeOH (1:1, 4ml). H_2O_2 (27% w/w solution in water, 1.6 ml, 12.4 mmol) was then added. The mixture was heated to reflux for 18 hours. Saturated $Na_2S_2O_3$ solution (3 ml) and ethyl acetate (10 ml) were then added. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (3x10 ml). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated. Flash column chromatography (eluting: 50% ethyl acetate: petrol) gave the title compound as a colourless oil (0.032g, 48%). [Found MH^+ (CI): 161.1534; $C_9H_{21}O_2$ requires *M*, 161.1542]; ν_{max} (thin film) 3360 (b, OH), 2958, 2932, 2873, 1723, 1468, 1390, 1762, 1120, 990 cm^{-1}; δ_H (300MHz) 3.66 (2H, t, J= 6.3 Hz, $HOC\underline{H}_2CH_2$-), 3.10 (1H, dd, J= 6.3 Hz, 1.5 Hz, -$CH(CH_3)C\underline{H}(OH)CH(CH_3)_2$), 1.90-1.30 (6H, m), 1.24 (1H, bs, $O\underline{H}$), 1.15 (1H, bs, $O\underline{H}$), 0.93, 0.89 (2x3H, d, J= 6.9 Hz, diastereotopic $CH(C\underline{H}_3)_3$), 0.90 (3H, d, J= 6.6 Hz, -$CH_2CH(C\underline{H}_3)CH(OH)$); δ_C (75MHz) 80.99, 63.30, 35.54, 30.15, 30.02, 27.42, 20.06, 16.45, 16.05; MS (EI^+) m/z 161 (M+1, <1%); (CI) m/z 178 (M+NH_4, 100%), 161 (MH^+, 25%).

4,6-Dimethyl-1,5-bis(4'-nitrobenzoyloxy)heptane (343)

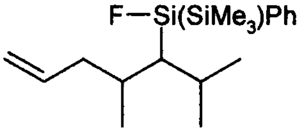


A solution of diol (342) (10 mg, 0.063 mmol) and DMAP (15 mg, 0.12 mmol) in THF (2 ml) was stirred at 0°C. A solution of 4-nitrobenzoyl chloride (0.12 g, 0.65 mmol) and triethylamine (0.06 ml, 0.95 mmol) in THF (2 ml) was added dropwise. The solution was stirred and allowed to attain ambient temperature. The mixture was then stirred at room temperature for 12 hours. Water (10 ml) and ether (10 ml) were then added. The organic layer was separated, and the aqueous layer extracted with ether (3x10 ml). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Flash column chromatography (eluting: 10% ethyl acetate: petrol) gave a white solid (20 mg, 43%) with a ^1H NMR spectrum consistent with the di(4-nitrobenzoyl) ester of the diol (342).

δ_H (300MHz) 8.35-8.10 (8H, m, **Ar**), 4.97 (1H, dd, J=6.9Hz, 5.4Hz, 5-C**H**), 4.34 (2H, t, J= 6.9 Hz, 1-C**H**$_2$), 2.15 (1H, m, 6-C**H**), 1.97 (1H, m, 4-C**H**), 1.40-1.10 (4H, m, 2-C**H**$_2$ and 3-C**H**$_2$), 1.00, 0.95 (6H, d, J=8.90Hz, 6-CH(C**H**$_3$)$_2$) -0.97 (3H, d, J=6.0Hz, 4-CH(C**H**$_3$)).

Oxidation of silacycle (269): Formation of 2,4-dimethyl-3-hydroxyhept-6-ene (344)

Stage 1



Silacycle (269) (0.05 g, 0.17 mmol) was dissolved in $CHCl_3$ (5 ml). $BF_3.2AcOH$ (0.07 g, 0.38 mmol) was then added. The mixture was refluxed for 18 hours. Saturated $NaHCO_3$ solution was then added (10 ml). The aqueous layer was extracted with $CHCl_3$ (3x15 ml). The organic layers were combined, dried over $MgSO_4$, filtered and concentrated to give the crude fluorosilane (349), (0.05 g, 92%). This was used without further purification in stage 2.

δ_F (188 MHz) –184.74; MS (EI^+) m/z 322 (M^+, 0.5%), 307 (M^+-CH_3, 1), 249 (M^+-$Si(CH_3)_3$, 37), 197 (22), 189 (15), 165 (59), 147 (18), 135 (93), 105 (32), 73 (100).

Stage 2

The fluorosilane from stage 1 was dissolved in MeOH/THF (1:1, 4ml). KF (0.02g, 0.28mmol) was added, followed by aqueous hydrogen peroxide (27% solution in water, 0.33ml, 2.63mmol). The mixture was heated to reflux, and stirred at this temperature for 18 hours. Saturated sodium thiosulfate solution was then added (2ml). The mixture was then extracted with ether (3x20ml). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Purification by flash column chromatography (eluting: 10% ethyl acetate: petrol) gave a product (0.03 g) whose ^{1}H NMR spectra was consistent with that for 2,4-dimethyl-3-hydroxyhept-6-ene (345) as reported in the literature.[129, 130]

δ_H (300MHz) 6.82 (1H, m, $CH_2{=}C\underline{\mathbf{H}}CH_2$-), 5.05 (2H, m, $C\underline{\mathbf{H}}_2{=}CHCH_2$-), 3.15 (1H, m, $CH(CH_3)C\underline{\mathbf{H}}(OH)CH(CH_3)_2$), 2.40(1H, m, $C\underline{\mathbf{H}}(CH_3)CH(OH)CH(CH_3)_2$, 2.00-1.70 (2H, m, $CH_2{=}CHC\underline{\mathbf{H}}_2CH(CH_3)$-), 1.70-1.60 (1H, m, $CH(OH)C\underline{\mathbf{H}}(CH_3)_3$, 1.30 (1H, b, $O\underline{\mathbf{H}}$), 1.00-0.85 (9H, m, 3x $C\underline{\mathbf{H}}_3$).

Appendix

Anomalous rearrangements in the reaction of acylpolysilanes with TMSNTf$_2$

Malcolm B. Berry,[b] Russell. J. Griffiths,[a] Dmitrii S. Yufit[a] and Patrick G. Steel*[a]†

[a] *Department of Chemistry, University of Durham, Science Laboratories, South Road, Durham, UK DH1 3LE*
[b] *GlaxoWellcome Research and Development, Gunnels Wood Road, Stevenage, Herts, UK SG1 2NY*

Reaction of acylpolysilanes with silylbistriflimides (R_3SiNTf_2) leads to novel silanols *via* a pathway involving two 1,2-migrations of Me_3Si groups from silicon to carbon and one migration of a R_3SiO unit from carbon to silicon; the X-ray structure of one example is reported.

In the course of an investigation of the use of silenes as reagents for novel transformations in organic synthesis we had need to generate silenes from acylpolysilanes in what is effectively a 1,3 silyl migration.[1] This is normally achieved through either thermal (T = *ca.* 180 °C) or photochemical initiation.[1,2] Neither of these methods is compatible with the range of functionality which we wished to explore. Consequently, in order to determine whether it was possible to generate silenes through the Lewis acid promoted 1,3-silyl shift of acylpolysilanes, we investigated the reaction of benzoylpolysilane with silyl based Lewis acids (TMSOTf, TMSNTf$_2$). Here we report that there is no evidence for the formation of silenes in this process (neither silene adducts nor silene dimers are detected) but rather a series of 1,2-migrations occurs to generate a silenium ion intermediate which subsequently undergoes nucleophilic capture.

Initial experiments involved the addition of trimethylsilyl triflate (TMSOTf) to a mixture of the polysilane and piperylene. However, these reactions were complicated by extensive diene polymerisation. Consequently we turned to the use of the corresponding silylbistriflimides (R_3SiNTf_2), readily available from the corresponding allylsilane and bis(trifluoromethylsulfonyl)imide, which has been reported to be more tolerant with respect to alkene polymerisation.[3] Whilst this strategy proved to be no more successful than TMSOTf in inhibiting diene degradation, addition of TMSNTf$_2$ to a solution of the polysilane in CH_2Cl_2 at −78 °C afforded a deep red colour. After stirring at this temperature for 12 h, aqueous workup followed by flash column chromatography afforded a colourless crystalline material in near quantitative yield. Infra-red spectroscopy revealed the presence of an OH group, whilst mass spectroscopy showed a molecular ion at *m/z* 442 which corresponded to the starting material plus Me_3SiOH. Chemical analysis confirmed this formula. However it proved difficult to fit this data with the NMR spectra which showed four $SiMe_3$ units and five different silicon signals. Fortunately it proved possible to grow crystals suitable for X-ray diffraction,‡ which revealed the structure as the silanol **2a** (Fig. 1).§

In order to verify that this was a general procedure we then repeated this experiment with various other acylpolysilanes (Table 1). Whilst 4-trifluoromethylbenzoylpolysilane **1b** and acetylpolysilane **1d** gave similar products, pivaloylpolysilane **1e** failed to react and the 4-methoxyphenyl analogue **2c** underwent rapid decomposition on attempted isolation. To account for these observations we suggest that the reaction follows the pathway outlined in Scheme 1. Initial activation of the carbonyl group by the Lewis acid generates the oxacarbenium ion **5** which is stabilised by three β-Me_3Si units and R^1. In the situation in which the neighbouring alkyl group provides no stabilisation there is no reaction (R = Bu^t). Two successive 1,2 migrations of a trimethylsilyl group from silicon to carbon accompanied by a 1,2 shift of a trimethylsilyloxy group from carbon to silicon then occur. Similar migrations of trimethylsilyl groups from silicon to an adjacent cationic centre are precedented.[4–7] The precise order of these events is not clear and these may be either concerted or stepwise pathways. Whilst a silyl cation may be invoked as an intermediate in this process we have obtained no evidence for this and Lewis base coordinated species **6** and **8** (X = NTf$_2^-$ or RCOSiR′$_3$) are probably more plausible. The resultant 'silenium ion' complex **8** is then hydrolysed by water on aqueous workup to produce the observed silanol. Use of MeOH in this final step leads to the

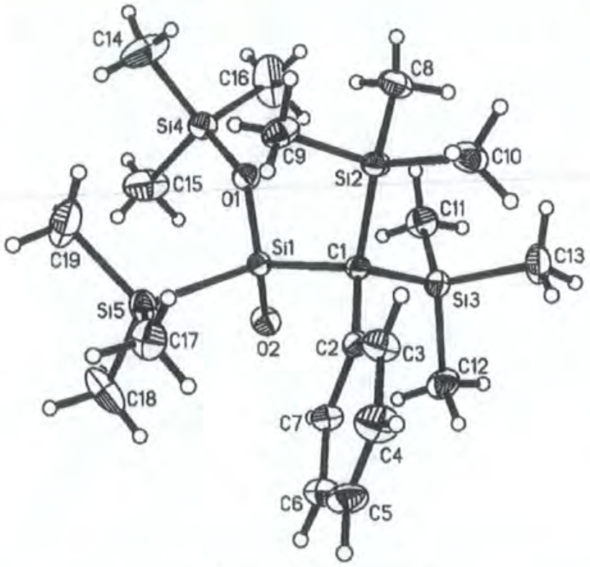
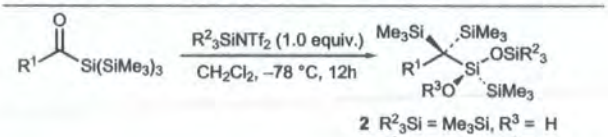


Fig. 1 Molecular structure of **2a**

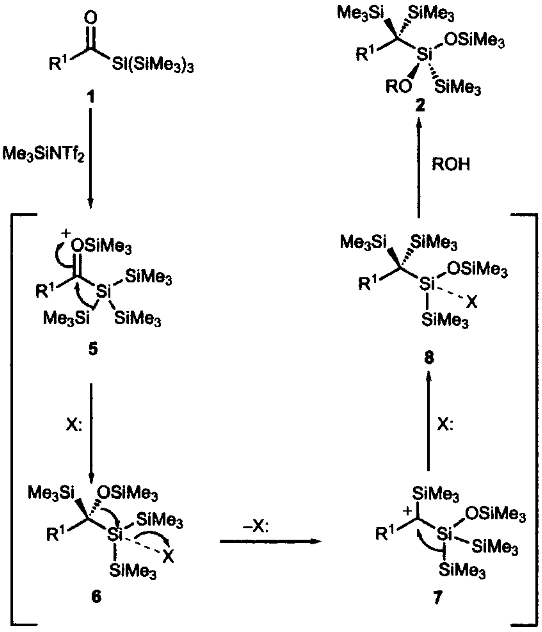
Table 1 Reaction of acylpolysilanes **1** with trialkylsilylbistriflimides



2 $R^2_3Si = Me_3Si, R^3 = H$
3 $R^2_3Si = Me_3Si, R^3 = Me$
4 $R^2_3Si = Bu^tMe_2Si, R^3 = H$

Entry	**1**	R^1	R$^2_3$Si	Product	Yield (%)[a,b]
1	**1a**	Ph	Me$_3$Si	**2a**	93
2	**1a**	Ph	Me$_3$Si[c]	**2a**	9
3	**1a**	Ph	Me$_3$Si	**3a**	89[d]
4	**1a**	Ph	Bu^{t}Me$_2$Si	**4a**	84
5	**1b**	*p*-CF$_3$C$_6$H$_4$	Me$_3$Si	**2b**	82
6	**1c**	*p*-MeOC$_6$H$_4$	Me$_3$Si	**2c**	—[e]
7	**1d**	Me	Me$_3$Si	**2d**	77
8	**1e**	Bu^t	Me$_3$Si	**2e**	n.r.

[a] Yields refer to purified isolated compounds. [b] All products gave satisfactory spectroscopic and analytical data. [c] 10 mol% of TMSNTf$_2$ was used. [d] MeOH was added as the quenching agent. [e] Product decomposed on attempted isolation.



Scheme 1 Mechanistic pathway for the reaction of acylpolysilanes **1** with trialkylsilylbistriflimides

corresponding methoxide analogue **3a** in equally good yield (Table 1, entry 3). Further evidence in support of this pathway come from the use of TBMSOTf as the Lewis acid. As predicted this leads to complete incorporation of the TBDMS group at the silyloxy position (Table 1, entry 4) as confimed by ^{29}Si NMR spectroscopy (**4a**: OSiBu^{t}Me$_2$ δ 9.48; **2a**: OSiMe$_3$ δ 5.44). Furthermore, use of substoichiometric quantities of the initiator produces the same product in a corresponding yield together with recovered starting material (Table 1, entry 2).

Similar structures have been reported by Brook in the reaction of tertiary alkyl acylpolysilanes (R = Bu^t, adamantyl and bicyclo[2.2.2]octyl) with TiCl$_4$.[4] This was accounted for by a similar mechanistic pathway although, in this latter case, a 1,3 methyl shift from one of the trimethylsilyl groups to the 'silenium ion' also occurs. The reason for this difference between the TiCl$_4$ and the bistriflimide promoted pathways is not obvious at the present time.

In conclusion we report a novel rearrangement of acylpolysilanes on reaction with silyl triflates. Attempts to tune this reactivity to generate silenes in a convenient fashion are in progress and will be reported in due course.

We thank GlaxoWellcome and the EPSRC for financial support of this work (studentship to R. J. G. and funding for D. S. Y., repectively), the EPSRC mass spectrometry service at Swansea for accurate mass determinations, Dr A. M. Kenwright and Mr I. H. McKeag for assistance with NMR experiments and Dr M. Jones for mass spectra. The referees are thanked for helpful comments regarding the mechanism of this transformation.

Notes and References

† E-mail: p.g.steel@durham.ac.uk

‡ *Crystal data* for **2a**: $C_{19}H_{42}O_2Si_5$, M = 442.98, monoclinic, space group $P2_1/n$, a = 15.3270(1), b = 10.6851(1), c = 16.8596(1) Å, β = 105.50(1)°, U = 2659.5(9) Å^3, $F(000)$ = 968, Z = 4, D_c = 1.106 mg m^{-3}, μ = 0.28 mm^{-1} (Mo-Kα, λ = 0.71073 Å), T = 120(1) K, 33156 reflections ($1.60 \leqslant \theta \leqslant 30.5°$) were collected on a Siemens SMART-CCD diffractometer (ω-scan, 0.3° per frame) yielding 7534 unique data (R_{merg} = 0.047). The structure was solved by direct-methods and refined by full-matrix least-squares on F^2 for all data using SHELXL software. All non-hydrogen atoms were refined with anisotropic displacement parameters, H-atoms were located on the difference map and refined isotropically. The H-atom of the OH group could not be located reliably and was not included in the refinement. Final $wR_2(F^2)$ = 0.1095 for all data (399 refined parameters), conventional $R(F)$ = 0.0411 for 5539 reflections with $I \geqslant 2\sigma$, GOF = 1.119. The largest peak on the residual map (0.62 e Å^{-3}) is located on the middle of one of the Si–Si bonds. CCDC 182/1000.

§ Attempts to achieve this transformation using TMSOTf afford a viscous oil which has similar spectroscopic properties to **2a** but whose structure is currently undefined. Details will be given in a full paper.

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Reactions of acylpolysilanes with silyl Lewis acids

Malcolm B. Berry,[b] Russell J. Griffiths,[a] Judith A. K. Howard,[a] Michael A. Leech,[a]
Patrick G. Steel *[a] and Dmitrii S. Yufit[a]

[a] *Department of Chemistry, University of Durham, Science Laboratories, South Road, Durham, UK DH1 3LE. E-mail: p.g.steel@durham.ac.uk*
[b] *Glaxo Wellcome Research and Development, Gunnels Wood Road, Stevenage, Herts, UK SG1 2NY*

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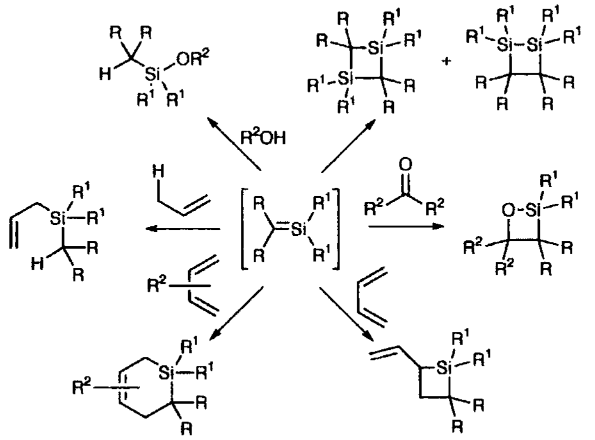
The reaction of acylpolysilanes with TMSOT and TMS(NTf$_2$) proceed *via* a series of 1,2 silyl and silyoxy shifts to afford the silanol products **5** and **6** respectively. A unified mechanistic pathway involving the formation of transient silenium ion complexes and silenes which rationalises these products is proposed. The structural assignment of the products is supported by X-ray structures for the phenyl **6a** and trifluoromethylphenyl **6b** substituted silanols.

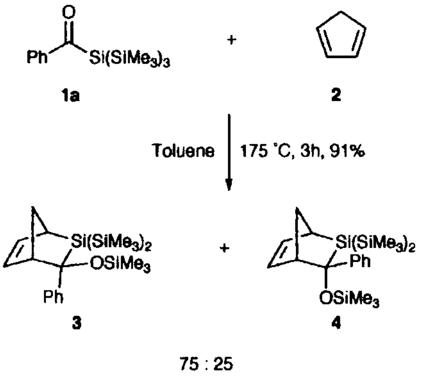
Introduction

Silenes, compounds containing a silicon–carbon double bond have been the object of some interest since their first recorded preparation in 1967.[1,2] Owing to their high reactivity, and in most cases transient existence, much of this effort has been focused on structural and bonding aspects with a particular emphasis on the preparation of stable isolable silenes.[3,4] In many cases evidence for the formation of silenes is obtained from the isolation of adducts from reactions with compounds of different functionalities including alcohols, alkenes and carbonyl compounds (Scheme 1).[5] However, despite this broad repertoire of chemistry there has been little effort to exploit the unique reactivity of these species in organic synthesis. With this objective in mind we have initiated a programme to explore this aspect of silene chemistry.



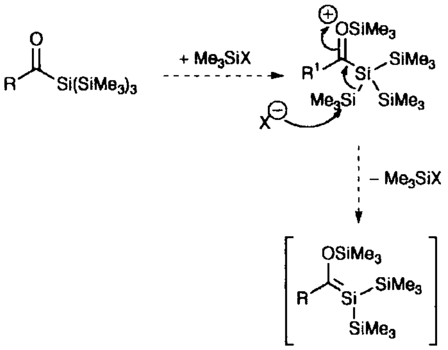
Scheme 1 Typical reactions of silenes.

In the first instance we elected to examine the diastereoselectivity of the Diels–Alder reaction of the relatively stable alkoxysilenes with a range of dienes. Brook has demonstrated that these silenes can be readily generated by either a thermal or photochemical mediated 1,3 silyl rearrangement of acylpolysilanes.[6] Using the former method it proved possible to generate the desired cycloadducts in good yields and with moderate diastereoselectivity (Scheme 2).[7]



Scheme 2 Thermal reaction of acylpolysilanes with dienes.

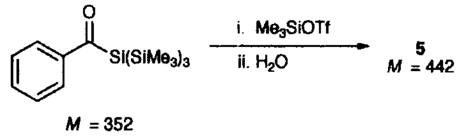
However, the high temperatures needed (~180–200 °C) limit the variation of functionality in both reaction partners, require the use of specialised apparatus (Carius tube facility) and, potentially, account for the less than ideal diastereoselectivity. Similar problems of scale, apparatus and limitation of compatibility of ancillary functionality affect the photochemical generation of these alkoxysilenes. Consequently, we sought alternative methods for silene generation and postulated that the treatment of the acylpolysilane with a silyl Lewis acid would lead, in a low temperature process, to a transient siloxysilene which could be trapped *in situ* by an appropriate diene (Scheme 3). In this paper we report the full details of our studies of the reactions of acylpolysilanes and silyl Lewis acids and the transformations of the resultant products.[8]



Scheme 3 Proposed reaction of acylpolysilanes with TMSOTf.

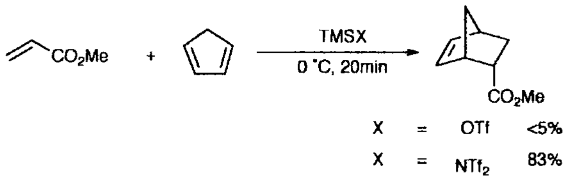
Results and discussion

In view of our goal of generating siloxysilene cycloadducts from the reaction of acylpolysilane and silyl Lewis acid in the presence of a diene we required ready access to acylpolysilanes. These are readily accessible through the reaction of the corresponding acid chloride with tris(trimethylsilyl)silyllithium following established literature protocols. Treatment of a mixture of benzoylpolysilane **1a** and piperylene (penta-1,3-diene) with, either a stoichiometric or catalytic amount of, trimethylsilyl triflate (Me_3SiOTf, TMSOTf) afforded a complex mixture of products dominated by polymerised diene. In order to ascertain that silene formation had occurred we then carried out the reaction in the absence of the diene with a view to isolating the corresponding silene dimer. Under these conditions, whilst no evidence for silene dimers could be detected, a single new component **5** was obtained of molecular mass 442 and containing five discrete silicon atoms (^{29}Si NMR). However, a structure could not be unequivocally assigned at this stage, *vide infra* (Scheme 4).



Scheme 4 Reaction of benzoylpolysilane with TMSOTf.

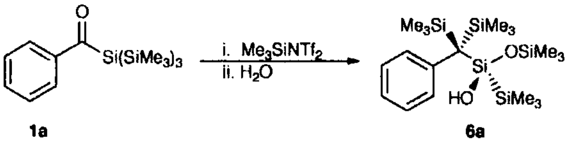
At this point in time, we became aware of a report by Mathieu and Ghosez *et al.* which advocated the use of trimethylsilylbis(triflimide) ($TMSNTf_2$, $Me_3SiN(CF_3SO_2)_2$) as an extremely powerful Lewis acid which does not cause the problems of alkene polymerisation frequently observed with TMSOTf (Scheme 5).[9] This reagent is readily prepared through



Scheme 5 Comparison of TMSOTf and $TMSNTf_2$.

the reaction of allyltrimethylsilane with bis(trifluoromethylsulfonyl)imide followed by vacuum distillation.

However, application of this reagent with benzoylpolysilane in the presence of piperylene proved to be no more successful with respect to diene degradation. In the absence of a diene the addition of a stoichiometric quantity of bistriflimide to a solution of benzoylpolysilane **1** in dichloromethane at −78 °C afforded a deep red solution which on aqueous work up and purification by flash chromatography afforded a single colourless crystalline product in near quantitative yield (Scheme 6).



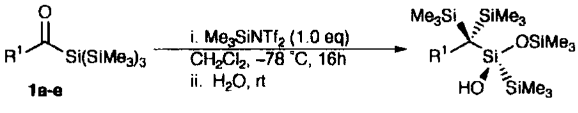
1a **6a**

Scheme 6 Reaction of benzoylpolysilane with $TMSNTf_2$.

This material was isomeric with that obtained from the reaction with TMSOTf with mass spectrometry indicating a molecular ion at 442 corresponding to the starting material plus Me_3SiOH. Elemental analysis confirmed this formula whilst infra-red spectroscopy revealed the presence of an OH group. However, it proved difficult to reconcile this data with the NMR spectra which showed four $SiMe_3$ units and five different silicon signals. Fortunately it proved possible to grow crystals suitable for X-ray diffraction which revealed the structure as the silanol **6a** (Fig. 1a).

Repeating the reaction with other acylpolysilanes demonstrated that this is a general pathway (Table 1). With the exception of the pivaloyl derivative all polysilanes react to give the

Table 1 Reaction of acylpolysilanes with trimethylsilylbistriflimides



1a-e **6 a-e**

Entry	1	R¹	Product	Yield (%)[a]
1	**1a**	Ph	**6a**	93
2	**1a**	Ph	**6a**	9[b]
5	**1b**	*p*-CF_3-C_6H_4	**6b**	82
6	**1c**	*p*-MeO-C_6H_4	**6c**	[c]
7	**1d**	Me	**6d**	77
8	**1e**	ᵗBu	**6e**	n.r.

[a] Yields refer to purified isolated compounds. [b] 10 mol% of $TMSNTf_2$ was used. [c] Product decomposed on attempted isolation.

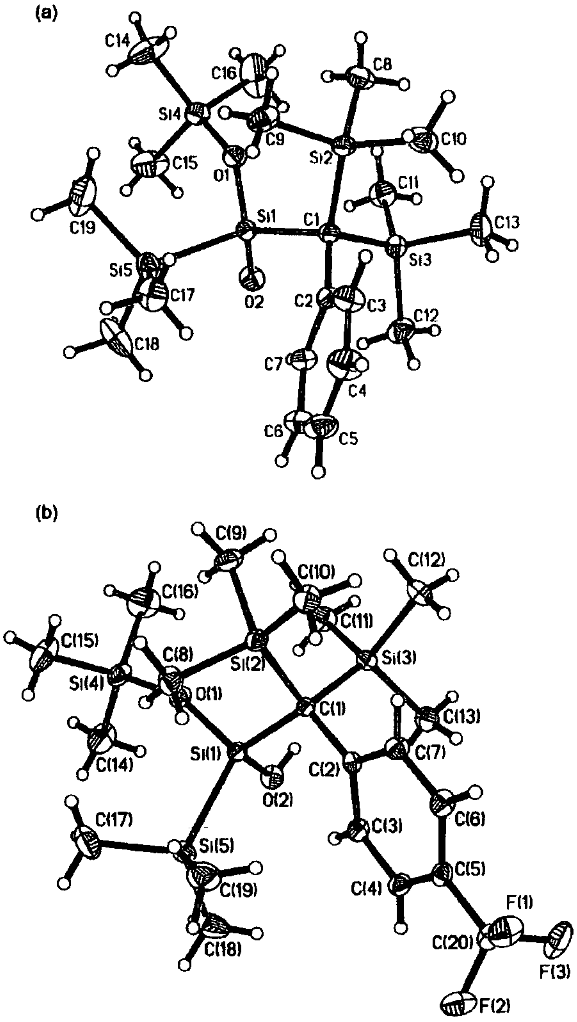


Fig. 1 Crystal structure of (a) silanol **6a** and (b) silanol **6b**.

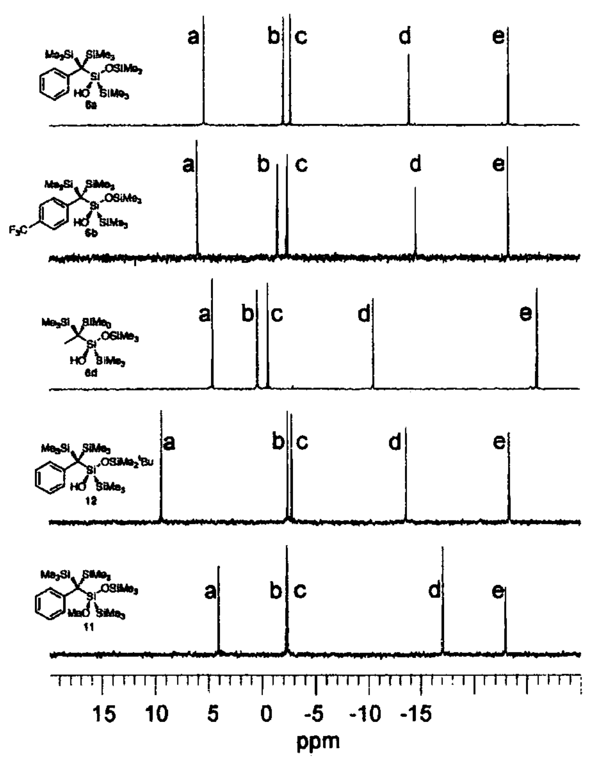
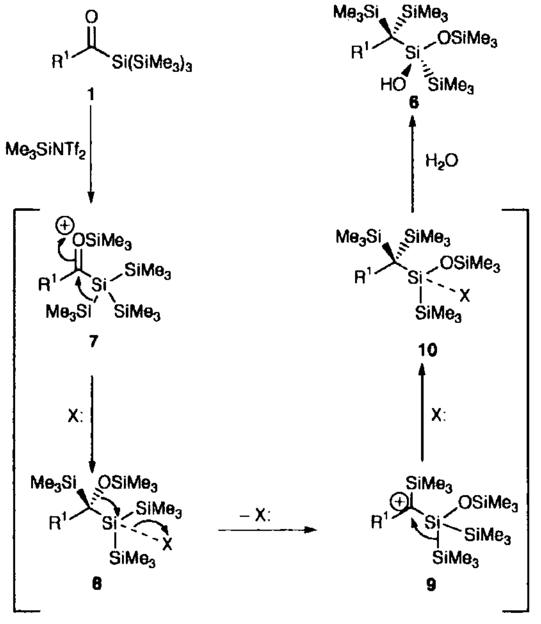


Fig. 2 ^{29}Si NMR spectra of TMSNTf$_2$ rearrangement products. a, O*Si*R$_3$; b, Me$_3$*Si*CSiMe$_3$; c, Me$_3$SiC*Si*Me$_3$; d, O-*Si*-O; e, Si-*Si*Me$_3$.

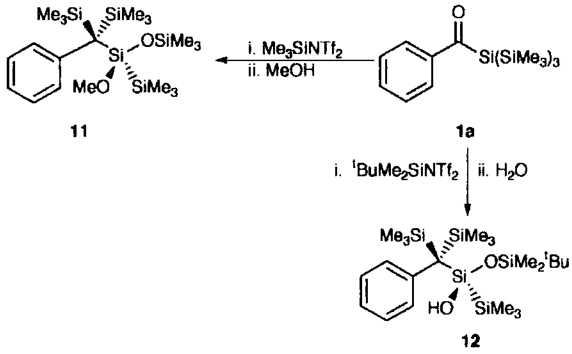
analogous product in good to excellent yields although the 4-methoxyphenyl derivative underwent decomposition upon attempted isolation. In all cases these compounds could be characterised by a range of analytical techniques including ^{29}Si NMR which showed five distinctive signals (Fig. 2). Confirmation that these related to the same series was obtained by a second crystal structure using the 4-trifluoromethylphenyl derivative **6b** (Fig. 1b).

To account for these observations we suggest that the reaction follows the pathway outlined in Scheme 7. Initial activation of the carbonyl group by the Lewis acid generates the oxacarbenium ion **7** which is stabilised by three β-Me$_3$Si units and the alkyl or aryl substituent, R^1. In the situation in which the acylpolysilane substituent provides little stabilisation for a neighbouring cationic centre there is no reaction (*e.g.* R = ^{t}Bu). A 1,2 migration of a trimethylsilyl group from silicon to carbon then occurs, followed by a 1,2 shift of a trimethylsilyloxy group from carbon to silicon and a second silicon to carbon trimethylsilyl group migration. Related migrations of trimethylsilyl groups from silicon to an adjacent cationic centre are precedented.[10–13] The precise order of these events is not clear and these may be either concerted or stepwise pathways. Whilst a silyl cation may be invoked as an intermediate in this process we have obtained no evidence for this and Lewis base co-ordinated species **8** and **10** (X = NTf$_2^-$ or RCOSiR'$_3$) are equally plausible. The resultant "silenium ion" complex **10** is then hydrolysed by water on aqueous workup to produce the observed silanol.



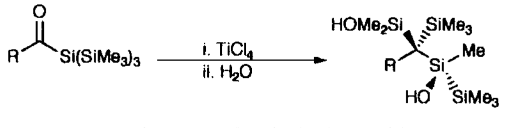
Scheme 7 Mechanistic pathway for the reaction of acylpolysilanes **1** with trialkylsilylbistriflimides.

To corroborate this pathway we then explored several variations including the use of substoichiometric quantities of bistriflimide and activating the reaction using *tert*-butyldimethylsilylbistriflimide (TBDMSNTf$_2$) (Scheme 8), prepared in an analogous fashion from *tert*-butyldimethylallylsilane and bis(trifluoromethylsulfonyl)imide. These reactions provided definitive evidence for the direct involvement of the silylbistriflimide in the reaction with the yield and degree of conversion being comparable to the stoichiometry (Table 1, run 2) and the incorporation of the TBDMS group into the product at the siloxy position as confirmed by ^{29}Si NMR spectroscopy (**12** OSi^{t}BuMe$_2$ δ = 9.48, **6a** OSiMe$_3$ δ = 5.44, Fig. 2). Finally, use of methanol to quench the reaction generated the corresponding methyl ether **11** consistent with the formation of a silenium ion complex as the final intermediate on the pathway.



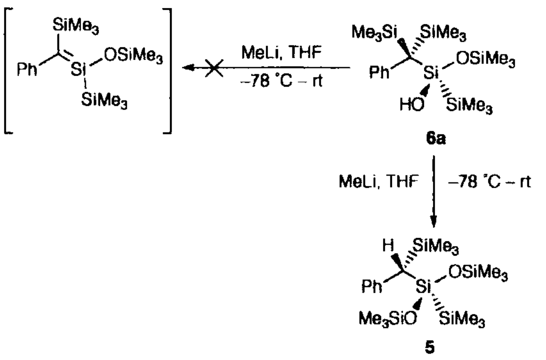
Scheme 8

Related structures have been reported by Brook *et al.* in the reaction of tertiary alkyl acylpolysilanes (R = ^{t}Bu, adamantyl and 2,2,2-bicyclooctyl) with titanium tetrachloride (Scheme 9).[12] This was accounted for by a similar mechanistic pathway although, in this latter case, a 1,3 methyl shift from one of the trimethylsilyl groups to the "silenium ion" also occurs. Reasons for this difference between the titanium tetrachloride and the bistriflimide promoted pathways are not obvious at the present time.



Scheme 9 Reaction of acylpolysilanes with TiCl$_4$.

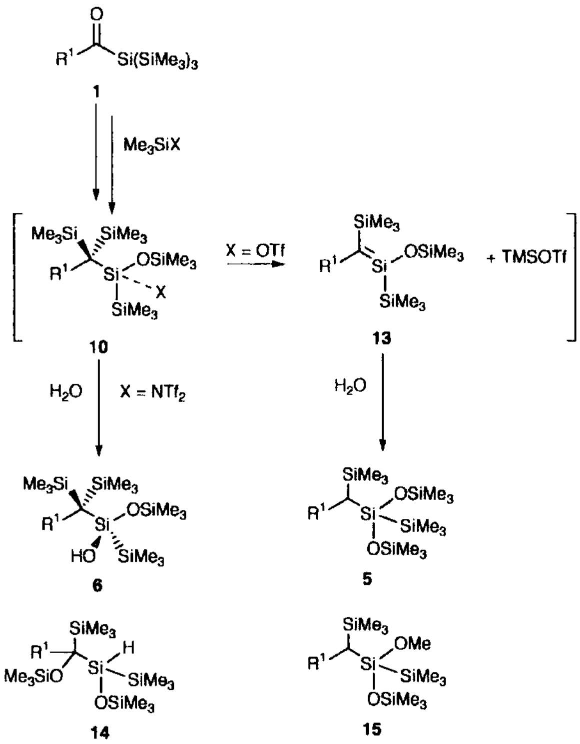
Although this rearrangement did not afford the desired silene dimer it occurred to us that the presence of α,β-hydroxysilane within this product might allow these silanols to function as convenient silene precursors through a Peterson type elimination. This method of silene generation has been exploited by Oehme and co-workers in the generation of transient alkyl substituted silenes.[14] Consequently, treatment of the silanols with MeLi was undertaken. In no case could any evidence for silene dimers or cycloadducts be observed. However, reaction of silanol **6a** with MeLi afforded the identical material to that obtained from the reaction of benzoylpolysilane with TMSOTf (Scheme 10). Subsequent NMR studies, using 2D H-C correlation experiments, allowed the assignment of structure as that shown in Scheme 10. Similar anionic Brook-type migrations of silyl groups to proximal oxy-anions have been observed in related systems using a number of different bases (MeLi, KH, NaH).[10] Attempts to achieve the Peterson elimination under acidic conditions (HF, HBF_4, H_2SO_4) failed, all variations merely returning unchanged silanol.



Scheme 10 Reaction of silanol **6a** with MeLi.

To account for these observations we suggest that the reaction of acylpolysilanes with silyl Lewis acids is initiated by activation of the carbonyl group followed by the 1,2 migrations as described above to afford silenium ion complex **10**. The more nucleophilic triflate anion then displaces a neighbouring trimethylsilyl group to generate a transient silene **13** which on addition of water undergoes nucleophilic attack by trimethylsilanol generated by hydrolysis of the residual TMSOTf. The less nucleophilic bistriflimide anion is not sufficiently active to promote the elimination to the silene and the hydrolysis product, silanol **6**, of intermediate complex **10** is isolated upon addition of water. Further evidence for this hypothesis is obtained through variation of the time and temperature of the TMSOTf mediated reaction. If the reaction mixture is maintained at −78 °C and quenched after a shorter period of time then both silanol **6** and bis(silyloxy)acetal **5** can be isolated. Larger scale versions of this reaction allow the isolation of small amounts (5–≤20% by NMR using ^{29}Si–^{1}H satellites) of the alternative regioisomer **14** by nucleophilic addition of trimethylsilanol to the silene **13**. Finally, quenching the reaction mixture with methanol leads to the corresponding methyl silyl ether **15** (Scheme 11).

In conclusion, a rearrangement involving a series of 1,2 shifts of silyl and silyloxy groups occur on treatment of acylpolysilanes with silyl Lewis acids. Silene intermediates can be invoked when the silyl counter ion is sufficiently nucleophilic (X = OTf) although all attempts to trap these species have, to date, proved unsuccessful. Current work is focused on circumventing these difficulties and exploring alternative mild methods of silene generation. These will be reported in due course.



Scheme 11 Overall mechanistic pathway for the reaction of acylpolysilanes with silyl Lewis acids.

Experimental

All reactions were undertaken in an inert gas atmosphere of dry nitrogen or argon in pre-dried glassware. Nuclear magnetic resonance (NMR) spectra were obtained on Varian Inova 500 (^{29}Si at 99.325 MHz), VXR-400 (^{1}H at 399.952 MHz, ^{13}C at 100.577 MHz), Unity-300 (^{1}H at 299.910 MHz, ^{13}C at 75.420 MHz) and Mercury-200 (^{1}H at 199.993 MHz, ^{13}C at 50.293 MHz) spectrometers with $CDCl_3$ as solvent ($\delta = 7.26$) and are recorded in ppm (δ units) downfield of tetramethylsilane ($\delta = 0$) with coupling constants quoted in Hertz (Hz). Infra-red (IR) spectra were recorded on a Perkin Elmer FT-IR 1720X spectrometer. Low-resolution mass spectra were recorded on VG Analytical 7070E and VG Autospec organic mass spectrometers, and gas chromatography–mass spectra (GC-MS) were recorded using a Hewlett Packard 5890 Series II gas chromatograph connected to a VG mass Lab trio 1000. Flash column chromatography was performed on silica (60–240 mesh). Melting points were determined using Gallenkamp melting point apparatus and are uncorrected. All solvents were distilled prior to use following standard protocols.[15] Petroleum ethers refer to the fraction boiling in the 40–60 °C range unless otherwise stated. Acylpolysilanes were prepared from the corresponding acid chloride following literature procedures.[6]

General procedure for reaction of acylpolysilanes with silylbistriflimides

A solution of acylpolysilane in dichloromethane (~0.3 M) was cooled to −78 °C. Silylbistriflimide (1 eq.) was then added. The solution became dark red in colour and was stirred at −78 °C for approximately 16 hours when saturated $NaHCO_3$ solution was added. The organic layer was separated, and the aqueous layer extracted with diethyl ether. The combined organic layers were then dried over $MgSO_4$, filtered, and concentrated to give the crude product which was purified as described below.

1-Hydroxy-1-[phenylbis(trimethylsilyl)methyl]-2,2,2-trimethyl-1-trimethylsilyloxydisilane 6a. A solution of benzoyltris(trimethylsilyl)silane (1.11 g, 3.30 mmol) was treated with trimethylsilylbistriflimide (1.12 g, 3.29 mmol) as described above to give an off-white solid. Recrystallisation from ethanol gave pure **6a** as colourless crystals (1.35 g, 93%); mp 92–93 °C

(Found: C, 50.27; H, 9.61. $C_{19}H_{42}O_2Si_5$ requires C, 51.52; H, 9.56%); ν_{max} (KBr disc)/cm^{-1} 3629, 3552 (br, -OH), 3055, 1945, 1686, 1593, 1497, 1439, 1403, 1264, 1150; δ_H (300 MHz) 7.52–7.01 (5H, m, Ar-H), 2.20 (1H, s, -O*H*), 0.23, 0.22, 0.21 (each 9H, s, 2 × $\text{C-Si(C}H_3)_3$, 1 × $\text{O-Si(C}H_3)_3$), −0.15 (9H, s, $\text{Si-Si(CH}_3)_3$); δ_C (75 MHz) 141.5, 131.7, 127.9, 123.8, 28.8, 3.87, 3.86, 2.8, −0.5; δ_{Si} 5.4, −2.0, −2.7, −13.9, −23.3; *m/z* (EI^+) 442 (14%, M^+), 427 (22, $M^+ - CH_3$), 411 (17), 369 (81, $M^+ - SiMe_3$), 353 (46, $M^+ - OSiMe_3$), 337 (44), 279 (48), 264 (40), 207 (33), 147 (47), 135 (31), 73 (100).

Crystal data for **6a** was reported in the preliminary communication.[8]

1-Hydroxy-1-[(4′-trifluoromethylphenyl)bis(trimethylsilyl)methyl]-2,2,2-trimethyl-1-trimethylsilyloxydisilane 6b

A solution of (4-trifluoromethylbenzoyl)tris(trimethylsilyl)silane (0.89 g, 2.12 mmol) was treated with trimethylsilylbistriflimide (0.76 g, 2.15 mmol) as described above to give an off-white solid. Recrystallisation from ethanol gave pure **6b** as colourless crystals (0.90 g, 82%); mp 68–69 °C (Found: C, 46.82; H, 8.38. $C_{20}H_{41}F_3O_2Si_5$ requires C, 47.01; H, 8.09%); ν_{max} (KBr disc)/cm^{-1} 3550 (br, OH), 3048, 2933, 2854, 1855, 1550, 1476, 1401, 1245, 1130; δ_H (250 MHz) 7.64–7.43 (4H, m, aromatic), 2.20 (1H, br s, -O*H*), 0.25, 0.22, 0.20 (each 9H, s, 2 × $\text{C-Si(C}H_3)_3$, 1 × $\text{O-Si(C}H_3)_3$), −0.14 (9H, s, $\text{Si-Si(CH}_3)_3$); δ_C (100 MHz) 146.7, 131.7, 125.8 (q, -*C*F_3), 29.8, 3.8, 3.6, 2.8, −0.5; δ_F (235 MHz) −62.6; δ_{Si} 6.1, −1.4, −2.3, −14.5, −23.2; *m/z* (EI^+) 510 (M^+, 3.4%), 495 ($M^+ - CH_3$, 2), 437 ($M^+ - SiMe_3$, 3), 420 ($M^+ - OSiMe_3$, 6), 147 (13), 73 (100), 71 (55).

Crystal data for **6b**:† $C_{20}H_{41}F_3O_2Si_5$, $M = 510.98$, triclinic, space group $P\bar{1}$, $a = 10.237(2)$, $b = 10.977(2)$, $c = 13.598(3)$ Å, $\alpha = 100.67(3)$, $\beta = 109.10(1)$, $\gamma = 90.40(3)°$, $U = 1415.2(5)$ Å^3, $F(000) = 548$, $Z = 2$, $D_c = 1.199$ mg m^{-3}, $\mu = 0.286$ mm^{-1} (Mo-Kα, $\lambda = 0.71073$ Å), $T = 120(1)$ K. 15765 reflections ($1.62 = \theta = 27.48°$) were collected on a Bruker SMART-CCD diffractometer (ω-scan, 0.3°/frame) yielding 6471 unique data ($R_{merg} = 0.023$). The structure was solved by direct methods and refined by full-matrix least squares on F^2 for all data using SHELXL software. All non-hydrogen atoms were refined with anisotropic displacement parameters, H-atoms were placed geometrically and refined with a riding model. Final $wR_2(F^2) = 0.0903$ and $R(F) = 0.0378$ for all data (284 refined parameters), GOF = 1.042, residuals min = −0.50 e Å^{-3} and max = 0.61 e Å^{-3}.

1-[1′,1′-Bis(trimethylsilyl)ethyl]-1-hydroxy-2,2,2-trimethyl-1-trimethylsilyloxydisilane 6d

A solution of acetyltris(trimethylsilyl)silane (0.73 g, 2.50 mmol) was treated with trimethylsilylbistriflimide (0.88 g, 2.50 mmol) as described above to give a crude oil. Purification by flash column chromatography (eluent: 5% ethyl acetate–petroleum ether) afforded the title disilane **6d** as a colourless oil (0.73 g, 77%) (Found: $(M + NH_4)^+$, 398.2218. $C_{14}H_{44}O_2NSi_5$ requires *M*, 398.2218); ν_{max} (LF)/cm^{-1} 3686, 3500 (broad, OH), 2950, 2904, 2864, 1461, 1406, 1254, 1044; δ_H (300 MHz) 1.95–1.80 (1H, br, -O*H*), 1.10 (3H, s, C*H_3*), 0.16 (18H, s), 0.10 (9H, s) (2 × $\text{C-Si(C}H_3)_3$, 1 × $\text{O-Si(C}H_3)_3$), −0.08 (9H, s, $\text{Si-Si(CH}_3)_3$); δ_C (50 MHz) 12.5, 6.3, 2.6, 0.9, 0.7, 0.1; δ_{Si} 4.7, 0.4, −0.5, −10.4, −25.9; *m/z* (EI^+) 365 ($M^+ - CH_3$, 3%), 349 (6), 307 ($M^+ - SiMe_3$, 17), 217 (35), 147 (14), 73 (100%).

1-Methoxy-1-[phenylbis(trimethylsilyl)methyl]-2,2,2-trimethyl-1-trimethylsilyloxydisilane 11

A solution of benzoyltris(trimethylsilyl)silane (0.85 g, 2.43 mmol) was treated with trimethylsilylbistriflimide (0.86 g, 2.43 mmol) as described above except that the reaction was quenched by the addition of methanol followed by water. The resultant crude oil was purified by flash column chromatography (eluent: petroleum ether) to afford the title ether **11** as a white solid (0.99 g, 89%); mp 207–208 °C (Found: C, 51.43; H, 10.14. $C_{20}H_{44}O_2Si_5$ requires C, 51.56; H, 9.70%); ν_{max} (KBr disc)/cm^{-1} 2955, 2899, 2834, 1594, 1497, 1446, 1410, 1255, 1101; δ_H (200 MHz) 7.56–7.02 (5H, m, aromatic), 3.64 (3H, s, -OC*H_3*), 0.34, 0.29, 0.26 (each 9H, s, 2 × $\text{C-Si(C}H_3)_3$, 1 × $\text{O-Si(C}H_3)_3$), −0.10 (9H, s, $\text{Si-Si(CH}_3)_3$); δ_C (50 MHz) 141.8, 131.9, 127.8, 123.7, 50.5, 29.0, 4.1, 3.7, 2.9, 0.4; δ_{Si} 4.1, −2.26, −2.34, −17.0, −22.9; *m/z* (EI^+) 457 (M^+, 4%), 441 ($M^+ - CH_3$, 8), 383 ($M^+ - SiMe_3$, 32), 147 (30), 73 (100).

1-Hydroxy-1-[phenylbis(trimethylsilyl)methyl]-2,2,2-trimethyl-1-(*tert*-butyldimethylsilyloxy)disilane 12

A solution of benzoyltris(trimethylsilyl)silane (1.03 g, 2.94 mmol) was treated with (*tert*-butyldimethylsilyl)bistriflimide (1.25 g, 3.16 mmol) as described above to give a crude oil. Purification by flash column chromatography (eluent: 5% ethyl acetate–petroleum ether) yielded the title disilane **12** as a clear oil (1.20 g, 84%) (Found: M^+, 484.2465. $C_{22}H_{48}O_2Si_5$ requires *M*, 484.2501); ν_{max} (LF)/cm^{-1} 3674 (s, -OH), 3054, 2955, 2897, 2858, 1593, 1497, 1472, 1361, 1253, 1151; δ_H (300 MHz) 7.55–7.10 (5H, m, aromatic), 2.30 (1H, br s, -O*H*), 0.96 (9H, s, $\text{-C(C}H_3)_3$), 0.23, 0.22 (9H each, 2 × $\text{C-Si(C}H_3)_3$), 0.18, 0.16 (3H, each, $\text{-Si(C}H_3)_2{}^t\text{Bu}$, diastereotopic), −0.15 (9H, s, $\text{Si-Si(C}H_3)_3$); δ_C (50 MHz) 141.7, 131.9, 127.9, 123.9, 29.4, 26.5, 18.8, 4.1, 0.0, −1.3, −1.5; δ_{Si} 9.5, −2.4, −2.7, −13.5, −23.3; *m/z* (EI^+) 484 (M^+, 1%), 469 ($M^+ - CH_3$, 2.5), 424 ($M^+ - {}^t\text{Bu}$, 1.5), 411 ($M^+ - SiMe_3$, 25), 147 (29), 73 (100%).

1-[Phenyl(trimethylsilyl)methyl]-2,2,2-trimethyl-1,1-bis(trimethylsilyloxy)disilane 5

A solution of 1-hydroxy-1-[phenylbis(trimethylsilyl)methyl]-2,2,2-trimethyl-1-trimethylsilyloxydisilane **6a** (0.10 g, 0.23 mmol) in diethyl ether (5 ml) was cooled to −78 °C. Methyllithium (1.6 M solution in diethyl ether, 0.15 ml, 0.23 mmol) was then added. The solution was allowed to warm to 0 °C over 5 h and then stirred for a further 12 h at this temperature. Saturated NH_4Cl solution was then added, the layers were separated and the aqueous layer extracted with diethyl ether (3 × 20 ml). The combined organic layers were dried over $MgSO_4$, filtered and concentrated to give the crude product. Flash column chromatography (eluent: petrol) gave the product as a white solid (0.075 g, 74%); mp 117–119 °C (Found: C, 51.28; H, 9.66. $C_{19}H_{42}O_2Si_5$ requires C, 51.49; H, 9.56%); ν_{max} (KBr disc)/cm^{-1} 2957, 2899, 1598, 1494, 1254, 1201, 1074, 1041; δ_H (500 MHz) 7.17–7.00 (5H, m, aromatic), 1.58 (1H, s, $\text{Ph(Me}_3\text{Si)C}H$), 0.15, 0.12 (2 × 9H, s, 2 × $\text{OSi(C}H_3)_3$ diastereotopic), 0.01 (9H, s, $\text{CHSi(Si(C}H_3)_3)$), −0.19 (9H, s, $\text{Si-Si(C}H_3)_3$); δ_C (100 MHz) 140.7, 129.7, 128.0, 123.5, 33.8, 2.5, 2.3, −0.1, −1.4; δ_{Si} 0.2, −0.8, −5.8, −31.7, −32.7; *m/z* (EI^+) 442 (M^+, 0.5%), 427 ($M^+ - CH_3$, 3%), 369 ($M^+ - SiMe_3$, 7%), 279 (40), 265 (12), 191 (29), 147 (19), 73 (100).

Reaction of benzoylpolysilane 1a with trimethylsilyl trifluoromethylsulfonate: 1-[phenyl(trimethylsilyl)methyl]-2,2,2-trimethyl-1,1-bis(trimethylsilyloxy)disilane 5 and 1-[phenyl(trimethylsilyl)(trimethylsilyloxy)methyl]-2,2,2-trimethyl-1-trimethylsilyloxydisilane 14

A solution of benzoyltris(trimethylsilyl)silane **1a** (1.24 g, 3.52 mmol) in dichloromethane (10 ml) was cooled to −20 °C. Trimethylsilyl trifluoromethanesulfonate (3.52 mmol) was then added. The solution was then stirred for approximately 14 h when saturated $NaHCO_3$ solution was added. The organic layer was separated, and the aqueous layer extracted with diethyl ether (3 × 20 ml). The combined organic layers were dried over $MgSO_4$, filtered and concentrated to give the crude product as an orange oil. Purification by flash column chromatography

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† CCDC reference number 207/379. See http://www.rsc.org/suppdata/p1/1999/3645 for crystallographic files in .cif format.

(eluent: petrol) gave the title products (colourless semisolid) as an inseparable mixture (1.25 g, 2.82 mmol, 80%). Both GC and ^{1}H NMR analyses indicated a ratio of **5**:**14** of 81:19. ν_{max} ($CHCl_3$)/cm^{-1} 3060, 2957, 2897, 1596, 1494, 1449, 1405, 1252, 1200; δ_H (500 MHz) 7.40–6.96 (5H, m, aromatic, both isomers), 5.26 (1H, s, Si*H*, minor), 1.59 (1H, s, Ph(Me_3Si)C*H*, major), 0.16 (9H, s, OSi(CH_3)$_3$, major and 2 × 9H, s, OSi(CH_3)$_3$, minor), 0.13 (9H, s, OSi(CH_3)$_3$, major), 0.09 (2 × 9H, s, PhC(OSiMe$_3$)Si(CH_3)$_3$ and Si(SiCH_3)$_3$, both minor), 0.01 (9H, s, PhCHSi(CH_3)$_3$, major), −0.18 (9H, s, Si-Si(CH_3)$_3$); δ_C (125 MHz) 141.9, 140.7, 130.9, 129.7, 128.0, 127.6, 123.5, 33.8, 2.5, 2.3, 2.3, 2.0, 1.7, −0.0, −1.4; *m*/*z* (EI$^+$) major: 442 (M$^+$, 1%), 369 (M$^+$ − SiMe$_3$, 10%), 279 (51), 265 (19), 191 (40), 147 (34), 73 (100); *m*/*z* (EI$^+$) minor: 442 (M$^+$, 1%), 427 (M$^+$ − SiMe$_3$, 8%), 368 (20), 280 (23), 265 (20), 147 (20), 135 (10), 73 (100).

1-[Phenyl(trimethylsilyl)methyl]-2,2,2-trimethyl-1-methoxy-1-trimethylsilyloxydisilane 15

A solution of benzoyltris(trimethylsilyl)silane **1a** (0.51 g, 1.46 mmol) in dichloromethane (10 ml) was cooled to −20 °C. Trimethylsilyl trifluoromethanesulfonate (1.46 mmol) was then added. The solution was stirred for approximately 14 h when methanol was added. After 1 h saturated $NaHCO_3$ solution was then added. The organic layer was separated, and the aqueous layer extracted with diethyl ether (3 × 20 ml). The combined organic layers were dried over $MgSO_4$, filtered and concentrated to give the crude product as a dark yellow oil. Purification by flash column chromatography (eluting: petrol) gave the title silane **15** as a colourless oil (0.33 g, 58%) (Found: M$^+$, 384.1792. $C_{17}H_{36}O_2Si_4$ requires *M*, 384.1792); ν_{max} (thin film)/cm^{-1} 3020, 2956, 2898, 2835, 1700, 1597, 1493, 1450, 1405, 1287, 1251, 1204; δ_H (400 MHz) 7.20–7.00 (5H, m, aromatic), 3.52 (3H, s, OCH_3), 1.60 (1H, s, Ph(Me$_3$Si)C*H*), 0.16 (9H, s, OSi(CH_3)$_3$), 0.01 (9H, s, PhCHSi(CH_3)$_3$), −0.17 (9H, s, Si-Si(CH_3)$_3$); δ_C (100 MHz) 140.4, 129.6, 128.1, 123.6, 50.8, 32.7, 2.4, −0.2, −1.0; *m*/*z* (EI$^+$) 384 (M$^+$, 2%), 369 (M$^+$ − CH$_3$, 22), 311 (M$^+$ − SiMe$_3$, 17), 265 (20), 221 (100), 117 (44), 73 (76).

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RESEARCH CONFERENCES ATTENDED

December 1996	Modern Aspects of Stereochemistry, University of Sheffield.
December 1997	Modern Aspects of Stereochemistry, University of Sheffield.
July 1998	12th International Conference on Organic Synthesis, Venice, Italy.

PRESENTATIONS BY THE AUTHOR

July 1998	12th International Conference on Organic Synthesis, Venice, Italy (*)
December 1998	Pfizer Organic Poster Symposium, London (*)
December 1998	ICI Poster Competition, University of Durham (*)
March 1999	SCI Postgraduate Symposium, University of Glasgow (**)

(*): Poster presentation

(**): Oral presentation

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