# ORGANOSILICON SURVEY 1986-THE SILICON-CARBON BOND

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# I. INTRODUCTION

This section of the Annual Survey of Organosilicon Chemistry covers the material appearing in volumes 104 and 105 of Chemical Abstracts. It is the intention to report on the silicon-carbon bond and carbofunctional organosilanes. It should be noted that in many instances equations and structures are written in general form with liberal use of R, Ar, TMS, TBS for alkyl, aryl, trimethylsilyl and tert-butyldimethylsilyl, respectively. These are used in addition to many of the commonly used acronyms for various reagents and solvents. As is necessarily the case, it is impossible to fully categorize all the chemistry into the sections as they are outlined and the reader is advised to consult all sections for a more complete coverage.

# II. BOOKS

Books that appeared on the general topic of organosilicon chemistry include, "Advances in Organosilicon Chemistry" (272 pages) [1], "Carbosilanes: Syntheses and Reactions" (258 pages) [2] and "Organosilicon and Bioorganosilicon Chemistry: Structure, Bonding, Reactivity and Synthetic Application" (298 pages) [3]. This last book contains several chapters dealing with a variety of topics, which deal with: Unsaturated Silicon Compounds (6 pages) [4], Di- and Polysilylated Systems (10 pages) [5], Silafunctional Compounds in Synthesis (12 pages) [6], Hydrosilylation and Metathesis of Vinylsilanes (12 pages) [7], Molecular Orbital Studies (12 pages) [8], Mechanistic Studies of Silicon Atoms and Silylenes (12 pages) [9], Shortlived Organosilicon Molecules and Molecular Ions (23 pages) [10], Unsaturated

Reactive Intermediates in Organosilicon Chemistry (7 pages) [11], Small Ring Polysilanes (7 pages) [12], Unstable Intermediates From Organohalosilanes and Alkali Metal Vapors (5 pages) [13], Insights into the Chemistry of Organosilicon Intermediates (12 pages) [14], Structure-Reactivity Correlations in Heterosilanes (5 pages) [15], Silicon-Transition Metal Chemistry (7 pages) [15], Sterically Hindered Organosilicon Compounds (8 pages) [17], Organosilicon Polymer-Supported Metal Complexes (6 pages) [18] and Ligand Effects on Stereochemistry and Reactivity of Organosilanes (7 pages) [19].

## III. REVIEWS

Reflecting the continuing extraordinary growth of organosilicon chemistry, several review articles were published since the last survey. Although not all of these deal directly with the silicon-carbon bond they are listed nonetheless. A number of these were written as a part of a book as listed above. Many were more general in nature including an update of the chemistry of organosilanes from the Corriu group (42 references) [20], a preparative chemist's view of the reaction pathways of organosilanes (40 references) [21], and the chemistry of organochlorosilanes (171 references) [22].

Other reviews were more specific in their coverage including the transition metal catalyzed reduction of tri- and dichloromethyl systems in the presence of a silane (78 references) [23], the molecular structure of silatranes (105 references) [24], chiral recognition in gas chromatographic analysis of enantiomers on chiral polysiloxanes (75 references) [25], directions in the study and applications of the hydrosilylation reaction (15 references) [26], asymmetric syntheses with chiral metal complex catalysts including hydrosilylation (86 references) [27], asymmetric hydrosilylation (112 references) [28], and metal-mediated cycloaddition reactions of 1,2-disilacyclobutenes with dienes (16 references) [29].

Not surprisingly, several reviews addressed the general topic of organosilanes in organic synthesis. These included the topic of silicon in organic synthesis (22 references) [30], selective carbon-carbon bond formation based on organosilicon reagents (24 references) [31], and the use of organosilicon reagents as protective groups in organic synthesis (210 references) [32]. In addition there were articles on silyl enol ethers in synthesis (17 references) [33], ylides via desilylation of α-silyl onium salts (66 references) [34], the preparation and applications to organic synthesis of trimethylsilyl polyphosphate (19 references) [35], trimethylsilyldiazomethane (50 references) [36], trimethylsilyl iodide (55 references) [37], thiazole chemistry including silylated thiazoles (47 references) [38], synthetic aspects of the chemistry of silylated thiazoles and oxazoles (35 references) [39], heterocyclizations employing vinylsilane terminators (40 references) [40], acyclic stereoselection via addition of achiral nucleophiles to chiral carbonyl compounds - particularly the reaction of α-alkyl-β-trimethylsilyl-β,γ-unsaturated carbonyl compounds (59 references) [41], silyl substituted cyclopropanes as synthetic reagents (146 references) [42], application of allylsilanes to synthesis (33 references) [43], selective syntheses with organosilicon compounds (12 references) [44], [3+2] cycloadditions of trimethylene methane and its synthetic equivalents- particularly the trimethylene methane generated from 2-[(trimethylsilyl)-methyl]allyl esters and Pd(0) (99 references) [45], vinyl- and ethynylsilane terminated cyclization reactions (105 references) [46], organic synthesis via [3.3]-sigmatropic rearrangements of allyl dithiocarbamates - several used to generate silyl reagents (56 references) [47], cobalt-mediated steroid syntheses - a description of the state of the art in this fascinating chemistry [48], and drug design by sila-substitution (41 references) [49].

Other reviews dealt with a variety of topics, among which were bioorganosilicon chemistry in the years 1980-1982 (40 references) [50], revised MNDO parameters for silicon [51], derivatives of azenes (63 references) [52], new aspects of silacycloheptatriene chemistry (24 references) [53], thermochemical kinetics - dealing with the heats of formation of a variety of high energy silicon species [54], from silylcarbinol to silaethylenes - an account of the many "Brook Rearrangements" (42 references) [55], photochemical behaviour of silenes derived from acylsilanes (16 references) [56], inorganic silylenes (119 references) [57], silylenes and related analogous carbon species (99 references) [58], organosilicon $\alpha$-cation radicals (15 references) [59], ion-molecule reactions in volatile silanes (103 references) [60], use of reactive organosilyl intermediates in the preparation of heterocyclic and catenated organosilanes (117 references) [61], the chemistry of disilaanthracenes (49 references) [62], silafunctional compounds - synthesis and reactivity (616 references) [63], alcoholysis of hydrosilanes (135 references) [64], a comparison of the nucleophilic substitution at silicon and at phosphorus (no references) [65], reactivity of the silicon-nitrogen bond (35 references) [66], reactions in the chlorosilane-silanol-siloxane systems (11 references) [67], chloropropyltrialkoxysilanes (153 references) [68], and finally, special silicon products developed in Poland (14 references) [69].

## IV. DISSERTATIONS

Several doctoral dissertations, available from Dissertation Abstracts, Ann Arbor, Michigan, dealing with silicon appeared. These include selective redistribution reactions of organosilanes in the presence of chloroplatinic acid [70], the rearrangement of O-silylketene acetals in α-silyl esters [70], isomerization reactions in organosilicon chemistry [71], structurally unique organosilanes - for example, 1,8-bis(trimethylsilyl)naphthalene [72], reactions of organosilicon substituted alcohols and amines with cationic platinum(II) carbonyl complexes [73], reactions of trimethylsilyl metal carbonyl complexes [74], applications of alkyne addition reactions for the synthesis of organosilanes [75], synthesis and properties of branched cyclosilanes [76], the chemistry of silylsilylenes [77], gas phase decomposition of dimethylsilane, ethynylsilane and disilane [78], study of the low temperature generation of silene [79], a theoretical study of silicon-centered radicals [80], generation and reaction of enolate anions - trapped with chlorosilanes [81], use of organosilicon synthons in organic synthesis [82], α-lithiosilanes [83], regiospecificity of ring openings of oxetanes and epoxides with trimethylsilyl cyanide - direct synthesis of a polycarbosilane polymer [84], solvolysis of conformationally constrained β-functionalized

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organosilanes [85], application of silyloxydienes in the construction of the Prelog-Djerassi lactone and 6-deoxyerythronolide-B [86] and mechanistic and synthetic aspects of N-1-trialkylsilylprop-2-en-1-yl iminium salts [87].

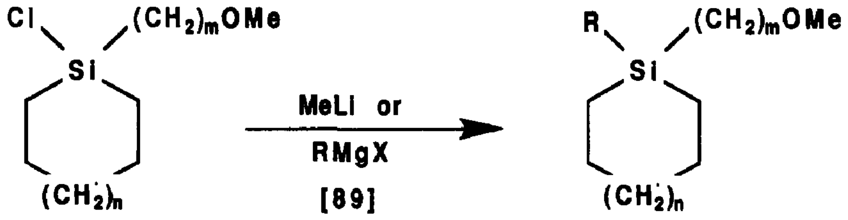
## V. ALKYLSILANES

### A. PREPARATION

Alkylhalosilanes can be prepared via the direct reaction of the alkyl halide with silicon metal at 250-350° C in the presence of tin, copper and/or other compounds. Thus, dimethyldichlorosilane was prepared in 90.44% yield by this process. (Eqn. 1)

$$Si + MeCl \xrightarrow[\substack{Sn/P\text{-}Cu\ alloy \\ 250\text{-}350^\circ \\ [88]}]{Zn/CuCl} \underset{90.44\%}{Me_2SiCl_2} \qquad (1)$$

Several alkylated silacycles were prepared in a straightforward manner as shown in Eqn. 2.



(2)

n= 0,1; m = 3,4

R = Me, $C_8H_{17}$; p-$ClC_6H_4CH_2$

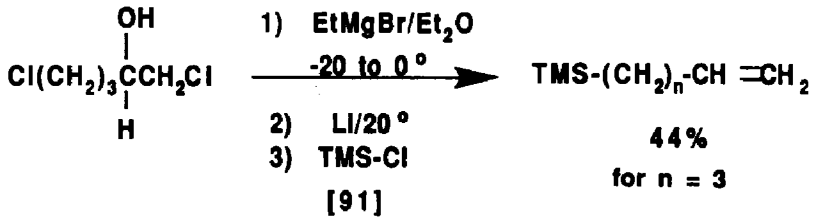
Trialkylsilyl nitriles were shown to react very well with a variety of proton exhangeable substrates resulting in the silylation of the substrate. They were also reacted with organolithium and Grignard reagents to provide the substituted organosilane. (Eqn. 3) The reaction of trimethylsilyl nitrile with n-butyllithium was used to provide a convenient route to the difficult to handle and store lithium cyanide.

$$\mathrm{TMS\text{-}CN} \xrightarrow[\mathrm{RMgX}]{\mathrm{RLi\ or}} \mathrm{R\text{-}TMS} \qquad (3)$$

[90]

14 examples including vinyl and ethynyl 35 - 80%

Chlorinated chlorohydrins were sequentially reacted with ethylmagnesium bromide, lithium metal and an electrophile to produce unsaturated addition products. One example of such a reaction employed trimethylchlorosilane as the electrophile. (Eqn. 4)



$$\mathrm{Cl(CH_2)_3\overset{OH}{\underset{H}{C}}CH_2Cl} \xrightarrow[\substack{2)\ \mathrm{Li}/20^\circ \\ 3)\ \mathrm{TMS\text{-}Cl} \\ [91]}]{\substack{1)\ \mathrm{EtMgBr/Et_2O} \\ -20\ \mathrm{to}\ 0^\circ}} \mathrm{TMS\text{-}(CH_2)_n\text{-}CH{=}CH_2} \qquad (4)$$

44% for n = 3

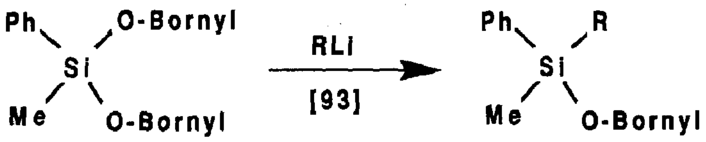
Treatment of tetrakis(trimethylstannyl)methane with a single equivalent of methyllithium and then trimethylchlorosilane gives all the possible products. (Eqn. 5) The same is true with the trimethyllead derivative.

$$\mathrm{(Me_3Sn)_4C} \xrightarrow[\substack{-\mathrm{Me_4Sn} \\ [92]}]{\mathrm{MeLi}} \mathrm{(Me_3Sn)_3CLi} \xrightarrow{\mathrm{TMS\text{-}Cl}} \qquad (5)$$

$$\mathrm{(Me_3Sn)_3CTMS}\ (40\%) + \mathrm{(Me_3Sn)_2C(TMS)_2}\ (23\%)$$

$$+\ \mathrm{Me_3SnC(TMS)_3}\ (6\%) + \mathrm{(TMS)_4C}\ (1\%) + \mathrm{(Me_3Sn)_4C}\ (30\%)$$

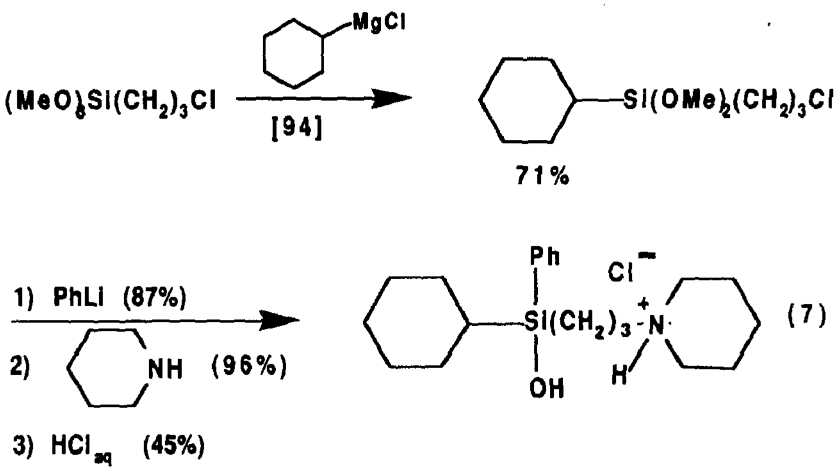
Selective substitution of one of the homochiral alkoxy groups from reasonable yields of the trisubstituted alkoxysilane with moderate diastereoselectivity. (Eqn. 6)



(6)

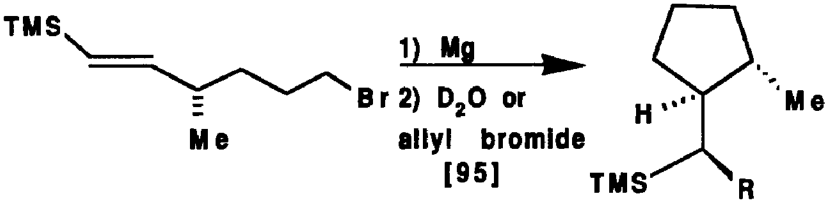
| R | % de | % Yield |
|---|---|---|
| Et | 50 | 39 |
| iPr | 25 | 79 |
| tBu | no rxn | |
| allyl | 50 | 76 |

The reaction sequence shown below was used to prepare the *antimuscarinic* agent cyclohexylphenyl(3-piperidinopropyl)silanol. (Eqn. 7)



(7)

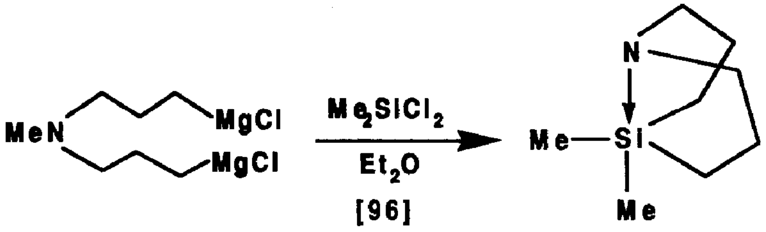
An intramolecular addition of a Grignard reagent to a vinylsilane provided a route to trimethylsilylmethylcyclopentanes. The trans vinylsilane gave excellent stereoselectivity, the structure being confirmed by an independent synthesis. (Eqn. 8) The cis vinylsilane, however, gave an equimolar mixture of diastereomers.



R = D; allyl

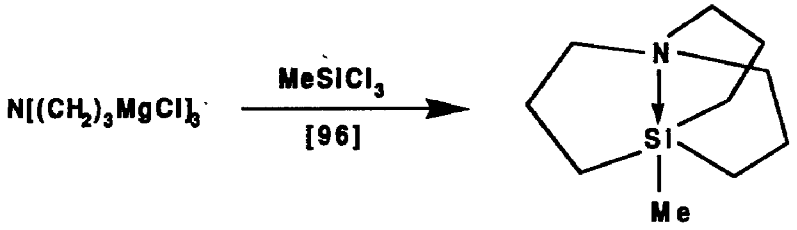
(8)

The Grignard reagents from bis(3-chloropropyl)methylamine and tris(3-chloropropyl)amine were used to prepare the pentavalent organosilanes **1** and **2**. (Eqns. 9, 10)



1

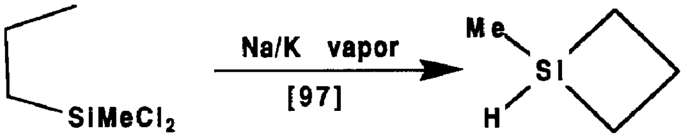
(9)



2

(10)

The gas phase dehalogenation of either n-propylmethyldichlorosilane or 3-chloropropyldimethylchlorosilane gives 1-methyl-1-silacyclobutane. (Eqns. 11, 12)



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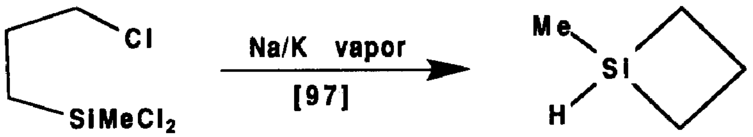
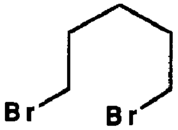
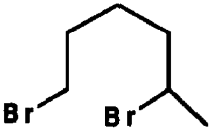


(12)

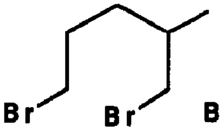
The 1,5-dibromopentanes **3** - **9** were reacted with dimethyldichlorosilane to give the silacylohexanes **10**. The lowest yields were found with dibromides **3** and **6**. (Eqn. 13) Not surprisingly, some chlorine-bromine exchange was also observed. The reactions were also carried out with methyldichlorosilane and phenylmethyldichlorosilane. In a similar reaction the 3-silabicyclo[3.2.1]octanes **11** were prepared. (Eqn. 14) A number of substitution reactions of both **10** and **11** were carried out in order to study the stereochemistry of the substitution reactions in these silacycles.



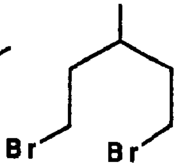
**3**



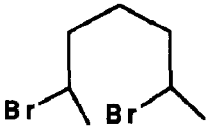
**4**



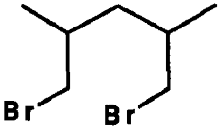
**5**



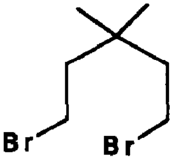
**6**



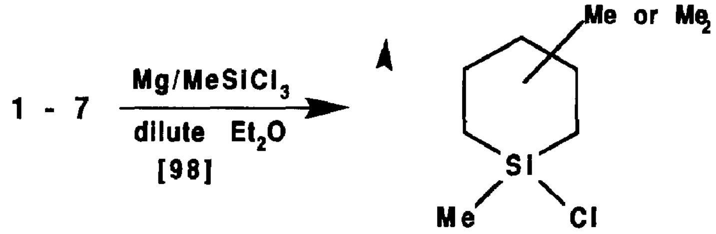
**7**



**8**



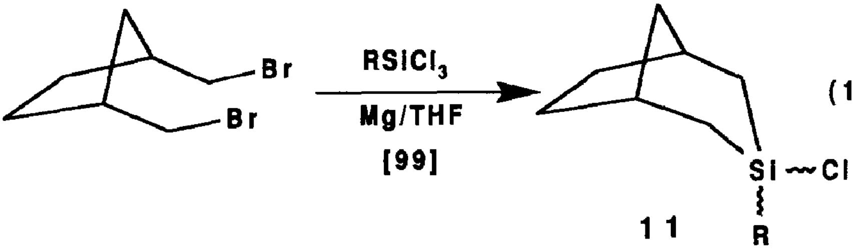
**9**



(13)

**10** 32 - 69%

MeHSiCl$_2$ and PhSiCl$_3$ also reacted



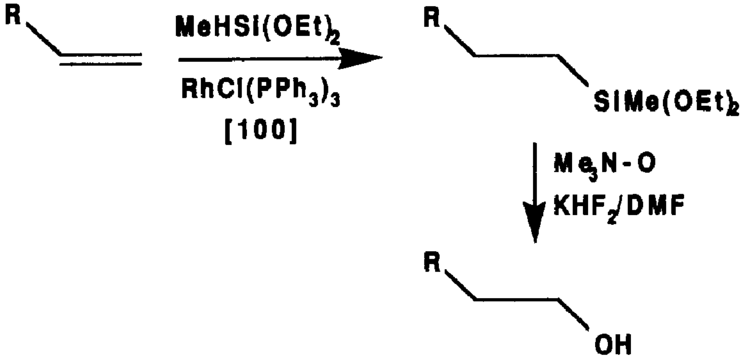
(14)

**11**

(R = Cl (20%); Me (50-60%); Ph (50%; endo:exo > 60:40)

## B. ALKYLSILANES--REACTIONS

It has been found that trimethylamine N-oxide will oxidize the silicon carbon bond providing the silicon is bonded to alkoxy groups. (Eqns. 15, 16) The advantage of this new procedure is that it is more tolerant of functional groups than the peracid oxidation procedure.



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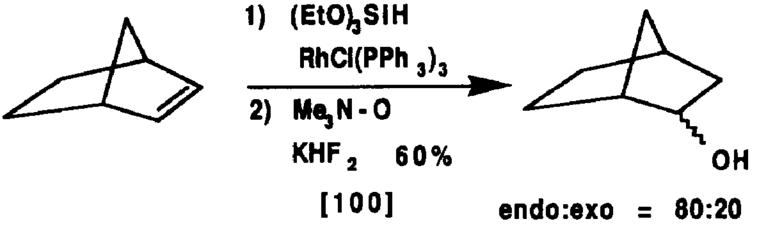


(16)

Tetrakis(trimethylsilyl)methane was reacted with iodine monochloride and iodine monobromide to give electrophilic cleavage of one of the methyl groups from each silicon moiety. (Eqn. 17) Trimethylchlorosilane was formed by electrophilic cleavage of tetramethylsilane. (Eqns. 18, 19, 20) A related reaction is seen in Eqn. 21.

$$(Me_3Si)_4C \ + \ I\text{-}X \xrightarrow[\text{[101]}]{} C(SiMe_2X)_4 \qquad (17)$$

X = Cl or Br

$$Me_4Si \ + \ CCl_4 \xrightarrow[\text{[102]}]{AlBr_3 \text{ or } AlCl_3} Me_3Si\text{-}Cl \qquad (18)$$

($CHCl_3$; $CH_2Cl_2$; $C_2Cl_6$; and $ClCH_2CH_2Cl$ also work)

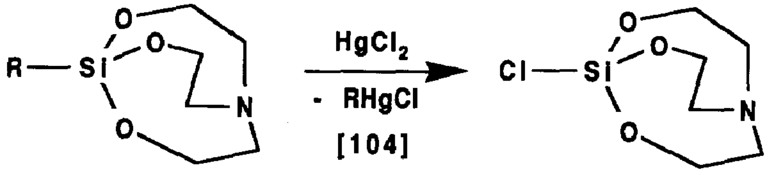
$$Me_4Si \ + \ MeSiCl_3 \xrightarrow[\text{[103]}]{AlCl_3 \text{ (cat)}} Me_3Si\text{-}Cl \qquad (19)$$

44% conversion

$PhSiCl_3$ also works

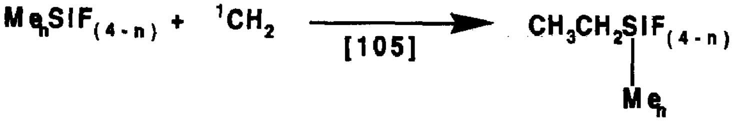
$$Me_4Si \ + \ ClCH_2Me_2Si\text{-}Cl \xrightarrow[\text{[103]}]{} \begin{cases} \xrightarrow[\text{pressure}]{\text{atm.}} TMS\text{-}Cl & (20) \\ \xrightarrow{\text{autoclave}} EtMe_2Si\text{-}Cl & (21) \end{cases}$$

It was shown that various groups could be electrophilically cleaved from silatranes with mercuric chloride. (Eqn. 22) The relative rates of reaction are Vi>Ph>p-ClPh>Me>Et>$^i$Pr>$C_6H_{11}$>$ClCH_2$>$Cl_2CH$>EtO.



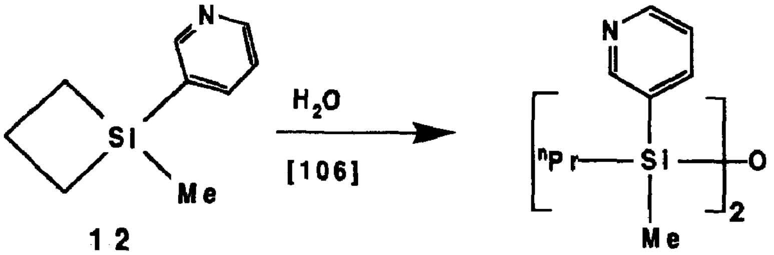
(22)

The kinetics of the insertion of singlet methylene into the C-H bond of methylfluorosilanes was determined. The relative rates were determined to be $Me_4Si > Me_3SiF > Me_2SiF_2 > MeSiF_3$. The reaction is shown in Eqn. 23. Some insertion into the Si-F bond of dimethyldifluorosilane is reported.



$$Me_nSiF_{(4-n)} + {}^1CH_2 \xrightarrow[{[105]}]{} CH_3CH_2\underset{\underset{Me_n}{|}}{Si}F_{(4-n)} \qquad (23)$$

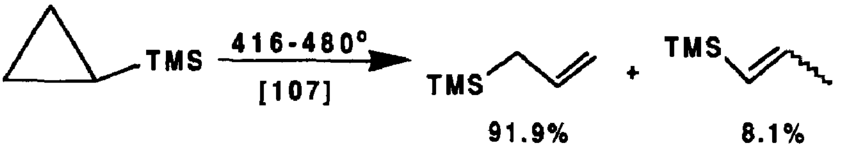
Silacyclobutane **12** reacts with water with opening of the endocyclic Si-C bond. Compound **12** is much more reactive towards water than the corresponding m-tolyl and p-dimethylaminophenyl systems. (Eqn. 24)



**1 2**

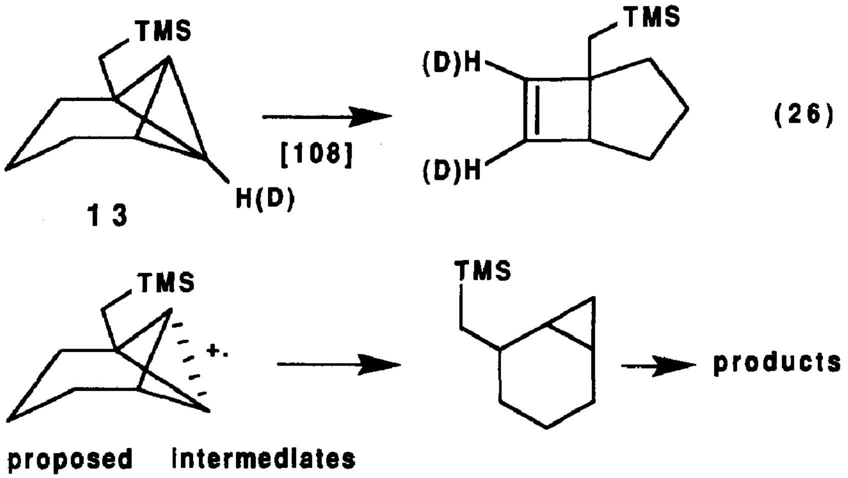
(24)

The kinetics of the thermal isomerization of cyclopropyltrimethylsilane were determined. Some evidence for anchimeric assistance by the cyclopropyl group was found. The reaction is shown in Eqn. 25.



(25)

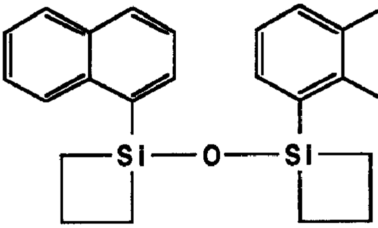
The trimethylsilylated tricycloheptane **13** was used to gain insight into the photoinduced rearrangement of the tricyclo[4.1.0.0$^{2,7}$]heptyl skeleton. The data is consistent with the argument that one-electron C-C bonds are subject to rearrangement if a suitable carbocation stabilizing group (such as a β-trimethylsilyl group) is present. (Eqn. 26)



(26)

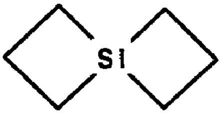
## C. ALKYLSILANES-OTHER STUDIES

The cleavage of the Si-C bond in triethylsilane by various metal catalysts (Cu, Ni, Rh, Pd, Pt) supported on Cab-o-Sil® was studied. [109] The structure of disiloxane **14**, prepared in 75% yield from the corresponding chlorosilane, was determined. It is a centrosymmetric dimer with a linear Si-O-Si linkage. [110]



**14**

A correlation of molar refraction with first-order molecular connectivity index was found for alkylsilanes. [111] The vibrational spectra of 4-silaspiro[3.3]heptane, **15**, were recorded. The data show the molecule to have puckered rings consistent with $C_2$ symmetry, but the data can also be analyzed assuming $D_{24}$ symmetry. [112]

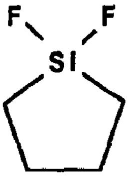


**15**

A quantum chemical analysis of silicon atom pentacoordination was reported. The formation of intramolecular pentacoordinate silicon and complex ions is discussed. [113] The stabilization of a carbocation by a γ-silicon group is proposed to be by a bridged structure and not *via* hyperconjugation. [114] A kinetic study of the gas phase reaction of iodine and tert-butyltrimethylsilane provided a β-silicon stabilization energy of ca. 12 kJ/mol for the $Me_2SiCMe_2CH_2$ radical. [115]

The measurement of $^{29}Si$ satellites in proton-decoupled $^{13}C$ NMR spectra with selective $^{29}Si$ decoupling was used in the assignment of lines in the $^{29}Si$ spectra of pertrimethylsilylated monosaccharides. [116] Tunneling frequencies of 15.8 and 24.0 MHz were determined for the slowly relaxing component of spin-lattice relaxation due to Me rotation in solid γ-tetramethylsilane. [117]

The molecular structure and pseudorotational motion of **16** was determined by gas phase electron diffraction. [118]

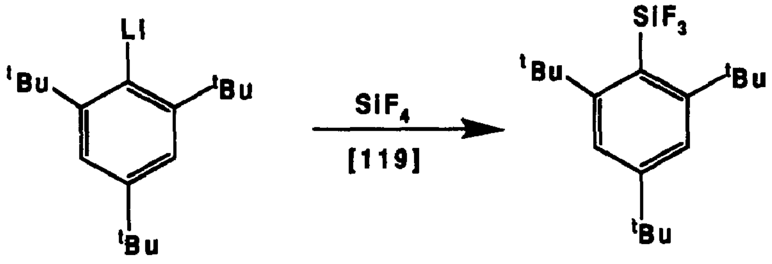


**16**

## VI. ARYLSILANES

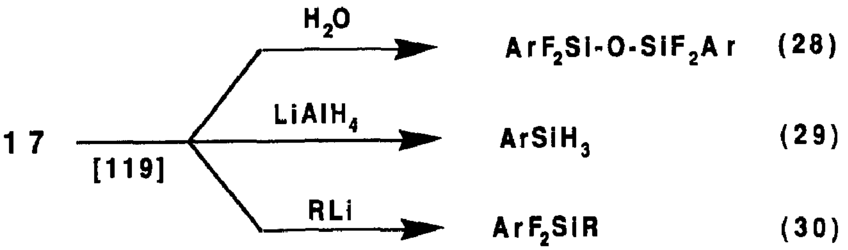
### A. PREPARATION

Several derivatives of 2,4,6-tri-tert-butylphenylsilane were reported. The best synthesis was the reaction of 2,4,6-tri-tert-butyl-phenyllithium with silicon tetrafluoride to form the aryltrifluorosilane from which other derivatives could be synthesized. (Eqns. 27, 28, 29. 30)



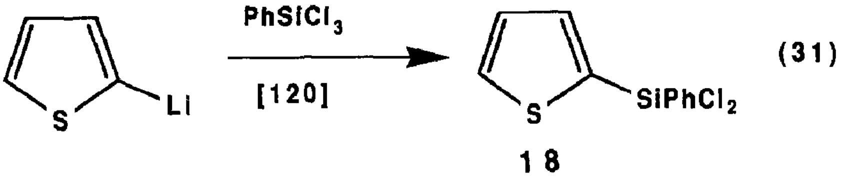
(27)

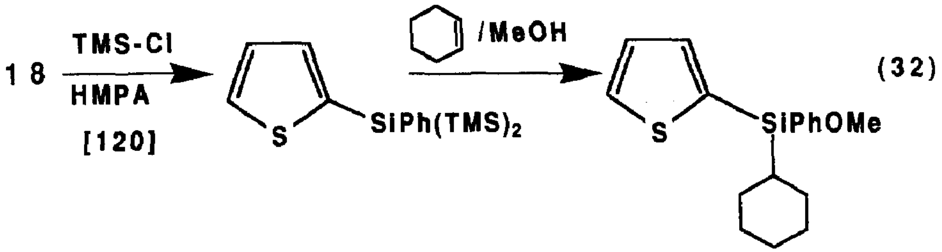
**17**



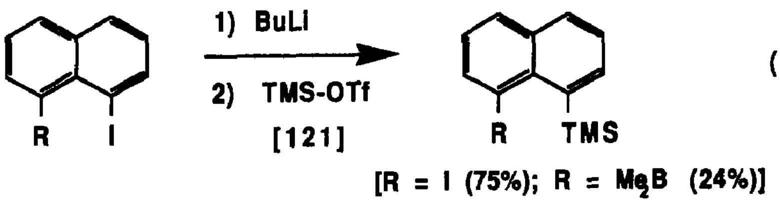
[R = Me(93%); $^t$Bu (60%); Ar (0%)]
Ar = as above

The reaction of phenyltrichlorosilane with 2-lithiothiophene led to 2-thiophenylphenyldichlorosilane from which other derivatives of this bis arylsilane were prepared. (Eqns. 31, 32)





Trimethylsilyltrifluoromethane sulfonate (trimethylsilyl triflate) was used to silylate some of the slower reacting aryllithium reagents. (Eqn. 33) A similar reaction with 1,1-dichloro-1-silacyclobutane is shown in Eqn. 34.



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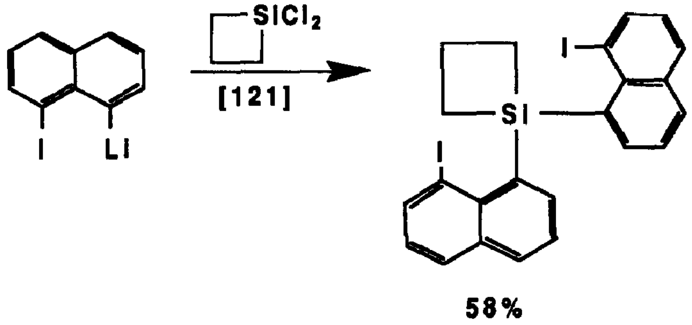
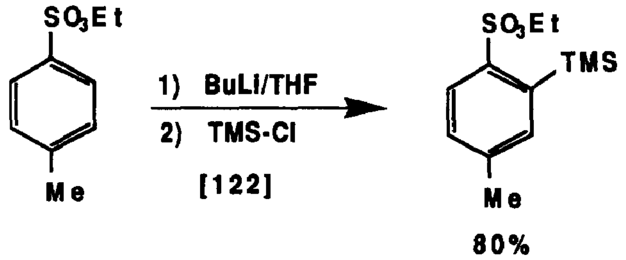


(34)

Three reports of ortho-lithiation-trimethylsilylation were published. These involved an arylsulfonate (Eqn. 35), an N,N-diethylcarbamate (Eqns. 36, 37, 38, 39), esters (Eqn. 40) and an oxazoline (Eqn. 41). The silylation of the esters to give **19** was carried out sequentially. The first trimethylsilyl group adds to position 5 and the second to position 3.



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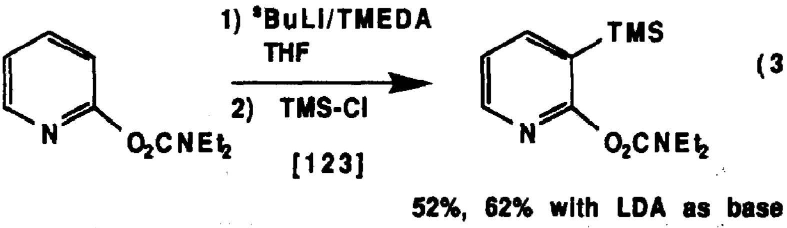

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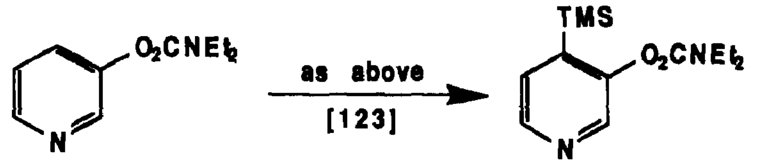
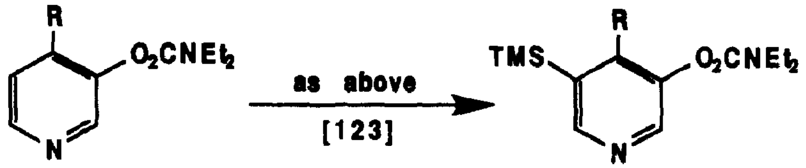


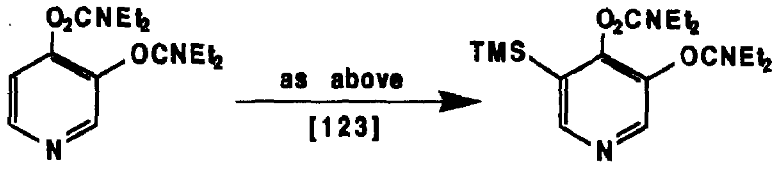
(37)

69%; 83% with LDA as base



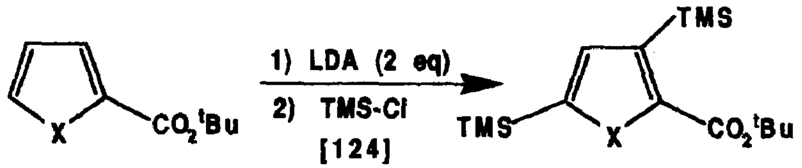
(38)

R = Br 65%; R = CONEt$_2$ 66%



(39)

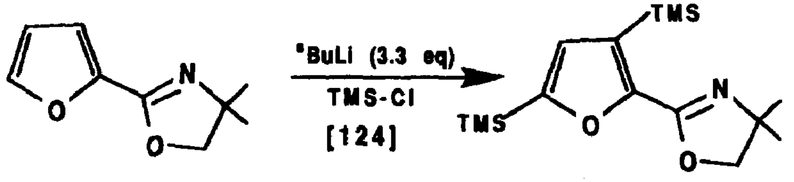
68%



(40)

19

(X = O, S, ca. 95%)

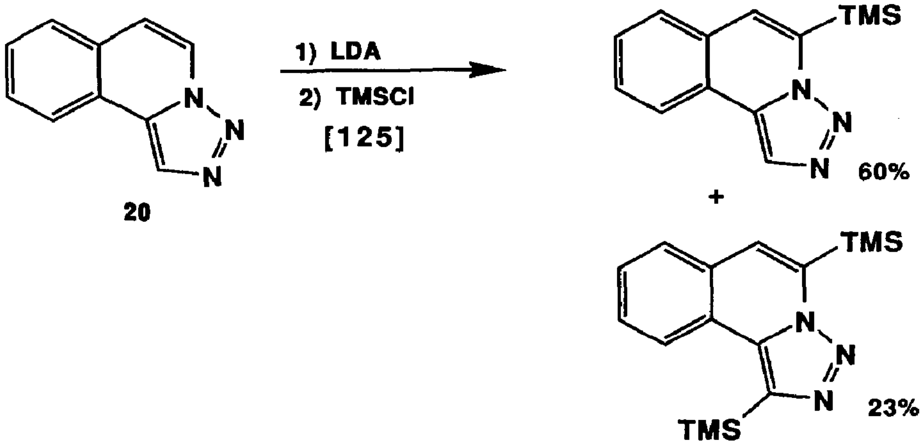


(41)

93%

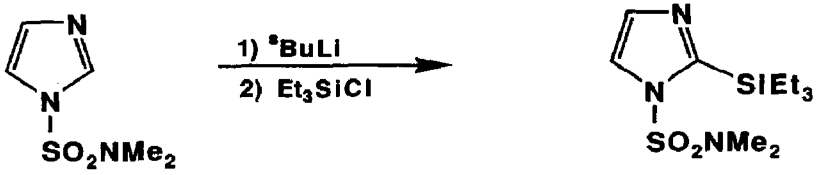
Metal-hydrogen exchange provided the lithium reagents of two heteroaryl systems, which were then silylated. Lithiation of the triazolopyridine **20** followed by trimethylsilylation produced both the mono- and bis-trimethylsilylaed materials. (Eqn. 42)

Triethylsilylation of the protected imidazole provides a route to 5-substituted imidazoles after a second substitution and desilylation. (Eqns. 43,44)



20

(42)



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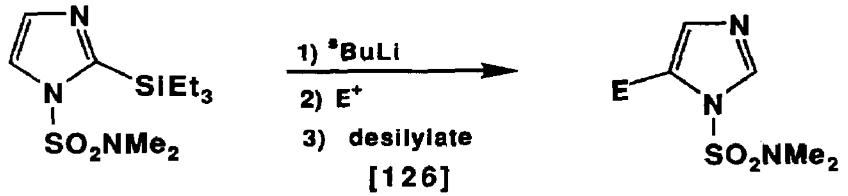
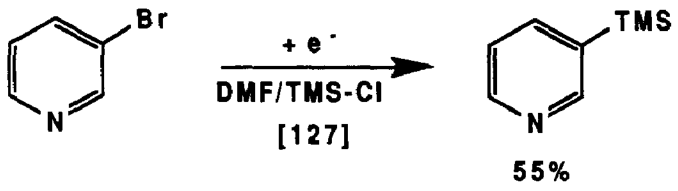


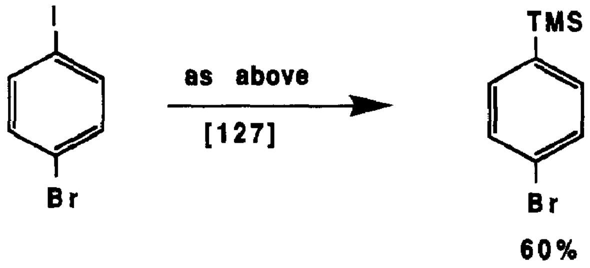
(44)

(E = D, Me, SMe, allyl, TMS, $PhCH_2$, Cl, $CPh_2OH$, $CO_2H$)

The electrochemical reduction of aryl bromides, or better, aryl iodides in the presence of trimethylchlorosilane provides the corresponding aryltrimethylsilane in moderate to good yields. (Eqns. 45, 46)

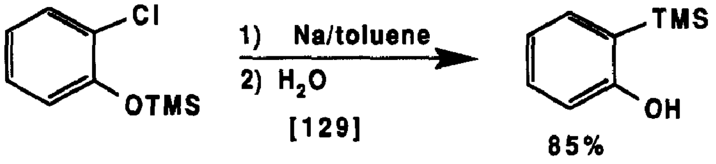


(45)



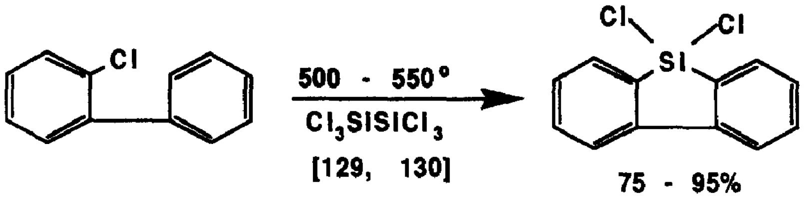
(46)

Treatment of trimethylsilylated o-chlorophenol with sodium metal in toluene gives, after trimethylsilyl migration from oxygen to the ortho carbon, o-trimethylsilylphenol in good yield. (Eqn. 47)

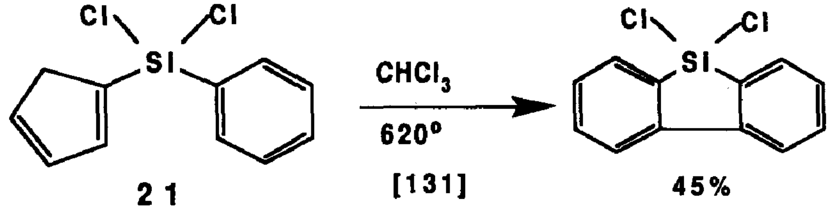


(47)

Thermolysis of o-chlorobiphenyl in the presence of hexachlorodisilane provides the dichlorosilafluorene in excellent yield. (Eqn. 48) A similar system was prepared by thermolysis of **21** in the presence of chloroform. (Eqn. 49)

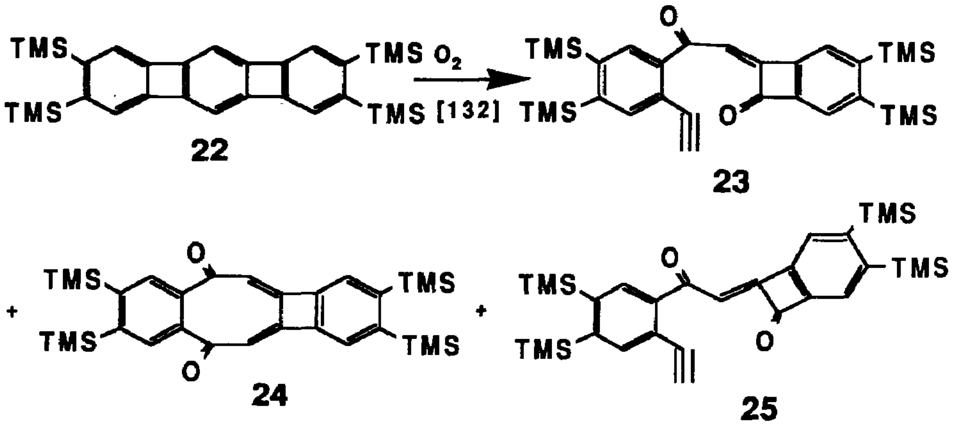


(48)



(49)

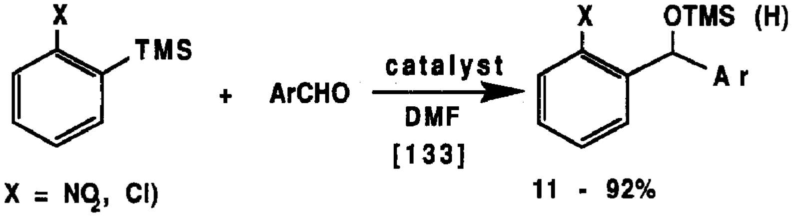
The photooxidation of arylsilane **22** gave products **23** - **25**. (Eqn. 50)



(50)

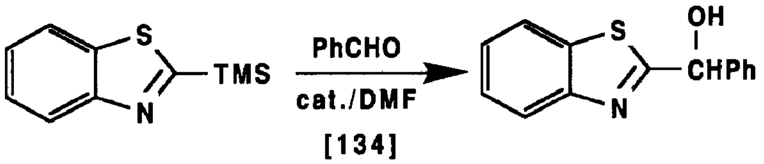
## B. ARYLSILANES-REACTIONS

The reaction of certain arylsilanes with fluoride ion or strongly nucleophilic oxygen anions in the presence of an electrophile has been used to electrophilically substitute aromatic systems. (Eqns. 51 - 54). This reaction has also been carried out with 2- and 3-trimethylsilylthiophene. [132] The reaction has been studied mechanistically using the general system shown in Eqn. 53. Not surprisingly, electron withdrawing groups such as nitro groups favored the reaction.



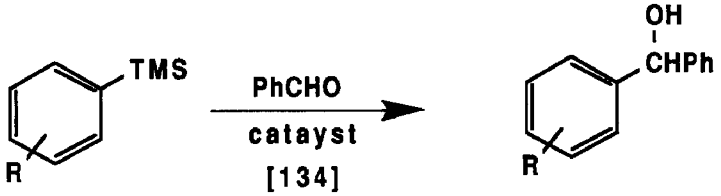
(51)

(other electrophiles added: DMF, MeCHO, ketones, $CO_2$, anhydrides)

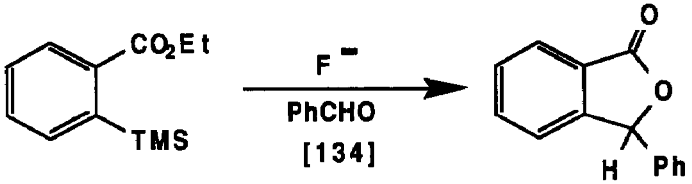


(52)

(best catalysts: KF, CsF, KO$^t$Bu, PhOK, KOAc)

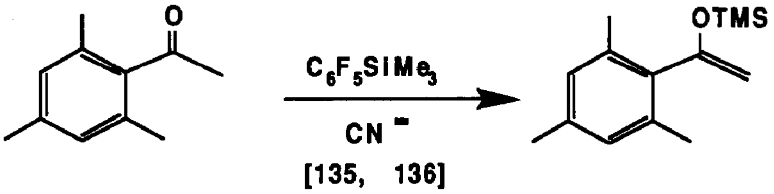


(53)



(54)

The reaction of pentafluorophenyltrimethylsilane with cyanide ion in the presence of enolizable ketones leads to trimethylsilyl enol ethers. (Eqns. 55, 56) It was found that potassium cyanide in the presence of a catalytic amount of 18-crown-6 greatly enhanced the reaction.



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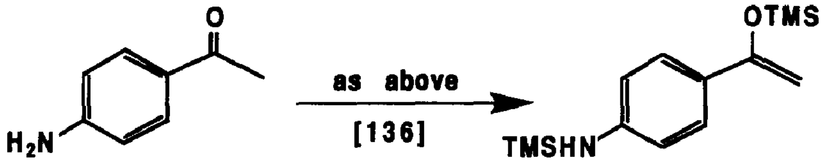
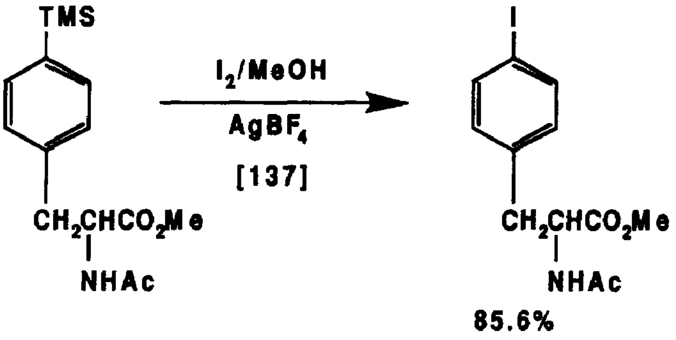
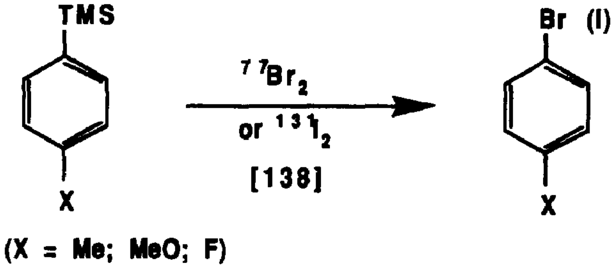


(56)

The direct iodination of aryltrimethylsilanes was used to provide iodophenylalanine. (Eqn. 57) The direct bromination and iodination of aryltrimethylsilanes was used to prepare radiolabelled aryl bromides and aryl iodides, respectively. (Eqn. 58) It was found that, in general, iodination was better than bromination and that tin was better than germanium, which was in turn better than silicon in this reaction.

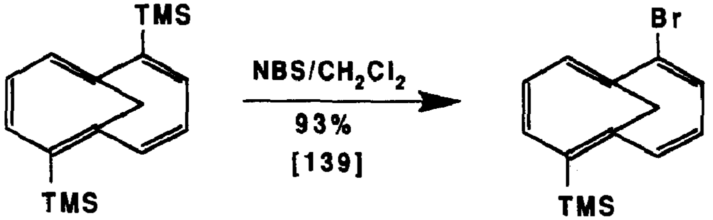


(57)



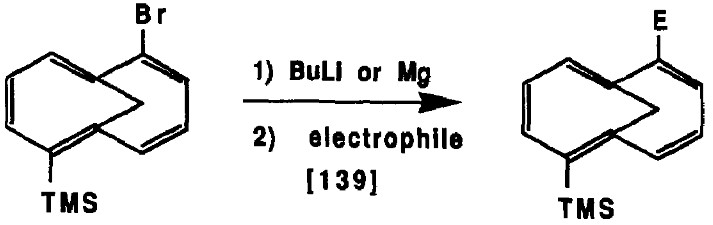
(58)

The selective bromodesilylation of the bis-trimethylsilyl-[10]-annulene **26**, prepared in nearly quantitative yield by lithium-bromine exchange followed by trimethylsilylation, was used to prepare 2-substituted-1,6-methano[10]annulenes. (Eqns. 59, 60)



**26**

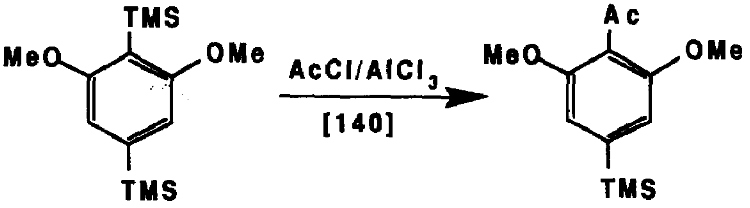
(59)



(60)

(E = Me, CO$_2$Me, CHO, $^t$BuO; yields = 65 - 80%)

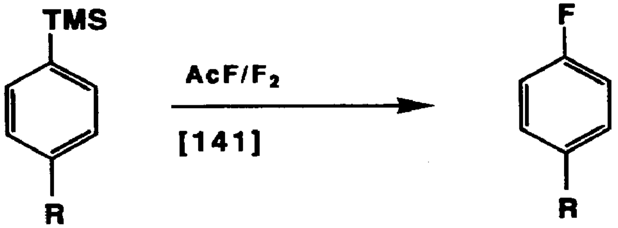
The regioselective acylation of the bis-trimethylsilyl derivative **27** was accomplished. (Eqn. 61) The selective removal of the trimethylsilyl flanked by the activating methoxy groups is, however, not surprising.



**27**

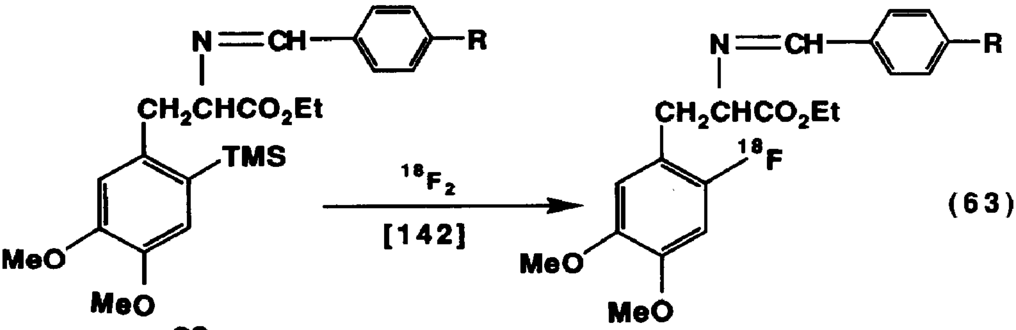
(61)

The direct fluorination of aryltrimethylsilanes was reported. (Eqn. 62) This was used as a way to regioselectively introduce $^{18}$F as is seen in the preparation of $^{18}F$ labelled 6-fluoro-L-dopa. (Eqn. 63) The requisite arylsilane **28** was prepared by treating the corresponding bromide with magnesium and trimethylchlorosilane.



(62)

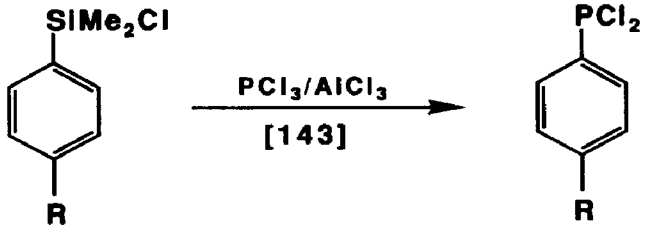
(R = H, Me, MeO, Cl, Br, OAc, Ac, TMS)



**28**

(63)

The electrophilic phosphinylation of arylsilanes has been reported. (Eqn. 64)

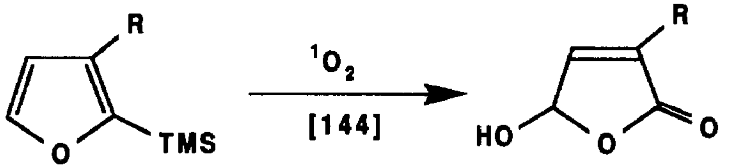


(64)

(R = H, Cl, Br, Me)

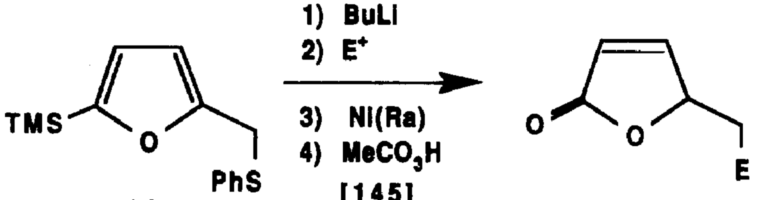
70 - 87%

Furans substituted in the 3-position and trimethylsilylated in the 2-position react with singlet oxygen to provide 5-hydroxy-3-substituted butenolides in excellent yields. (Eqn. 65) This approach to substituted butenolides was expanded using the thiophenoxymethyl trimethylsilylfuran **29**. (Eqn. 66) One such sequence leading to cis-quercus lactone is shown. (Eqn. 67)



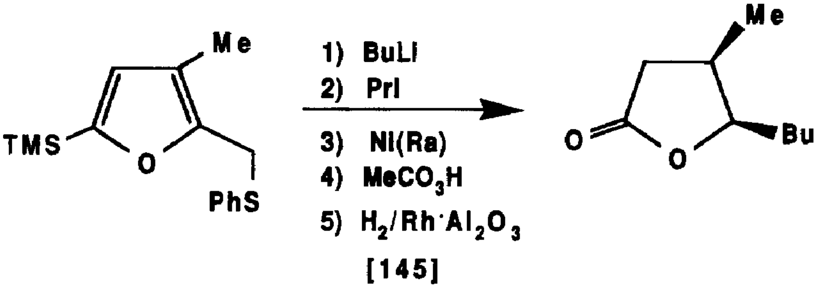
4 examples 93 - 94%

(65)



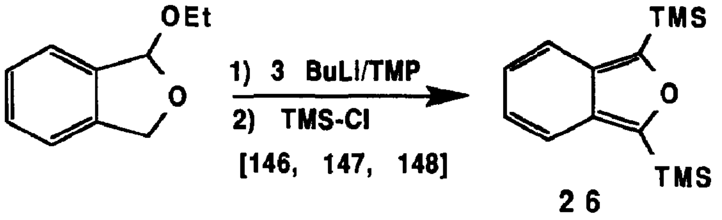
**29**

(66)

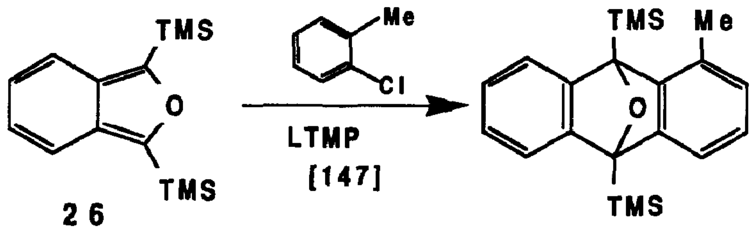


(67)

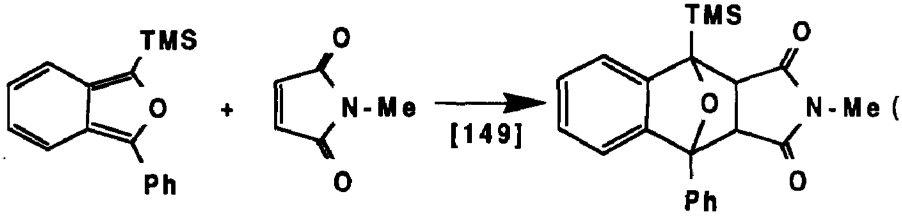
Trimethylsilylated isobenzofurans were prepared and used very successfully in the preparation of substituted aromatic polycyclic compounds *via* cycloaddition to a number of *in situ* generated benzynes. It is possible to desilylate the products. The synthesis of one of the key silylated isobenzofurans **30** is given in Eqn. 68. Some representative examples of the cycloaddition reactions are shown in Eqns. 68 - 70.



(68)

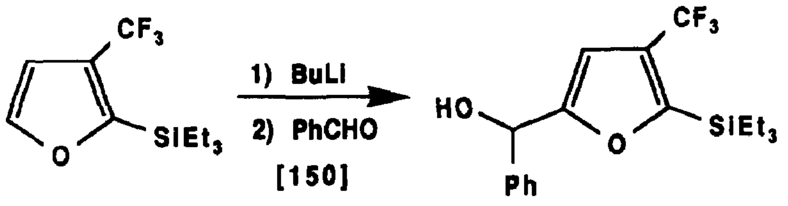


(69)



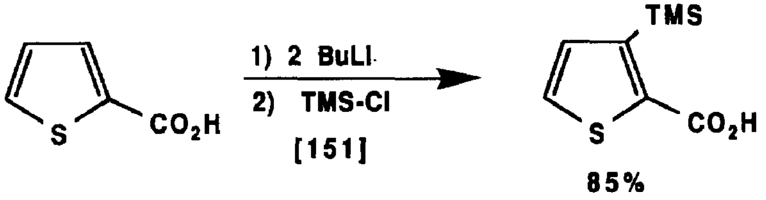
(70)

Triethylsilylation of 3-trifluoromethylfuran was used to protect the 2-position and thus allow substitution of the 5-position as shown in Eqn. 71. Again protiodesilylation provides the silicon-free material.

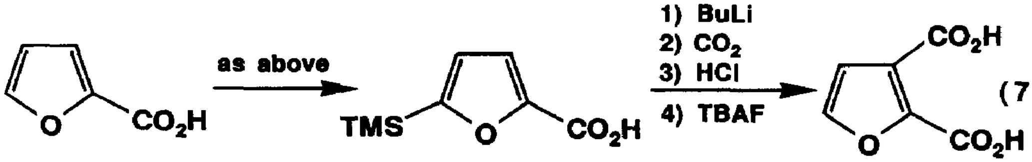


(71)

Lithiation-trimethylsilylation of thiophene 2-carboxylic acid gives the 3-trimethylsilyl derivative in good yield. (Eqn. 72) Similar treatment of furan 2-carboxylic acid gives the 5-trimethylsilyl product **31**. Lithiation-carboxylation-protiodesilylation of this material provides furan 2,3-dicarboxylic acid in excellent overall yield. (Eqn. 73)



(72)



**31**

(73)

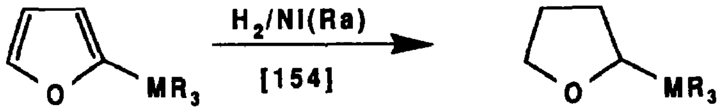
Phenylfluorosilanes were shown to react with potassium fluoride/18-crown-6 to give the corresponding fluorosiliconates in excellent yields. (Eqn. 74)

$$\mathrm{Ph_nSiF_{4\text{-}n}} \xrightarrow[\substack{\text{18-C-6/toluene} \\ [152]}]{\text{KF}} \mathrm{Ph_nSiF_{5\text{-}n}^{-}\ K^{+}\ 18\text{-}C\text{-}6} \qquad (74)$$

Some phenylfluorosilanes were prepared from the corresponding chlorosilanes and zinc fluoride. A key step in the preparation of sym-tetrafluorodiphenyldisilane was the chlorodephenylation of hexaphenyldisilane. (Eqn. 75)

$$Ph_3SiSiPh_3 \xrightarrow[\text{[153]}]{HCl} Cl_2PhSiSiPhCl_2 \xrightarrow{ZnF_2} F_2PhSiSiPhF_2 \quad (75)$$

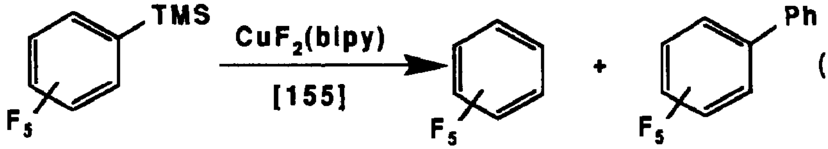
Various 2-substituted furans were hydrogenated. (Eqn. 76) The relative rates of reaction with Raney-Nickel catalyst were $CH_3$ > $^tBu$ > $Me_3Si$ > $Me_3Ge$.



(76)

$R_3M$ = $CH_3$, tBu, $Me_3Si$, $Me_3Ge$)

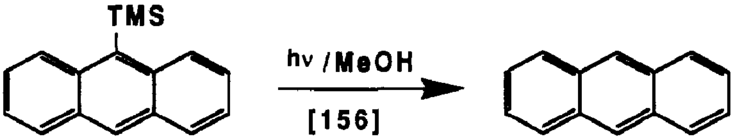
Pentafluorophenyltrimethylsilane was dearylated with copper (II) fluoride bipyridyl complex. A small amount of phenylpentafluorobenzene was also produced in this reaction. (Eqn. 77)



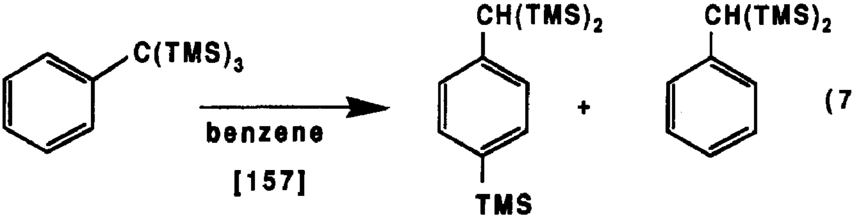
(77)

Photolysis of 9-trimethylsilylanthracene in methanol results in clean protiodesilylation. (Eqn. 78) Photolysis of tris(trimethylsilyl)methylbenzene gives the rearranged product **32**. (Eqn. 79) A radical mechanism supported by experimental evidence is proposed. Photolysis of 2-trimethylsilylthiophenes gives polymeric products, whereas photolysis of 2-trimethylsilyl-N-methylpyrrole gives the 3-trimethylsilyl derivative.

(Eqns. 80, 81) Similar treatment of N-methyl-2,5-bis(trimethylsilyl)-pyrrole gives initially the 2,3-disilylated material, which photoisomerizes virtually quantitatively to N-methyl-3,4-bis(trimethylsilyl)-pyrrole. (Eqn. 82) Finally, photolysis of **33** gives the photocyclomer **34**. (Eqn. 83)

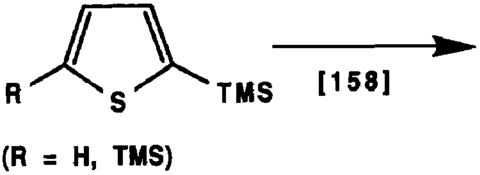


(78)

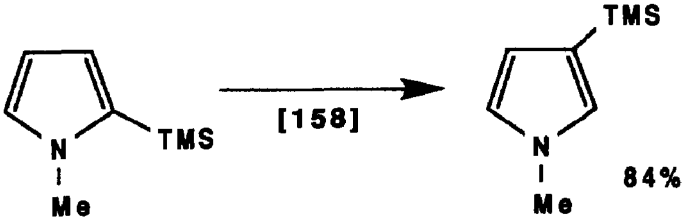


**32**

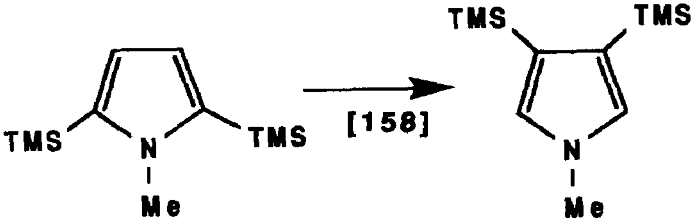
(79)



(80)



(81)



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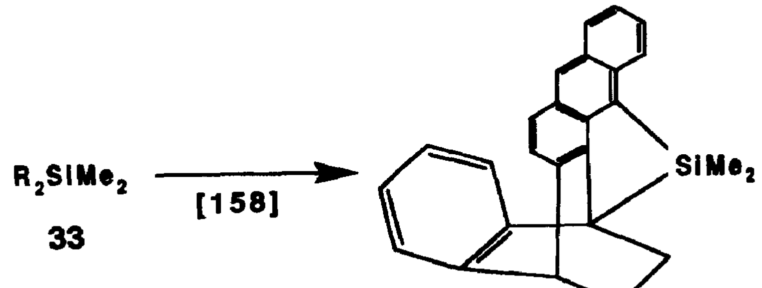


(83)

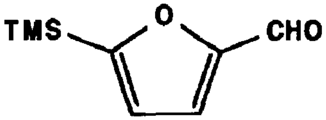
33

(R = 9-anthranyl)

34

## ARYLSILANES--OTHER STUDIES

A variety of 5-substituted furanyltrimethylsilanes was prepared by standard chemistry. LCAO-CNDO/2MO analysis of the electronic structures of **35** and **36** were done. [160]



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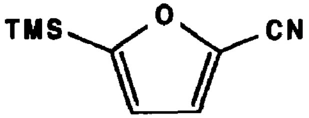
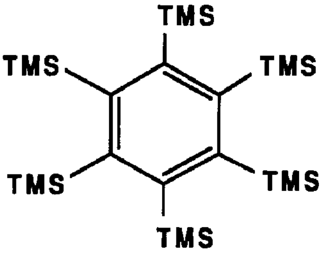


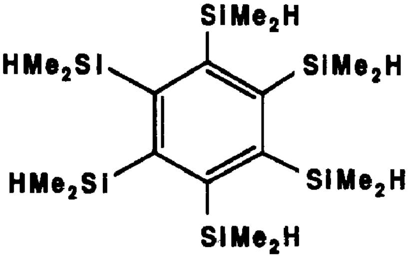
36

The structural parameters for hexakis(trimethylsilyl)benzene **37** were calculated and compared with the calculated and experimental values for hexa(tert-butyl)benzene and hexa(trimethylgermyl)benzene. The calculated ground state for **37** is $D_3$. [161]



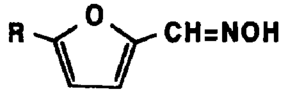
**37**

The dynamic stereochemistry of hexa(dimethylsilyl)benzene **38** has been studied. Empirical-force-field (EFF) calculations show it to have $C_{6h}$ ground state geometry. Variable temperature NMR measurements on the chromium tricarbonyl complex of **38** show that the dimethylsilyl group rotational barrier is 14.2 kcal/mol compared to a rotational barrier of 15.7 kcal/mol calculated for **38** itself. [162]

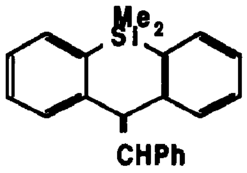


**38**

Some NMR studies were carried out on arylsilanes. These include an NMR analysis of systems of the general structure **39** and in particular where R = trimethylsilyl . [163] An NMR analysis of the boat-boat inversion of **40** showed $\Delta G^{\#}_{298}$ = 53.5 kJ/mol. [164] Silatranes **41** were prepared and their crystal structures determined. NMR analysis of the stereoisomers in solution were performed as well. [165]



39



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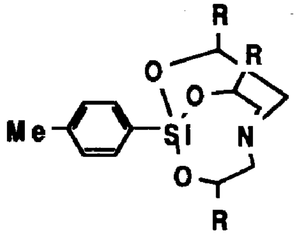
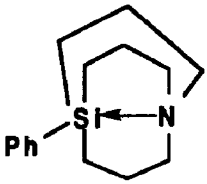


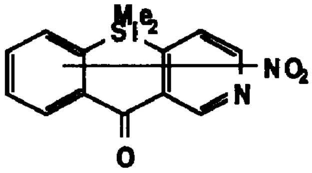
41

The crystal structure of 1-phenylcarbosilatrane **42** was determined by x-ray diffraction. The Si-N bond distance is 2.291(1) A, which is 0.13 A longer than that found in phenylsilatrane. [166]



42

Cation radicals of several alkyl- and silylsubstituted benzenes in frozen trichlorofluoromethane were studied by ESR. All substituents were found to be electron donating to the benzene cation. The results may shed light on the conformational necessities of hyperconjugation. [167] A mass spectral study of nitro substituted dihydrosilaazanthrones **43** was conducted. [168] A discussion of the aromaticity of the silacyclopentadienyl **44** and 1-silafluorenyl anions **45** based on NMR analysis was presented. [169]



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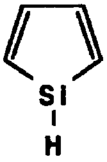

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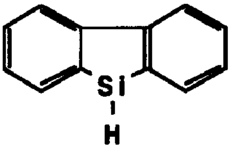


45

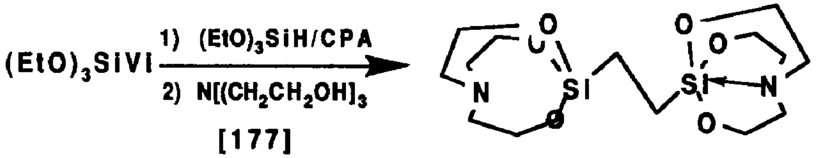
# VII. HYDROSILYLATION

## A. GENERAL

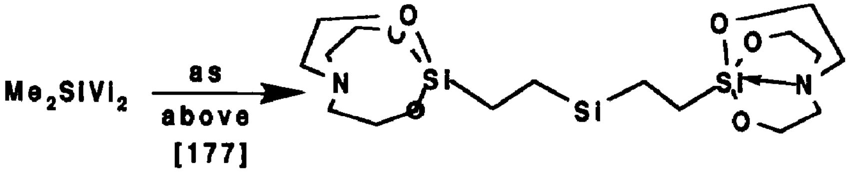
It has been demonstrated that the reaction of cyclooctadienylplatinum(II) chloride with triethoxysilane forms colloidal platinum as the active catalyst, thus accounting for the fact that an induction period is observed in the hydrosilylation reaction. [170] Evidence has been presented for a radical-cation mechanism in the hydrosilylation of olefins with triethyl-silane and triethoxysilane. [171] The kinetics of the hydrosilylation of acetylene and vinylmethyldichlorosilane with methyldichlorosilane were determined. Rate constants of $1.1 \times 10^4$ and $3.1 \times 10^4$ L/mol-sec were observed. [172] The kinetics of the addition of trimethyoxysilane to 1-decene with bis(triphenylphosphine)platinum oxide catalysis was studied. The reaction was found to be first order in 1-decene. [173] The regio- and stereochemistry of the hydrosilylation of 1-hexyne and phenylacetylene catalyzed by various rhodium complexes was studied. [174] A detailed study of the hydrosilylation of vinylsilanes of the general structure $Me_nSiVi_{4-n}$ (n = 0-3) was made. Thus, a variety of catalysts and solvent systems were investigated. [175] The regioselectivity of the hydrosilylation of styrene with methyldichlorosilane in the presence of ion exchange supported group VIII metal complexes was studied. Thus, KU-2-Ni(II) gave 94% of the α-isomer, whereas AB-17-[Ir(III)Cl6] gave 100% of the β-isomer. [176]

## B. HYDROSILYLATION--ALKENES

The hydrosilylation of vinyltriethoxysilane, 1,5-hexadiene and divinyldimethylsilane with triethoxysilane, catalyzed by chloroplatinic acid (CPA), was used as an approach to linked silatranyl structures. Two examples are shown in Eqns. 84a and 84b.



(84a)



(84b)

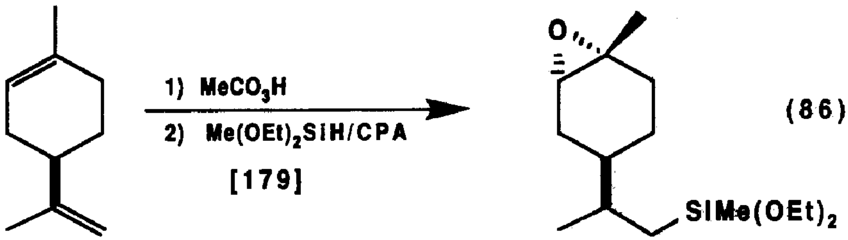
A series of 1,2-bissilylated ethanes were prepared *via* the hydrosilylation of vinylsilanes. Other minor products were also obtained from this hydrosilylation. The yields ranged from moderate to excellent. (Eqn. 85)

$$R_3SiCH{=}CH_2 \xrightarrow[\text{[178]}]{R_3'SiH/CPA} R_3SiCH_2CH_2SiR_3' \qquad (85)$$

[$R_3Si$ = $Me_nSiCl_{3-n}$ (n=0-3); $Vi_3Si$]

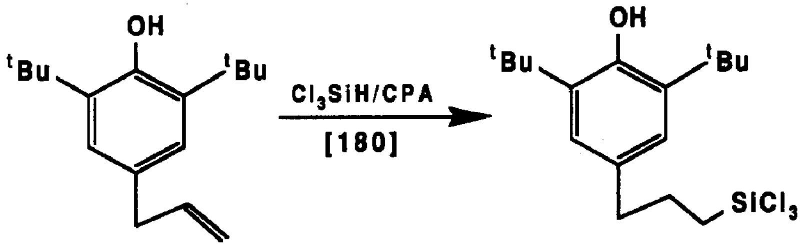
[$R_3'Si$ = $Me_nSiCl_{3-n}$ (n=0-3); $Me_2PhSi$; $MePh_2Si$; $Ph_3Si$]

Several terpenes were sequentially epoxidized and then hydrosilylated with diethoxysilane. The products were useful as polymer and paint additives. One example is shown. (Eqn. 86)



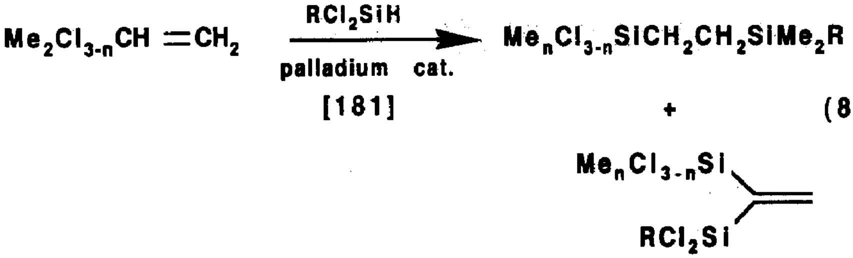
(86)

A series of 2,6-di-tert-butyl-4-alkylsilyl phenols was prepared *via* hydrosilylation of the appropriate unsaturated 4-alkyl-2,6-di-tert-butylphenol as illustrated in Eqn. 87.



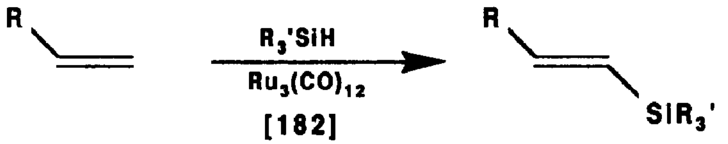
(87)

The hydrosilylation of vinylsilanes with various palladium catalysts was studied. It was found that vinyltrichlorosilane reacts with trichlorosilane to give predominantly the 1,1-bis(trichlorosilyl)ethylene, whereas the others give almost exclusively the 1,2-bis silylated ethanes. (Eqn. 88)

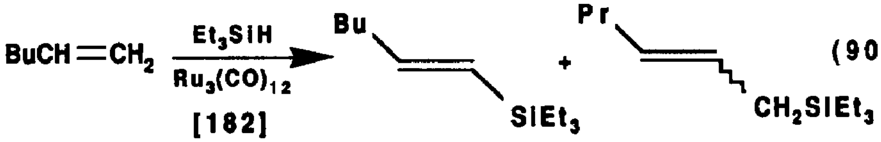


(88)

The trirutheniumdodecacarbonyl catalyzed hydrosilylation of alkenes results in the direct formation of vinylsilanes from the alkene. (Eqn. 89) When allylic protons are present in the alkene some allylsilane is also formed. (Eqn. 90) One equivalent of alkene is used to take up the hydrogen so that the general procedure utilizes an equivalent of 1-hexene for this purpose.



(89)



(90)

The triethylsilylated iridium (III) complexes **46** and **47** were prepared according to Eqn. 91 and used as catalysts for the hydrosilylation of olefins. (Eqn. 92)

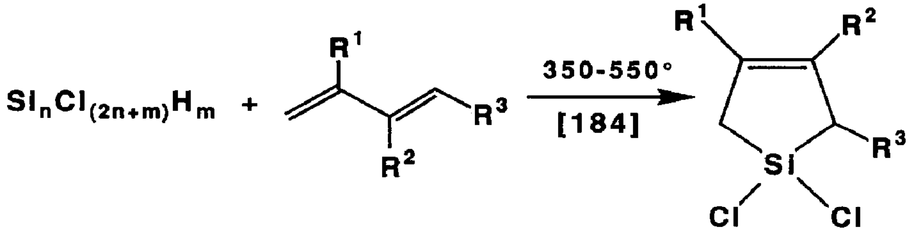
$$1/2\ \ [\mathrm{Ir(OMe)(COD)}]_2 \xrightarrow[\text{- }\mathrm{MeOSiEt_3}]{\mathrm{Et_3SiH/L}} \mathrm{IrH_2(SiEt_3)(COD)L} \qquad (91)$$

[183] $\mathrm{L = Ph_3P}$ **46**

$\mathrm{L = Ph_3As}$ **47**

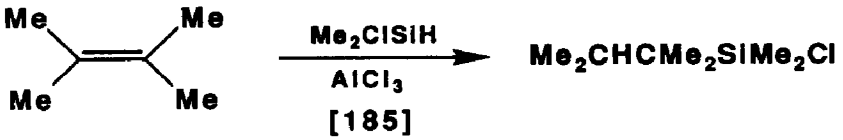
$$\mathrm{BuCH{=}CH_2} \xrightarrow[\textbf{46}\text{ or }\textbf{47}]{\mathrm{Et_3SiH}} \mathrm{C_6H_{14} + C_6H_{11}SiEt_3 + C_6H_{13}SiEt_3} \qquad (92)$$

The thermal gas-phase hydrosilylation of 1,3-butadienes provides the corresponding silacyclopentene. (Eqn. 93)

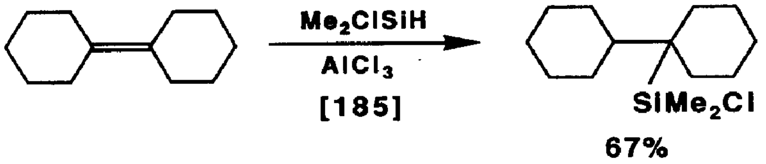


(93)

The hydrosilylation of tetrasubstituted olefins takes place with aluminum trichloride catalysis. This was used to prepare (2,3-dimethyl-2-butyl)dimethylchlorosilane (thexyldimethylchlorosilane) in excellent yield. (Eqn. 94) Other tetrasubstituted olefins react similarly as is seen from Eqn. 95.



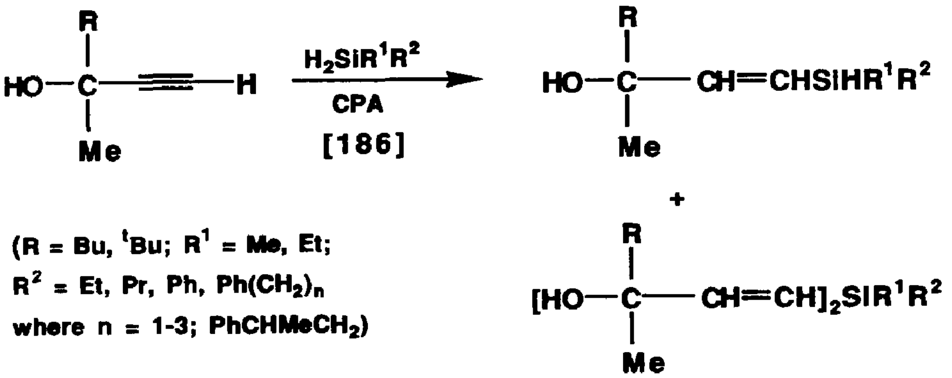
(94)



(95)

## C. HYDROSILYLATION-ALKYNES

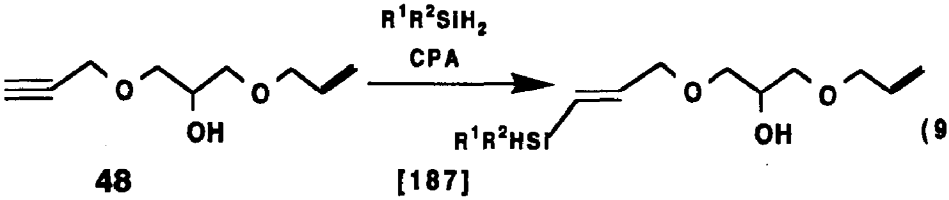
Several propargyl alcohols were hydrosilylated with dihydrosilanes to provide the corresponding vinylsilane containing an Si-H bond in addition to the divinylsilane resulting from dihydrosilylation. (Eqn. 96)



(R = Bu, $^tBu$; $R^1$ = Me, Et;
$R^2$ = Et, Pr, Ph, $Ph(CH_2)_n$
where n = 1-3; $PhCHMeCH_2$)

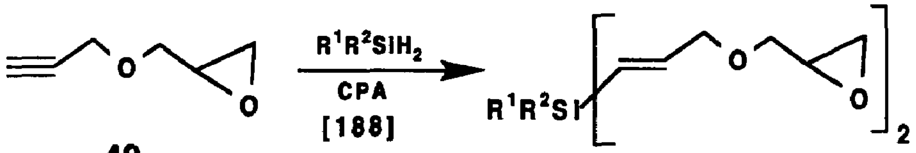
(96)

In a related study the propargyl alcohol **48** was reacted with several dihydrosilanes to give the vinylsilanes containing an Si-H bond. (Eqn. 97) The oxirane **49** was similarly treated to give the divinylsilanes *via* hydrosilylation with both Si-H bonds. (Eqn. 98) The divinylsilane was obtained from the hydrosilylation of **50**. (Eqn. 99) A similar approach was used to prepare the vinylated disiloxanes as seen in Eqn. 100.



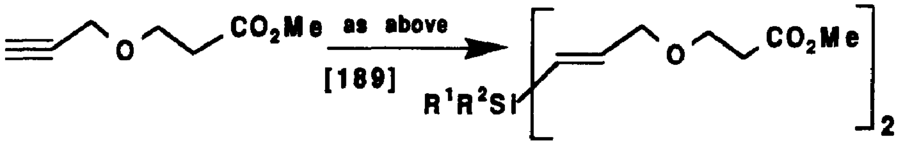
**48**

(97)



**49**

(98)

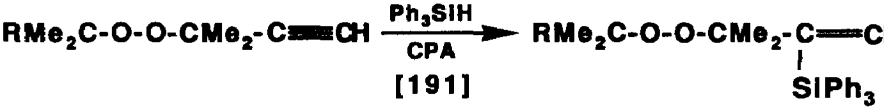


(99)

**50**

(100)

Propargyl peroxides were hydrosilylated with triphenylsilane. (Eqn. 101) Propargyl chloride was hydrosilylated with various silanes. (Eqn. 102)



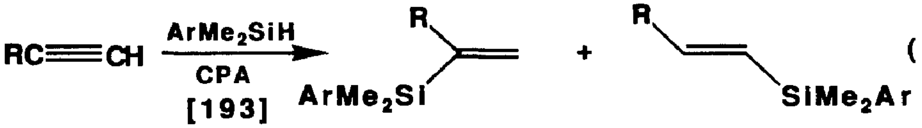
$$RMe_2C\text{-}O\text{-}O\text{-}CMe_2\text{-}C{\equiv}CH \xrightarrow[\text{CPA}]{Ph_3SiH} RMe_2C\text{-}O\text{-}O\text{-}CMe_2\text{-}\underset{SiPh_3}{C}{=}CH_2 \quad (101)$$

[191]

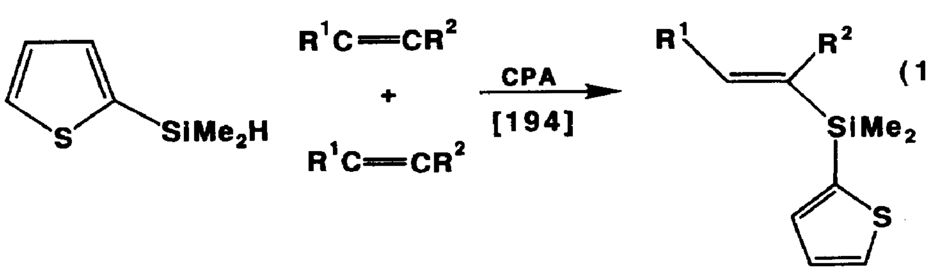
(R = Me, Et, Pr, $C_5H_{11}$)

55 - 66%

Various arylated hydrosilanes were used to hydrosilylate terminal alkynes providing both the α- and trans β-ethenylsilanes. (Eqn. 103) Dimethyl(2-thiophenyl)silane was used to hydrosilylate acetylenes. When carried out in the presence of an alkene, only the triple bonded species reacted. (Eqn. 104)

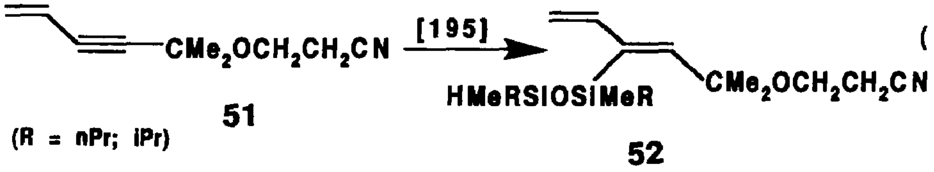


(103)

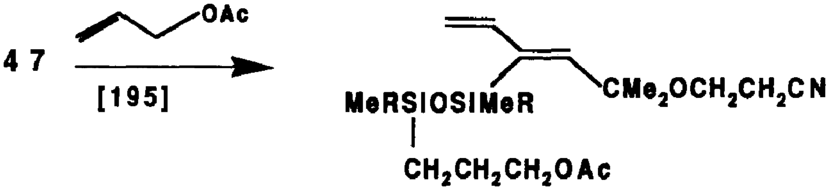


(104)

Enyne **51** was hydrosilylated with 1,3-dihydrodisiloxanes at the triple bond with the silicon adding to the 3-position of the enyne. (Eqn. 105) The monosilylated product **52**, which still contains an Si-H bond, was further reacted in one case with allyl acetate. (Eqn. 106)

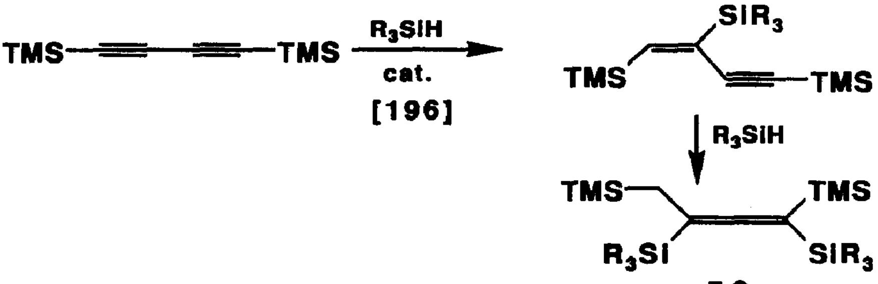


**51** **52** (105)

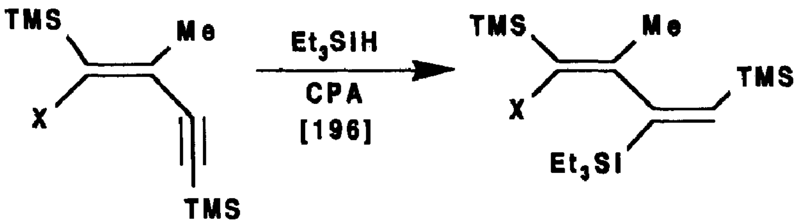


(106)

Bis(trimethylsilyl)butadiyne hydrosilylates first to place the silyl group on the 2-position. The second hydrosilylation occurs in a 1,4 manner to give the tetrasilylated allene **53**. (Eqn. 107) On the other hand the 3-methylated enynes **54** and **55** react with triethylsilane to give the 1,2 addition product. (Eqn. 108)



**53** (107)



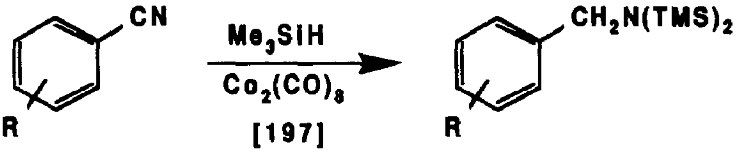
(108)

X = H **54**
X = Br **55**

X = H **56** 71%
X = Br **57** 93%

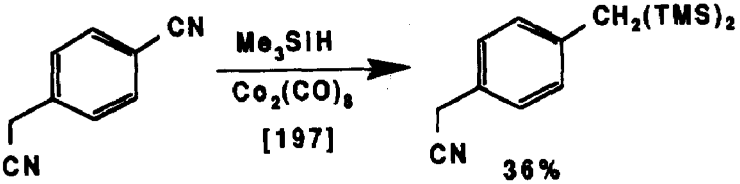
## D. HYDROSILYLATION–OTHER

Aromatic nitriles are reductively silylated with trimethylsilane in the presence of dicobalt octacarbonyl. The yields range from poor to excellent. (Eqn. 109) Only the aromatic nitrile groups react. (Eqn. 110) Trialkylsilanes were shown to react with oxiranes in the presence of dicobalt octacarbonyl. (Eqn. 111) Unfortunately, a mixture of products is obtained. In a like manner oxetanes were reacted with trialkylsilanes and dicobalt octacarbonyl, but in this case the products are those of a silylhydroformylation reaction. (Eqn. 112)



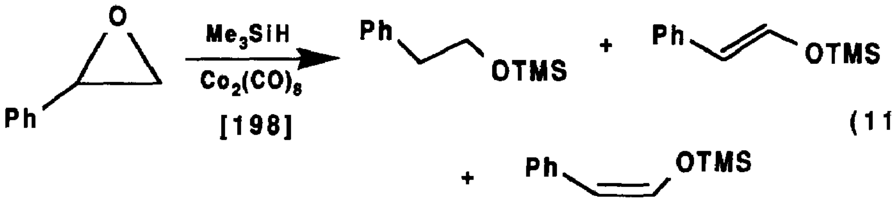
(109)

10 examples: 11 - 91%

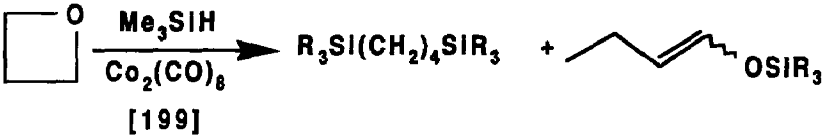


(110)

36%

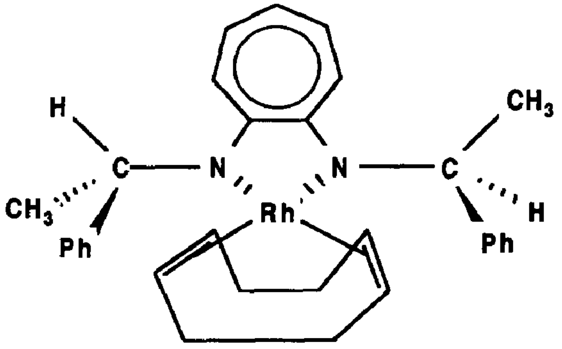


(111)



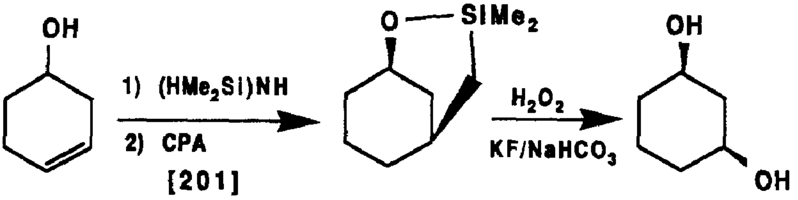
(112)

Diphenylsilane was used as the hydrosilylating agent in the asymmetric reductive silylation of acetophenone employing optically active rhodium complexes wherein the ligands bound to the rhodium are optically active ligands derived from tropone. Unfortunately, the ee of the ultimate product, 1-phenylethanol was very low in all cases. This changed somewhat for the better when (+)-norphos or (-)-diop were used as cocatalysts. One of the rhodium catalysts is shown in structure **58**. [200]

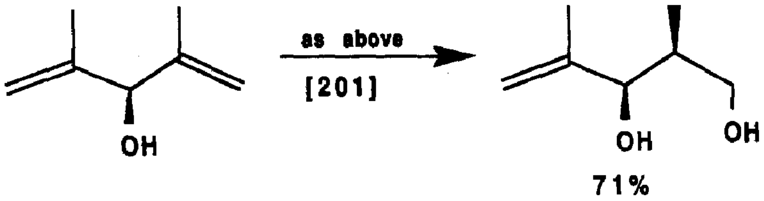


**58**

A sequence involving silylation of an unsaturated alcohol with sym-tetramethyldisilazane followed by intramolecular hydrosilylation and oxidation provides a stereoselective route to diols. Two such examples are shown. (Eqns. 113, 114)



(113)

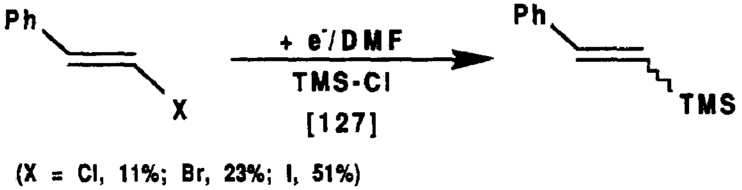


(114)

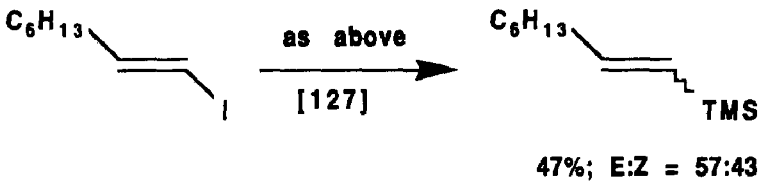
## VIII. VINYLSILANES

### A. PREPARATION

The electrochemical reductive silylation of vinyl halides was accomplished. (Eqns. 115, 116)

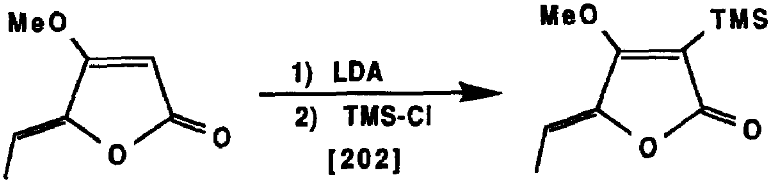


(115)



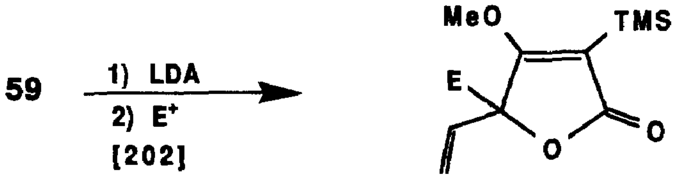
(116)

Not surprisingly several vinylsilanes were prepared by the reaction of a vinyl organometallic reagent, usually a vinyllithium reagent, and a chlorosilane. Most often the intrigue in these reactions is in the method of preparation of the vinyl organometallic reagent or the application of the vinylsilane prepared. The methylenol ether of 4-ethylidenetetronic acid was metallated and then reacted with trimethylchlorosilane to give **59**. (Eqn. 117) Deprotonation of this material gave a lithium reagent that reacted at the 4-position, (Eqn. 118) with the exception of acylation, which provided some of the dienol acetate **60**, which itself was cycloadded to dimethylacetylene dicarboxylate. (Eqns. 119, 120)



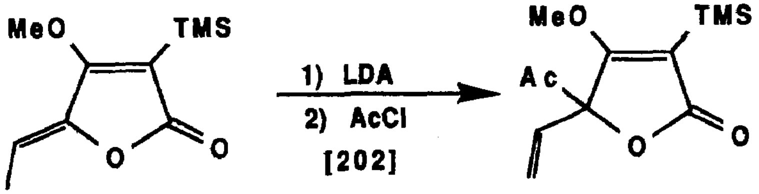
**59**

(117)

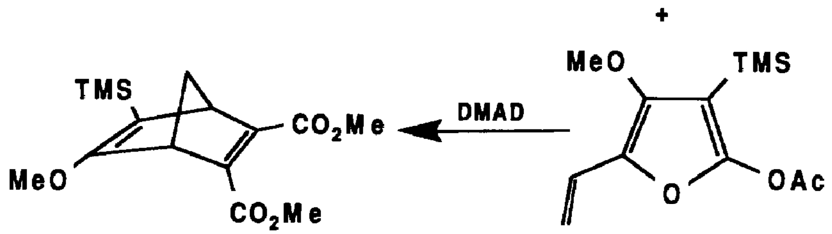


(118)

($E^+$ = MeI; PhCHO; PrCHO)



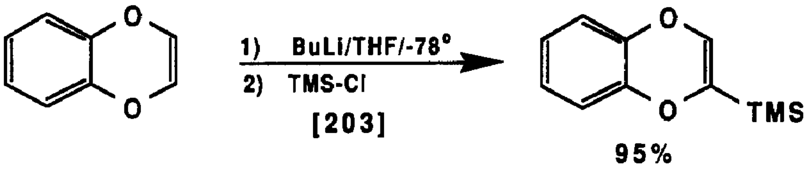
(119)



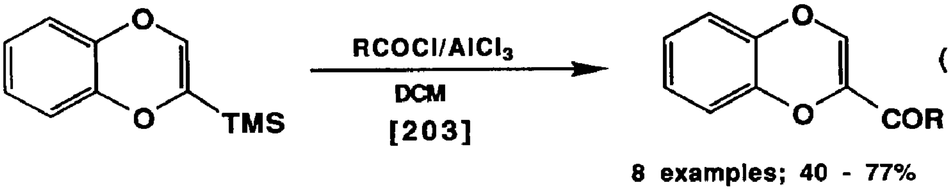
**60**

(120)

Benzodehydro-1,4-dioxane was lithiated and trimethylsilylated. (Eqn. 121) The resulting vinylsilane was used to prepare several enones. (Eqn. 122)

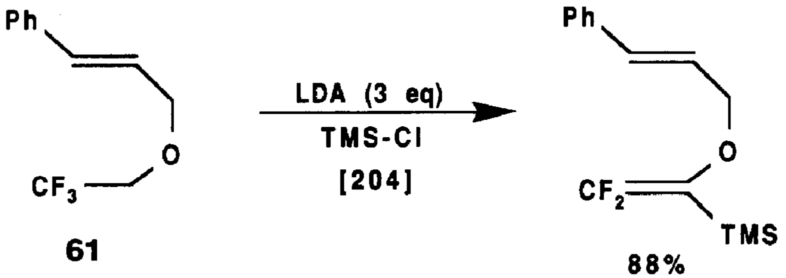


(121)



(122)

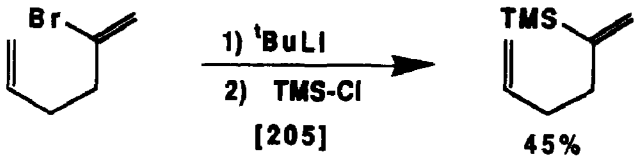
Deprotonation of trifluoroethyl allyl ether **61** provides a vinyllithium reagent, which was trimethylsilylated. (Eqn. 123)



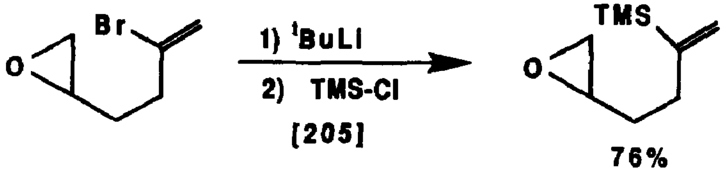
**61**

(123)

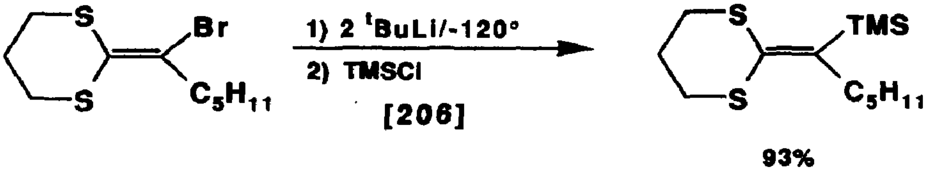
Vinyl bromides were subjected to metal-halogen exchange with the resulting vinyllithium reagent being trimethylsilylated. Examples are given in Eqns. 124-127. The last example actually involves a migration of a trimethylsilyl group.



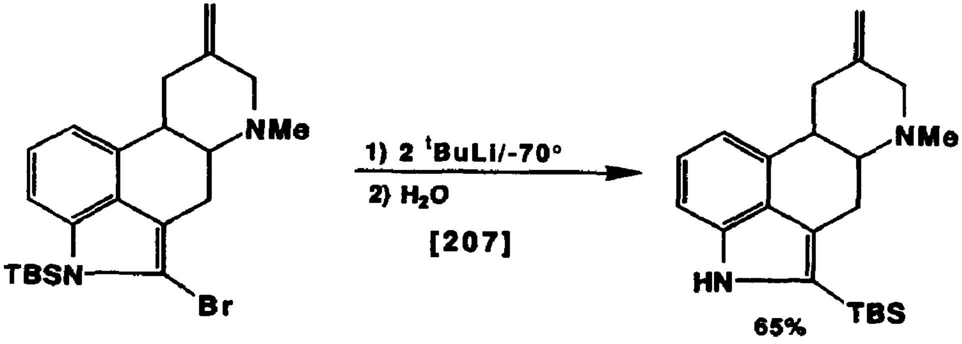
(124)



(125)

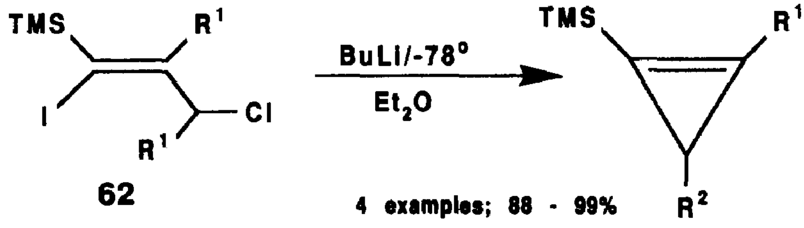


(126)



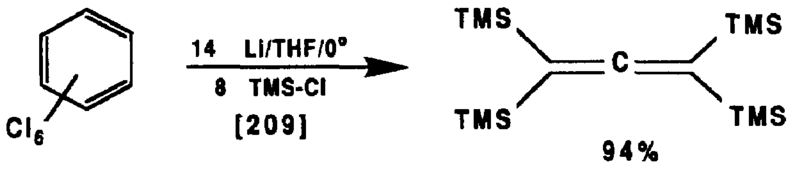
(127)

Trimethylsilylcylopropenes were prepared from vinylsilanes **62** as shown in Eqn. 128.



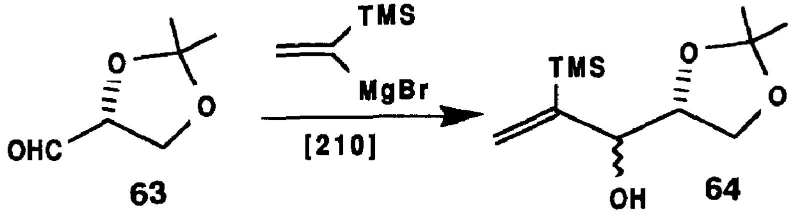
(128)

The reaction of hexachlorobenzene with lithium and trimethylchlorosilane produces tetrakis(trimethylsilyl)allene in excellent yield. (Eqn. 129)



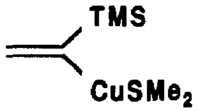
(129)

Vinylsilanes were prepared from the reaction of α-metallated vinylsilanes with various electrophiles. α-Trimethylsilylvinylmagnesium bromide was reacted with aldehyde **63** to give **64**. The copper reagent prepared from the Grignard reacted even better. (Eqn. 130) This Grignard reagent was also cross-coupled with vinyl bromides to give 3-trimethylsilyl-1,3-butadienes. (Eqn. 131) The lithium reagent **65** was reacted with a variety of electrophiles including methanol, iodomethane, benzaldehyde, butanal, cyclohexanone, benzoyl chloride, acetyl chloride, trimethylchlorosilane, -germane and -stannane. (Eqn. 132) The reaction with aldehydes and cyclohexanone were much better in the presence of boron fluoride etherate.

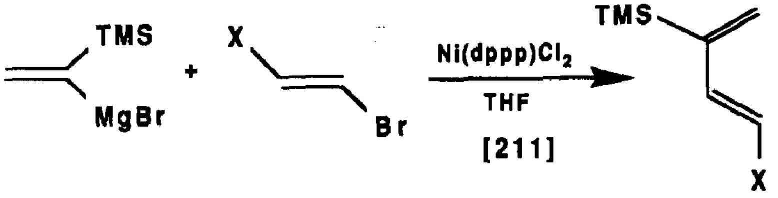


63 64 (130)

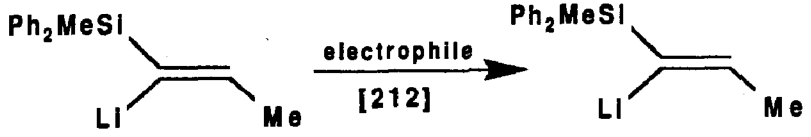
85%; syn:anti = 1:3



(gave all syn product)

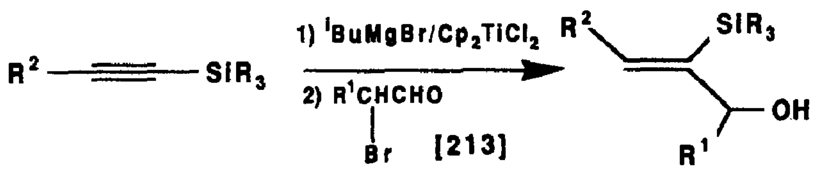


(131)



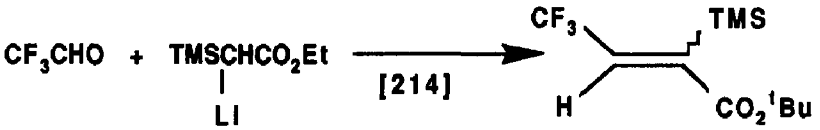
65 (132)

The titanium (IV) catalyzed hydromagnesiation of ethynylsilanes provides the corresponding α-silyl-α-bromomagnesiovinylsilane, which can be reacted with electrophiles. The reaction with α-bromoaldehydes was reported. (Eqn. 133)



(133)

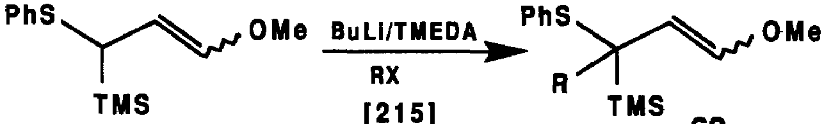
Tert-butyl lithio(trimethylsilyl)acetate was reacted with trifluoroacetaldehyde to give vinylsilane **66**. (Eqn. 134)



**66**

(134)

α-Thiophenoxyallylsilane **67** was alkylated to give key intermediate **68** (Eqn. 135), which was used to prepare β-trimethylsilyl-α, β-unsaturated aldehydes (Eqn. 136) and β-trimethylsilyl-α, β-unsaturated ketones *via* intermediate **69** (Eqns. 137, 138)

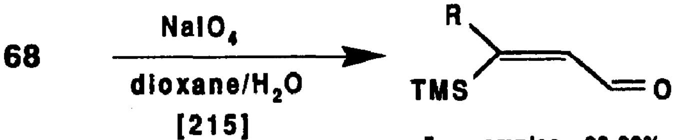


**67**

**68**

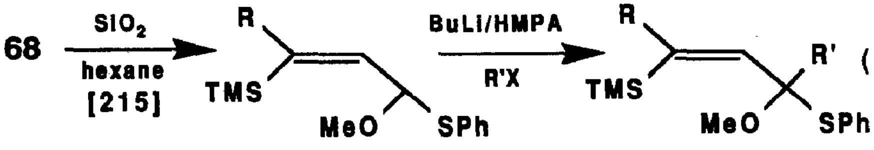
5 examples; 69-80%

(135)



5 examples 62-80%

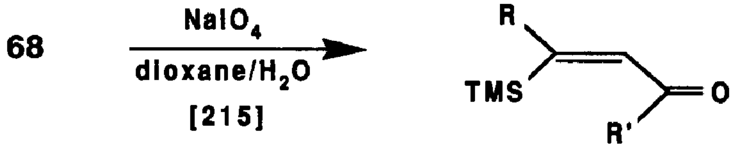
(136)



4 examples; 83-92%

**69**

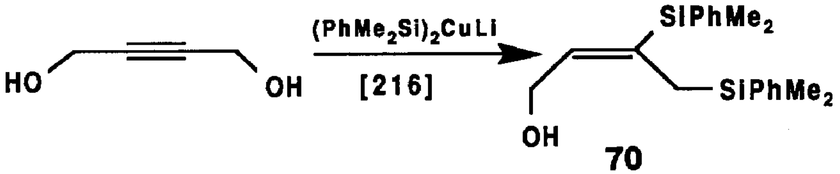
(137)



4 examples; 48-62%

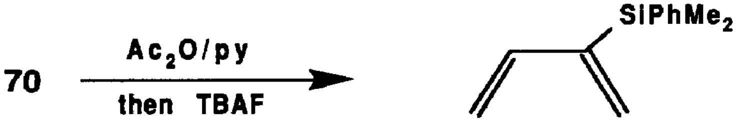
(138)

The addition of silyl organometallic reagents to triple bonds was employed for the preparation of vinylsilanes. The reaction of 3-butyn-1,4-diol with lithium bis(phenyldimethylsilyl)cuprate gave 3,4-bis(trimethylsilyl)-2-buten-1-ol **70**. (Eqn. 139) This was converted to the acetate (98% yield) and the acetate deacetoxysilylated with fluoride ion to produce 2-(phenyldimethylsilyl)-1,3-butadiene. (Eqn. 140) This silylated diene was reacted with maleic anhydride to give the cycloadduct. (Eqn. 141) Diene **71** could also be prepared directly from **70** by treatment with p-toluenesulfonic acid.



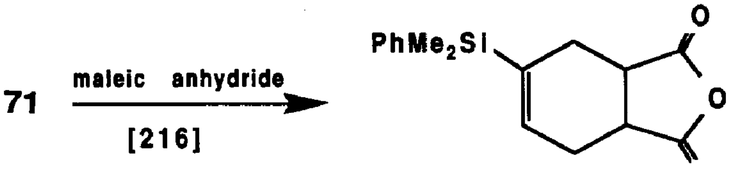
**70**

(139)



**71**

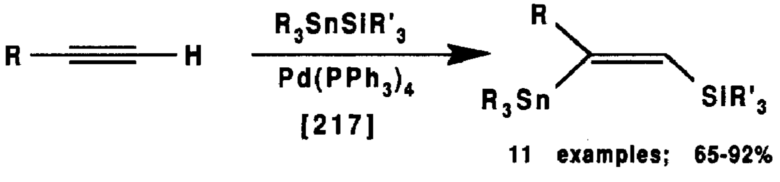
(140)



65%

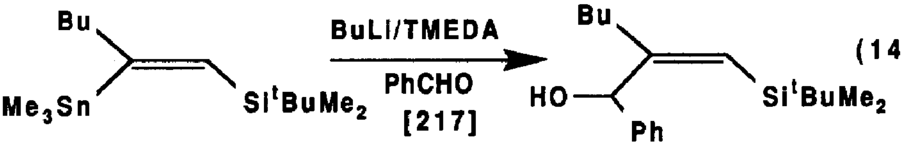
(141)

The Si-Sn bond can be added across the triple bond of terminal acetylenes with palladium (0) catalysis. (Eqn. 142) The silicon adds to the terminal carbon. The resulting vinylsilanes, which are also vinylstannanes undergo some useful reactions. (Eqns. 143, 144, 145)

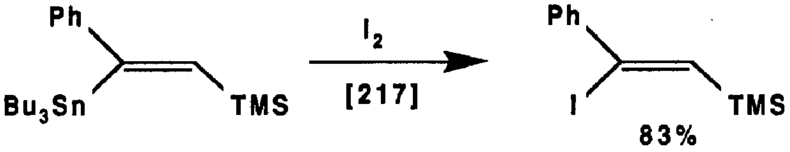


(142)

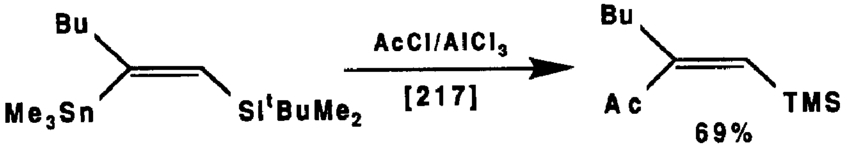
($R_3Sn$ = $Me_3Sn$, $Bu_3Sn$, $Ph_3Sn$; $R'_3Si$ = $Me_3Si$, ${}^tBuMe_2Si$)



(143)

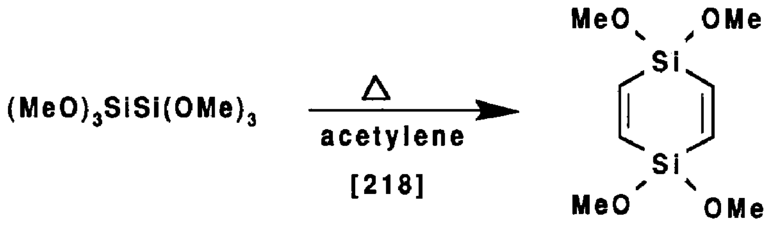


(144)



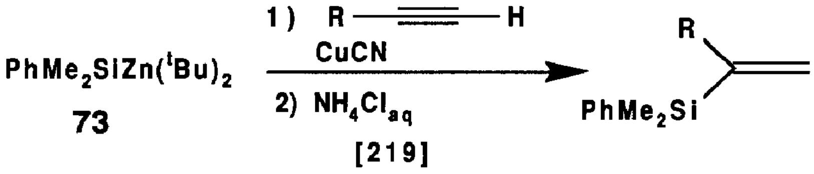
(145)

Hexamethoxydisilane was added to acetylene itself under pyrolytic conditions to give disilacycle **72**. (Eqn. 146)



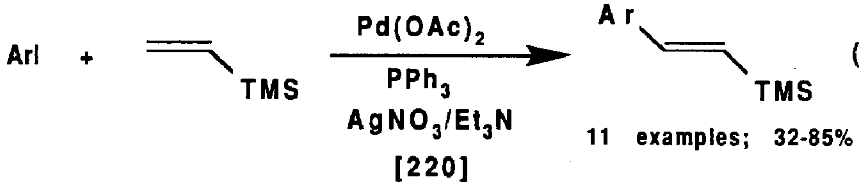
**72** (146)

Phenyldimethylsilyllithium was converted to silylzincate **73**, which was added to acetylenes to give the corresponding vinylsilane with the silicon adding to the more substituted carbon. (Eqn. 147) The addition to the internal unsaturation occurs, but without regioselectivity.

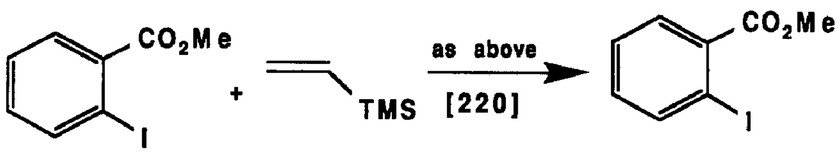


(147)

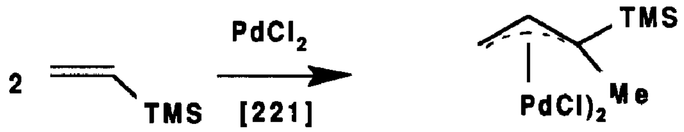
Vinyltrimethylsilane was arylated with aryl iodides in the presence of palladium (II) acetate and silver nitrate. (Eqns. 148, 149) Vinyltrimethylsilane was reacted with palladium (II) chloride to provide a silylated π-allylpalladium complex **74**, which was reacted with nucleophiles to give vinylsilanes. (Eqn. 150)



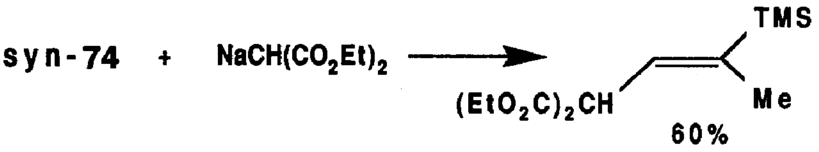
(148)



(149)



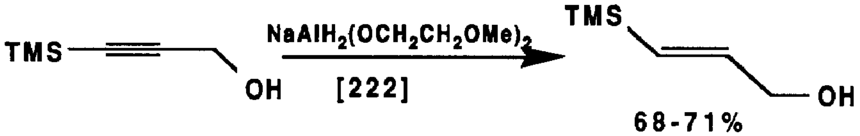
**74**



(150)

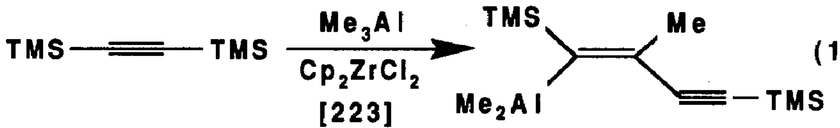
**anti-74** gives the (Z) isomer

A convenient synthesis of (E)-3-(trimethylsilyl)-2-propen-1-ol, a valuable precursor to several useful carbofunctional vinylsilanes was reported. (Eqn. 151)



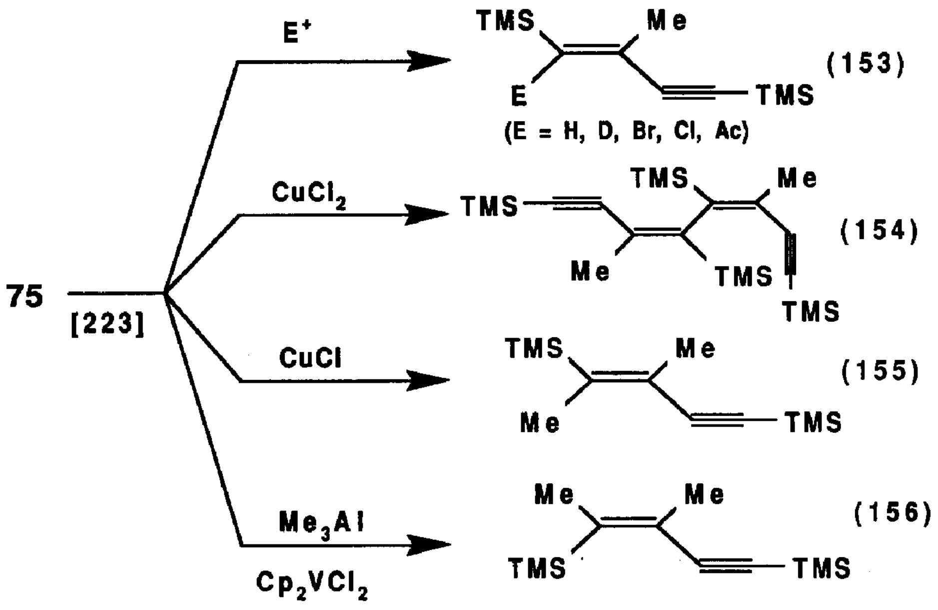
(151)

Treatment of 1,4-bis(trimethylsilyl)-1,3-butadiyne with trimethylaluminum leads to a variety of silylated enynes via intermediate **75** as shown in Eqns. 152-155.

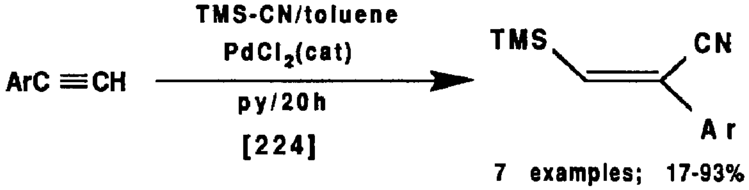


**75**

(152)

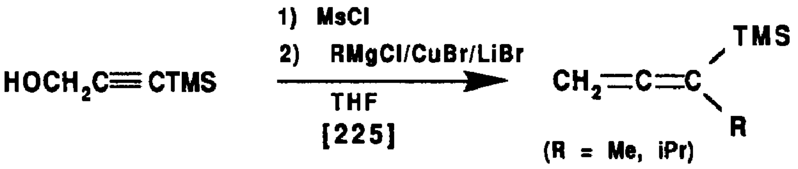


Trimethylsilyl nitrile can be added to aryl acetylenes according to Eqn. 157. The addition is cis.

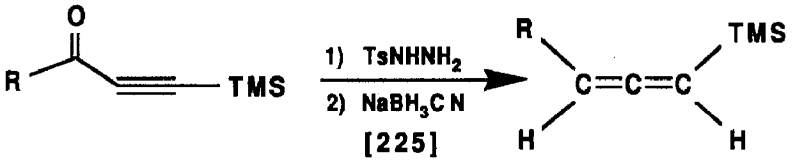


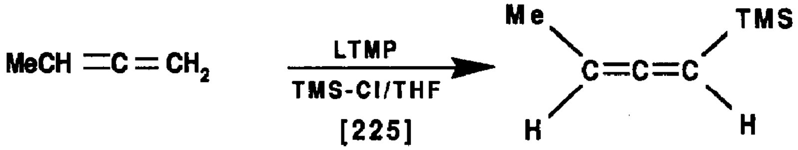
(157)

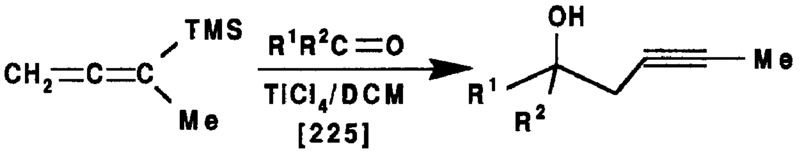
Allenyltrimethylsilanes were prepared by three routes as shown. (Eqns. 158, 159, 160) These were employed in the preparation of homopropargylic alcohols. (Eqn. 161)



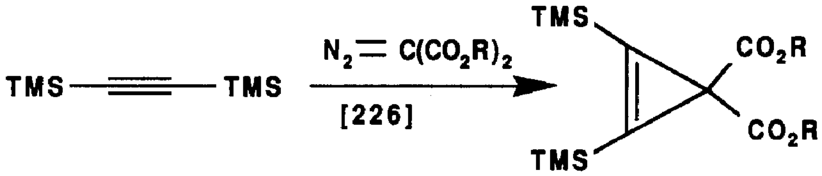
(158)

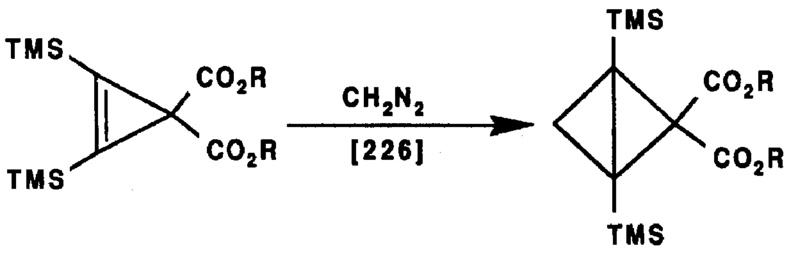

(159)


(160)

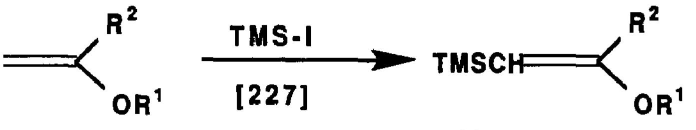

(161)

Bis(trimethylsilyl)acetylene was reacted with α-diazo malonic esters to give trimethylsilylcyclopropenes, which were also reacted with diazomethane to give the silylated bicyclobutanes. (Eqns. 162, 163) Desilylation of the silylated cyclopropenes is possible with potassium fluoride.


(162)


(163)

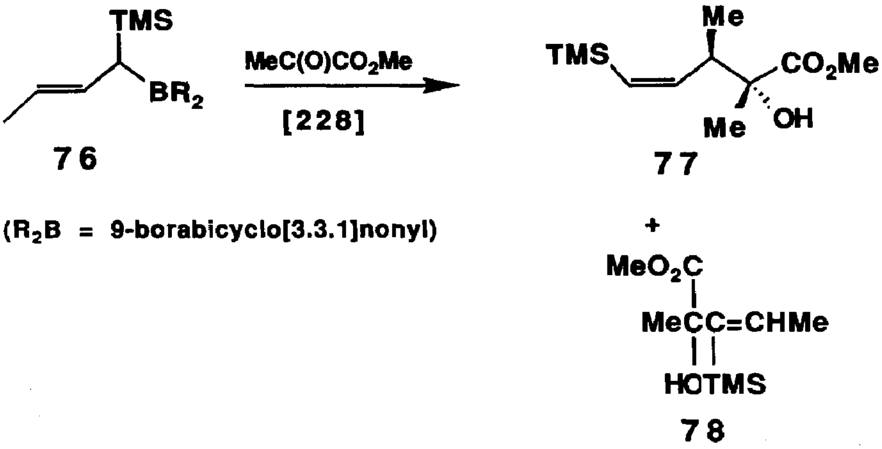
Enol ethers were shown to react directly with trimethylsilyl iodide to give vinylsilanes, presumably *via* addition elimination. (Eqn. 164)



(164)

($R^1$ = Me, Bu; $R^2$ = $CH_3$, $CH_2CH_3$)

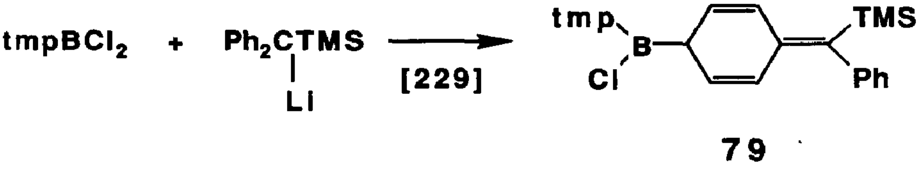
α-Borylallylsilane **76** was reacted with methyl pyruvate to give vinylsilanes **77** and **78**. (Eqn. 165)



(165)

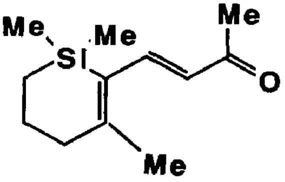
($R_2B$ = 9-borabicyclo[3.3.1]nonyl)

Tetramethylpiperidinoboron dichloride, (tmp)$BCl_2$, reacts with α-lithiobenzhydryltrimethylsilane to give **79**. (Eqn. 166)



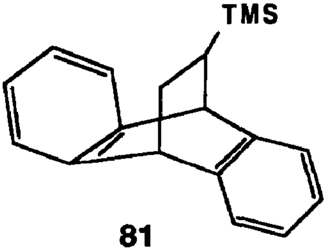
(166)

A nine-step improved synthesis of **80** was reported. [230]



**80**

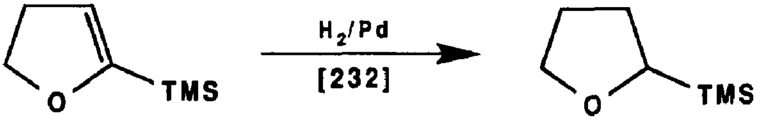
The kinetics of the retro-Diels-Alder reaction of **81** was studied. The reaction is first order with k = 146 x $10^{-5}$ $sec^{-1}$ with a relative rate of 123 versus the protonated analog. [231]



**81**

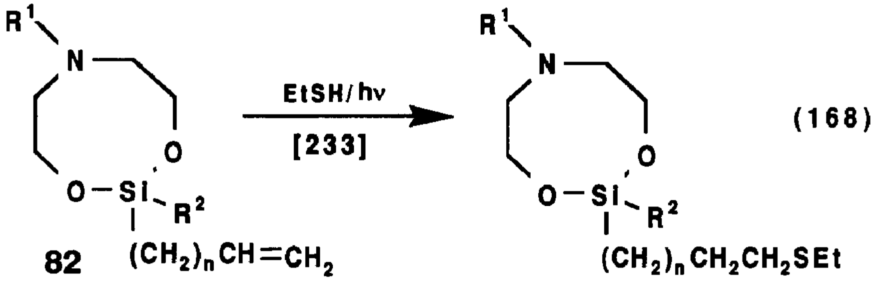
## B. VINYLSILANES--REACTIONS

The hydrogenation of (4,5-dihydro-2-furyl)silanes and germanes was carried out to give the tetrahydrofurylsilanes. (Eqn. 167) The hydrogenation of bis(4,5-dihydro-2-furyl)dimethylsilane occurred in a stepwise manner with isolation of the monoreduced intermediate possible.



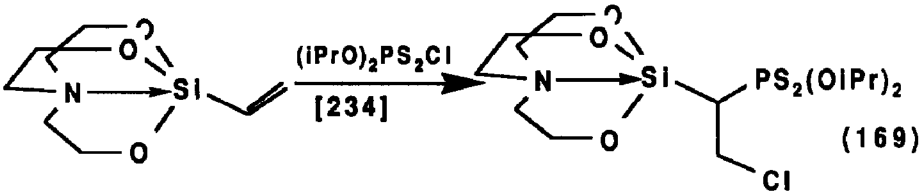
(167)

The vinyl (and allyl) silanes **82** were reacted with ethyl mercaptan to give the addition products in good yield. (Eqn. 168) Vinylsilatrane was reacted with diisopropylthiophosphorylsulfenyl chloride (Eqn. 169) and diisopropylthiophosphorylsulfenic acid (Eqn. 170) to give the addition products. Benzenesulfonyltribromomethane was added to vinyltrimethylsilane thermally or photochemically to give **83**.

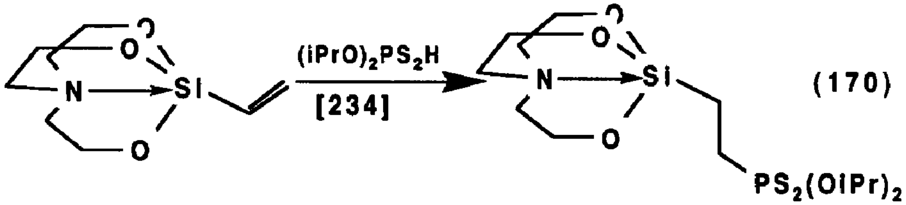


(168)

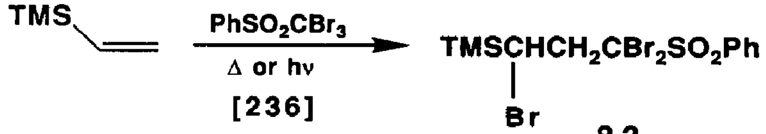
($R^1$ = H, Me, Ph; $R^2$ = Me, Et); n = 0, 1)



(169)



(170)

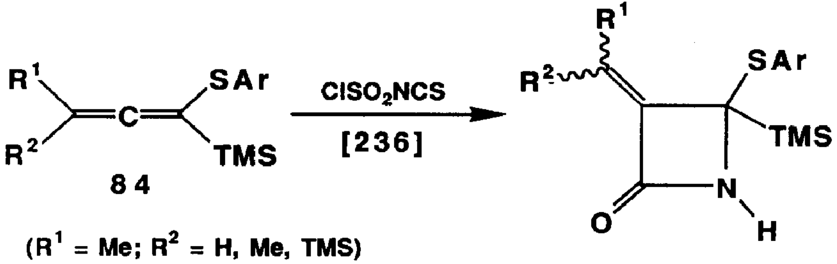


(171)

**83**

46% with Δ; 81% with hν

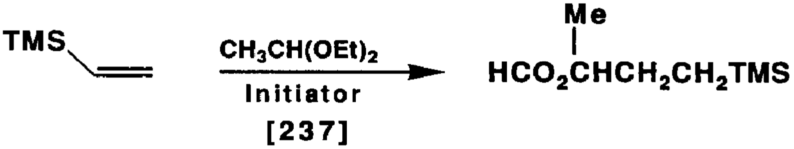
The cycloaddition of isothiocyanotosulfonyl chloride with allenylsilanes **84** provides an entry into α-alkylidene-β-lactams. (Eqn. 172) The initially formed α-functional organosilanes can be protiodesilylated with fluoride ion.



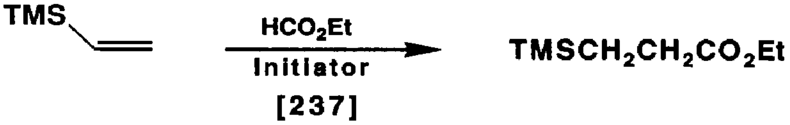
(172)

($R^1$ = Me; $R^2$ = H, Me, TMS)

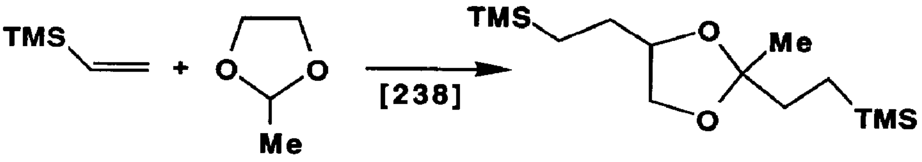
Vinyltrimethylsilane was reacted with 1,1-diethoxyethane and with ethyl formate under catalysis with free radicals to give the products shown in Eqns. 173 and 174.



(173)

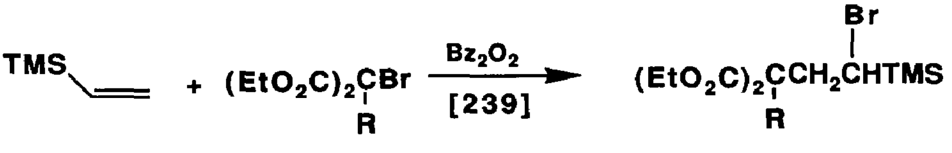


(174)

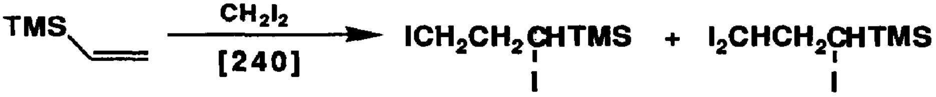


(175)

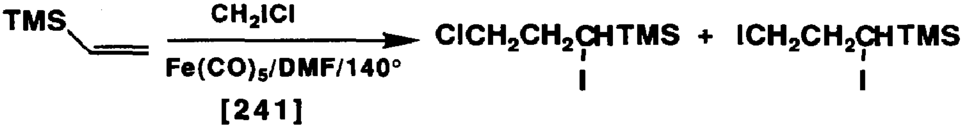
α-Bromomalonates were added to vinyltrimethylsilane under free radical conditions. (Eqn. 176) Diiodomethane was added to vinyltrimethylsilane under free radical conditions or with iron pentacarbonyl. (Eqn. 177) Iodochloromethane was also added to vinyltrimethylsilane. (Eqn. 178)



$$\text{TMS-CH=CH}_2 + (\text{EtO}_2\text{C})_2\text{C(R)Br} \xrightarrow[\text{[239]}]{\text{Bz}_2\text{O}_2} (\text{EtO}_2\text{C})_2\text{C(R)CH}_2\text{CH(Br)TMS} \quad (176)$$

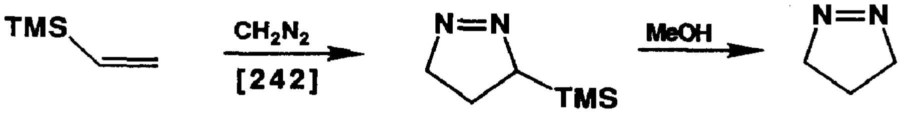


$$\text{TMS-CH=CH}_2 \xrightarrow[\text{[240]}]{\text{CH}_2\text{I}_2} \text{ICH}_2\text{CH}_2\text{CH(I)TMS} + \text{I}_2\text{CHCH}_2\text{CH(I)TMS} \quad (177)$$

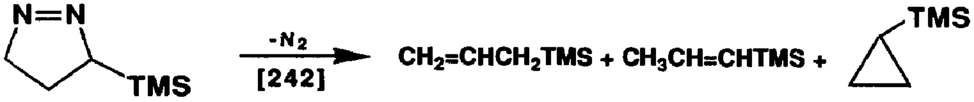


$$\text{TMS-CH=CH}_2 \xrightarrow[\text{Fe(CO)}_5\text{/DMF/140°}\ \text{[241]}]{\text{CH}_2\text{ICl}} \text{ClCH}_2\text{CH}_2\text{CH(I)TMS} + \text{ICH}_2\text{CH}_2\text{CH(I)TMS} \quad (178)$$

Diazomethane was added to vinyltrimethylsilane. (Eqn. 179) The adduct was protiodesilylated with methanol and lost molecular nitrogen to give allyltrimethylsilane, (Z) and (E) 1-propenyltrimethylsilanes and, as the major product, cyclopropyltrimethylsilane. (Eqn. 180)

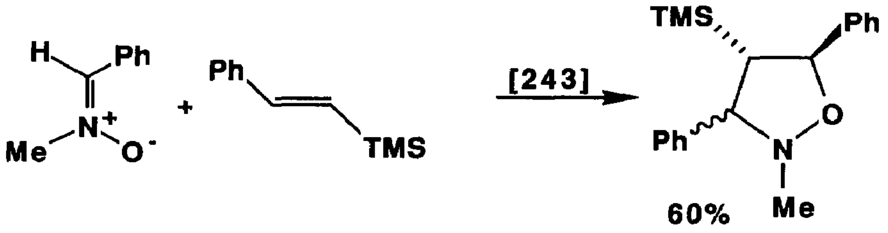


(179)

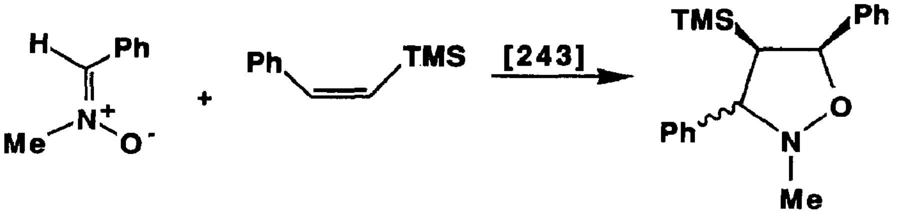


(180)

The cycloaddition of nitrones with vinylsilanes was carried out. The reaction is stereoselective with respect to the geometry of the vinylsilane. (Eqns. 181, 182)

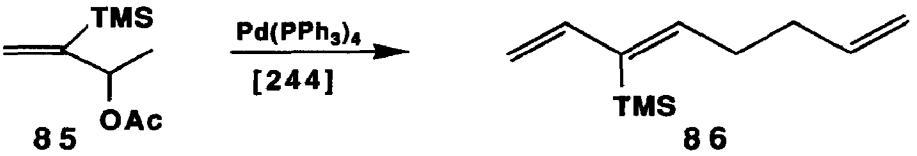


(181)

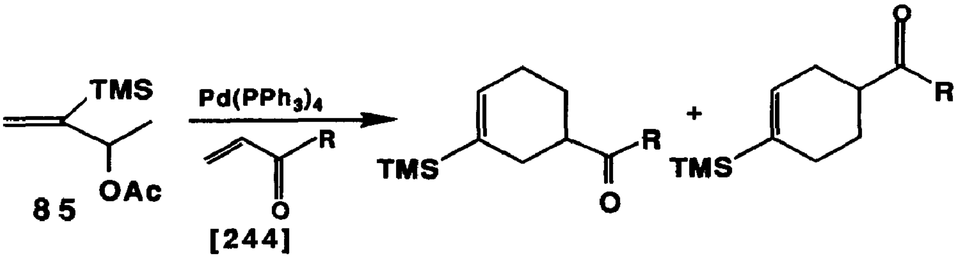


(182)

Treatment of vinylsilane **85** with palladium(O) failed to give 2-trimethylsilyl-1,3-butadiene, but gave **86** instead. (Eqn. 183) When treated with palladium(O) in the presence of a dienophile **85** gave the cycloadduct in moderate yield. (Eqn. 184)



(183)



(184)

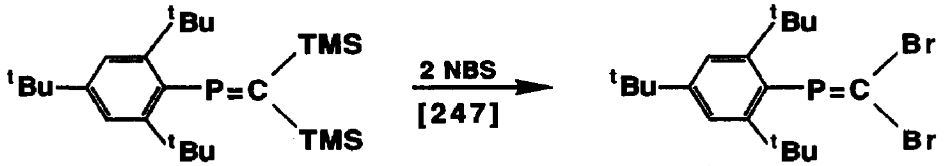
Hydrochloric acid was added to vinylchlorosilanes in the presence of various metal chlorides. (Eqns. 185, 186)

$$R_n(CH_2{=}CH)_{4-n}Si \xrightarrow[\text{[245]}]{\text{HCl/catalyst}} R_nCl_{4-(n+k)}Si(CH{=}CH_2)_k \qquad (185)$$

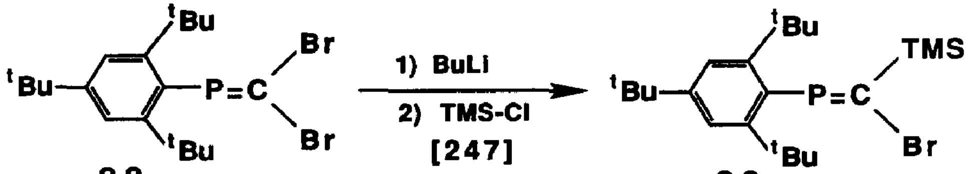
(catalyst = $AlCl_3$, $FeCl_3$, $SbCl_3$, $SnCl_4$)

$$R_m(CH{=}CH_2)_{4-(m+n)}Si(Cl)_n \xrightarrow[\text{[246]}]{\text{HCl/catalyst}} R_mCl_{n+1}Si(CH{=}CH_2)_{3-(m+n)} \qquad (186)$$

The electrophilic substitution of vinylsilanes was used as an entry into several systems. Dibromomethylenephosphine **88** was prepared from the corresponding vinylsilane **87**. (Eqn. 187) The dibromide **88** was used to prepare vinylsilane **89**. (Eqn. 188)

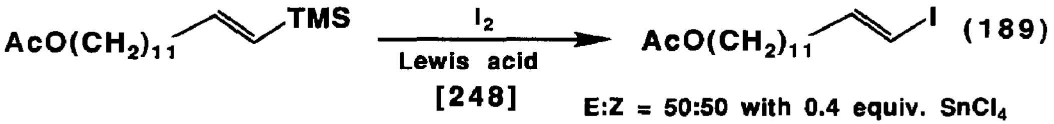


**87** **88** (187)



**88** **89** (188)

The iododesilylation of vinylsilanes to produce vinyl iodides was found to be "tunable" in terms of the stereoselectivity by the amount of Lewis acid employed in the reaction. This was employed as a key step in the preparation of insect pheromones which are precise mixtures of (Z) and (E) olefins. (Eqn. 189)



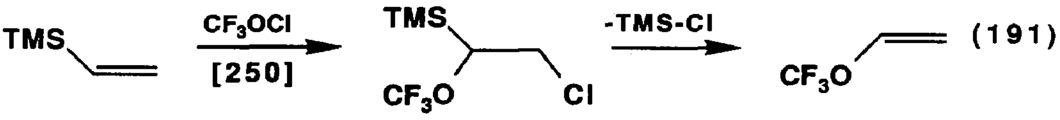
E:Z = 50:50 with 0.4 equiv. $SnCl_4$
E:Z = 80:20 with 1.1 equiv. $AlCl_3$

The very sterically crowded tris(trimethylsilylmethyl)dimethylvinylsilane **90** was reacted with various electrophiles to give desilylation as shown in Eqn. 190.

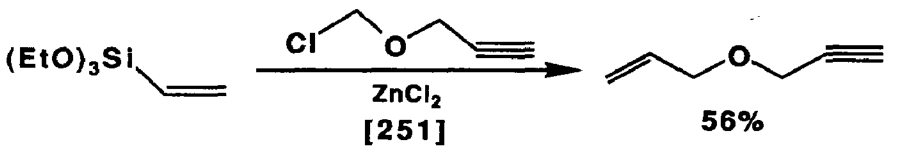
$$\underset{\mathbf{90}}{(TMS)_3CSiMe_2CH{=}CH_2} \xrightarrow[\substack{-CH_2{=}CHY \\ [249]}]{X\text{-}Y} (TMS)_3CSiMe_2X \qquad (190)$$

($X\text{-}Y = ClI, Br_2, I_2, CF_3CO_2H$)

Trifluoromethoxy chloride reacts with vinyltrimethylsilane to give trifluoromethylvinyl ether *via* an addition elimination process. (Eqn. 191) The same reaction occurs with vinyltrimethoxysilane and vinyltrichlorosilane.

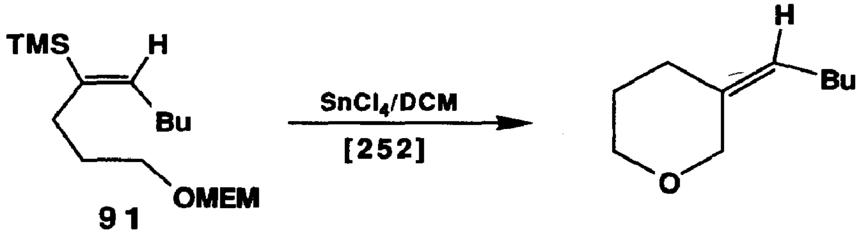


Propargyloxymethylation of vinyltriethoxysilane was accomplished from chloromethylpropargyl ether and zinc chloride. (Eqn. 192)



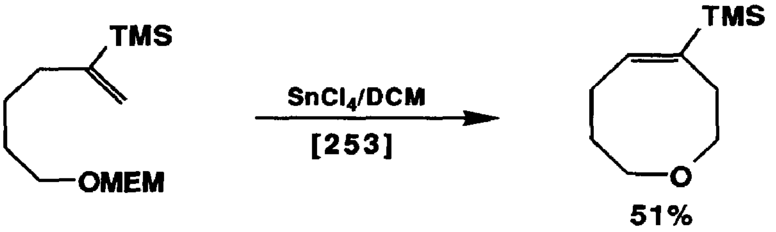
(192)

The intramolecular cyclization of vinylsilane **91** and similar systems was shown to be very highly stereospecific. (Eqn. 193) In the formation of larger rings the trimethylsilyl group is not lost. (Eqn. 194)



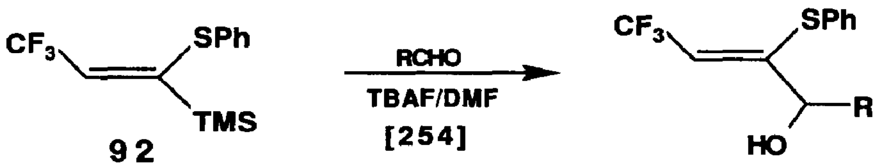
**91**

(193)



(194)

Vinylsilane **92** was looked at as an entry into trifluoromethylated organic molecules. It condenses with aldehydes under fluoride ion catalysis. (Eqn. 195)

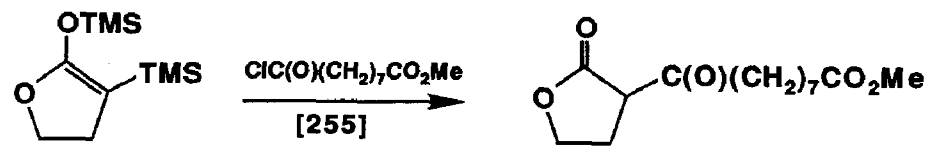


**92**

(195)

(8 examples: 34-90%)

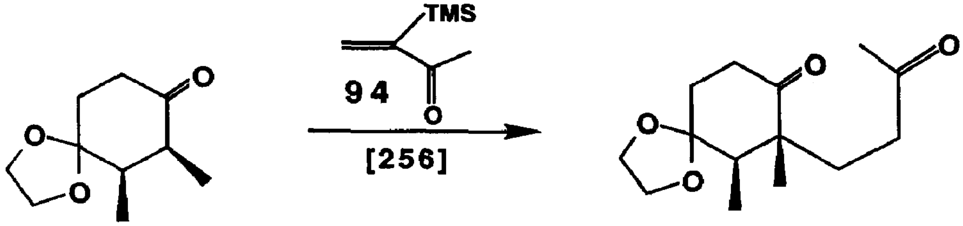
Vinylsilane **93** reacts as a trimethylsilylketene acetal with acid chlorides to give γ-keto-γ-lactones. (Eqn. 196)



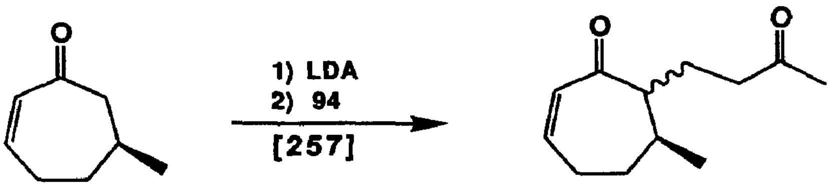
**93**

(196)

3-Trimethylsilylbut-3-en-2-one **94** was used in directing the addition of an enolate towards conjugate addition as opposed to 1,2-addition. (Eqn. 197) A second example is shown in Eqn. 198 as a key step in the preparation of racemic Clavularin B.

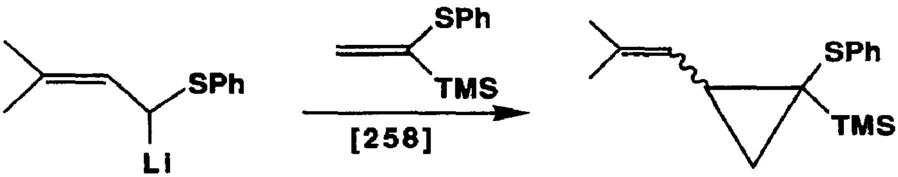


(197)



(198)

α-Thiophenoxytrimethylsilylcyclopropanes were nicely prepared via the addition of α-thiophenoxyallyllithium reagents to α-thiophenoxyvinyltrimethylsilane. (Eqn. 199)

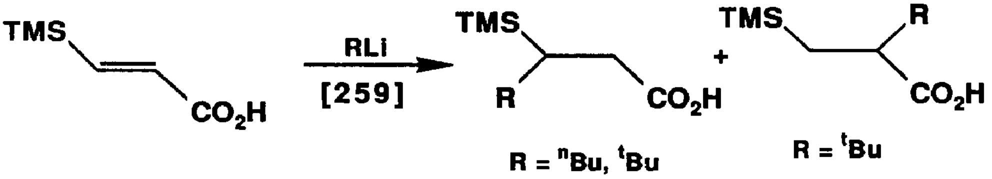


(199)

100%

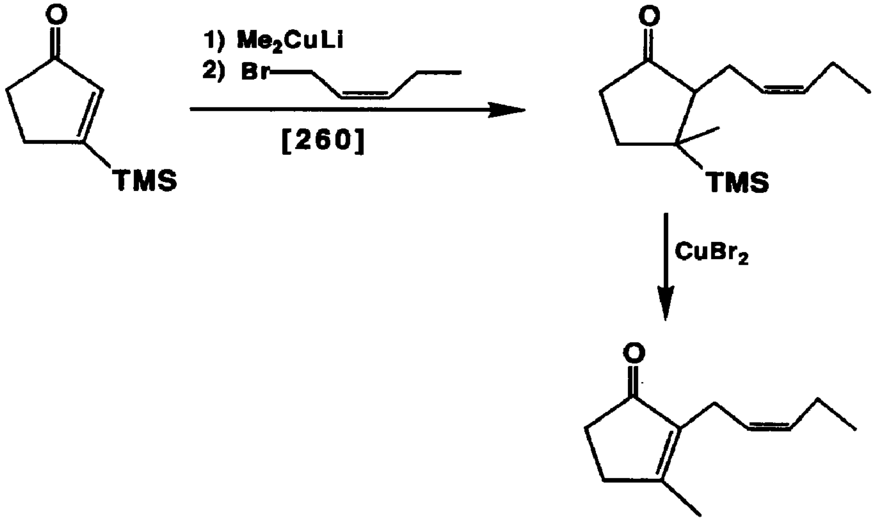
5 examples; 76-100%

(E) β-Trimethylsilylacrylic acid reacted with n-butyllithium to give the product of Michael addition after protonation, but with tert-butyllithium to give considerable amounts of the anti-Michael addition. (Eqn. 200) Interestingly, the (E) β-phenylacrylic acid showed the same behaviour.



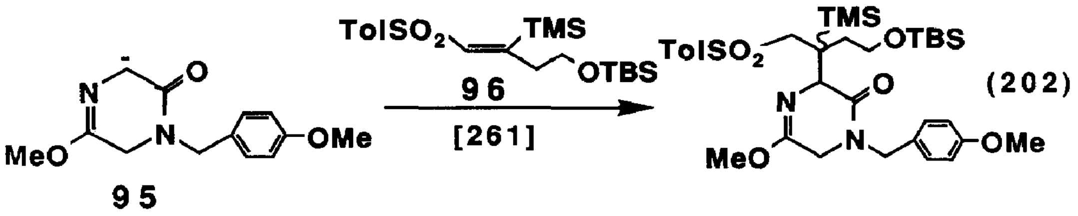
(200)

The addition of lithium dimethylcuprate to β-trimethylsilylcyclopent-2-enone was a key step in the preparation of jasmone. A second key step involving the silicon group was the regio-selective bromination-elimination sequence as shown. (Eqn. 201)

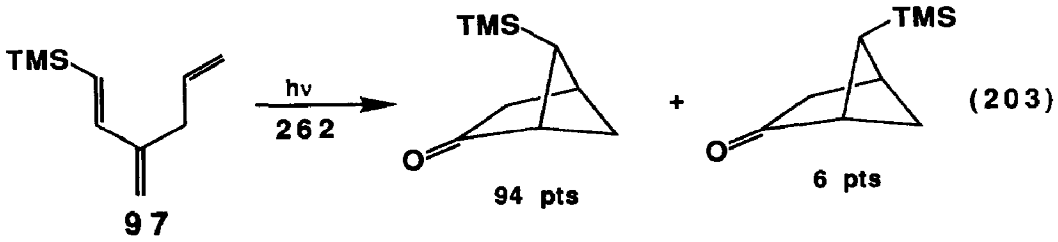


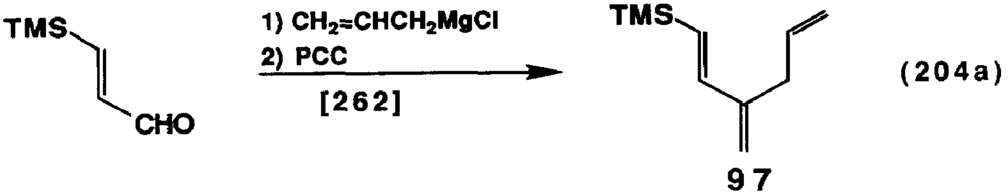
(201)

A key step in a synthesis of bicyclomycin was the addition of anion **95** to trimethylsilylsulphone **96**. (Eqn. 202)

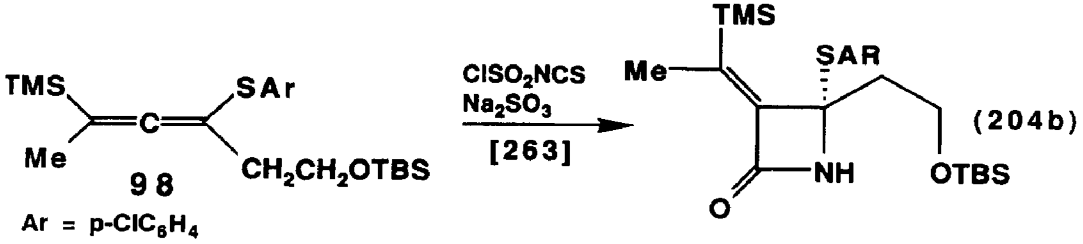


The intramolecular photocyclization of the trimethylsilylated 1,5-diene **92** was accomplished. (Eqn. 203) The requisite diene was prepared as shown in Eqn. 204a.

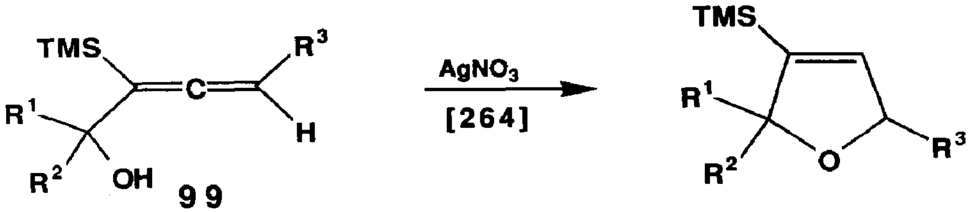




The addition of chlorosulfonyl nitrile to allenylsilane **98** was a key step in a formal synthesis of racemic thienamycin. (Eqn. 204b)

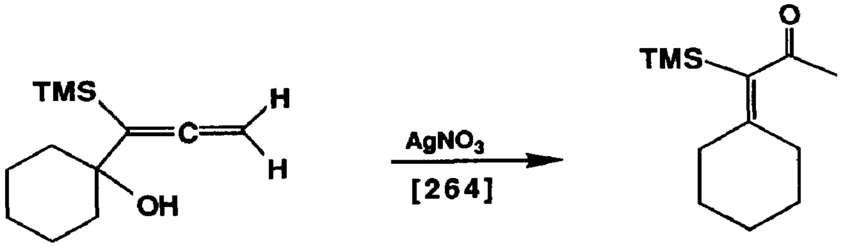


Allenylsilanes **98** were cyclized to the silylated dihydrofurans in good yields. (Eqn. 205) Some reactions took another route as seen in Eqn. 206.



(205)

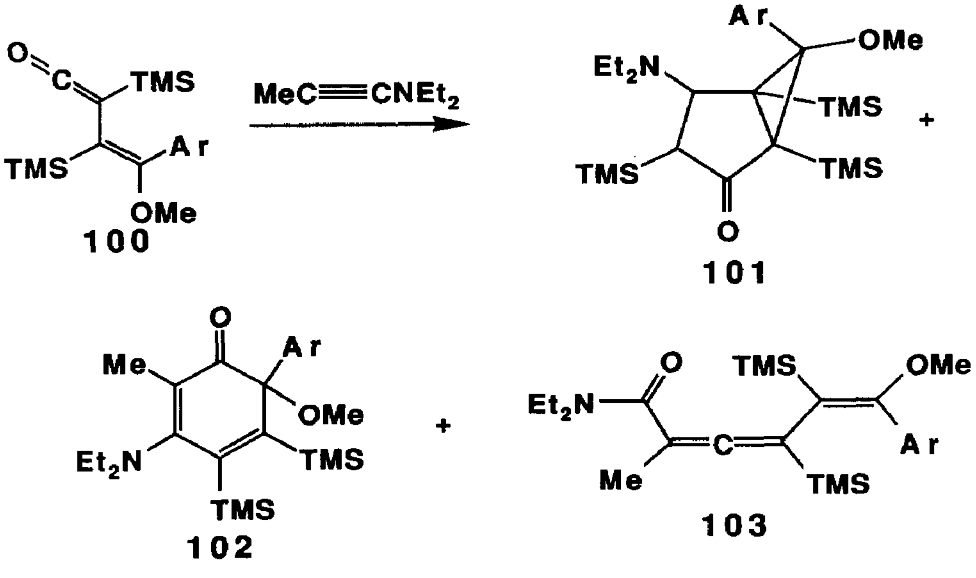
6 examples: 42-72%



(206)

24%

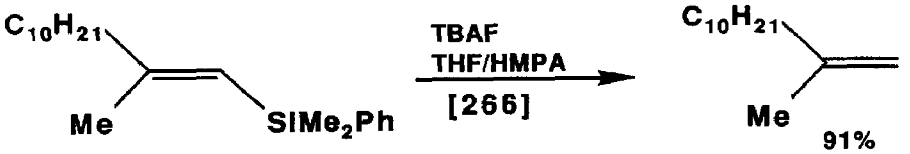
The cycloaddition of diethylpropynylamine to the trimethylsilylated vinyl ketene **100** gave **101**, **102** and **103**. (Eqn. 207)



(207)

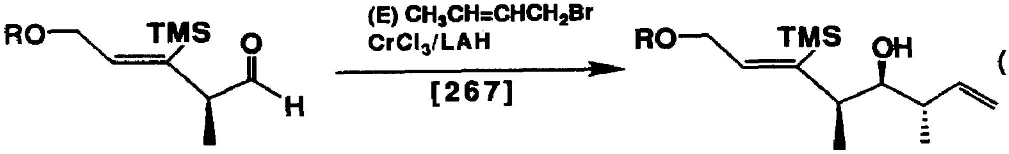
Ar = p-H, Me or $CF_3$-$C_6H_4$

It was found that the silicon-vinyl bond is readily cleaved with fluoride ion when the silyl group is the phenyldimethylsilyl group. (Eqn. 208) The allyldimethylsilyl and alkoxydimethylsilyl groups are also readily cleaved from the vinyl moiety under these conditions.

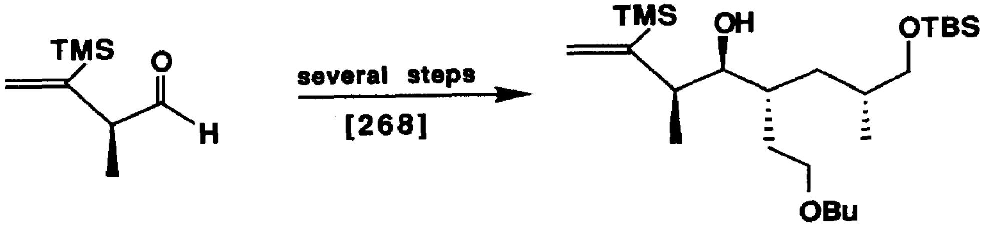


(208)

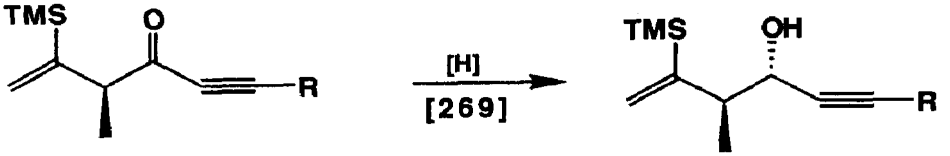
The trimethylsilyl group attached to a vinyl group was employed as a large hydrogen in several instances in order to better direct the stereoselectivity of a reaction at another site in the molecule. Some examples are shown in eqns. 209-212. All four stereoisomers of **104** were prepared. [271]



(209)

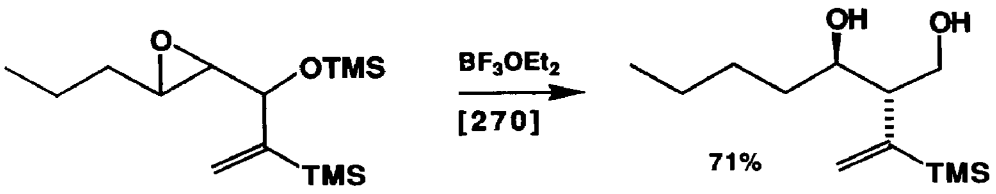


(210)

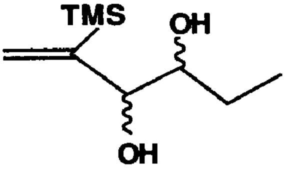


(211)

5 examples; threo:erythro 8:1 to >91:1



(212)

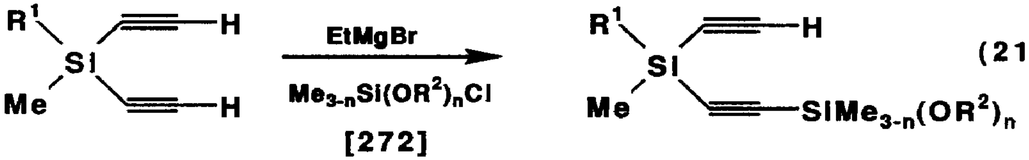


**104**

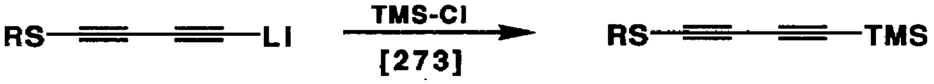
# IX. ETHYNYLSILANES

## A. PREPARATION

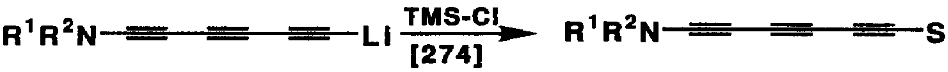
Diethynylsilanes were deprotonated and silylated to provide novel ethynylsilanes. (Eqn. 213) Thio-substituted silylated 1,3-butadiynes were prepared in a straightforward manner (Eqn. 214) as were amino-substituted silylated 1,3,5-hexatriynes (Eqn. 215).



(213)

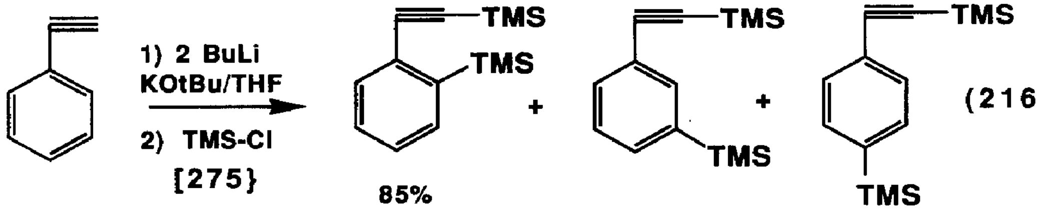


(214)



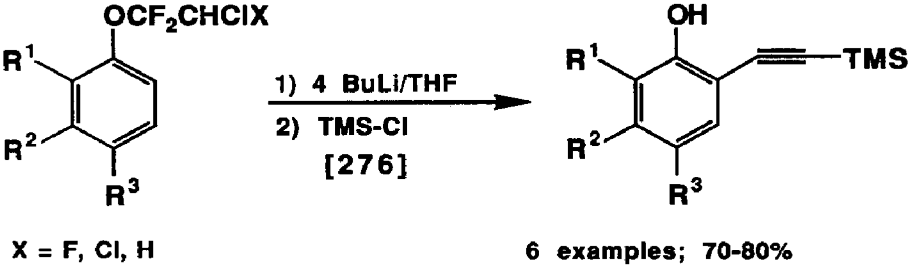
(215)

Phenylacetylene can be dimetallated with butyllithium and potassium tert-butoxide and, therefore, disilylated as well. (Eqn. 216)



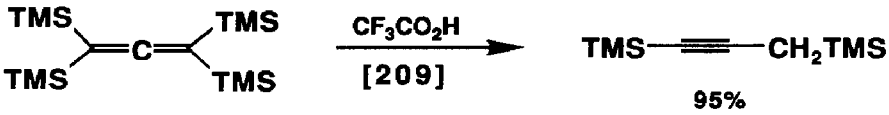
(216)

o-Hydroxyarylacetylenes were prepared from haloethyl aryl ethers upon treatment with butyllithium and a rearrangement followed by trimethylsilylation. (Eqn. 217)



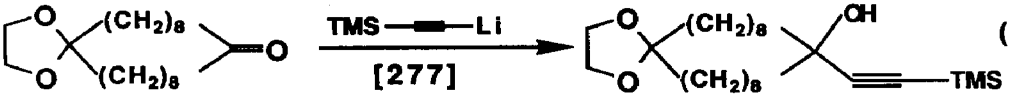
(217)

Tetrakis(trimethylsilyl)allene is converted to 1,3-bis(trimethylsilyl)propyne upon treatment with 2 equivalents of trifluoroacetic acid. (Eqn. 218)



(218)

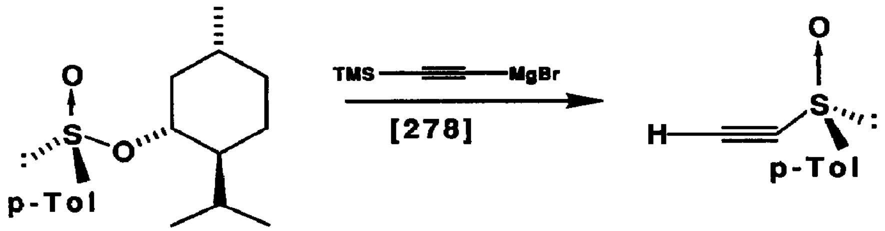
A number of ethynylsilanes were prepared from existing ethynylsilanes. Trimethylsilylethynyllithium was reacted with monoprotected diketone **105** in a key step leading to the synthesis of the first bicyclic cumulatriene. (Eqn. 219)



**105**

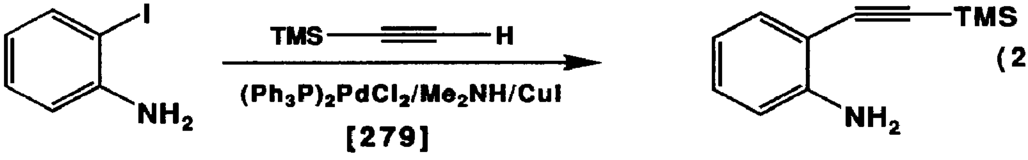
(219)

Trimethylsilylethynylmagnesium bromide was reacted with optically active sulfoxides to produce optically active ethynylsulfoxides. (Eqn. 220)



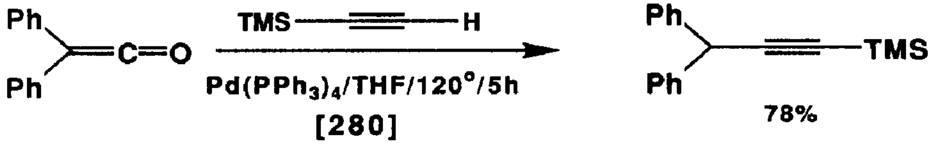
(220)

Trimethylsilylacetylene was coupled with aryl iodides in the presence of a palladium(II) catalyst to give the arylethynylsilanes, which could be protiodesilylated. (Eqn. 221)



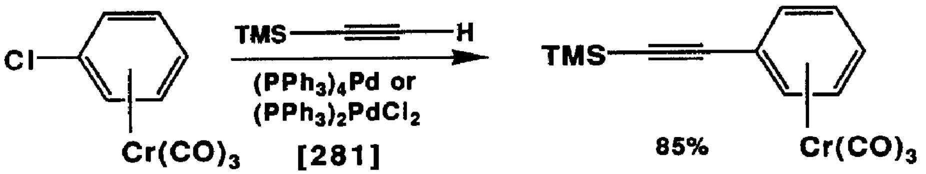
(221)

Trimethylsilylacetylene was also reacted with diphenylketene to give benzhydrylethynyltrimethylsilane. (Eqn. 222)



(222)

Trimethylsilylacetylene was reacted with the chromium tricarbonyl complex of chlorobenzene to give the ethynylaryl chromium complex. (Eqn. 223)

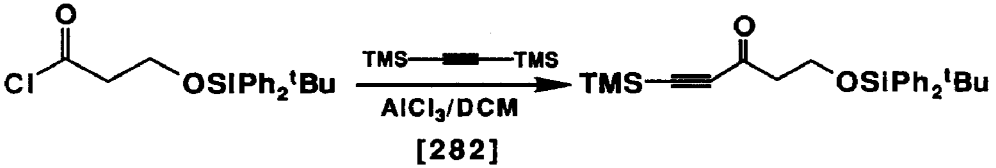


(223)

Trimethylsilylacetylenes figured into the general strategy for the synthesis of monohydroxyeicosatetraenoic acids. Two of the applications are shown below. (Eqns. 224, 225)

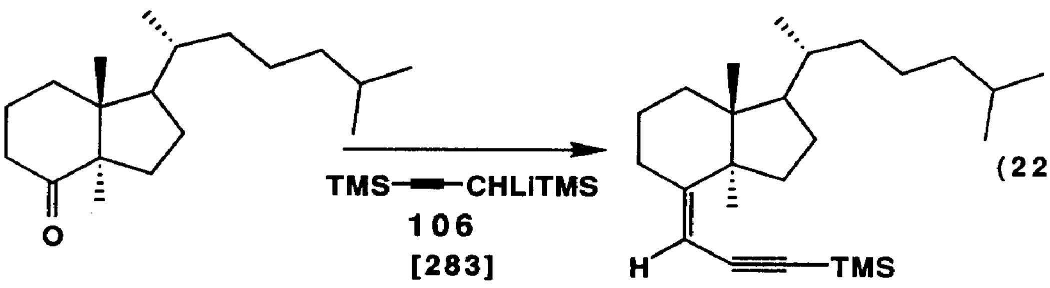
$$BrMg-C\equiv C-(CH_2)_3C(OMe)_3 \xrightarrow[[282]]{TMS-C\equiv C-CH_2OTs} TMS-C\equiv C-CH_2-C\equiv C-(CH_2)_3C(OMe)_3$$

(224)

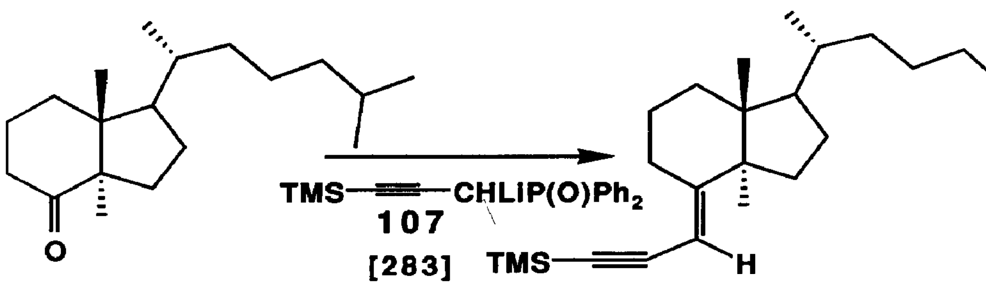


(225)

Lithiated ethynylsilanes **106** and **107** reacted with a vitamin D derived ketone to give (Z) and (E) stereoisomers, respectively. (Eqns. 226, 227)

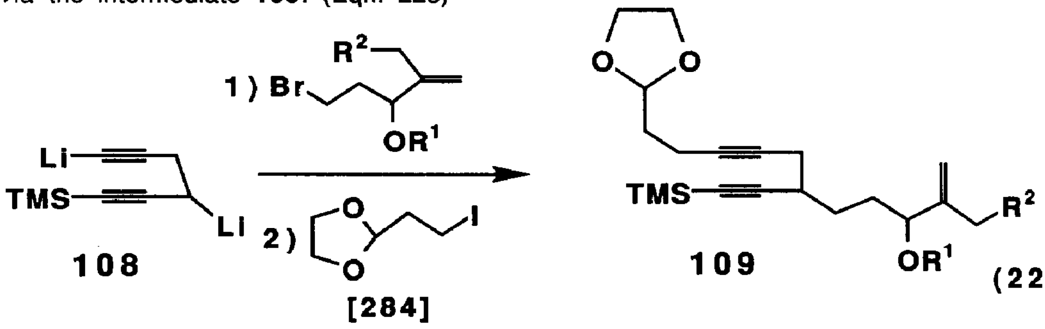


(226)



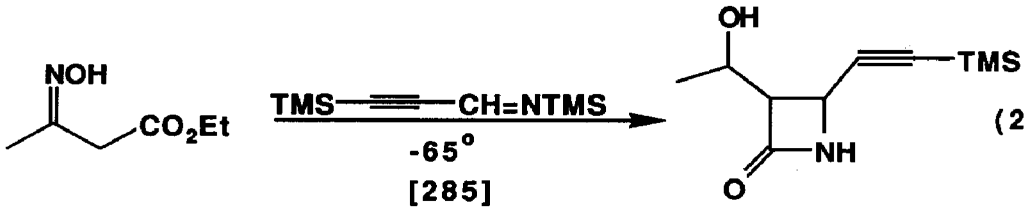
(227)

Dilithium reagent **108** was employed in the synthesis of B-ring aromatic steroids *via* the intermediate **109**. (Eqn. 228)



(228)

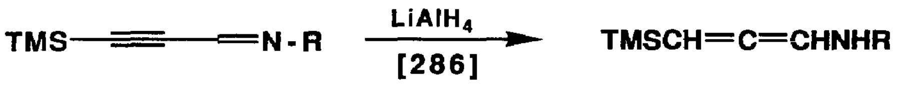
Trimethylsilylethynyl substituted azetidinone derivatives were prepared. (Eqn. 229)



(229)

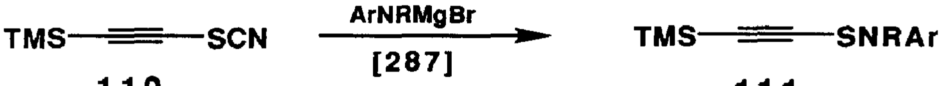
Trimethylsilylated propargyl amines were obtained by reduction of trimethylsilylethynyl imines. (Eqn. 230) In the case of alkylated imines the products were the allenyl imines. (Eqn. 231)

$$\mathrm{TMS}{-}{\equiv}{-}{=}\mathrm{N\text{-}Ar} \xrightarrow[\text{[286]}]{\mathrm{LiAlH_4}} \mathrm{TMS}{-}{\equiv}{-}\mathrm{CH_2NHAr} \qquad (230)$$



(231)

Trimethylsilylethynyl thiocyanate **110** was converted to the N-aryl sulfenamides **111**. (Eqn. 232)

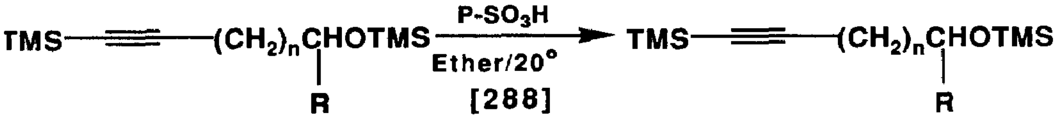


**110** **111**

(232)

**3 examples; 43 - 46%**

A method employing a polymer supported sulfonic acid was used to selectively desilylate a trimethylsilyl ether in the presence of an ethynyltrimethylsilyl group. (Eqn. 233)

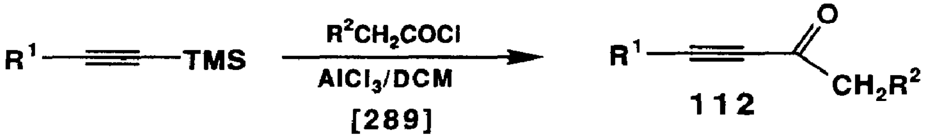


**n = 0, 2, 3; P = polymer**

(233)

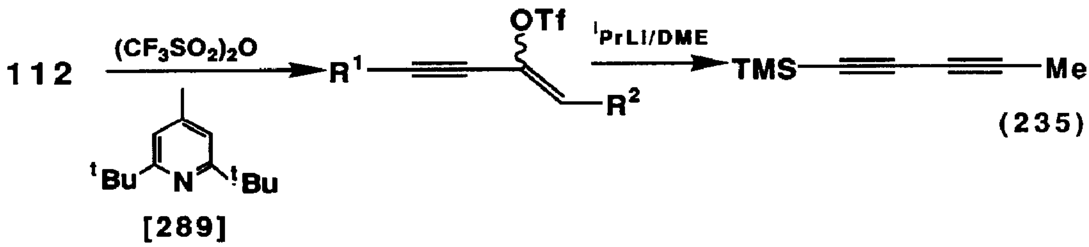
### B. ETHYNYLSILANES--REACTIONS

Several examples of the electrophilic substitution of ethynylsilanes were reported. Ethynylsilanes were acylated (Eqn. 234) and the resulting ethynyl ketones converted to enol triflates and then to trimethylsilylated 1,3-diynes (Eqn. 235)



**112**

(234)



(235)

Ethynylsilanes were converted to nitroacetylenes upon treatment with nitronium tetrafluoroborate in dichloromethane in the presence of fluoride ion. (Eqn. 236)

$$\mathrm{TMS{-}C{\equiv}C{-}TMS} \xrightarrow[\mathrm{DCM/F^-}]{\mathrm{NO_2^+\ BF_4^-}} \mathrm{TMS{-}C{\equiv}C{-}NO_2} \qquad (236)$$

[290]

The reaction of hypervalent iodine with ethynylsilanes gives ethynyliodonium salts according to Eqn. 237.

$$\mathrm{R{-}C{\equiv}C{-}TMS} \xrightarrow[\mathrm{Et_3OBF_4/DCM}]{\mathrm{(PhIO)_n}} \mathrm{R{-}C{\equiv}C{-}\overset{+}{I}{-}Ph\quad BF_4^+} \qquad (237)$$

[291] 5 examples; 56-75%

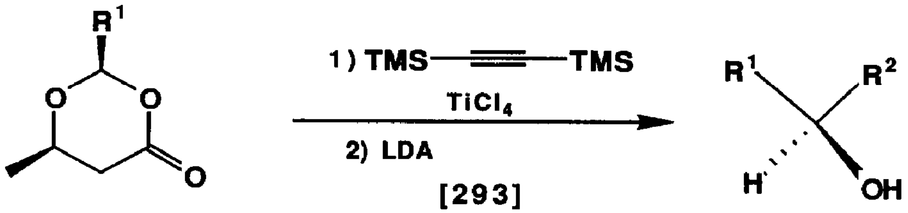
Alkylation of ethynylsilanes is possible with tertiary alkyl chlorides, again in an electrophilic process. (Eqn. 238) The bis alkylation of bis(trimethylsilyl)acetylene is possible as well. (Eqn. 239)

$$\mathrm{R^1{-}C{\equiv}C{-}TMS} \xrightarrow[\mathrm{[292]}]{\mathrm{R^2Cl/AlCl_3/DCM}} \mathrm{R^1{-}C{\equiv}C{-}R^2} \qquad (238)$$

$$\mathrm{TMS{-}C{\equiv}C{-}TMS} \xrightarrow[\mathrm{[292]}]{\mathrm{R^2Cl/AlCl_3/DCM}} \mathrm{R^2{-}C{\equiv}C{-}R^2} \qquad (239)$$

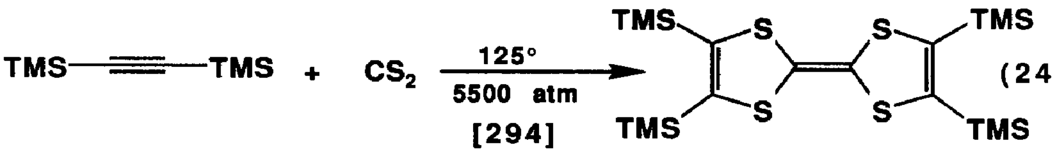
$R^2$ = ${}^t$Bu, 1-adamantyl, $Me_2CHCH_2CMe_2$; $R^1$ = Ph, Me, H, ${}^t$Bu

Bis(trimethylsilyl)acetylene was used to ethynylate optically active 1,3-dioxan-4-ones to give optically active alcohols. (Eqn. 240)



(240)

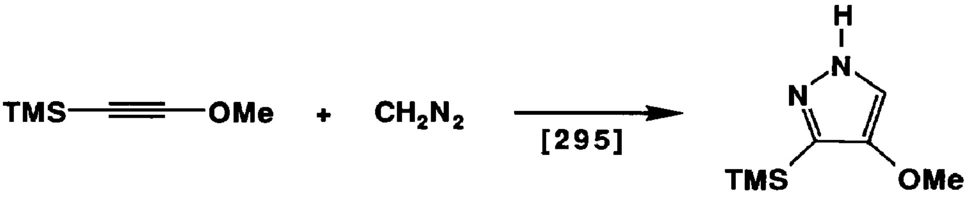
Bis(trimethylsilyl)acetylene was reacted with carbon disulfide to provide the silylated fulvalene **113** in good yield. (Eqn. 241)



**113**

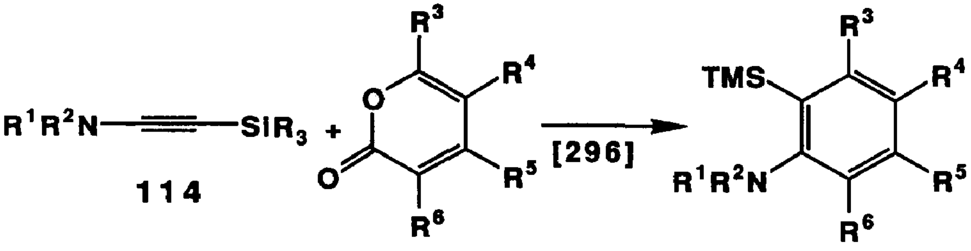
(241)

Trimethylsilylmethoxyacetylene was reacted with diazomethane to give the cycloadduct in a regiospecific manner. (Eqn. 242)



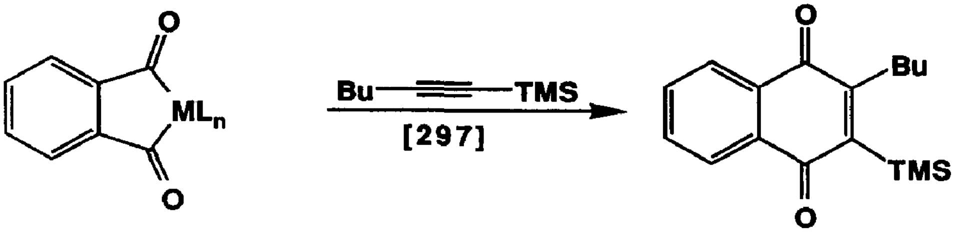
(242)

The ynaminylsilanes **114** were reacted with α-pyrones in a Diels-Alder fashion with extrusion of carbon dioxide to give anilines. (Eqn. 243) In addition to the ynaminyltrimethylsilane the triphenylsilyl acetylenes were also investigated as was the phenyldimethylsilyl version.



(243)

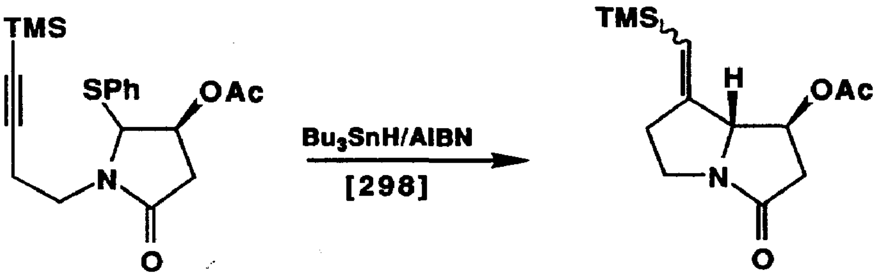
Phthaloyliron and cobalt complexes were reacted with acetylenes to produce naphthoquinones. One such reaction involved 1-trimethylsilylhexyne. (Eqn. 244)



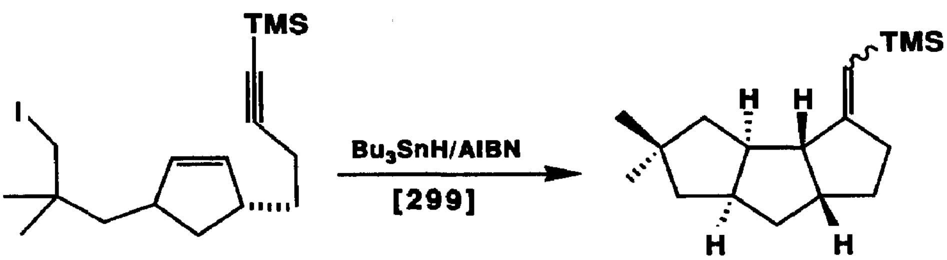
(244)

[$ML_n$ = $Fe(CO)_4$ (22%); $Co(PPh_3)_2Cl$ (68%)]

Radical initiated cyclizations of trimethylsilylated acetylenes was accomplished as shown in Eqns. 245 and 246.

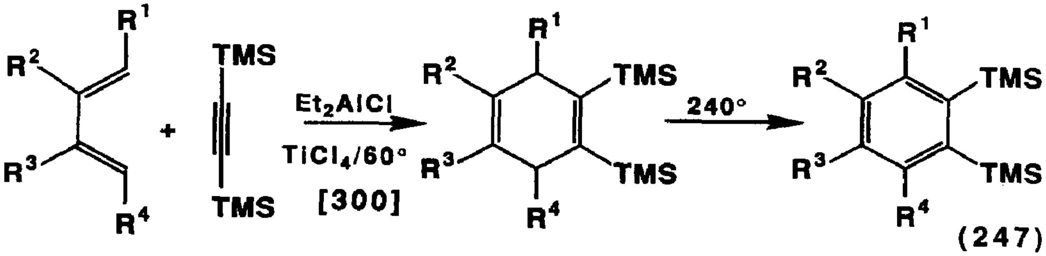


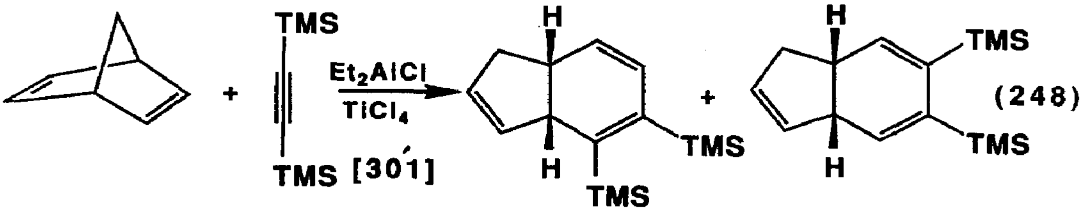
(245)



(246)

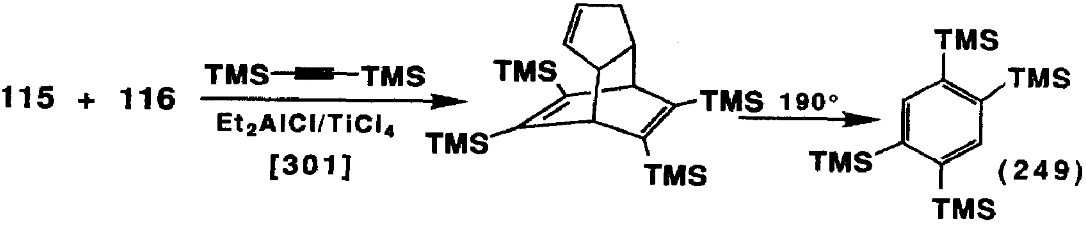
Bis(trimethylsilyl)acetylene was cycloadded to 1,3-butadienes with Lews acid catalysis. (Eqn. 247) This same ethynylsilane was added to norbornadiene to provide trimethylsilylated cyclohexadienes, (Eqn. 248) which were in turn cycloadded to the silylated acetylene. A retro Diels-Alder reaction on the product of this reaction gives 1,2,4,5-tetrakis(trimethylsilyl)benzene. (Eqn. 249)



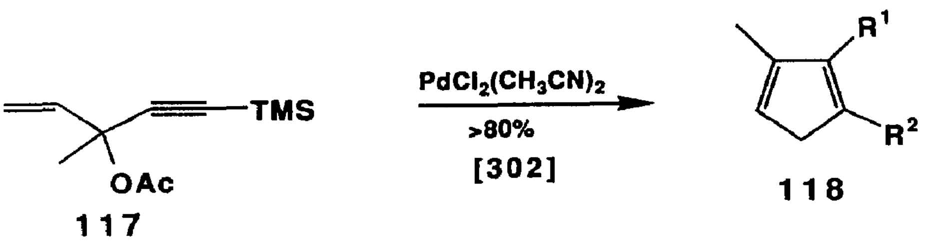


**115** formed at 20°

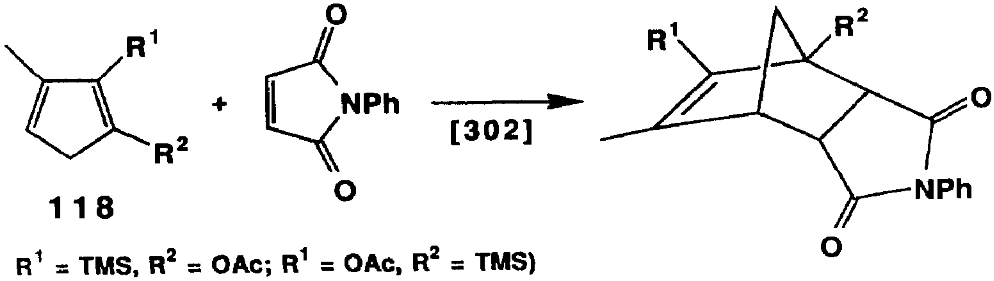
**116** formed at 60°



The ethynylsilane **117** reacted with palladium (II) to give two isomeric cyclopentadienes, both of which were subjected to Diels-Alder reaction with N-phenylmaleimide. (Eqns. 250, 251)



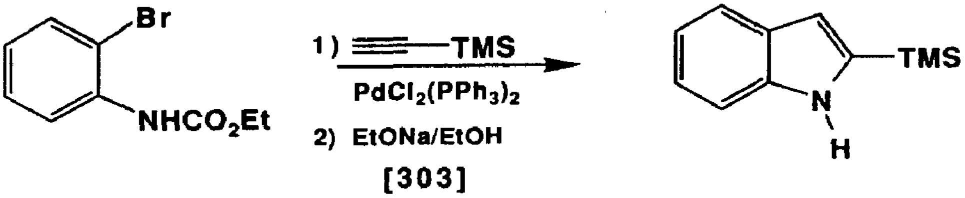
(250)



(251)

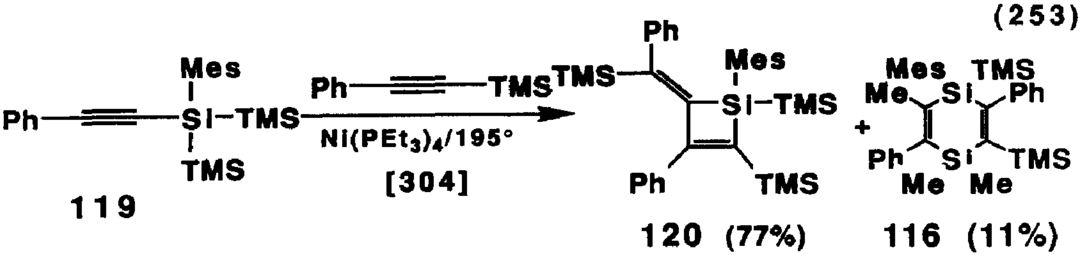
R$^1$ = TMS, R$^2$ = OAc; R$^1$ = OAc, R$^2$ = TMS)

Trimethylsilylacetylene was reacted with α-bromoanilines in the presence of a palladium (II) catalyst to give 2-trimethylsilylindole. (Eqn. 252)

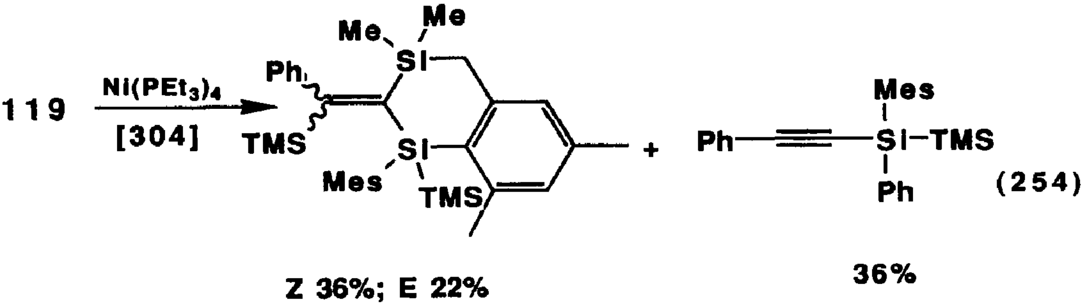


(252)

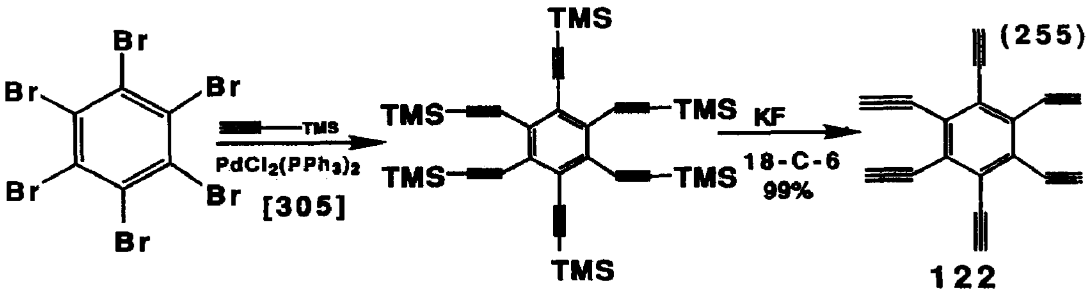
Heating ethynylsilane **119** in the presence of trimethylsilylphenylacetylene and nickel(0) gives silacyclobutene **120** and disilacyclohexadiene **121**. (Eqn. 253) In the absence of the trimethylsilylphenylacetylene the products are those shown in Eqn. 254.


(253)

119 → 120 (77%) + 116 (11%)

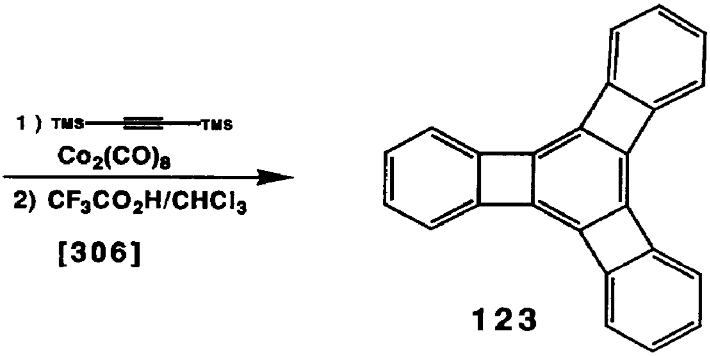

(254)

Hexabromobenzene was reacted with trimethylsilylacetylene in the presence of palladium(II) to give a 28 percent yield of hexa(trimethylsilylethynyl)benzene, which could be protiodesilylated in nearly quantitative yield to hexaethynylbenzene. (Eqn. 255) The hexaethynylbenzene was converted to a bond isolated cyclohexatriene in a sequence involving bis(trimethylsilyl)acetylene. (Eqn. 256)


(255)

122

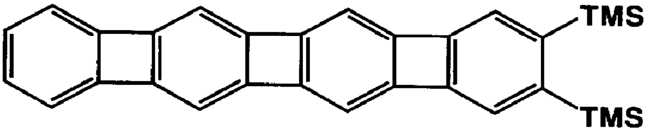
**122**



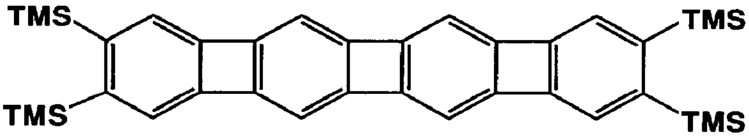
**123**

(256)

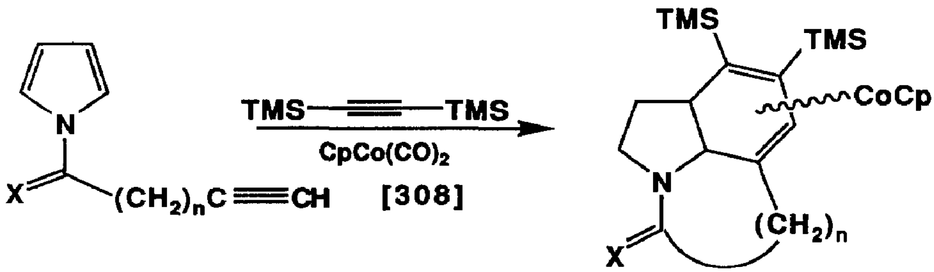
2,3-Bis(trimethylsilyl)[4]phenylene **124** and 2,3,8,9-tetrakis(trimethylsilyl)[4] phenylene **125** were prepared using the cobalt-mediated cyclization with bis(trimethyl silyl)acetylene. [307]



**124**



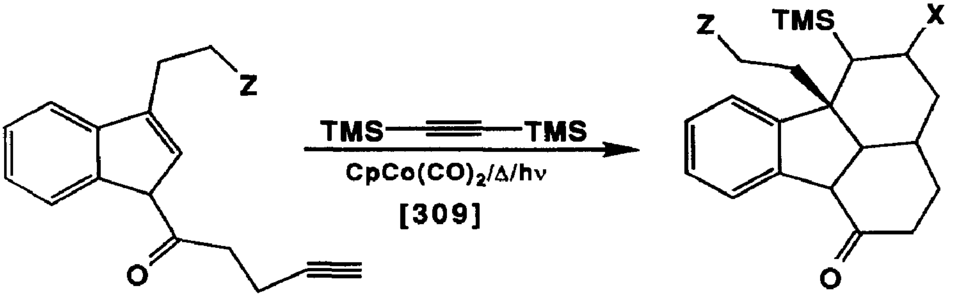
The cobalt-mediated [2 + 2 + 2] cycloadditions of ethynylsilanes to the 2,3-double bond of pyrroles provides a convenient entry into fused dihydroindoles. (Eqn. 257) A similar reaction with the 2,3-double bond of indoles results in an entry into the novel 4a,9a-dihydro-9H-carbazole nucleus. (Eqn. 258) In related chemistry the silylated steroid nucleus**126** was prepared (Eqn. 259) as was the cobalt complex of cyclobutadiene **127** (Eqn. 260). Finally, dicobaltoctacarbonyl was used to cyclize **128** to prepare bicyclo[3.3.0]octenones. (Eqn. 261)



(257)

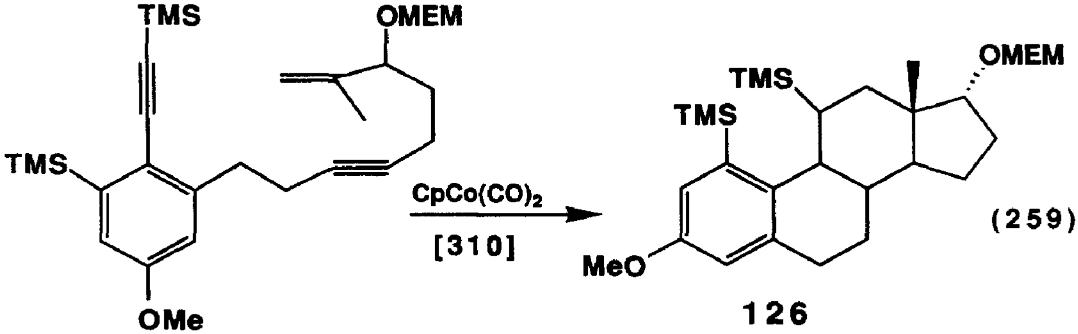
( X = O; CH$_2$; n = 2, 3, 4)

(major product except where n = 4)



(258)

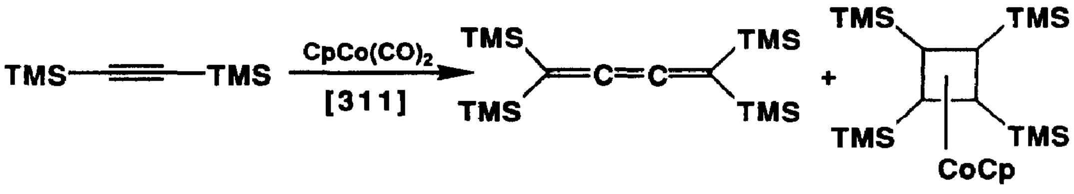
( Z = NHAc, NPhth, OTBS)



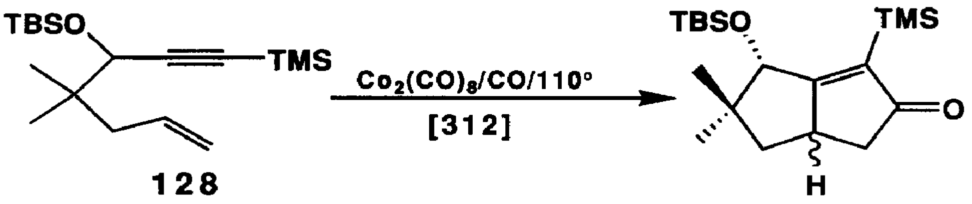
(259)

**126**

(260)



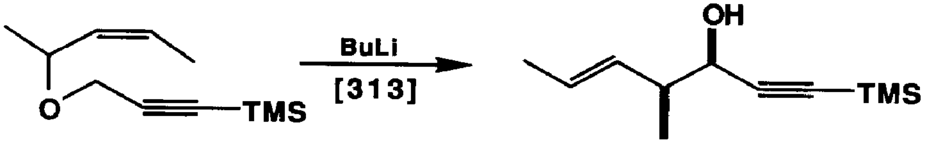
**127**



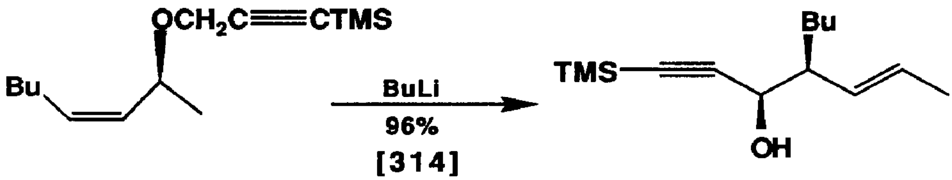
128

(261)

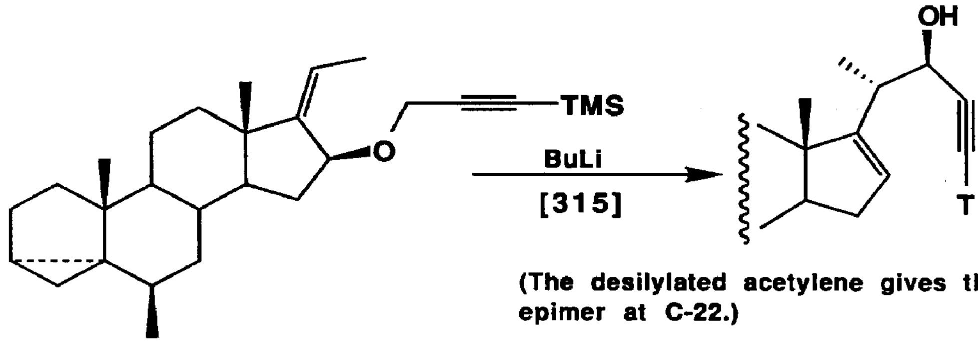
Trimethylsilylated acetylenes were employed in [2,3]Wittig rearrangements mostly in an effort to gain further control over the stereochemistry of the reaction. Examples



(262)

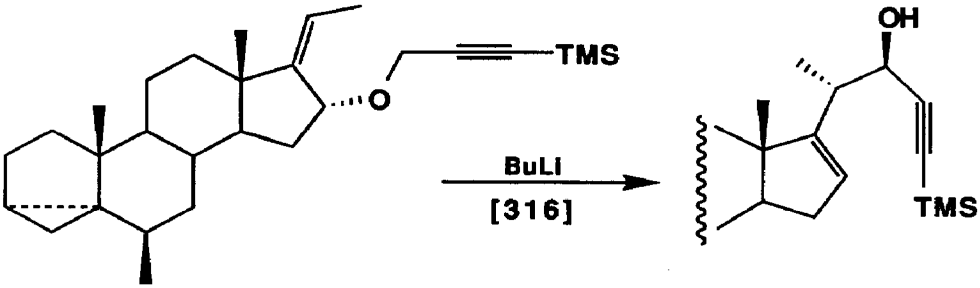


(263)



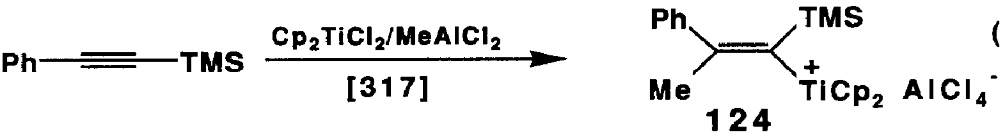
(264)

(The desilylated acetylene gives the epimer at C-22.)



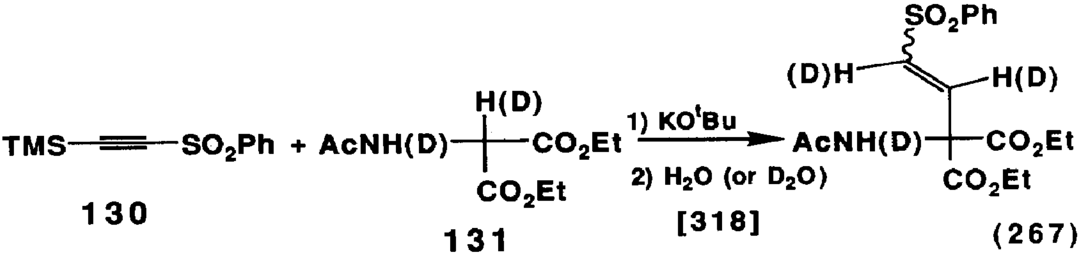
(265)

Trimethylsilylphenylacetylene was reacted with bis(cyclopentadienyl)titanium dichloride in the presence of methylaluminum dichloride to give the addition product **129**. Compound **129** was subjected to x-ray analysis. (Eqn. 266)

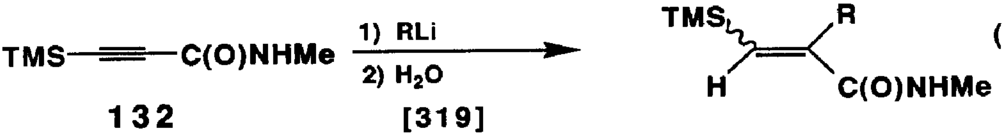


(266)

The addition of nucleophiles to ethynylsilanes containing an electron withdrawing group was reported. The silylated sulfone **130** was reacted with amidomalonate **131** to lead to racemic vinylglycine. (Eqn. 267) Silylated ethynylamide **132** reacted with organolithium reagents in the reverse manner to give the α-substituted products rather than the β-substituted ones. (Eqn. 268)



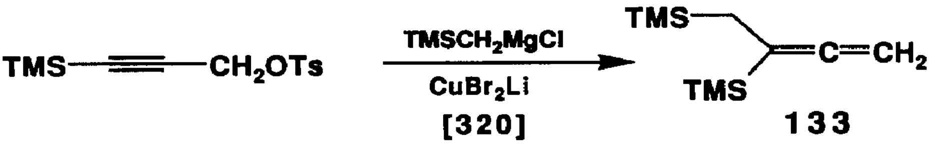
(267)



(268)

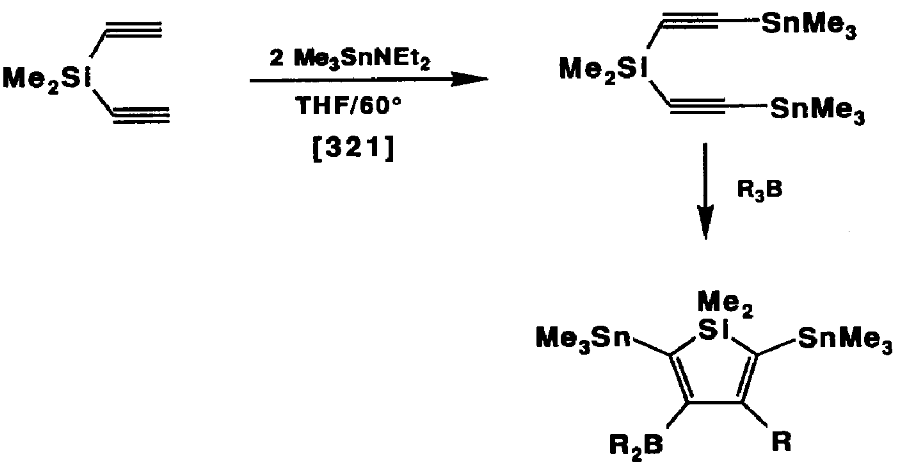
(92 - 100% of product)

Trimethylsilylmethylmagnesium chloride adds to the tosylate of 3-trimethylsilylpropargyl alcohol to give disilylated allene **133**. (Eqn. 29)

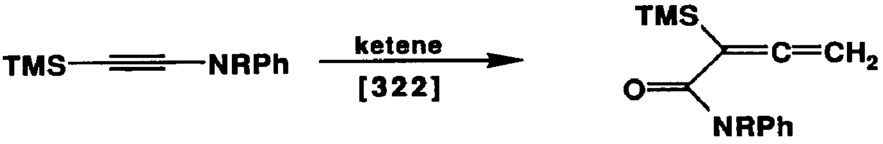


(269)

Diethynyldimethylsilane was stannylated and the resulting material cyclized with organoboranes. (Eqn. 270)



(270)



(271)

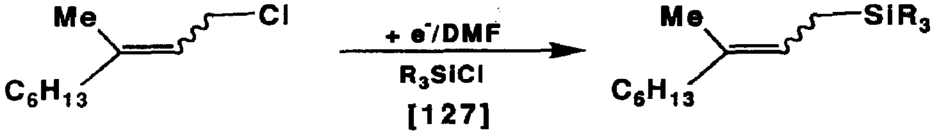
## C. ETHYNYLSILANES-OTHER STUDIES.

The kinetics of the base cleavage of ethynylsilanes showed that methoxy ligands on silicon can enhance the reaction electronically and inhibit the reaction sterically. [323] The kinetics of the thermal decomposition of ethynylsilane itself showed that there are four channels of decomposition, three *via* silirane and the fourth *via* the usual 1,1-hydrogen elimination. [324] The Penning ionization electron spectra of some trimethylsilylacetylenes were obtained. [325]

# X. ALLYLSILANES

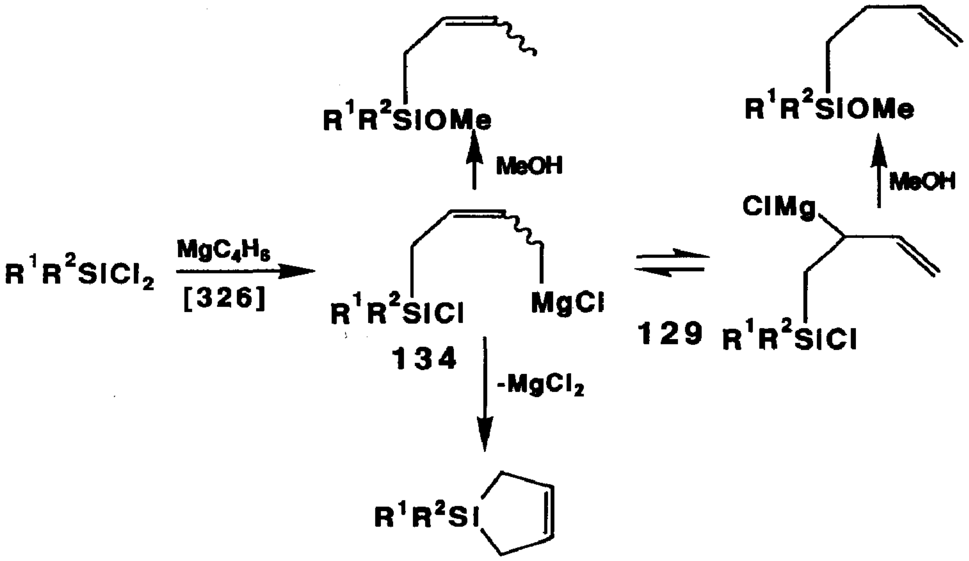
## A. PREPARATION

Allylsilanes were prepared electrochemically from allyl chlorides and chlorosilanes. (Eqn. 272)

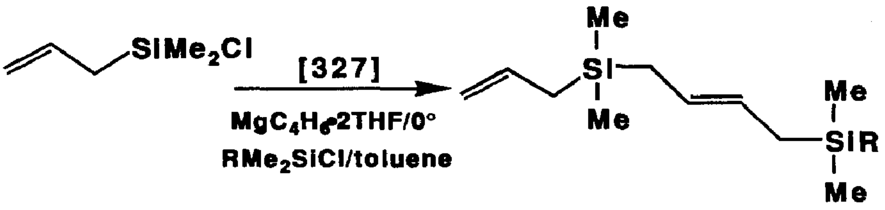


(272)

Allylsilanes were prepared from the reaction of disubstituted dichlorosilanes and butadienemagnesium. The observed products suggest the intermediacy of a silyl-substituted crotyl organomagnesium species **134**. (Eqn. 273) This reagent was employed in the synthesis of some 1,3-disilyl-2-butenes. (Eqn. 274)

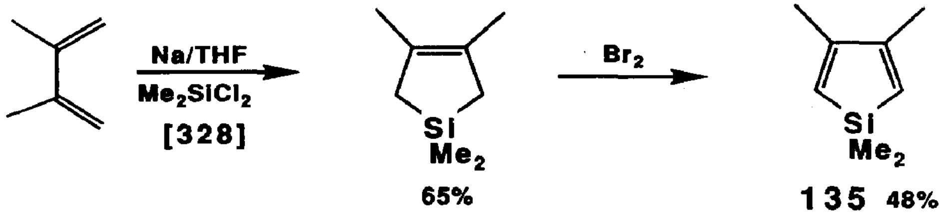


(273)



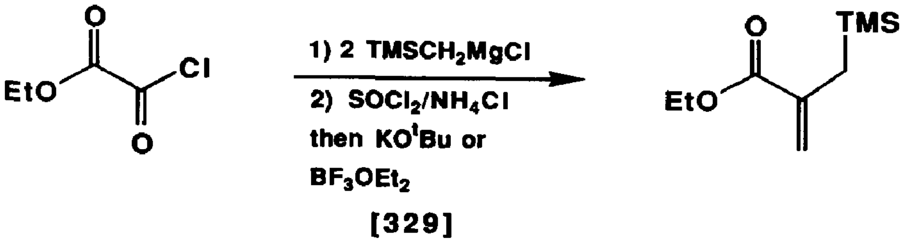
(274)

Treatment of 2,3-dimethyl-1,3-butadiene with dimethyldichlorosilane and sodium metal in tetrahydrofuran gives the 1-silacyclopent-3-ene. Bromination of this material gave the silole **135**. (Eqn. 275)

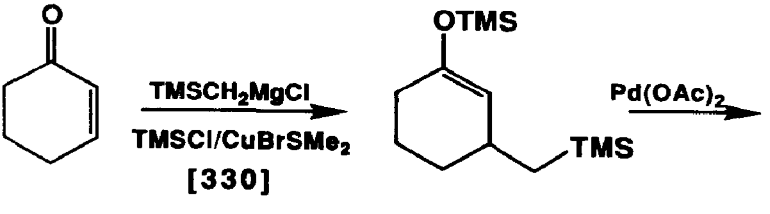


(275)

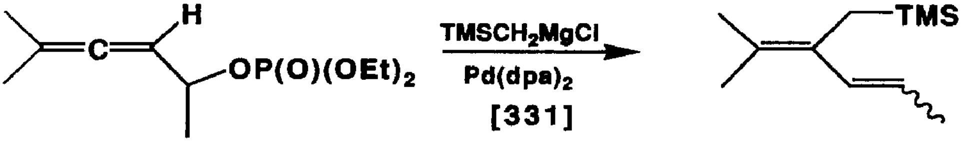
Trimethylsilylmethylmagnesium chloride, a readily available Grignard reagent, was the starting material for the preparation of allylsilanes as illustrated in the following examples. (Eqns. 276-278)



(276)

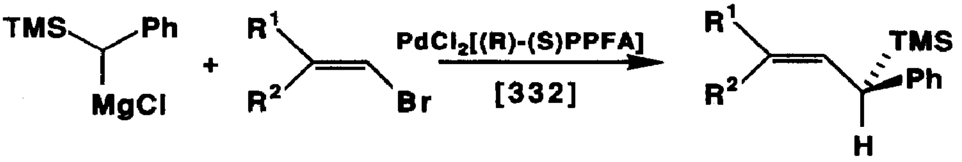


(277)



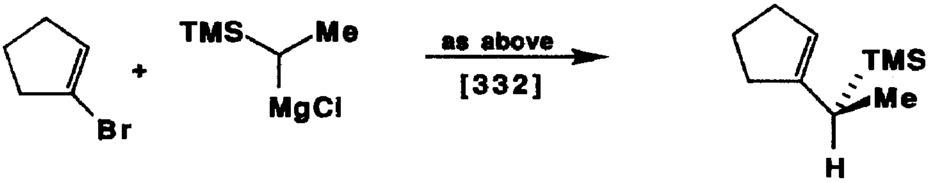
(278)

Optically active allylsilanes were prepared *via* the coupling of α-trimethylsilyl Grignard reagents and vinyl bromides. Two such examples are shown below. (Eqns. 279, 280)



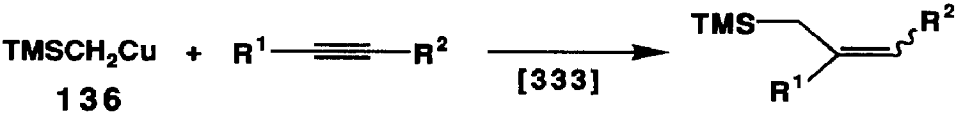
(279)

**5 examples; 42-95% yield**
**24-95% R**



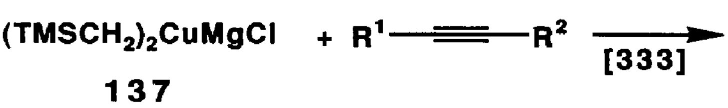
(280)

Trimethylsilylmethylcopper **136** and chloromagnesium bis(trimethylsilylmethyl)-cuprate **137** were added to acetylenes to give allylsilanes. (Eqns. 281, 282) Reagent **136** was reacted with epoxy acetylenes to give allenes, which are at the same time allylsilanes. (Eqn. 283) A similar reaction was carried out with 4-mesyloxy-allenes. (Eqn. 284)

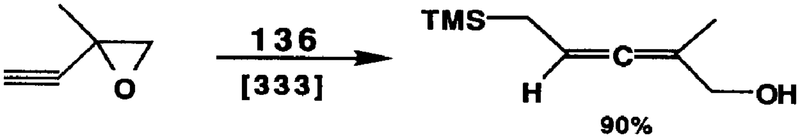


(281)

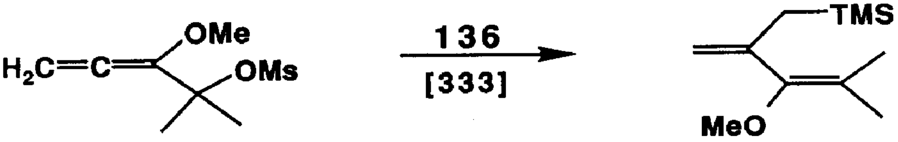
**8 examples; 70-98%**



(282)

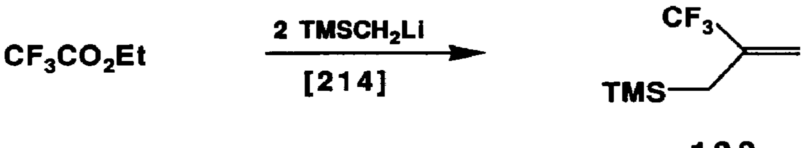


(283)



(284)

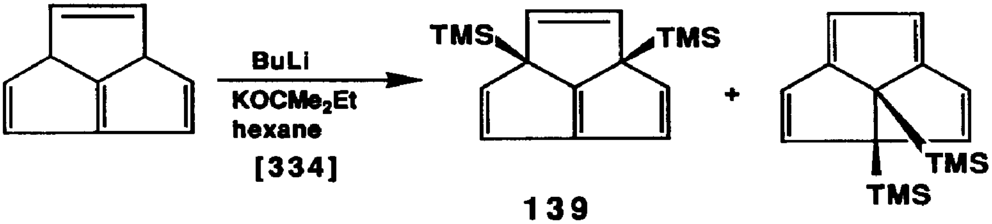
Trimethylsilylmethyllithium was reacted with ethyl trifluoroacetate to give the fluorinated allylsilane **138**. (Eqn. 285)



**138**

(285)

Direct metallation of acepentalene followed by trimethylsilylation provided the intriguing allylsilanes **139** and **140**. (Eqn. 286)

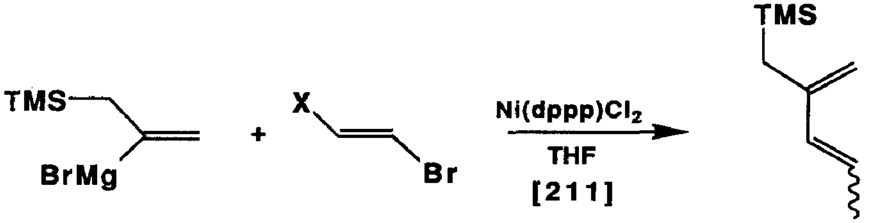


**139**

**140**

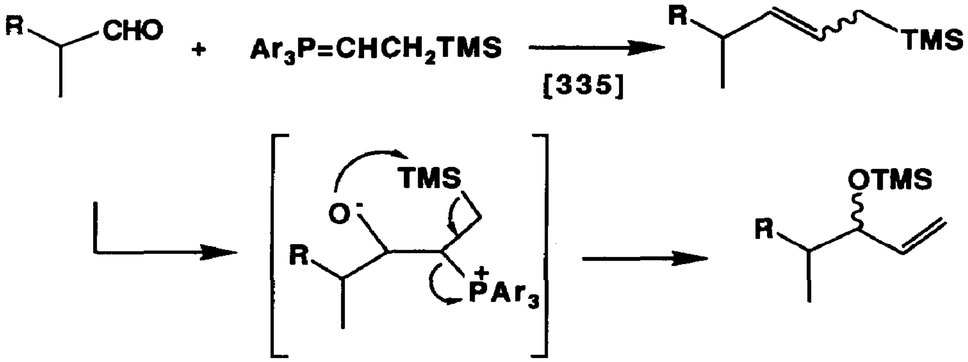
(286)

3-Trimethylsilyl-2-propenylmagnesium bromide was coupled with vinyl bromides to give 2-trimethylsilylmethyl-1,3-butadienes. (Eqn. 287) These were used in Diels-Alder reactions.



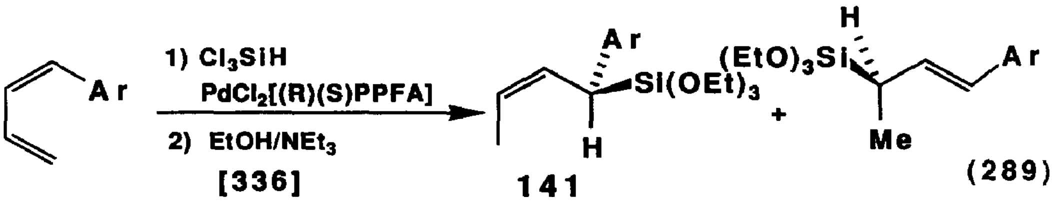
(287)

The reaction of [2-(trimethylsilyl)ethylidene]triarylphosphoranes (the Seyferth-Wittig reagent) with aldehydes was shown to proceed via two different pathways leading to trimethylsilylated allylic alcohols in addition to allylsilanes. *o*- and *p*-methoxyphenyl ligands on phosphorus favored the silylated allyl alcohol formation. (Eqn. 288)



(288)

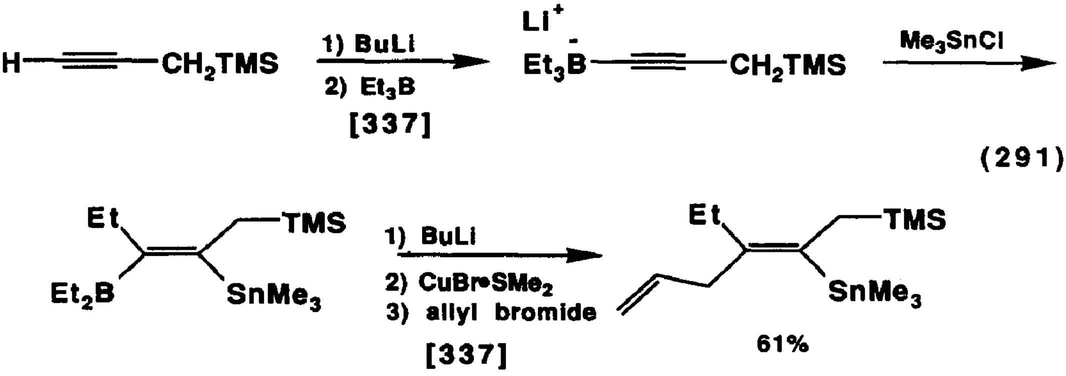
The hydrosilylation of 1-aryl-1,3-butadienes with trichlorosilane and a chiral catalyst results in the formation of allylsilanes optically active at carbon. (Eqn. 289) In one case the allylsilane was converted to an optically active allyl alcohol. (Eqn. 290)



(289)

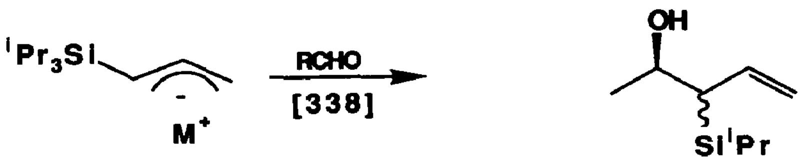
(290)

Trisubstituted vinylstannanes were prepared starting from 3-trimethylsilylpropyne as illustrated in Eqn. 291.



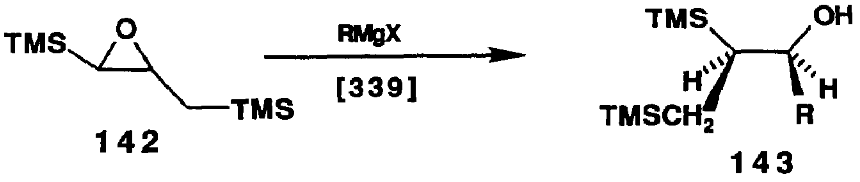
(291)

Deprotonation of allyltriisopropylsilane followed by reaction of the resulting lithium reagent with various other metal species and then with aldehydes produces β-hydroxy- allylsilanes as syn/anti mixtures, except with tributyltin chloride which gives only syn product. (Eqn. 292) Only a small amount of γ-attack was found.



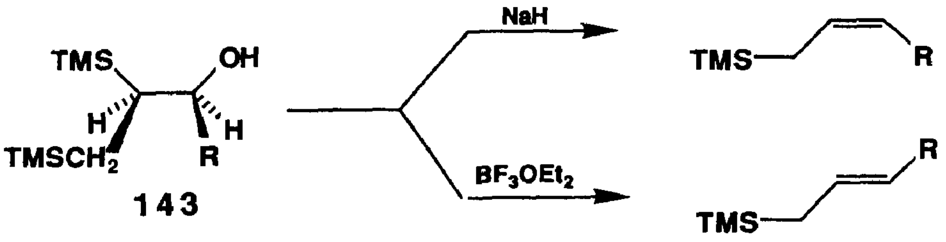
(292)

The reaction of Grignard reagents with disilylated epoxide **142** produces a β-hydroxysilane **143** (Eqn. 293), which, after a Peterson elimination, gives allylsilanes in a stereospecific manner. (Eqn. 294)



**142** **143**

(293)

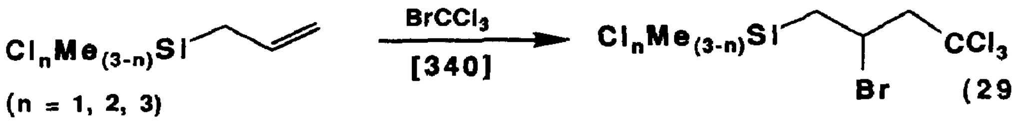


**143**

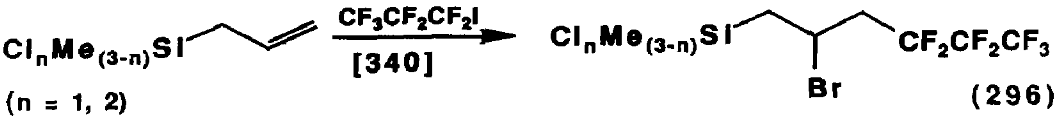
(294)

## B. ALLYLSILANES--REACTIONS

The addition of various reagents to the double bond of allylsilanes was reported. Bromotrichloromethane was added to allylsilanes under photolytic conditions to give the β-bromo regioisomer. (Eqn. 295) In a like manner 1-iodoheptafluoropropane was added to the same allylsilanes. (Eqn. 296)

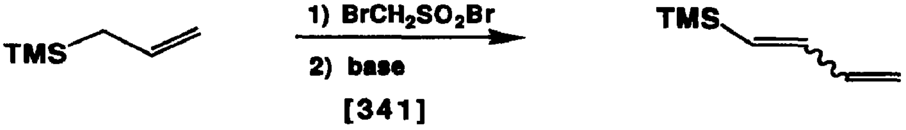


(295)

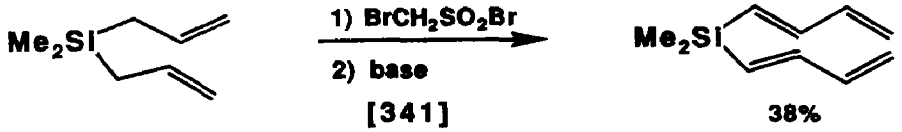


(296)

Bromomethylsulfonyl bromide was added to allylsilanes and the adduct treated with base to give silylated 1,3-dienes. (Eqns. 297, 298)

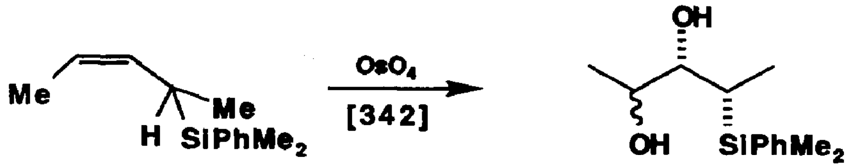


(297)



(298)

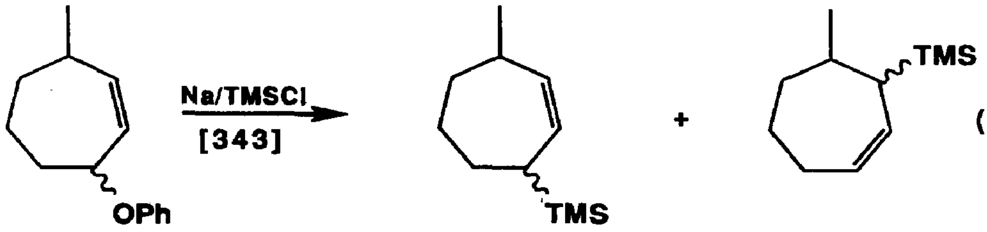
The osmylation of allylsilanes was shown to be independent of hyperconjugation effects. The results are consistent with steric effects. (Eqn. 299)



(299)

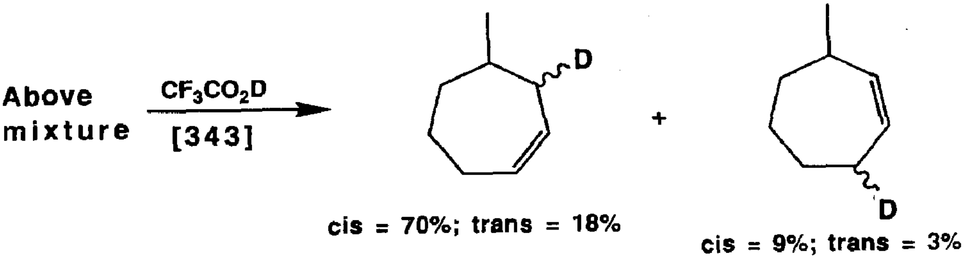
syn = 78%; anti = 22%

The stereochemistry of acidolysis of cyclohept-2-enyltrimethylsilanes showed that the protonation (deuteration) occurs gamma and anti to the silicon. (Eqn. 301) The starting allylsilanes were prepared according to Eqn. 300. The results were the same for the corresponding tin system.



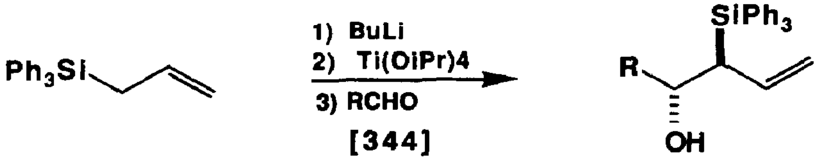
(300)

(70% cis; 17% trans) (3% cis; 10% trans)



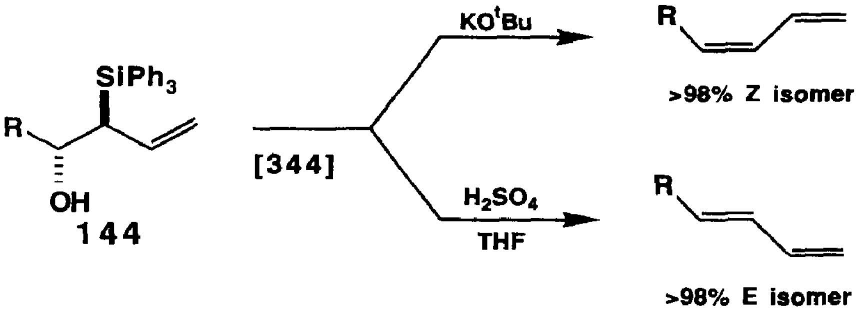
(301)

The deprotonation of allylsilanes with butyllithium followed by metal-metal exchange with titanium tetraisopropoxide provides a reagent that reacts regioselectively with aldehydes at the α-position. Elimination of the resulting β-hydroxysilane produces 1,3-dienes in a highly stereoselective manner. (Eqns. 302, 303) Deprotonation of allyltriisopropylsilane gives a lithium reagent which preferentially alkylates at the less sterically demanding γ-position. (Eqn. 304)

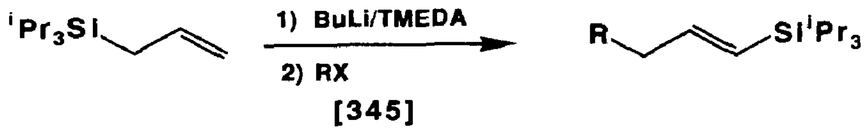


144

(302)

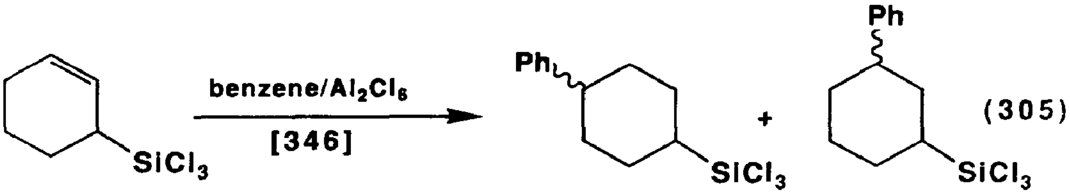


(303)



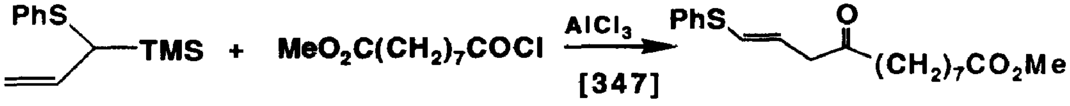
(304)

3-Cyclohexenyltrichlorosilane was reacted with benzene in the presence of aluminum chloride and hydrochloric acid to give arylation of the double bond in what is likely a Friedel-Crafts alkylation of the aromatic ring. (Eqn. 305)

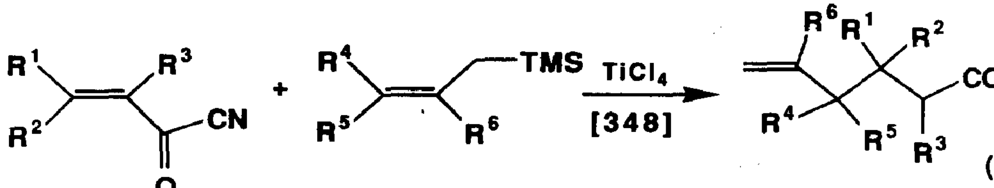


(305)

Allylsilanes were employed in the allylation of acid chlorides (Eqn. 306), α, β-unsaturated acyl nitriles (Eqn. 307) and γ-lactones (Eqn. 308) Simple iminium salts were reacted with allylsilanes in aqueous medium. (Eqn. 309)

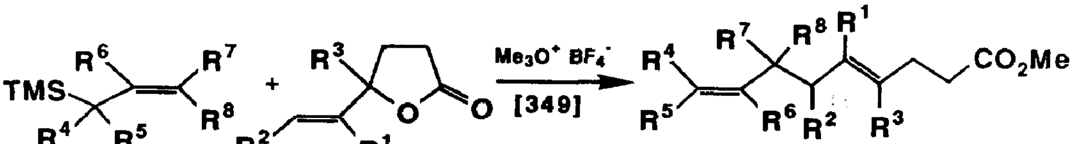


(306)

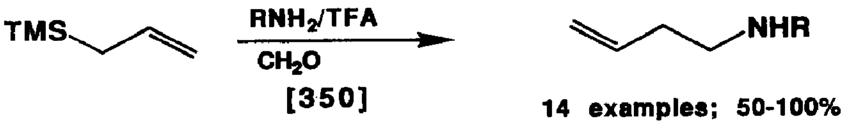


(307)

12 examples
nearly quantitative



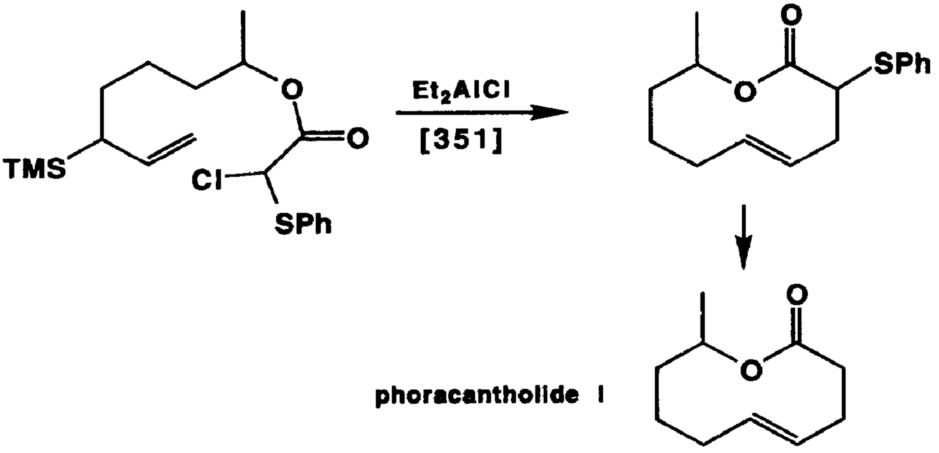
(308)



(309)

14 examples; 50-100%

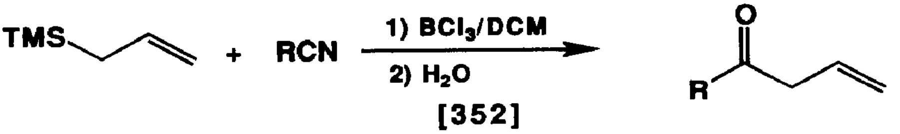
The reaction of allylsilanes with α-chloro-α-thiophenoxy esters was carried out in an intramolecular fashion in order to prepare phoracantholide I. (Eqn. 310)



(310)

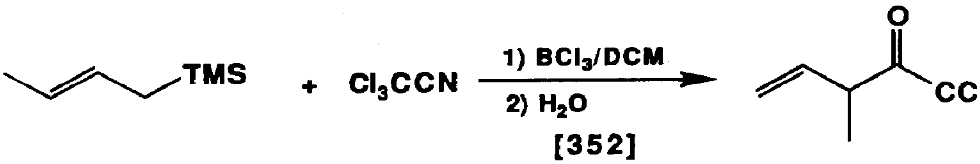
phoracantholide I

The reaction of allylsilanes with alkyl nitriles provides, after hydrolysis, β, γ-unsaturated ketones in good to excellent yields. (Eqns. 311, 312)



(311)

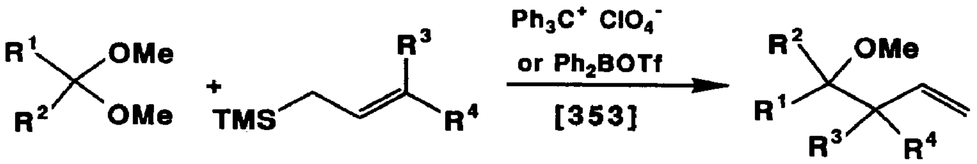
(8 examples 38-86%)



(312)

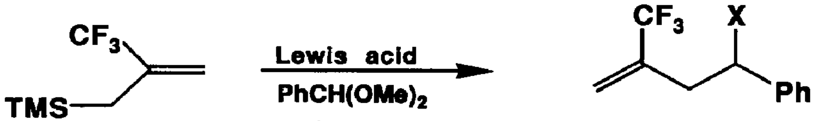
79%

The use of allylsilanes in the allylation of acetals and ketals to homoallylic ethers has continued to be investigated as can be seen in the several examples shown below. Diphenylboryl triflate and trityl perchlorate serve very well as catalysts for the allylation of acetals and ketals. (Eqn. 313) The allylsilane **145** provides a route towards the introduction of the trifluoromethyl group into various systems as seen in Eqn. 314. The hemiacetal **146** was nicely allylated with allyltrimethylsilane. (Eqn. 315) Interestingly, the reaction of **146** with trimethylsilylnitrile gives substitution of the hydroxyl group by a nitrile group. The optically active acetal 147 was allylated with a high degree of stereoselectivity. (Eqn. 316) Its diastereomer gave a 9:1 ratio of stereoisomers under the same conditions.



(313)

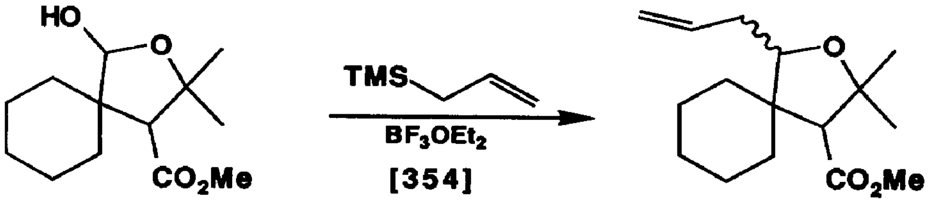
**with trityl perchlorate 7 examples 57-90%**
**with diphenylboryl triflate 4 examples 69-77%**



**145**

(314)

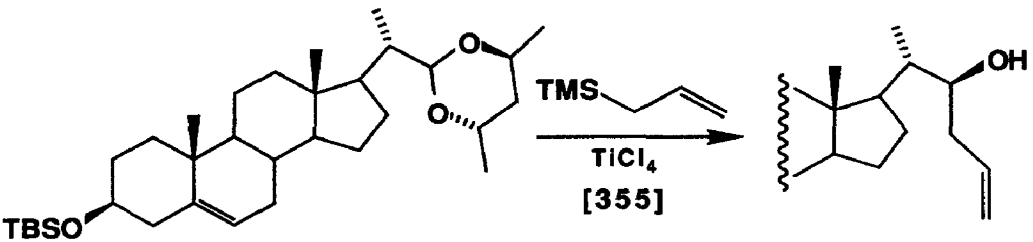
**LA = $TiCl_4$, X = Cl**
**LA = TMSOTf, X = OMe**



(315)

**146**

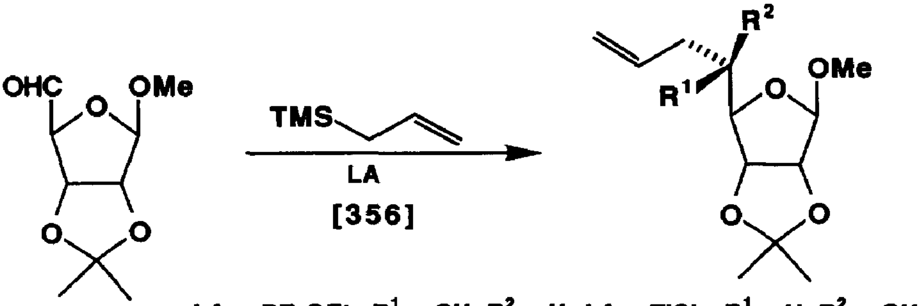
**cis:trans = 1:4**



**147**

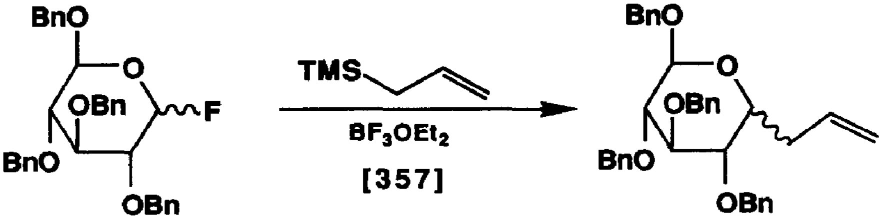
(316)

It is interesting to note that the allylation of **148** takes place at the aldehyde functionality rather than the acetal or ketal groups. (Eqn. 317) Glycosyl fluorides were shown to react with allyltrimethylsilane in the presence of a Lewis acid catalyst. (Eqn. 318)



(317)

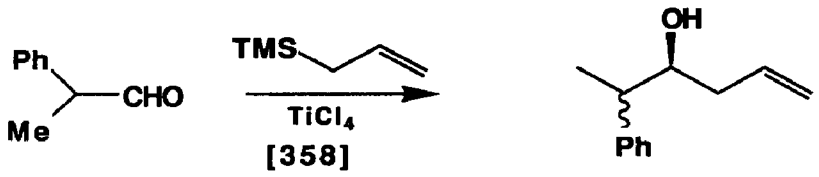
**148** LA = $BF_3OEt_2$ $R^1$ = OH, $R^2$ = H; LA = $TiCl_4$, $R^1$ = H, $R^2$ = OH



(318)

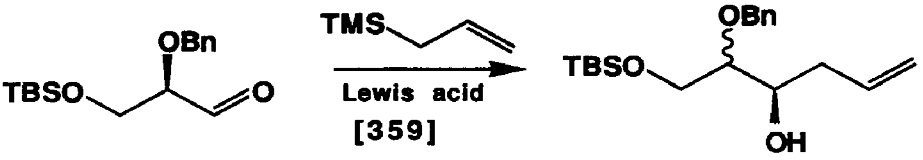
Preferential Cram stereoselectivity was observed in the titanium tetrachloride catalyzed allylation of 2-phenylpropanal (Eqn. 319). Chelation ($TiCl_4$) and non-chelation ($BF_3OEt_2$) control was observed in the allylation of protected glyceraldehyde.

(Eqn. 321) The structure and electronic nature of the benzaldehyde boron trifluoride complex was presented and discussed in terms of the reactions of aldehydes and ketones with allyltrimethylsilane, enol silyl ethers and trimethylsilylnitrile. [360]



Cram:anti-Cram = 70:30

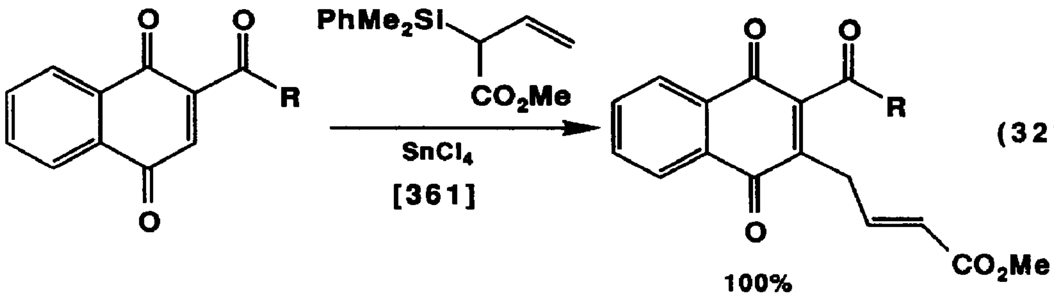
(319)



TiCl$_4$ or SnCl$_4$ >98% syn; BF$_3$OEt$_2$ 81% anti

(320)

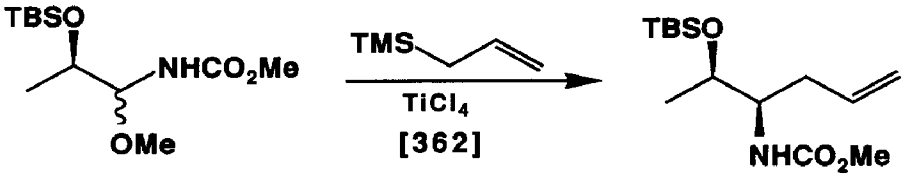
An approach to pyranonaphthoquinone antibiotics involves the allylation of 2-alkanoyl-1,4-quinones. (Eqn. 321)



100%

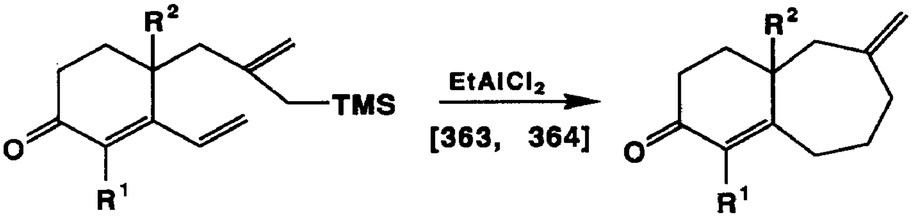
(321)

The allylation of the N,O-acetal of threonine gave the desired product with high diastereoselectivity. (Eqn. 322)



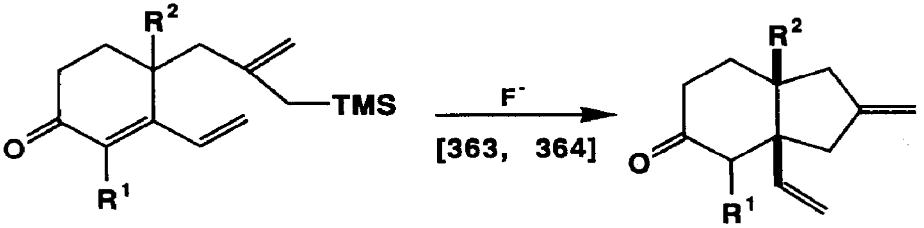
(322)

The intramolecular allylation of dienone **149** was carried out with both Lewis acid catalysis and fluoride ion catalysis. The results show that δ-attack is favored by Lewis acid catalysis and β-attack by fluoride ion catalysis. (Eqns. 323, 324) A small amount of the bicyclic material was also formed in one case. Further examples were reported [365] as were the geometric constraints on the reaction [366].



**149**

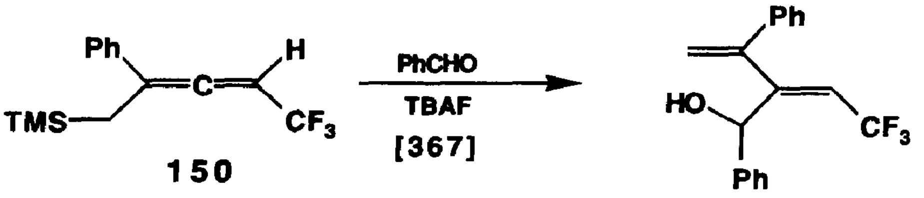
(323)



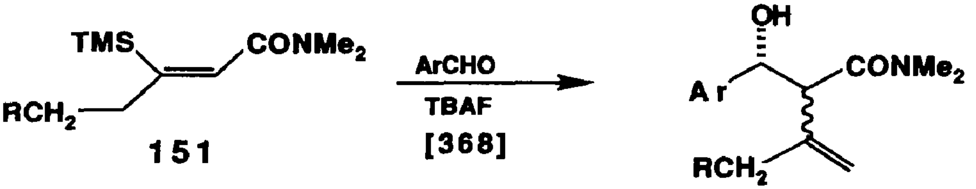
**149**

(324)

Fluoride-induced allylation of electrophiles with allylsilanes was studied. The allylsilane **150** was reacted with benzaldehyde in the presence of tetra-n-butyl ammonium fluoride, a well known soluble source of fluoride ion. (Eqn. 325) Aryl aldehydes were reacted with allylsilane **151** to give predominantly the syn product. (Eqn. 326)



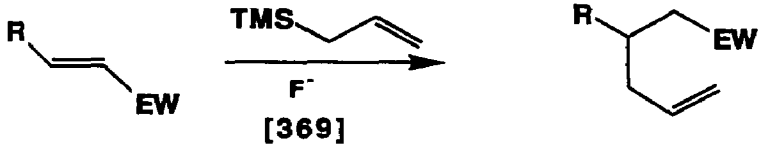
(325)



(326)

**4 examples; 58-98%**
**with TiCl$_4$ syn>anti**

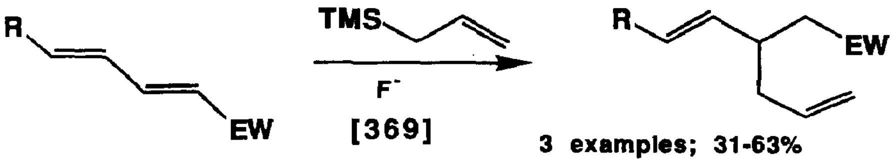
A general procedure for the fluoride ion-induced reaction of allylsilanes with α, β-unsaturated esters and nitriles, but not amides, was reported. (Eqn. 327) This methodology is more general than that for the cuprates and the Lewis acid catalyzed procedures. α, β, γ, δ-unsaturated systems react at the β-position. (Eqn. 328) The reaction was applied to an intramolecular system as well. (Eqn. 329)



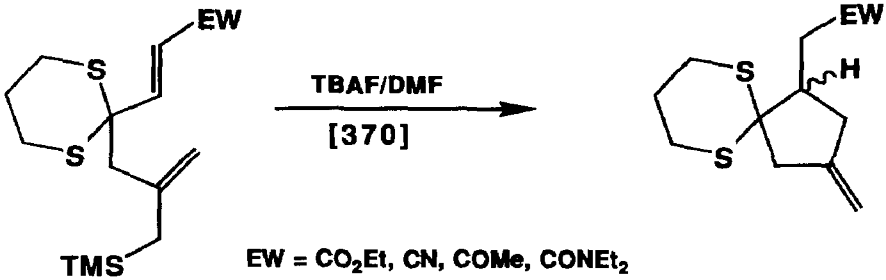
(327)

**5 examples; none with enolizable hydrogens**

**EW = CN, CO$_2$Et**

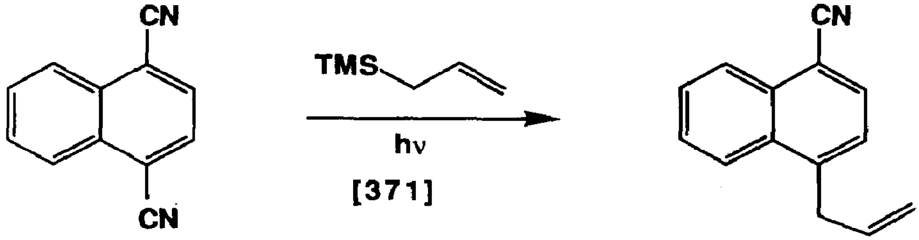


(328)

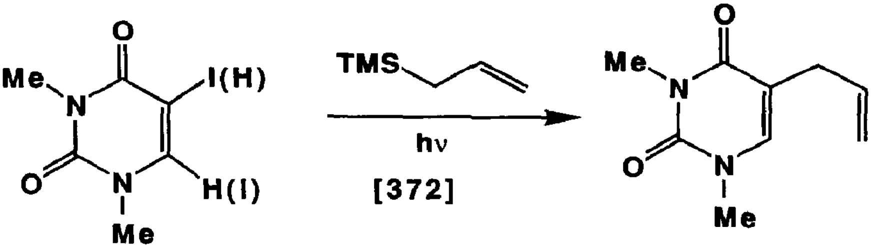


(329)

Allyltrimethylsilane was photochemically reacted with 1,4-dicyanopolyaromatic compounds (Eqn. 330) and 5- and 6-iodo uracils (Eqn. 331).

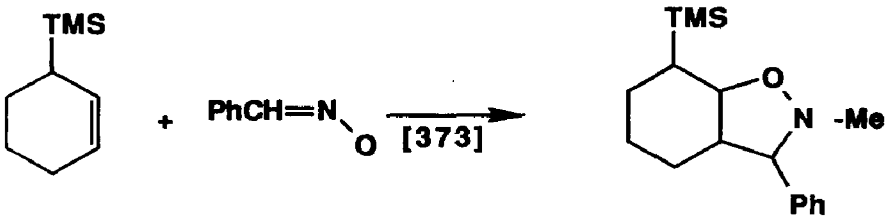


(330)

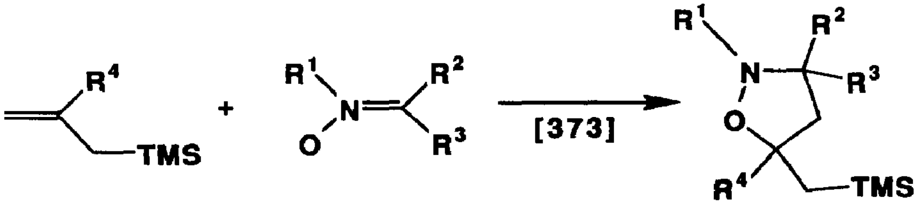


(331)

Allyltrimethylsilane was cycloadded to nitrones (Eqns. 332, 333) and to nitrile oxides (Eqn. 334).

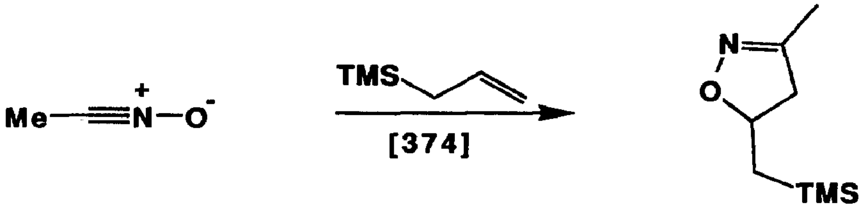


(332)



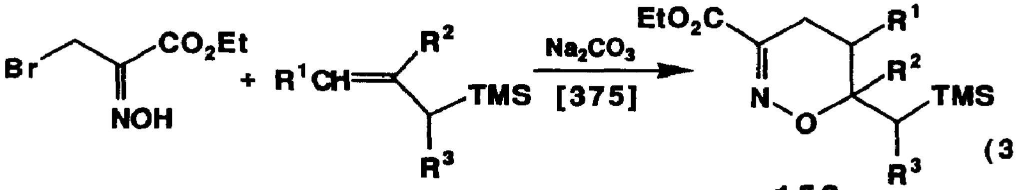
(333)

4 examples; 83-94%



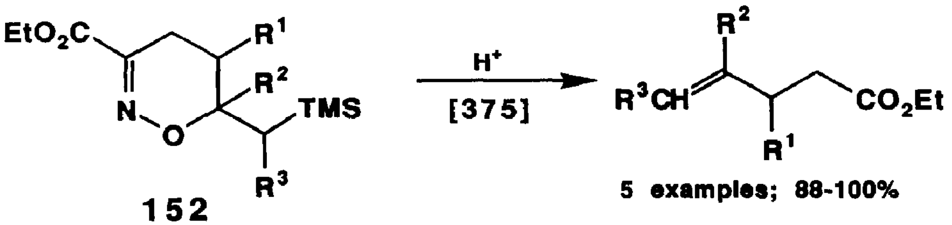
(334)

Allylsilanes react with α-halo oximes in the presence of sodium carbonate to give the dihydrooxazines **152**, which upon treatment with acid produce γ, δ-unsaturated esters in excellent yields. (Eqns. 335, 336)



**152**

(335)

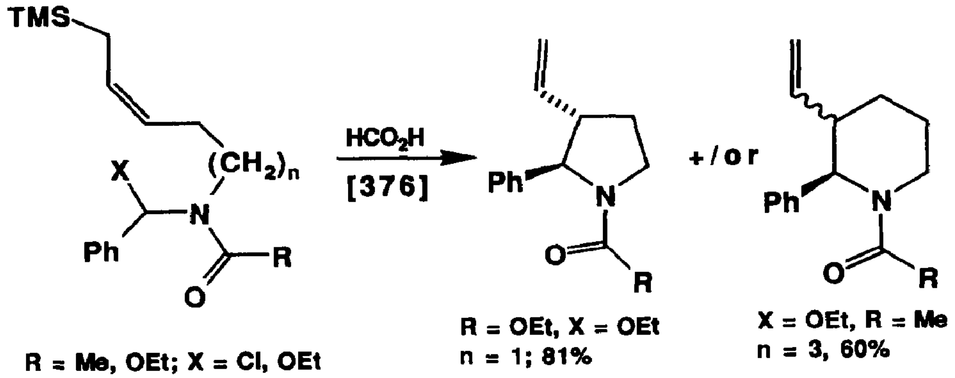


**152**

5 examples; 88-100%

(336)

An intramolecular cyclization of an allylsilane and an acyliminium ion was reported. (Eqn. 337)



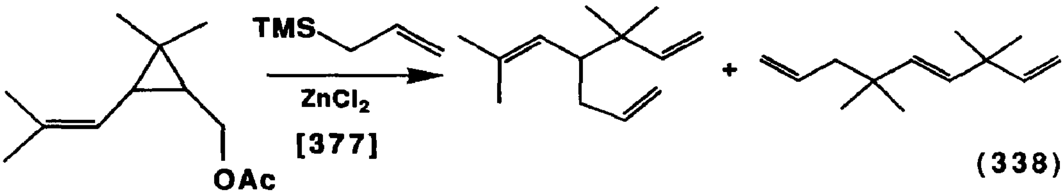
R = Me, OEt; X = Cl, OEt

R = OEt, X = OEt
n = 1; 81%

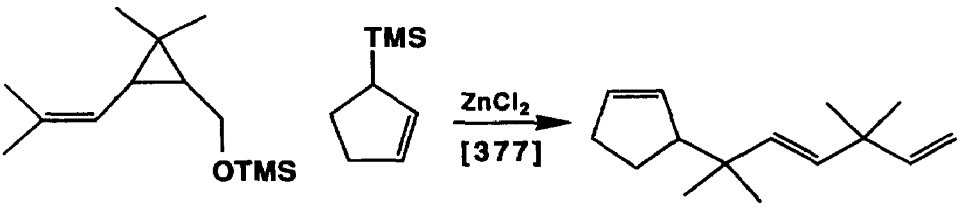
X = OEt, R = Me
n = 3, 60%

(337)

Allylsilanes react with chrysanthemic acid derivatives under the influence of Lewis acids to give ring opening with cleavage of the $C_1$-$C_3$ bond. (Eqns. 338, 339)



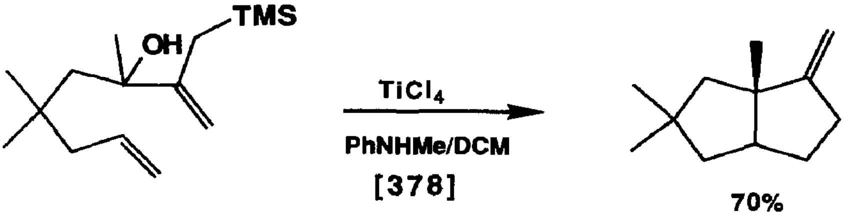
(338)



(339)

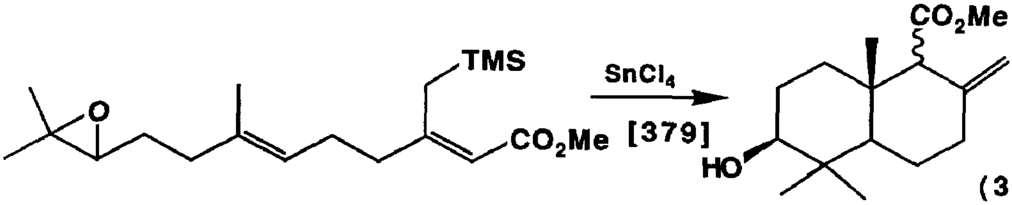
other systems also studied

Unsaturated trimethylsilylmethallyl alcohols were cyclized as shown in the example in Eqn. 340.

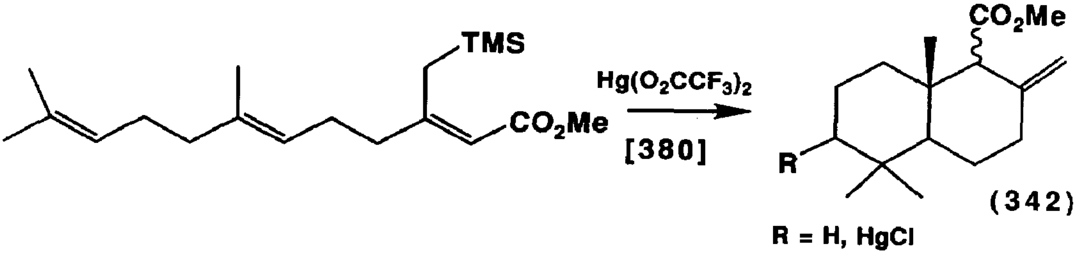


(340)

The electrophilic cyclizations of allylsilanes as key steps in the preparation of racemic karahana ether and labdadienoic acid (Eqn. 341) and racemic isodrimenin (Eqn. 342) were reported.

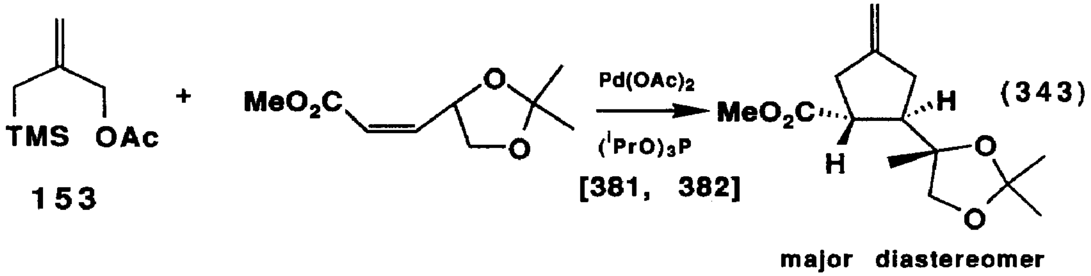


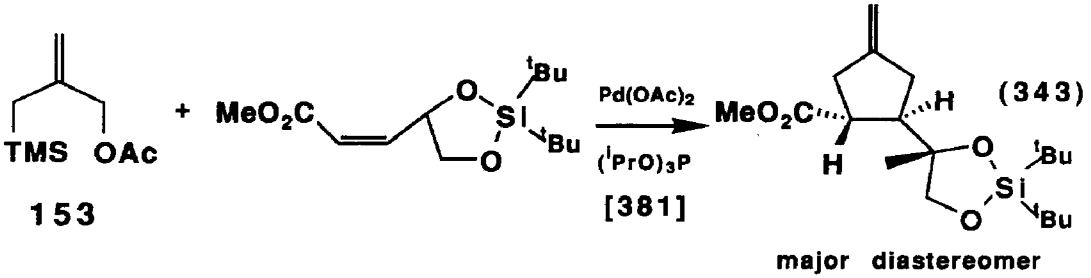
(341)



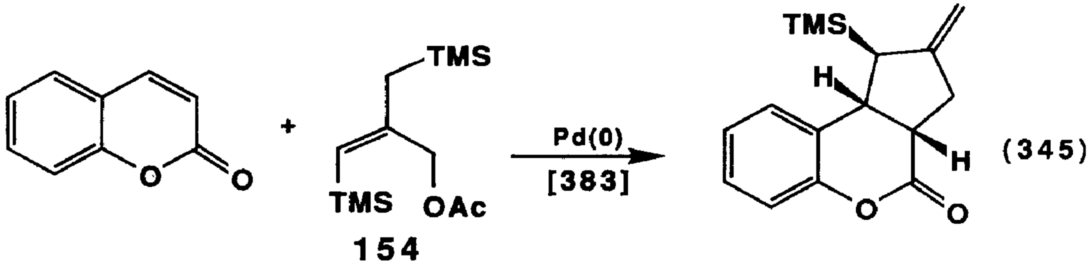
(342)

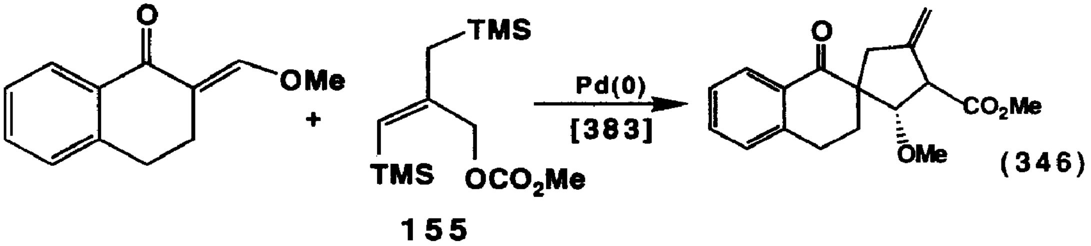
Work with the functionalized allylsilane **153** as a route to trimethylenemethane palladium complexes used in [3+2] cycloadditions continued with a look at the diastereoselectivity of the cyclization step. (Eqns. 343, 344)



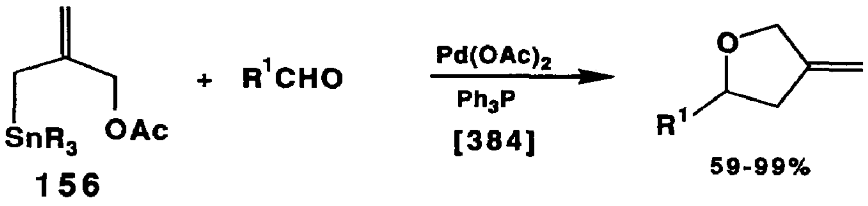


The reagent **154** was found to react normally to give the expected exo-methylene cyclopentane upon cycloaddition (Eqn. 345), but the carbonate derivative **155** results in carboxylative trimethylenemethane cycloaddition (Eqn. 346).



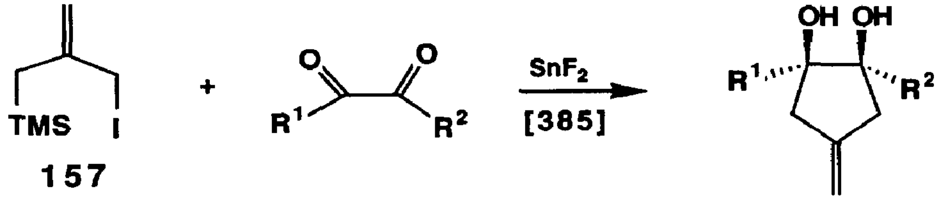


To test theory, which indicates that the trimethylenemethane palladium complex should be nucleophilic, the allyltin system **156** was reacted with aldehydes in the presence of palladium(II) to give the corresponding heterocycles. (Eqn. 347)



(347)

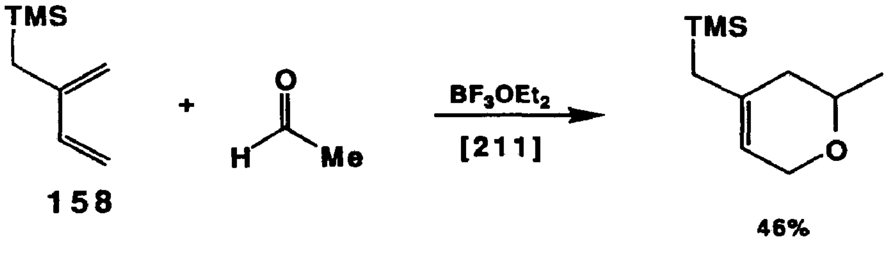
In a related cycloaddition, although vastly different mechanistically, the allylsilane **157** was reacted with 1,2-diketones in the presence of a tin difluoride catalyst. (Eqn. 348) The diastereoselectivity in this reaction is extremely high.



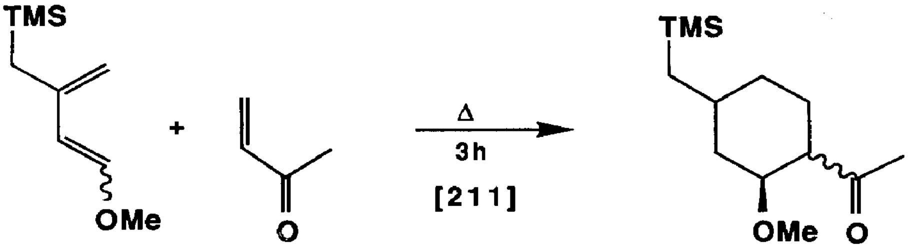
(348)

**9 examples; 0-88% yield**
**diastereoselectivity 7.5:1 to 100:0**

The trimethylsilylated 1,3-butadienes **158** and **159** were employed in [2+4] cycloadditions as shown in Eqns. 349 and 350.



(349)

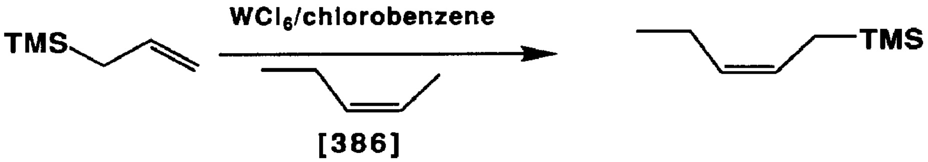


**159**

70%

(350)

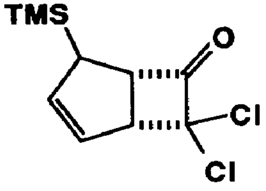
Allyltrimethylsilane was reacted with cis-2-pentene in the presence of tungsten hexachloride to give a metathesis derived product. (Eqn. 351)



(351)

## C. ALLYLSILANES--OTHER STUDIES

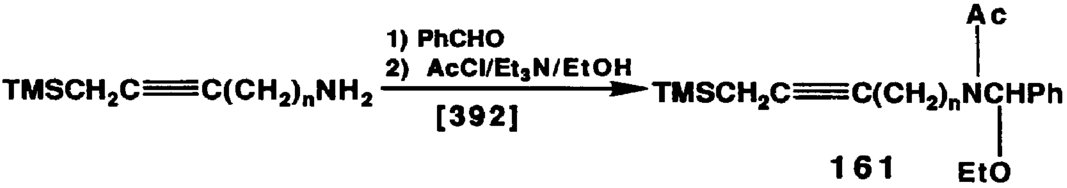
The allylsilane **160** was used in the preparation of racemic sarkomycin. [387] Calculations and experimental evidence were presented to account for the anti electrophilic addition of electrophiles to allylsilanes. [388] The torsional potential function of allylsilane has been calculated using MM2 and ab initio methods. The most stable geometry is with a C=C-C-Si dihedral angle of 102-104° and the least stable is that with a dihedral angle of 0° or 180°. [389] Calculations (6-31G*) on the silacyclopentadiene anion show that the ground state is the $C_s$ pyramidal structure. The planar $C_{2v}$ form is the transition state for pyramidal inversion. It was calculated that the silacyclopentadiene anion has only about 3% of the resonance stability of the carbon analog. [390] The $^{60}$Co ionization of allylsilanes to give cation radicals were shown by esr measurements to have a large polarization of the SOMO due, presumably, to enhanced σ-π conjugation. [391]



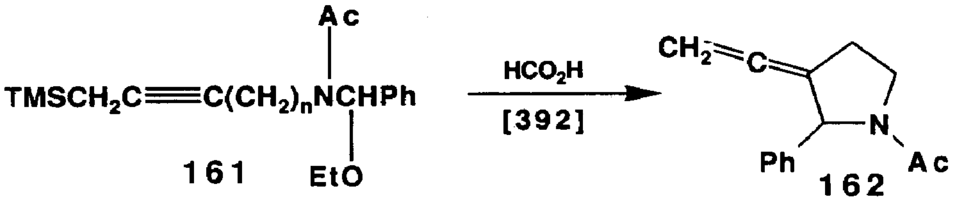
**160**

## XI. PROPARGYLSILANES

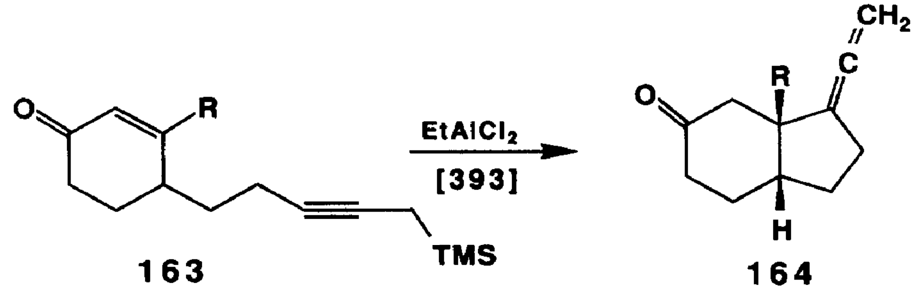
Three reactions of propargylsilanes were reported. The propargylsilane **161**, prepared as shown in Eqn. 352, was subjected to acid catalyzed cyclization to provide the exo-cyclic allenylpyrrole **162**. (Eqn. 353) The propargylsilane **163** was cyclized to exocyclic allenylcyclopentane **164**. (Eqn. 354) In a similar reaction the intramolecular cyclization with an enone as the electrophile was accomplished. (Eqn. 355) Other examples were presented as well. The propargylsilane **165** was used as a synthon for α-carboethoxyvinylsilanes via its reaction with aldehydes and ketones. (Eqns. 356, 357)



$$\mathrm{TMSCH_2C{\equiv}C(CH_2)_nNH_2} \xrightarrow[\text{[392]}]{\text{1) PhCHO} \quad \text{2) AcCl/Et}_3\text{N/EtOH}} \underset{\textbf{161}}{\mathrm{TMSCH_2C{\equiv}C(CH_2)_n\overset{Ac}{N}\underset{EtO}{C}HPh}} \qquad (352)$$

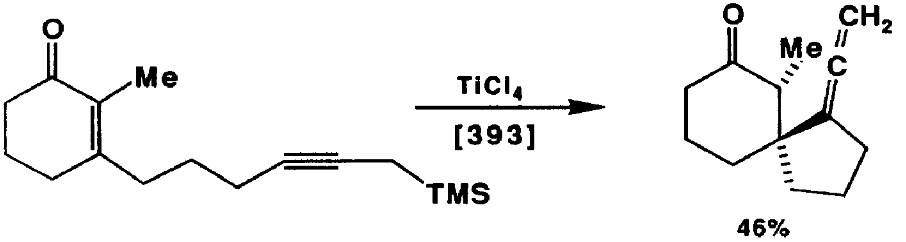


(353)

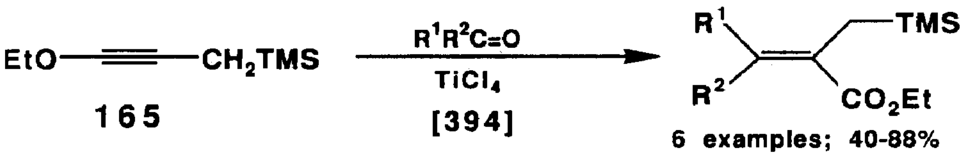


R = H (50%); R = Me (87%)

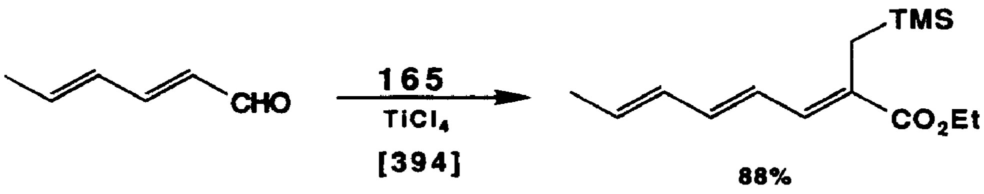
(354)



(355)



(356)

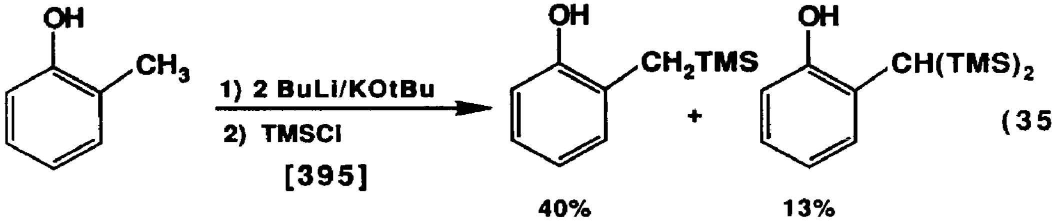


(357)

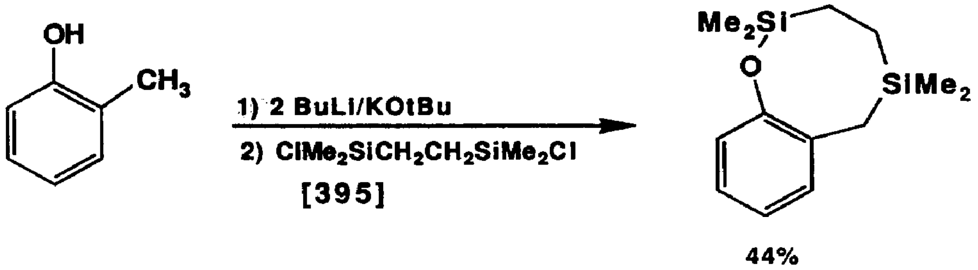
# XII. BENZYLSILANES

## A. PREPARATION

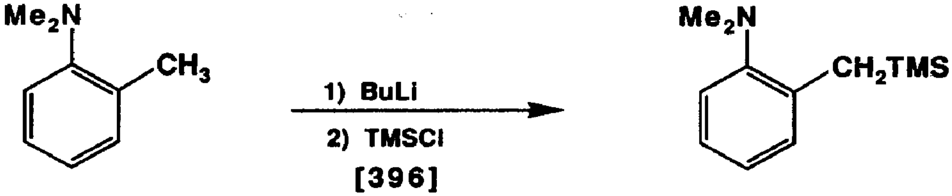
The preparation of benzylsilanes via the reaction of benzyllithium reagents was accomplished with the dianion of ortho-cresol (Eqns. 358, 359) and the anion of ortho-methyl N,N-dimethylaniline (Eqn. 360) The product from the anion of the aniline was further deprotonated and substituted. (Eqn. 361)



(358)



(359)



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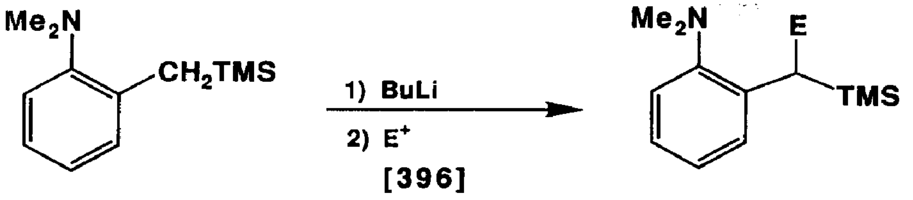
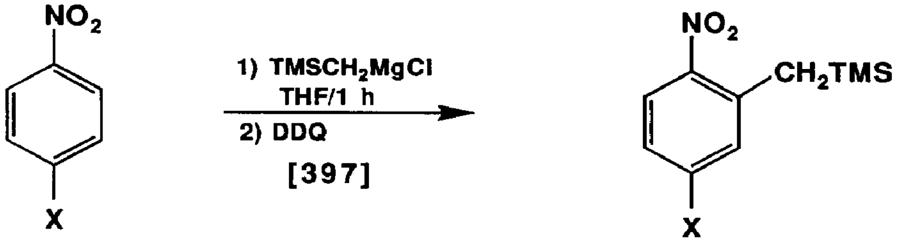


(E = D, Me$_3$Sn, PhMeBrSn, TMS)

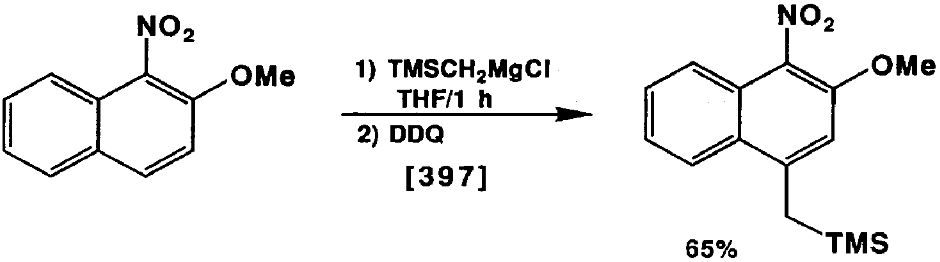
(361)

α-Silylated organometallic reagents were employed in the synthesis of benzylsilanes from nitroaromatics as seen from the examples shown in Eqns. 362 and 363.



9 examples; 53-90%

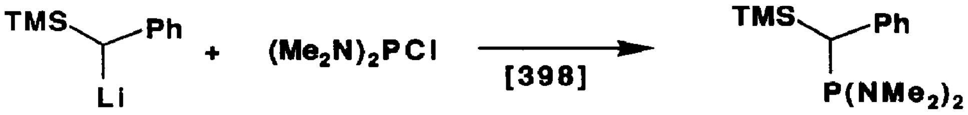
(362)



65%

(363)

The lithium reagent of benzyltrimethylsilane was reacted with bis(dimethylamino)phosphorus chloride to give **166**. (Eqn. 364)

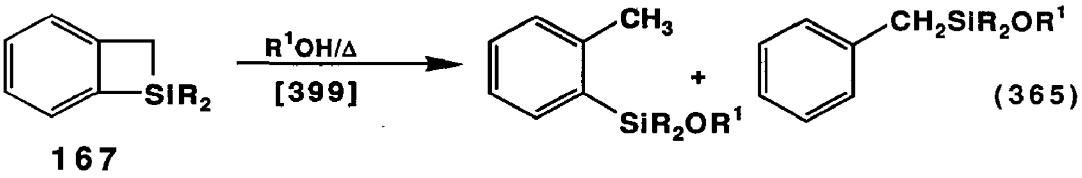


**166**

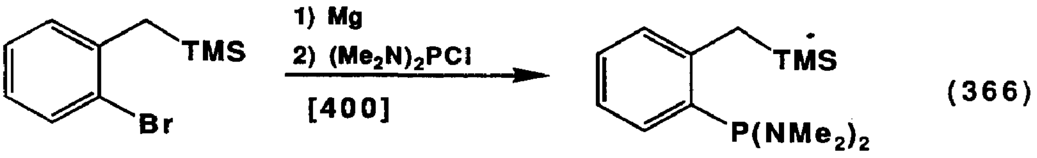
70-75%

(364)

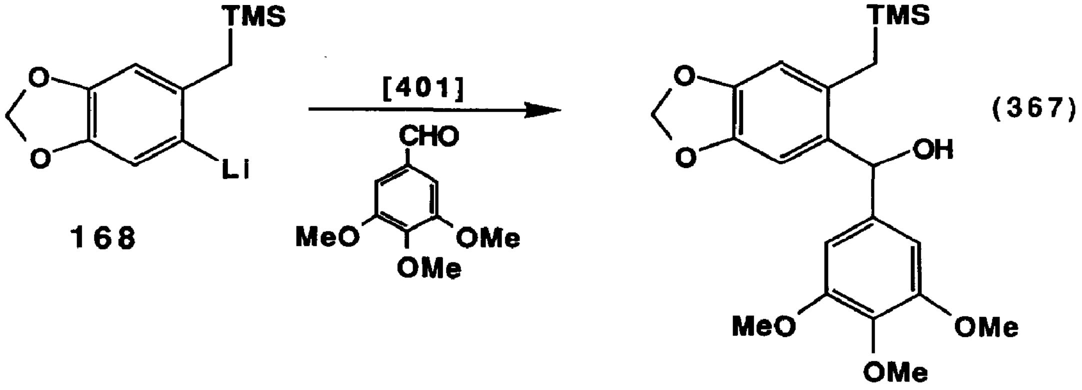
The benzosilacyclobutane **167** reacts with alcohols to give a mixture of the ortho-silyltoluene and the benzylsilane resulting from cleavage of the benzyl-silicon bond and the phenyl-silicon bond, respectively. (Eqn. 365)



Ortho-bromobenzyltrimethylsilane was functionalized via the corresponding Grignard reagent. (Eqn. 366)

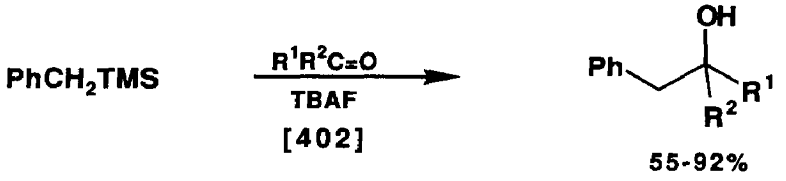


The ortho-lithiated benzylsilane **168** was used in an approach to the synthesis of podophyllotoxins. (Eqn. 367)

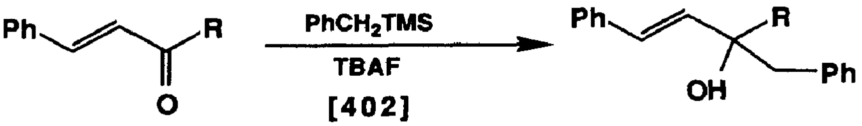


## B. BENZYLSILANES--REACTIONS

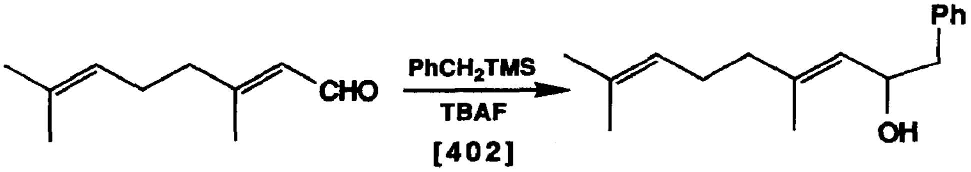
Benzylsilanes react with ketones and aldehydes under the influence of fluoride ion to give benzylation of the carbonyl group. (Eqn. 368) 1,2-Addition is observed with α,β-unsaturated systems. (Eqns. 369, 370) This was carried over to heterocyclic benzylic silanes. (Eqn. 371)



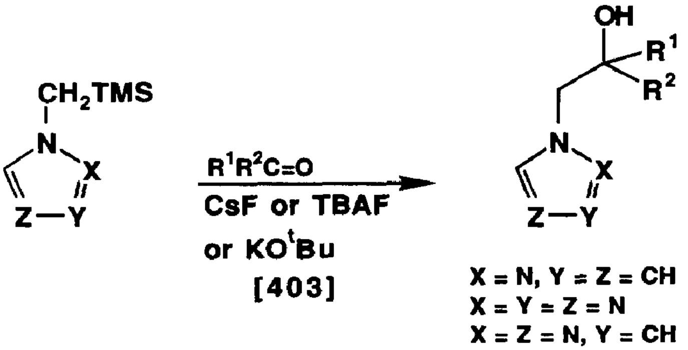
(368)



(369)

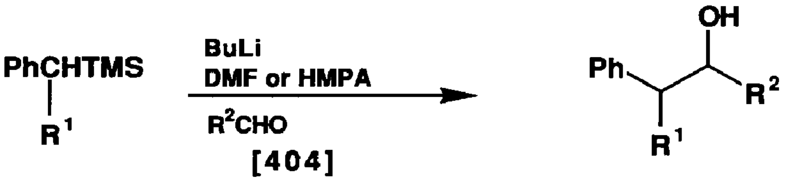


(370)



(371)

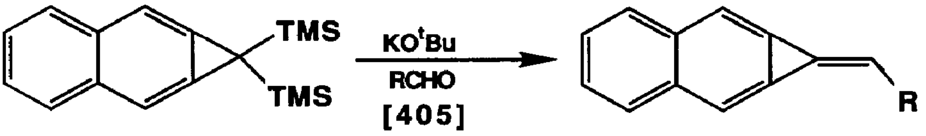
Substituted benzyltrimethylsilanes were treated with butyllithium in DMF or HMPA solvent and then an aldehyde to provide 2-phenylethanol derivatives. It is interesting that desilylation occurs here rather than simple deprotonation. (Eqn. 372)



(372)

($R^1$ = H, MeO, THPO, OTMS; $R^2$ = Ph, p-$MeC_6H_4$, p-$MeOC_6H_4$, styryl, Pr, $^i$Pr, $^t$Bu)

Cyclopropenes have been prepared via the reaction of **169** with aldehydes in the presence of tert-butoxide ion. (Eqn. 373)

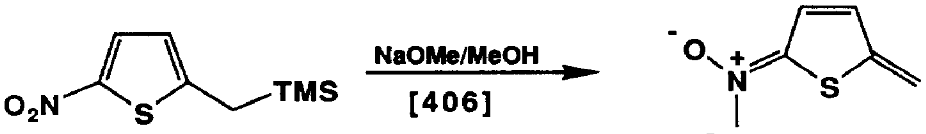


(373)

**169**

**6 examples; 10-100%**

The benzyltrimethylsilane **170** was used to generate the anion **171** as shown in Eqn. 374.

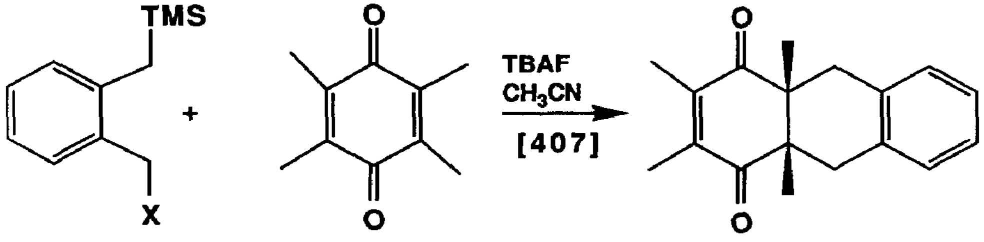


(374)

**170**

**171**

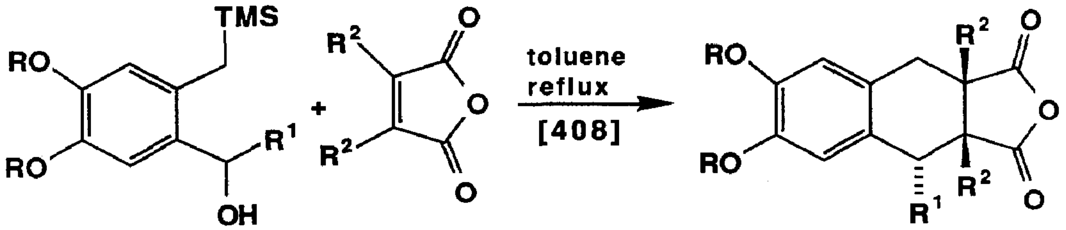
The benzylsilane entry into "in situ" generated o-quinodimethane intermediates continued to be used synthetically. Thus, they were trapped with p-quinones to give tetrahydro-1,4-anthracenediones. (Eqn. 375)



(375)

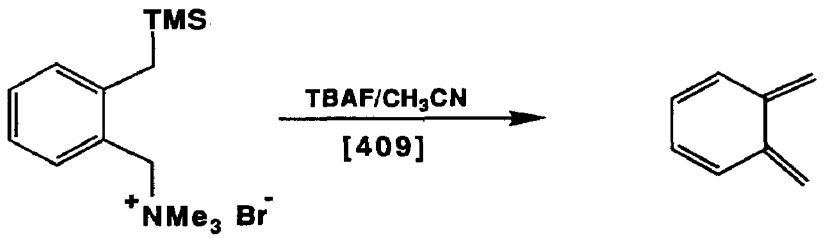
X = NMe$_3$Br (44%), X = OAc (61%)

A thermal benzo-Peterson reaction was used to generate o-quinodimethanes and hence tetrahydronaphthalenes. (Eqn. 376)



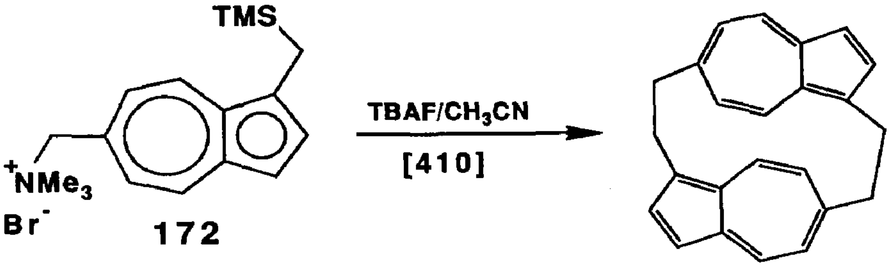
51-72% (376)

This approach was also used to prepare o-quinodimethane for direct observation of this reactive intermediate. (Eqn. 377)



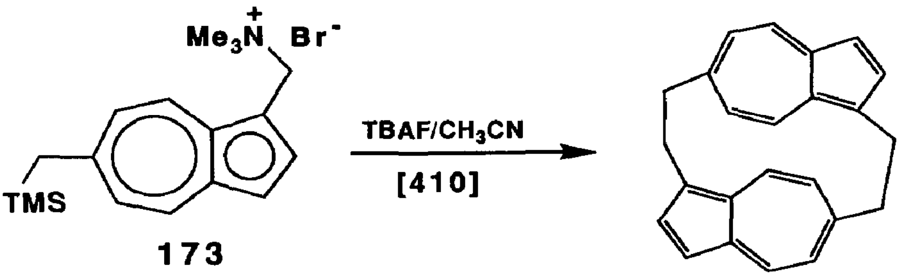
(377)

Both benzylsilanes **172** and **173** were used to prepare anti[2.2](1,6)azulenophane *via* intermediate **174**. (Eqns. 378, 379)



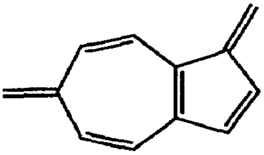
**172**

(378)



**173**

(379)



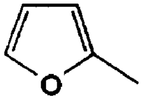
**174**

## C. BENZYLSILANES--OTHER STUDIES

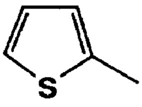
The kinetics of the cleavage of a series of benzylic silanes in methanolic sodium methoxide was studied. (Eqn. 380) The relative rates observed were **176** > **177** > **178** > **175**.

$$\mathrm{RCH_2TMS} \xrightarrow[50^\circ]{\mathrm{NaOMe/MeOH}} \mathrm{RCH_3} + \mathrm{MeOSiMe_3} \qquad (380)$$

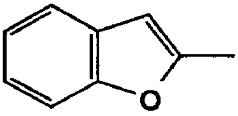
[411]



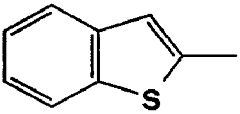
**175**



**176**



**177**

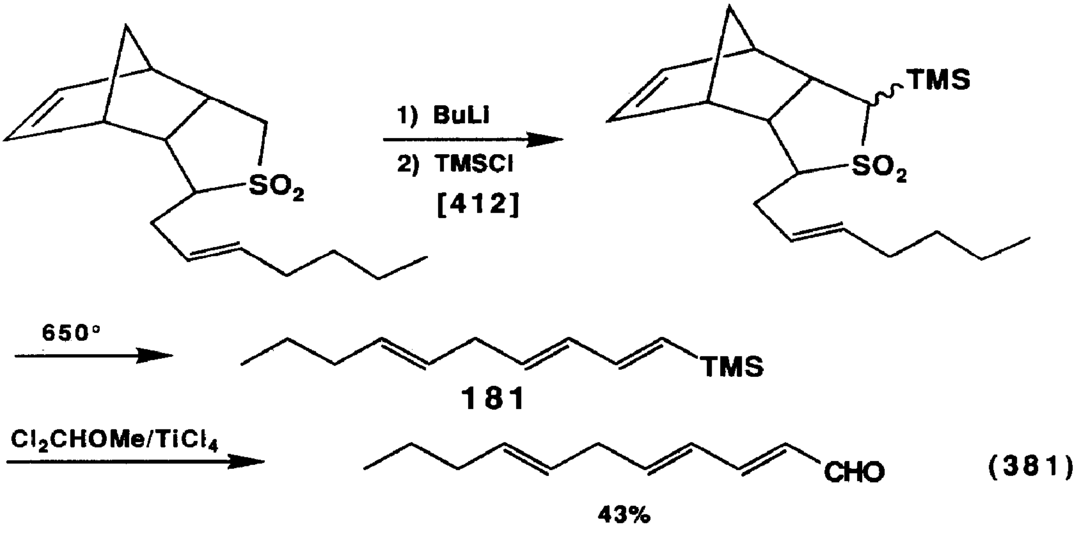


**178**

# XIII. α-FUNCTIONAL ORGANOSILANES

## A. PREPARATION

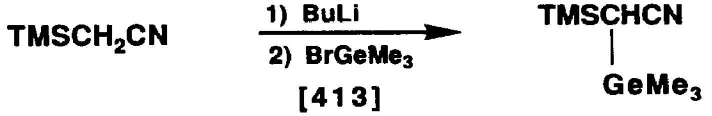
As expected the reaction of α-functionalized organometallic, principally organolithium reagents, with chlorosilanes was a popular entry into α-functional organosilanes. Metallation-trimethylsilylation of the sulfone **179** results in the preparation of the α-trimethylsilylated sulfone **180**, which upon thermolysis gives silylated triene **181**. The vinylsilane **181** was converted to the corresponding aldehyde in moderated yield. (Eqn. 381)



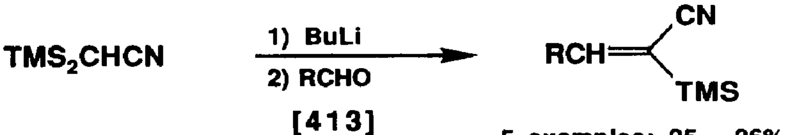
Trimethylsilylacetonitrile was converted to the bis(trimethylsilyl)acetonitrile

(Eqn. 382), the α-trimethylgermyl-α-trimethylsilylacetonitrile (Eqn. 383) and the bis trimethylsilyl material to α-trimethylsilyl acrylonitriles (Eqn. 384).

$$\mathrm{TMSCH_2CN} \xrightarrow[\substack{2)\ 2\ \mathrm{TMSCl} \\ [413]}]{1)\ 2\ \mathrm{BuLi}} \mathrm{TMS_2C{=}C{=}NTMS} \xrightarrow{\mathrm{H_2O}} \mathrm{TMS_2CHCN} \qquad (382)$$



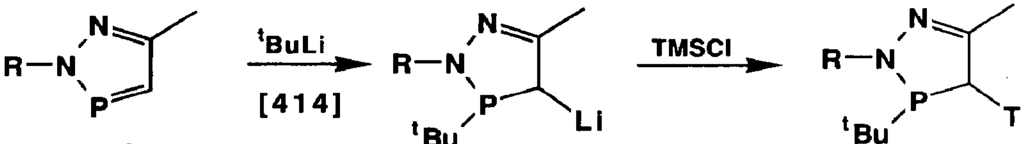
$$\mathrm{TMSCH_2CN} \xrightarrow[\substack{2)\ \mathrm{BrGeMe_3} \\ [413]}]{1)\ \mathrm{BuLi}} \underset{\mathrm{GeMe_3}}{\mathrm{TMSCHCN}} \qquad (383)$$



5 examples; 25 - 96%

(384)

Reaction of tert-butyllithium with the diazophosphole **182** results in a lithium reagent, which was trapped with trimethylchlorosilane. (Eqn. 385)



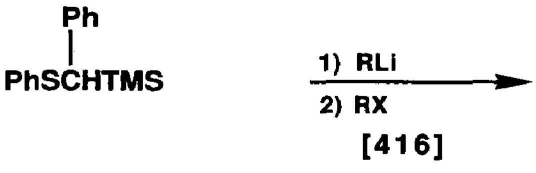
**182**

(385)

Lithiated perfluoroethers were reacted with chlorosilanes to give the corresponding perfluorinated silyl derivatives. (Eqn. 386)

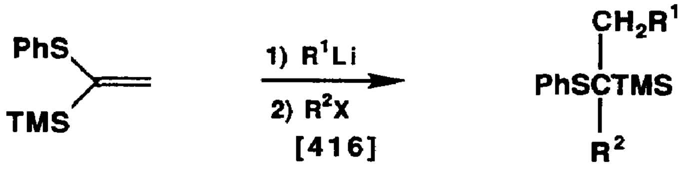
$$\mathrm{R^1{}_fOR^2{}_fLi} + \mathrm{R^3{}_3SiCl} \xrightarrow[{[415]}]{} \mathrm{R^1{}_fOR^2{}_f\text{-}SiR^3{}_3} \qquad (386)$$

Existing α-trimethylsilyl sulfides were used to prepare further alkylated derivatives of these highly useful materials as shown in Eqns. 387-389.



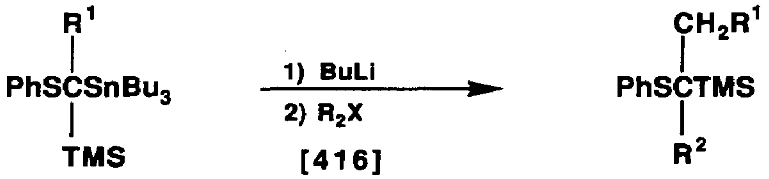
$$\mathrm{PhS\overset{Ph}{C}HTMS} \xrightarrow[\text{2) RX} \quad [416]]{\text{1) RLi}} \mathrm{PhS\overset{Ph}{\underset{R}{C}}TMS}$$

(387)



$$\mathrm{PhS(TMS)C{=}CH_2} \xrightarrow[\text{2) } R^2X \quad [416]]{\text{1) } R^1Li} \mathrm{PhS\overset{CH_2R^1}{\underset{R^2}{C}}TMS}$$

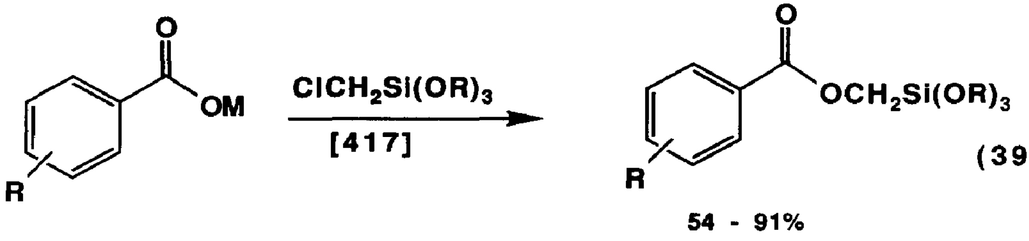
(388)



$$\mathrm{PhS\overset{R^1}{\underset{TMS}{C}}SnBu_3} \xrightarrow[\text{2) } R_2X \quad [416]]{\text{1) BuLi}} \mathrm{PhS\overset{CH_2R^1}{\underset{R^2}{C}}TMS}$$

(389)

The reaction of carboxylic acid salts with chloromethylsilanes was used to prepare several silylmethyl esters as seen in Eqns. 390-392.



(390)

$$\mathrm{KO_2C(CH_2)_nCO_2K} \xrightarrow[{[418]}]{\mathrm{R_3SiCH_2Cl/DMF}} \mathrm{R_3SiCH_2O_2C(CH_2)_nCO_2CH_2SiR_3}$$

(391)

$$ClCH_2Me_2SiCl \xrightarrow[{[419]}]{RCO_2^-/DMF} RCO_2CH_2Me_2SiO_2CR \qquad (392)$$

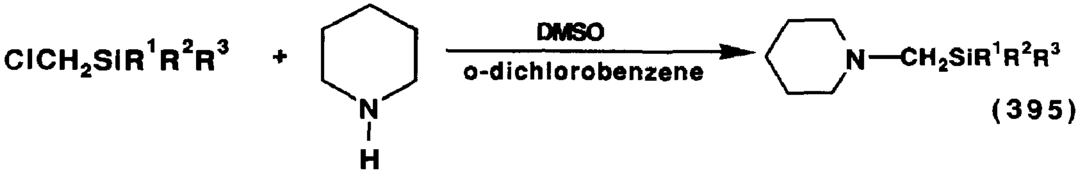
Halomethylsilanes were the silicon-containing starting materials for other α-functional organosilanes as well. Trimethylsilylmethylselenides were prepared according to Eqn. 393. An NMR study of the intramolecular interaction of the acetylacetamidomethylsilane **183**, prepared according to Eqn. 394, was carried out. The kinetics of the reaction of chloromethylsilanes with piperidine according to Eqn. 395, were studied. The nucleophilic aminomethylation of aldehydes was accomplished with reagents such as **184**, prepared as shown in Eqn. 396. Silylmethyl-1,2,4-triazoles were shown to have fungicidal properties. Chloromethyldimethylchlorosilane reacts with silylated derivatives of hydroxycarbamic acid to give reaction only at the silicon-chlorine bond. (Eqn. 397) A similar reaction is seen with bis(trimethylsilyl)-carbodiimide. (Eqn. 398)

$$RSeLi + TMSCH_2X \xrightarrow[{[420]}]{} RSeCH_2TMS \qquad (393)$$

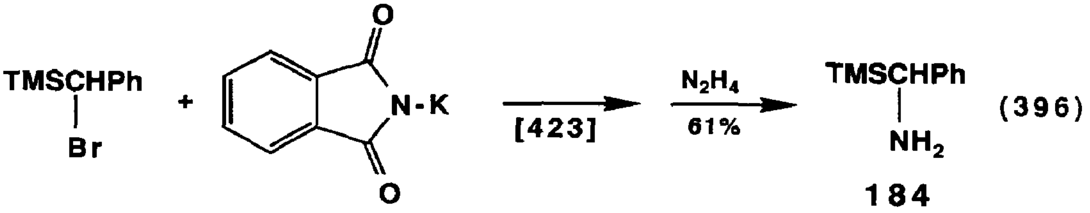
(X = Cl, Br; R = Me, Ph)

**183**

(394)

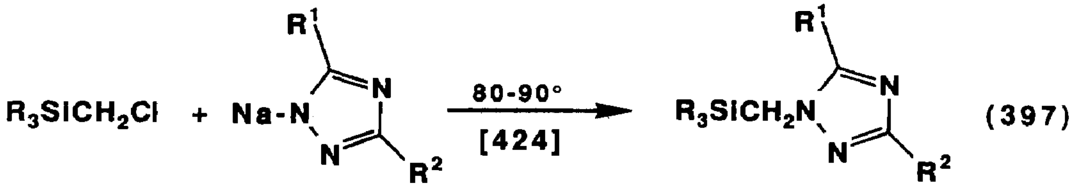


(395)

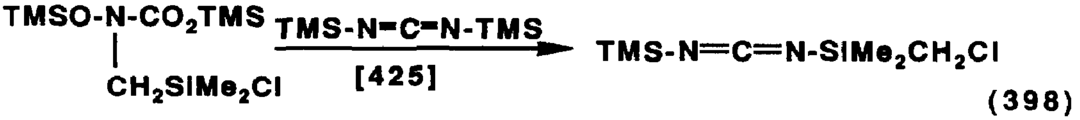


**184**

(396)



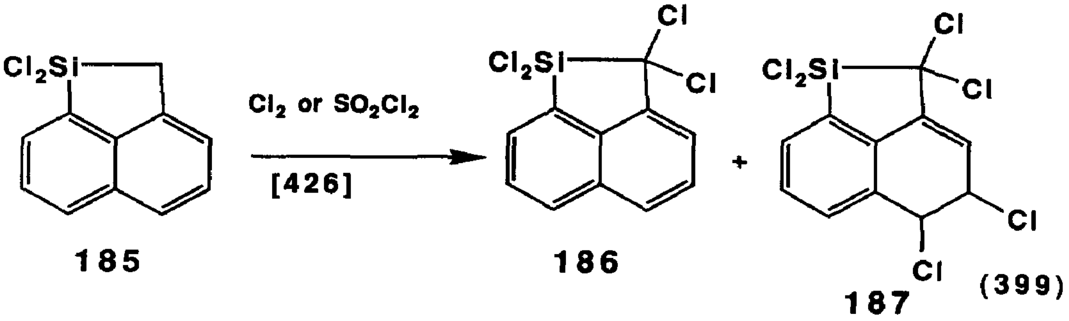
(397)



$$\underset{\displaystyle CH_2SiMe_2Cl}{TMSO\text{-}N\text{-}CO_2TMS} \xrightarrow[\text{[425]}]{TMS\text{-}N{=}C{=}N\text{-}TMS} TMS\text{-}N{=}C{=}N\text{-}SiMe_2CH_2Cl$$

(398)

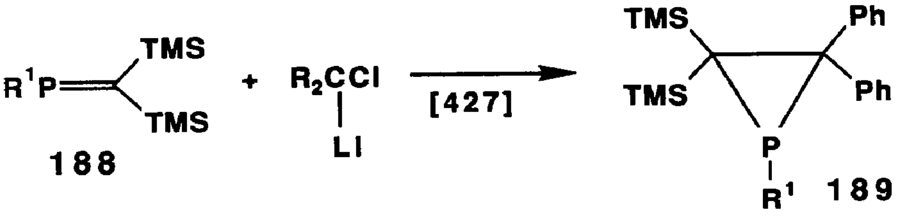
The chlorination of silaacenaphthene **185** gives the α,α-dichloro derivative **186** and the hexachloro material **187**. (Eqn. 399)



**185** **186** **187**

(399)

The silylated phosphaalkene **188** was converted to the α,α-disilylated phosphacyclopropane **189**. (Eqn. 400)



188

189

R¹ = Ph, ᵗBu

(400)

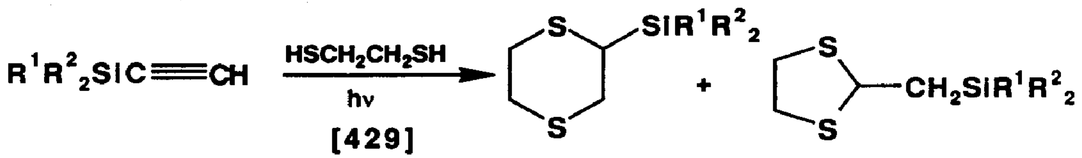
1-Hexynyldimethylsilane was reacted with dichlorocarbene, generated from sodium trichloroacetate, to give the corresponding dichloromethylsilane. (Eqn. 401) Its reaction with chloroform and potassium tert-butoxide on the other hand results in cleavage of the hexynyl group leading to (dichloromethyl)tert-butoxydimethylsilane. (Eqn. 402)

$$\mathrm{BuC{\equiv}CSiMe_2H} \xrightarrow[\text{[428]}]{\mathrm{Cl_3CCO_2Na}} \mathrm{BuC{\equiv}CSiMe_2CHCl_2} \quad (401)$$

20%

$$\mathrm{BuC{\equiv}CSiMe_2H} \xrightarrow[\text{[428]}]{\mathrm{CHCl_3/{}^tBuOK}} \mathrm{{}^tBuOSiMe_2CHCl_2} \quad (402)$$

Ethynylsilanes were reacted with 1,2-dimercaptoethane under photolytic conditions to produce the α- and β-functional silanes **190** and **191**. (Eqn. 403)



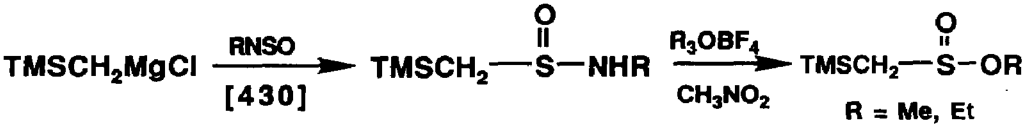
190

191

(403)

Trimethylsilylmethylmagnesium chloride was converted to trimethylsilylmethyl sulfinic acid (Eqn. 404) and derivatives (Eqn. 405).

$$\mathrm{TMSCH_2MgCl} \xrightarrow[\substack{2)\ \mathrm{H_2O} \\ [430]}]{1)\ \mathrm{SO_2}} \mathrm{TMSCH_2SO_2H} \xrightarrow{25^\circ} \begin{array}{c}\mathrm{TMSCH_2SOH} \\ + \\ \mathrm{TMSCH_2SO_3H}\end{array} \qquad (404)$$



$$\mathrm{TMSCH_2MgCl} \xrightarrow[[430]]{\mathrm{RNSO}} \mathrm{TMSCH_2{-}\overset{\overset{\displaystyle O}{\|}}{S}{-}NHR} \xrightarrow[\mathrm{CH_3NO_2}]{\mathrm{R_3OBF_4}} \mathrm{TMSCH_2{-}\overset{\overset{\displaystyle O}{\|}}{S}{-}OR}$$

$$\mathrm{R = Me,\ Et}$$

(405)

Tris(trimethylsilyl)methyllithium was reacted with elemental tellurium and selenium to provide the corresponding α-silylatated ditellurides and diselenides, respectively. (Eqn. 406) These could be converted to the tritellurides or triselenides (Eqn. 407) or even the mixed tetra- and tri substrates **192** and **193**. (Eqns. 408, 409)

$$\mathrm{(TMS)_3CLi} + \mathrm{Z} \xrightarrow[[431]]{} \mathrm{(TMS)_3\text{-}Z\text{-}Z\text{-}C(TMS)_3} \qquad (406)$$

$$\mathrm{Z = Te,\ Se}$$

$$\mathrm{(TMS)_3\text{-}Z\text{-}Z\text{-}C(TMS)_3} \xrightarrow[[431]]{\mathrm{H_2O/O_2}} \mathrm{(TMS)_3\text{-}Z\text{-}Z\text{-}Z\text{-}C(TMS)_3} \qquad (407)$$

$$\mathrm{Z = Te,\ Se}$$

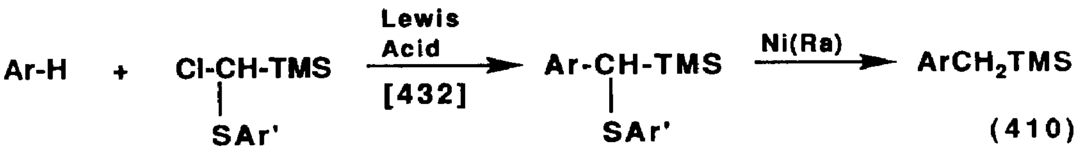
$$\mathrm{(TMS)_3\text{-}Te\text{-}Te\text{-}C(TMS)_3} \xrightarrow[\substack{2)\ \mathrm{Se_2Cl_2} \\ [431]}]{1)\ 2\ \mathrm{Li}} \mathrm{(TMS)_3\text{-}Te\text{-}Se\text{-}Se\text{-}Te\text{-}C(TMS)_3}$$

**192** (408)

$$(TMS)_3\text{-Te-Se-Se-Te-C}(TMS)_3 \xrightarrow[{[431]}]{Hg} (TMS)_3\text{-Te-Se-Te-C}(TMS)_3 \quad (409)$$

**193**

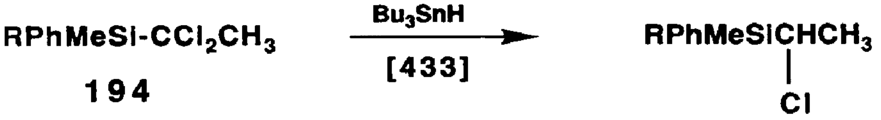
It is, of course, possible to convert one α-functional organosilane into another. This was used in the preparation of some benzylsilanes via the α-thiophenoxysilanes, formed via a Friedel-Crafts reaction. (Eqn. 410)



$$\text{Ar-H} + \text{Cl-}\underset{\substack{|\\ \text{SAr'}}}{\text{CH}}\text{-TMS} \xrightarrow[{[432]}]{\text{Lewis Acid}} \text{Ar-}\underset{\substack{|\\ \text{SAr'}}}{\text{CH}}\text{-TMS} \xrightarrow{\text{Ni(Ra)}} \text{ArCH}_2\text{TMS} \quad (410)$$

**7 examples; 72-98%**

The diastereoselectivity of the reduction of α,α-dichloroethylsilanes **194** was studied. (Eqn. 411) It was found that the diastereoselectivity is very low with the exception of the system where R is mesityl.

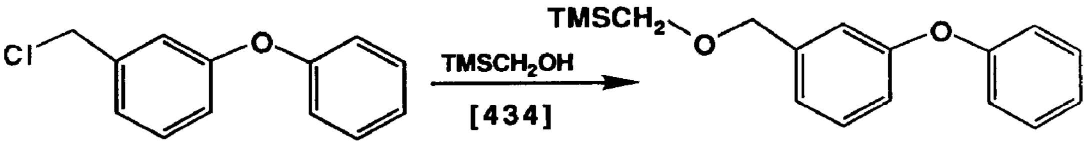


$$\text{RPhMeSi-CCl}_2\text{CH}_3 \xrightarrow[{[433]}]{Bu_3SnH} \text{RPhMeSi}\underset{\substack{|\\ \text{Cl}}}{\text{CH}}\text{CH}_3 \quad (411)$$

**194**

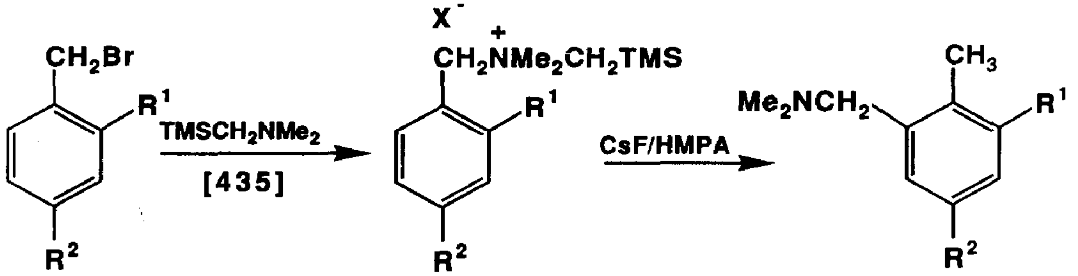
(R = c-$C_6H_{11}$, $^i$Pr, $^t$Bu, Mes)

Trimethylsilylmethanol was converted to the benzylic ether **195**, which was found to kill house flies very efficiently. (Eqn. 412) This material was also prepared from chloromethyltrimethylsilane and the sodium salt of the benzyl alcohol.



**195** (412)

Trimethylsilylmethyldimethylamine was converted to benzylammonium salts, which were reacted with fluoride ion to give the product of a Sommelet-Hauser rearrangement. (Eqn. 413)



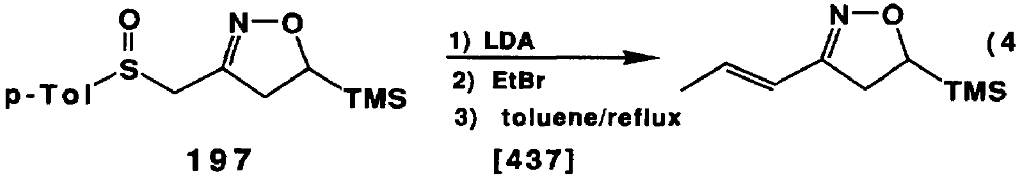
7 examples; 65-84% (413)

Tris(trimethylsilyl)methylmercaptan thermally rearranges to the S-silylated material **196**, which was in turn further derivatized. (Eqns. 414, 415)

$$(TMS)_3CSH \xrightarrow[\text{[436]}]{230^\circ} \underset{\mathbf{196}}{(TMS)_2CHSTMS} \qquad (414)$$

$$\underset{\mathbf{196}}{(TMS)_2CHSTMS} \xrightarrow{RSOCl} (TMS)_2CSS(O)R \qquad (415)$$

The α-functional silane **197** was derivatized via the sulfoxyl functionality as shown. (Eqn. 416)



**197**

(416)

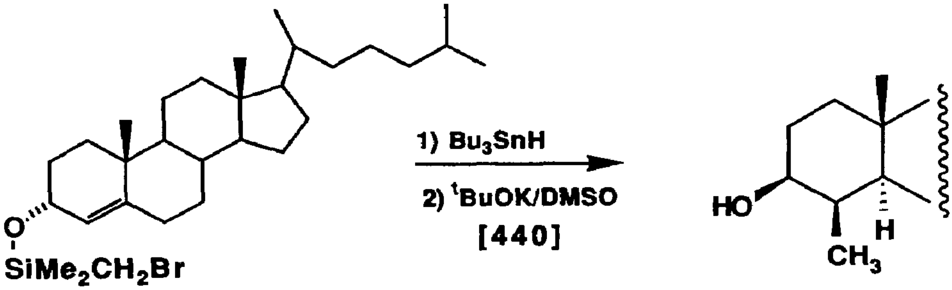
New α-functional organosilanes were also prepared by the exchange of ligands on an α-functional organosilane. (Eqns. 417, 418)

$$\mathrm{F_3SiCH_2SAc} + \mathrm{TMSOTMS} \xrightarrow[\text{[438]}]{\mathrm{CCl_4}} \mathrm{(TMSO)_2FSiCH_2SAc} \qquad (417)$$

$$\mathrm{CF_3SiF_3} \xrightarrow[\substack{\mathrm{Bu_2O/-78^\circ} \\ \text{[439]}}]{\mathrm{LiAlH_4}} \mathrm{CF_3SiH_3} \qquad (418)$$

## B. α-FUNCTIONAL ORGANOSILANES--REACTIONS

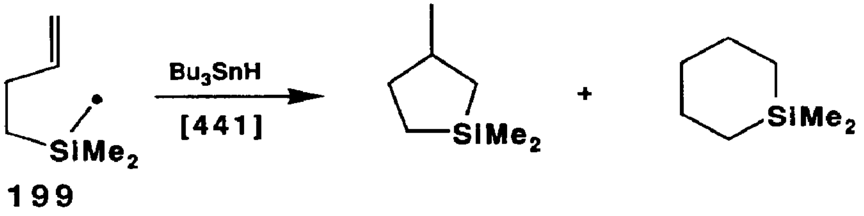
The bromomethyldimethylsilylated steroidal alcohol **198** was subjected to reductive cyclization and then protiodesilylation in order to stereospecifically introduce the methyl group at C-4. (Eqn. 419) Other examples were also investigated.



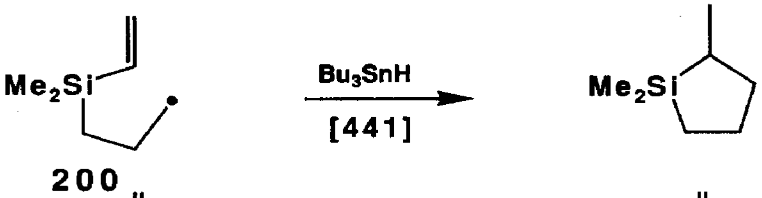
**198**

(420)

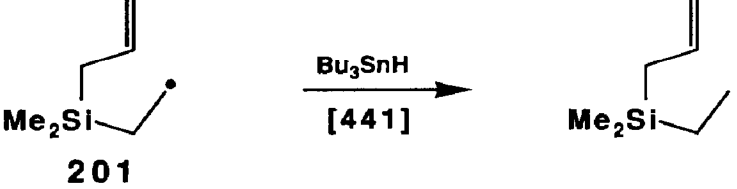
3-Buten-1-yldimethylsilylmethyl radical **199** was generated and the cyclization products analyzed. The endo-trig mode of cyclization was preferred. (Eqn. 421) The γ-silyl radical **200** also prefers the endo mode of cyclization, whereas the beta silyl radical **201** undergoes reduction with only a small amount of cyclization.



(421)

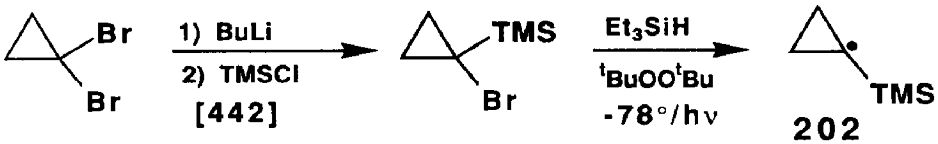


(422)



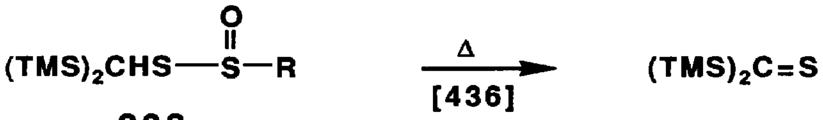
(423)

The configurational geometry of the α-trimethylsilylcyclopropyl radical **202** was studied. It was found to be configurationally planar. (Eqn. 424)



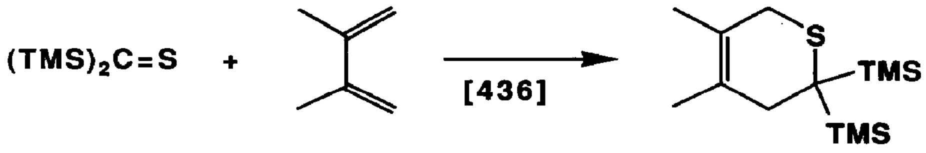
(424)

Bis(trimethylsilyl)thione can be generated by thermolysis of bis(trimethylsilyl)-dithioformate **203**. (Eqn. 425) This reactive intermediate can be trapped with dienes. (Eqn. 426)



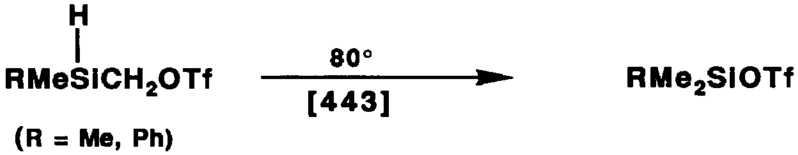
$$(TMS)_2CHS{-}\overset{O}{\overset{\|}{S}}{-}R \xrightarrow[\text{[436]}]{\Delta} (TMS)_2C{=}S \qquad (425)$$

203

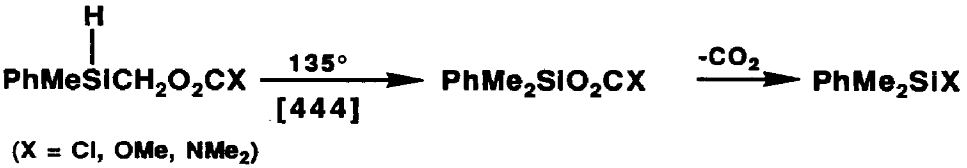


(426)

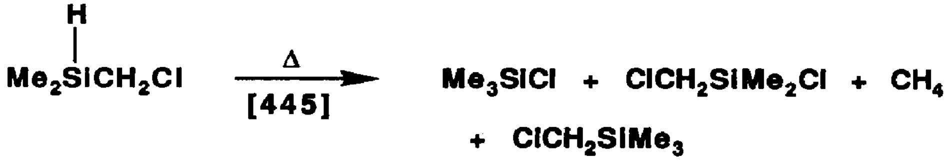
The thermal rearrangement of α-functional hydridosilanes was investigated. The migration of the hydride group from silicon to the α-carbon requires relatively low temperatures. It has been shown that the leaving group from the a-carbon can be a trifluoromethane sulfonate or carbonate moiety. (Eqns. 427, 428) In addition, the kinetics of the thermal rearrangement of chloromethyldimethylsilane were studied. (Eqn. 429)



$$\underset{(R\,=\,Me,\,Ph)}{RMe\overset{H}{\overset{|}{Si}}CH_2OTf} \xrightarrow[\text{[443]}]{80°} RMe_2SiOTf \qquad (427)$$

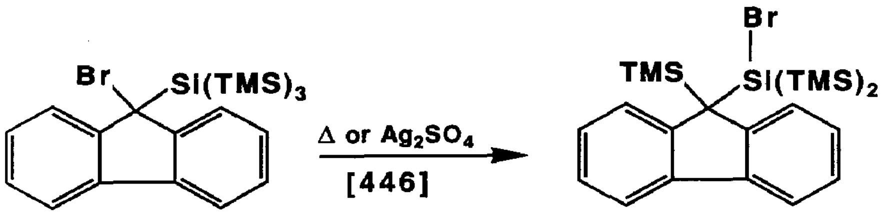


$$\underset{(X\,=\,Cl,\,OMe,\,NMe_2)}{PhMe\overset{H}{\overset{|}{Si}}CH_2O_2CX} \xrightarrow[\text{[444]}]{135°} PhMe_2SiO_2CX \xrightarrow{-CO_2} PhMe_2SiX \qquad (428)$$



$$Me_2\overset{H}{\overset{|}{Si}}CH_2Cl \xrightarrow[\text{[445]}]{\Delta} Me_3SiCl + ClCH_2SiMe_2Cl + CH_4 + ClCH_2SiMe_3 \qquad (429)$$

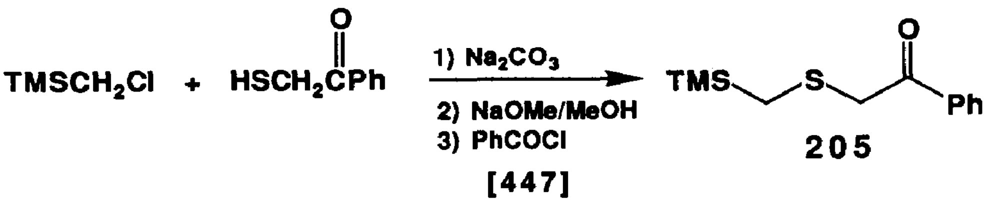
A thermal rearrangement of the α-bromotris(trimethylsilyl)silylfluorene **204** was reported. (Eqn. 430)



**204**

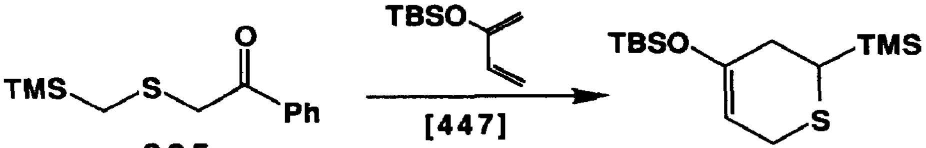
(430)

Photolysis of α-thioorganosilane **205**, prepared according to Eqn. 431, in the presence of dienes gives the cycloadduct of the diene with trimethylsilylthiocarbaldehyde (Eqn. 432).



**205**

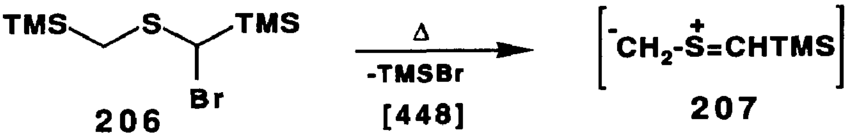
(431)



**205**

(432)

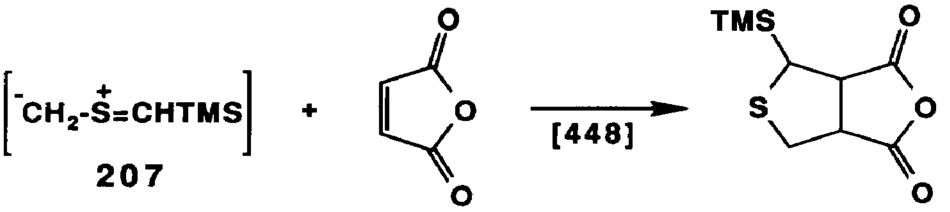
Thermolysis of α-functional silane **206** provides the thiocarbonyl ylide **207**. (Eqn. 433) This material cycloadds to activated dipolarophiles. (Eqn. 434)



**206**

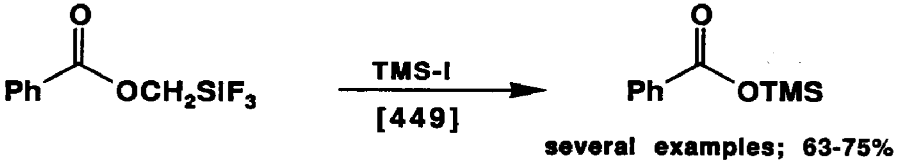
**207**

(433)

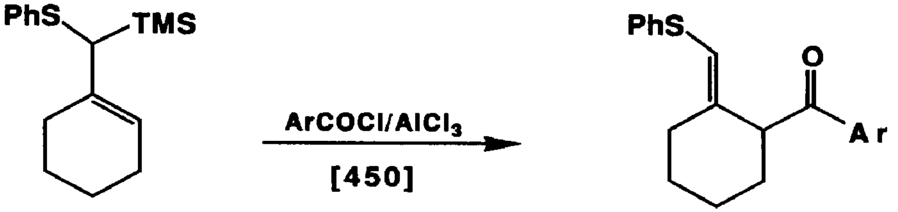


(434)

Trifluorosilylmethyl benzoate was transesterified with trimethyliodosilane. (Eqn. 435) Presumably iodomethyltrifluorosilane is the other product of this reaction. α-Thiophenoxylsilane **208**, which reacts as an allylsilane, was acylated according to Eqn. 436.



(435)

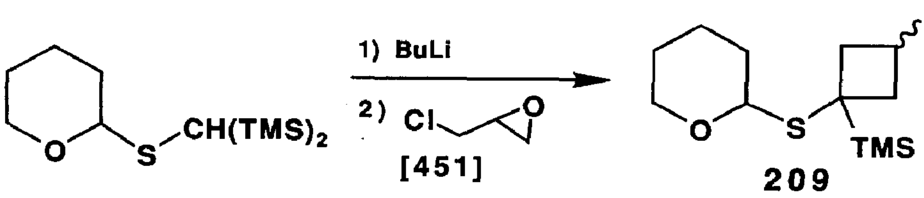


(436)

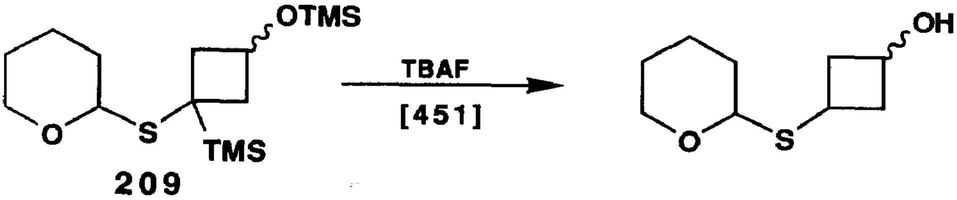
## C. α-FUNCTIONAL ORGANOSILANES--REACTIONS WITH FLUORIDE ION

The combination of a variety of carbofunctional organosilanes and fluoride ion to bring about otherwise difficult chemistry is one of the fastest growing areas of organosilicon chemistry as applied to synthesis. Of particular interest in the application of the strong chemoselectivity is the reaction of α-functional organosilanes with fluoride ion to generate a reactive species in the presence of an electrophile. It is for this reason that a separate section is devoted to this specific topic.

The α-thio organosilane **209**, prepared as shown, (Eqn. 437) is protiodesilylated with tetrabutylammonium fluoride (TBAF) in THF. (Eqn. 438)

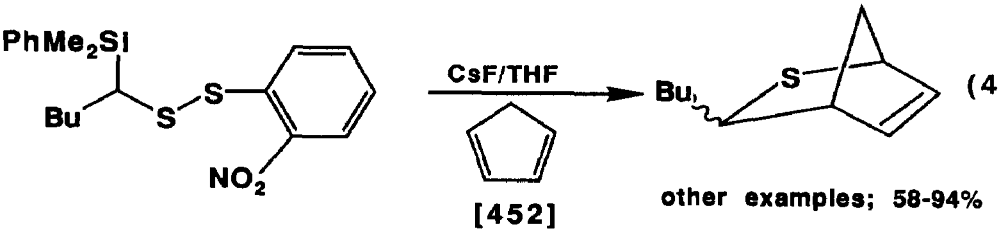


(437)



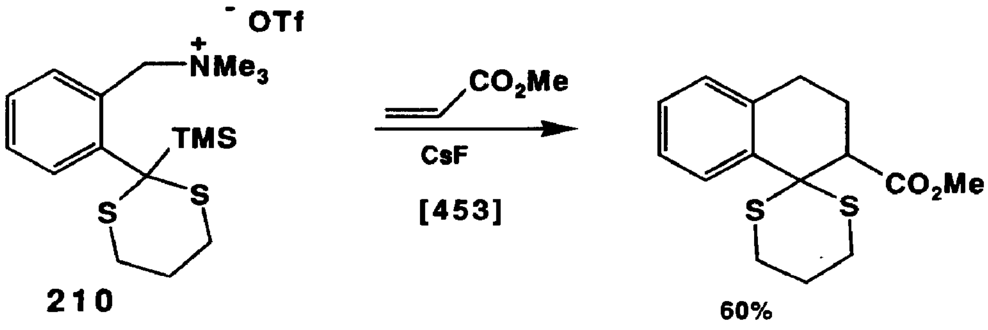
(438)

α-Trimethylsilyldisulfides can be treated with fluoride ion to generate the unstable thioaldehydes. Using this technique these reactive intermediates can be chemoselectively produced in the presence of a diene resulting in cycloadditions. (Eqn. 439)



(439)

The trimethylsilylated dithiane **210** was used to generate the functionalized o-quinonodimethane, which was trapped with methyl acrylate. (Eqn. 440)

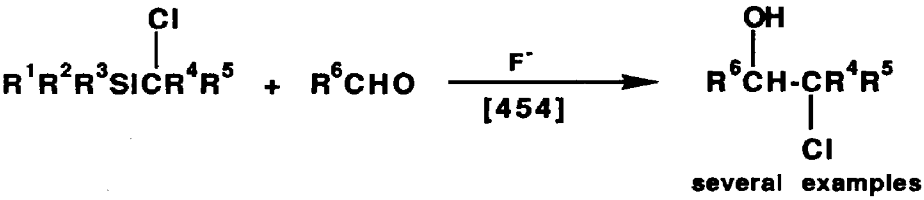


**210**

60%

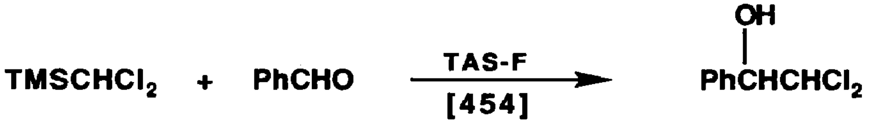
(440)

Treatment of α-chloroalkylsilanes with fluoride ion in the presence of aldehydes and ketones results in the corresponding chlorohydrins. (Eqns. 441, 442)



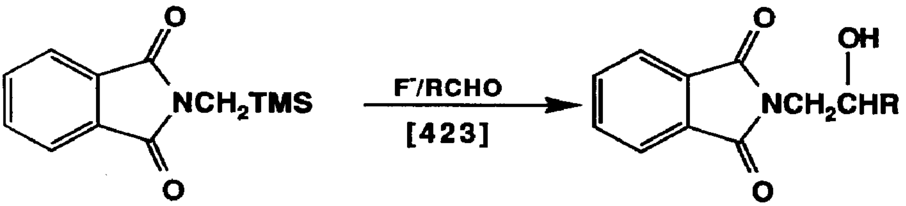
$$R^1R^2R^3Si\overset{Cl}{C}R^4R^5 + R^6CHO \xrightarrow[\text{[454]}]{F^-} R^6\overset{OH}{C}H\text{-}\underset{Cl}{C}R^4R^5 \qquad (441)$$

several examples



$$TMSCHCl_2 + PhCHO \xrightarrow[\text{[454]}]{\text{TAS-F}} Ph\overset{OH}{C}HCHCl_2 \qquad (442)$$

The phthalimidomethyltrimethylsilane **211** and related materials were reacted with aldehydes in the presence of fluoride ion (CsF or TBAF) to give the desired adducts. (Eqn. 443) Some protiodesilylation is also observed in these reactions.

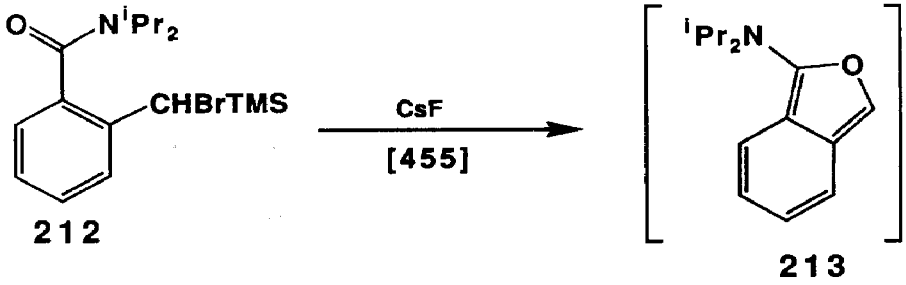


**211**

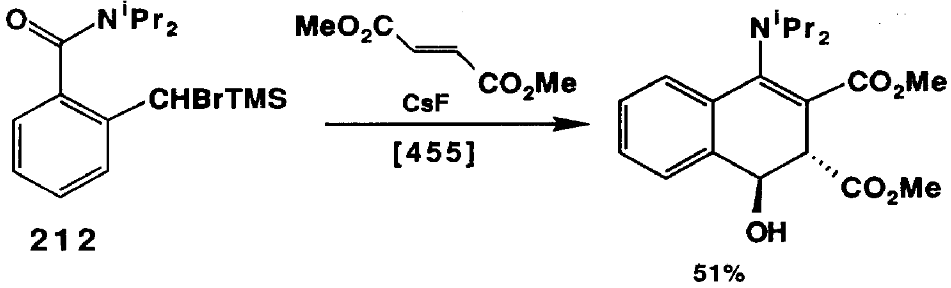
7 examples; 24-60%

(443)

The diisopropylaminobenzofuran **213** was generated 'in situ' from α-bromosilane **212** and cesium fluoride. (Eqn. 444) It was possible to carry this reaction out in the presence of activated dienophiles.as seen in the example shown in Eqn. 445.



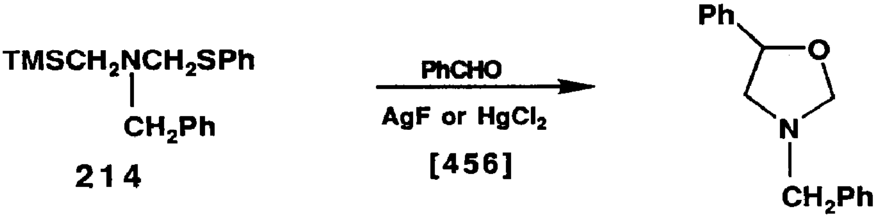
(444)



(445)

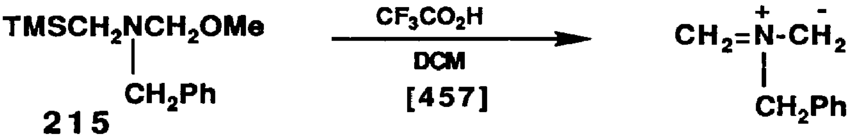
One of the more exciting applications of the combination of organosilanes with fluoride ion to directly generate reactive intermediates in the presence of other substrates has been the generation of azomethine ylides. Perhaps more than any other instances of the reactivity of fluoride ion and organosilanes these examples illustrate the high degree of chemoselectivity of fluoride for silicon allowing for a variety of electrophiles to be present in the reaction mixture. Since the azomethine ylides discussed below were all reacted with various dipolarophiles, only representative examples will be given here.

α-Thiophenoxyaminosilane **214**, preparable in multigram quantities and stable, is a precursor to N-benzylazomethine ylide, which undergoes various cycloadditions. (Eqn. 446)



(446)

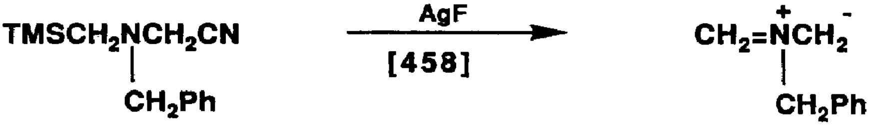
In a similar example it was found that trifluoroacetic acid will also serve to liberate the azomethine ylide from methoxy precursor **215**. (Eqn. 447) This methodology would not work well with acid sensitive substrates, however.



$$\underset{\textbf{215}}{\mathrm{TMSCH_2\underset{\substack{|\\ CH_2Ph}}{N}CH_2OMe}} \xrightarrow[\text{DCM}\ [457]]{\mathrm{CF_3CO_2H}} \mathrm{CH_2{=}\underset{\substack{|\\ CH_2Ph}}{\overset{+}{N}}{-}\overset{-}{C}H_2}$$

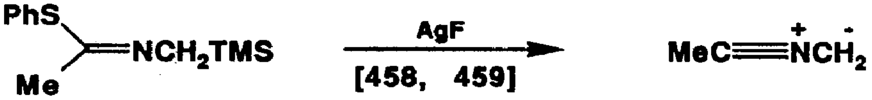
(447)

A listing of other azomethine ylides along with their silyl precursors is given below. (Eqns. 448-452) All of these materials undergo the expected cycloadditions when generated in the presence of the dipolarophile.

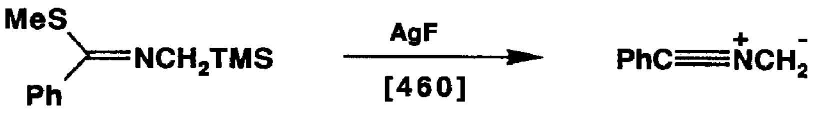


$$\mathrm{TMSCH_2\underset{\substack{|\\ CH_2Ph}}{N}CH_2CN} \xrightarrow[[458]]{\mathrm{AgF}} \mathrm{CH_2{=}\underset{\substack{|\\ CH_2Ph}}{\overset{+}{N}}\overset{-}{C}H_2}$$

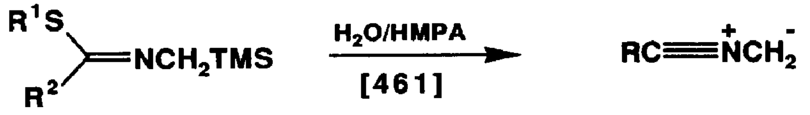
(448)



(449)

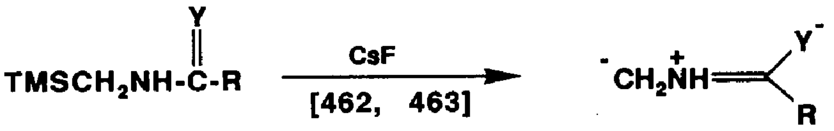


(450)



(451)

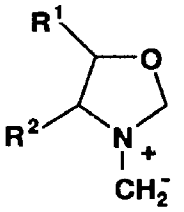
fluoride ion also serves here



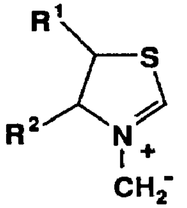
(452)

(Y = NPh, N-$C_6H_{11}$, S

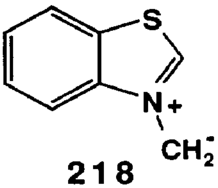
It proved not possible to successfully trap the ylides **216**, **217** and **218** due to rearrangements of the initial cycloadducts. [464, 465]



**216**

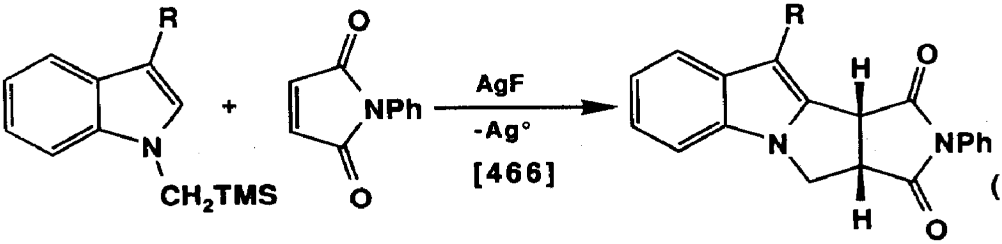


**217**

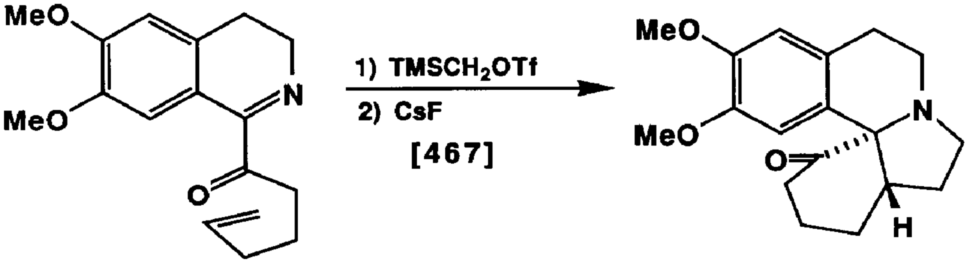


**218**

The preparation and reaction of cyclic azomethine ylides is, however, possible. One such ylide was used in an approach to pyrrolo[1,2-a]indoles. (Eqn. 453) The intramolecular cyclization shown in Eqn. 454 is a key step in an approach to the erythrinane skeleton.

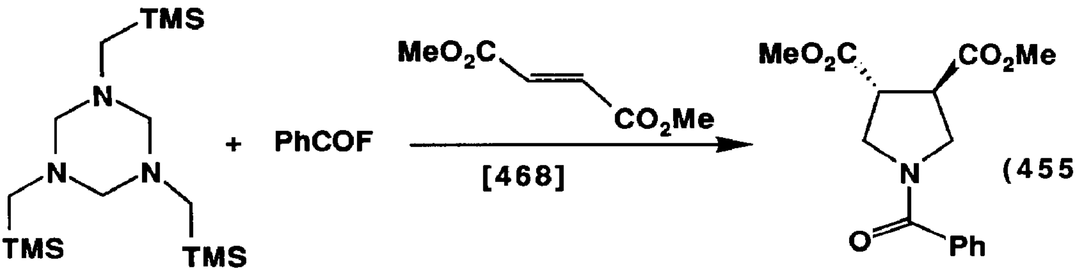


(453)



(454)

Compound **219** reacts with acyl fluorides to produce the simplest azomethine ylide, which can be trapped with dipolarophiles. (Eqn. 455)

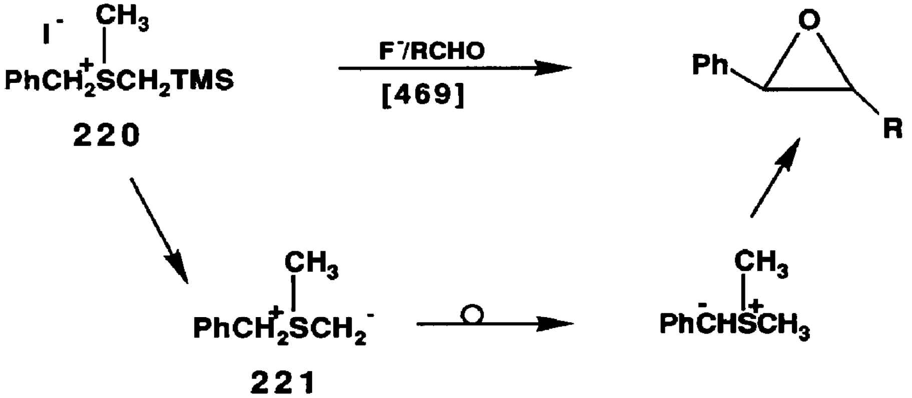


**219**

(455)

**6 examples; 60-82%**

Treatment of trimethylsilylmethylsulfonium salt **220** with fluoride ion in the presence of an aldehyde produces epoxides and not the expected five-membered ring. This has now been attributed to a [2,3]-sigmatropic rearrangement of the sulfur ylide to the more stable benzyl ylide **221**. (Eqn. 456)



(456)

## D. α-METALATED ORGANOSILANES

The synthesis of a wide variety of α-metalated organosilanes was reported. Trimethylsilylmethyllithium was prepared in excellent yield. (Eqn. 457) This highly useful material was converted to tris(trimethylsilylmethyl)aluminum (Eqn. 458), which was in turn converted to bis(trimethylsilylmethyl)bromoaluminum *via* disproportionation with aluminum bromide (Eqn. 459). Trimethylsilylmethylmagnesium chloride was reacted with indium iodide to give tris(trimethylsilylmethyl)indium, again in excellent yield. (Eqn. 460)

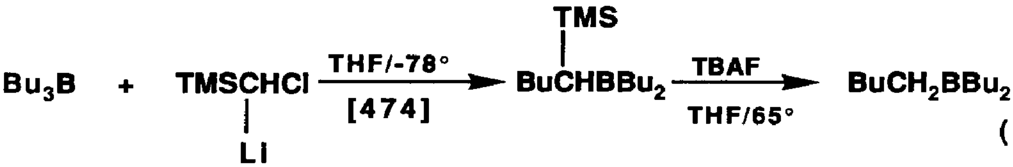
$$\mathrm{TMSCH_2Cl} \quad + \quad 2\ \mathrm{Li} \quad \xrightarrow[\text{[470]}]{\qquad\qquad} \quad \mathrm{TMSCH_2Li} \qquad (457)$$

$$3\ \mathrm{TMSCH_2Li} \quad + \quad \mathrm{AlBr_3} \quad \xrightarrow[\text{[471]}]{\qquad\qquad} \quad \underset{85\%}{\mathrm{(TMSCH_2)_3Al}} \qquad (458)$$

$$\mathrm{AlBr_3} \quad + \quad 2\ \mathrm{(TMSCH_2)_3Al} \quad \xrightarrow[\text{[472]}]{\qquad\qquad} \quad 3\ \underset{94\%}{\mathrm{BrAl(CH_2TMS)_2}} \qquad (459)$$

$$3\ \mathrm{TMSCH_2MgCl} \quad + \quad \mathrm{InI_3} \quad \xrightarrow[\text{[473]}]{\qquad\qquad} \quad \mathrm{(TMSCH_2)_3In} \qquad (460)$$

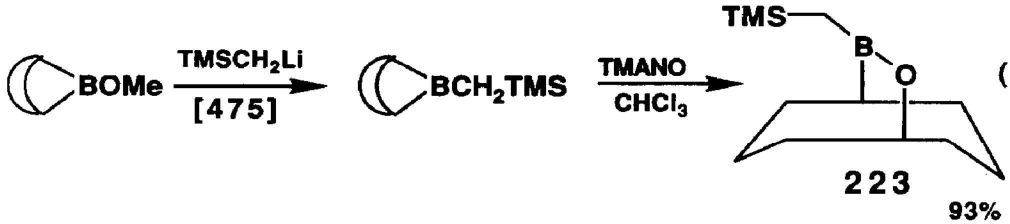
Trimethylsilylchloromethyllithium **222** was reacted with organoboranes to give addition followed by a migration of a group from boron to carbon with displacement of the chloride ion providing, ultimately, the α-boryl organosilane. Lithium reagent **222** was thus used to homologate organoboranes since it proved possible to protiodesilylate the α-boryl organosilanes. (Eqn. 461)



$$Bu_3B + TMSCH(Li)Cl \xrightarrow[\text{[474]}]{THF/-78°} BuCH(TMS)BBu_2 \xrightarrow[THF/65°]{TBAF} BuCH_2BBu_2 \quad (461)$$

**222**

Trimethylsilylmethyllithium reacts with B-methoxy-9-BBN to give the α-boryl organosilane, which when oxidized with trimethylamine N-oxide gives borinate ester 223. (Eqn. 462)

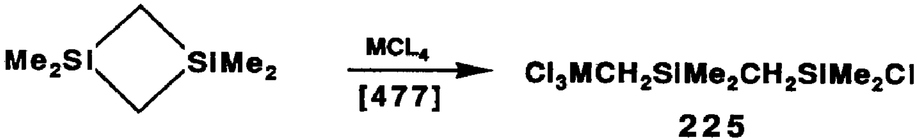


**223** (462)

Chloromethylsilanes were reacted with bis(triethylgermyl)mercury to give the bis(silylmethyl)mercury systems. (Eqn. 463)

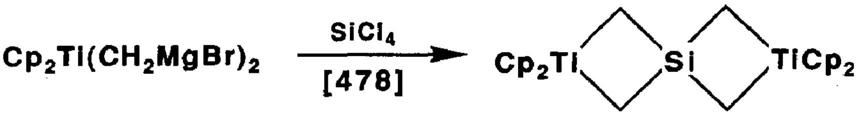
$$(Et_3Ge)_2Hg + ClCH_2SiMe_nCl_{3-n} \xrightarrow[\text{[476]}]{[O]} (Cl_{3-n}Me_nSiCH_2)_2Hg \quad (463)$$

Disilacyclobutane **224** reacts with zirconium or hafnium tetrachloride to give the ring opened α-metallo organosilanes **225**. (Eqn. 464)



**224** (464)

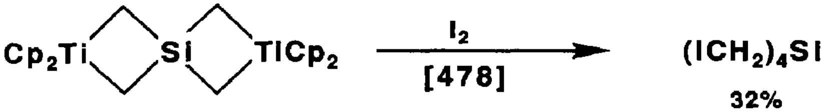
Di-Grignard reagent **226** reacts with silicon tetrachloride to give the silaspirocycle **227** in good yield. (Eqn. 465) This material reacts with iodine and trimethyltin chloride to give the products shown in Eqns. 466 and 467, respectively.



**226**

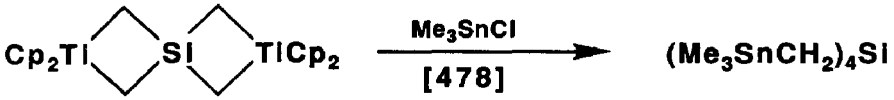
**227** 48%

(465)



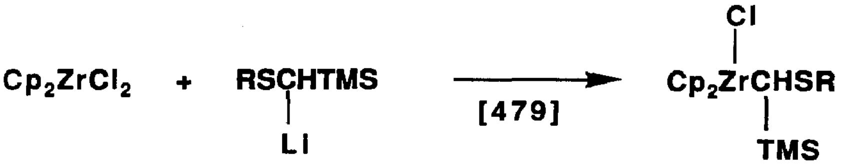
32%

(466)



(467)

α-Lithiotrimethylsilyl sulfide **228** was reacted with bis(cyclopentadienyl)dichloro zirconium to give **229**. (Eqn. 468)



$$Cp_2ZrCl_2 + \underset{\displaystyle Li}{RSCHTMS} \xrightarrow[{[479]}]{} \overset{\displaystyle Cl}{\underset{\displaystyle TMS}{Cp_2ZrCHSR}}$$

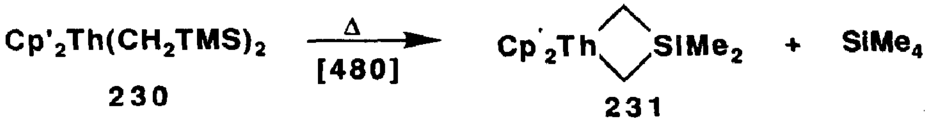
**228**

**229**

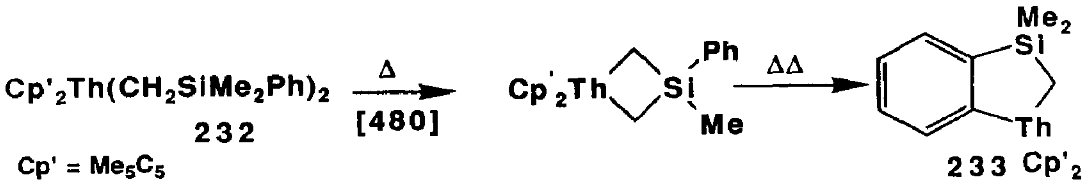
R = Me, Ph

(468)

Bis(trimethylsilylmethyl)dicyclopentadienylthorium complex **230** thermally eliminates tetramethylsilane and metallocycle **231**. (Eqn. 469) The phenylated system **232** gives phenyltrimethylsilane and, upon further heating, metallocycle **233**. (Eqn. 470)

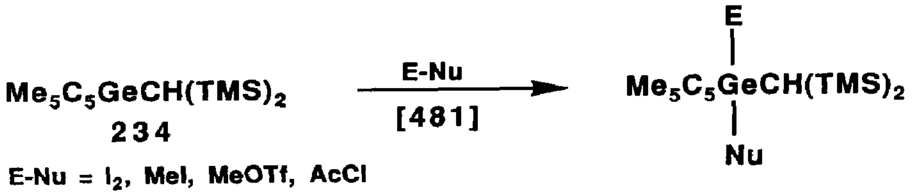


(469)



(470)

The α,α-bis(trimethylsilyl)germylene **234** was reacted with a number of electrophiles to give the products of addition to the germanium as shown in general form. (Eqn. 471) Tetrafluoroboric acid results in degermylation. (Eqn. 472)

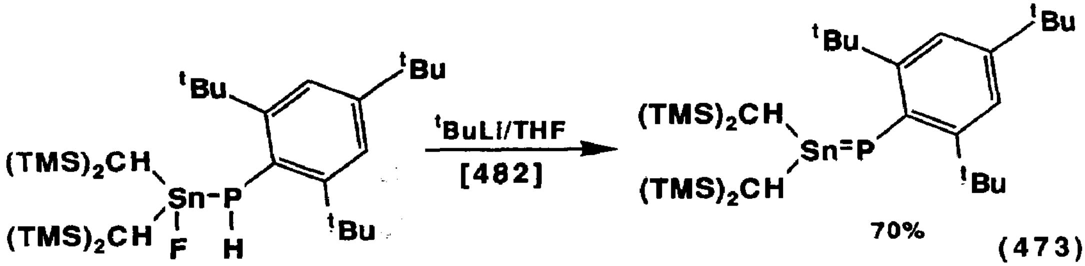


$$\underset{\mathbf{234}}{\mathrm{Me_5C_5GeCH(TMS)_2}} \xrightarrow[\text{[481]}]{\text{E-Nu}} \mathrm{Me_5C_5}\underset{\mathrm{Nu}}{\overset{\mathrm{E}}{\mathrm{Ge}}}\mathrm{CH(TMS)_2} \qquad (471)$$

E-Nu = $I_2$, MeI, MeOTf, AcCl

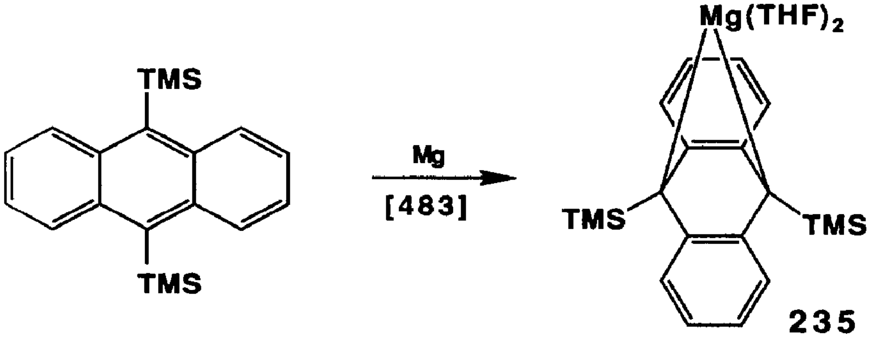
$$\mathrm{Me_5C_5GeCH(TMS)_2} \xrightarrow[\text{[481]}]{\mathrm{HBF_4}} \mathrm{Me_5C_5Ge^+\,BF_4^-} + \mathrm{(TMS)_2CH_2} \qquad (472)$$

The bis(trimethylsilyl)methyl group was employed to allow the preparation of the tin phosphorus double bond as shown. (Eqn. 473)



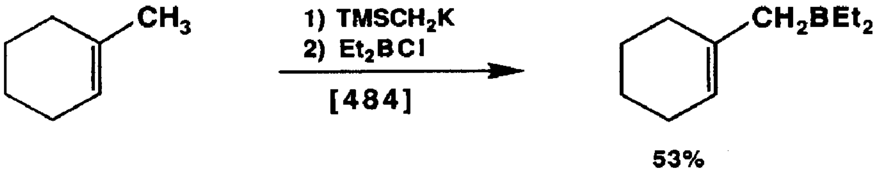
(473)

9,10-Bis-(trimethylsilyl)anthracene has been reacted with magnesium metal to give complex **235**, the structure of which has been determined. (Eqn. 474)



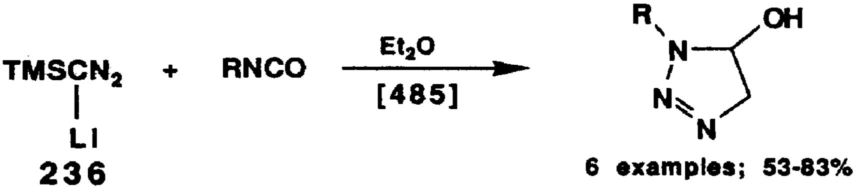
(474)

Trimethylsilylmethylpotassium was used to deprotonate the allylic position of olefins. The resulting allyl anions were reacted with dialkylboron chlorides to form the allylic bornaes. (Eqn. 475)

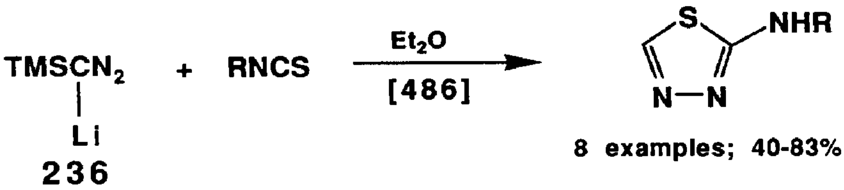


(475)

α-Lithiotrimethylsilyldiazomethane **236** was used in a number of cyclizations. The reaction of **236** with isocyanates provides 1-alkylated-5-hydroxy-1,2,3-triazoles. (Eqn. 476) It reacts with isothiocyanates in ether to give 2-amino-1,3,4-thiadiazoles. (Eqn. 477) These same reagents in THF give 1-substituted-5-thioalkyl-1,2,3-triazoles. (Eqn. 478)

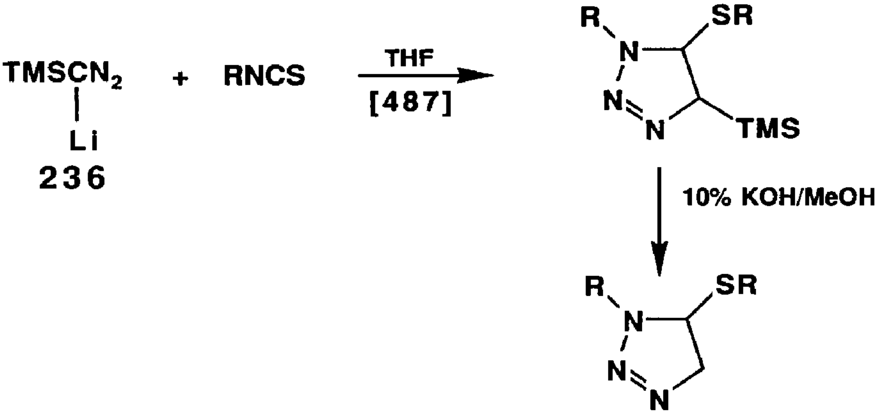


(476)



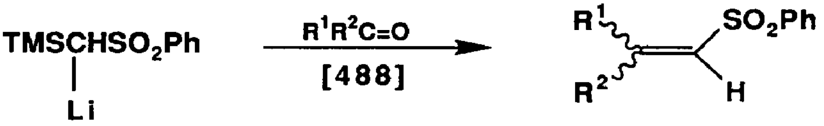
8 examples; 40-83%

(477)



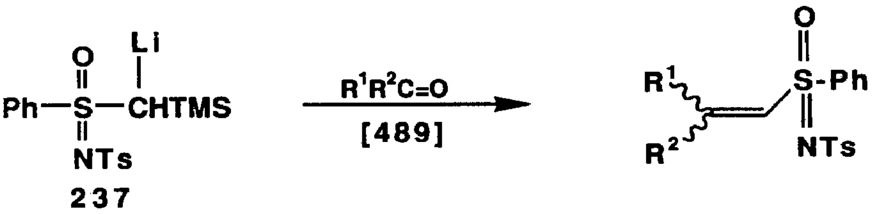
(478)

Several α-metalated organosilanes were employed in the Peterson olefination of aldehydes and ketones. Phenyl trimethylsilylmethyl sulfone was deprotonated and condensed with aldehydes and ketones to provide an entry into vinyl sulfones. (Eqn. 479) A variety of functional groups can be tolerated in this reaction. A similar sequence was accomplished with the silylated sulfoximine 237. (Eqn. 480)



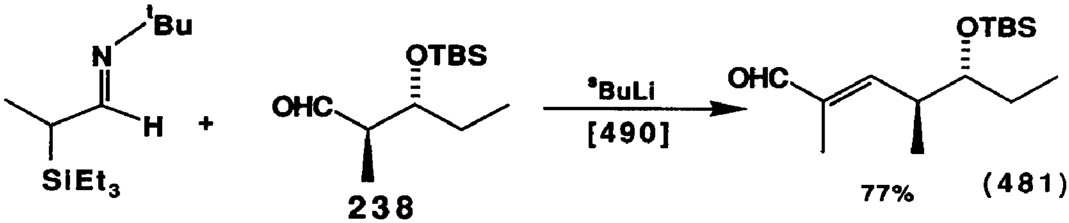
12 examples; 50-92%

(479)



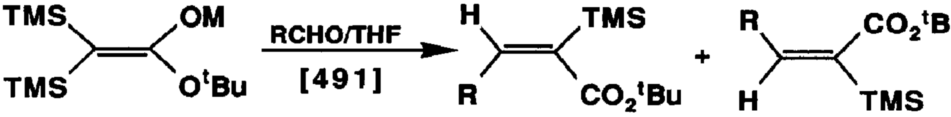
(480)

A difficult extension of aldehyde **238** was accomplished with the α-triethylsilyl-tert-butylimine of propionaldehyde as shown. (Eqn. 481) No other reagent succeeded in this transformation.



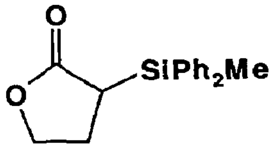
(481)

Tert-butyl bis(trimethylsilyl)acetate was deprotonated and the counterion varied to check the (Z) to (E) ratio of the adducts with aldehydes. (Eqn. 482) The ratio was found to depend on both the counterion and the R group of the aldehyde with non-complexing metals such as potassium favoring the (E) isomer and chelating type metal ions such as lithium, magnesium and aluminum favoring the (Z) isomer and a larger R group favoring the (E) isomer.

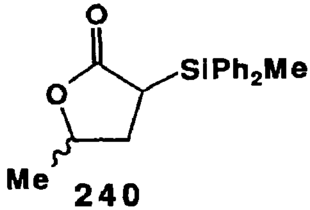


(482)

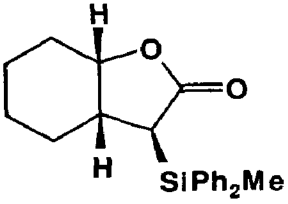
The three α-(methyldiphenylsilyl)lactones **239**, **240** and **241** were deprotonated and the resulting lithium reagent condensed with aldehydes to produce α-methylene lactones. Compound **241** only condensed with butanal with other substrates simply undergoing deprotonation. (Eqn. 483) Reagent **240** was used in a short synthesis of racemic ancepsenolide. (Eqn. 484)



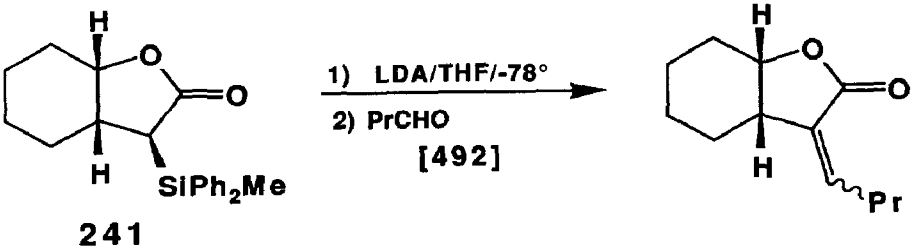
**239**



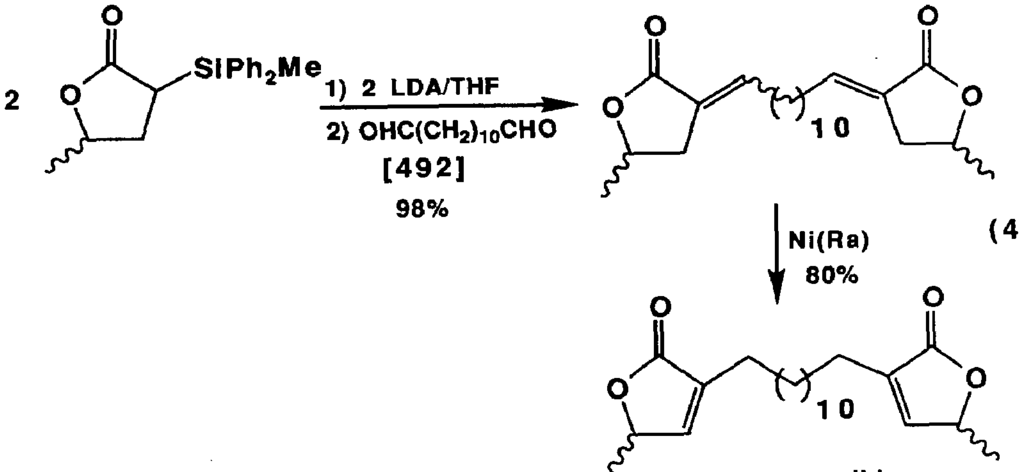
**240**



**241**



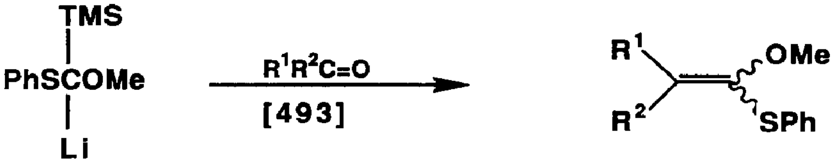
(483)



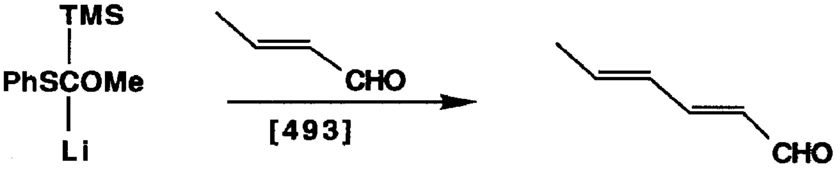
(484)

ancepsenolide

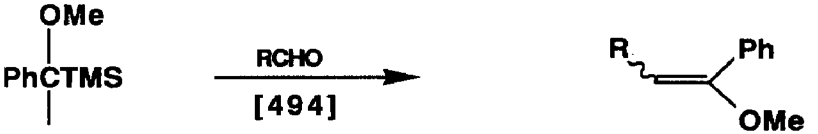
Some α-functionalized lithiated organosilanes were used in the Peterson olefination. Thus (methoxy)(thiophenoxy)trimethylsilylmethyllithium was reacted with aldehydes and ketones to give ketene O,S-acetals along with some deprotonation. (Eqn. 485) The reaction with crotonaldehyde occurs in a 1,2 fashion. (Eqn. 486) The reaction of trimethylsilyl-α-methoxybenzyllithium with aldehydes and ketones gives the expected olefins. (Eqn. 487)



(485)



(486)

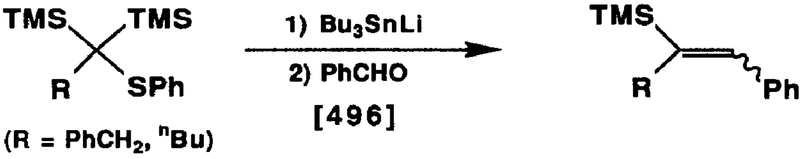


12 examples; 62-92%

(487)

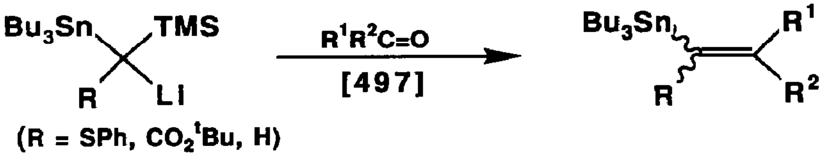
Several α-thio lithium reagents were studied with regards to their mode of addition to α,β-unsaturated ketones. Included in this study were trimethylsilyl-(thiophenoxy)methyllithium, trimethylsilylbis(thiophenoxy)methyllithium and bis(trimethylsilyl(thiophenoxy)methyllithium. The addition of HMPA or DME to the solvent mixture enhanced the 1,4-addition as did formation of the copper reagents. [495]

Bis(trimethylsilyl)methyllithium reagents, formed by the reaction of tributyltin-lithium on the corresponding thiophenyl ether, were reacted with benzaldehyde to give the vinylsilane. (Eqn. 488)



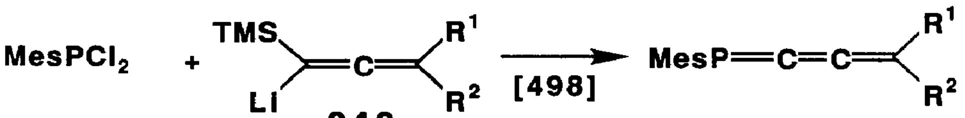
(488)

α-(Trimethylsilyl)tri-n-butylstannylmethyllithium reagents react with aldehydes and ketones to give vinylstannanes and not the vinylsilane. (Eqn. 489)



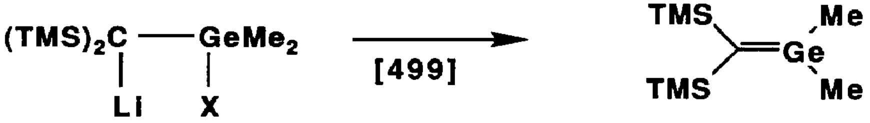
(489)

α-Trimethylsilyllithium reagent **242** was used to prepare 1-phospha-1,2,3-butatriene. (Eqn. 490) Reagent **243** led to germene **244** as ascertained by trapping experiments with 2,3-dimethyl-1,3-butadiene. (Eqn. 491)



**242**

(490)



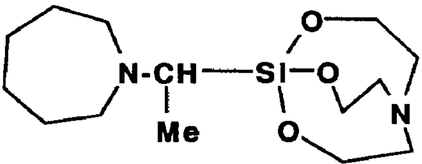
**243**

**244**

(491)

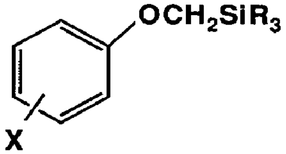
## E. α-FUNCTIONAL SILANES--OTHER STUDIES

The gas phase structure of trifluoromethylsilane has been determined. [500] An x-ray structure determination of **245** was done. [501]

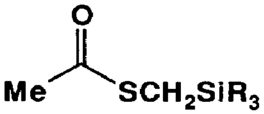


**245**

The $^{13}C$ and $^{29}Si$ NMR spectra were taken for several chloromethylsilanes and the chemical shifts correlated with Taft $\sigma^*$ constants. [502] Infrared studies were carried out on phenoxymethylsilanes **246** and charge transfer complexes were formed formed between these materials and tetracyanoethylene. [503] The IR, UV, $^1H$, and $^{29}Si$ NMR spectra were taken for compounds of the general structure 247. Intramolecular interaction is found when the silicon contains a fluorine ligand. [504]



**246**



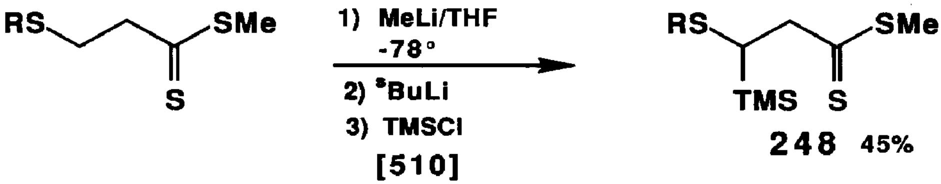
**247**

The photoelectron spectra of thioalkoxymethylsilanes were determined. [505] A series of trimethylsilylmethyl oxonium and halonium ions was studied by $^1H$, $^{13}C$ and $^{29}Si$ spectroscopy. [506] The configurational instability of α-silyl-α-alkenyllithium reagents was investigated. It was concluded that the π accepting ability of the silyl group was a determining factor. [507] Molecular mechanics calculations were carried out on trichloromethyltrichlorosilane. [508] The effect of reaction conditions and a new model for the addition of carbanions to carbonyl derivatives was the thrust of a mecahnistic study of the Peterson reaction. [509]

# XIV. β-FUNCTIONAL ORGANOSILANES

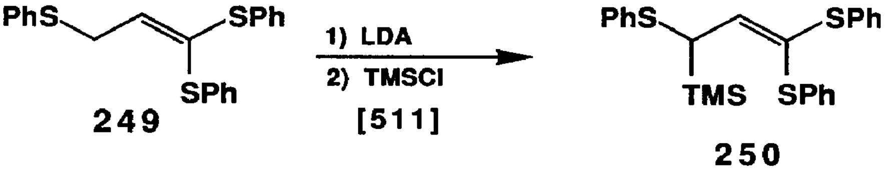
## A. PREPARATION

Double lithiation-trimethylsilylation of β-thiosubstituted dithiopropanoates gives the β-trimethylsilyldithio ester **248**. (Eqn. 492)



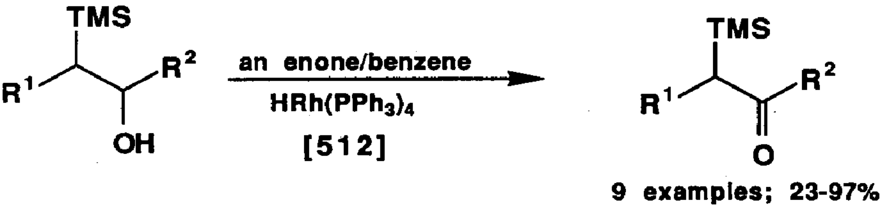
(492)

A similar, but distinct, system was prepared in which the trisulfide **249** is deprotonated and silylated to give the β-thiophenoxy allylsilane **250**. (Eqn. 493)



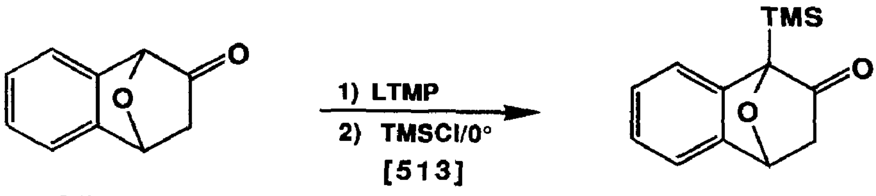
(493)

β-Hydroxysilanes, readily available materials, were nicely oxidized by enones in the presence of Wilkinson's catalyst to the correspondiong β-ketosilanes. (Eqn. 494)



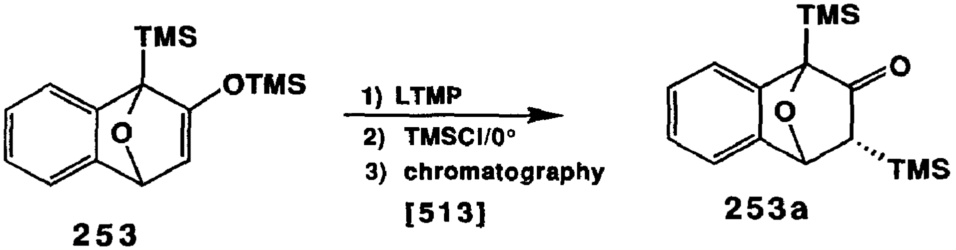
(494)

Oxabicyclo ketone **251** reacts with lithium tetramethylpiperidide and then trimethylchlorosilane at 0° to give β-ketosilane **252**. (Eqn. 495) At -78° the trimethylsilyl enol ether is obtained. Deprotonation-trimethylsilylation of **252** gives **253**, which upon chromatography produces the β-ketosilane **253a**. (Eqn. 496)



**251** **252**

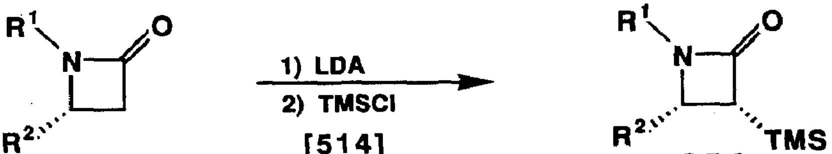
(495)



**253** **253a**

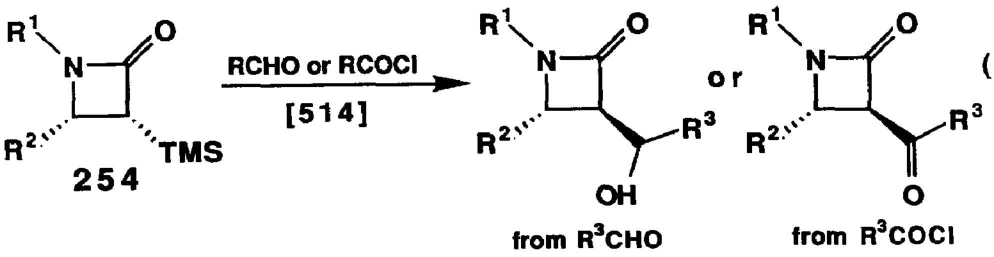
(496)

Deprotonation-trimethylsilylation of β-lactams provides the α-trimethylsilyl lactam **254**. (Eqn. 497) These substrates were employed in the preparation of derivative azetidinones. (Eqn. 498)



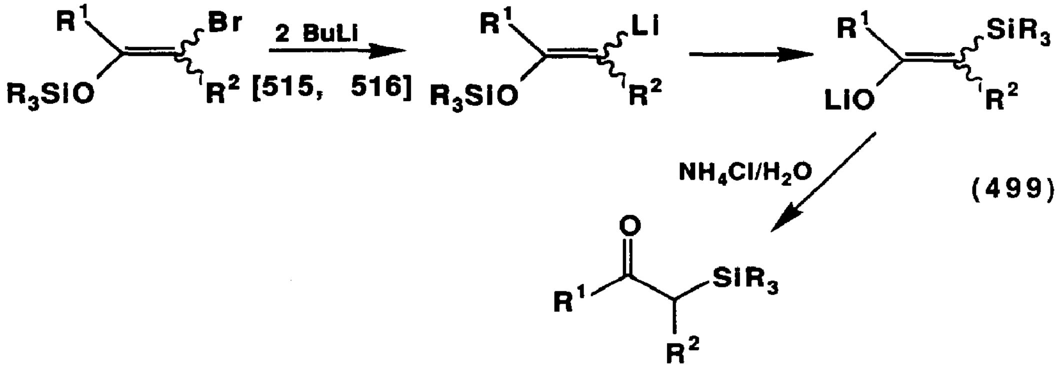
**254**

(497)



(498)

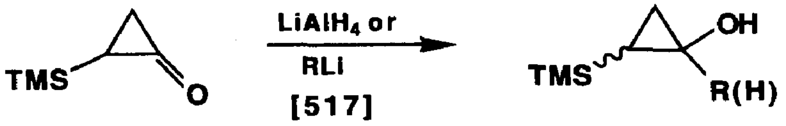
The deprotonation-silylation of α-bromo ketones gives the α-bromo enol silyl ether, which in turn undergoes lithium-bromine exchange with the resulting lithium reagent undergoing a rearrangement to the α-silyl enolate ion. This upon hydrolysis gives the β-ketosilane. (Eqn. 499)



(499)

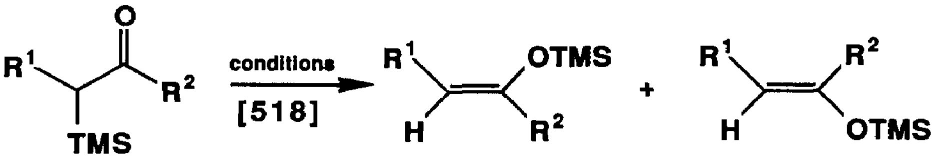
## B. β-FUNCTIONAL SILANES--REACTIONS

The α-trimethylsilylcyclopropanone was reacted with lithium aluminum hydride or lithium reagents to give β-hydroxysilanes. (Eqn. 500)



(500)

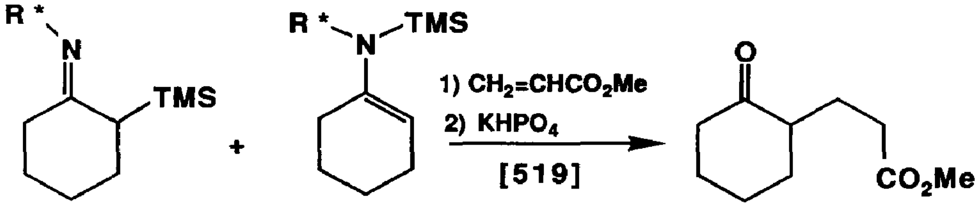
It has long been known that β-ketosilanes rearrange to the enol silyl ether. It has now been shown that this rearrangement can be carried out in a stereoselective manner. (Eqn. 501)



(501)

| | | |
|---|---|---|
| **Thermolysis (neat)** | **minor** | **major** |
| **$HRh(CO)(PPh_3)_3$/105°** | **minor** | **major** |
| **TMSOTf (10 mole %)/HMDS** | **major** | **minor** |
| **TMSI(5 mole %)/$HgI_2$/DCM** | **major** | **minor** |

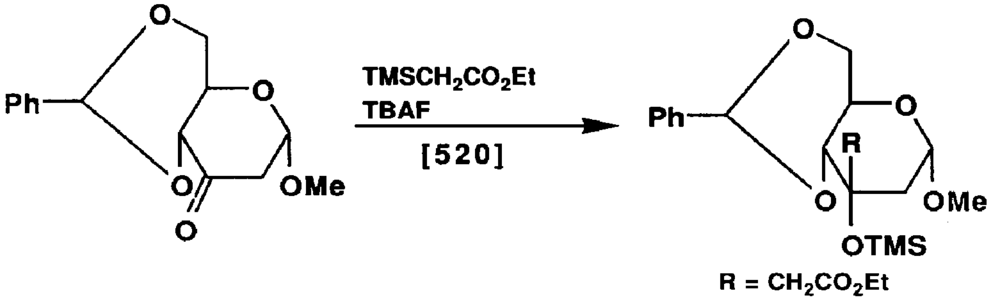
α-Trimethylsilyl imines and/or their isomeric (tautomeric) N-trimethylsilyl enamines react with α,β-unsaturated esters to produce δ-keto esters upon hydrolysis. (Eqn. 502) An optically active form of the reaction is shown. The ee depends on the ratio of the the isomeric starting materials.



(502)

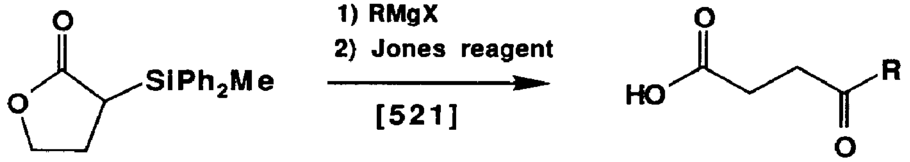
**R* = (S) 1-phenylethyl** **15-60 % ee**

Ethyl trimethylsilylacetate was employed in the acetoxylation of ketosugars. This reaction was carried out in the presence of fluoride ion catalysis. (Eqn. 503)

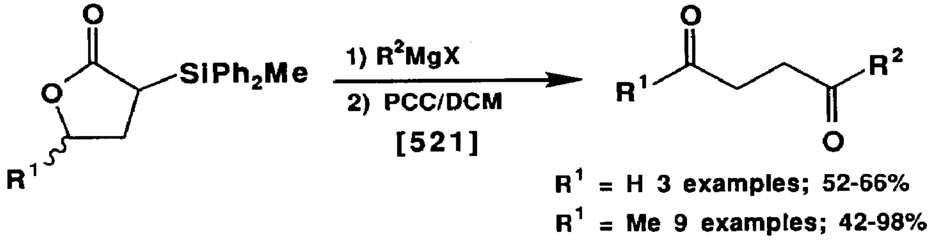


(503)

α-Methyldiphenylsilyl-γ-butyrolactone was reacted with Grignard reagents and the intermediate products oxidized with Jones reagent to give 4-oxo acids in moderate to good yield. (Eqn. 504) In a similar development 4-oxo aldehydes and 4-oxo ketones were prepared. (Eqn. 505)

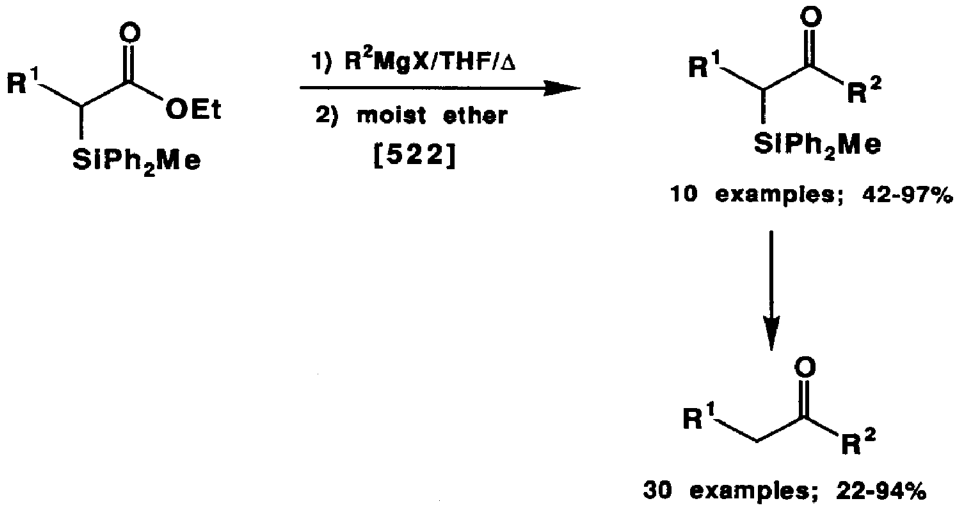


(504)



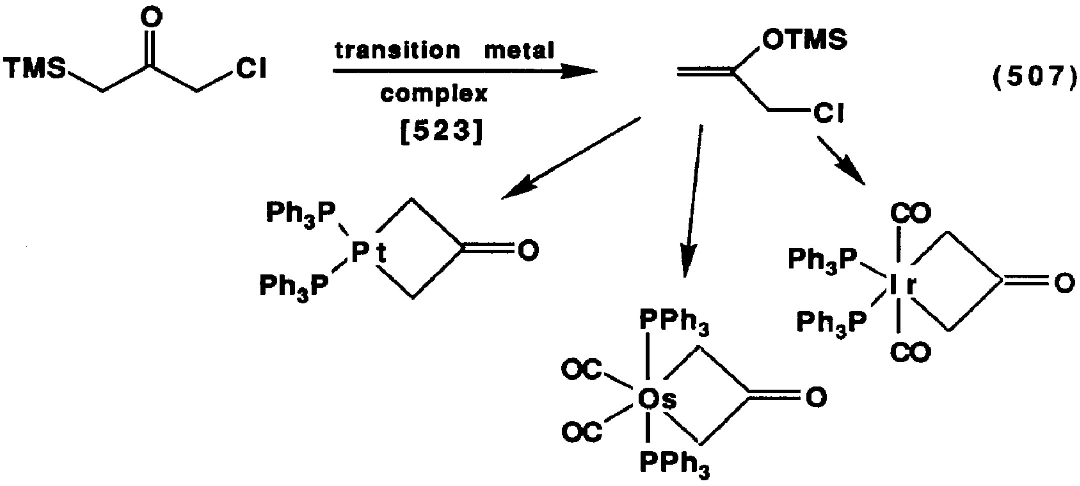
(505)

α-Methyldiphenylsilyl esters, when reacted with Grignard reagents, provide α-methyldiphenylsilyl ketones, which can be protiodesilylated to the corresponding ketone providing an ester to ketone route. (Eqn. 506) It is possible to carry out the ester to ketone transformation without isolation of the α-silyl ketone.



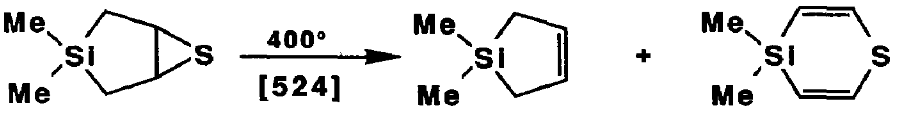
(506)

1-Trimethylsilyl-3-chloro-2-propanone was rearranged to its enol silyl ether, which was in turn reacted with low valent osmium, iridium or platinum complexes to give metallocyclobutanones. (Eqn. 507)



(507)

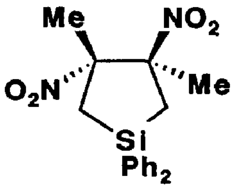
Pyrolysis of **255** gives mainly 1,1-dimethylsilacyclopent-3-ene and 1,1-dimethylsila-2-thiacyclohexa-3,5-diene. (Eqn. 508) Mass spectral fragmentation of **255** gave only the silacyclopentene.



**255**

(508)

The x-ray structure of **256** shows it to have a configuration of between a half-chair and an envelope. The NMR spectrum of a solution indicates it to have the half-chair configuration. [525]

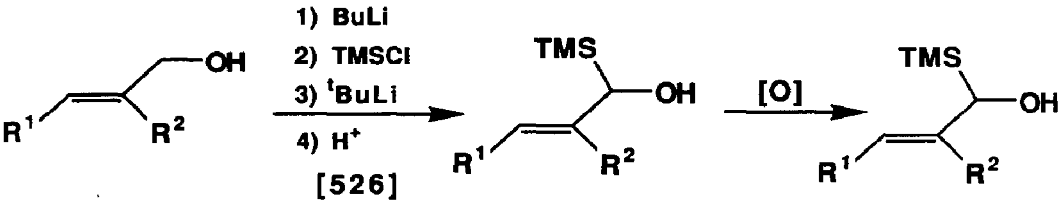


**256**

# XV. MISCELLANEOUS FUNCTIONAL ORGANOSILANES

## A. ACYLSILANES-PREPARATION

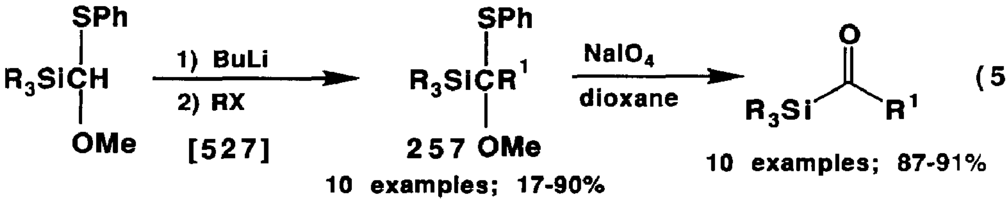
An interesting and highly useful entry into α,β-unsaturated acylsilanes involves O-trimethylsilylation, a Brook rearrangement to the α-trimethylsilyl allyl alcohol and then an oxidation with the Swern or Corey-Kim reagent. (Eqn. 509)



(509)

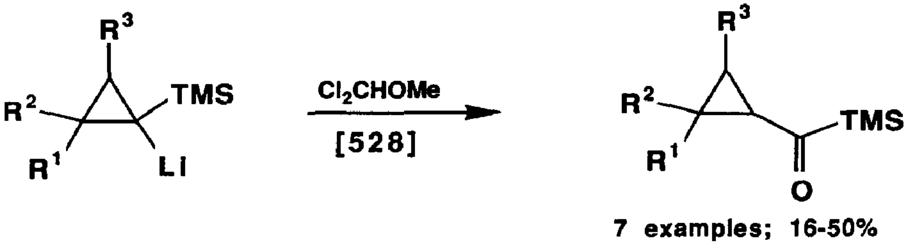
**3 examples; 64-79%**

Reminiscent of the original preparation of acylsilanes by Brook and coworkers who used the dithiane acyl anion equivalent, the silylated methoxy(phenylthio) acyl anion equivalent **257** was used to synthesize acylsilanes. (Eqn. 510)

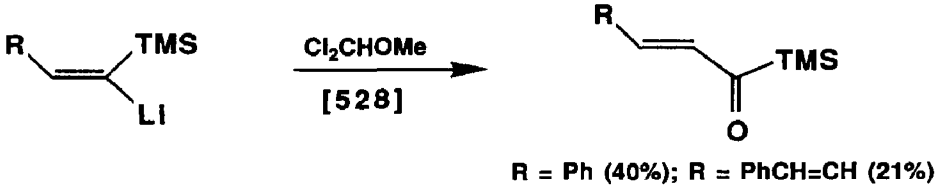


(510)

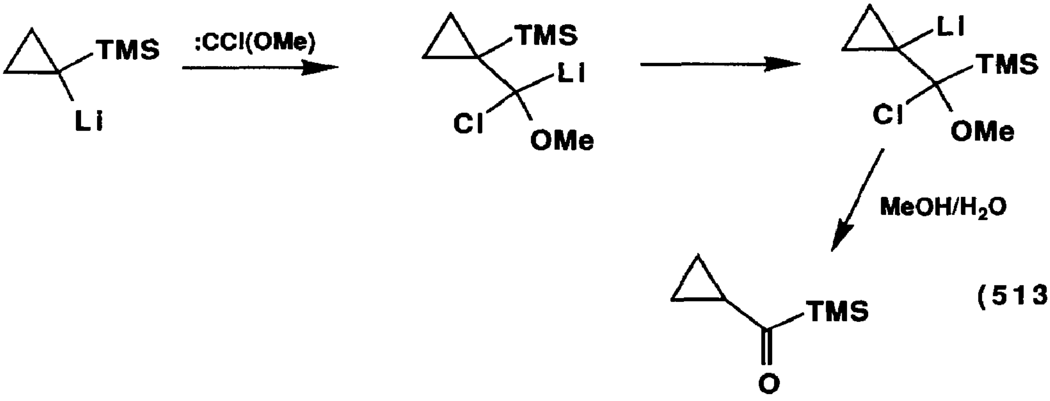
The reaction of α-trimethylsilyl lithium reagents with (dichloromethyl)methyl ether results in the formation of acylsilanes in moderate yield. (Eqns. 511, 512) The reaction presumably proceeds via chloromethoxy carbene according to Eqn. 513.



(511)

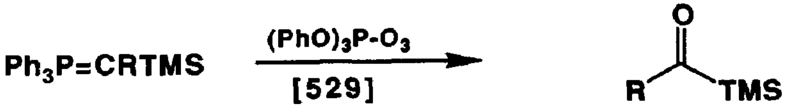


(512)

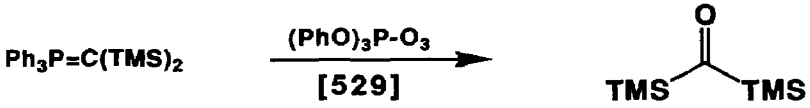


(513)

α-Trimethylsilylated Wittig reagents can be directly oxidized with triphenoxyphosphine ozone complex to acylsilanes. (Eqns. 514, 515)

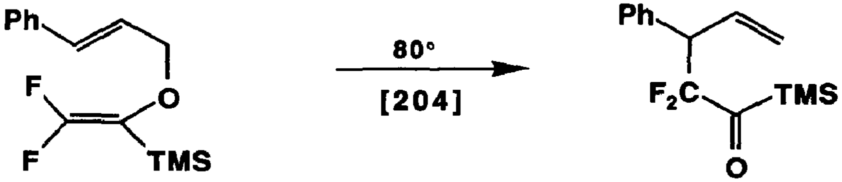


(514)



(515)

Thermolysis of α-trimethylsilyl vinyl allyl ether **258** gave acylsilane **259**. (Eqn. 516)

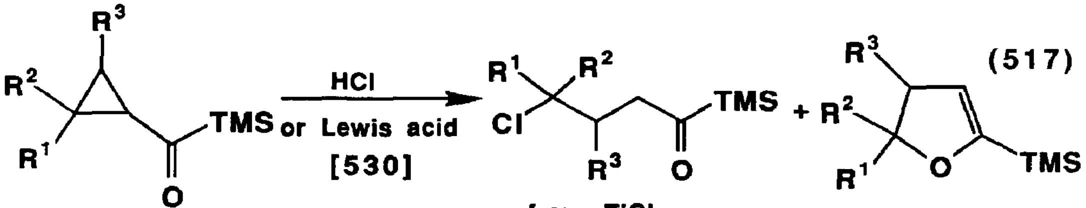


**258** **259**

(516)

## B. ACYLSILANES - REACTIONS

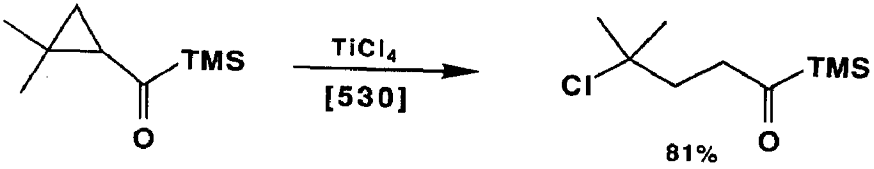
Trimethylsilylcyclopropyl ketones were ring opened with hydrochoric acid or Lewis acids to provide γ-chloroacylsilanes or 2-trimethylsilyl-4,5-dihydrofurans. (Eqns. 517, 518)



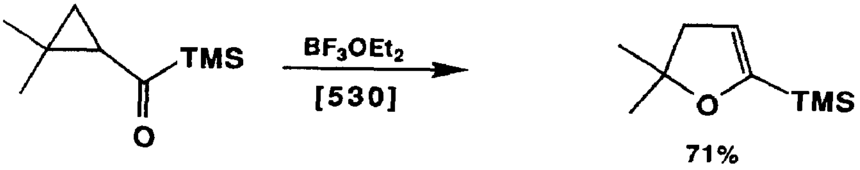
(517)

from $TiCl_4$

from HCl, $SnCl_4$, or $BF_3OEt_2$

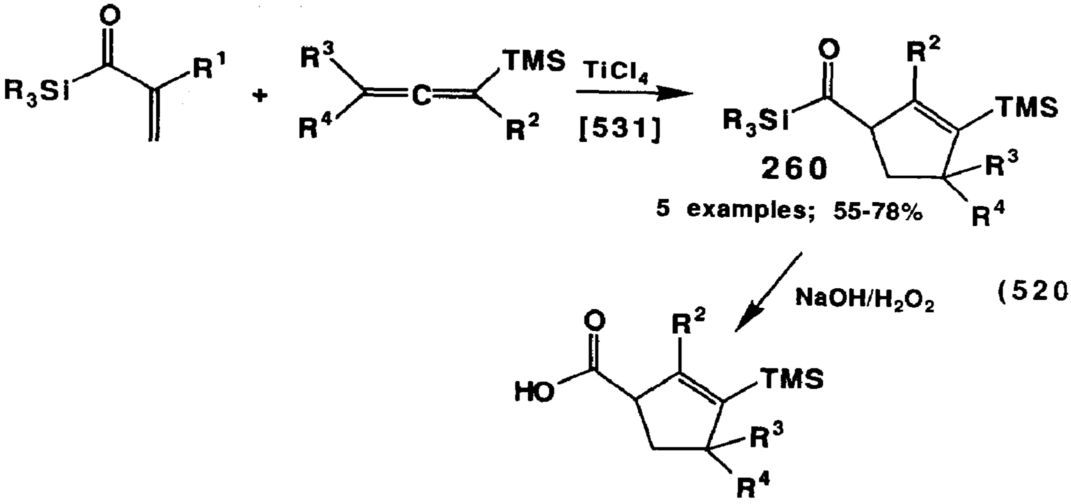


(518)

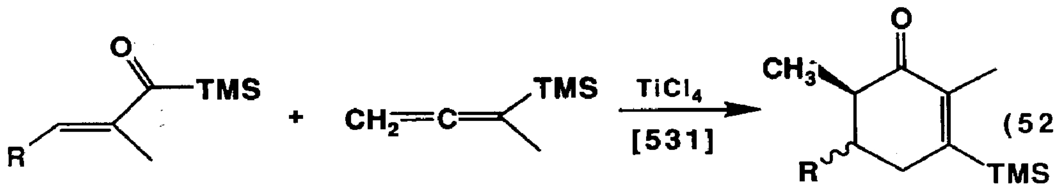


(519)

α,β-Unsaturated acylsilanes were cycloadded to allenylsilanes to give the acylsilanes **260**, which were converted to the corresponding carboxylic acids. (Eqn. 520) Six membered rings from a 3+3 cycloaddition are also observed. (Eqn. 521)

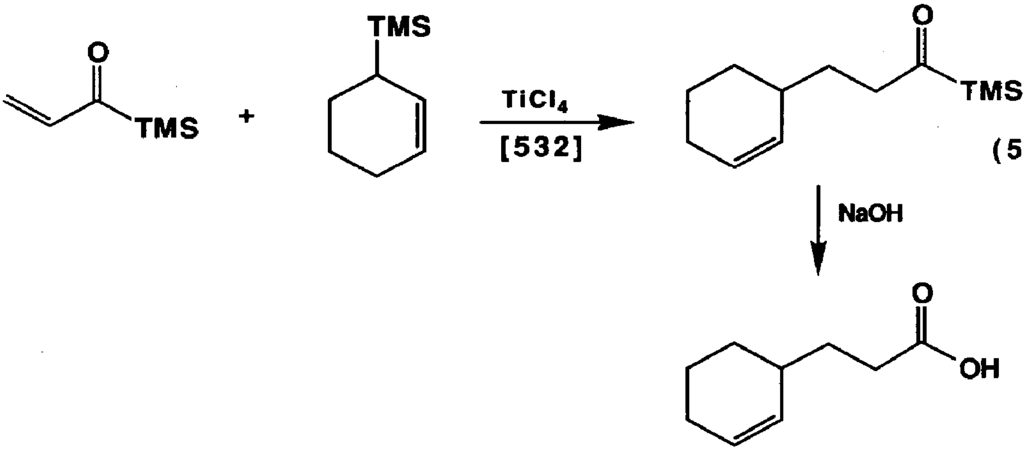


(520)



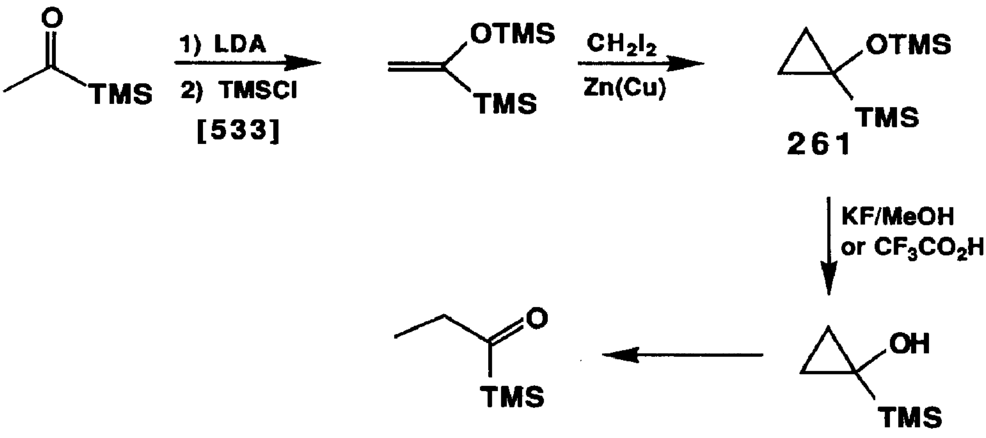
(521)

The conjugate addition of allylsilanes to acylsilanes was accomplished. Conversion of the acylsilane functionality to a carboxylic acid results in the formation of δ,ε-unsaturated acids. (Eqn. 522)

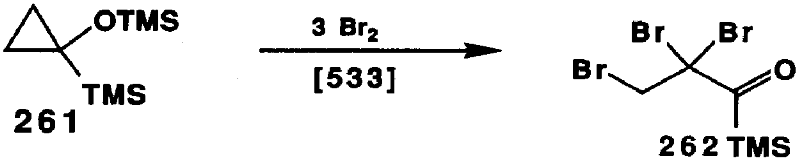


(522)

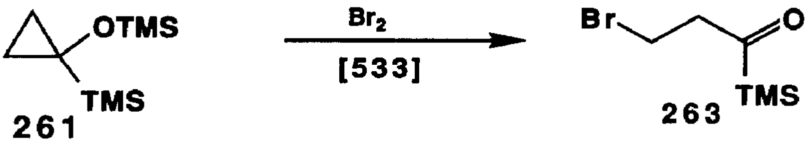
Acyltrimethylsilane itself was deprotonated and trimethylsilylated to give the enol silyl ether, which was in turn cyclopropanated, desilylated, and ring opened to propionyltrimethylsilane. (Eqn. 523) Ring opening of the silylated intermediate **261** with bromine gives the tribromoacylsilane **262** or **263** depending on the amount of bromine employed. (Eqns. 524, 525) The γ-bromoacylsilane **263** can be converted to the enone **264**. (Eqn. 526)



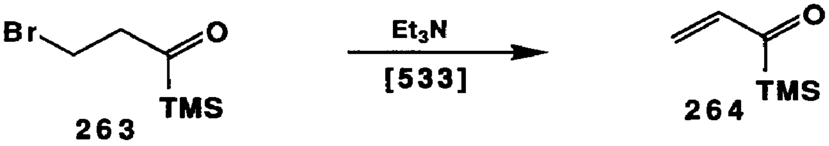
(523)



(524)

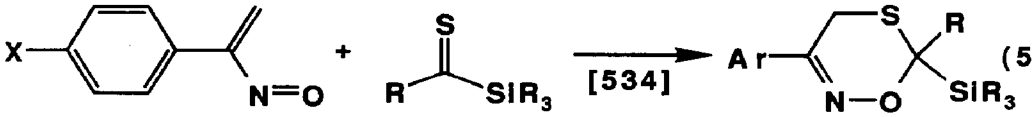


(525)



(526)

Silylthiones were cycloadded to nitrosoalkenes as shown in Eqn. 527.

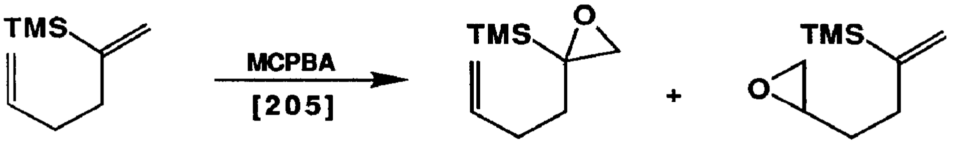


(527)

X = H; R = Ph; $R_3Si$ = $Ph_3Si$ 91%
X = H; R = Ph; $R_3Si$ = $Me_3Si$ 60%

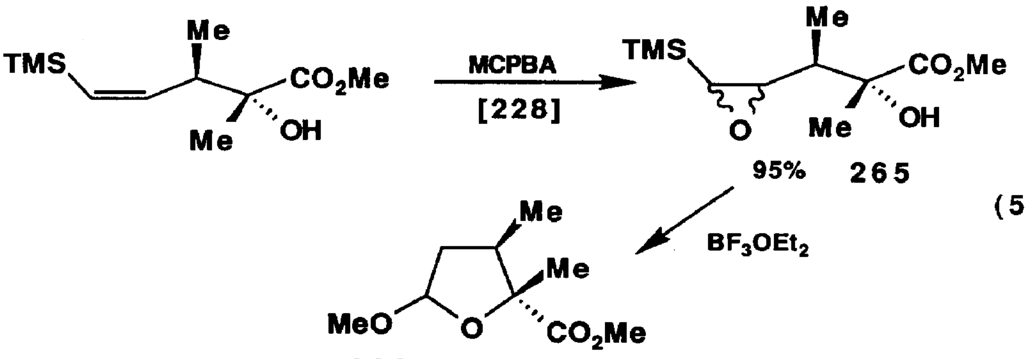
## C. EPOXYSILANES

The epoxidation of a 2-trimethylsilyl substituted terminal olefin is faster than that of a mono-substituted terminal olefin as seen from the example in Eqn. 528.



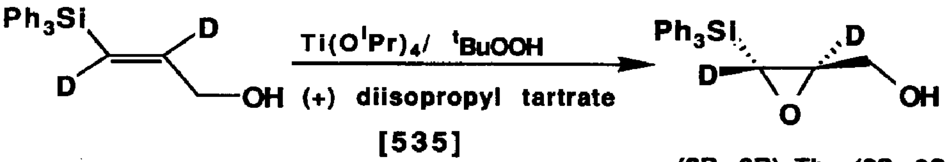
7.7 pts 1 pt (528)

Epoxysilane **265** was prepared and reacted with boron trifluoride etherate to give the tetrahydrofuran **266**. (Eqn. 529)



**266** 90% (529)

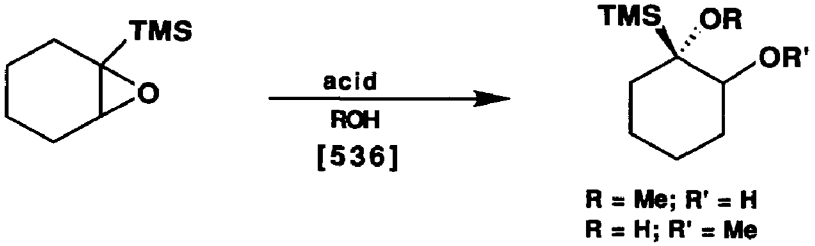
The (R,R) and (S,S) oxiranes **266** and **267** were prepared via a Sharpless oxidation of (E) 1-(triphenylsilyl)-1,2-dideuteriopropenol. (Eqn. 530)



(530)

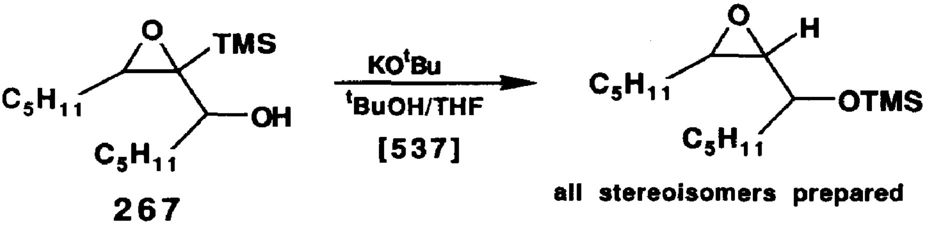
**(2R, 3R) The (2S, 3S) arises from the (-) tartrate**

The regio- and stereoselectivity of the acid-induced gas phase ring opening of an epoxysilane with methanol or water was determined. (Eqn. 531) It was determined that the intrinsic electronic properties of the oxonium ion intermediate are solely responsible for the regio- and stereochemistry.



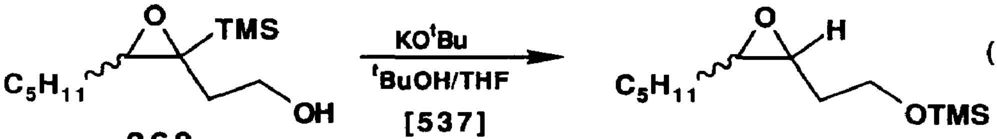
(531)

The hydroxy substituted epoxysilanes **267** and **268** undergo trimethylsilyl migration and concomitant protonation. (Eqns. 532, 533)



**267**

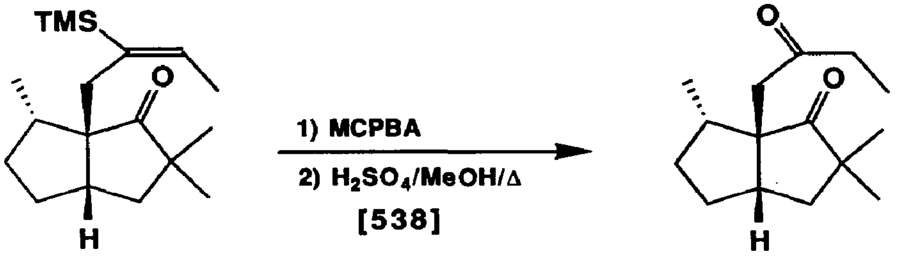
(532)



**268**

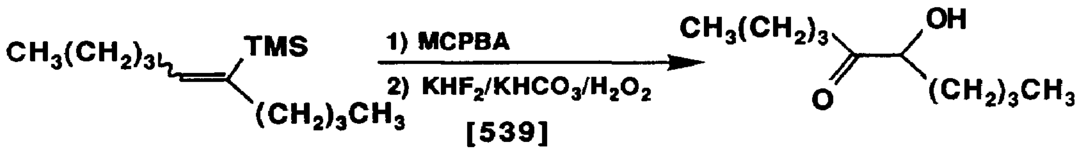
(533)

Epoxysilanes were used as intermediates to ketones in approaches to angular triquinanes. (Eqn. 534)



(534)

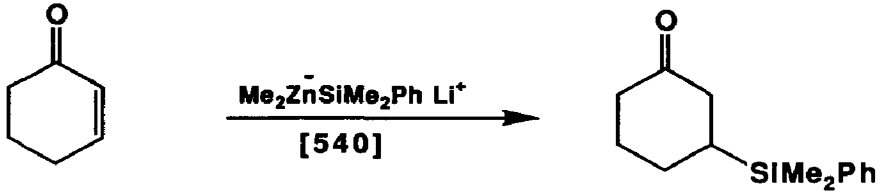
The epoxidation of alkenylsilanes followed by oxidative cleavage of the silicon-carbon bond results in the formation of α-hydroxy ketones in good yield. (Eqn. 535)



(535)

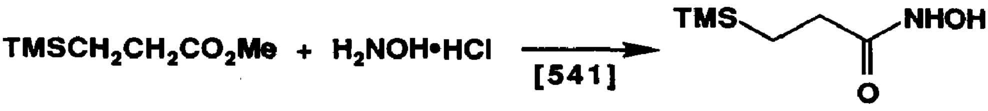
## D. γ-FUNTIONAL ORGANOSILANES

Phenyldimethylsilyllithium was converted to the dimethylzincate and this species reacted with enones to provide γ-phenyldimethylsilyl ketones in good yield. (Eqn. 536)



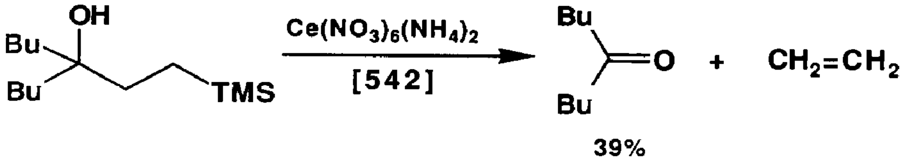
(536)

γ-Trimethylsilyl esters were converted to the corresponding hydroxamic acid with hydroxylamine hydrochloride. (Eqn. 537)

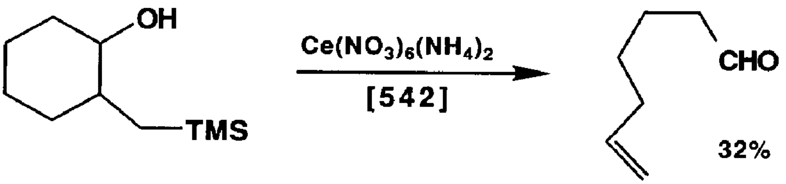


(537)

γ-Hydroxysilanes can be oxidatively fragmented in moderate yield. (Eqns. 538, 539)

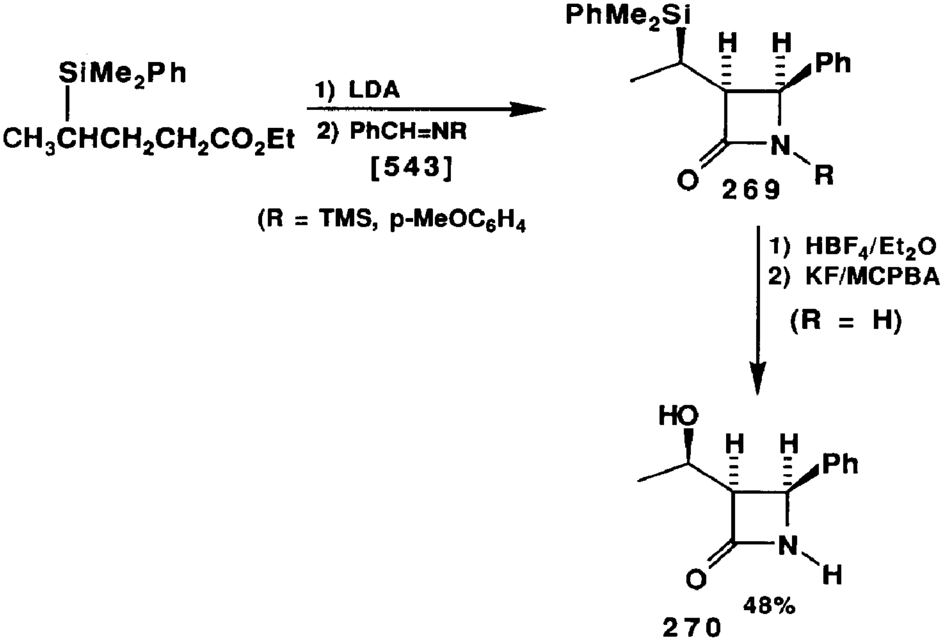


(538)



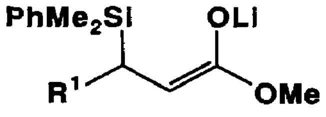
(539)

Ethyl 3-phenyldimethylsilylbutyrate was deprotonated and the resulting enolate reacted with imines to provide β-lactams **269**. Oxidation of the carbon-silicon bond gave the azetidinones **270**. (Eqn. 540)

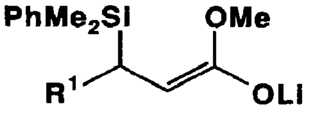


(540)

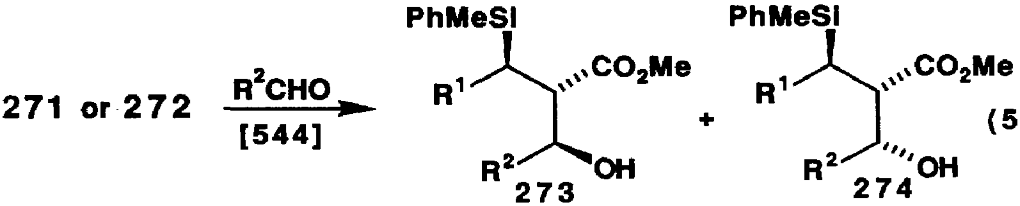
The diastereoselectivity of the reaction of β-silyl enolates **271** and **272** with aldehydes was investigated. The (E) enolate **271** gives the anti, anti product **273** whereas the (Z) enolate **272** gives predominantly the anti, syn product **274**. (Eqn. 541)



**271**



**272**

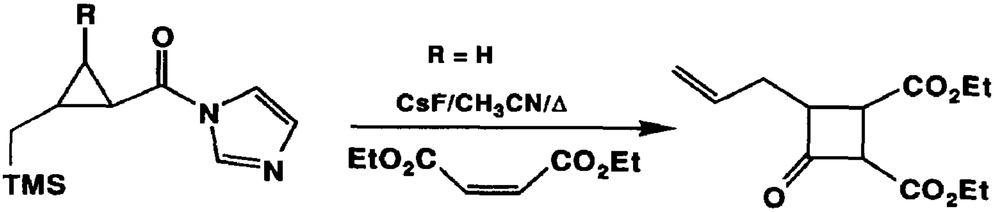


**273** **274** (541)

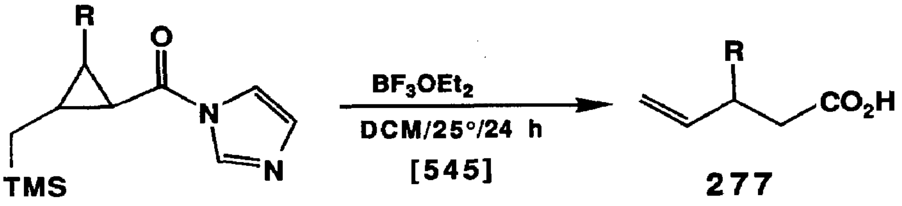
major product from **271** major product from **272**

## E. OTHER FUNCTIONAL ORGANOSILANES

The *trimethylsilylmethylcyclopropyl amide* **275**, *when treated with fluoride ion in* the presence of a dipolarophile, gives cyclobutanone **276**. (Eqn. 542) On the other hand, ring opening with boron trifluoride etherate gives the unsaturated acids **277**.
(Eqn. 543a)

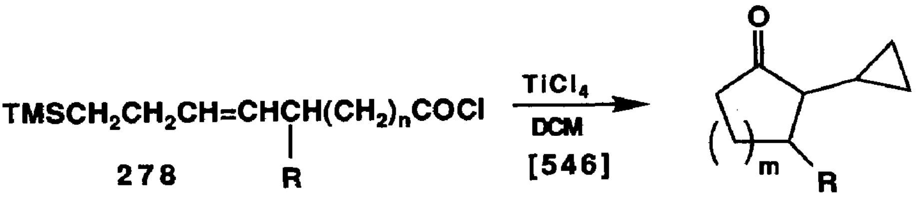


**275** **276** (542)



**275** **277** (543a)

The homoallylic silanes **278** were cyclized with titanium tetrachloride. (Eqn. 545b)



$TMSCH_2CH_2CH{=}C\underset{|\atop R}{H}CH(CH_2)_nCOCl$

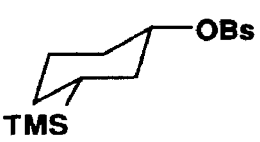
**278**

R = H, $^n$Bu; n = 2-5

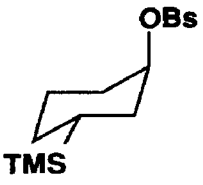
m = 1-4

(543b)

The solvolyses of cis and trans-3-(trimethylsilyl)cyclohexyl p-bromobenzenesulfonates, **279** and **280**, respectively, were studied. It was found that the cis isomer hydrolyzes faster than the trans isomer and it is argued that this is due to a W effect in the stabilization of the incipient carbocation by the trimethylsilyl group. [547]



**279**

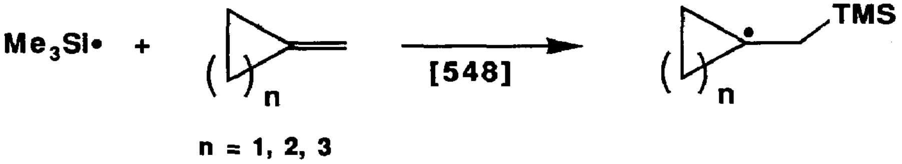


**280**

# XVI. REACTIVE ORGANOSILICON SPECIES

## A. SILYL RADICALS

The trimethylsilyl radical was reacted with exo-methylenecycloalkanes to produce trimethylsilylmethylcycloalkanes. (Eqn. 544)



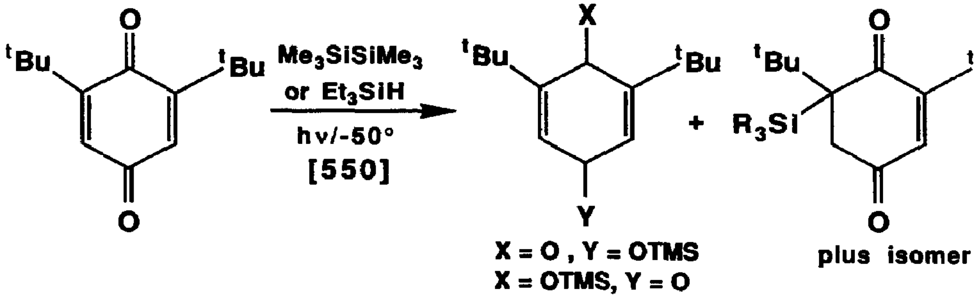
(544)

Trifluorosilyl radicals, generated via a low temperature radiofrequency glow discharge or plasma of hexafluorodisilane, were reacted in the vapor phase with vaporsof cadmium and zinc to give bis(trifluorosilyl)cadmium and bis(trifluorosilyl)-zinc, respectively. (Eqn. 545)

$$F_3Si\bullet \;+\; M \xrightarrow{\hspace{2em}}_{[549]} (F_3Si)_2M \qquad (545)$$

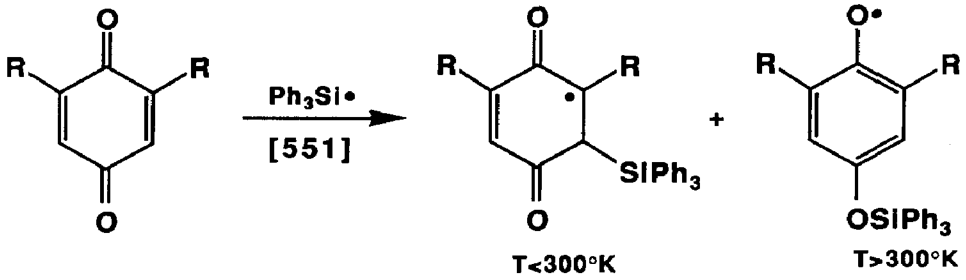
M = Cd, Zn

Trimethylsilyl or triethylsilyl radicals were added to p-benzoquinones. The reaction was shown to proceed through two pathways. (Eqn. 546)

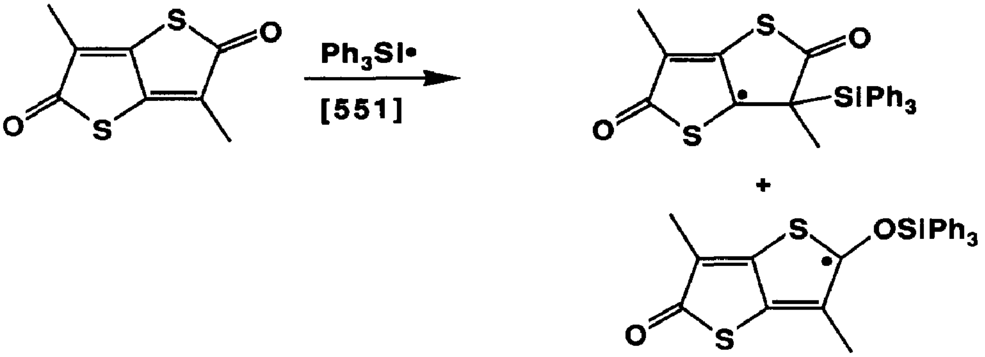


(546)

The regioselectivity of the addition of silyl radicals to enones and p-quinones was studied. Some results are shown in Eqns. 547 and 548.

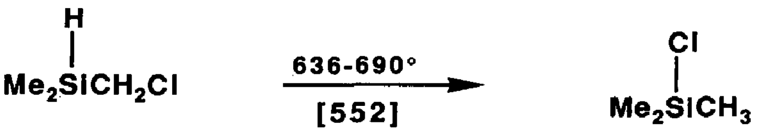


(547)



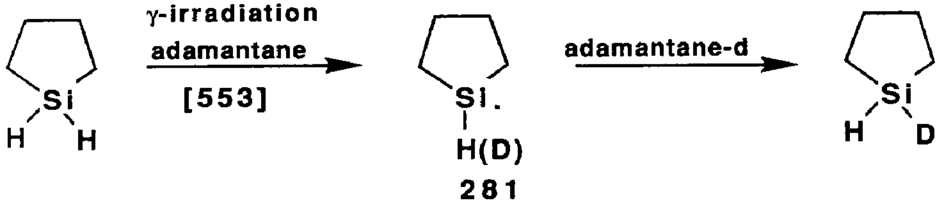
(548)

It was shown that the rearrangement of the thermally generated chloromethyldimethylsilyl radical goes by two pathways, a concerted dyotropic rearrangement and a free radical process. (Eqn. 549)



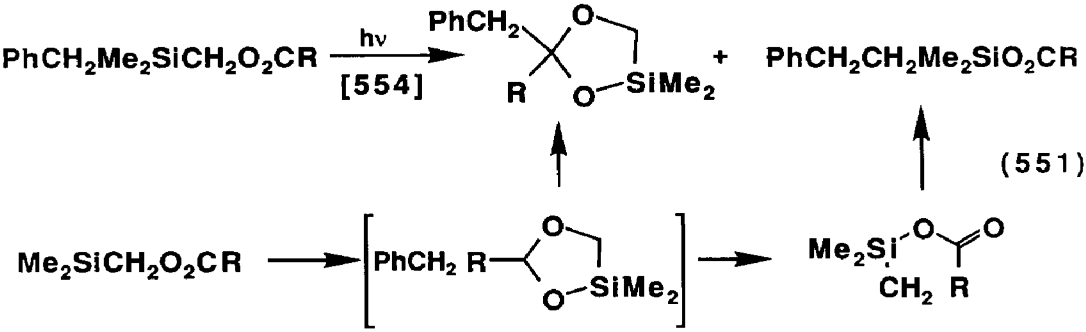
$$\mathrm{Me_2\overset{H}{\overset{|}{S}}iCH_2Cl} \xrightarrow[\text{[552]}]{636\text{-}690^\circ} \mathrm{Me_2\overset{Cl}{\overset{|}{S}}iCH_3} \qquad (549)$$

ESR studies were used to show that silacyclopentyl radical, **281**, reacts reversibly with adamantane and deuterated adamantane at room temperature. (Eqn. 550)



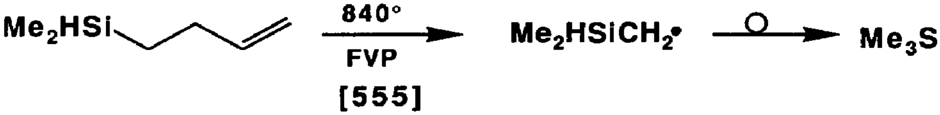
(550)

The photolysis of benzyl(acyloxymethyl)silanes proceeds through the intermediacy of benzyl and silyl radicals. Deuterium labelling showed it to be a cage process. (Eqn. 551)



(551)

Evidence for the isomerization of dimethylsilylmethyl radical to trimethylsilyl radical via the 1,2-migration of hydrogen was found from the pyrolysis of 4-(dimethylsilyl)-1-butene, which loses an allyl radical. (Eqn. 552)



(552)

A determination of the abstraction of hydrogen from triethylsilane with pentacarbonylrhenium radical was determined to be $9.6x10^5$ $Lmol^{-1}s^{-1}$ at 20°. [556] The relative rates of reaction of ethyldichlorosilyl radical with olefins was determined. [557] A gas phase kinetic study of the thermal reactions of tert-butoxy radicals with phosphine, germane and trimethylsilane was done. [558] It was found that the pentamethyldisilane is a better hydrogen donor than triethylsilane towards tert-butoxy radicals. [559] The phenylpentamethyldisilyl cation radical is an Si-Si σ–cation radical like that of the hexamethyldisilane cation radical and not a weakly perturbed phenyl cation radical like that of phenyltrimethylsilane. [560] The esr spectrum of octaisopropylcyclotetrasilane and octaisobutylcyclotetrasilane show them to be bent and not rapidly interconverting. [561]

## B. SILYLENES

It was found that dimethylsilylene will abstract chlorine atoms from chloromethanes. (Eqn. 553)

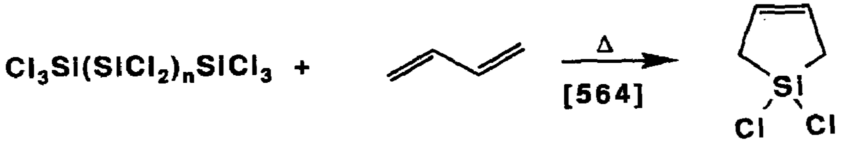
$$(Me_3Si)_6 \xrightarrow[CCl_4]{h\nu} C_2Cl_6 + Me_2SiCl_2 + ClMe_2SiMe_2SiMe_2SiCl \qquad (553)$$

[562]

Alkylmethyldichlorosilanes, when reacted with sodium/potassium in the gas phase, give products consistent with silylene intermediates. (Eqn. 554) Silyl radicals and silylmethyl radicals were also generated from the reaction of the approriate chlorides and sodium/potassium. [563] Perchlorinated polysilanes give dichlorosilylene upon thermolysis. (Eqn. 555)

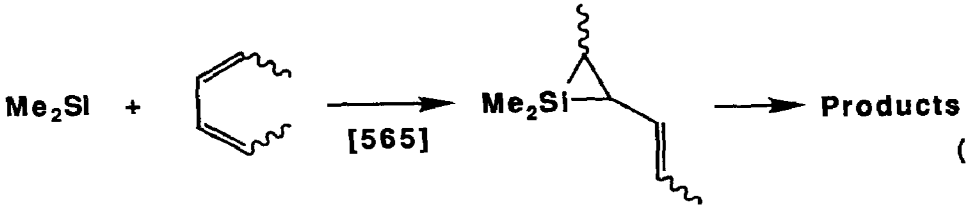
$$RCH_2CH_2MeSiCl_2 \xrightarrow[300^\circ]{Na/K} RCH_2CH_2MeSi \longrightarrow RCH{=}CH_2 + MeHSi \qquad (554)$$

$$[563]$$



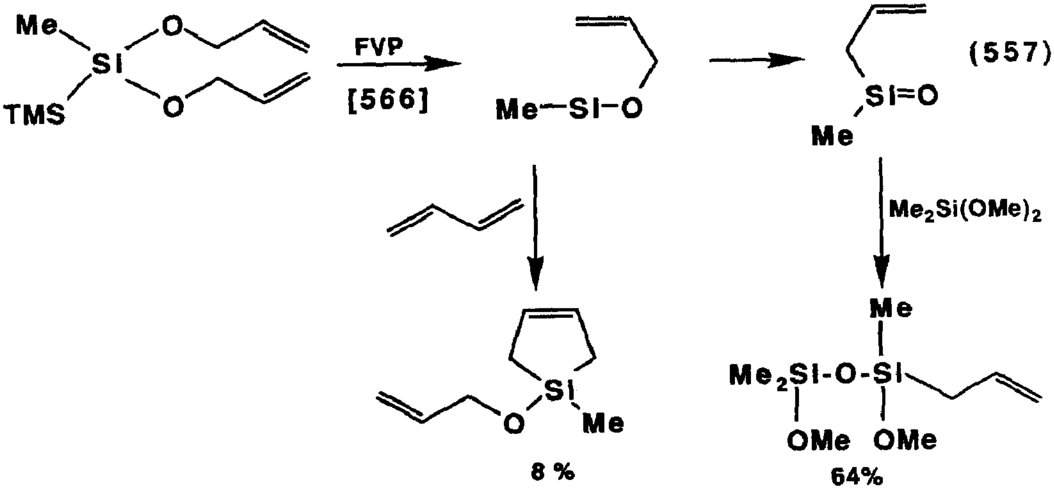
(555)

It is argued that dimethylsilylene, generated from sym-dimethoxytetramethyldisilane, reacts via a concerted 1,5-sigmatropic H-shift in the rearrangement of originally formed vinylsilacyclopropane intermediates. (Eqn. 556)



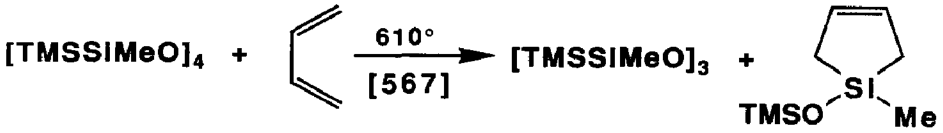
(556)

Flash vacuum pyrolysis of (trimethylsilyl)methyldiallyloxysilane gives methylallyloxysilylene, which rearranges to allylmethylsilanone leading to products consistent with this postulate. (Eqn. 557)



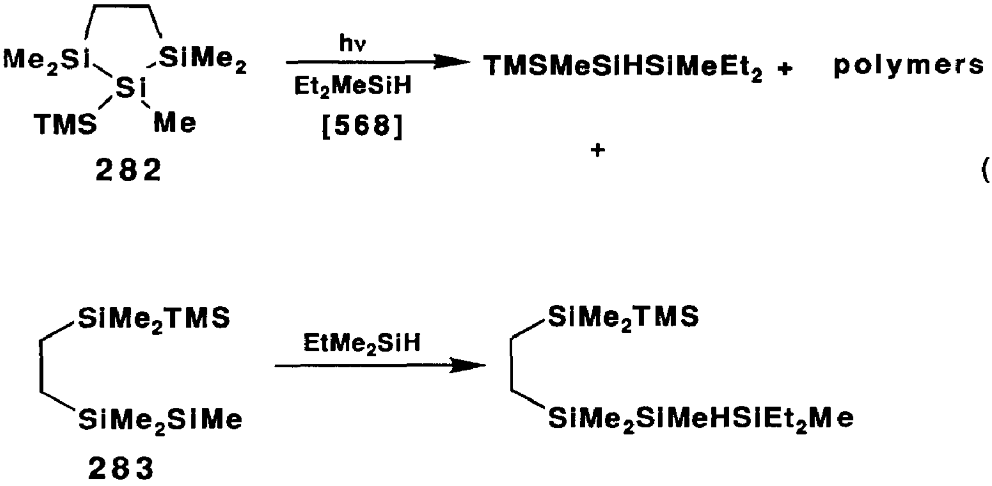
(557)

1,3,5,7-tetramethyl-1,3,5,7-tetrakis(trimethylsilyl)cyclotetrasiloxane was pyrolyzed to give products consistent with the formation of methyltrimethylsiloxysilylene. (Eqn. 558) The exact mechanism for the derivation of this silylene is not understood at the moment.



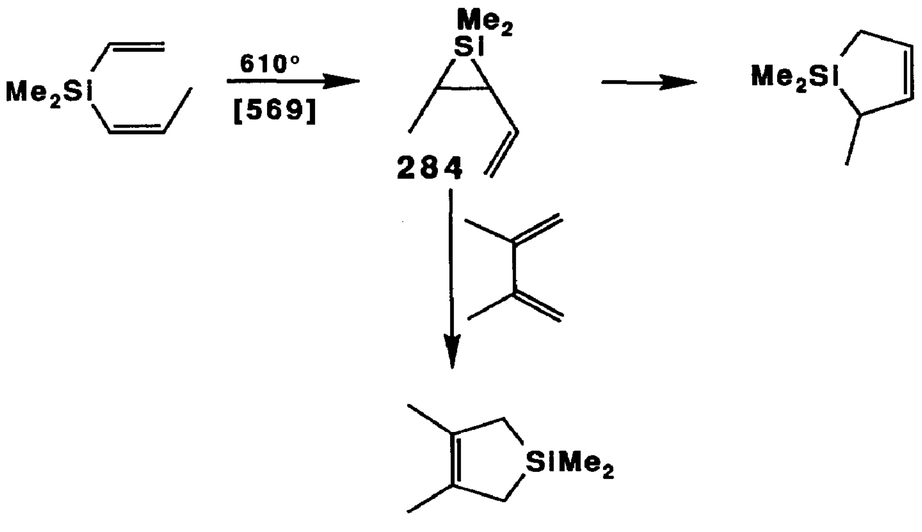
(558)

Photolysis of silane **282** gives methyl(trimethylsilyl)silylene as the principal intermediate; silylene **283** is also formed. (Eqn. 559)



(559)

The pyrolysis of dimethyl(cis-1-propenyl)vinylsilane generates dimethylsilylene via silacyclopropane **284**. (Eqn. 560)



(560)

The kinetics and mechanism of the thermolysis of 1,3-disilacyclobutane 1,3-dimethyl-1,3-disilacyclobutane, and 1,1,3,3-tetramethyl-1,3-disilacyclobutane was investigated. A 1,3-hydrogen shift was proposed for the hydride containing species. [570] The mechanism for the thermal decomposition of dimethylsilane was studied. The shock induced reaction is accelerated by free-radical and silylene chains, which cannot be trapped. [571] The mechanism and kinetics of the decomposition of silane in the presence of olefins and acetylene was investigated. The results show that silyl radical and hydrogen radical are not involved in the reaction. [572] The generation of dimethylsilylene in the gas phase and its reaction with fluoride ion gives dimethylfluorosilylide ion; the reaction with amide ion gives $MeSiCH_2^-$ and the reaction with 1,3-butadiene gives 1,1-dimethyl-1-silacyclopent-3-ene. Other reactions were also studied. [573] The photolysis of dimethyldiazidosilane in an argon matrix provided dimethylsilylene for spectroscopic measurements. [574]

The gas phase reactions of transition metals with methylsilanes produces transition metal complexes of silylene itself. (Eqn. 561)

$$Ti^+ + MeSiH_3 \xrightarrow[{[575]}]{} \underset{94\%}{TiSiCH_4^+} + H_2 + \underset{6\%}{TiSiH_2} + CH_4 \quad (561)$$

The relative rates of reaction of silylene with 1,3-butadiene, acetylene, and methanol were studied. [576] The thermolysis of bis(trimethylsilyl)silane gives trimethylsilylsilylene, which rearranges to trimethyldisilene. Other rearrangements are also observed. [577] The kinetics of the isomerization of 1-methylsilene to dimethylsilylene were determined by trapping with 1,3-butadiene. A free energy of activation of 42.5 kcal/mol was found, which is in agreement with a calculated value of 42.2 kcal/mol. [578] The ultraviolet spectrum of dimethylsilylene, which shows an absorption at 450 nm, has been shown to be in agreement with theory.[579] The structures and energies of singlet silacyclopropenylidene and 14 higher lying $C_2SiH_2$ isomers have been studied theoretically. Structure **285** was found to be the most stable followed by **286** and **287** with all others being very high in energy. [580]

**285**

$CH_2{=}C{=}Si$

**286**

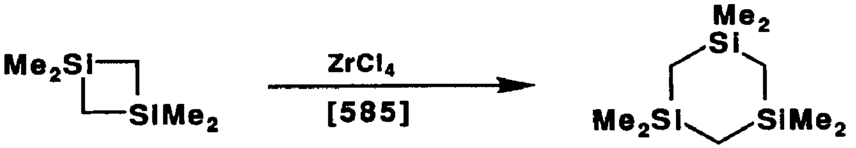
$HSi{\equiv}H$

**287**

The photolysis of trisilane to disilane and silylene was studied by a pseudopotential method. The lower-lying excited states were calculated and analyzed. [581] Calculations were carried out for the synchronous 1,4-addition of silylene ($^1A_1$) to s-cis-buta-1,3-diene. The reaction is initiated by an electrophilic step involving the HOMO of butadiene and the empty p orbital of $SiH_2$. [582] The most stable structure for bis-(cyclopentadienyl)silylene is the bis-monohapto isomer, with an angle of 105.4°. [583]

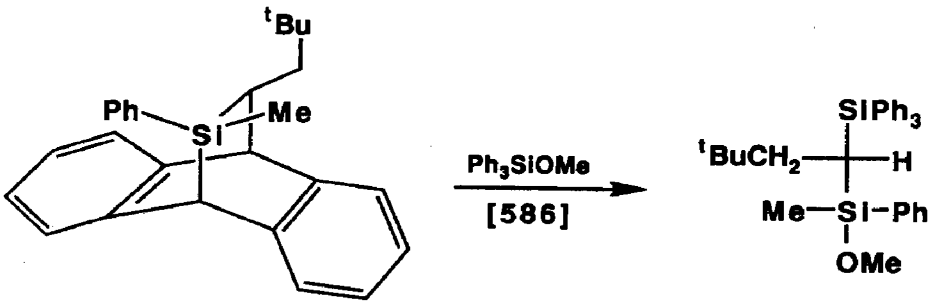
## C. SILENES

The reaction of 1,1,3,3-tetramethyl-1,3-disilacyclobutane with zirconium tetrachloride produces 1,1,3,3,5,5-hexamethyl-1,3,5-trisilacyclohexane via the intermediacy of 1,1-dimethylsilene. (Eqn. 562)



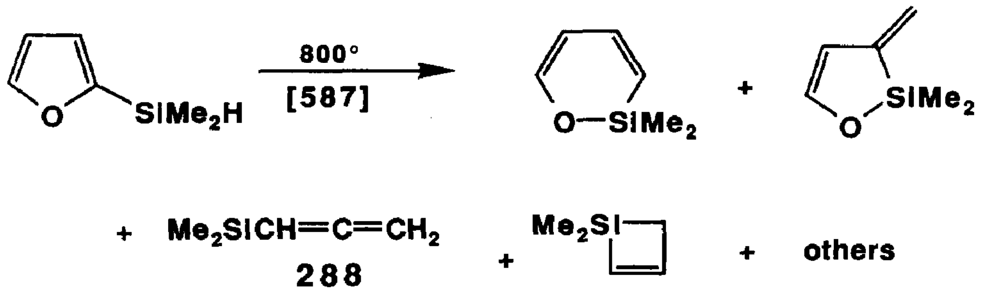
(562)

The stereochemistry of the the addition of triphenylmethoxysilane to a silene was shown to be stereospecific syn addition. (Eqn. 563) The x-ray crystal structure of the adduct showed it to be the R,S;S,R diastereomers.



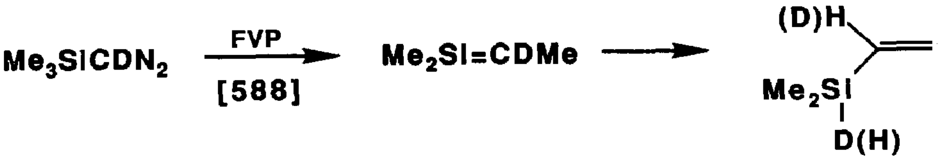
(563)

The flash vacuum pyrolysis (FVP) of 2-(dimethylsilyl)furan gives 1,1-dimethyl-1-silacyclobutene as one of the products. It is argued that this product arises from the intermediacy of silene **288**. (Eqn. 564)



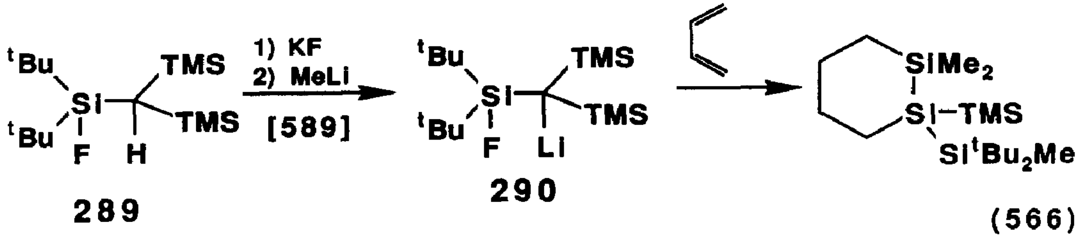
(564)

Evidence for the [1,3]-sigmatropic H migration from a methyl group of 1,13-trimethylsilene to the π-bonded silicon was provided from the pyrolysis of trimethylsilyldeuterodiazomethane. (Eqn. 565)



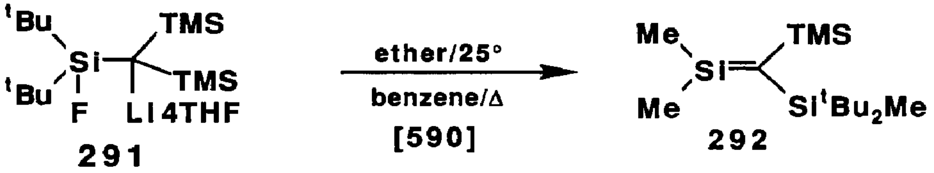
(565)

The very sterically impeded organosilane **289** was used as an entry into several potential precursors to stable silenes. Only the material **290** was found to yield the silene and then in the presence of butadiene as a trapping agent. (Eqn. 566) In the absence of a trapping agent secondary products were obtained.



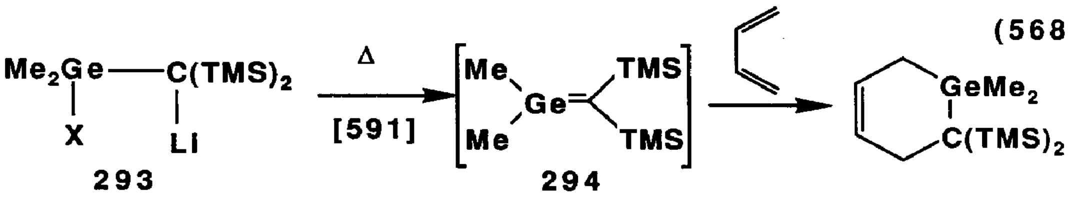
(566)

The intermediate **291** eliminated lithium fluoride in ether at room temperature, whic be an excellent entry into the silene **292** as a tetrahydrofuran complex, which could be made THF free upon heating in benzene and azeotropic removal of the THF. (Eqn. 567) The thusly produced silene showed slow decomposition at 60° and the NMR spectra ($^1$H and $^{13}$C) showed a rapid methyl exchange process occurring. This material was reacted with a variety of reagents. including alcohols, HBr, bromine, boron trifluoride olefins, and ketones.



(567)

In analogous chemistry the germanium compound **293** gave the germene **294** trapped as the cycloadduct with butadiene. (Eqn. 568)

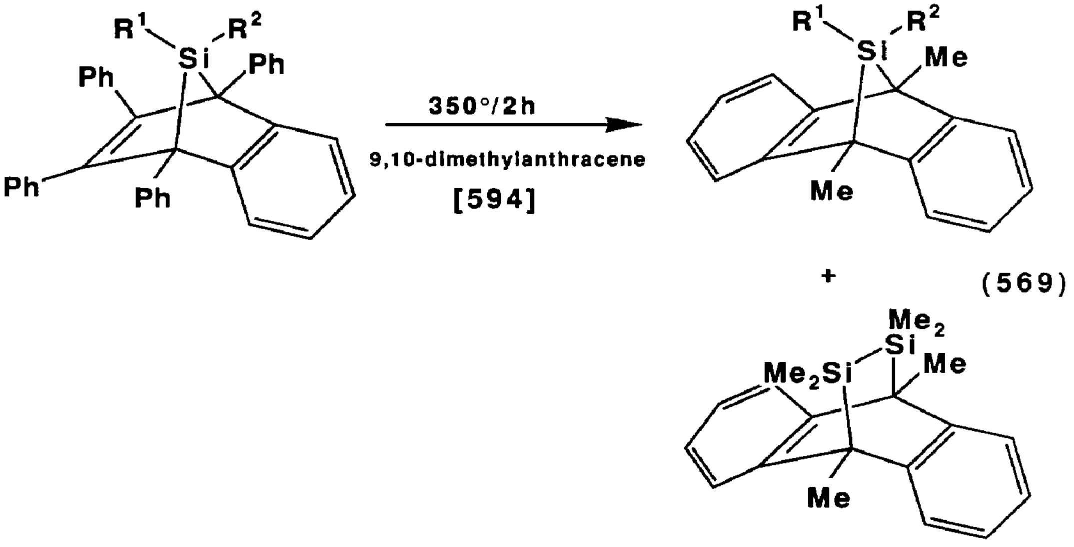


(568)

Ab initio MO calculations on the reaction of atomic hydrogen and silene have been made. The activation energy for the addition to the silicon center is less than that for the carbon center. [592] The geometries for the lowest singlet and triplet states of silacyclobutadiene have been calculated. [593]

## D. DISILENES

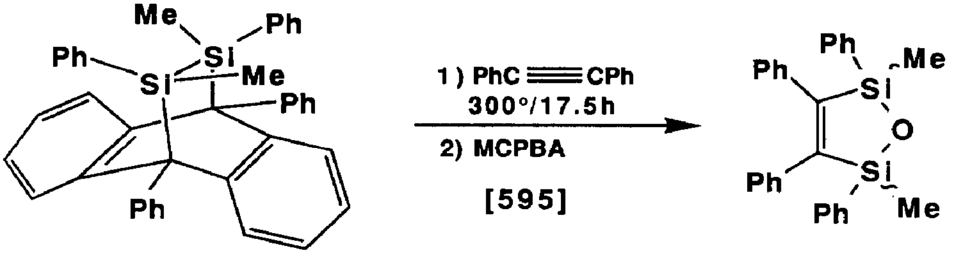
Silylenes and disilenes were generated and trapped according to Eqn. 569.



(569)

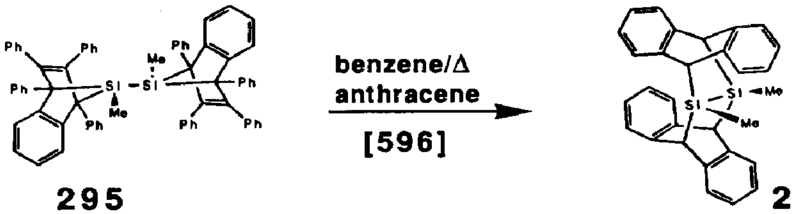
for $R^1$ and $R^2$ = Me

The stereochemistry of the addition of a disilene to diphenylacetylene was investigated by oxidation of the resulting disilane with meta-chloroperbenzoic acid. (Eqn. 570) Since the product proved to be a mixture of diastereomers it was concluded that the cycloaddition proceeded via a diradical.



(570)

Compound **295** was used as a synthon for the silicon-silicon triple bond, a disilyne, which when trapped with anthracene gave **296**. (Eqn. 571)

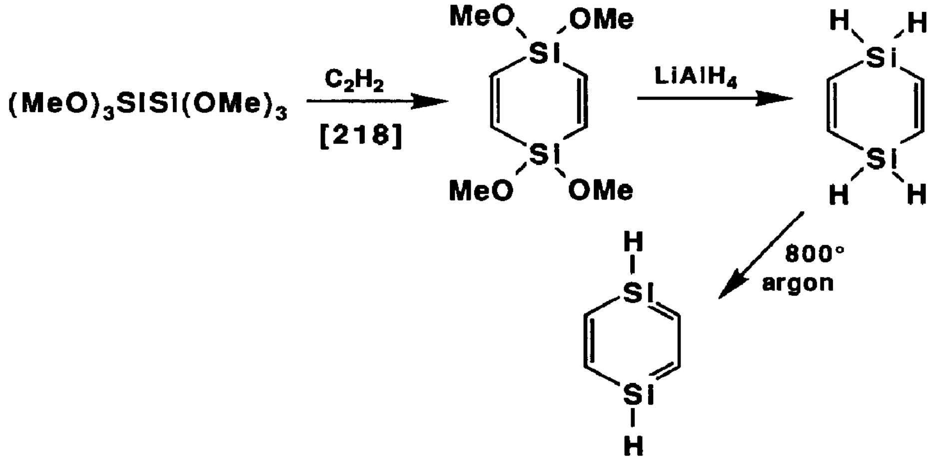


**295** **296**

(571)

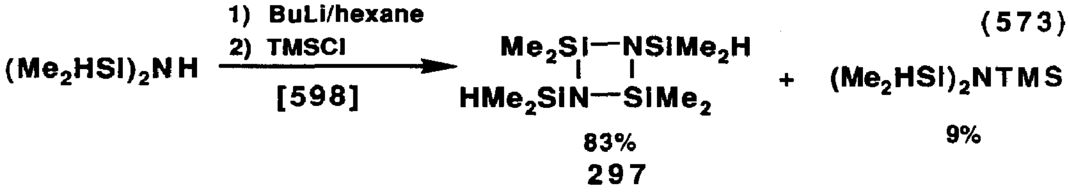
## E. OTHER REACTIVE ORGANOSILANE SPECIES

Hexamethoxydisilane was reacted with acetylene and the resulting disilacyclohexadiene reduced. Pyrolysis of this material provided 1,4-disilabenzene in an argon matrix. (Eqn. 572) The relative stabilities of 1,4-disilabenzene and its valence isomers have been calculated. Indications are that the planar form, the Dewar form and a silylene isomer have similar thermodynamic stabilities. There is reduced aromaticity in the silabenzenes. [597]



(572)

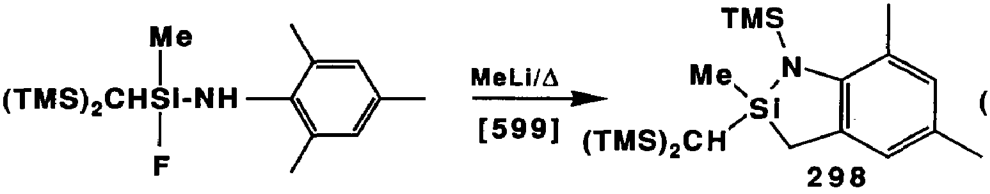
It was found that when bis(dimethylsilyl)amine is treated with n-butyllithium in hexane and the resulting solution reacted with trimethylchlorosilane only a 9 percent yield of the expected trimethylsilylated amine was formed along with an 83 percent yield of the cyclodisilazane **297**. It is postulated that this material arises from the intermediacy of a silaimine. (Eqn. 573)



**297**

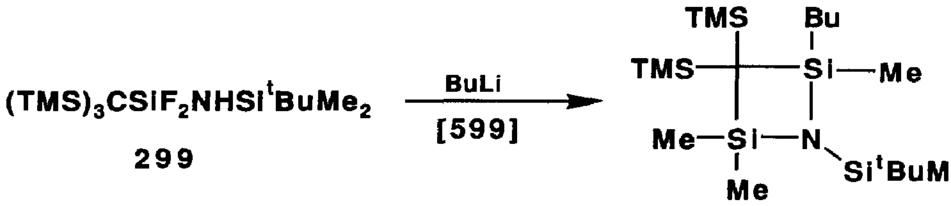
(573)

A silaimine is proposed as the key intermediate in the formation of the silacycle **298**. (Eqn. 574) The silylated material **299** gives a similar reaction. (Eqn. 575)



**298**

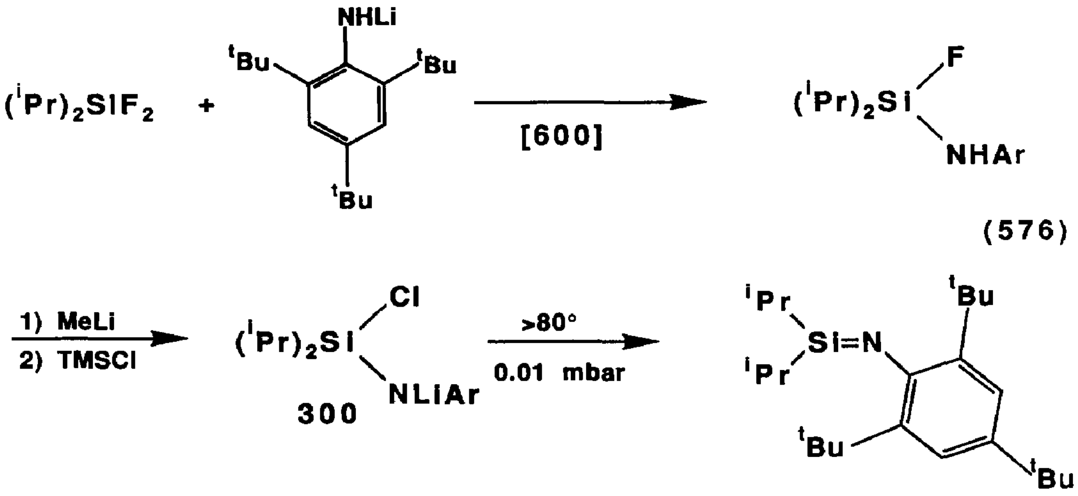
(574)



**299**

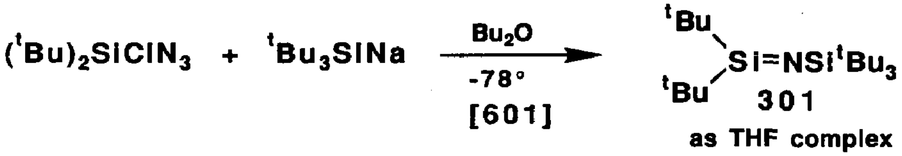
(575)

The first free silaimine was isolated according to the scheme outlined in Eqn. 576. Thus reaction of diisopropyldifluorosilane with lithium 2,4,6-tri-tert-butylanilide gives the substitution product, which can be lithiated. Treatment of this lithium salt with trimethylchlorosilane results in a ligand exchange to provide the chloride **300**, which undergoes elimination above 80° to produce the silaimine in high yield. This orange, crystalline material melts without decomposition or dimerization to a red liquid. It shows a $^{29}Si$ resonance at 60.3 ppm, consistent with an $sp^2$ hybridized silicon.



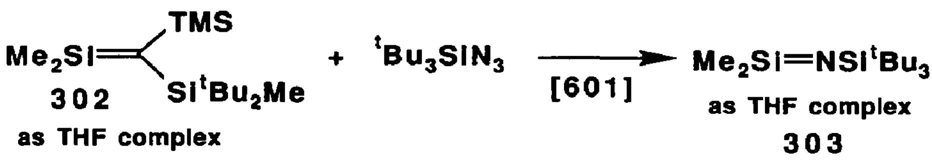
(576)

Di-tert-butylchloroazidosilane reacts with tri-tert-butylsilyl sodium to give silaimine **301**. (Eqn. 577) Tri-tert-butylsilyl azide reacts with silene **302** to give silaimine **303**. (Eqn. 578) An x-ray structure was obtained for **303**.



$$({}^tBu)_2SiClN_3 + {}^tBu_3SiNa \xrightarrow[-78^\circ\ [601]]{Bu_2O} ({}^tBu)_2Si{=}NSi{}^tBu_3 \quad (577)$$

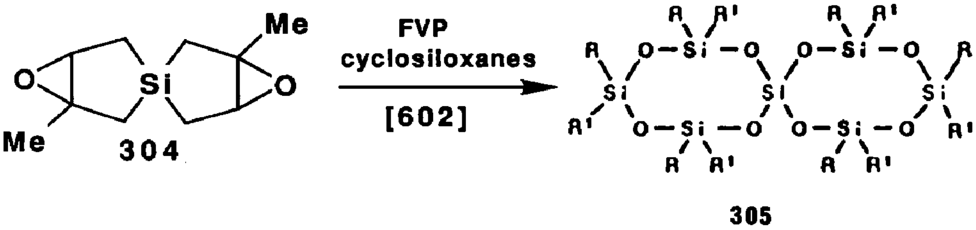
**301** as THF complex



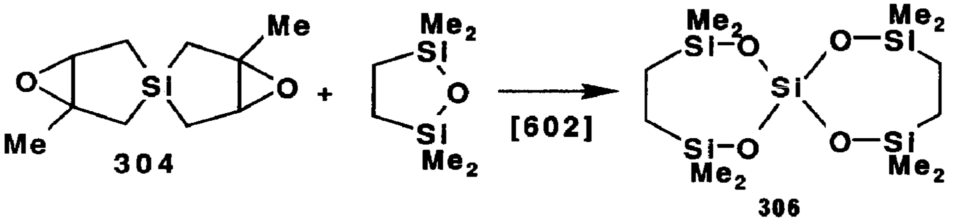
$$Me_2Si{=}C(TMS)(Si{}^tBu_2Me) + {}^tBu_3SiN_3 \xrightarrow[{[601]}]{} Me_2Si{=}NSi{}^tBu_3 \quad (578)$$

**302** as THF complex; **303** as THF complex

The flash vacuum pyrolysis of diepoxysilane **304** in the presence of cyclosiloxanes gives the spirocyclosiloxanes **305** and **306**. (Eqns. 579, 580) With no trapping agent a high surface area silica is formed.



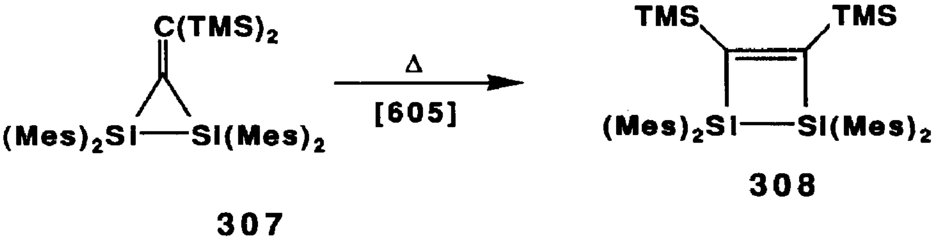
(579)



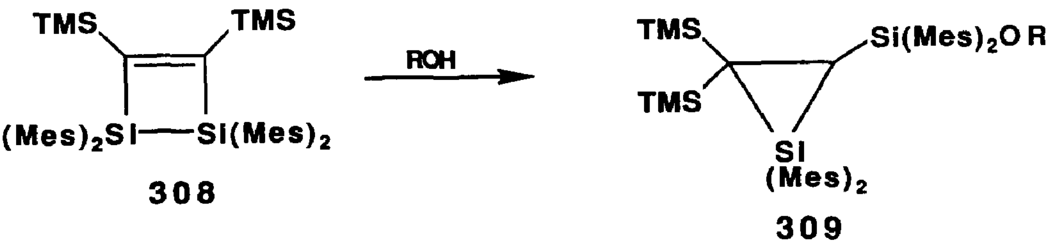
(580)

Force constants, total energies, and molecular and electronic structures were calculated for silanethione and dimethylsilanethione. The silanethione is more stable than the isomeric silylene. [603] Calculations indicate that it is more difficult to form the silicon-sulfur double bond than the silicon-oxygen double bond. [604]

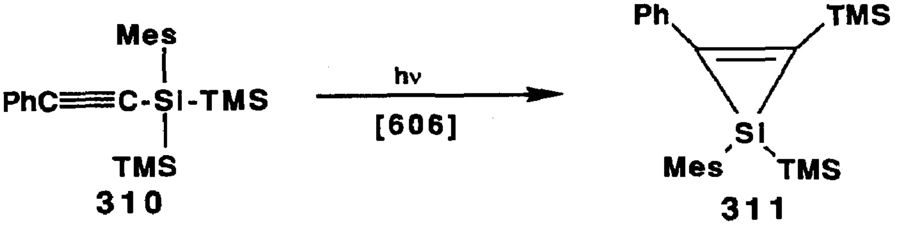
The disilacyclobutene **308**, prepared by the thermolysis of disilacyclopropane **307**, was reacted with alcohols to give the silacylopropane **309**. (Eqn. 581)



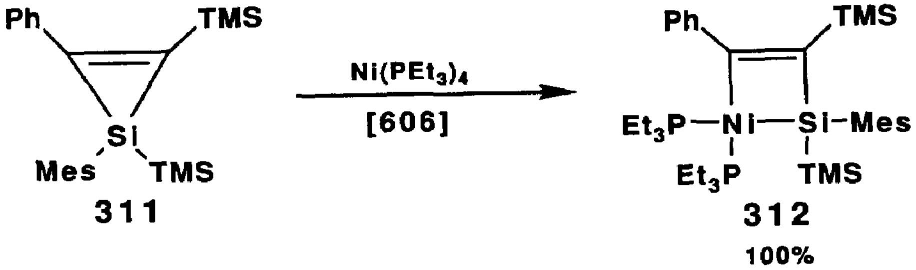
(581)



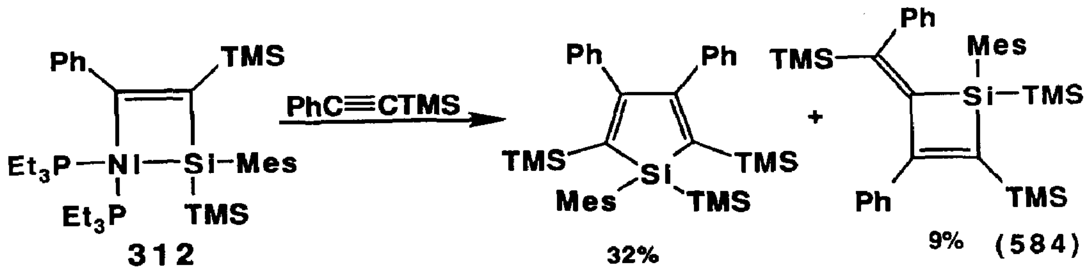
Photolysis of ethynylsilane **310** gives silacyclopropene **311**. (Eqn. 582) This was reacted with tetrakis(triethylphosphine)nickel(O) to give metallocycle **312**. (Eqn. 583) This interesting metallocycle was reacted with trimethylsilylphenyl acetylene (Eqn. 584) and thermally gave C-H insertion (Eqn. 585)



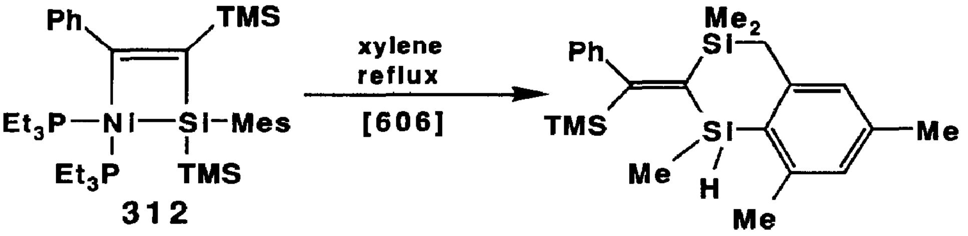
(582)



(583)

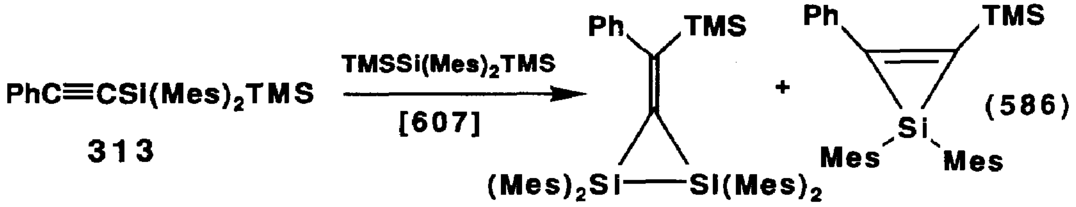


(584)

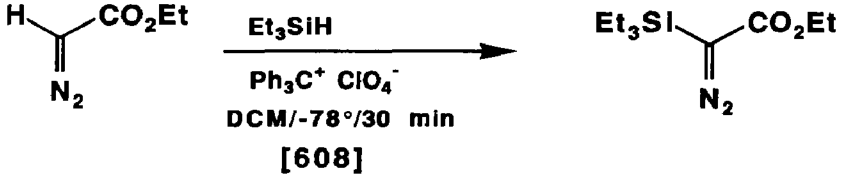


(585)

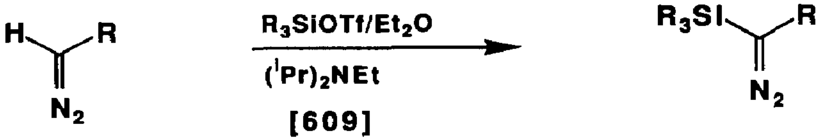
The generation of dimesitylsilylene in the presence of ethynylsilane **313** gives a mixture of the exo-methylenesilacyclopropane and silacyclopropene. (Eqn. 586)



Ethyl diazoacetate was reacted with triethylsilane in the presence of trityl perchlorate to give ethyl triethylsilyldiazoacetate in nearly quantitative yield. (Eqn. 587) Trimethylsilyl triflate reacts with diazoalkanes to give silyldiazoalkanes. (Eqn. 588) Ethyl pentamethyldisilyldiazoacetate gives the bissilylketene **314** upon photolysis. It is proposed, and substantiated by trapping with methanol, that the silene **315** is the intermediate in the reaction. (Eqn. 589)

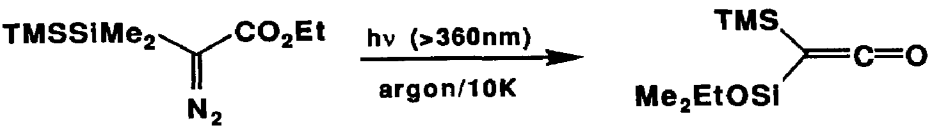


(587)



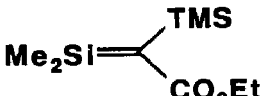
**8 examples; 68-82%**

(588)



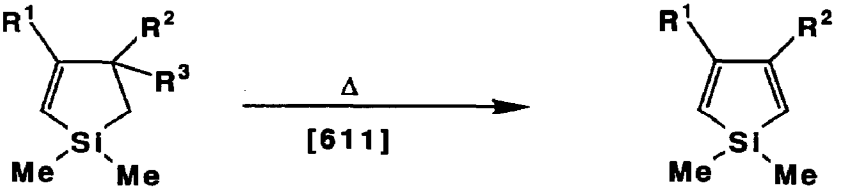
314

(589)



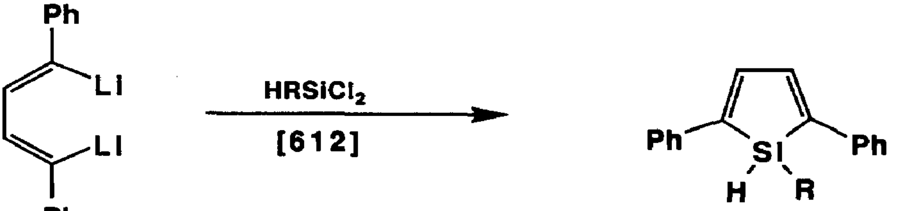
315

Siloles were prepared via the thermal elimination of carbamates and dithiocarbonates as shown in Eqn. 590. Siloles were also prepared by the reaction of 1,4-diphenyl-1,4-dilithio-1,3-butadiene and dichlorosilanes. (Eqn. 591) The siloles prepared in this way were reacted with bis(1,5-cyclooctadiene)nickel(O). (Eqn. 592) Siloles were utilized in Diels-Alder cycloadditions. (Eqns. 593, 594, 595)



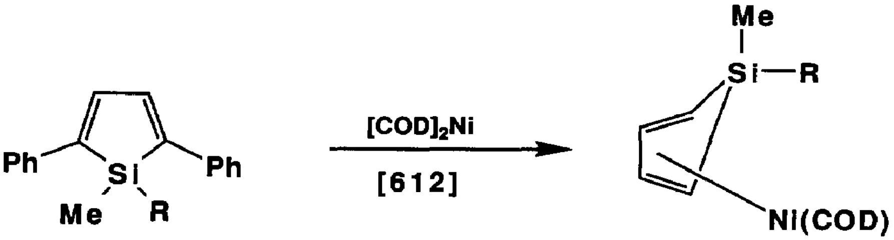
(590)

($R^3$ = OCONHPh; OCSSMe)

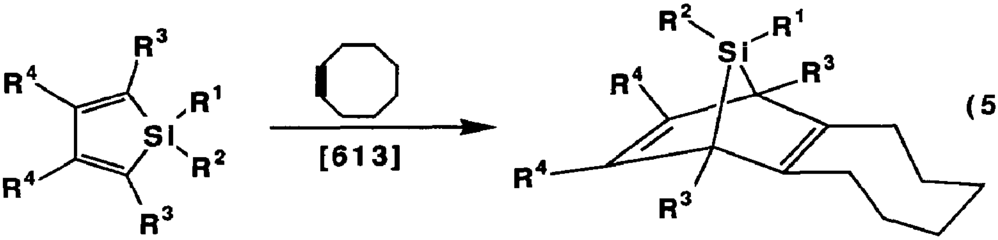


(591)

(R = vinyl, Me)

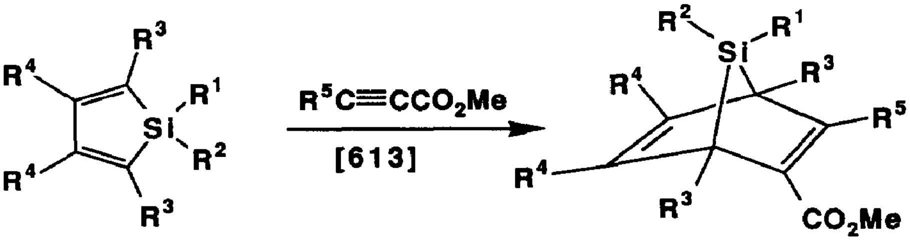


(592)



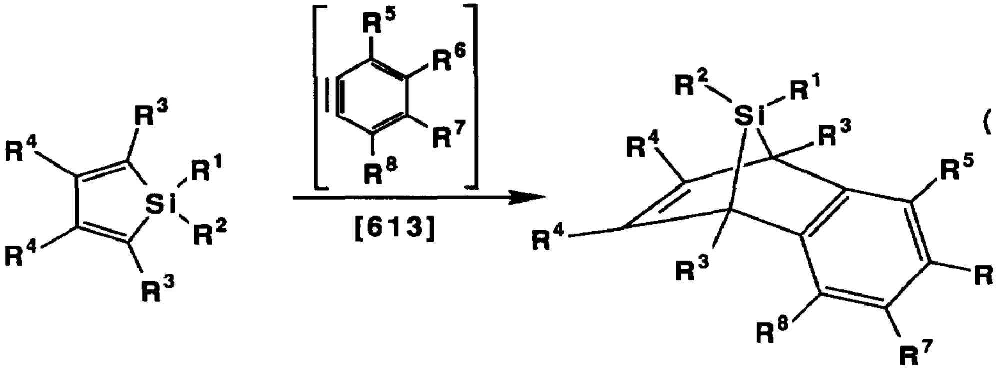
(593)

7 examples; 40-83%



(594)

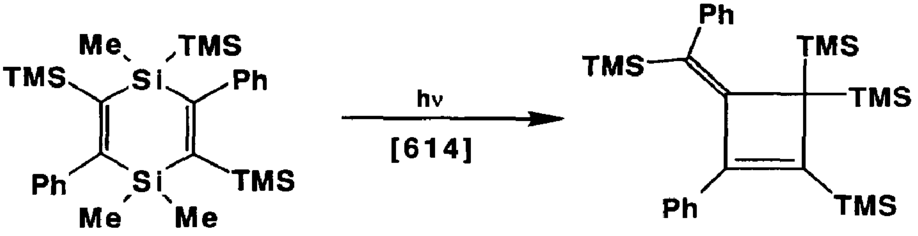
7 examples; 20-90 %



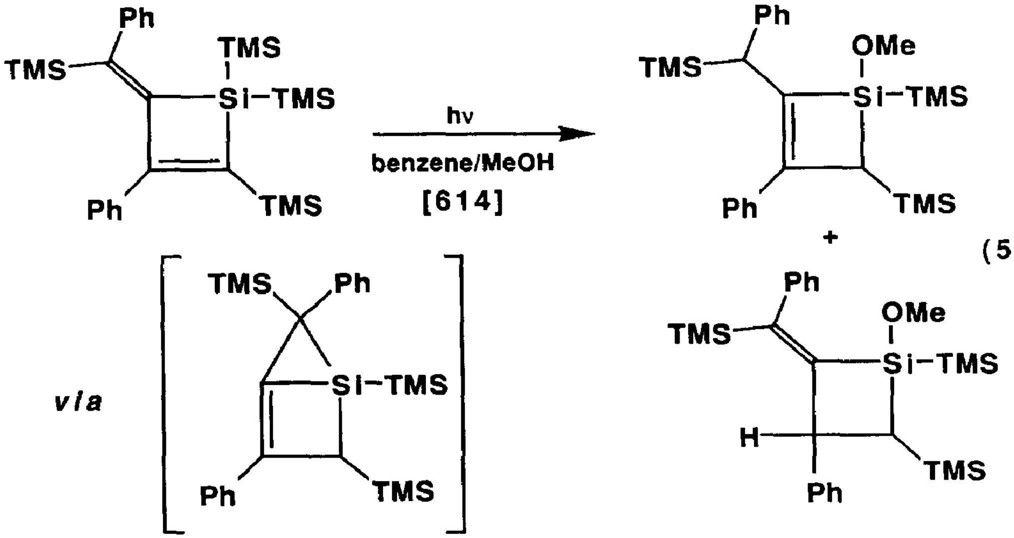
(595)

14 examples; 9-92 %

It is argued that a silacyclopropane is the intermediate in the photolysis of alkylidene silacyclobutenes (Eqn. 597), formed by photolysis of 1,4-disilacyclohexadienes (Eqn. 596). The thermolysis of silacyclobutenes in the absence (Eqn. 598) and presence (Eqn. 599) of methanol was carried out. A silylene intermediate is proposed.



(596)



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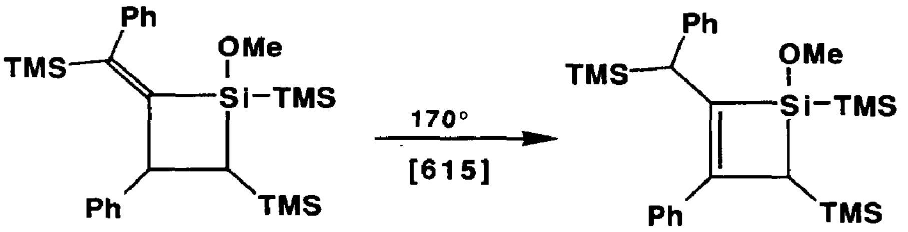
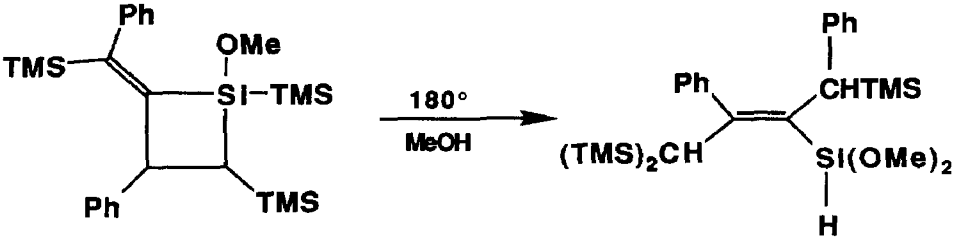


(598)

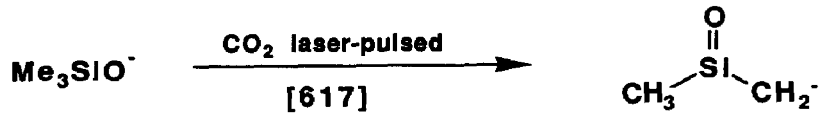


(599)

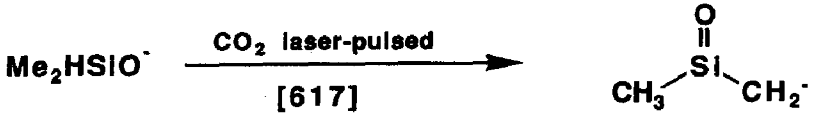
The triphenylsilyl cation was generated from the reaction of triphenylsilane and trityl perchlorate. (Eqn. 600) All evidence is consistent with an ionic species.

$$Ph_3SiH + Ph_3C^+ ClO_4^- \xrightarrow[{[616]}]{} Ph_3Si^+ ClO_4^- + Ph_3CH \qquad (600)$$

The enolate of trimethylsilanone was generated in the gas phase according to Eqns. 601, 602.



$$Me_3SiO^- \xrightarrow[{[617]}]{CO_2\ \text{laser-pulsed}} CH_3Si(=O)CH_2^- \qquad (601)$$



$$Me_2HSiO^- \xrightarrow[{[617]}]{CO_2\ \text{laser-pulsed}} CH_3Si(=O)CH_2^- \qquad (602)$$

**Acknowledgements:** I would like to thank Mr. Roy Anderson and Dr. Craig Blankenship for thorough readings of this manuscript.

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