ORGANOSILICON SURVEY 1985. THE SILICON-CARBON BOND

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I. INTRODUCTION

This section of the Annual Survey of Organosilicon Chemistry covers material appearing in volumes 102 and 103 of Chemical Abstracts. It is the intention to report on the silicon-carbon bond and carbofunctional organosilicons. It should be noted that in many instances equations and structures are written in general form with liberal use of R, Ar, TMS and TBS for alkyl, aryl, trimethylsilyl and tert-butyldimethylsilyl, respectively. 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. REVIEWS

A total of 44 reviews appeared, not all of which dealt with the silicon-carbon bond, but which are included nonetheless. The number of references to be found in each review is given in parentheses.

The two most comprehensive reviews to appear were the Organosilicon Survey-The Silicon-Carbon Bond-1983 (447) [1] and Silafunctional compounds: Synthesis and Reactivity: Annual Survey-1983 (559) [2].

Synthetic applications was again the theme for a number of reviews. These included applications of organosilicon reagents in pharmaceutical synthesis (23) [3], application of organosilicon compounds to synthesis (15) [4], organic synthesis with boron, phosphorus and silicon reagents (>30) [5], silicon in silylation reactions (0) [6], the properties and applications of trimethylsilyltriflate (5) [7], reactions of ions formed from trimethylsilyltriflate (25) [8], the synthesis, reactions and antihypertensive, antibacterial and anticancer activities of α- and β-aminoalkylsilanes (50) [9], acylation and alkylation of enol silyl ethers (43) [10], reactive enolates from enol silyl ethers (48) [11], selective carbon-carbon bond formation using silyl enol ethers (18) [12], application of methyl 2-(triorganosilyl)-3-butanoate to pyranonaphthaquinone antibiotics (73) [13], preparation and alkylation of silyl enol ethers (21) [14], oxoalkylation of carbonyl compounds via enol silyl ethers and silyl ketene acetals (35) [15], cyanation of enol silyl ethers and silyl ketene acetals (30) [16], synthetic organic reactions via reactive nucleophiles generated by silyl group rearrangements (37) [17], organic synthesis with silyl rearrangement (20) [18], Lewis acid cleavage of silicon-carbon bonds with carbon-carbon bond formation (107) [19], synthetic applications of chloromethyltrimethylsilane (122) [20], allylsilanes in organic synthesis (115) [22], pentadienylmetal compounds (84) [23], synthesis and utilization of compounds with chiral silicon centers (75) [24], azomethine ylides from α-aminosilanes (36) [25].

Other reviews dealt with a variety of topics. Thus reviews appeared dealing with alkynyl, alkenyl and alkylsilanes (26) [26], organosilicon chemistry: silicon age is coming, dealing with a variety of topics (33) [27], silicone (4) [28], structure, properties and uses of organosilicon compounds (0) [29], preparation and application of organosilicon compounds of chemical vapor deposition (37) [30], structure and chemistry of silatranes (88) [31], use of organosilathianes for the synthesis of sulfur-containing organic compounds (0) [32], interaction of vinylsilylacetylenes with group II organometallics (15) [33], synthesis of nitro containing silacyclopentanes and silacyclopentenes (6) [34], mechanism of hydrosilylation of olefins with Ni(II) complexes (9) [35], effects of ligands on the hydrosilylation via Ni(II) catalysis (6) [36], silylenes (125) [37], arynes, carbenes, nitrenes and silylenes (100) [38], highly reactive organophosphorus species stabilized by steric protection, which includes silylation (92) [39], reactivity of organosilicon derivatives of phosphorus (137) [40], silane photochemistry (205) [41], silyl, germyl and stannyl derivatives of azenes (88) [42], chemistry of carbanions in the gas phase, some carbanions generated by fluoride on organosilicons (7) [43] and photoelectron spectroscopy in organometallic chemistry (9) [44].

III. DISSERTATIONS

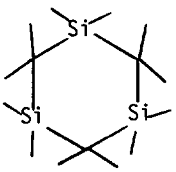
Several dissertations, available from Dissertation Abstracts, Ann Arbor, Michigan, dealing with silicon appeared. These include the trimethylsilyl group in organic synthesis [45], silicon-mediated synthesis of bibenzyl systems [46], the chemistry of 1-piperidino-1-trimethylsilyloxycyclopropane [47], 2-bromo-3-(trimethylsilyl)propene: a bifunctional conjunctive reagent [48], electrophilic ring opening of epoxides with chlorotrimethylsilane [49], flash vacuum pyrolysis of trimethyl (trichloromethyl)silane with benzaldehyde [50], synthesis of carbocyclic silanes via organosilicon reactive intermediates [51], the regiochemistry of alkenylsilyl, alkenyldisilanyl and alkenylsilyloxy radical cyclizations [52], esr study of the singly occupied orbital in cyclosilane anion radicals [53], synthesis and reactions of [2-(trimethylsilylmethyl) benzyl]trialkylammonium iodide: o-xylylene precursors [54], and a multinuclear NMR study of organosilanes [55].

IV. ALKYLSILANES

A. Preparation

The catalytic formation of silanes on copper-silicon alloys has been studied. The rates of formation of silanes from chloromethane and silicon were measured at atmospheric pressure and 520-620^{o}K. A variety of catalyst variations were investigated. [56] Tableting a Si-Cu alloy containing Si, Cu, Al, Fe and Ti and sintering at 1100-1300^{o} in nitrogen gave catalysts for the direct reaction. Best selectivity was found with from 0.2 to 0.8 weight percent titanium present. [57] A catalyst with from 10-57 weight percent aluminum and 0.05 to 5 percent titanium and silicon powder was used to best methylate methyltrichlorosilane to chlorotrimethylsilane and tetramethylsilane. [58]

Dichloromethane, chloroform and carbon tetrachloride have been reacted with elemental silicon and the products reduced with lithium aluminium hydride. In addition to already known silicon products, several silicon rich viscous compounds were found. Separation by HPLC showed that dichloromethane leads to $Si_nC_{n-1}H_{4n}$ (n=4-12 with two H_3Si termini) and 1 with chains attached to carbon or silicon. Chloroform reacts to give unbranched chains and chains with 1 or 2 carbon branches and 2 with 1, 2 or 3 silyl groups attached to carbon. [59]



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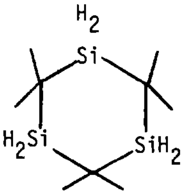


2

The vat residues from ethylchlorosilane production showed chloroethane, ethyldichlorosilane, ethyltrichlorosilane, toluene, diethyldichlorosilane, triethylchlorosilane, tetraethylsilane and hexaethyldisiloxane as well as linear and cyclic siloxanes. [60] The reaction of tetraethoxysilane, chloroethane and magnesium in an organic solvent containing toluene and diethyldichlorosilane or silicon tetrachloride gives more triethylchlorosilane. (Eqn. 1)

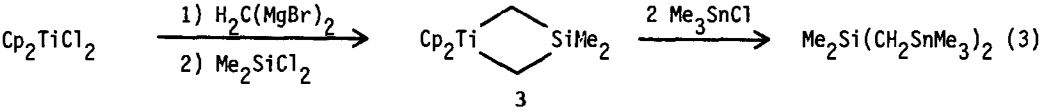
$$EtCl \quad + \quad (EtO)_4Si \quad + \quad Mg \xrightarrow[\substack{\text{toluene;} \\ Et_2SiCl_2 \\ SiCl_4 \\ [61]}]{\text{solvent}} Et_3SiCl + Et_3SiOEt + Et_3SiOSiEt_3 \quad (1)$$

Tris(dimethylphenylsilyl)methyllithium can be prepared and reacted with some electrophiles. (Eqn. 2)

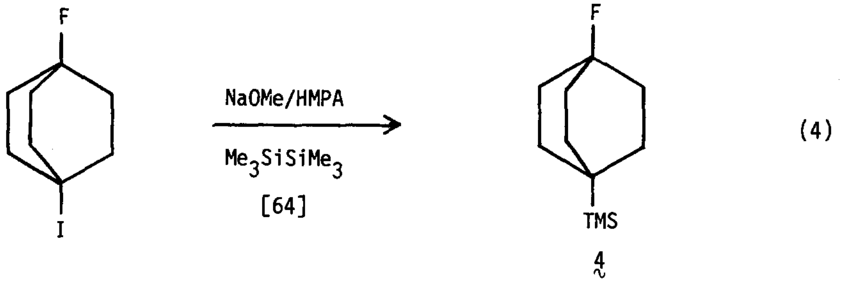
$$(PhMe_2Si)_3CH \xrightarrow[\text{2) } E^+ \text{ [62]}]{\text{1) MeLi/THF}} (PhMe_2Si)_3 \qquad (2)$$

E^+ = MeI; Me_2HSiCl; $MeHSiCl_2$; but not TMSCl

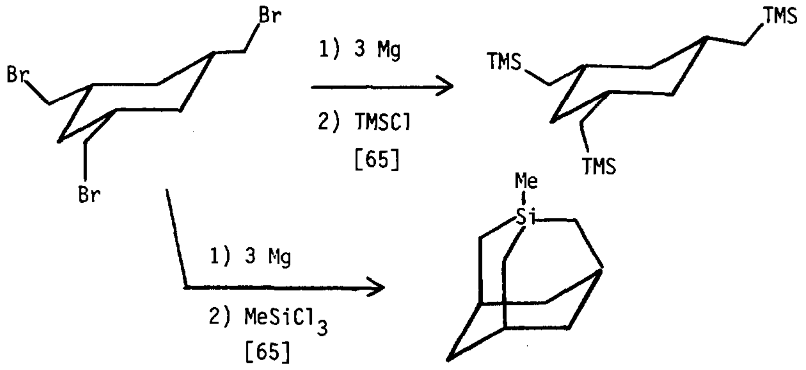
Bis(bromomagnesio)methane reacts with Cp_2TiCl_2, which in turn reacts with dimethyldichlorosilane to form **3**. Compound **3** can be stannylated. (Eqn. 3)



The bridgehead silylated system **4** was prepared by reaction of trimethylsilylsodium on the corresponding iodide. (Eqn. 4).



The reaction of magnesium with cis-1,2,3-tris(bromomethyl)-cyclohexane gives the tri-Grignard reagent, which was reacted with trimethylchlorosilane and methyltrichlorosilane as shown. (Eqns. 5 and 6)



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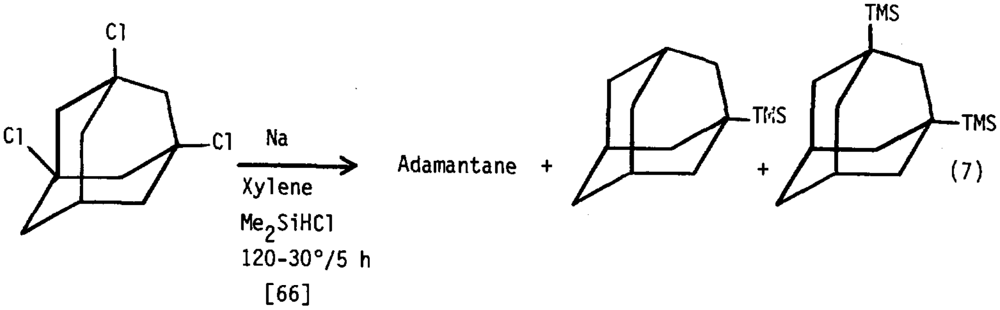
(6)

The reaction of bridgehead chlorinated adamantanes with sodium in xylene in the presence of dimethylchlorosilane or trimethylchlorosilane gives the results shown below. (Eqns. 7 and 8) On the other hand the reaction of dimethylphenylsilyllithium with bridgehead brominated adamantanes gives excellent yields of the silylated materials. (Eqn. 9)



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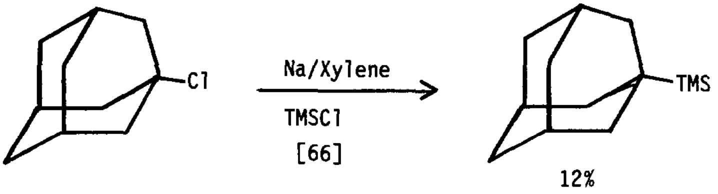

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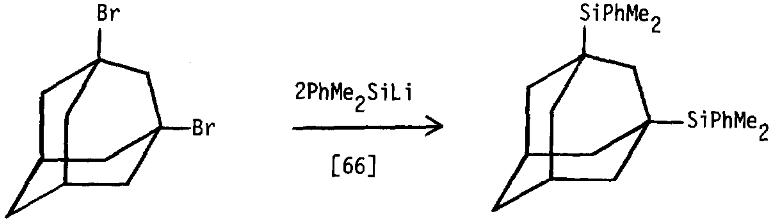

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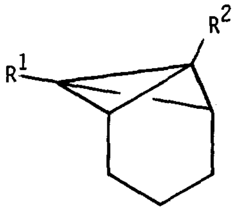
The bicyclobutanes **5-10** have been dilithiated and trimethylsilylated to give the disilylated products in 15-70 percent yield. [67]



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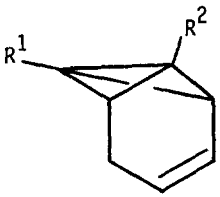

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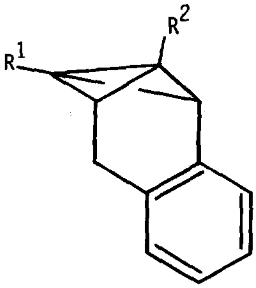

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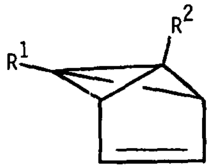

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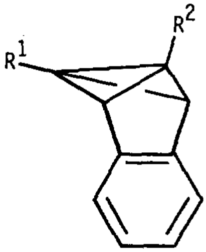

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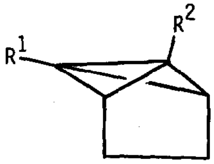

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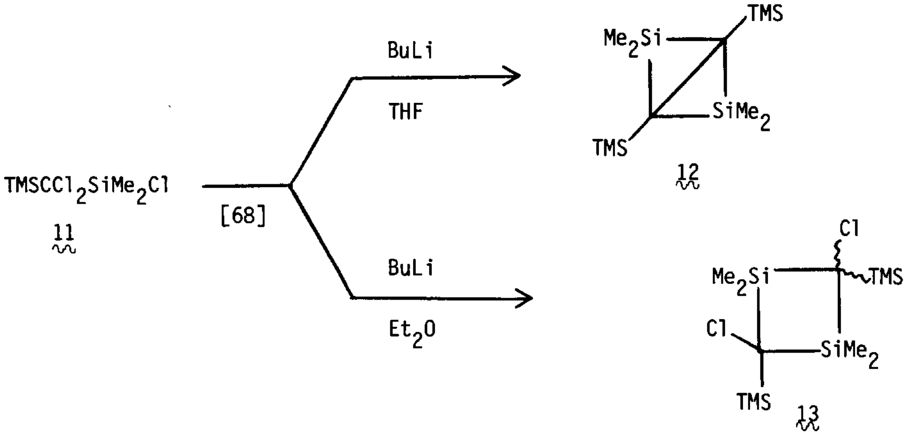
$R^1, R^2 = H; R^1, R^2 = Li$

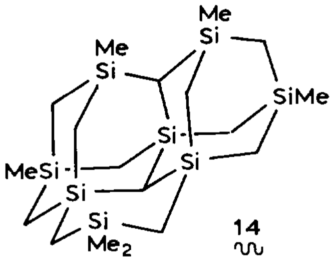
Treatment of **11** with n-butyllithium in THF gives the disilabicyclobutane **12**, whereas in ether the reaction gives the diastereomeric 1,3-disilacyclobutanes **13**. Both isomers of **13** were shown to be intermediates in the formation of **12**. (Eqns. 10 and 11)



(10)

(11)

Finally, a series of silaadamantane structures containing the Me-Si group in 1,3 arrangements have been prepared and characterized. A representative example is shown in structure **14**. [69, 70]



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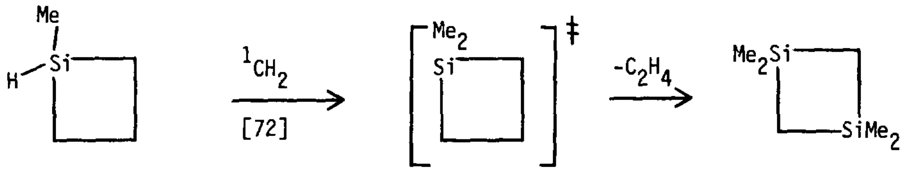
B. Reactions

Tetramethylsilane has been reacted with adamantane under the influence of aluminum bromide to produce mono- to polymethylated adamantanes. (Eqn. 12)

$$\text{Adamantane} \xrightarrow[\substack{40\text{-}70^\circ \\ [71]}]{Me_4Si/AlBr_3} \begin{array}{l}\text{mono- to polymethylated} \\ \text{Adamantanes}\end{array} \qquad (12)$$

The insertion of singlet methylene ($^1CH_2$) into 1-methyl-1-silacyclobutane provides an activated (∿115 kcal/mol) 1,1-dimethyl-1-silacyclobutane, which then leads to the same products as does photolysis of 1,1-dimethyl-1-silacyclobutane, namely ethylene and 1,1,3,3,-tetramethyl-1,3-disilacyclobutane. (Eqn. 13)



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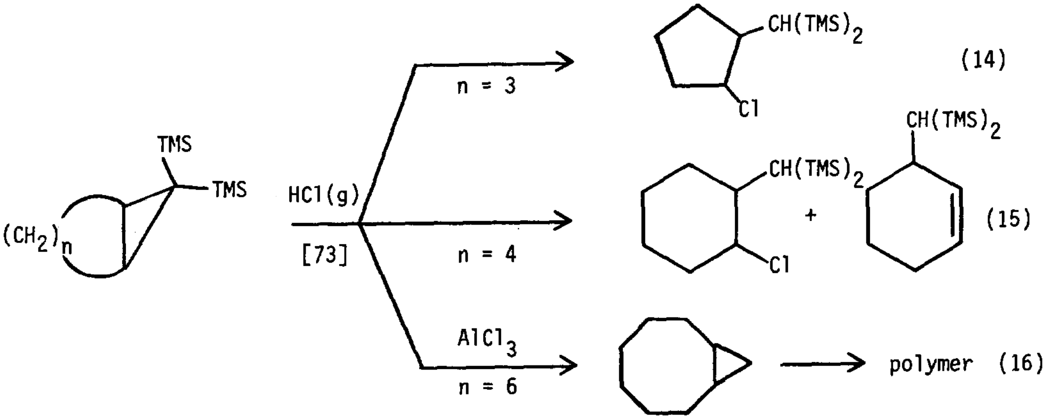
Bis (trimethylsilyl)bicyclo[n.1.0]alkanes react with acids to readily substitute one of the trimethylsilyl groups and/or open the cyclopropane ring. (Eqns. 14-16)

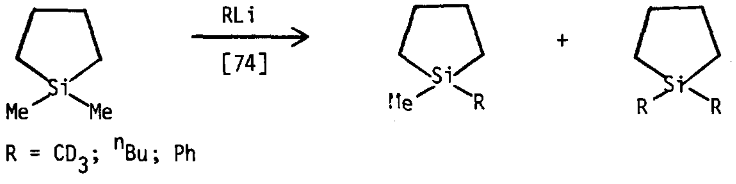


(14)

(15)

(16)

1,1-Disubstituted silacyclopentanes were shown to undergo an exchange reaction with lithium reagents presumably via an ate-complex intermediate. The exchange is 100 fold faster in THF than in ether. (Eqn. 17) Some deprotonation is also observed. (Eqn. 18)



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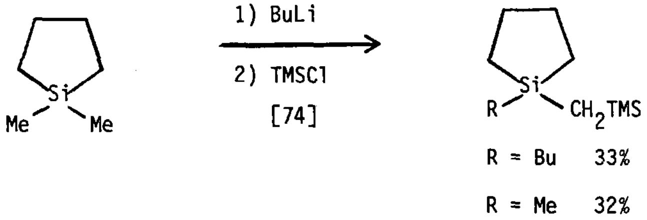
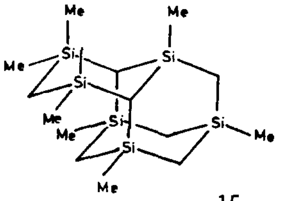


(18)

C. Other

A reverse phase HPLC system employing nucleosil 5-C18 methanol: hexane was shown to work well for the separation of complex carbosilane and silylphospine mixtures. Examples of the components in the carbosilane test mixture used are given in structures **15**-**18**. [75]



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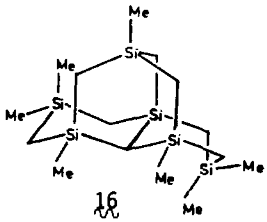

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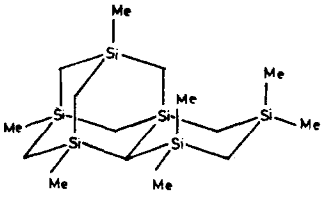

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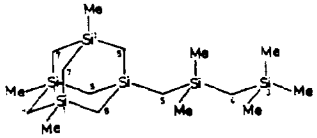
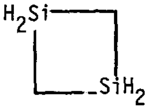


18

Several spectral studies of alkylsilanes were reported. The electron energy loss spectra of the silicon 2p, 2s, carbon 1s and valence shells of tetramethylsilane were recorded. [76] The vibrational overtone spectra of gaseous methyl substituted silanes ($MeSiH_3$ Me_2SiH_2, Me_3SiH and Me_4Si) between 12,800 and 18,200 cm^{-1} have been recorded. [77] The IR (3500-50 cm^{-1}) and Raman (3500-20 cm^{-1}) spectra of gaseous, liquid and solid cyclobutylsilane have been recorded. The equatorial silyl group is the preferred conformation in the vapor and liquid state and the only conformation in the solid state. [78] A planar structure for 1,1,3,3,-tetrachloro-1,3-disilacyclobutane has been established by its IR and Raman spectra. [79] The far IR, mid-IR and Raman spectra of **19-23** have been carried out and the ring bending transition frequencies determined. All but **21** have equilibrium ring conformations which are nonplanar. [80]



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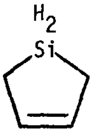

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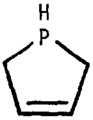

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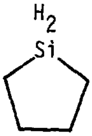
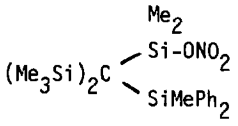


23

The mass spectra of some high molecular weight tetraalkylsilanes with one small and three long groups (C_{20}-C_{32}) were recorded. The dominant course of fragmentation involved the loss of alkyl groups. With chains longer then n-hexyl a rearrangement was observed in which alkanes were eliminated, for example, hexyl gave methane, heptyl gave ethane, octyl gave propane and so on. [81] The mass spectra of α-trimethylsiloxy-ω-methyl(ethoxy)silyl alkanes and 1-oxa-2,2-methyl(ethoxy)-2-silacycloalkanes were reported. [82] The fragmentations of saturated organosilanes were determinated by on-line deuteration. [82a]

The structure of bis (trimethylsilyl)methyllithium by electron diffraction in the gas phase showed it to be monomeric with the trimethylsilyl groups twisted ca. 9 degrees from the reference position. [83] The structure of **24** showed it to have no symmetry. The ^{1}H NMR at ambient temperature shows two silicon methyl resonances (not considering the MePh$_2$Si one, which does not change with temperature) and eight silicon methyl signals at -90°. [84]

Ab initio calculations for **25** (M=C, Si) have been carried out. For both compounds the most stable structure is twisted (distorted pyramidal). The planar structure is higher in energy by 66.2 (Si) and 32.3 (C) kcal/mol. The energy increases monotonically in going from the distorted pyramidal to the planar structure. The possible decomposition mode to extrude disilene is predicted to be unfavorable. [85]



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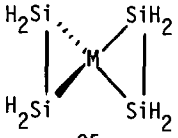

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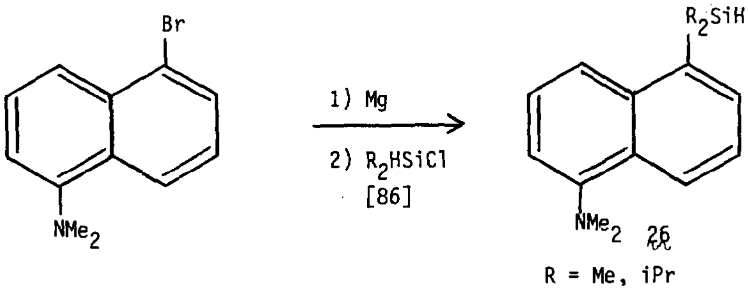
V. ARYLSILANES

A. Preparation

The reaction of arylmagnesium halides generated prior to the addition of the chlorosilane (Eqns. 19-21, 23, 25-27) or "in situ" together with the chlorosilane provides arylsilanes. The tertiary silanes **26** and the 10-anthranyl derivatives (see Eqn. 49) are fluorescent hydroxyl protecting groups that can distinguish between primary and secondary hydroxyls. Silaketone **27** was prepared by three routes as shown in equations 22-24. The aryl chlorides were best reacted with Rieke's activated magnesium metal. Further examples are given in equations 25 and 26. The benzosilacyclobutanes **28** were prepared according to equation 27.



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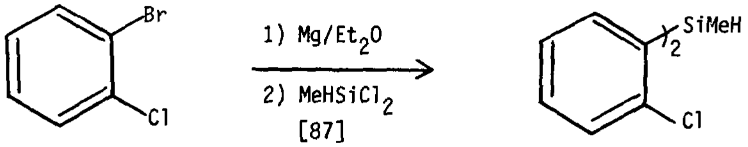

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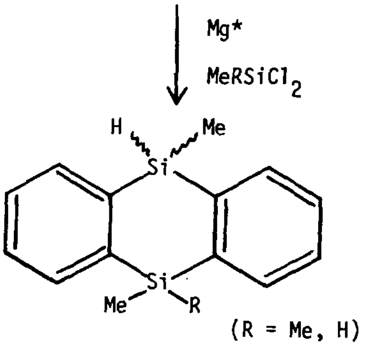

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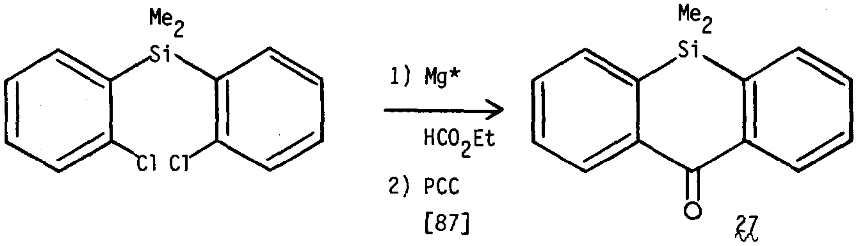

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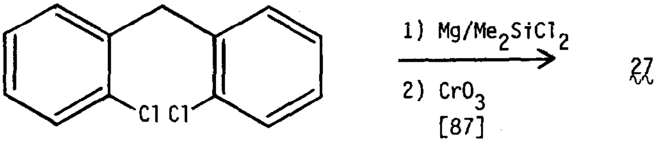

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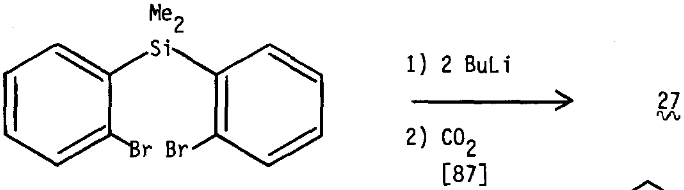

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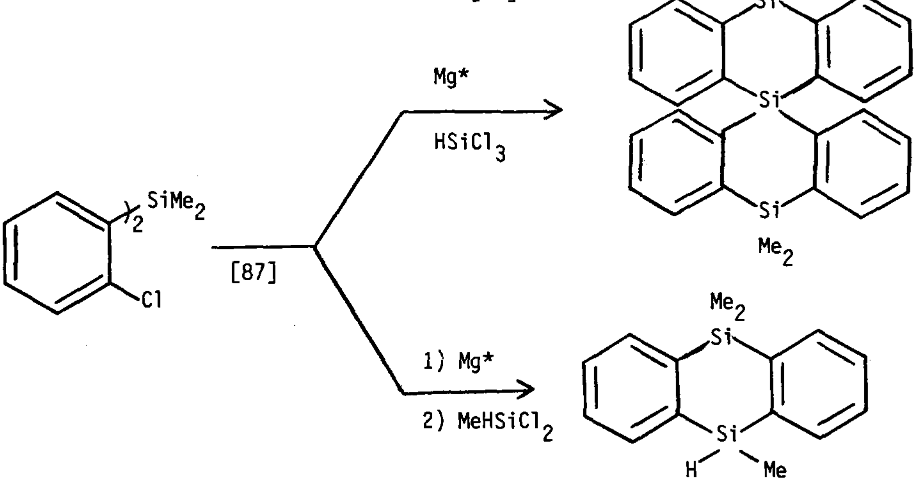

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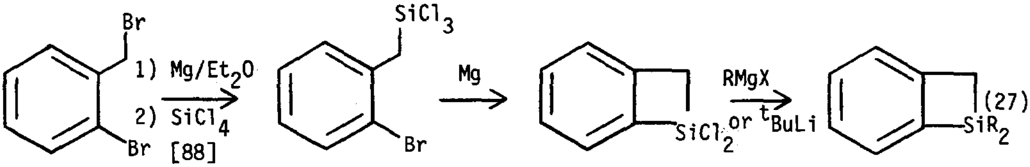
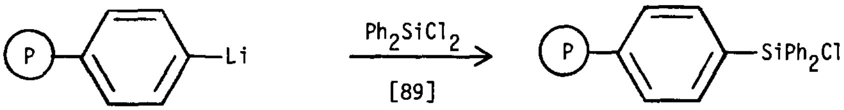
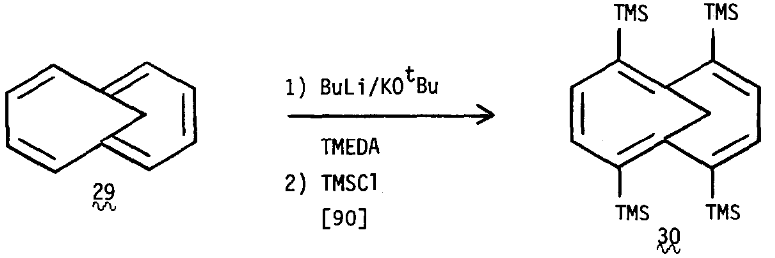


(R = Me (90%); Ph (88%); Et (86%); iPr(83%); ^{t}Bu (55%)

Direct lithiation of aryl systems was used to provide aryllithium reagents, which were then reacted with chlorosilanes to give arylsilanes. Examples are shown in equations 28-48. This technique was used to provide polymer supported organosilyl protecting groups, which were applied to the monoprotection of 1,9-nonane diol. (Eqn. 28) The 1,6-methano[10]annulene **29** was lithiated and trimethylsilylated to give **30** which was subjected to an x-ray structure determination. (Eqn. 29) A host of furan and thiophene derivatives have been selectively lithiated and silylated. These are shown in equations 30-36. Compounds of the structure **29** were tested for analgesic and antiinflammatory activity. Equation 36 demonstrates the difference in reactivity between the two different lithiated positions, with the 3-lithio position being the more reactive of the two. The results shown in equations 30 and 34-36 illustrate the directive effect of the carboxyl and amide groups on the lithiation reaction. The reaction shown in equation 32 demonstrates the utility of lithium diisopropyl amide in direct lithiation as opposed to the lithium-bromine exchange that occurs with butyllithium.



(28)



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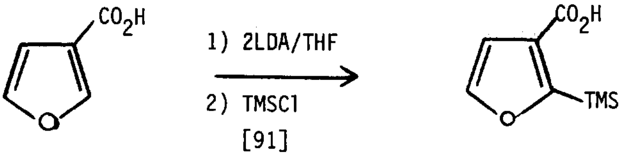
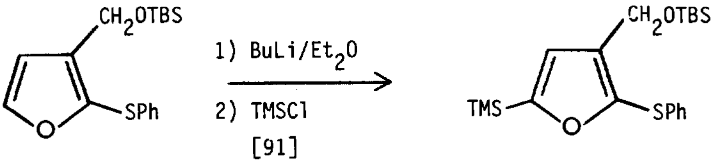


(30)



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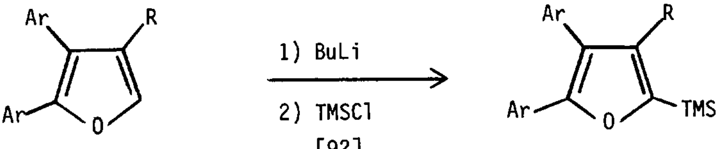
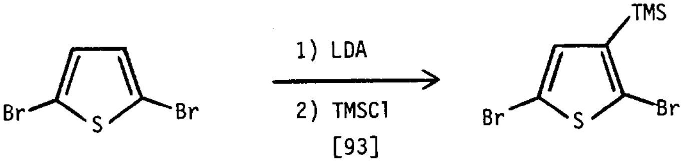


31

(32)



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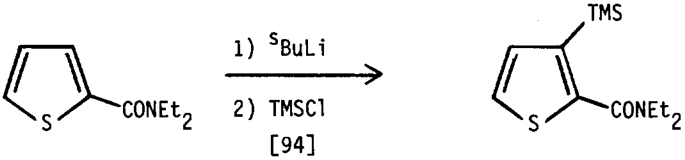

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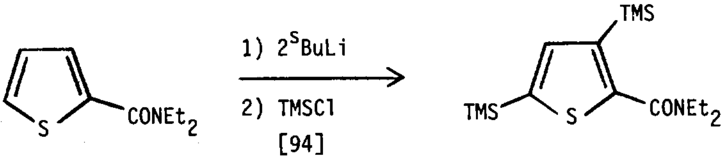
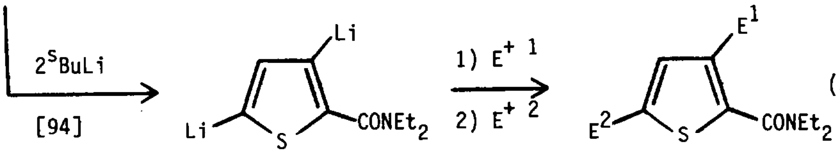


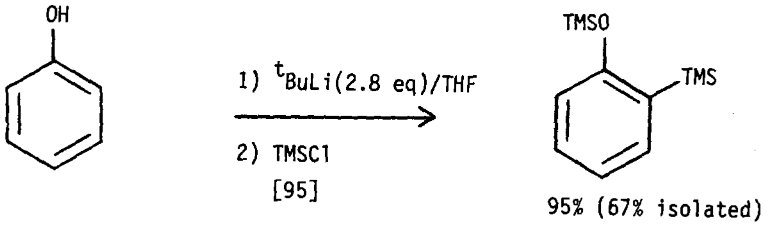
(35)



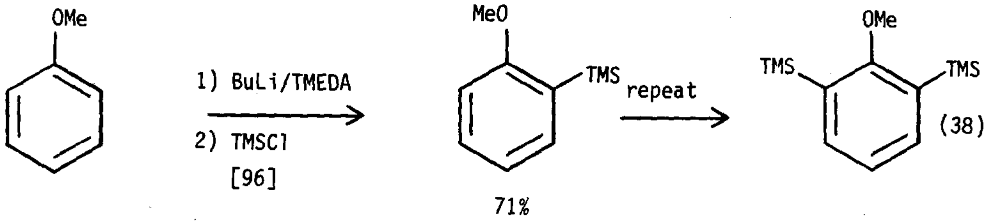
(36)

E^1	E^2	%
TMS	H	40
MeS	TMS	26
TMS	MeS	35

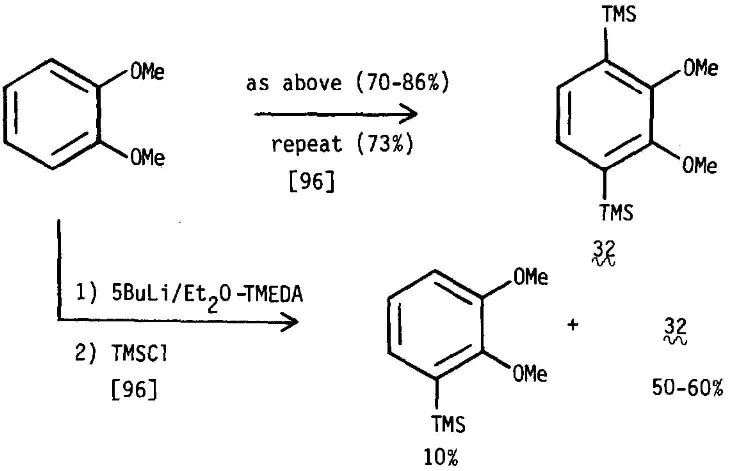
Conditions were found for the direct ortho-lithiation of phenol. (Eqn. 37) The systematic lithiation of a series of methoxybenzenes gave the results shown in equations 38-45. In summary it was determined that direct lithiation would provide dilithio reagents **35-37** in good yield, **38-39** incompletely and **40-41** not at all. The effect of dialkylamino groups on the regiochemistry of the lithiation of o-carbamoyl phenols was investigated. Two examples are shown here. (Eqns. 46-48) In general with the strong ortho directing carbamoyloxy group the least hindered ortho position is attacked. (Eqn. 46) The weaker directing methoxyl group gives lithiation ortho to both groups. (Eqn. 47) The methoxymethyl group gives either or both products depending on the dialkylamino substituents and the solvent. (Eqn. 48)



(37)

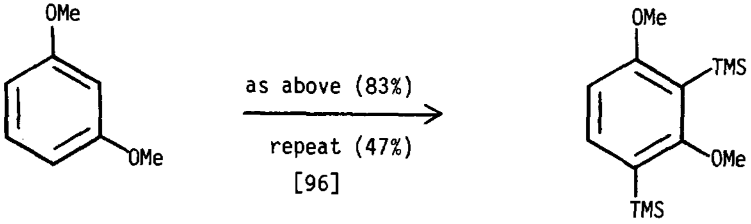


(38)

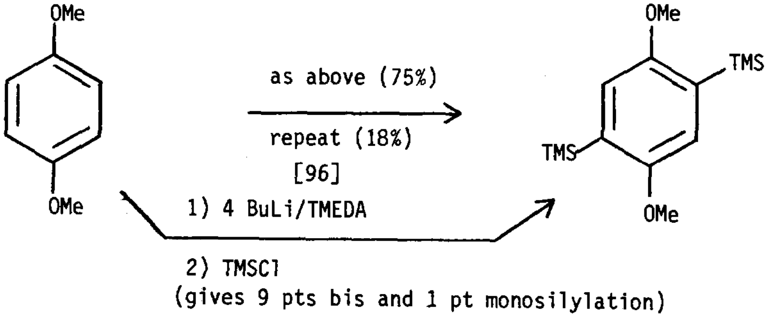

OMe
OMe
as above (70-86%)
repeat (73%)
[96]
TMS
OMe
OMe
TMS
32
1) 5BuLi/Et$_2$O-TMEDA
2) TMSCl
[96]
OMe
OMe
TMS
10%
+
32
50-60%

(39)

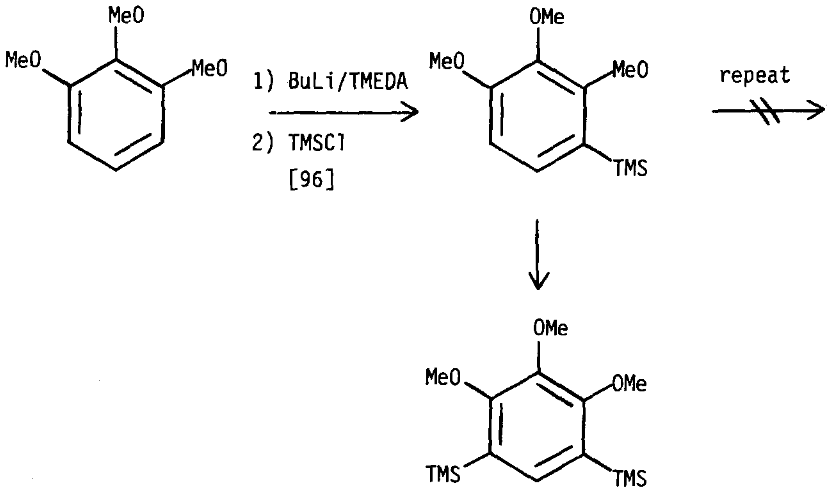
(40)


OMe
OMe
as above (83%)
repeat (47%)
[96]
OMe
TMS
OMe
TMS

(41)

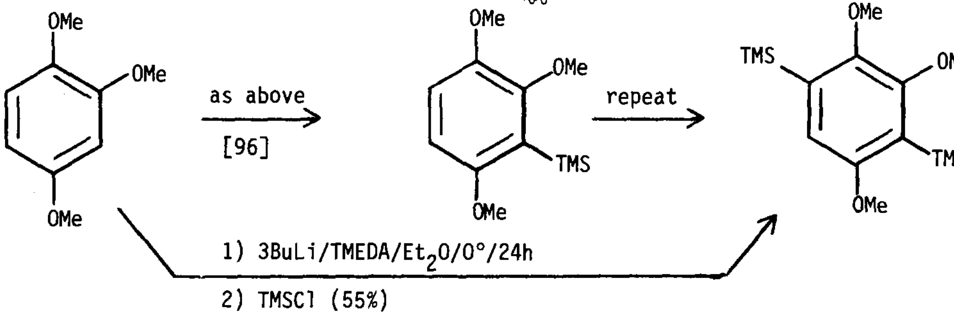

OMe
OMe
as above (75%)
repeat (18%)
[96]
OMe
TMS
TMS
OMe
1) 4 BuLi/TMEDA
2) TMSCl
(gives 9 pts bis and 1 pt monosilylation)

(42)

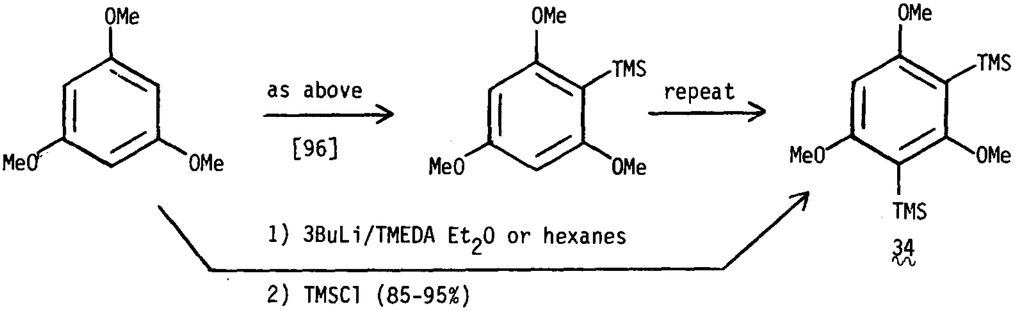

1) BuLi/TMEDA
2) TMSCl
[96]
repeat
MeO
OMe
TMS

(43)

33

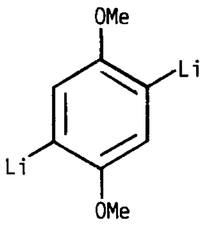

as above
[96]
repeat
1) 3BuLi/TMEDA/Et$_2$O/0°/24h
2) TMSCl (55%)
OMe
TMS

(44)

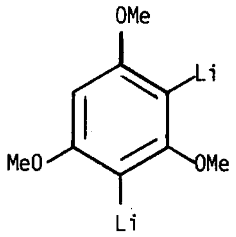

as above
[96]
repeat
1) 3BuLi/TMEDA Et$_2$O or hexanes
2) TMSCl (85-95%)
OMe
MeO
TMS

(45)

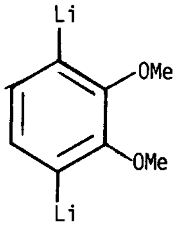
34



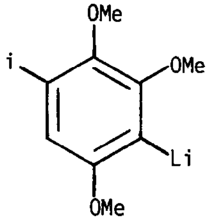
35



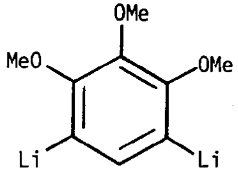
36



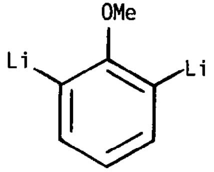
37



38



39



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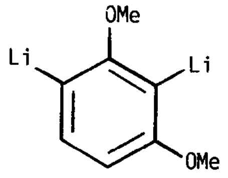

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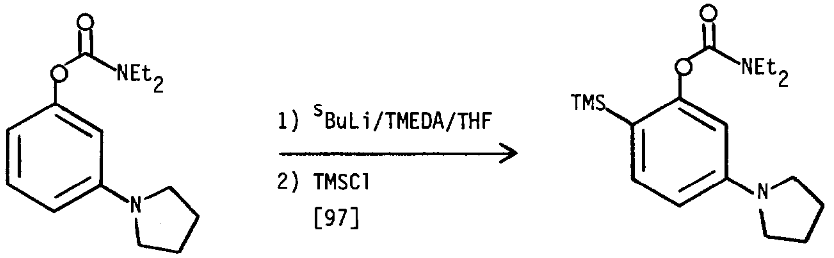
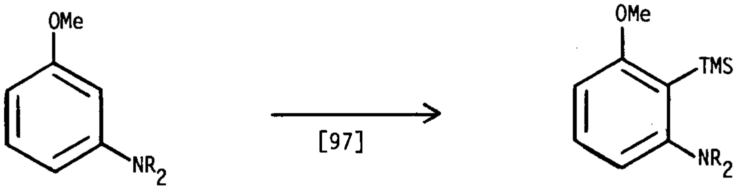
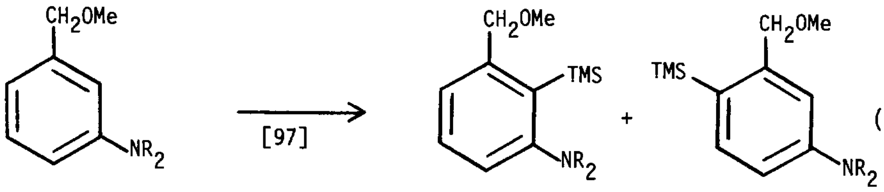


(46)



(47)

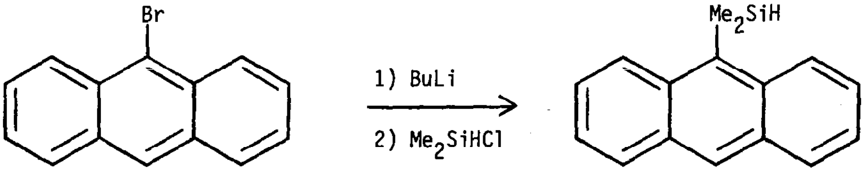
(R_2N = piperidino; morpholino)



(48)

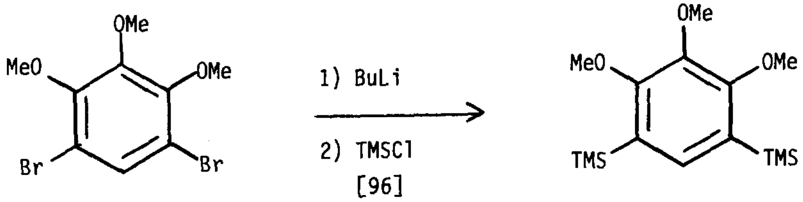
(R_2N = pyrrolidino; piperidino; morpholino)

Lithium-bromine exchange followed by silylation provides routes to arylsilanes. Examples are shown in equations 49-55 compound **42** was also employed as a fluorescent silylating agent for primary alcohols. (see Eqn. 19) The results shown in equation 50 show an alternate entry into silylated **39** as does equation 52 for silylated **36**. The reaction of 2,5-dibromothiophene provides the interesting by-product **43** with one equivalent of butyllithium (Eqn. 53) and the expected results with two equivalents (Eqn. 54). Lithium-bromine exchange provided a route to the 1,6-disilaperfluorotriptycene **44**. (Eqn. 55)

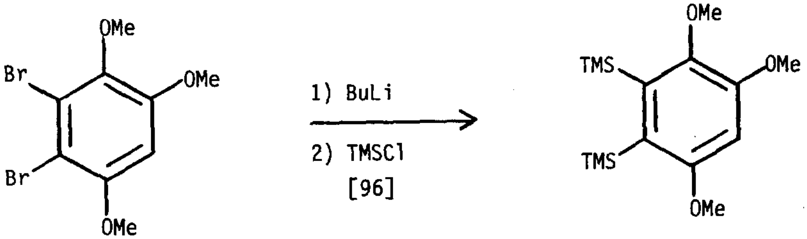


42

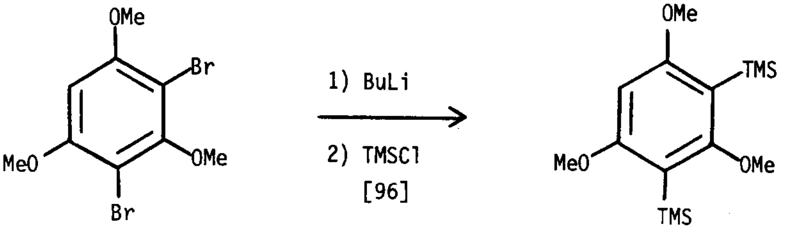
(49)



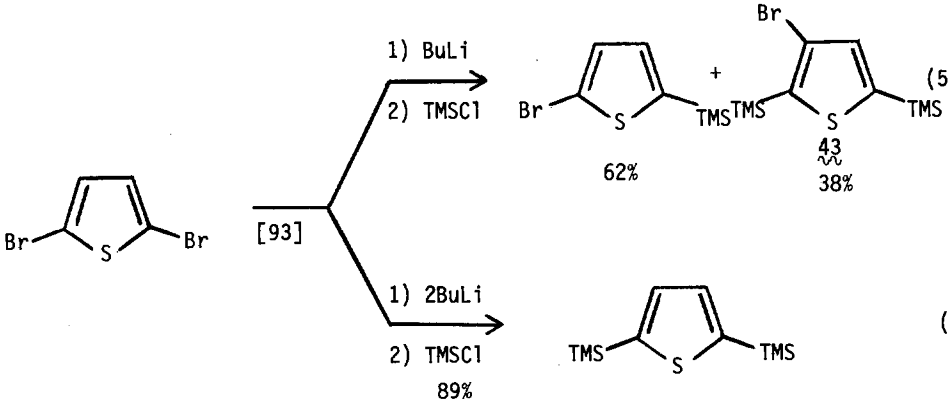
(50)



(51)

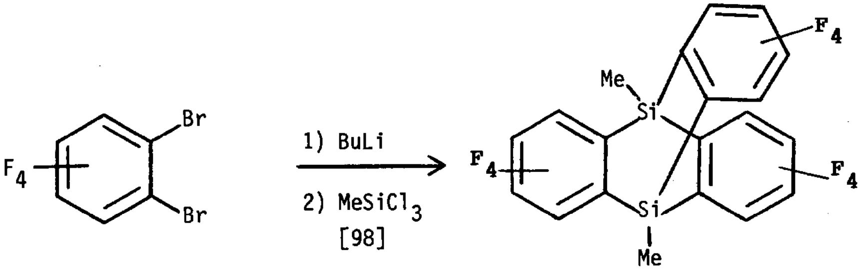


(52)



(53)

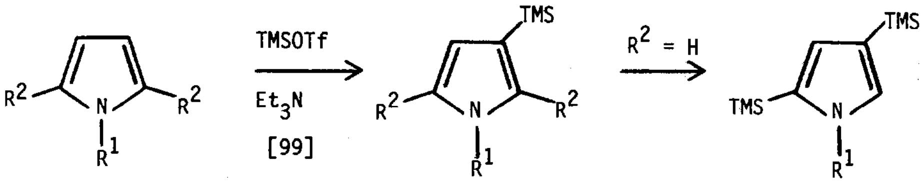
(54)



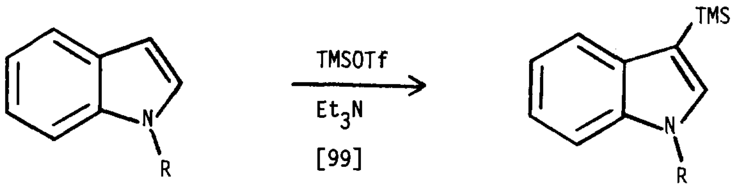
44

(55)

Other entries into arylsilanes were varied. Treatment of pyrroles with trimethylsilyltriflate provided the results shown in equation 56. Similarly treatment of N-protected indoles gave 3-trimethylsilyl indoles. (Eqn. 57)



(56)

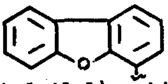


(57)

[R = Me (81%); $PhCH_2$ (69%); TMS (54%)]

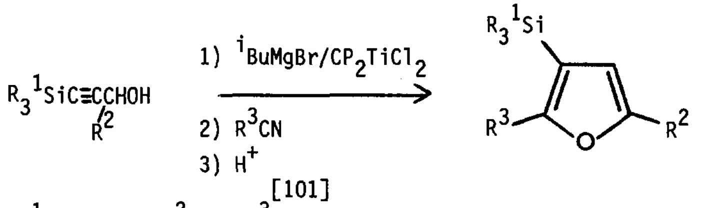
Aryl iodides and one aryl bromide were silylated under electrochemical conditions. (Eqn. 58)

$$\mathrm{ArI} + \mathrm{TMSCl} \xrightarrow[{[100]}]{+e^-} \mathrm{Ar\text{-}TMS} \qquad (58)$$

Ar = Ph (70%), p-MeC_6H_4 (53%), p-BrC_6H_4 (60%),  (89%)

3-bromopyridine gave 55% yield of 3-(trimethylsilyl)pyridine

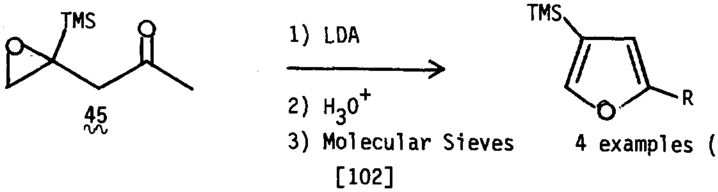
3-(Trialkylsilyl)furans were prepared from 1-silyl propargyl alcohols as shown in equation 59.



(59)

(R^1 = alkyl; R^2 and R^3 = H, alkyl, aryl, aralkyl)

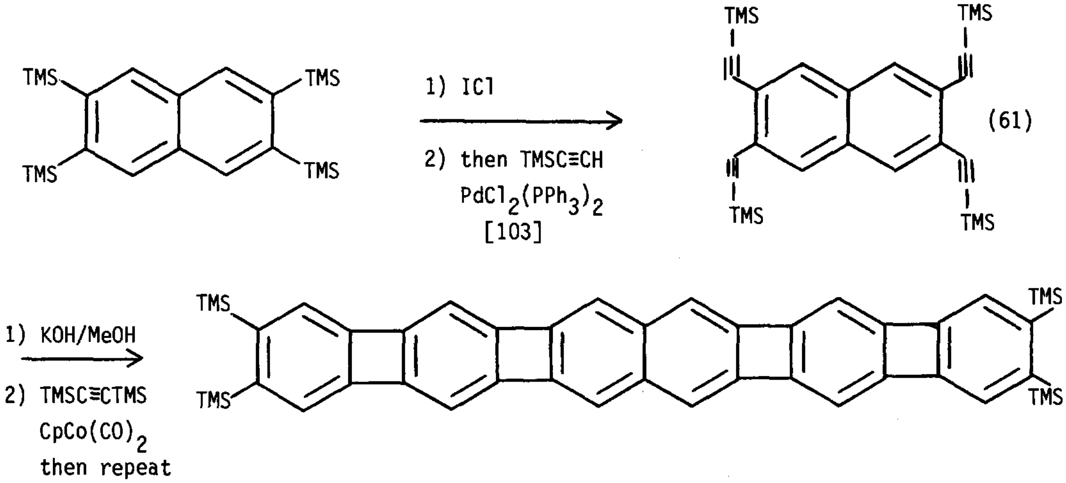
The epoxysilanes **45** can be treated sequentially with a strong base, acid and molecular sieves to provide the 2-substituted 4-(trimethylsilyl) furans in good yield. (Eqn. 60)



(60)

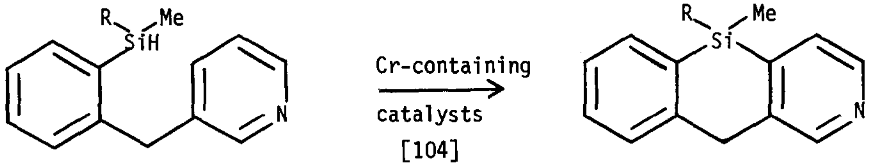
4 examples (71-82%)

The $CpCo(CO)_2$ catalyzed cyclization of acetylenes with bis(trimethylsilyl)acetylene provided the route to some (o-phenylene)naphthalenes. (Eqn. 61)



(61)

Chromium containing catalysts brought about the dehydrocyclization shown in equation 62, albeit in very low yield. Calcium atoms were reacted with benzene vapor and this product treated with chlorotrimethyl or chlorotriethylsilane to give arylsilanes and silanes. (Eqn. 63)



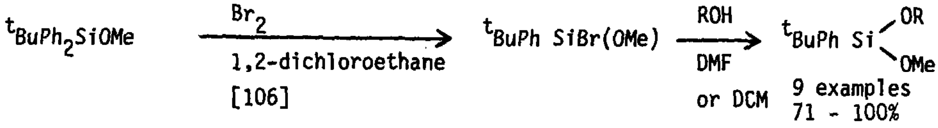
(62)

$$\mathrm{Ca} \xrightarrow[\text{benzene}]{900^\circ} \text{Condensed ca/benzene} \xrightarrow[[105]]{R_3SiCl} PhSiR_3 \quad + \quad R_3SiH \qquad (63)$$

	$PhSiR_3$	R_3SiH	
R=Me	43	57	14.2%
R=Et	40	60	8.0%

B. Reactions

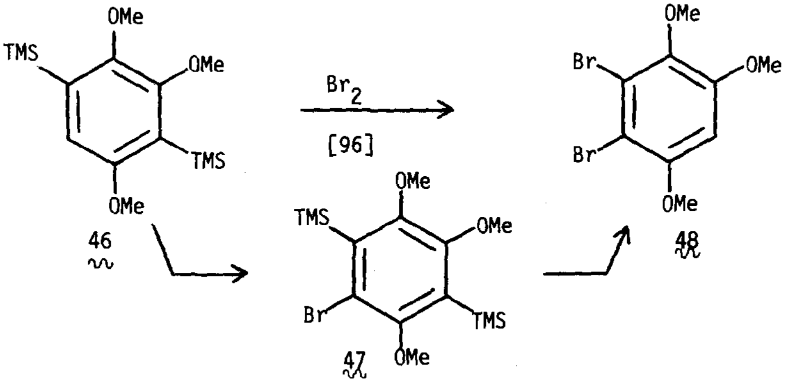
Tert-butylmethoxyphenylsilyl ethers were formed from the corresponding tert-butylmethoxyphenylbromosilane, which was formed via a bromodesilylation reaction. (Eqn. 64) These silyl ethers are extremely labile to fluoride ion for selective deprotection.



$$^{t}BuPh_2SiOMe \xrightarrow[\text{1,2-dichloroethane}\ [106]]{Br_2} {}^{t}BuPh\,SiBr(OMe) \xrightarrow[\text{DMF or DCM}]{ROH} {}^{t}BuPh\,Si(OR)(OMe)$$

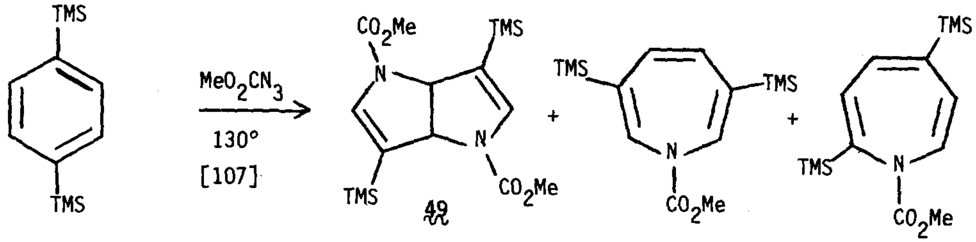
(64)

It appears that the unusual bromodesilylation of **46** proceeds via prior direct bromination to **47**, which the gives **48**. (Eqn. 65)



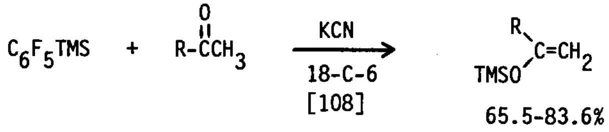
(65)

1,4-Bis(trimethylsilyl)benzene reacted with methyl azocarboxylate to give **49** as shown. (Eqn. 66)



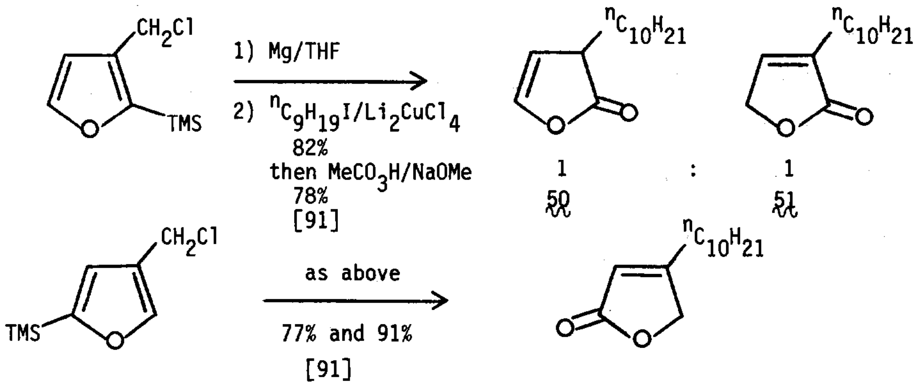
(66)

The reaction of trimethyl(pentafluorophenyl)silane with enolizable ketones in the presence of cyanide ion provides enol silyl ethers in good yield. (Eqn. 67)



(67)

The (trimethylsilyl)furans **50** and **51**, obtained in a straightforward manner from the acid formed in equations 30 and 31, respectively, were converted to the 3- and 4-alkylbutenolides. (Eqns. 68 and 69)

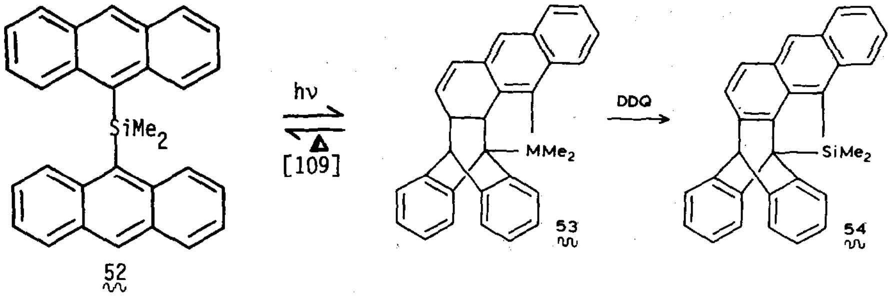


50 **51**

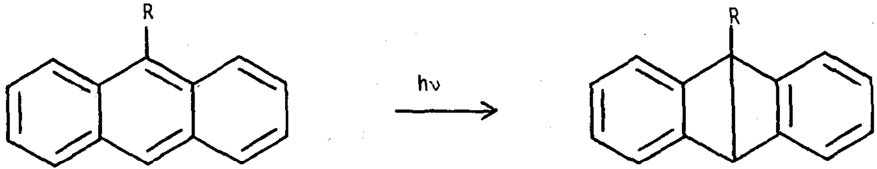
(68)

(69)

Photolysis of **52** gave the intramolecular cycloaddition product **53**, which with DDQ gave the fully aromatic **54**. Thermally **53** regenerates **52**. (Eqn. 70) Although 9-tert-butyl and 9-isopentylanthracenes photoisomerize to the Dewar isomers, the corresponding trimethylsilyl and dimethylphenylsilyl derivatives do not. (Eqn. 71)



(70)



(71)

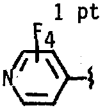
(R = TMS or PhMe$_2$Si do not isomerize)

Aryltrimethylsilanes were reacted with xenon difluoride in the presence of metal fluorides to give biaryls and protiodesilylation. (Eqn. 72)

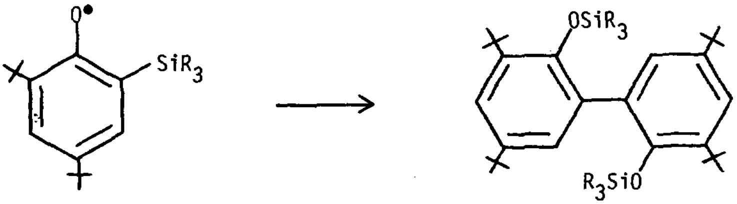
$$\mathrm{ArTMS} + \mathrm{XeF_2} \xrightarrow[\mathrm{MF/-20^\circ}]{\mathrm{CH_3CN}} \text{Ar-Ar} + \text{Ar-H} + \text{Xe} + \text{TMSF} \qquad (72)$$

60-70% [111] — Ar-Ar: 1 pt; Ar-H: 2-3 pts

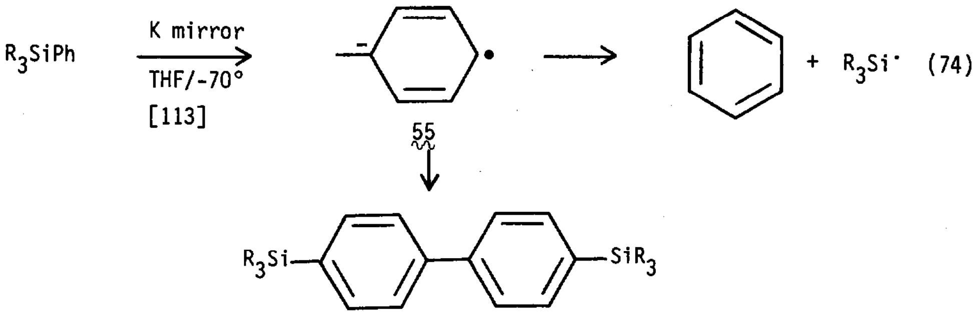
Ar = C_6H_5; C_6F_5;



Ortho silyl phenoxy radicals rearrange and couple. (Eqn. 73) Arylsilanes were converted to their anion radicals **55**, which were studied by esr. The esr data is useful in predicting the reactions. The major decomposition pathways are cleavage and coupling. (Eqn. 74)

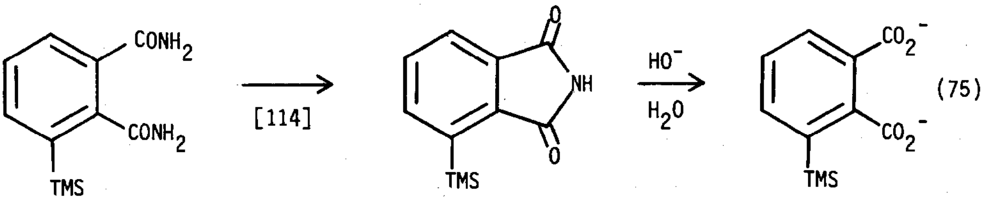


(73)



(74)

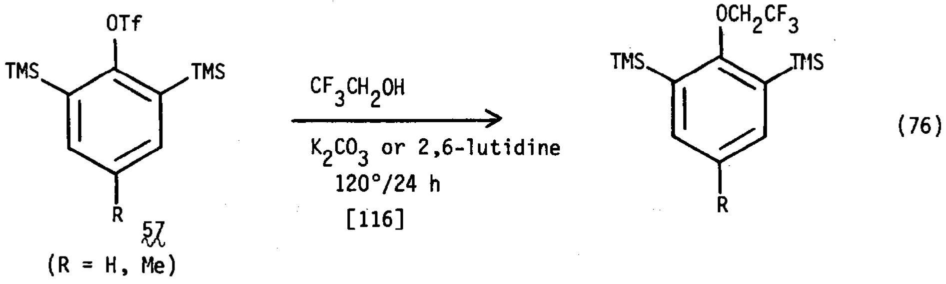
Ammonolysis and hydrolysis of the phthalimide **56** can be accomplished with desilylation. (Eqn. 75)



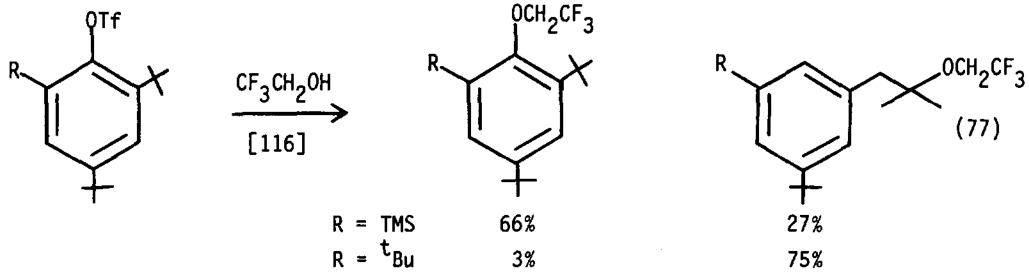
56

(75)

Consistent with theoretical predictions [115] (see next section) the silylated aryltriflate **57** was solvolyzed according to equation 76 in a first order reaction. The reaction showed (R=H) $k_1 = 1.36 \times 10^{-4}\ s^{-1}$ (lutidine at 100°C) $\Delta H^{\neq} = 26.5$ kcal/mol (80-100°C) and $\Delta S^{\neq} = -5.5$ cal deg $^{-1}$ mol $^{-1}$ at 100^0. The ortho tert-butyl substituted analogs also undergo the solvolysis, but with some rearrangement also taking place. (Eqn. 77)



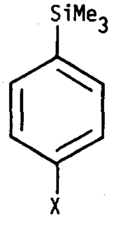
(76)



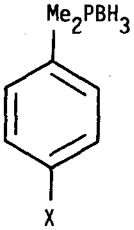
(77)

C. Other Studies

A ^{13}C NMR study of compounds **58** and **59** were carried out and, based on the chemical shift of the ipso C-X carbon, it was determined that the H_3BPMe_2 group is a better π-acceptor than the Me_3Si group [117]. The ^{29}Si NMR spectra of $Me_{2-n}Ph_nSiX_2$ (X=H, Me, Ph, F, Cl, NR_2, OR) indicate that the shifts seen as methyls are replaced by phenyls are determined by the electronegativity and donor ability of X. [118] The inductive, hyperconjugative and d-orbital effects in $PhSiMe_3$, $PhSiH_3$ and $PhSiF_3$ as compared to their carbon counterparts (calcd. and observed HOMO and LUMO levels) showed that hyperconjugation is the main effect for $PhSiMe_3$ and $PhSiH_3$, but d-orbitals are more important for $PhSiF_3$. [119]

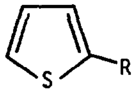


58



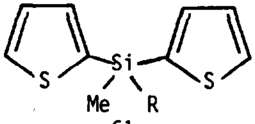
59

Electron distributions were calculated (MO LCAO CNDO/2) for compounds **60** and **61** [120] as well for **62** [121].

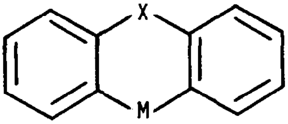


60

R=H, $\mathrm{Sihe_2H,SiMe_3}$



61

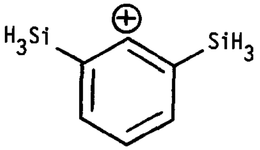


62

X = 0; NEt

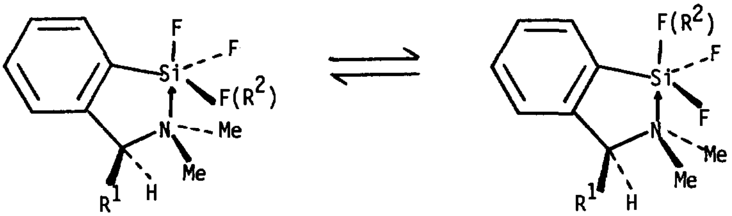
M = CH_2; $SiMe_2$; $GeCl_2$

It has been calculated that two ortho silyl groups should add enough stability (∿ 25 kcal/mol) to permit the formation of the aryl cation **63**. [115] (see Eqns. 76 and 77 for chemical verification of this prediction).



63

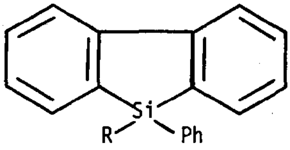
The temperature dependence ^{1}H and ^{19}F NMR data for **64** is consistent with a pseudorotation process at silicon rather than an opening and reclosing of the complex. (Eqn. 78)



(78)

64

The crystal structures of **65** (R=H, Ph) were determined. [123]



65 (R = H, Ph)

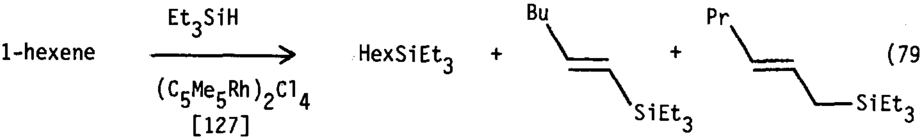
VI. HYDROSILYLATION

A. General

Kinetic studies of the hydrosilylation of 1-heptene with Me_2ArSiH and an immobilized catalyst were carried out. [124] The kinetics of the hydrosilylation of several alkenes with $PhMe_2SiH$ and $MeCl_2SiH$ with a fixed platinum catalyst were also reported. [125] Kinetic studies on the triisopropylsilane hydrosilylation of **66** showed the reaction to have an E_{act} of 40-50 kJ/mol. [126]

B. Alkenes

The rhodium catalyzed hydrosilylation of 1-hexene gives three products with the vinylsilane formed predominantly at lower temperatures and higher alkene:silane ratios. (Eqn. 79) The hydrosilylation of other alkenes are given in equations 80-90 without further comment.

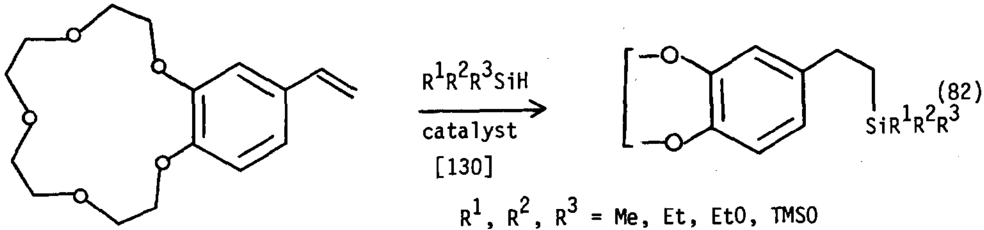


(79)

$$\text{1-Ad-CH=CH}_2 \xrightarrow[\text{[128]}]{R^1R^2_2SiH} \text{1-Ad-CH}_2\text{CH}_2\text{SiR}^2_2\text{R}^1 \qquad (80)$$

1-Ad = 1-Adamantyl

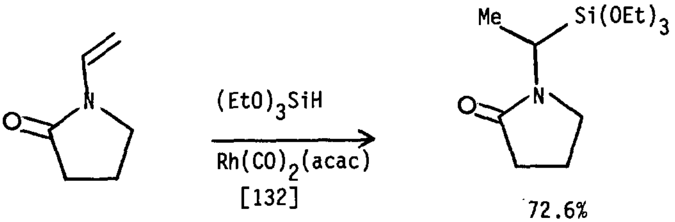
$$\text{Et}_3\text{SiCH=CH}_2 \xrightarrow[\substack{H_2PtCl_6 \\ [129]}]{Cl_3SiH} \text{Et}_3\text{SiCH}_2\text{CH}_2\text{SiCl}_3 \qquad (81)$$



(82)

R^1, R^2, R^3 = Me, Et, EtO, TMSO
studied complexing and phase transfer activity

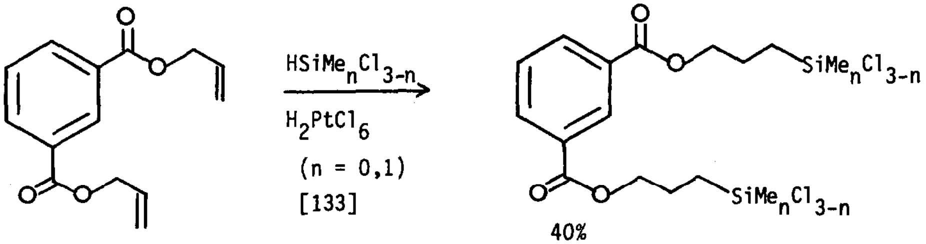
$$\text{CH}_2\text{=CHCN} + \text{Cl}_3\text{SiH} \xrightarrow[\substack{Et_4NCl \\ [131]}]{\text{electrolysis}} \text{Cl}_3\text{SiCH}_2\text{CH}_2\text{CN} \qquad (83)$$



(84)

72.6%

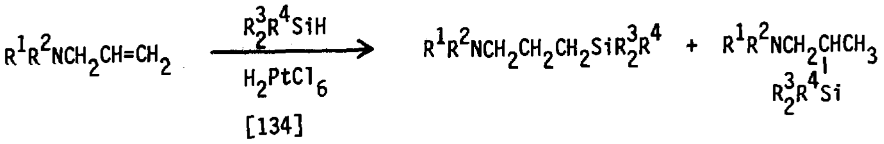
(shows neurotropic and psychotropic activity)



(85)

40%

(n = 0, 1)



$$R^1R^2NCH_2CH=CH_2 \xrightarrow[\substack{H_2PtCl_6 \\ [134]}]{R^3_2R^4SiH} R^1R^2NCH_2CH_2CH_2SiR^3_2R^4 + R^1R^2NCH_2\underset{\underset{R^3_2R^4Si}{|}}{C}HCH_3$$

(86)

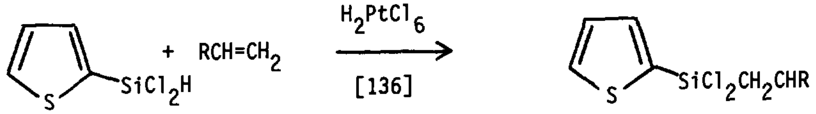
R^1 = Et, Pr, Bu, allyl, benzyl
R^2 = H, alkyl
R^3,R^4 = Et, EtO, Me, Ph

$$R^1CH_2CH_2OCH_2CH=CH_2 \xrightarrow[[135]]{R^2MeSiH_2} R^1CH_2CH_2OCH_2CH_2CH_2SiHMeR^2$$

(87)

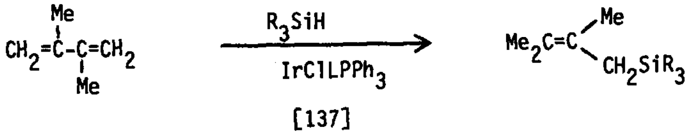
8 - 50 %

R^1 = glycidyloxy, MeO_2C
R^2 = Me_2CHCH_2, $Ph\underset{\underset{Me}{|}}{C}HCH_2$, $Ph(CH_2)_n$, $Me(CH_2)_n$, (n = 0-3)



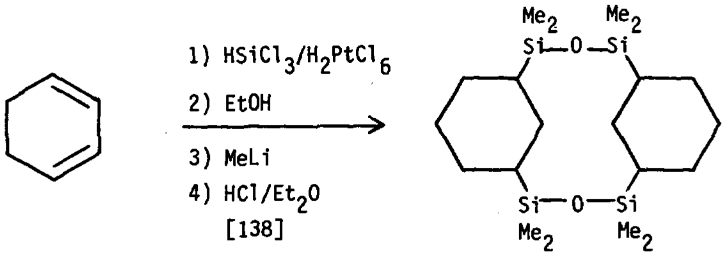
(88)

(R = Bu; C_5H_{11}; C_8H_{17}; CN; CH_2CN; CH_2Cl; CH_2OPh)



(89)

R = Et, EtO; L = cyclooctene



(90)

C. Alkynes

The hydrosilylations involving alkynes are shown in equations 91-99 and are presented without further comment.

$$\mathrm{PrC{\equiv}CH} \xrightarrow[\mathrm{IrClLPPh_3}\ [137]]{\mathrm{Et_3SiH}} \mathrm{PrCH{=}CHSiEt_3} \tag{91}$$

62 - 100%

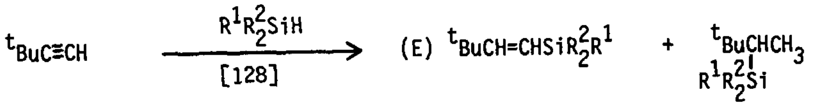
70 - 83% Z isomer

L = cyclooctene

$$\mathrm{1\text{-}Ad\text{-}C{\equiv}CH} \xrightarrow[[128]]{\mathrm{R^1R^2_2SiH}} (E)\ \mathrm{1\text{-}Ad\text{-}CH{=}CHSiR^2_2R^1} \tag{92}$$

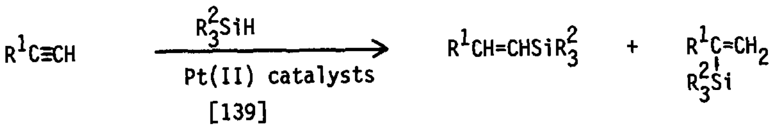
R^1 = 2-thienyl, Cl, Ph; R^2 = Me

R^1,R^2 = Et

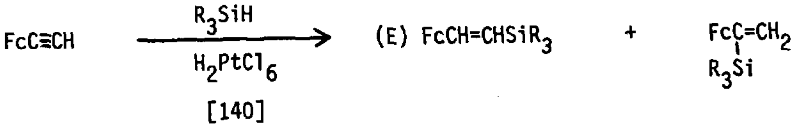


$$\mathrm{{}^tBuC{\equiv}CH} \xrightarrow[[128]]{\mathrm{R^1R^2_2SiH}} (E)\ \mathrm{{}^tBuCH{=}CHSiR^2_2R^1} + \mathrm{{}^tBuCH(SiR^2_2R^1)CH_3} \tag{93}$$

75 - 91% 3 - 5%



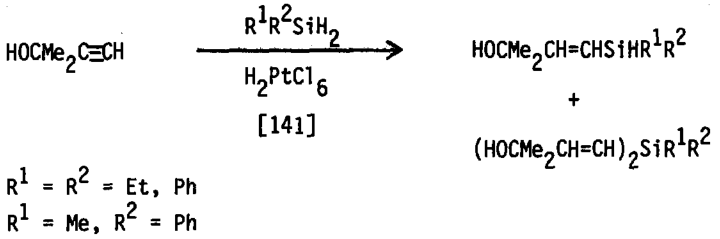
$$\mathrm{R^1C{\equiv}CH} \xrightarrow[\mathrm{Pt(II)\ catalysts}\ [139]]{\mathrm{R^2_3SiH}} \mathrm{R^1CH{=}CHSiR^2_3} + \mathrm{R^1C(SiR^2_3){=}CH_2} \tag{94}$$



$$\mathrm{FcC{\equiv}CH} \xrightarrow[\mathrm{H_2PtCl_6}\ [140]]{\mathrm{R_3SiH}} (E)\ \mathrm{FcCH{=}CHSiR_3} + \mathrm{FcC(SiR_3){=}CH_2} \tag{95}$$

Fc = ferrocenyl

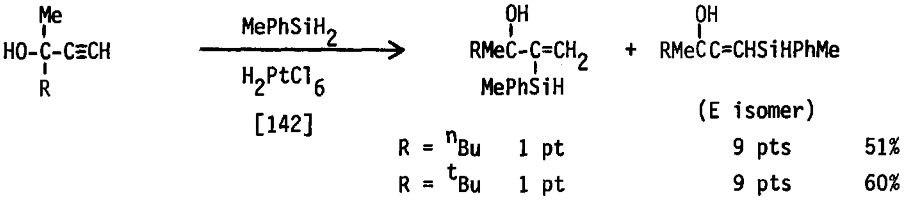
R = Ph	100%	0%
R = Et	80%	20%



$$\mathrm{HOCMe_2C{\equiv}CH} \xrightarrow[\mathrm{H_2PtCl_6}\ [141]]{\mathrm{R^1R^2SiH_2}} \mathrm{HOCMe_2CH{=}CHSiHR^1R^2} + \mathrm{(HOCMe_2CH{=}CH)_2SiR^1R^2} \qquad (96)$$

$R^1 = R^2 = \mathrm{Et, Ph}$

$R^1 = \mathrm{Me}, R^2 = \mathrm{Ph}$

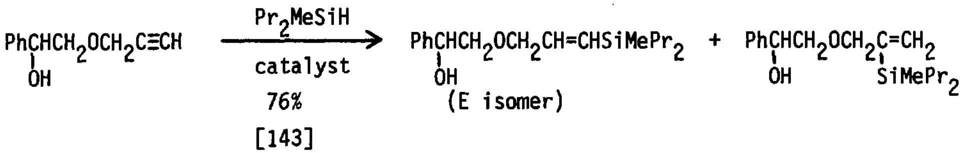


$$\mathrm{HO{-}\overset{Me}{\underset{R}{C}}{-}C{\equiv}CH} \xrightarrow[\mathrm{H_2PtCl_6}\ [142]]{\mathrm{MePhSiH_2}} \mathrm{RMe\overset{OH}{C}{-}\underset{MePhSiH}{C}{=}CH_2} + \mathrm{RMe\overset{OH}{C}C{=}CHSiHPhMe} \qquad (97)$$

(E isomer)

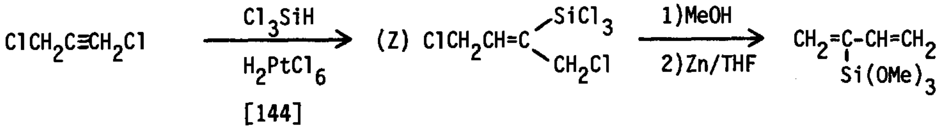
R = ^{n}Bu 1 pt 9 pts 51%

R = ^{t}Bu 1 pt 9 pts 60%



$$\mathrm{Ph\underset{OH}{C}HCH_2OCH_2C{\equiv}CH} \xrightarrow[\text{catalyst}\ 76\%\ [143]]{\mathrm{Pr_2MeSiH}} \mathrm{Ph\underset{OH}{C}HCH_2OCH_2CH{=}CHSiMePr_2} + \mathrm{Ph\underset{OH}{C}HCH_2OCH_2\underset{SiMePr_2}{C}{=}CH_2} \qquad (98)$$

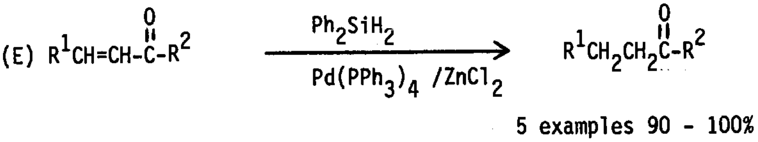
(E isomer)



$$\mathrm{ClCH_2C{\equiv}CH_2Cl} \xrightarrow[\mathrm{H_2PtCl_6}\ [144]]{\mathrm{Cl_3SiH}} \mathrm{(Z)\ ClCH_2CH{=}C}\begin{smallmatrix}\mathrm{SiCl_3}\\ \mathrm{CH_2Cl}\end{smallmatrix} \xrightarrow[\mathrm{2)Zn/THF}]{\mathrm{1)MeOH}} \mathrm{CH_2{=}\underset{Si(OMe)_3}{C}{-}CH{=}CH_2} \qquad (99)$$

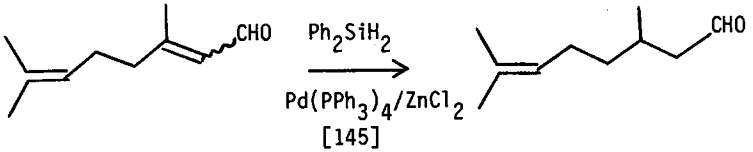
D. Other

The reaction of diphenylsilane with enones and α,β-unsaturated aldehydes in the presence of zinc chloride and palladium (O) gives net reduction of the C=C. (Eqns. 100 and 101) Methyl cinnamate and cinnamonitrile failed to react. The enantioselective reduction of acetophenone with catalysts, optically active diphosphine ligands and $\mathrm{Ph_2SiH_2}$ or 1-$\mathrm{NpPhSiH_2}$ was carried out with 10-40 percent ee. (Eqn. 102) The hydrosilylation of dioxolanes and dioxanes **64** (n=0,1) gives the products shown. (Eqn. 103)

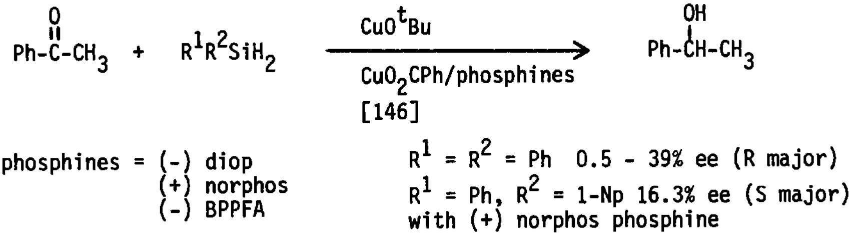


$$(E)\ R^1CH{=}CH{-}\overset{O}{\overset{\|}{C}}{-}R^2 \xrightarrow[Pd(PPh_3)_4\ /ZnCl_2]{Ph_2SiH_2} R^1CH_2CH_2\overset{O}{\overset{\|}{C}}{-}R^2 \qquad (100)$$

5 examples 90 - 100%



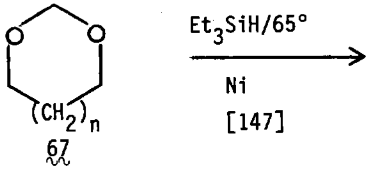
(101)



$$Ph{-}\overset{O}{\overset{\|}{C}}{-}CH_3 + R^1R^2SiH_2 \xrightarrow[CuO_2CPh/phosphines\ [146]]{CuO^tBu} Ph{-}\overset{OH}{\overset{|}{C}H}{-}CH_3 \qquad (102)$$

phosphines = (-) diop
(+) norphos
(-) BPPFA

$R^1 = R^2 = Ph$ 0.5 - 39% ee (R major)
$R^1 = Ph$, R^2 = 1-Np 16.3% ee (S major)
with (+) norphos phosphine



67

$$\longrightarrow Et_3SiOEt + \underset{13\text{-}14\%}{Et_3SiO(CH_2)_{n+2}OSiEt_3} \qquad (103)$$

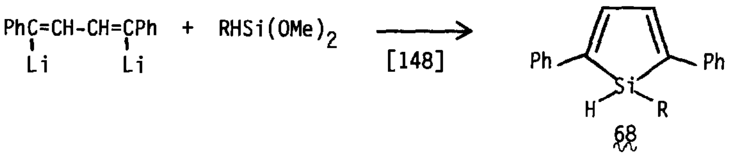
$$+ \underset{3\text{-}5\%}{MeO(CH_2)_{n+2}OSiEt_3} + \underset{12\text{-}14\%}{EtOCH_2O(CH_2)_{n+2}OSiEt_3}$$

VII. VINYLSILANES

A. Preparation

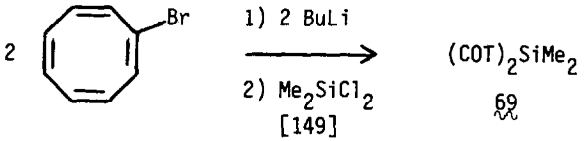
A variety of methods appeared for the preparation of vinylsilanes, due in large part to their synthetic utility. These are organized as closely as possible into the following general approaches: the reaction of vinylmetallic reagents with halo (or related) silanes, additions of organometallic reagents to ethynylsilanes and the products derived from these derivatives, addition of silylmetallic reagents to acetylenes, thermal reactions and miscellaneous approaches.

Silacyclopentadienes, **68**, were prepared from the dimethoxysilanes, which were better than the dichlorosilanes, as shown. (Eqn. 104)



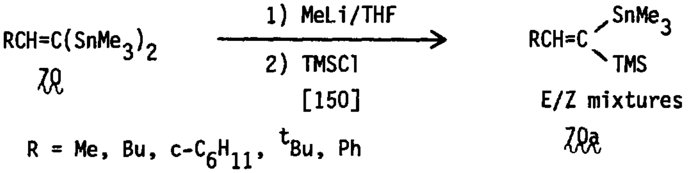
(104)

Bis-(cyclooctatetraenyl)dimethylsilane **69** was prepared from the lithium reagent. The product **69** was converted to its anion radical, the esr spectrum of which showed the Me_2Si group not to be strongly electron-withdrawing. (Eqn. 105)



(105)

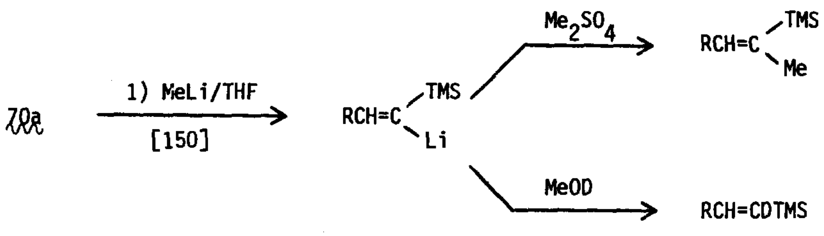
The α,α-distannyl alkenes **70** could be used to prepare vinylsilanes wherein both trimethyltin moieties can sequentially be converted to the vinyllithium reagents. (Eqns. 106 and 107)



$$RCH{=}C(SnMe_3)_2 \xrightarrow[\text{2) TMSCl}\ [150]]{\text{1) MeLi/THF}} RCH{=}C\begin{smallmatrix}SnMe_3\\TMS\end{smallmatrix} \qquad (106)$$

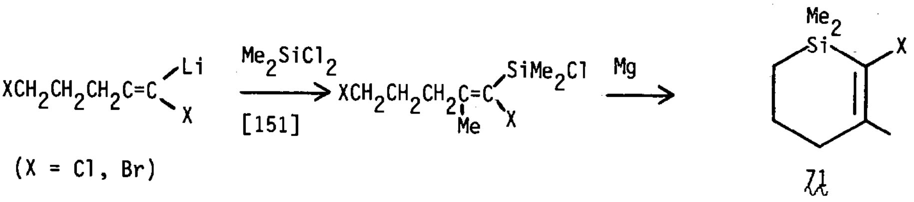
70, 70a: E/Z mixtures

R = Me, Bu, c-C_6H_{11}, ${}^tBu$, Ph

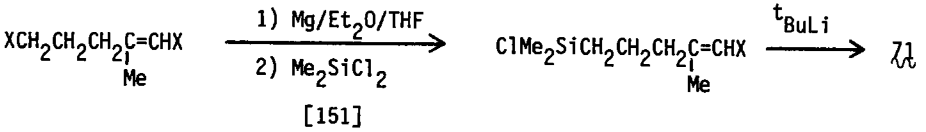


(107)

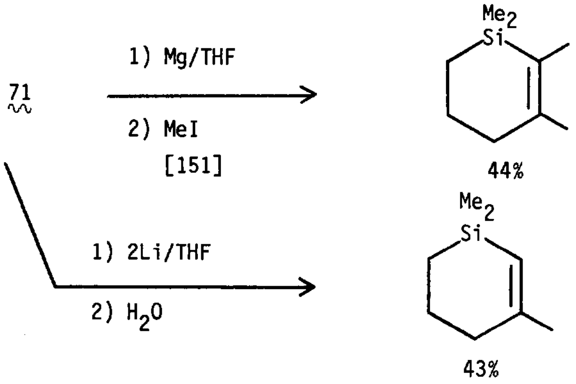
Silacyclohex-2-enes were prepared by cyclization of α-halo vinylsilanes as shown. (Eqn. 108) The reverse mode also works. (Eqn. 109) The cyclic system 71 could be converted to dehalo derivatives. (Eqns. 110 and 111)



(108)



$$XCH_2CH_2CH_2\underset{Me}{C}{=}CHX \xrightarrow[\text{2) } Me_2SiCl_2 \ [151]]{\text{1) } Mg/Et_2O/THF} ClMe_2SiCH_2CH_2CH_2\underset{Me}{C}{=}CHX \xrightarrow{{}^tBuLi} 71 \qquad (109)$$



(110)

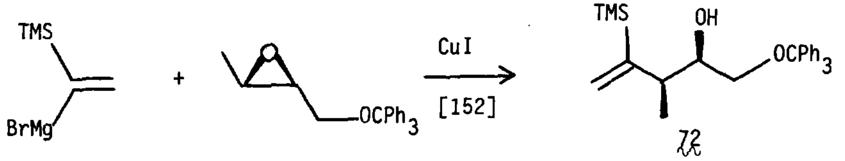
(111)

Electrolysis of a vinyl iodide in the presence of chlorotrimethylsilane gives the vinylsilane, but stereochemistry is lost in the process. (Eqn. 112) (see Eqn. 58 for a similar reaction)

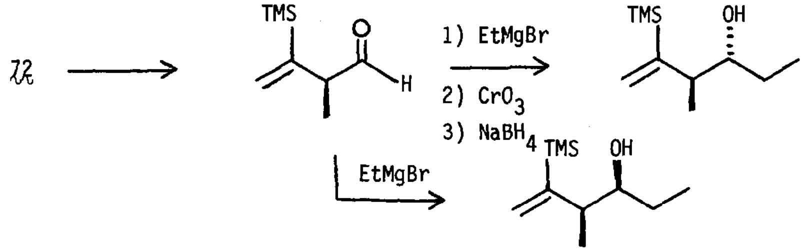
$$^{n}C_6H_{11}CH{=}CHTMS \xrightarrow[\substack{TMSCl\\ [100]}]{+e^-} {}^{n}C_6H_{11}CH{=}CHTMS \qquad (112)$$

$$47\% \text{ yield } E/Z = 57/43$$

α-Trimethylsilylvinylmagnesium bromide was condensed with epoxides in the presence of cuprous iodide. This was used to prepare all four stereo isomers of α-methylhomoallyl alcohols, two of which are shown here. (Eqns. 113-115)



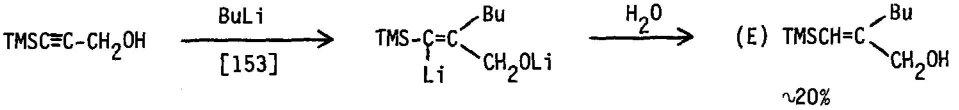
(113)



(114)

(115)

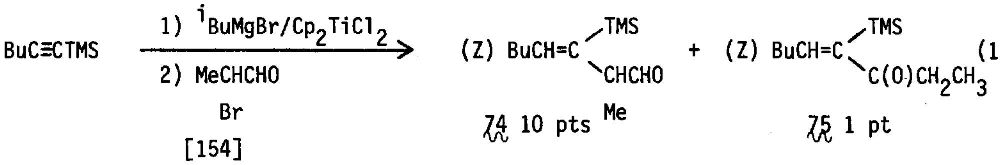
Butyllithium can be added to ethynylsilane 73 and the resulting vinyllithium reagent protonated. The reaction gives many side reactions, however. (Eqn. 116)



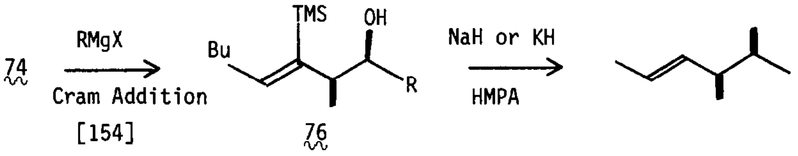
$$\mathrm{TMSC{\equiv}C\text{-}CH_2OH} \xrightarrow[\text{[153]}]{\text{BuLi}} \mathrm{TMS\text{-}\underset{Li}{C}{=}C\begin{matrix}\diagup Bu\\ \diagdown CH_2OLi\end{matrix}} \xrightarrow{\mathrm{H_2O}} \text{(E) } \mathrm{TMSCH{=}C\begin{matrix}\diagup Bu\\ \diagdown CH_2OH\end{matrix}} \quad (116)$$

∿20%

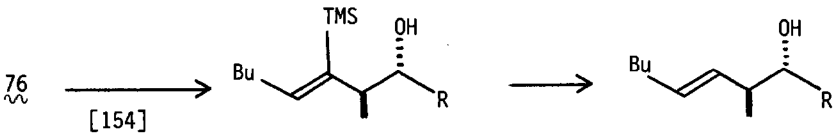
The hydridomagnesiation of ethynylsilanes continues to provide useful reagents for the preparation of vinylsilanes. In this latest report these were used to arrive at the same general homoallylic alcohols as shown in equations 114 and 115. (Eqns. 117-120)



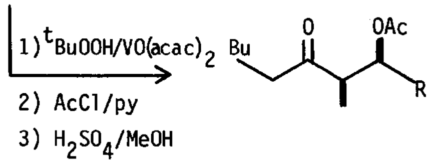
$$\mathrm{BuC{\equiv}CTMS}\ \xrightarrow[\substack{\text{2) MeCHCHO}\\ \text{Br}\\ [154]}]{\text{1) }^{i}\text{BuMgBr/Cp}_2\text{TiCl}_2}\ \underset{\underset{\sim}{74}\ \text{10 pts}}{\text{(Z) BuCH=C}\begin{matrix}\text{TMS}\\ \text{CHCHO}\\ \quad\text{Me}\end{matrix}}\ +\ \underset{\underset{\sim}{75}\ \text{1 pt}}{\text{(Z) BuCH=C}\begin{matrix}\text{TMS}\\ \text{C(O)CH}_2\text{CH}_3\end{matrix}}\qquad(117)$$



(118)

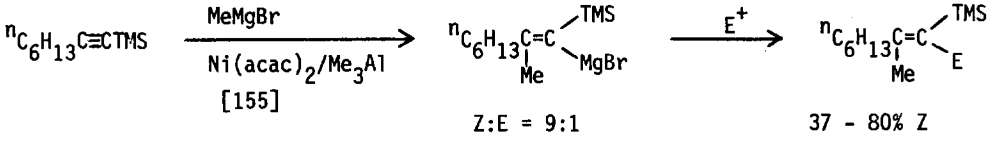


(119)



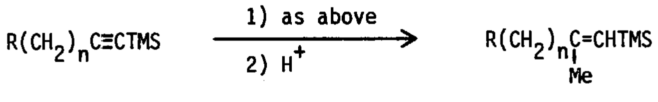
(120)

The addition of MeMgBr to ethynylsilanes provides α-trimethylsilylvinylmagnesium bromides which can be reacted with electrophiles. (Eqns. 121 and 122) The method was also applied to the synthesis of farnesol.



$$^{n}\mathrm{C_6H_{13}C{\equiv}CTMS}\ \xrightarrow[\substack{\text{Ni(acac)}_2\text{/Me}_3\text{Al}\\ [155]}]{\text{MeMgBr}}\ \underset{\text{Z:E = 9:1}}{^{n}\mathrm{C_6H_{13}}\underset{\text{Me}}{\mathrm{C}}\mathrm{=C}\begin{matrix}\text{TMS}\\ \text{MgBr}\end{matrix}}\ \xrightarrow{E^{+}}\ \underset{\text{37 - 80\% Z}}{^{n}\mathrm{C_6H_{13}}\underset{\text{Me}}{\mathrm{C}}\mathrm{=C}\begin{matrix}\text{TMS}\\ \text{E}\end{matrix}}\qquad(121)$$

$(E = H, CH_2OH, \underset{\text{Me}}{CHOH}, I, CH{=}CH_2, CH_2{=}CHCH_2)$

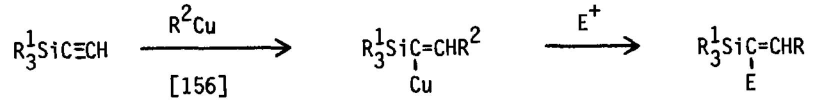


$$\mathrm{R(CH_2)_nC{\equiv}CTMS}\ \xrightarrow[\text{2) H}^{+}]{\text{1) as above}}\ \mathrm{R(CH_2)_n}\underset{\text{Me}}{\mathrm{C}}\mathrm{=CHTMS}\qquad(122)$$

(E) isomer

$R = NEt_2, \underset{\text{Me}}{OCHOEt}; n = 2,3$

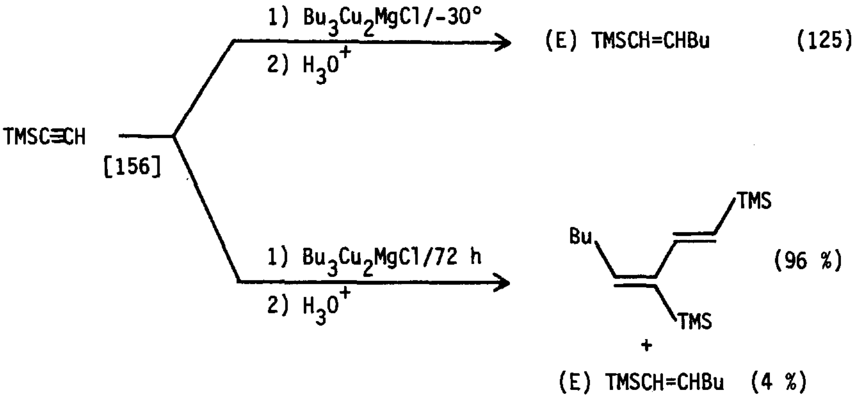
Organocopper (I) species can be added to ethynylsilanes and the α-silylvinyl copper (I) species reacted with electrophiles to produced substituted vinylsilanes. (Eqn. 123) Dialkylcuprates and higher order cuprates also add. (Eqns. 124-126)



$$R^1_3SiC\equiv CH \xrightarrow[[156]]{R^2Cu} R^1_3Si\underset{Cu}{C}{=}CHR^2 \xrightarrow{E^+} R^1_3Si\underset{E}{C}{=}CHR \qquad (123)$$

R^1 = Ph; R^2 = Et, iPr, tBu, c-hexyl (R^2 = Me)
R^1 = Me; R^2 = iPr, tBu, c-hexyl (only branched systems); E = H, Cl, Br, I, CN, Me_3Sn, Me, allyl

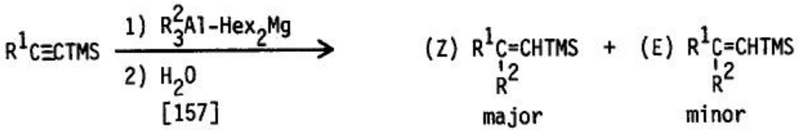
$$R^1_3SiC\equiv CH \xrightarrow[2)\ H_3O^+ \quad [156]]{1)\ R^2_2CuMgCl} (E)\ R^1_3SiCH{=}CHR^2 \qquad (124)$$



(125)

(126)

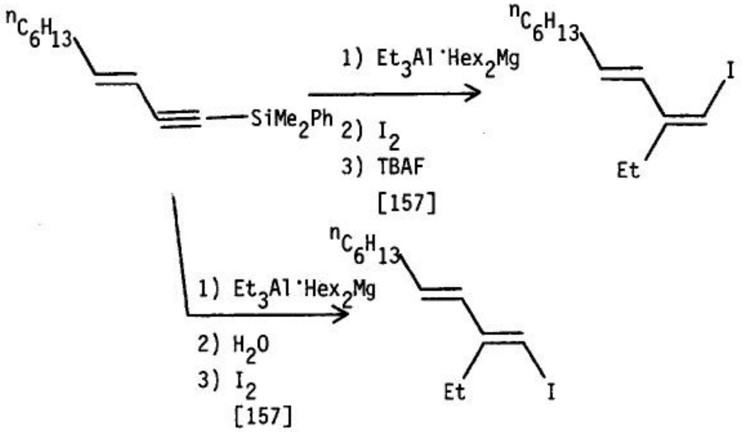
The carboalumination of ethynylsilanes is possible in the presence of di-n-hexylmagnesium. The newly formed vinyl-aluminum bond can be protonated or iodinated (Eqns. 127-130) or the vinyl-aluminum bond can be protonated and the resulting vinylsilane iodinated. (Eqn. 129)



$$R^1C{\equiv}CTMS \xrightarrow[\text{2) } H_2O \;\; [157]]{\text{1) } R^2_3Al\text{-}Hex_2Mg} (Z)\ R^1\underset{R^2}{C}{=}CHTMS \;(\text{major}) + (E)\ R^1\underset{R^2}{C}{=}CHTMS \;(\text{minor}) \qquad (127)$$

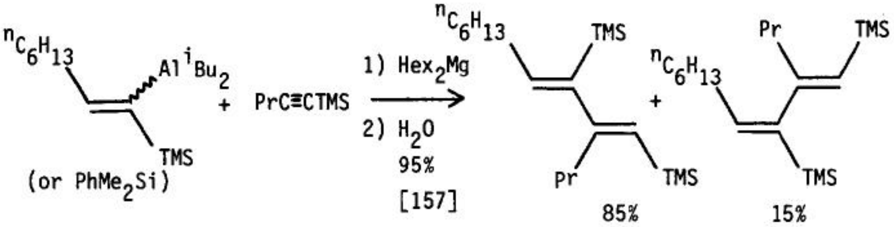
$R^1 = {}^nC_6H_{13}$, Ph, 1-cyclohexenyl, $PhMe_2SiC{\equiv}C$-

R^2 = Et, Pr



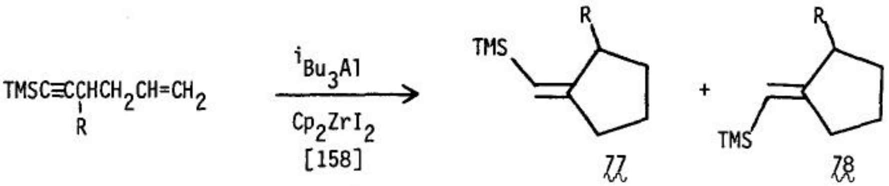
(128)

(129)



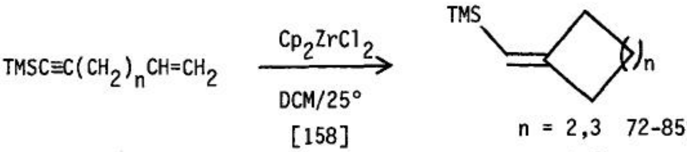
(130)

The carbometalation of certain unsaturated ethynylsilanes can be carried out with concomitant cyclization to vinylsilanes, a process which provides functionalized vinylsilanes in a straightforward manner. (Eqns. 131-135) These can be of further use. (Eqns. 136 and 137) A further functionalized system is shown in equation 138.



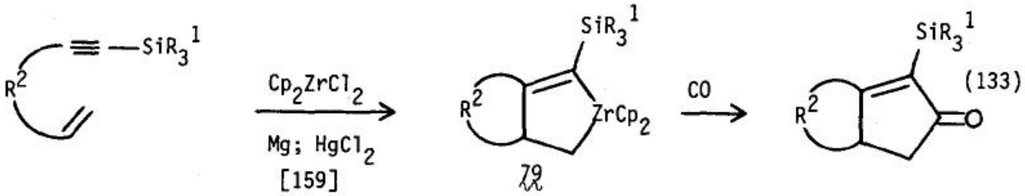
(131)

R = Me 1:1 mixture of 77 and 78
with ^{i}Bu$_3$Al-^{i}Bu$_2$AlOMe 4:1 mixture
with R = OH; ^{i}Bu$_3$Al-Cp$_2$ZrCl$_2$ 9:1 mixture
Thermal equilibrium gives 3:97 mixture.



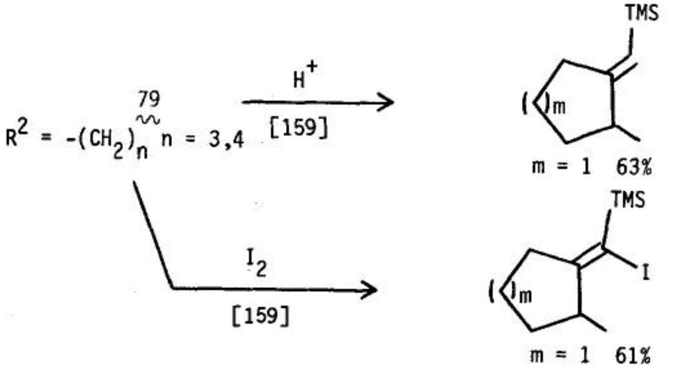
(132)

n = 2,3 72-85%
n = 1,4 no cyclization



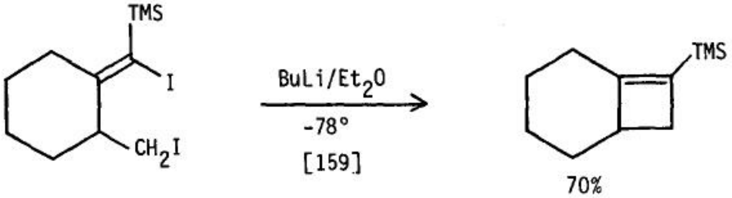
(133)

[R^2 = C$_3$ or C$_4$ chain (55-65%); $\mathrm{Me_2C}{<}^{\mathrm{CH_2}}_{\mathrm{CH_2}}$ (50%); Me$_2$CCH$_2$CH$_2$ (62%); R^1 = alkyl]

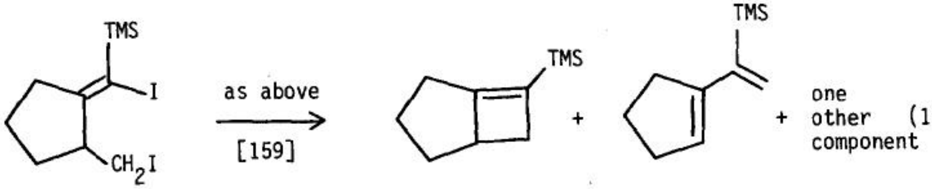


(134)

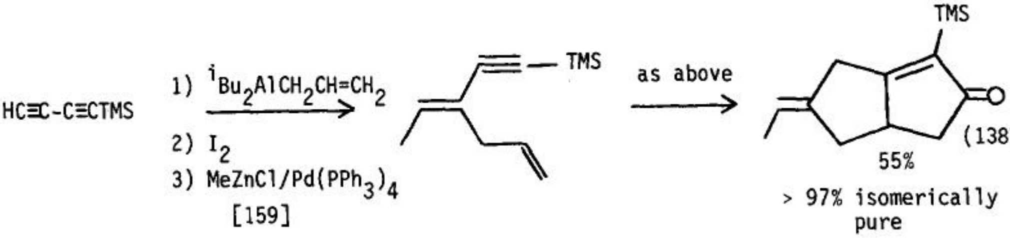
(135)



(136)



(137)

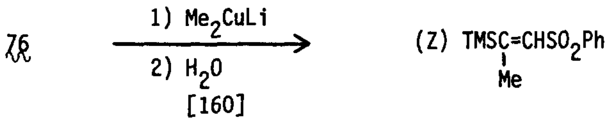


(138)

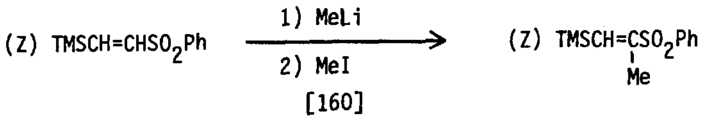
Trimethylsilylated ethynylsulfones can be hydrometalated (Eqns. 139 and 140) or carbometalated (Eqn. 141). The analogous vinylic systems undergo lithiation with methyllithium (Eqns. 142 and 143) or carbomagnesiation (Eqn. 145). One obtains overall reduction with Ni(0) followed by protonolysis (Eqn. 144)

$$\mathrm{TMSC{\equiv}CSO_2Ph} \xrightarrow[{[160]}]{} \xrightarrow[\text{2) } D_2O]{\text{1) DIBAH}} (E)\ \mathrm{TMSCD{=}CDSO_2Ph} \qquad (139)$$

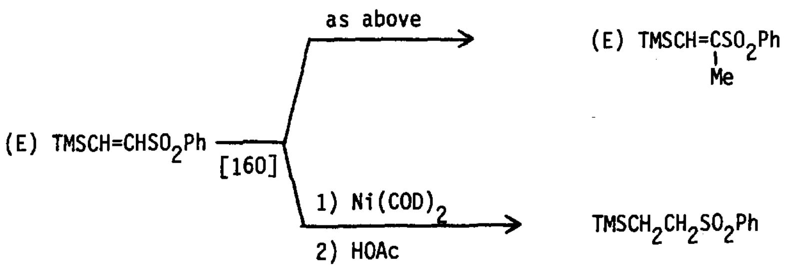
$$\xrightarrow[\text{2) HOAc}]{\text{1) } Ni(COD)_2} (Z)\ \mathrm{TMSCH{=}CHSO_2Ph} \qquad (140)$$



$$\mathbf{76} \xrightarrow[\text{2) } H_2O\ {[160]}]{\text{1) } Me_2CuLi} (Z)\ TMS\underset{Me}{C}{=}CHSO_2Ph \qquad (141)$$

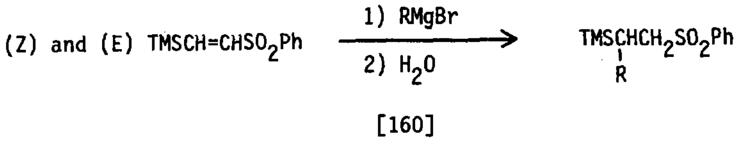


$$(Z)\ TMSCH{=}CHSO_2Ph \xrightarrow[\text{2) } MeI\ {[160]}]{\text{1) } MeLi} (Z)\ TMSCH{=}\underset{Me}{C}SO_2Ph \qquad (142)$$



$$(E)\ TMSCH{=}CHSO_2Ph \xrightarrow[{[160]}]{\text{as above}} (E)\ TMSCH{=}\underset{Me}{C}SO_2Ph \qquad (143)$$

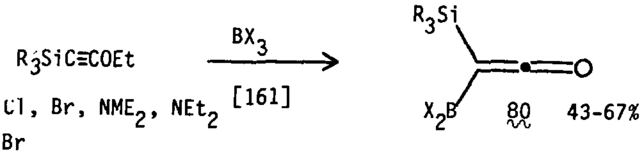
$$(E)\ TMSCH{=}CHSO_2Ph \xrightarrow[\text{2) } HOAc]{\text{1) } Ni(COD)_2} TMSCH_2CH_2SO_2Ph \qquad (144)$$



$$(Z)\text{ and }(E)\ TMSCH{=}CHSO_2Ph \xrightarrow[\text{2) } H_2O\ {[160]}]{\text{1) } RMgBr} TMS\underset{R}{C}HCH_2SO_2Ph \qquad (145)$$

R = Ph, allyl

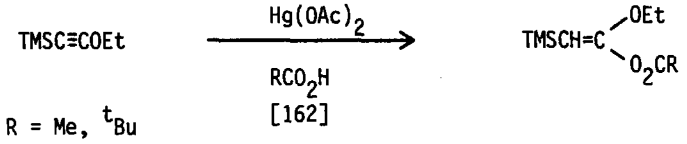
Trimethylsilylethoxy acetylene was reacted with BX_3 (X-Cl, Br, NR_2) to give the dimetallated ketenes 80. (Eqn. 146) The same acetylene can be carboxymercurated with concomitant loss of the mercury group. (Eqn. 147)



$$R_3SiC{\equiv}COEt \xrightarrow[{[161]}]{BX_3} \qquad (146)$$

80 43-67%

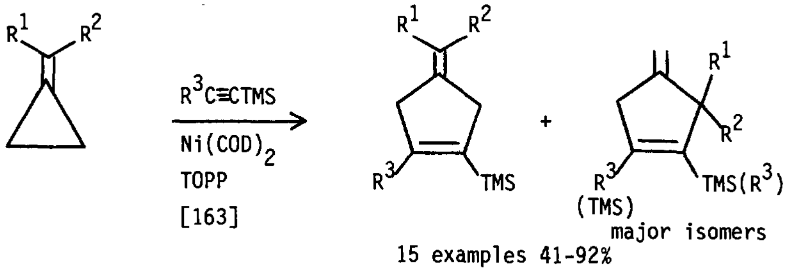
R = Me; X = Cl, Br, NME_2, NEt_2
R = Et; X = Br



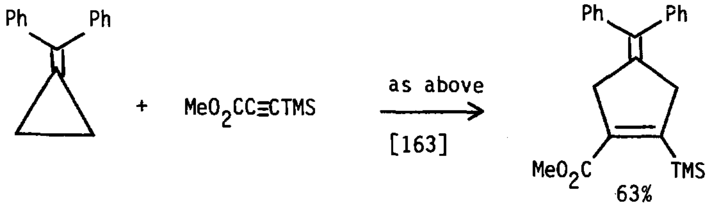
$$\mathrm{TMSC{\equiv}COEt} \xrightarrow[\mathrm{RCO_2H}\ [162]]{\mathrm{Hg(OAc)_2}} \mathrm{TMSCH{=}C(OEt)(O_2CR)} \qquad (147)$$

$\mathrm{R = Me,\ {}^tBu}$

In a somewhat related reaction ethynylsilanes were cycloadded to methylenecyclopropanes under catalysis by Ni(0). (Eqn. 148) The ring substituted products predominate with the exception of the example shown in equation 149.

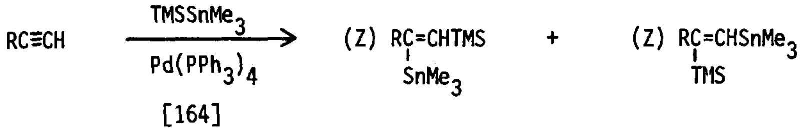


(148)



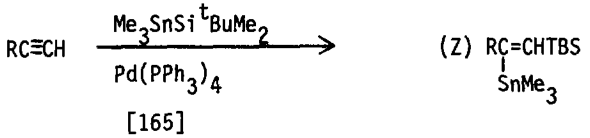
(149)

Silylmetallic reagents will add to acetylenes. The metal attached to silicon can be tin (Eqns. 150 and 151), copper (Eqn. 152), manganese (Eqns. 153-156) or lithium (Eqn. 157). It is fitting to mention at this point that the silicon-tin bond will add to allenes (Eqn. 158) or cyclohexenones (Eqn. 159) and that the bis(trimethylsilyl)cuprate was added to an α,β-unsaturated lactone (Eqn. 160).



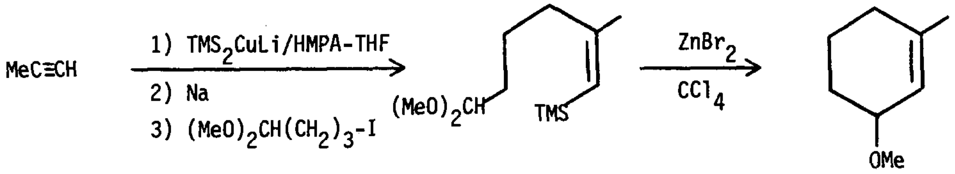
$$RC\equiv CH \xrightarrow[\text{Pd(PPh}_3)_4\ [164]]{\text{TMSSnMe}_3} (Z)\ \underset{\text{SnMe}_3}{RC}=CHTMS + (Z)\ \underset{\text{TMS}}{RC}=CHSnMe_3 \qquad (150)$$

R = Bu, Ph, Me_2NCH_2, $MeOCH_2$, $HOCH_2$, $\underset{Me}{HOCH}$, $HOCMe_2$, $HOCH_2CH_2$



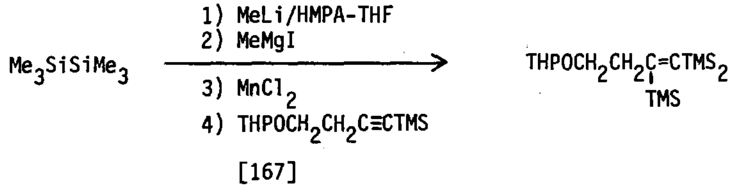
$$RC\equiv CH \xrightarrow[\text{Pd(PPh}_3)_4\ [165]]{\text{Me}_3\text{SnSi}^t\text{BuMe}_2} (Z)\ \underset{\text{SnMe}_3}{RC}=CHTBS \qquad (151)$$

R = Ph (93%), Bu (74%), iPr (67%), tBu (10%), $NC(CH_2)_3$ (90%)

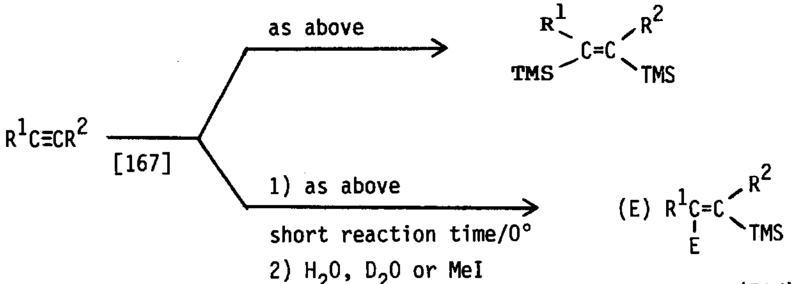


(152)

$$(MeO)_2CH(CH_2)_3C\equiv CH \xrightarrow[\substack{\text{2) MeI (78 \%) then}\\ \text{ZnBr}_2/\text{CCl}_4\ \text{(55 \%)}\\ [166]}]{\text{1) TMS}_2\text{CuLi/HMPA-THF}}$$



$$Me_3SiSiMe_3 \xrightarrow[\substack{\text{3) MnCl}_2\\ \text{4) THPOCH}_2\text{CH}_2\text{C}\equiv\text{CTMS}\\ [167]}]{\substack{\text{1) MeLi/HMPA-THF}\\ \text{2) MeMgI}}} THPOCH_2CH_2\underset{\text{TMS}}{C}=CTMS_2 \qquad (153)$$

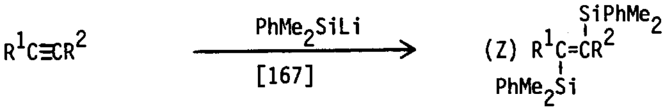


(154)

(155)

E = H, D or Me (70%)

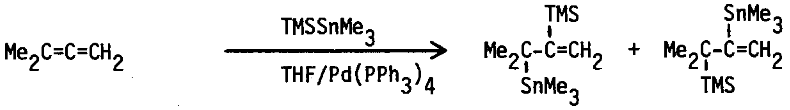
$$\mathrm{TMSC{\equiv}CTMS} \xrightarrow[\text{[167]}]{\text{as above}} \mathrm{TMS_2C{=}CTMS_2} \qquad (156)$$



$$\mathrm{R^1C{\equiv}CR^2} \xrightarrow[\text{[167]}]{\mathrm{PhMe_2SiLi}} \text{(Z) } \mathrm{R^1}\underset{\mathrm{PhMe_2Si}}{\mathrm{C}}{=}\overset{\mathrm{SiPhMe_2}}{\mathrm{C}}\mathrm{R^2} \qquad (157)$$

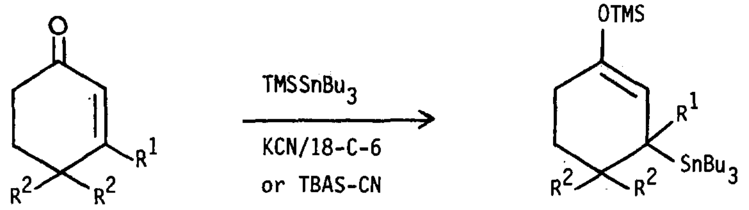
3 examples 51 - 70%

(Me_3SnLi and Bu_3SnLi also work in this reaction)



$$\mathrm{Me_2C{=}C{=}CH_2} \xrightarrow[\mathrm{THF/Pd(PPh_3)_4}]{\mathrm{TMSSnMe_3}} \mathrm{Me_2}\underset{\mathrm{SnMe_3}}{\mathrm{C}}\text{-}\overset{\mathrm{TMS}}{\mathrm{C}}{=}\mathrm{CH_2} + \mathrm{Me_2}\underset{\mathrm{TMS}}{\mathrm{C}}\text{-}\overset{\mathrm{SnMe_3}}{\mathrm{C}}{=}\mathrm{CH_2} \qquad (158)$$

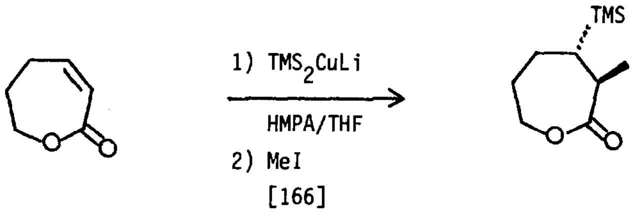
67%
[164]



(159)

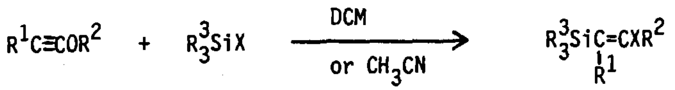
Me$_3$Si, PhMe$_2$Si and BuMe$_2$Si systems work, but Et$_3$Si and ^{t}BuMe$_2$Si do not.

R^1	R^2	%
H	H	75
Me	H	77
H	Me	68



(160)

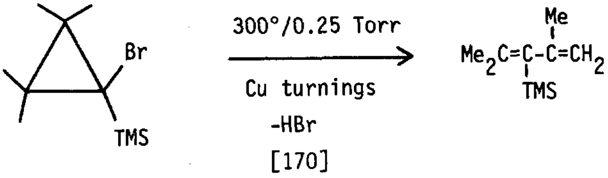
Silyl halides have been shown to add to acetylenic ethers as shown below. (Eqn. 161)



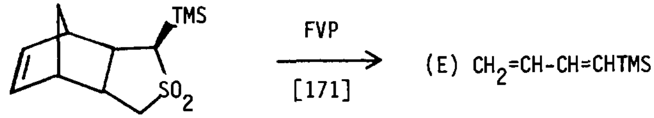
$$R^1C{\equiv}COR^2 \; + \; R^3_3SiX \xrightarrow[\text{or } CH_3CN]{\text{DCM}} R^3_3Si\underset{R^1}{\underset{|}{C}}{=}CXR^2 \qquad (161)$$

R^1 = H, alkyl; R^2 = alkyl; X = Cl, Br, I

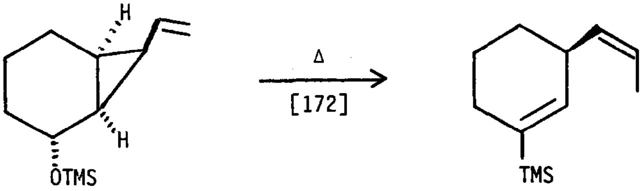
Some interesting thermal rearrangements provided vinylsilanes. These are shown in equations 162-168. The mechanism of the reactions shown in equation 166-168 have been studied mechanistically.



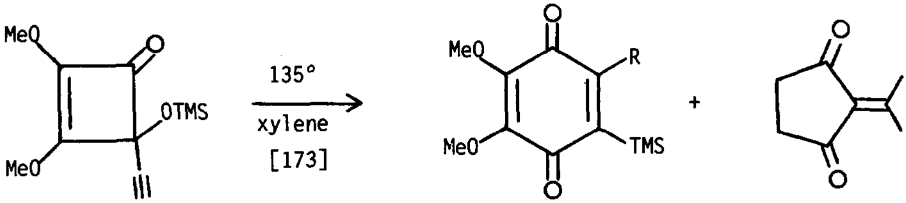
(162)



(163)



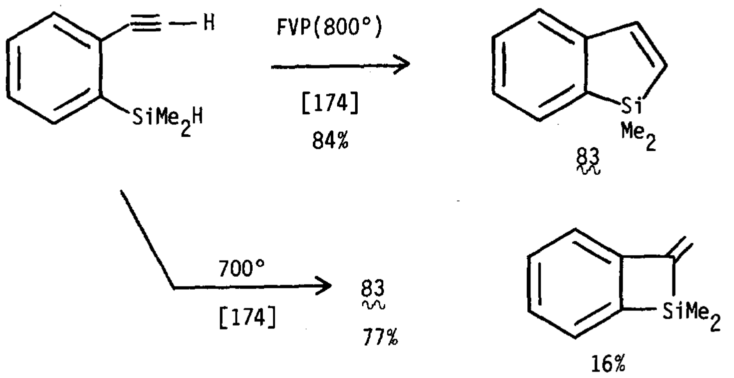
(164)



(165)

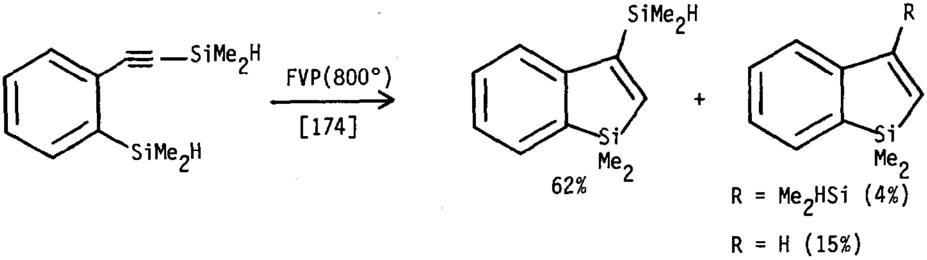
81 82

R	% 81	% 82
EtO_2C	--	33
Ph	13	52
Bu	75	--
$PhCH_2$	74	--
$TMSOCH_2$	80	--



(166)

(167)



(168)

A variety of other entries into vinylsilanes were reported. These are given in equations 169-181. 1,3-Bis(trimethylsilyl)-propyne was lithiated and then carefully protonated to give a mixture of the 1,3-bis(trimethylsilyl)allene and the starting material. (Eqn. 169) Both enantiomers of the allene could be observed by ^{1}H NMR in the presence of a shift reagent. An α-alkoxy allylsilane was deprotonated and the resulting lithium reagent quenched with benzaldehyde at both the α- and γ-positions with α-attack resulting in a Peterson elimination to produce the dienes. (Eqn. 170) Other conditions give more γ-attack. 1,3-Dichloropropene reacts with Mg/TMSCl to give **84** (Eqn. 171), which serves as a precursor to a variety of vinylsilanes via cuprate addition (Eqn. 172), reaction with an enolate (Eqn. 173) or reaction with magnesium and then a ketone or aldehyde (Eqn. 174). A sulfoxide was reacted with an excess of LDA in the presence of trimethylchlorosilane to give an α-thiophenoxyvinylsilane. (Eqn. 175) Trimethylsilyltriflate adds to the β-position of ketene acetals in the presence of triethylamine. (Eqn. 176) Vinyl triflates can be coupled with (E)-2-(trimethylstannyl)vinyltrimethylsilane. (Eqns. 177-179) This reaction was used in conjunction with a Nazarov cyclization to prepare $\Delta^{9(12)}$capnellane. (Eqn. 179) 2-(Trimethylsilyl)-1,3-butadiene was dimerized thermally and with Ni(0). (Eqn. 180) Finally **84** was converted to **89**, which in turn was deprotonated to **90**. (Eqn. 181) The structures of **84** and **90** were determined.

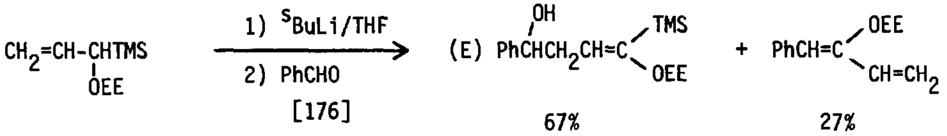
$$\mathrm{TMSC{\equiv}CCH_2TMS} \xrightarrow[\text{2) Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}]{\text{1) }^{t}\text{BuLi/THF}} \mathrm{TMSCH{=}C{=}CHTMS} + \mathbf{81} \qquad (169)$$

55% 45%

80%

[175]

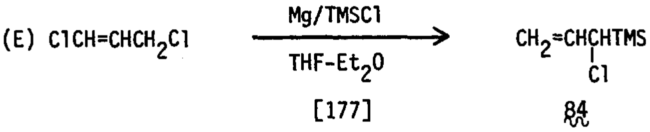
separated by reverse phase HPLC



$$\mathrm{CH_2{=}CH{-}\underset{\displaystyle OEE}{CH}TMS} \xrightarrow[\text{2) PhCHO}]{\text{1) }^{s}\text{BuLi/THF}} \text{(E) } \mathrm{Ph\overset{OH}{C}HCH_2CH{=}C(TMS)(OEE)} + \mathrm{PhCH{=}C(OEE)(CH{=}CH_2)}$$

(170)

[176] 67% 27%

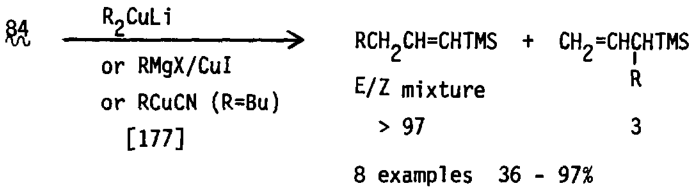


$$\text{(E) } \mathrm{ClCH{=}CHCH_2Cl} \xrightarrow[\text{THF-Et}_2\text{O}]{\text{Mg/TMSCl}} \mathrm{CH_2{=}CH\underset{\displaystyle Cl}{C}HTMS}$$

(171)

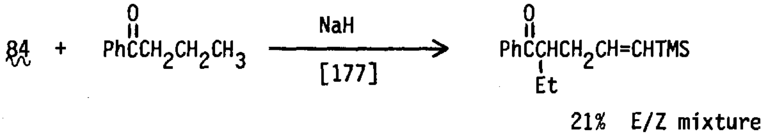
[177]

84



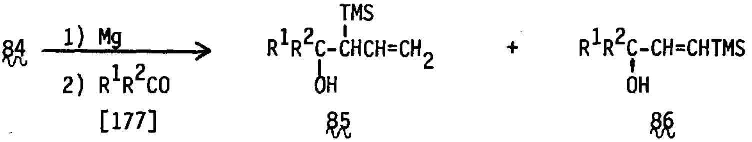
$$\mathbf{84} \xrightarrow[\text{or RMgX/CuI, or RCuCN (R=Bu), [177]}]{R_2CuLi} \underset{\substack{\text{E/Z mixture}\\ >97}}{RCH_2CH{=}CHTMS} + \underset{3}{CH_2{=}CH\underset{R}{C}HTMS} \qquad (172)$$

8 examples 36 - 97%



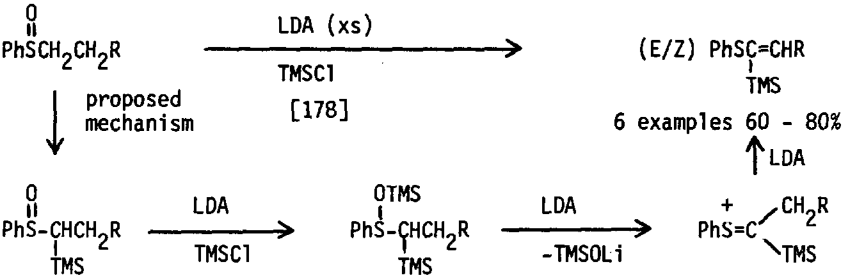
$$\mathbf{84} + Ph\overset{O}{\overset{\|}{C}}CH_2CH_2CH_3 \xrightarrow[{[177]}]{NaH} Ph\overset{O}{\overset{\|}{C}}\underset{Et}{C}HCH_2CH{=}CHTMS \qquad (173)$$

21% E/Z mixture



$$\mathbf{84} \xrightarrow[\substack{2)\ R^1R^2CO\\ [177]}]{1)\ Mg} \underset{\mathbf{85}}{R^1R^2\underset{OH}{C}\text{-}\overset{TMS}{C}HCH{=}CH_2} + \underset{\mathbf{86}}{R^1R^2\underset{OH}{C}\text{-}CH{=}CHTMS} \qquad (174)$$

R^1	R^2	conditions	%**85**	%**86**	%Yield
iPr	H	Et_2O/0°	76	24	76
iPr	H	THF/-78°	94	6	--
Ph	H	Et_2O/0°	66	34	81
Ph	H	THF/-75°	82	18	--
$-(CH_2)_5-$		Et_2O	0	100	83
$-(CH_2)_5-$		THF	--	--	88
Ph	Me	Et_2O	0	100	79



$$Ph\overset{O}{\overset{\|}{S}}CH_2CH_2R \xrightarrow[\substack{TMSCl\\ [178]}]{\text{LDA (xs)}} (E/Z)\ PhS\underset{TMS}{C}{=}CHR \qquad (175)$$

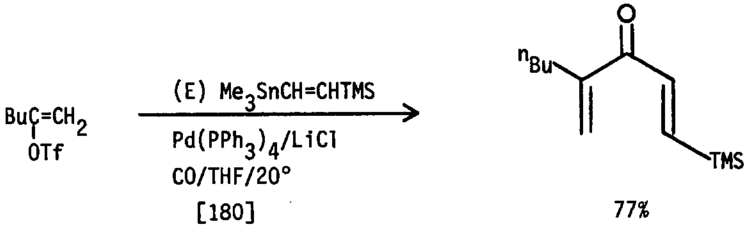
6 examples 60 - 80%

proposed mechanism

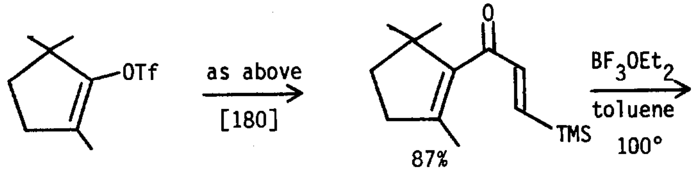
$$Ph\overset{O}{\overset{\|}{S}}\text{-}\underset{TMS}{C}HCH_2R \xrightarrow[TMSCl]{LDA} Ph\overset{OTMS}{S}\text{-}\underset{TMS}{C}HCH_2R \xrightarrow[-TMSOLi]{LDA} Ph\overset{+}{S}{=}C\begin{smallmatrix}CH_2R\\ TMS\end{smallmatrix} \xrightarrow{LDA} (E/Z)\ PhS\underset{TMS}{C}{=}CHR$$

$$R^1CH{=}C(OR^2)_2 \xrightarrow[\text{Et}_3\text{N/0-5° to RT}\ [179]]{\text{TMSOTf}} RC{=}C(OR^2)_2 \quad \text{9 examples 30 - 87\%} \qquad (176)$$

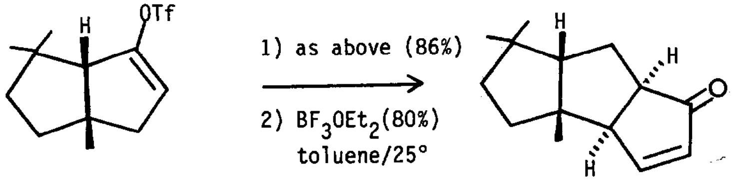
R^1 = H; R^2 = Me, Et, Pr, iBu, $MeOCH_2CH_2$, Ph, $Me_2NCH_2CH_2$
R^1 = Me; R^2 = Et
R^1 = Cl; R^2 = $MeOCH_2CH_2$



(177)

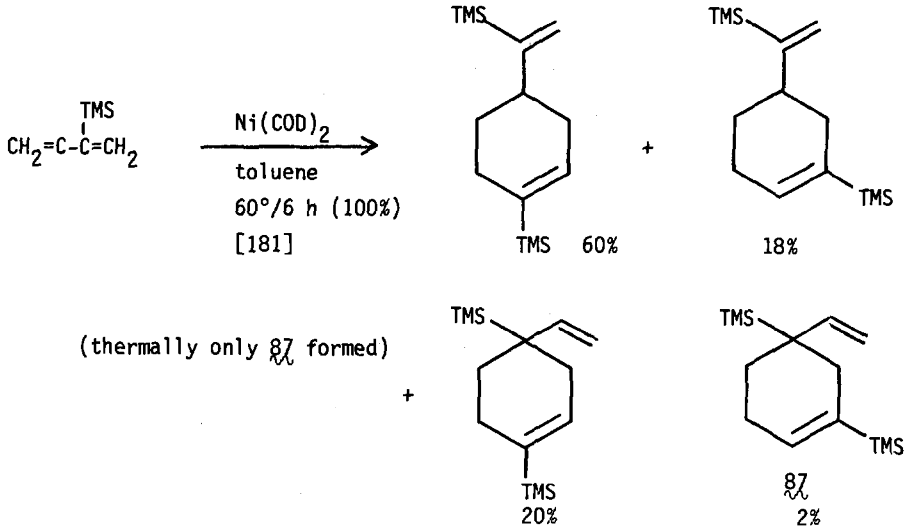


(178)

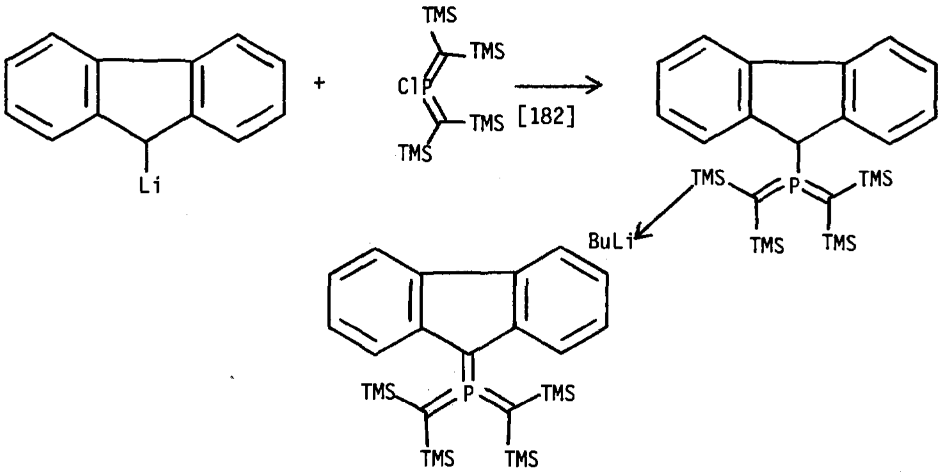


$\Delta^{9,12}$ capnellane

(179)



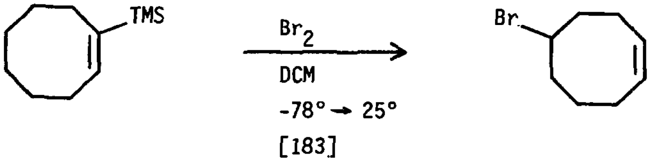
(180)



(181)

B. Reactions

Several addition reactions to vinylsilanes were reported. Treatment of (E)-1-(trimethylsilyl)cyclooctene results in a transannular bromodesilylation. (Eqn. 182)

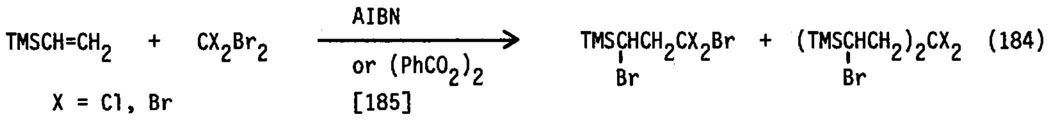


(182)

The regiospecific addition of HCl to vinylmethyldichlorosilane has been reported. (Eqn. 183) The radical addition of dibromodichloromethane or carbon tetrabromide to trimethylvinylsilane occurs to give the mono- or the bis product. (Eqn. 184) The addition of the Cl-N bond was used as an entry into trimethylsilylated aziridines. (Eqns. 185-187)

$$MeCl_2SiCH{=}CH_2 \xrightarrow[FeCl_2 \text{ or } TaCl_5]{HCl} MeCl_2SiCH_2CH_2Cl \qquad (183)$$

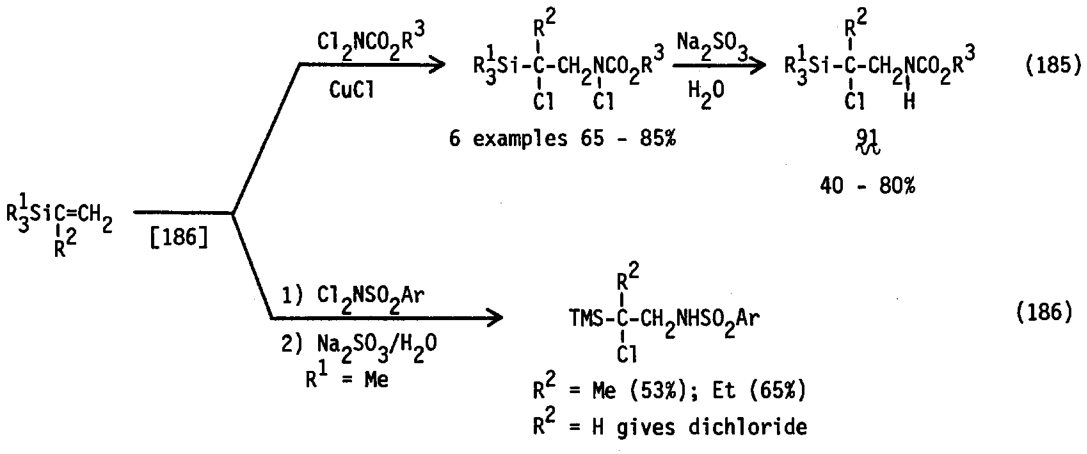
[184]



$$TMSCH{=}CH_2 + CX_2Br_2 \xrightarrow[\text{or } (PhCO_2)_2]{AIBN} TMS\underset{Br}{C}HCH_2CX_2Br + (TMS\underset{Br}{C}HCH_2)_2CX_2 \qquad (184)$$

X = Cl, Br

[185]



$R^1_3SiC(R^2){=}CH_2$ [186]

$Cl_2NCO_2R^3$, CuCl → $R^1_3Si\text{-}C(R^2)(Cl)\text{-}CH_2N(Cl)CO_2R^3$ → (Na_2SO_3, H_2O) $R^1_3Si\text{-}C(R^2)(Cl)\text{-}CH_2N(H)CO_2R^3$ (185)

6 examples 65 - 85%

91

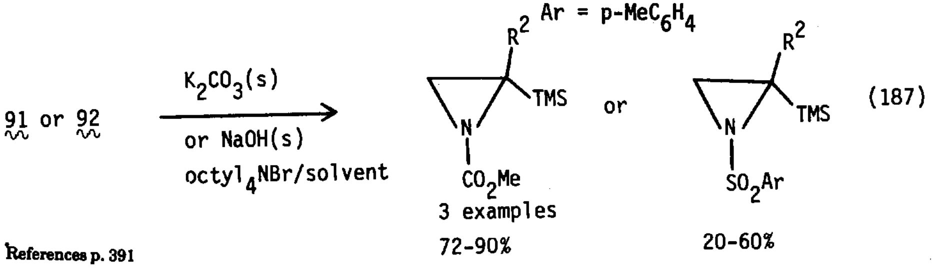
40 - 80%

1) Cl_2NSO_2Ar 2) Na_2SO_3/H_2O, R^1 = Me → $TMS\text{-}C(R^2)(Cl)\text{-}CH_2NHSO_2Ar$ (186)

R^2 = Me (53%); Et (65%)

R^2 = H gives dichloride

Ar = p-MeC_6H_4

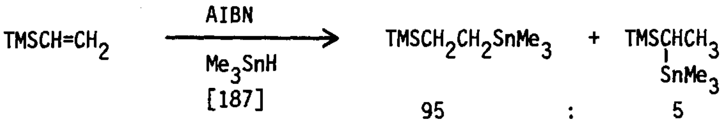


3 examples

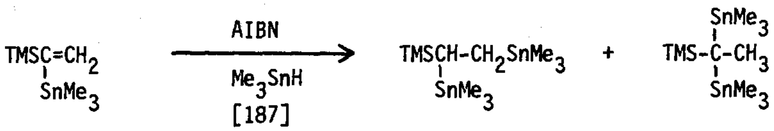
72-90%

20-60%

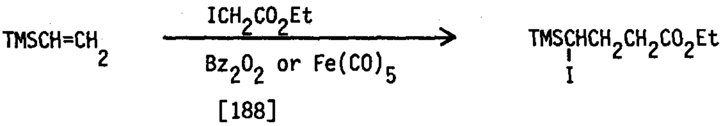
The hydrostannylation of vinylsilanes is shown in equations 188 and 189. The radical-induced addition of ethyl iodoacetate to give the γ-iodo-γ-trimethylsilyl ester was reported. (Eqn. 190) The addition of thiols to vinylsilanes was reported for several systems. (Eqns. 191-195) The allyl systems were also looked at. The resulting products were converted to the corresponding silatranes. Dialkyl- or diarylphosphine oxides add to vinylsilanes. (Eqn. 196)



$$\mathrm{TMSCH{=}CH_2} \xrightarrow[\mathrm{Me_3SnH}\ [187]]{\mathrm{AIBN}} \underset{95}{\mathrm{TMSCH_2CH_2SnMe_3}} + \underset{5}{\mathrm{TMS}\underset{\mathrm{SnMe_3}}{\mathrm{C}}\mathrm{HCH_3}} \qquad (188)$$



$$\mathrm{TMS}\underset{\mathrm{SnMe_3}}{\mathrm{C}}\mathrm{{=}CH_2} \xrightarrow[\mathrm{Me_3SnH}\ [187]]{\mathrm{AIBN}} \mathrm{TMS}\underset{\mathrm{SnMe_3}}{\mathrm{C}}\mathrm{H{-}CH_2SnMe_3} + \mathrm{TMS{-}}\overset{\mathrm{SnMe_3}}{\underset{\mathrm{SnMe_3}}{\mathrm{C}}}\mathrm{{-}CH_3} \qquad (189)$$



$$\mathrm{TMSCH{=}CH_2} \xrightarrow[\mathrm{Bz_2O_2\ or\ Fe(CO)_5}\ [188]]{\mathrm{ICH_2CO_2Et}} \mathrm{TMS}\underset{\mathrm{I}}{\mathrm{C}}\mathrm{HCH_2CH_2CO_2Et} \qquad (190)$$

$$\mathrm{(EtO)_3Si(CH_2)_nCH{=}CH_2} \xrightarrow[h\nu\ [189]]{\mathrm{RSH}} \mathrm{(EtO)_3Si(CH_2)_nCH_2CH_2SR} \qquad (191)$$

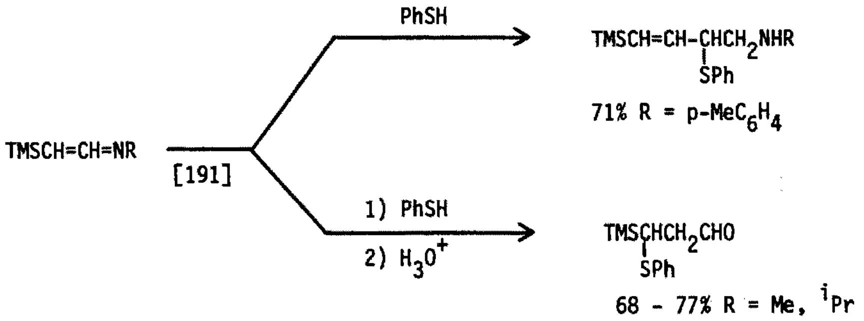
R = Me, Et, tBu

$$\mathrm{X_3SiCH{=}CH_2} \xrightarrow[[189]]{\text{as above}} \mathrm{X_3SiCH_2CH_2SR} \qquad (192)$$

X = F, Cl

$$(R^1O)_3Si(CH_2)_nCH{=}CH_2 \xrightarrow[h\nu \\ {[190]}]{R^2SH} (R^1O)_3Si(CH_2)_nCH_2CH_2SR^2 \qquad (193)$$

R^1,R^2 = Me, Et; Me, ${}^tBu$; ${}^tBu$, Et (n = 0)
R^1,R^2 = Me, Me; Et, Et; ${}^tBu$, Et (n = 1)



$$TMSCH{=}CH{=}NR \xrightarrow[{[191]}]{PhSH} TMSCH{=}CH\text{-}\underset{SPh}{\underset{|}{C}}HCH_2NHR \qquad (194)$$

71% R = p-MeC_6H_4

$$TMSCH{=}CH{=}NR \xrightarrow[{[191]}]{1)\ PhSH;\ 2)\ H_3O^+} TMS\underset{SPh}{\underset{|}{C}}HCH_2CHO \qquad (195)$$

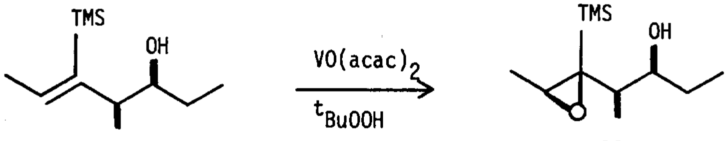
68 - 77% R = Me, ${}^iPr$

$$R^1(R^2O)_2SiCH{=}CH_2 + R^3_2P(O)H \xrightarrow[{[192]}]{AIBN} R^1(R^2O)_2SiCH_2CH_2P(O)R^3_2 \qquad (196)$$

R^1 = Me, Et, Pr, Bu, Ph
R^2 = Me, Et
R^3 = Et, Pr, Ph

8 examples 21.8 - 49.4%

The epoxidation of vinylsilanes proved very useful in the stereoselective preparation of polyhydroxy acyclic systems. Two such studies are shown here. The first (Eqns. 197-198) was involved in a synthesis of the C_2-C_7 fragment of 6-deoxyerythronolide and the second in a synthesis of (±)blastimycinone (Eqn. 199) The diols **94** were converted to substituted furans as shown. (Eqn. 200) A specific example is given. (Eqn. 201)

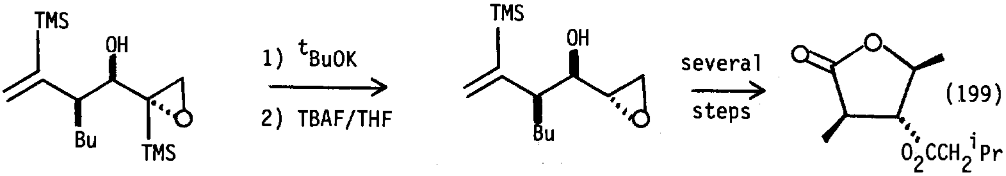


(197)

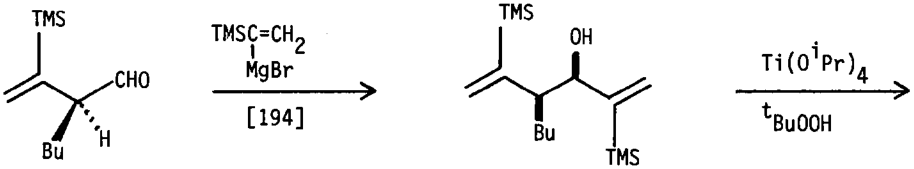
93 > 99:1 selectivity
MCPBA gives 4:1

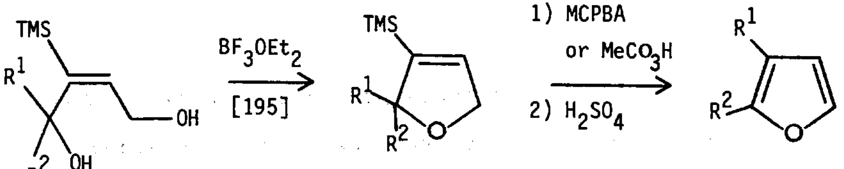
(198)

> 99:1



(199)

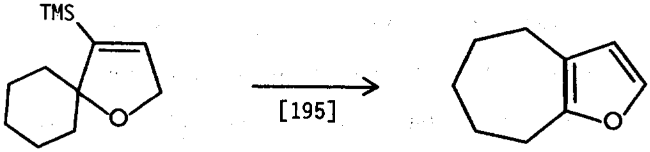




94

(200)

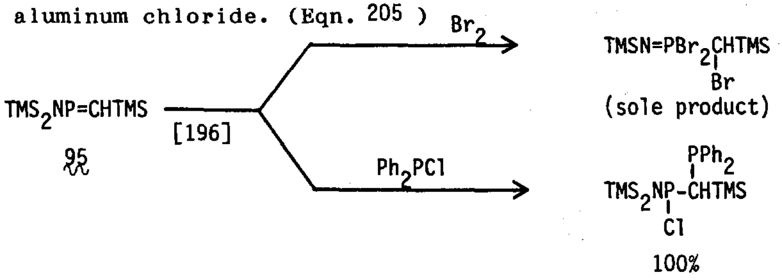
49-95%



(201)

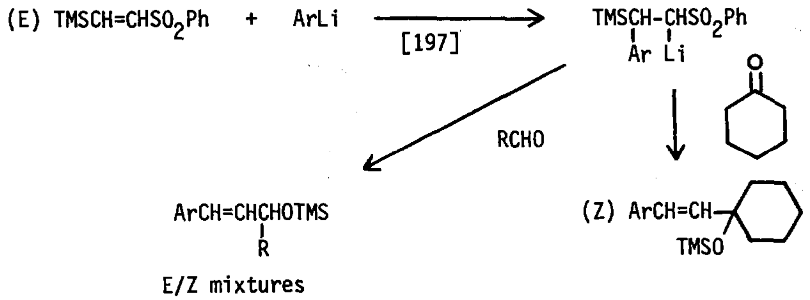
92%

Some miscellaneous additions are also given. The silylated ylide **95** undergoes addition reactions. (Eqns. 202 and 203) The silylated vinylsulfone **96** adds aryllithium reagents. The newly formed anion was then reacted with aldehydes to give, after silyl migration-elimination, the silylated allyl alcohols. (Eqn. 204) Vinylsilanes were added to adamantanes under the influence of aluminum chloride. (Eqn. 205)



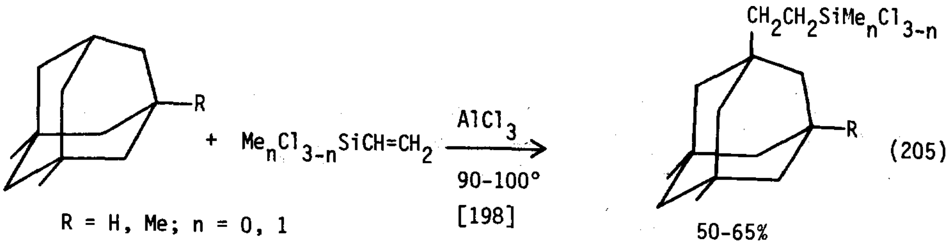
(202)

(203)



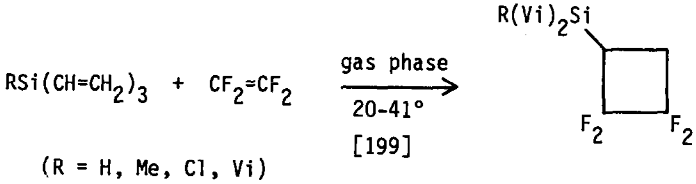
(204)

R = $PhCH_2CH_2$, Ph, iPr, n-C_5H_{11}
Ar = Ph, p-$MeOC_6H_4$

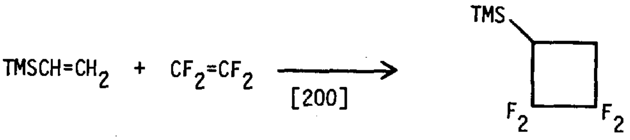


(205)

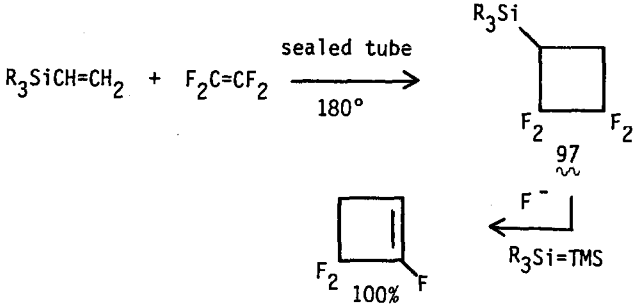
Cycloadditions involving vinylsilanes were reported. The [2+2] cycloadditions with tetrafluorethylene were studied. Examples are shown in equations 206-208. Pyrolysis of **97** gave polyfluorocyclic and bicyclic system. Vinylsilatranes were reacted with cyclopentadiene. The allyl systems were also employed. (Eqn. 209) Vinylsilanes served as the dipolarophile in cycloadditions with nitrones. (Eqn. 210)



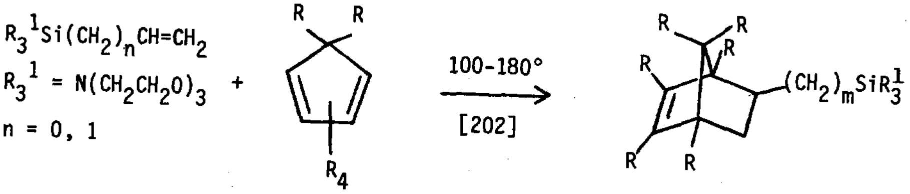
(206)



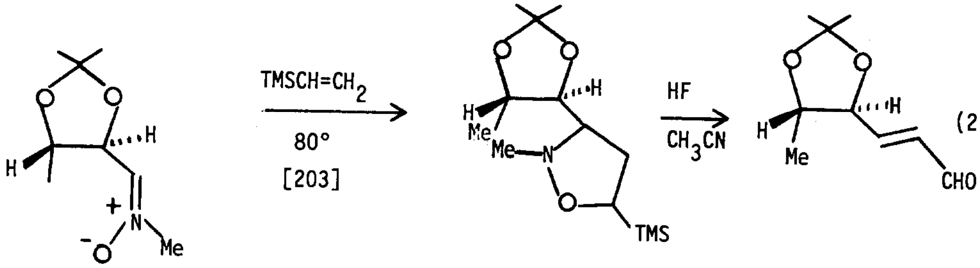
(207)



(208)

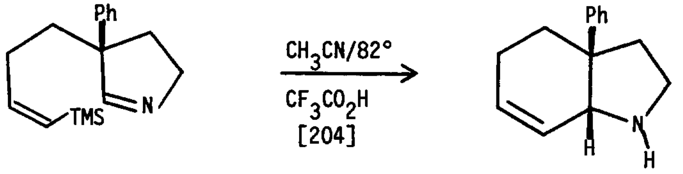


(209)



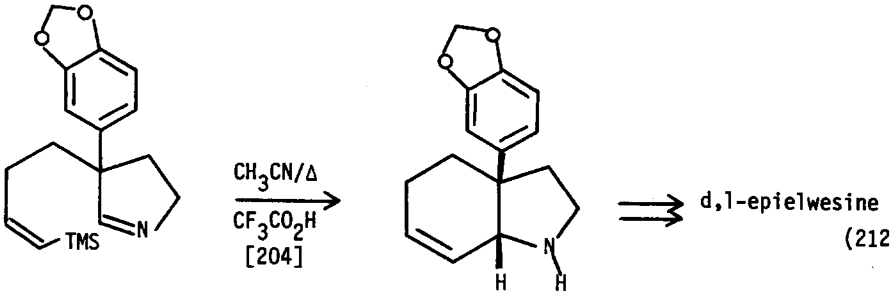
(210)

Vinylsilanes were intramolecularly cyclized with imines as shown in equations 211 and 212. Compound **98** was carried on to the alkaloid d,l-epielwesine. The synthesis of the requisite imines can be found in reference 205.



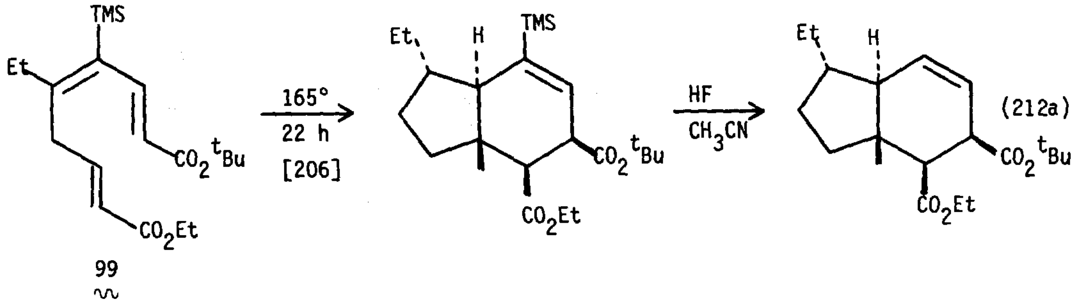
(211)

The (E) isomer does not cyclize.



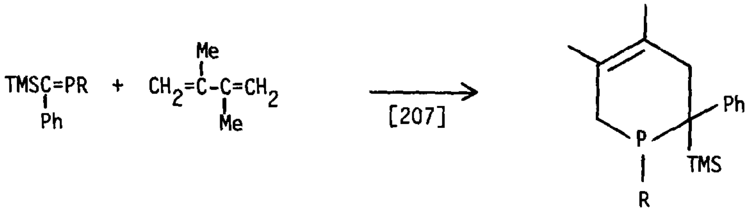
(212)

Vinylsilanne **99** prepared in a standard fashion was thermally cyclized. (Eqn. 212a)

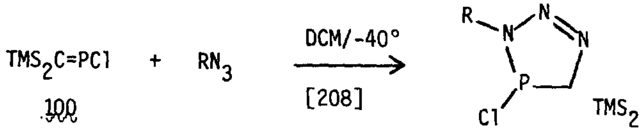


(212a)

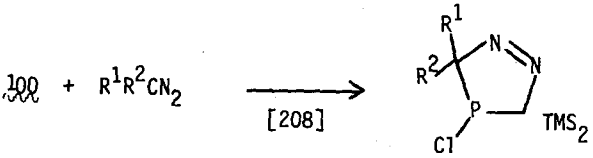
Silylated phosphorus ylides were shown to undergo cycloadditions. These are shown below. (Eqns. 213-221)



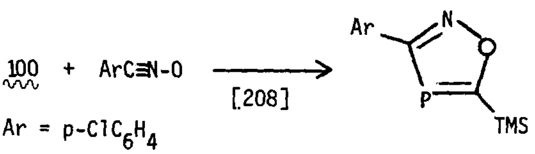
(213)



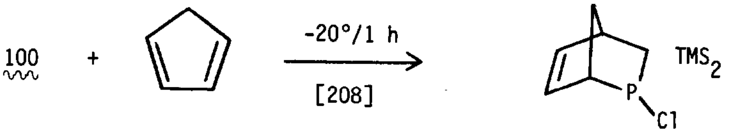
(214)



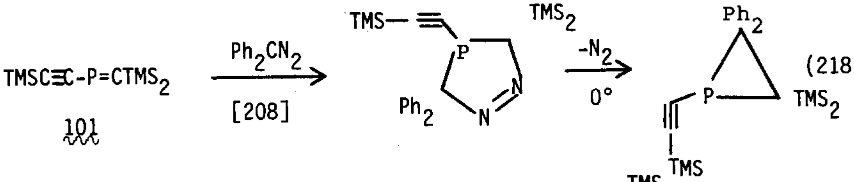
(215)



(216)



(217)



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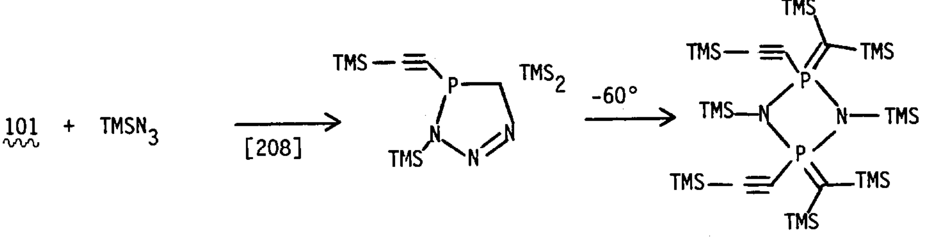

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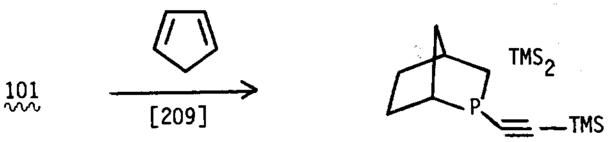

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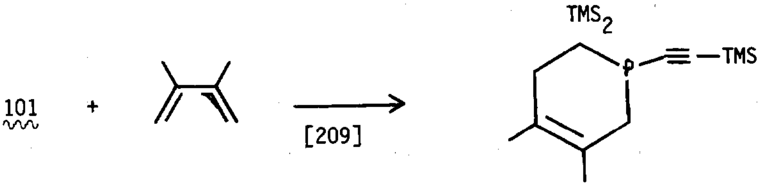
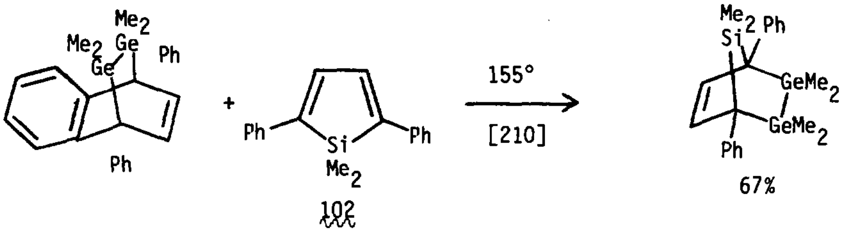


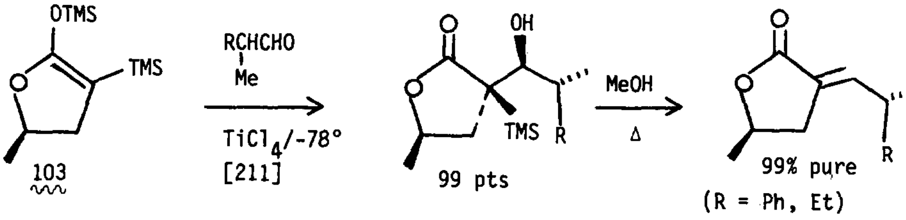
(221)

Silacyclopentadiene **102** served as the diene for the trapping of tetramethyldigermene, itself generated by a retro-Diels-Alder process. (Eqn. 222)



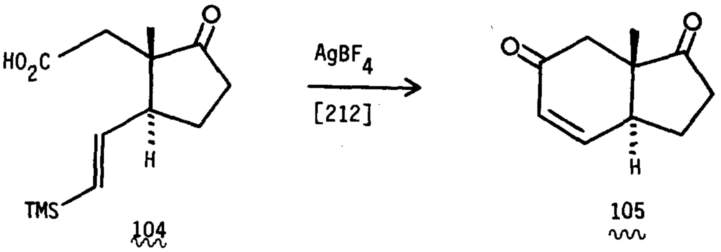
(222)

Some interesting applications of the reaction of vinylsilanes under the influence of Lewis acids appeared. The optically active vinylsilane **103**, which is also an enol silyl ether and which reacts primarily as an enol silyl ether in concert with the vinylsilane functionality, leads to the optically active α-alkylidene lactones with high stereoselectivity. (Eqn. 223)



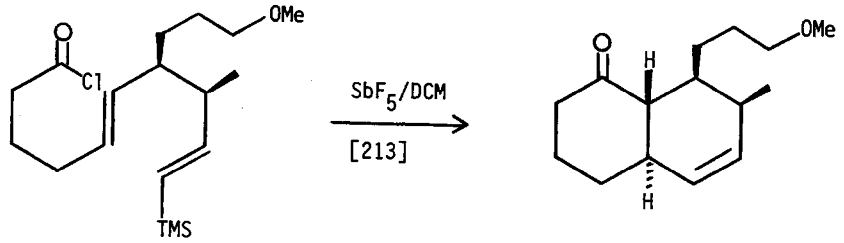
(223)

The acid **104**, prepared in a straightforward manner, was cyclized in the presence of $AgBF_4$ to give the trans-hydrindanedione **105**. (Eqn. 224) A similar system is shown in equation 225. A version of this cyclization where two rings are formed is seen in equation 226.



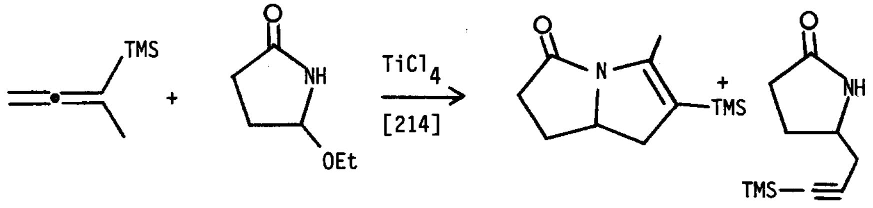
(224)

(225)

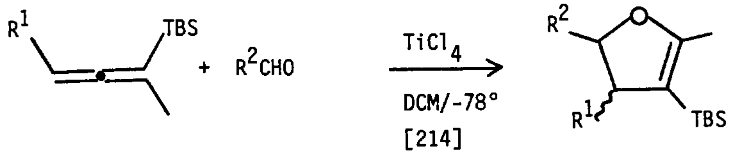


(226)

Allenenylsilanes were cyclized with γ-lactams and aldehydes. (Eqns. 227 and 228)

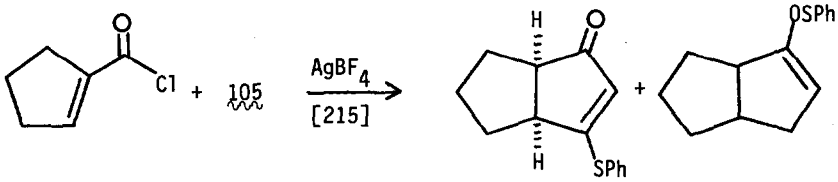


(227)

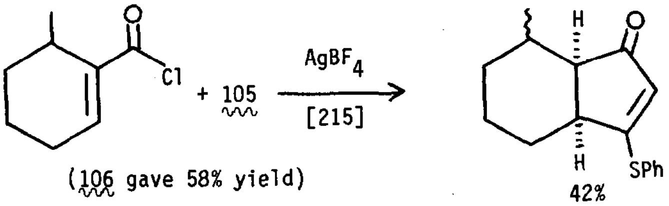


(228)

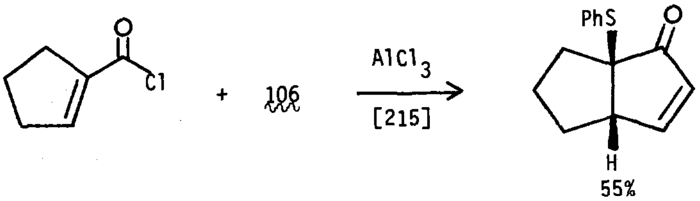
The α- and β-thiophenoxy vinylsilanes **105** and **106** respectively, were used in cyclopentenone annulations. The reagent **105** reacts via stabilization of the positive charge by the thiophenoxy group (i.e. α to sulfur) whereas in **106** both the trimethylsilyl and thiophenoxy are arranged so as to stabilize the positive charge (i.e. α to sulfur and β to silicon). The final products are a result of rearrangements, however. Examples of the cyclizations are given in equations 229-232.



(229)



(230)



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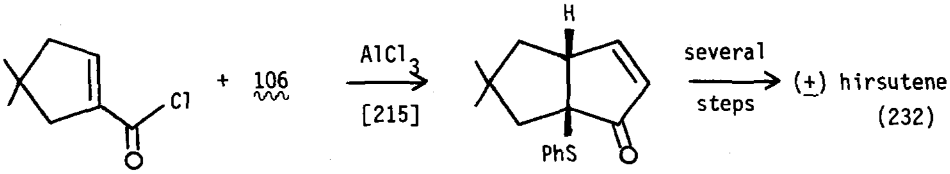
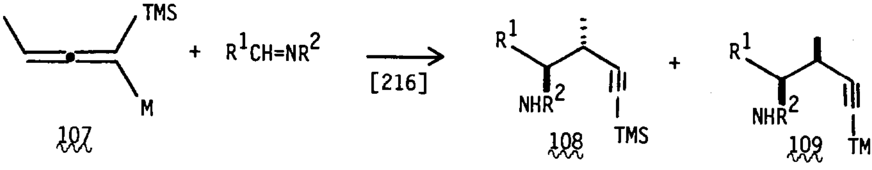
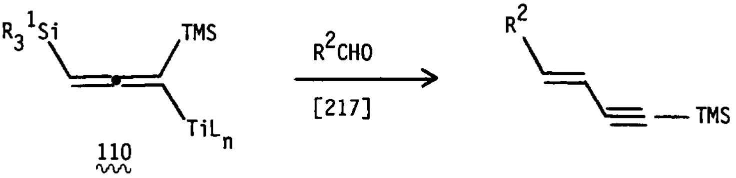


(232)

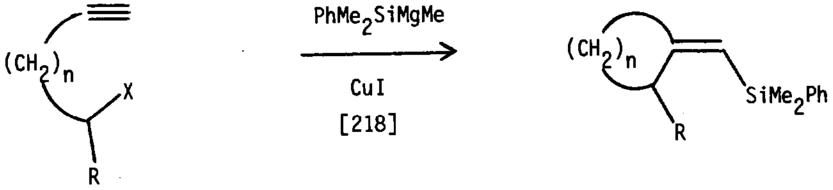
Metalated vinylsilanes, some of which we have seen already, were reacted with carbon electrophiles in an inter- or intramolecular sense. The allenenylsilanes **107** were reacted with imines to give predominantly the threo amino acetylenes. (Eqn. 233) The corresponding titanium derivatives **108** reacted with aldehydes to give enynes, the result of a Peterson-type elimination. (Eqn. 234) An intramolecular cyclization process was possible according to equations 235 and 236. (See Eqns. 131-138 for some similar transformations.)



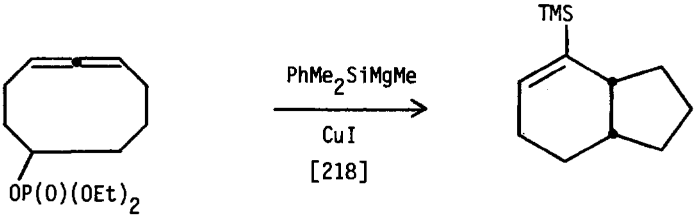
(233)



(234)

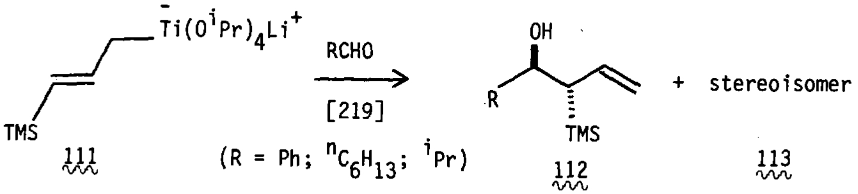


(235)



(236)

Vinylsilanes which are metalated in an allylic position, reagents which can be derived from the vinylsilane or allysilane, can be reacted with aldehydes and ketones to give α or γ- attack. The titanium reagent **111** (from lithiation-titanation of trimethylallylsilane) reacts with aldehydes α to silicon with good diastereoselectivity. (Eqn. 237) The resulting β-hydroxysilanes can be eliminated to Z or E-dienes. (Eqns. 238 and 239) Even acetophenone reacts with diastereoselectivity. (Eqns. 240-242)



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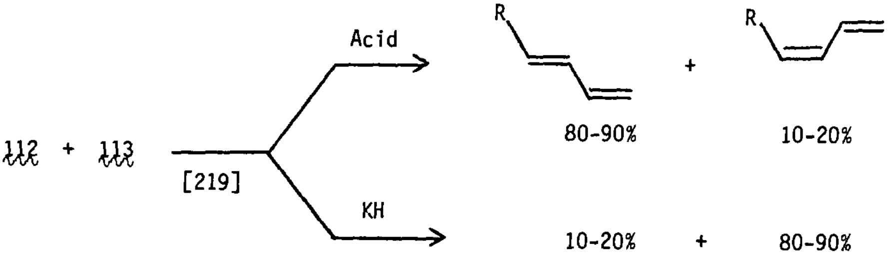
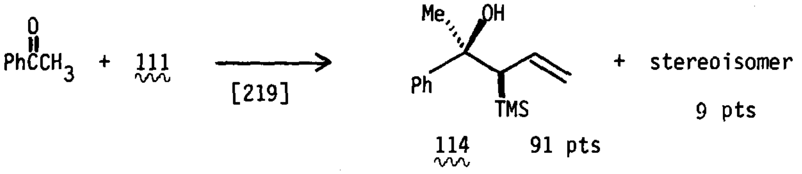
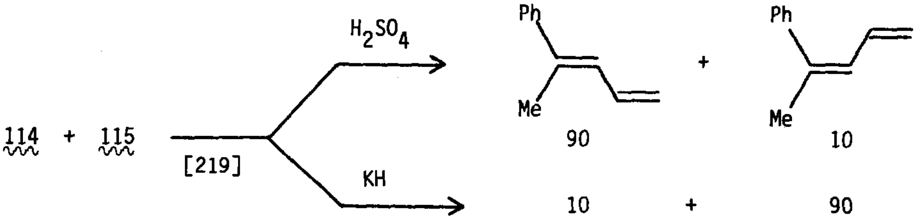


(238)

(239)



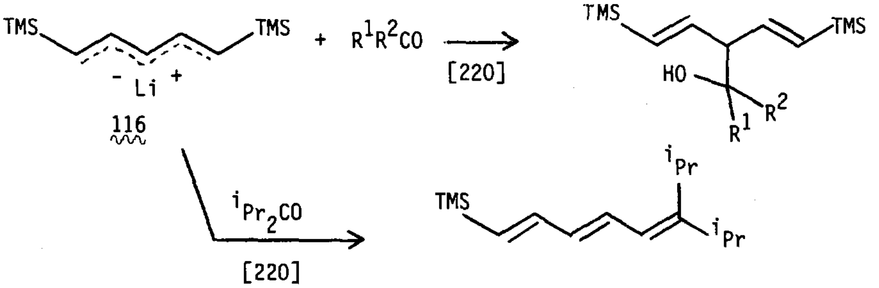
(240)



(241)

(242)

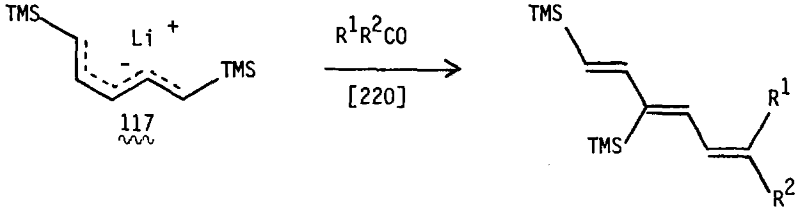
1,5-Bis(trimethylsilyl)pentadienyllithium **116** reacts with aldehydes and ketones at C-3 (Eqn. 243) with the exception of diisopropyl ketone, which reacts at C-1 and gives a Peterson elimination (Eqn. 244). The 1,3,5-tris(trimethylsilyl)pentadienyllithium reagent **117** reacts at C-1 to give the Peterson olefination products. (Eqn. 245) The dianion of **118** reacted with diisopropyl ketone to give the bis-Peterson olefination polyene **119**. (Eqn. 246) Various modifications on the reactivity of 1-(trimethylsilyl)pentadienyl anion were studied. Thus, changing the metal to MgBr gave more C-3 attack, addition of $Cu(PBu_3)_3$ more C-3 attack. Treatment with $B(OMe)_3$ and oxidation gave allylic alcohol **120**. (Eqn. 247)



116

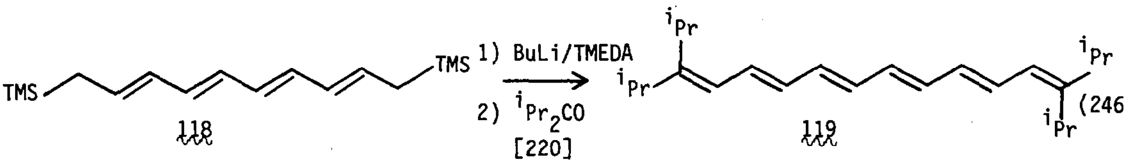
(243)

(244)



117

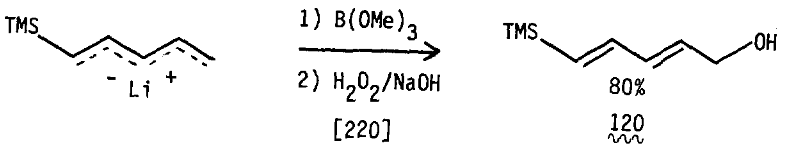
(245)



118

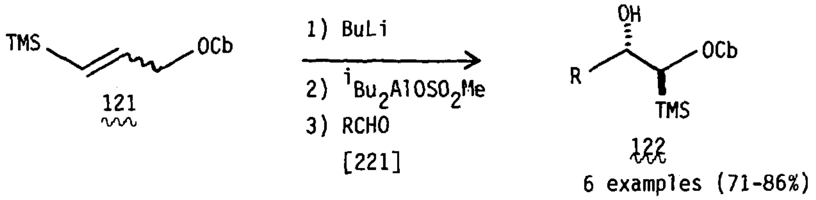
119

(246)

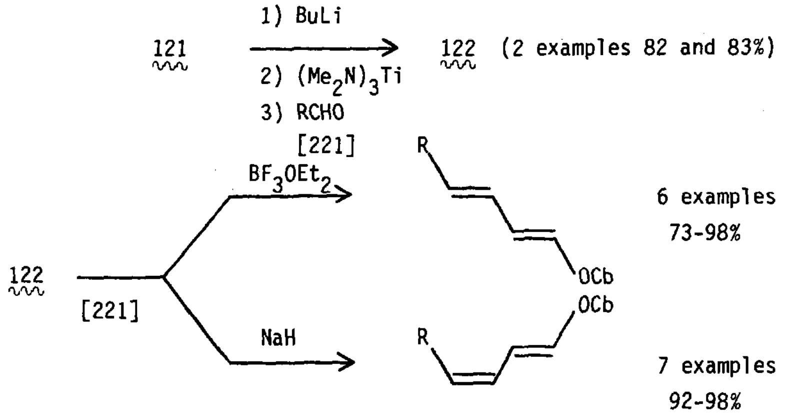


(247)

The carbamoyloxy vinylsilanes **121** were lithiated and the lithium reagents either eliminated or titanated. These new reagents reacted with aldehydes to give β-hydroxysilanes, which were then converted to E,E or Z,E enol carbamates as shown below. (Eqns. 248-251)



(248)

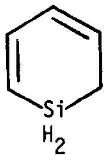


(249)

(250)

(251)

Treatment of silacyclohexadiene **123** with ^{t}BuLi/TMSCl gives ten products the results of substitution, addition, deprotonation and ring opening. [222]



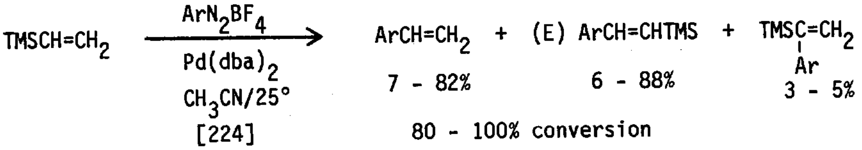
123

Vinylsilanes were shown to undergo a variety of coupling or substitution reactions catalyzed by transition metal complexes. Examples are given below. (Eqns. 252-255)

$$\mathrm{RCH{=}CHTMS} + \mathrm{PhPdOAc} \xrightarrow[\text{[223]}]{} \mathrm{RCH{=}C(Ph)TMS} + \mathrm{R(Ph)C{=}CHTMS} + \mathrm{RCH{=}CHPh} + \mathrm{R(Ph)C{=}CH_2} \qquad (252)$$

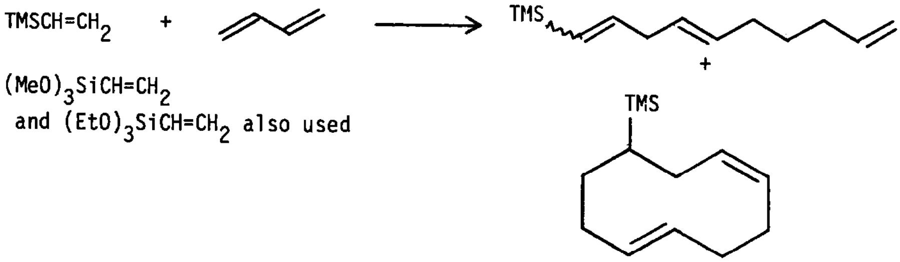
$\mathrm{R = Ph,\ {}^{n}C_6H_{13},\ MeOCH_2}$

34 - 78% conversion



$$\mathrm{TMSCH{=}CH_2} \xrightarrow[\substack{\mathrm{Pd(dba)_2} \\ \mathrm{CH_3CN/25°} \\ [224]}]{\mathrm{ArN_2BF_4}} \underset{7\,-\,82\%}{\mathrm{ArCH{=}CH_2}} + \underset{6\,-\,88\%}{\mathrm{(E)\ ArCH{=}CHTMS}} + \underset{3\,-\,5\%}{\mathrm{TMS\underset{|\atop Ar}{C}{=}CH_2}} \qquad (253)$$

80 - 100% conversion



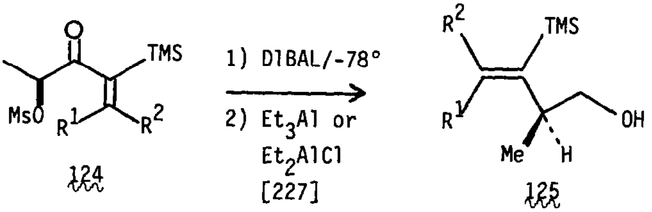
(254)

$\mathrm{(MeO)_3SiCH{=}CH_2}$
and $\mathrm{(EtO)_3SiCH{=}CH_2}$ also used

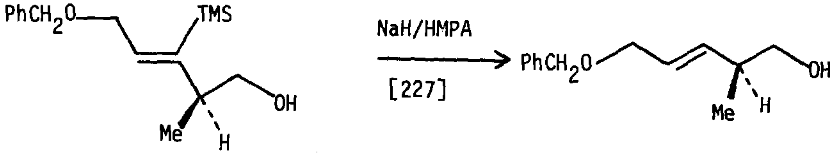
$$\mathrm{TMSCH{=}CH_2} + \mathrm{RX} \xrightarrow[\text{[226]}]{(\pi\text{-allylPdCl})_2} \mathrm{RCH{=}CH_2} \qquad (255)$$

R = 1-Np, 1-pyridyl, m-9-carbamoyl, Ph, $\mathrm{XC_6H_4}$; X = Br, I.

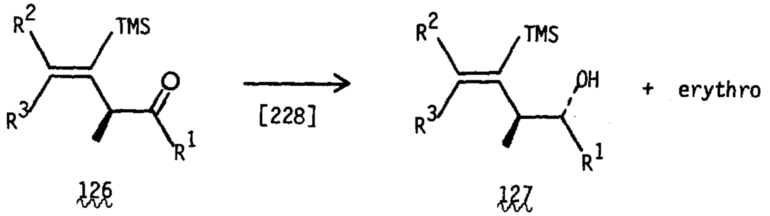
Some miscellaneous reactions of vinylsilanes are given in the equations below. (Eqns. 256-259) The vinylsilane **124** was useful in the synthesis of homoallylic alcohols chiral at C-2. (Eqns. 256 and 257) The vinylsilane group migrates during the reaction and the products are enantiomerically pure. In a similar vein **126** were used to prepare optically pure 1,3 -diols chiral at C-2. (Eqns. 258 and 259)



(256)

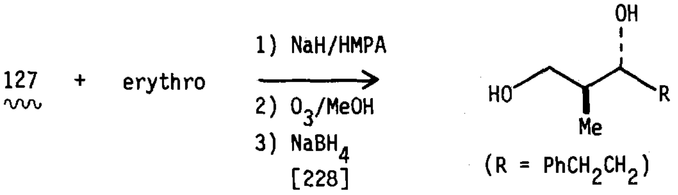


(257)



(258)

R^1	R^2	R^3	"H^-"		
$PhCH_2CH_2$	H	H	DIBAH	89	11
"	Bu	H	"	94	6
"	H	Bu	"	>99	<1
"	H	H	L-selectride	>99	<1
"	Bu	H	"	"	"
"	H	Bu	"	"	"

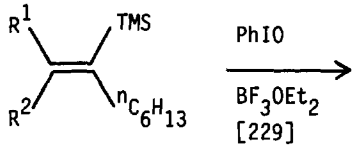


(259)

Hypervalent iodine in the presence of boron fluoride etherate converts (Z)- or (E)-vinylsilanes containing a β-hydrogen to acetylenes. (Eqns. 260 and 261)

$$\text{(Z) or (E) RCH=CHTMS} \xrightarrow[\text{BF}_3\text{OEt}_2\ [229]]{\text{PhIO}} \text{RC≡CH} \qquad (260)$$

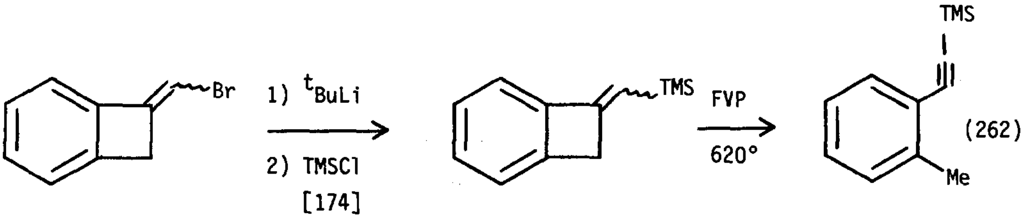
from (Z) 4 examples 61 - 99%
from (E) 3 examples 73 - 98%



$^nC_6H_{13}C{\equiv}C^nC_6H_{13}$ (261)

R^1 = $^nC_6H_{13}$; R^2 = H 79%
R^1 = H; R^2 = $^nC_6H_{13}$ 52%

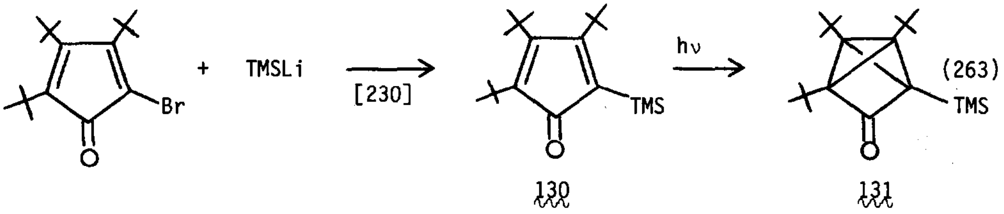
The vinylsilane **128**, prepared as shown, gives acetylene **129** upon flash vacuum pyrolysis. (Eqn. 262)



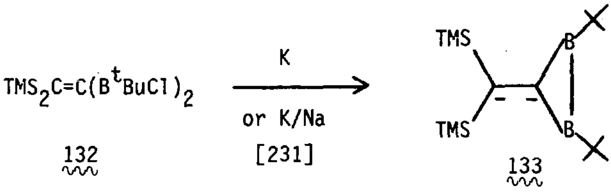
(262)

128 **129**

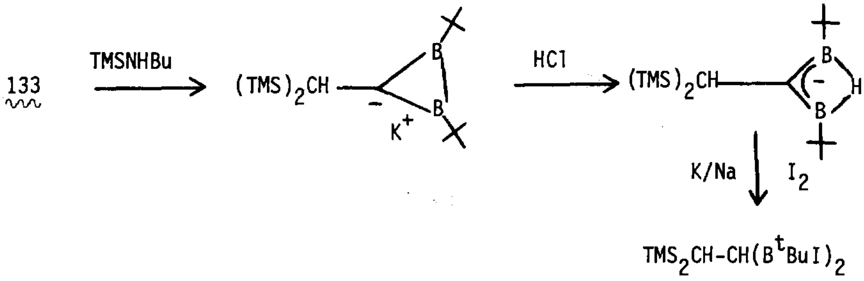
Trimethylsilylcyclopentadienone **130**, prepared as shown, undergoes photolysis to give **131**. (Eqn. 263) The highly metallated **132** can be converted to its dianion, which can be selectively protonated and then iodinated as illustrated. (Eqns. 264 and 265)



(263)



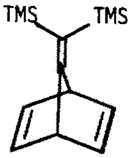
(264)



(265)

C. Other Studies

The kinetic isotope effect of the insertion of isopropylidene carbene into Et_3SiH (and Et_3SiD) was studied. It was determined that the reaction trajectory is nonlinear. [232] A variety of (E)-bis(silyl)ethylenes were studied by IR. [233] the photoelectron and the ^{13}C NMR spectra of **134** were studied and compared with other similar systems. [234] The conformations of **135-137** were studied by ^{1}H NMR. [235] An electron diffraction study of **138** was carried out and it was determined that the ring is nearly planar. [236] The antimicrobial properties of several polyfunctional unsaturated alkyl(aryl)silanes were studied. [237]



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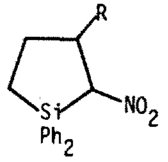

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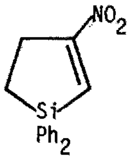

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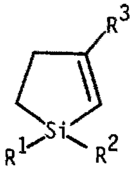
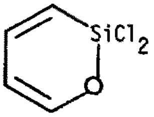


137



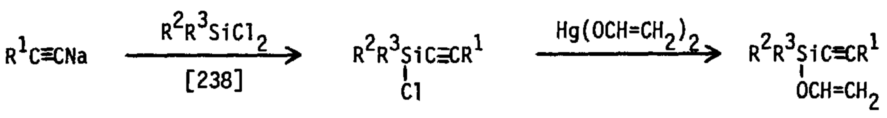
138

VIII. ETHYNYLSILANES

A. Preparation

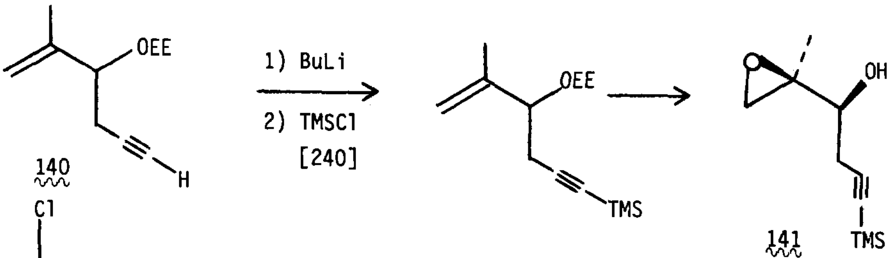
Several approaches towards the synthesis of ethynylsilanes appeared. These range from the simple reaction of an ethynylmetallic reagent with a chlorosilane through manipulation of an existing ethynylsilane to some cross coupling approaches.

The reaction of an active ethynylmetallic reagent with a chlorosilane is, of course, a straightforward entry into these increasingly useful species. A number of examples appeared. These are given below. Ethynylsodium reagents were reacted with dichlorosilanes to give the monoadducts, which were converted to enol silyl ethers. (Eqn. 266) Propynylmagnesium bromide was reacted with (chloromethyl)dimethylchlorosilane and the product of this converted to its Grignard reagent, which was in turn reacted with the above chlorosilane. This process can be repeated and ultimately stopped by reaction with trimethylchlorosilane to give the "polymeric" material **139**. (Eqn. 267) Acetylene **140** was lithiated and silylated as shown. The olefinic ethynylsilane was subjected to Sharpless epoxidation ((+) diisopropyl tartrate, $^tBuOOH/Ti(O^iPr)_4$) to give **141**. (Eqn. 268) Advantage was taken of the direct conversion of 1,1-dichloroalkenes to ethynyllithium reagents to convert **142** to **143**, which was then transformed into **144**. (Eqn. 269) Bis(bromomagnesio)acetylene was reacted with a series of disilylalkanes **145** to give the cyclic ethynylsilanes **146**. (Eqn. 270) (Z)-1-Methoxybut-1-en-3-yne **147** a commercially available enyne, was doubly deprotonated with butyllithium and silylated to give butadiyne **148** in good yield. (Eqn. 271) This material is a convenient, easily handled source of the volatile 1,3-butadiyne. Dilithiation of **148** followed by reaction with a single equivalent of trimethylchlorosilane gives **149**, which then can be reacted with other electrophiles. (Eqn. 272) **147** can be singly lithiated at -72^{o} and then silylated to give **150** (Eqn. 273), which can be lithiated at the 3-position and reacted with electrophiles to provide **151** (Eqn. 274).

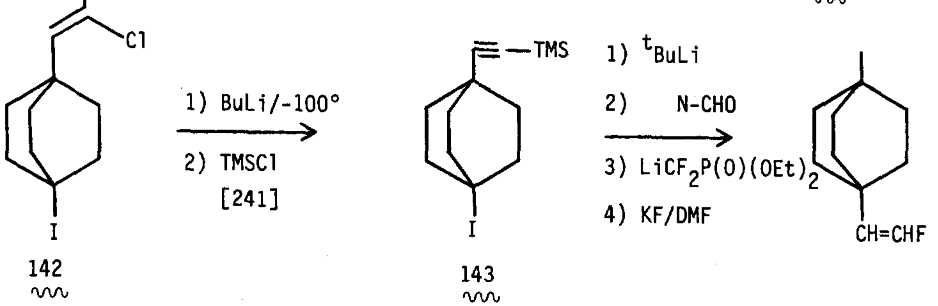


$$R^1C{\equiv}CNa \xrightarrow[{[238]}]{R^2R^3SiCl_2} R^2R^3\underset{Cl}{\underset{|}{Si}}C{\equiv}CR^1 \xrightarrow{Hg(OCH{=}CH_2)_2} R^2R^3\underset{OCH=CH_2}{\underset{|}{Si}}C{\equiv}CR^1 \qquad (266)$$

R^1 = H, Bu, Ph; R^2 = Me, H; R^3 = H, Vi, Ph



(268)



(269)

$$BrMgC{\equiv}CMgBr \xrightarrow[\text{[242]}]{Me_2ClSi\text{-}(CH_2)_n\text{-}SiMe_2Cl\ (145)} [Me_2Si\text{-}C{\equiv}C\text{-}(CH_2)_n]_m \quad (270)$$

146

observed cyclic products were where:

n = 0 m = 2,3
n = 1 m = 2, 3, 4
n = 2 m = 2, 3, 4
n = 3 m = 1 (trace), 2
n = 4 m = 1 (trace), 2

$$(Z)\ MeOCH{=}CHC{\equiv}CH \xrightarrow[\text{2) TMSCl } -25\rightarrow25° \text{ [243]}]{\text{1) 2 BuLi/}-25°} TMSC{\equiv}C\text{-}C{\equiv}CTMS \quad (271)$$

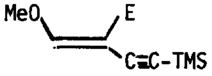
147 148 80%

$$\underset{147}{} \xrightarrow[\text{2) TMSCl (1 eq)}\ [243]]{\text{1) 2 BuLi}} \underset{149}{\text{LiC}\equiv\text{C-C}\equiv\text{CTMS}} \xrightarrow{E^+} \text{E-C}\equiv\text{C-C}\equiv\text{CTMS} \qquad (272)$$

E^+	%
H_3O^+	71
EtCHO	76
TMSCl	80

$$\underset{147}{} \xrightarrow[\text{2) TMSCl}\ [243]]{\text{1) BuLi/-72°}} \underset{150}{\text{(Z) MeOCH=CHC}\equiv\text{CTMS}} \qquad (273)$$

$$\underset{150}{} \xrightarrow[\text{2) } E^+\ [243]]{\text{1) BuLi/DME/-72°}}$$



151

(274)

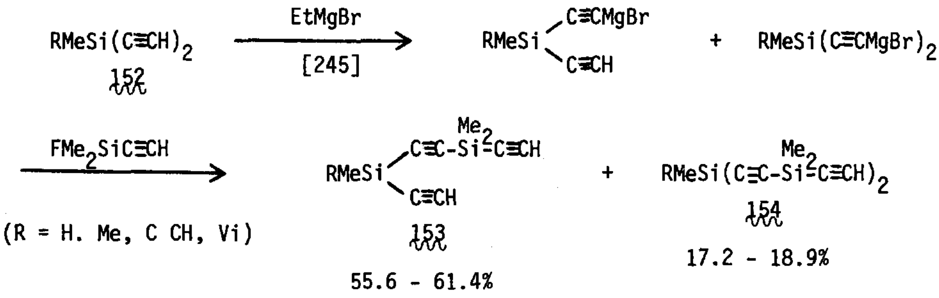
E^+ = MeOH (92%), MeOD (92%), MeI (78%), BuI (73%), $Me_2C=CHCH_2Br$ (74%), EtCHO (86%), Me_2CO (77%)

Silylethynyl organometallic reagents served as the source of several ethynylsilanes. Several silylethynyl Grignard reagents were reacted with trifluoro(chloromethyl)silane to give the bis adducts. One example is shown. (Eqn. 275) Bis-ethynylsilanes **152** were converted to mixtures of **153** and **154** as shown. (Eqn. 276) Trimethylsilylethynylmagnesium bromide was coupled to (E)-dichloroethylene to give both the (Z)- and (E)-products **155**, which could be separated. These served as precursors to the hexa-1,5-diyn-3-enes, which had to be maintained at low temperature. (Eqn. 277) Trimethylsilylethynyllithium was reacted with epoxides in the presence of trimethylgallium. (Eqn. 278)

This same reagent was Michael added to enone **156**. (Eqn. 279) Cerium reagents were used effectively to add to β-tetralones. (Eqn. 280) The chlorozinc reagent **157** reacted in a 1,3 manner with the propargyl chlorides **158** to give allenenyl systems. (Eqn. 281) The silylated ethynyltin reagents **159** and **160** were coupled with acid chlorides (Eqns. 282 and 283) or vinyl triflates (Eqn. 284).

$$\mathrm{TMSC{\equiv}CMgBr} + \mathrm{F_3SiCH_2Cl} \xrightarrow[\text{[244]}]{} \underset{65.8\%}{\mathrm{(TMSC{\equiv}C)_2SiFCH_2Cl}} \qquad (275)$$

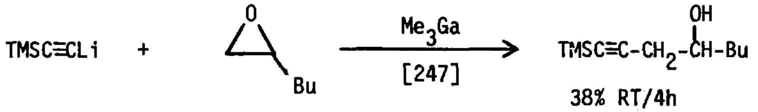
(other $\mathrm{R_3SiC{\equiv}CMgBr}$ used also with yields of 30.5 - 78.5%)



(276)

$$\mathrm{TMSC{\equiv}CMgBr} \xrightarrow[\substack{\mathrm{Cl_2Pd(dppp)} \\ \text{[246]}}]{\text{(E) ClCH=CHCl}} \text{(E) and (Z) } \underset{155}{\mathrm{TMSC{\equiv}C\text{-}CH{=}CH\text{-}C{\equiv}CTMS}} \qquad (277)$$

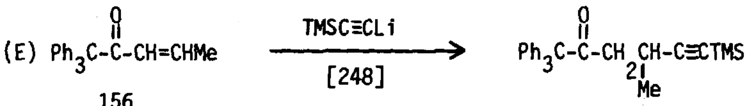
(dppp = $\mathrm{Ph_2P(CH_2)_3PPh_2}$)



(278)

38% RT/4h

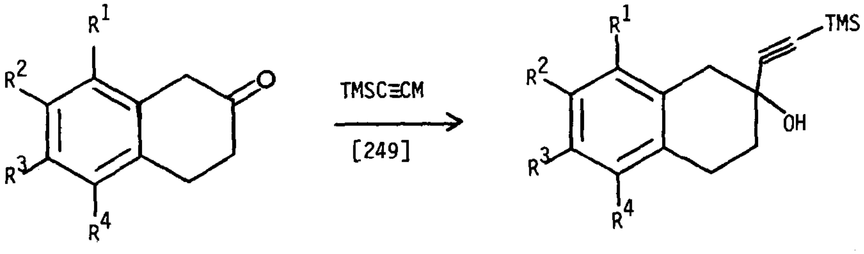
79% reflux/40 min



$$(E)\ Ph_3C\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH{=}CHMe \xrightarrow[\text{[248]}]{TMSC\equiv CLi} Ph_3C\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2\underset{Me}{\underset{|}{C}H}\text{-}C\equiv CTMS \qquad (279)$$

156

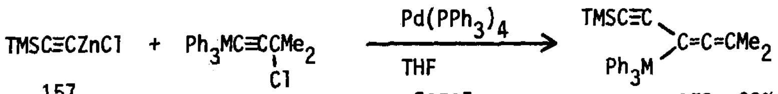
66%



(280)

[M = $CeCl_2$ or Ce as $(TMSC\equiv C)_3Ce$]

6 examples (55-100%)

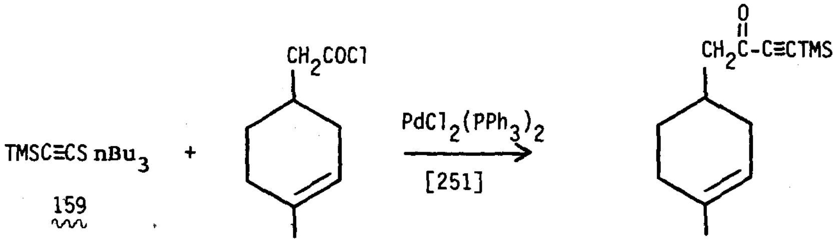


(281)

157

158 98%

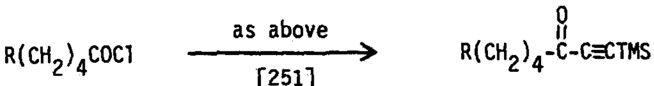
(M = Ge, Sn)



(282)

159

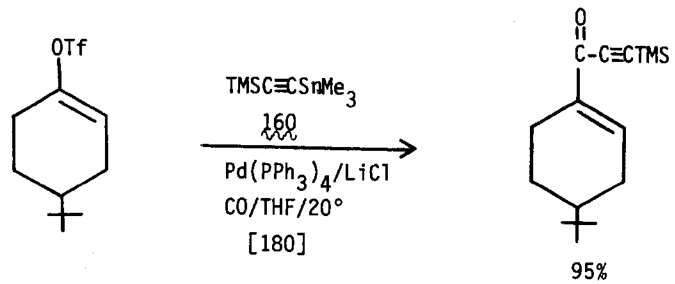
31%



$$R(CH_2)_4COCl \xrightarrow[\text{[251]}]{\text{as above}} R(CH_2)_4\text{-}\overset{O}{\overset{\|}{C}}\text{-}C\equiv CTMS \qquad (283)$$

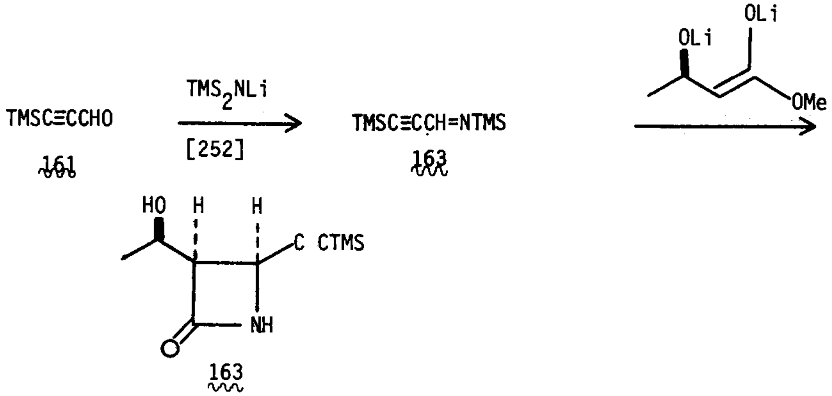
R = Vi 44%

R = Et 58%

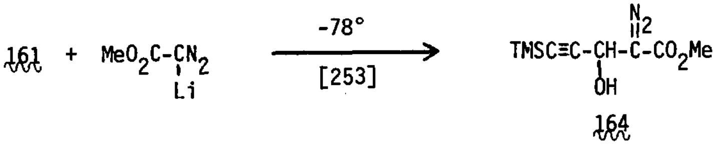


(284)

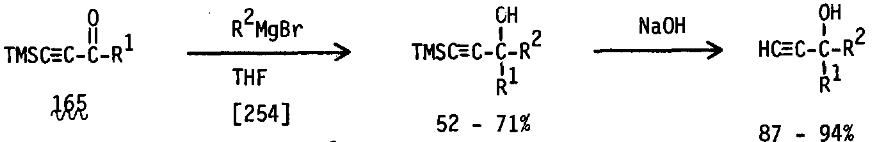
Reports of the reactions of some functionalized ethynylsilanes wherein the ethynylsilyl unit remains intact appeared. The aldeheyde **161** was converted to its silylated imine **162**, which was further converted to β-lactam **163**. (Eqn. 285) **161** was also converted to the remarkably functionalized **164**. (Eqn. 286) The related ketones **165** were reacted with Grignard reagents to give silylated propargyl alcohols and, after desilylation, propargyl alcohols. (Eqn. 287) The vinyl and ethynyl derivatives were converted to enynals. (Eqns. 288 and 289) In a related sequence arylated enynes were produced. (Eqn. 290) The trimethylsilylethynyl moiety proved to be an excellent dummy ligand for copper(I)-mediated Michael additions. Two examples are shown, both of which involve an active ethynylsilane reagent as well. (Eqns. 291 and 292)



(285)

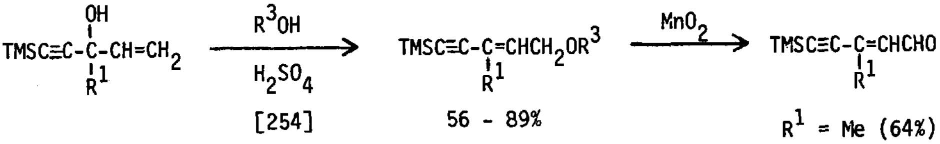


(286)



(287)

(R^1 = Me, Ph, p-MeC$_6$H$_4$; R^2 = Vi, CH C.



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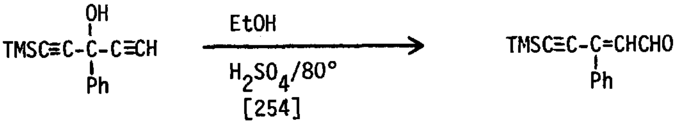

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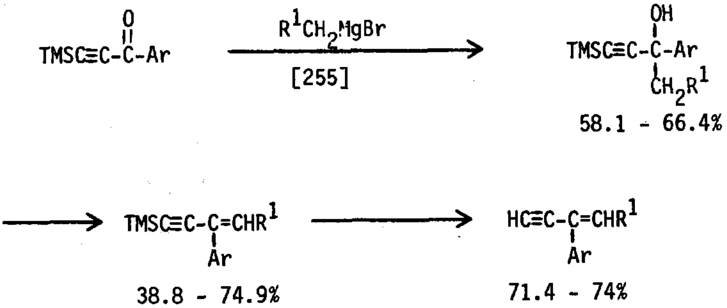
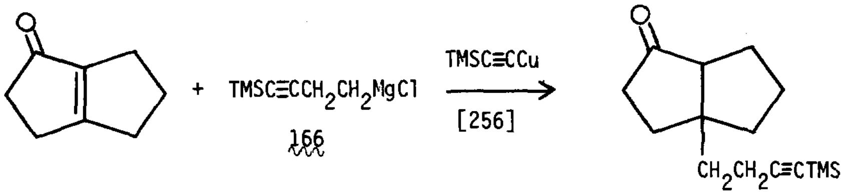
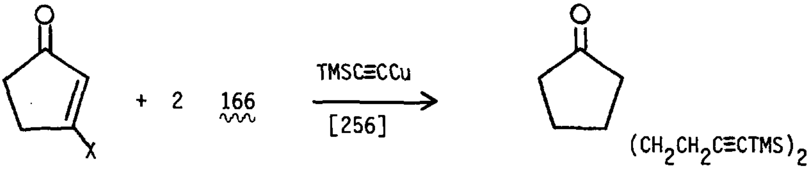


(290)

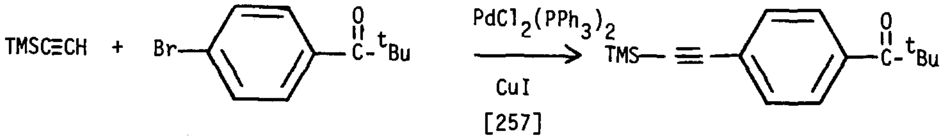


(291)

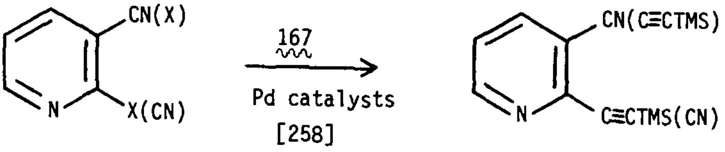


(292)

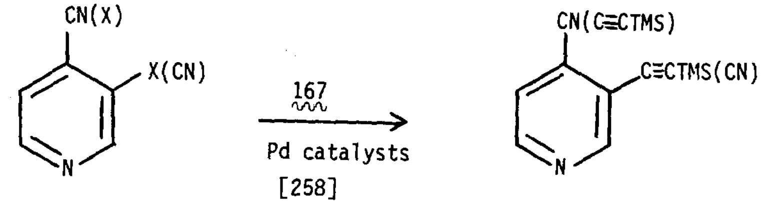
Some interesting and useful coupling reactions of ethynylsilanes and their derivatives were reported. Trimethylethynylsilane itself was coupled with aryl halides. (Eqns. 293-295) The reaction is regiospecific. Coupling of this material to vinyl chlorides in a sterospecific manner is also possible. (Eqns. 296 and 297) Trimethylsilylethynyl bromide was coupled to the Grignard reagentsof 9-iodocarboranes. (Eqn. 298) Silanes and terminal acetylenes were coupled under hydrosilylation conditions in the presence of iodine. (Eqn. 299)



(293)



(294)



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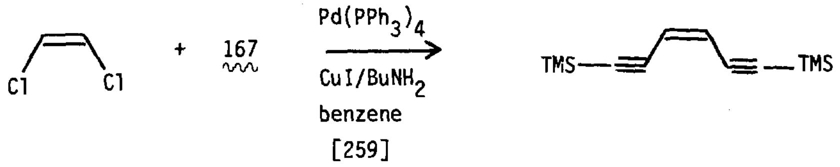

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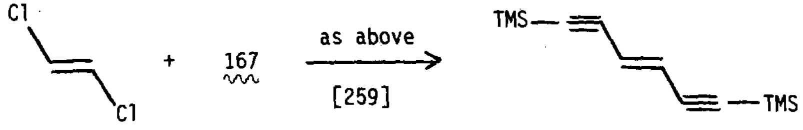


(297)

$$\text{o- and m-HCB}_{10}\text{H}_9\text{CH-9-MgI} \xrightarrow[\text{Pd(PPh}_3)_4 \; [260]]{\text{TMSC}\equiv\text{CBr}} \text{o- (or m-) HCB}_{10}\text{H}_9\text{-9-C}\equiv\text{CTMS} \quad (298)$$

$$R^1_2R^2SiH \; + \; R^3C\equiv CH \xrightarrow[I_2 \; [261]]{H_2PtCl_6} R^1_2R^2SiC\equiv CR^3 \quad (299)$$

34 - 96%

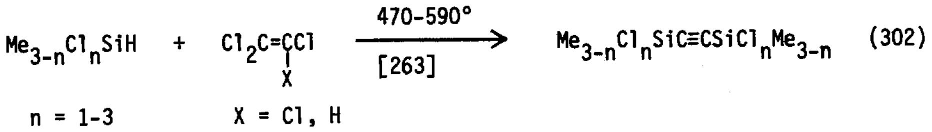
$R^1 = R^2 = Me, Et$; $R^1 = Me$, $R^2 = nC_5H_{11}, iC_5H_{11}, nC_6H_{13}$

$R^3 = Bu, Ph, TMS$

Some miscellaneous entries into ethynylsilanes are given. Sulfone **168** reacts with organolithium or organomagnesium reagents to give ethynylsilanes. (Eqn. 300) Bis(trimethylsilyl)-propynoate was prepared by decarboxylation of **169**. (Eqn. 301) Silanes were thermally reacted with tri- or tetrachloroethylene to give bis-silylacetylenes. (Eqn. 302)

$$\underset{\mathbf{168}}{\text{TMSC}\equiv\text{CSO}_2\text{Ph}} \xrightarrow[\text{or RMgX}\ [160]]{\text{RLi}} \text{TMSC}\equiv\text{CR} \qquad (300)$$

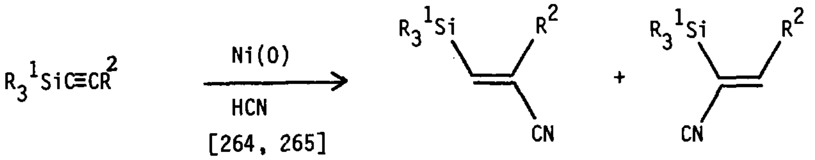
$$\underset{\mathbf{169}}{\text{TMSO}_2\text{CC}\equiv\text{CCO}_2\text{TMS}} \xrightarrow[66°\ [262]]{\text{Et}_3\text{N}} \text{TMSC}\equiv\text{CCO}_2\text{TMS} \qquad (301)$$



$$\underset{n\,=\,1\text{-}3}{\text{Me}_{3-n}\text{Cl}_n\text{SiH}} + \underset{X\,=\,\text{Cl, H}}{\text{Cl}_2\text{C}=\underset{\substack{|\\ \text{X}}}{\text{C}}\text{Cl}} \xrightarrow[[263]]{470\text{-}590°} \text{Me}_{3-n}\text{Cl}_n\text{SiC}\equiv\text{CSiCl}_n\text{Me}_{3-n} \qquad (302)$$

B. Reactions

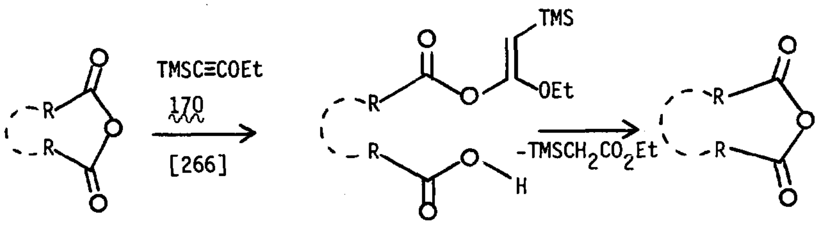
Additions to ethynylsilanes were reported. The addition of HCN catalyzed by Ni(0) was studied. (Eqn. 303) The α to β-cyanovinylsilane ratio depends in general on the steric requirements of the silyl group and the other substituent on the acetylene. The reaction of **170** with diacids gives acid anhydrides in nearly quantitative yields. (Eqn. 304) The reaction proceeds via addition product **171**. Specific examples are shown. (Eqns. 305 and 306) Trimethylsilylpropiolyl chloride reacts with indole and benzimidiazole to give the β-substituted-α, β-unsaturated amides **172** and **173**, respectively. (Eqns. 307 and 308) The reaction is fast. In the indole case desilylation does not occur.



(303)

Ni(0) = Ni[P(OPh)$_3$]$_4$; $R_3{}^1Si$ = Me$_3$Si, ^{t}BuMe$_2$Si, Ph$_3$Si

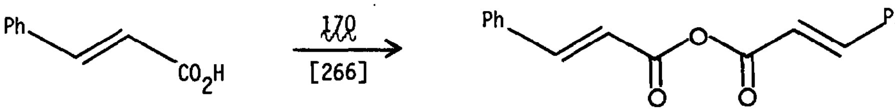
R^2 = H, Me, Bu, ^{t}Bu, Ph



171

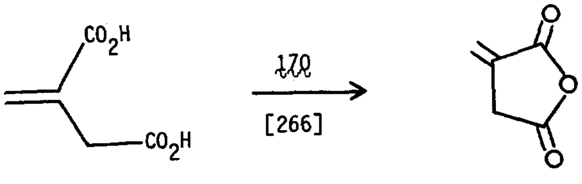
12 examples
(90-100%)

(304)



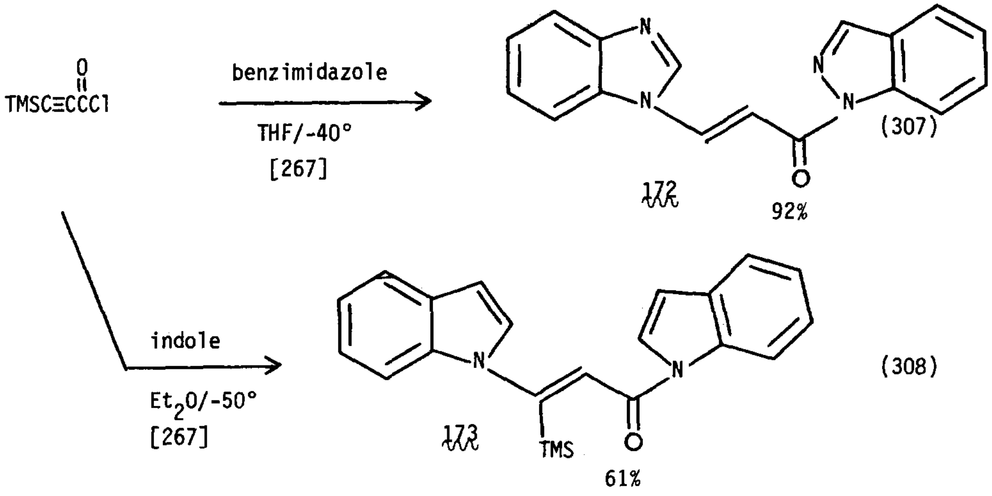
(305)

100%



(306)

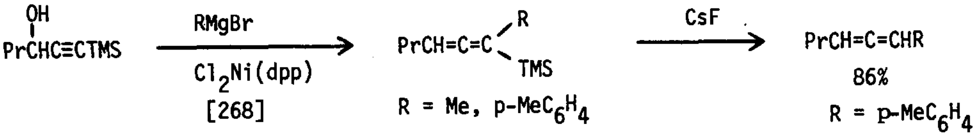
100%



(307)

(308)

Organometallics have been added to ethynylsilanes, other examples of which are to be found in the vinylsilane section. 1-Silylated propargyl alcohols add Grignard reagents in the presence of Ni(II) to give allenenylsilanes in excellent yield. These can be protiodesilylated to allenes. (Eqns. 309 and 310) Isopropylmagnesium bromide gives reduction. (Eqn. 311) Ethynylsilanes have been reacted with pentaborane to give trivinylboranes **173a** and nido-(TMS)RC$_2$B$_4$H$_6$ **173b**. (Eqns. 312 and 313) The trivinylborane **173a** can be prepared quantitatively via hydroboration of the ethynylsilane with borane-THF at 0^o. (Eqn. 314) Bis(trimethylsilyl)acetylene reacts to give nido (TMS)$_2$C$_2$B$_4$H$_6$, [TMSCH=C(TMS)]$_2$BH dimer and **173b**. (Eqn. 315) A crystal structure of **173b** was obtained. Hydroalumination of ethynylsilanes played a key role in the preparation of silylated cyclopentenes (Eqn. 316), when smaller and larger rings were not possible (Eqns. 317 and 318) and (+) 15 (S) pumiliotoxin A (Eqn. 319).



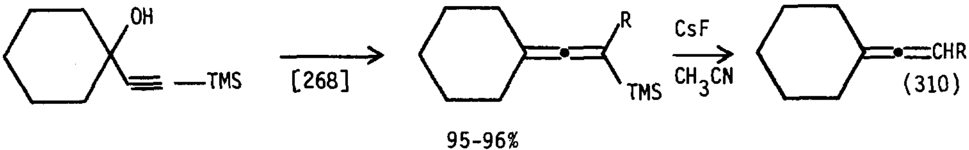
$$\overset{OH}{PrCHC}\equiv CTMS \xrightarrow[\substack{Cl_2Ni(dpp)\\ [268]}]{RMgBr} PrCH=C=C\begin{matrix}R\\ TMS\end{matrix} \xrightarrow{CsF} PrCH=C=CHR$$

R = Me, p-MeC_6H_4

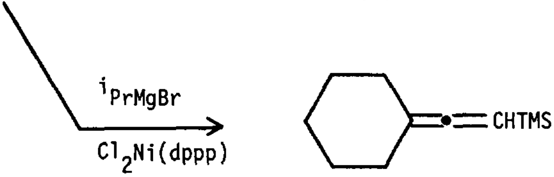
86%

R = p-MeC_6H_4

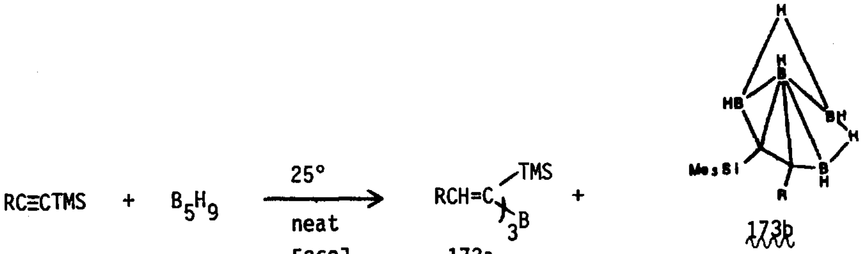
(309)



(310)



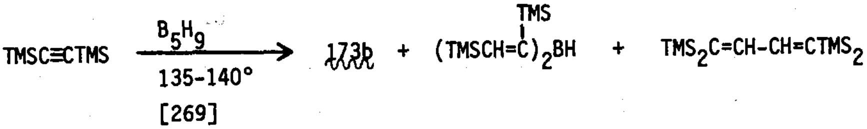
(311)



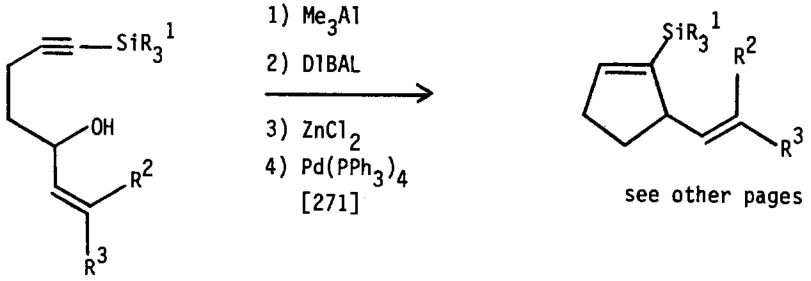
173a **173b** (312)

$$RC\equiv CTMS \quad + \quad B_5H_9 \xrightarrow[\substack{\text{sealed tube}\\ [269,\ 270]}]{135°} \mathbf{173a} \qquad (313)$$

$$RC\equiv CTMS \xrightarrow[[269]]{BH_3/THF/0°} \mathbf{173a} \qquad (314)$$



$$TMSC\equiv CTMS \xrightarrow[\substack{135\text{-}140°\\ [269]}]{B_5H_9} \mathbf{173b} + (TMSCH=\overset{TMS}{C})_2BH + TMS_2C=CH\text{-}CH=CTMS_2 \qquad (315)$$



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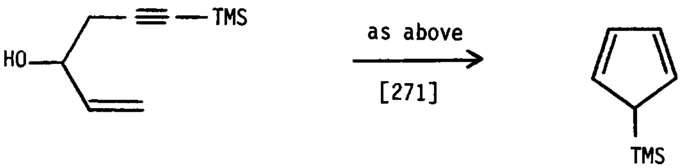

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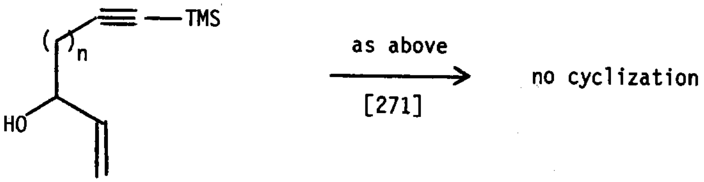
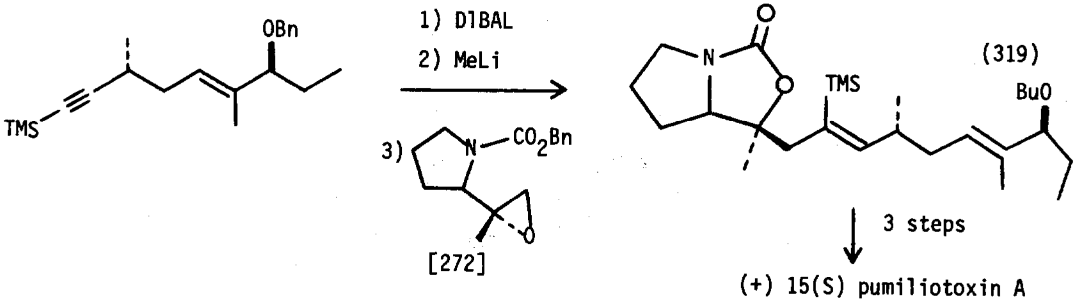
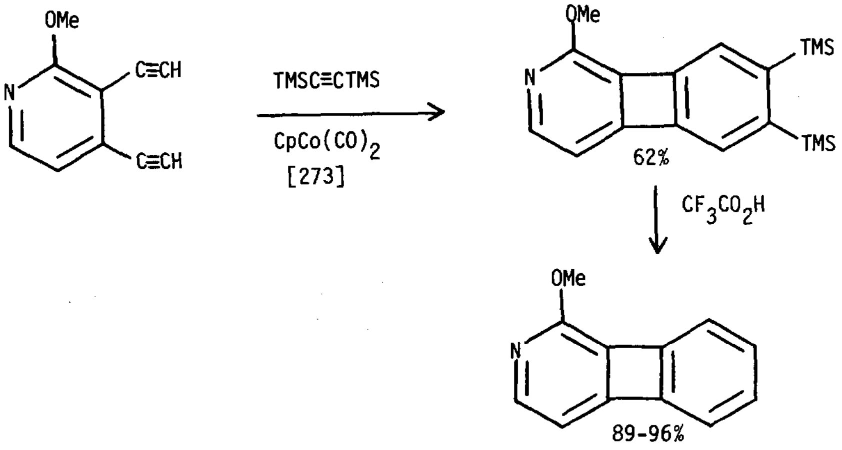


(318)



(319)

Several cyclizations of ethynylsilanes were reported during the year. Cobalt catalyzed processes continue to be useful. (Eqns. 320-322) (see also Eqn. 61 for another example of this).



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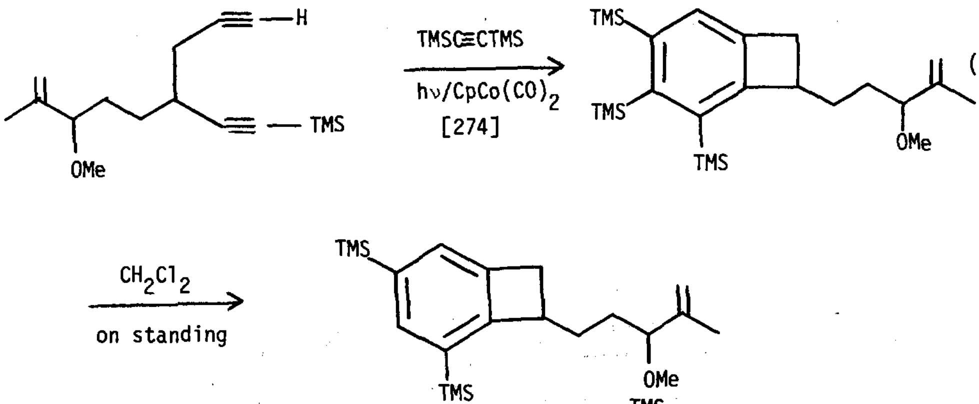
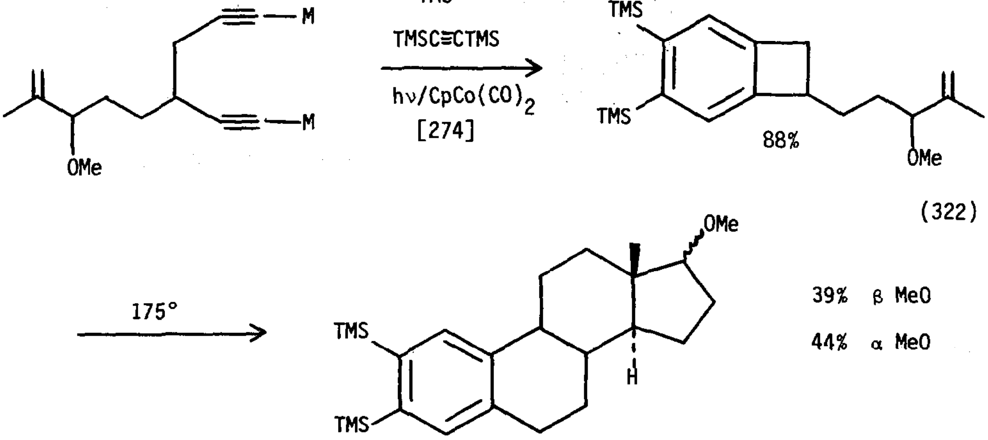
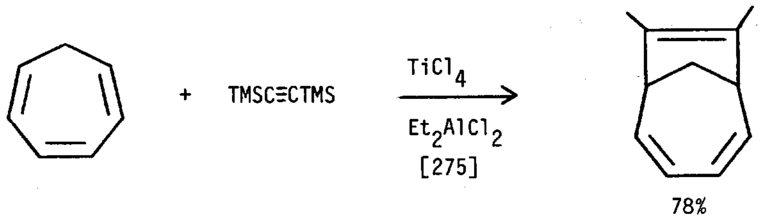


(321)

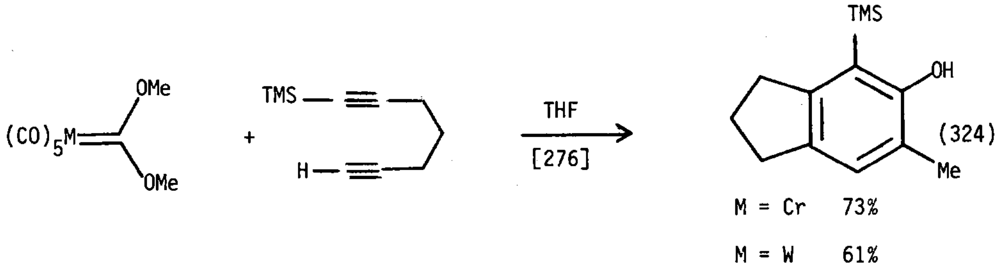


(322)

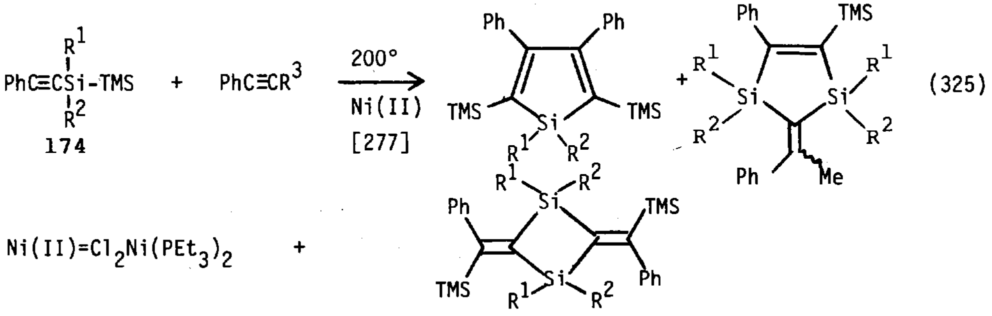
Bis-(trimethylsilyl)acetylene undergoes a 6 + 2 cycloaddition with cycloheptatriene in the presence of $TiCl_4$-Et_2AlCl. (Eqn. 323) Carbene chromium or tungsten complexes react with silylated diacetylenes to give benzene derivatives. (Eqn. 324)

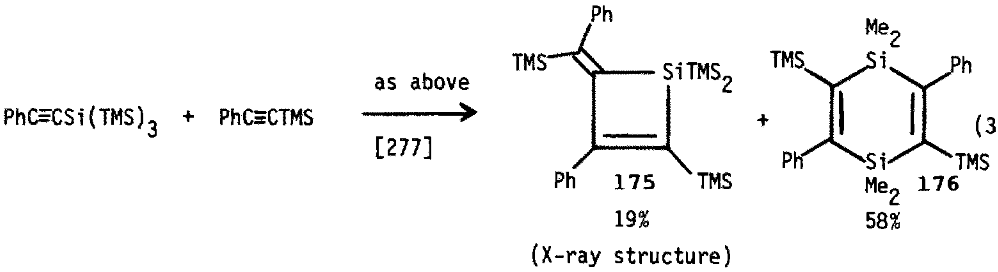


(323)



Several cyclic products were obtained from the thermal Ni(II) catalyzed reaction of compounds of the type **174** with acetylenes. (Eqns. 325 and 326)



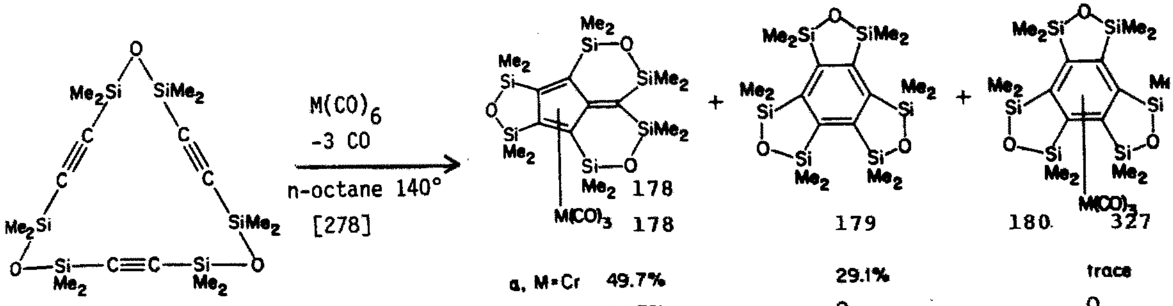


175 19% (X-ray structure)

176 58%

(326)

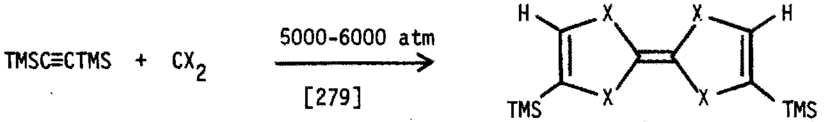
The cyclic triyne **177** when treated with group VI hexacarbonyls gives the cyclic products **178-180** in the yields shown. (Eqn. 327)



177 178 179 180 327

	178	179	180
a, M=Cr	49.7%	29.1%	trace
b, M=Mo	84.7%	0	0
c, M=W	18.1%	2.0%	0

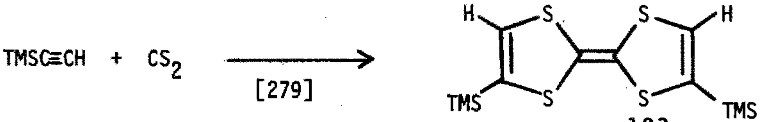
Bis(trimethylsilyl)acetylene and ethynyltrimethylsilane were reacted with carbon disulfide and carbon diselenide to give the thia- and selenafulvalenes **181-183**. (Eqns. 328 and 329)



X = S (65%); X = Se (20%)

181 182

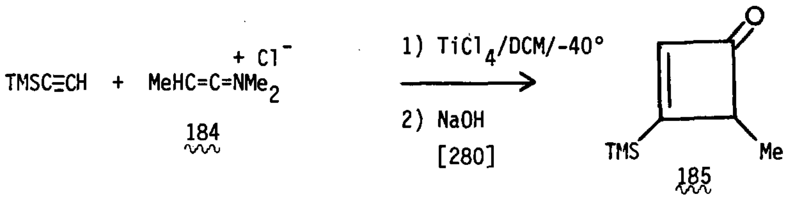
(328)



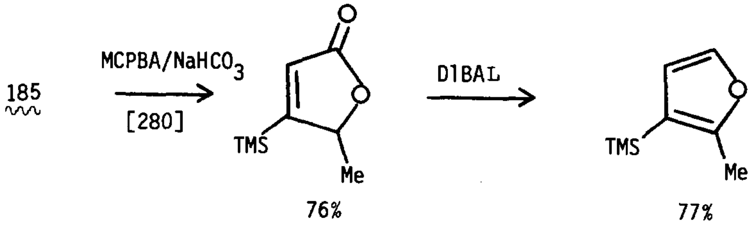
25% 183

(329)

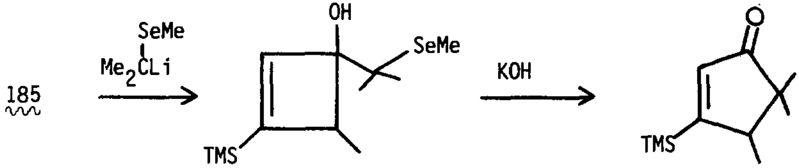
Ethynyltrimethylsilane was reacted with **184** to give silylated cyclobutenones. (Eqn. 330) These were converted to silylated furans (Eqn. 331) and silylated cyclopentenones (Eqn. 332).



(330)

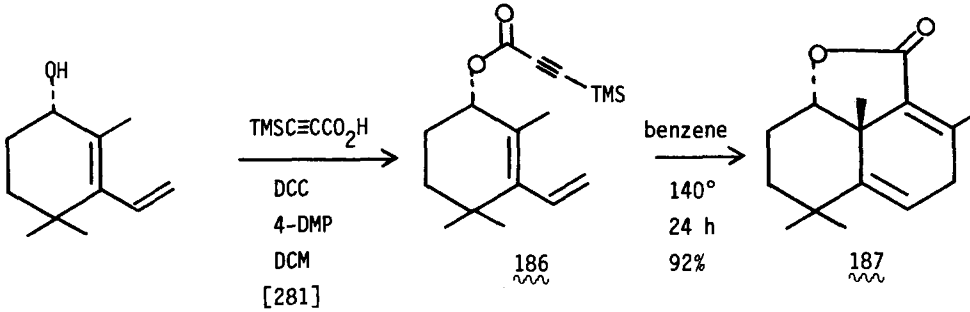


(331)



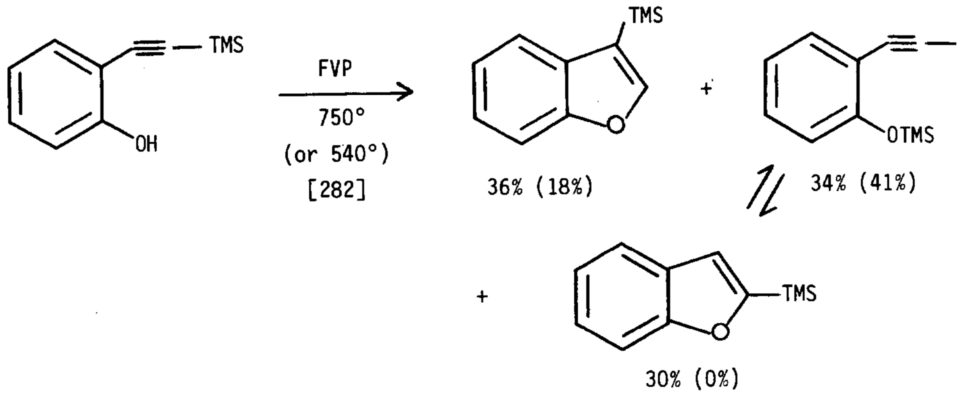
(332)

Trimethylsilylpropiolic acid was converted to ester **186**, which thermally gave an intramolecular Diels-Alder reaction to **187**. (Eqn. 333)

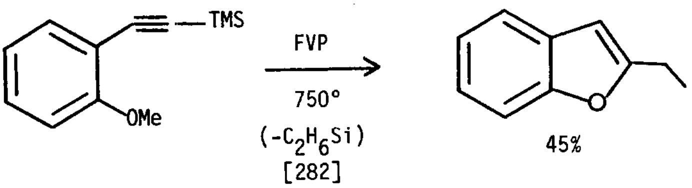


(333)

Ortho-trimethylsilylethynyl phenols were flash vacuum pyrolyzed to give silylbenzofurans. A number of systems were investigated in studying the mechanism. Only a representative sampling is shown here. (Eqns. 334 and 335)

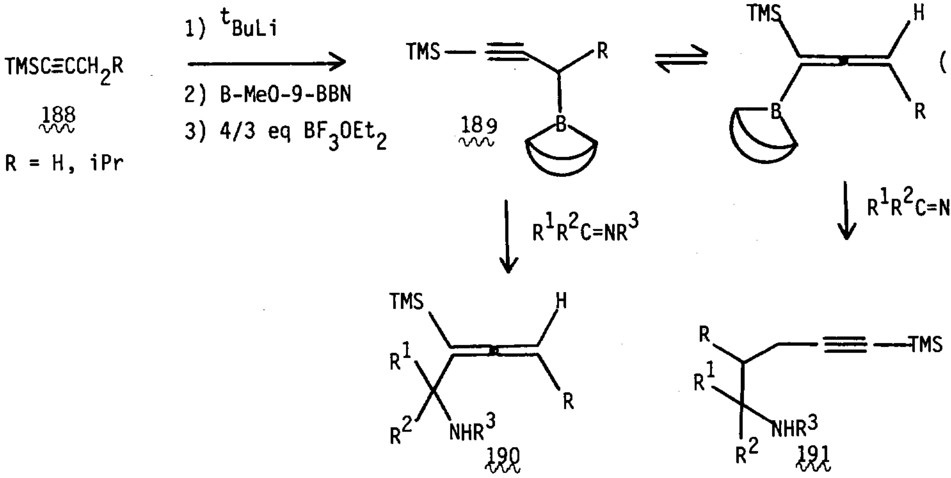


(334)

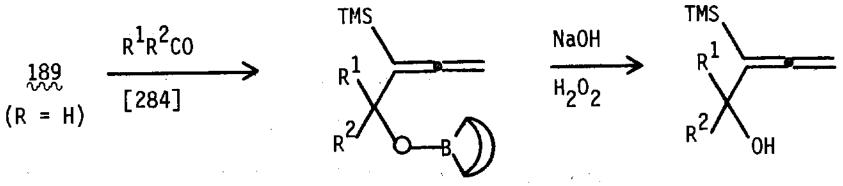


(335)

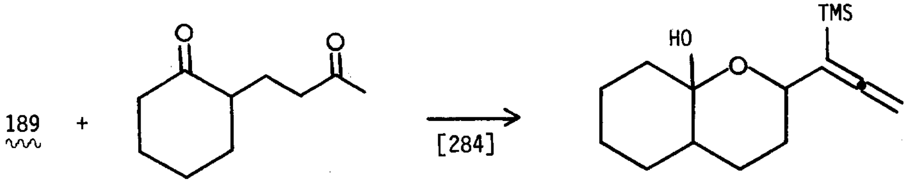
Some reactions of 3-metallo-1-trimethylsilyl alkynes were reported. Lithiation-borylation of 1-trimethylsilyl alkynes **188** provides the propargylborane **189**, which reacts with imines to give α-allenic **190** or β-acetylenic amines **191**. (Eqn. 336) This same system **189** (R = H) was reacted with aldehydes and ketones to give α-allenic alcohols. As shown below some aldehyde-ketone and even ketone-ketone and ketone-ester selectivity is possible with this reagent. (Eqns. 337-340) 1-Trimethylsilyl-3-iodopropyne was reacted with tin in the presence of aluminum and the resulting organometallic reacted with aldehydes. The α-allenic to β-acetylenic alcohol ratio is very solvent dependent. (Eqn. 341)



(336)

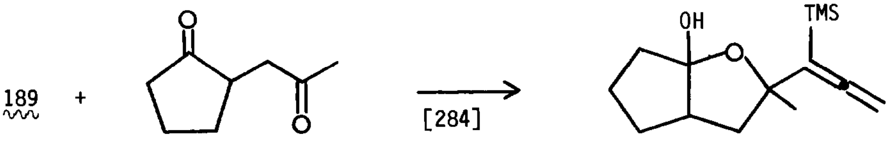


(337)

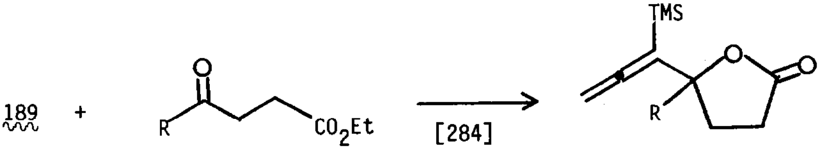


(338)

86%



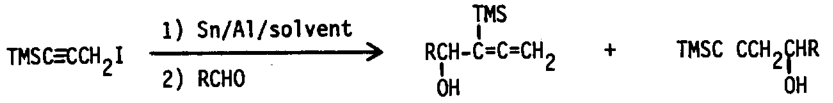
(339)



(340)

R = Me (95%)

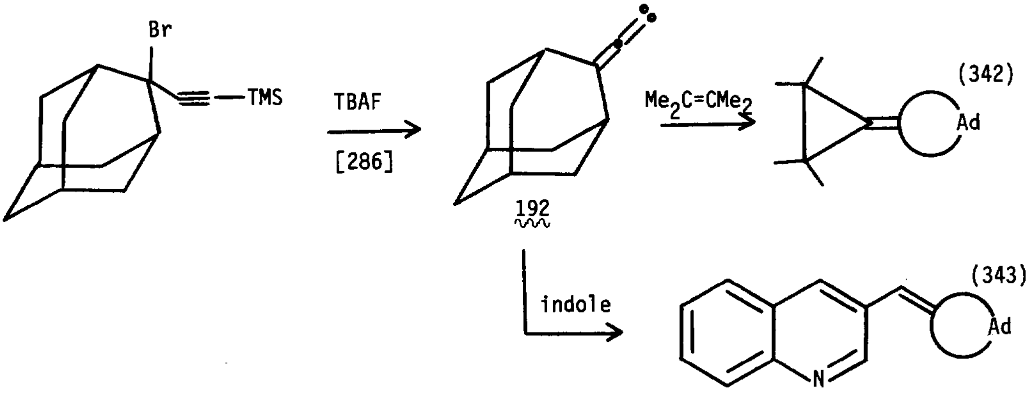
R = Ph (79%)



$$\mathrm{TMSC{\equiv}CCH_2I} \xrightarrow[\text{2) RCHO}]{\text{1) Sn/Al/solvent}} \underset{\mathrm{OH}}{\mathrm{RCH}}\text{-}\overset{\mathrm{TMS}}{\mathrm{C}}\mathrm{=C=CH_2} + \mathrm{TMSC\ CCH_2}\underset{\mathrm{OH}}{\mathrm{CHR}} \qquad (341)$$

R	solvent	%	%	% Yield
$^nC_6H_{13}$	CH_3CN/DMSO	95	5	88
Ph	"	90	10	88
(E) MeCH=CH	"	92	8	60
H		100	0	79
$^nC_6H_{13}$	Diglyme	8	92	75
Ph	"	11	89	69
(E) MeCH=CH	"	9	91	64
H	"	95	5	53

Some miscellaneous reactions of ethynylsilanes are given below. The vinylidene carbene **192** was formed and trapped as shown in equations 342 and 343. An ethynylsilane was cross coupled with 1-azidoadamantane. (Eqn. 344) Ethynyltrimethylsilane reacts with [hydroxy(tosyloxy)iodo] benzene to give **193**. (Eqn. 345)



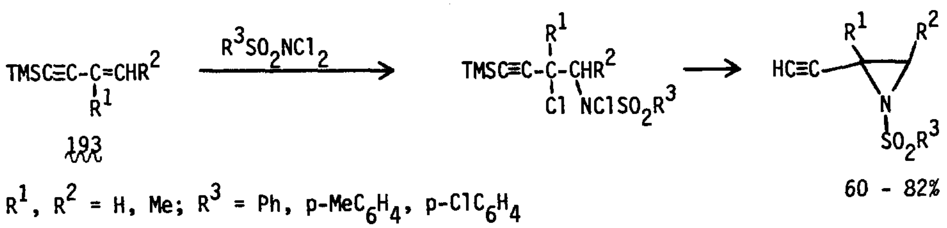
(342)

(343)

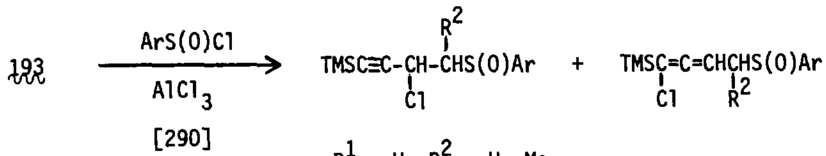
$$\text{1-Ad-N}_3 \quad + \quad \text{PhC}{\equiv}\text{C-TMS} \xrightarrow[\text{[287]}]{\mathrm{AlCl_3}} \text{1-Ad-C}{\equiv}\text{C-Ph} \qquad (344)$$

$$\mathrm{TMSC{\equiv}CH} + \mathrm{PhI(OH)OTs} \xrightarrow[\text{[288]}]{\mathrm{CHCl_3}} \underset{\textbf{193}\ \ 22\%}{\mathrm{TsOCH{=}CHPhIOTs}} \qquad (345)$$

Three papers dealt with additions to 1-trimethylsilyl vinylacetylenes. These additions occur predominantly, though not exclusively, at the double bond and not the triple bond. (Eqns. 346-350) (see Eqns. 390 and 391 for other similar examples)


(346)

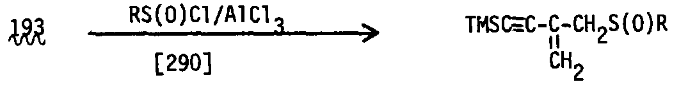
R^1, R^2 = H, Me; R^3 = Ph, p-MeC_6H_4, p-ClC_6H_4


(347)

$$\underset{\textbf{193}}{} \xrightarrow[\substack{\mathrm{AlCl_3}\\ \text{[290]}}]{\mathrm{ArS(O)Cl}} \mathrm{TMSC{\equiv}C\text{-}\underset{Cl}{CH}\text{-}\overset{R^2}{C}HS(O)Ar} + \mathrm{TMS\underset{Cl}{C}{=}C{=}CH\underset{R^2}{C}HS(O)Ar}$$

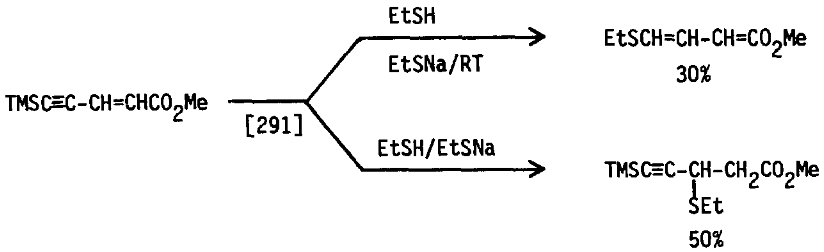
R^1 = H; R^2 = H, Me

Ar = p-XC_6H_4 X = H, Me, Cl


(348)

$$\textbf{193} \xrightarrow[\text{[290]}]{\mathrm{RS(O)Cl/AlCl_3}} \mathrm{TMSC{\equiv}C\text{-}\underset{\underset{CH_2}{\|}}{C}\text{-}CH_2S(O)R}$$

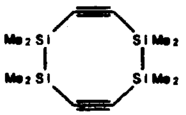
R = Me, Ph, p-ClC_6H_4,p-MeC_6H_4



$$\mathrm{TMSC{\equiv}C\text{-}CH{=}CHCO_2Me} \xrightarrow[\text{[291]}]{} \begin{cases} \xrightarrow[\mathrm{EtSNa/RT}]{\mathrm{EtSH}} \underset{30\%}{\mathrm{EtSCH{=}CH\text{-}CH{=}CO_2Me}} & (349) \\ \xrightarrow{\mathrm{EtSH/EtSNa}} \underset{50\%}{\mathrm{TMSC{\equiv}C\text{-}\underset{SEt}{CH}\text{-}CH_2CO_2Me}} & (350) \end{cases}$$

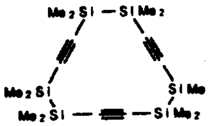
C. Other Studies

The thermal decomposition of ethynylsilane has been studied in detail. [292] The electronic effects of substituents on ethynylsilanes were investigated by IR, ^{1}H NMR, UV spectroscopy and by MO calculations. A mesomeric effect is argued. [243] The photoelectron (PE) spectra of cyclic ethynylsilanes **194-196** were carried out and the results compared with those of MINDO/3 and MNDO calculations. [294]



194

195

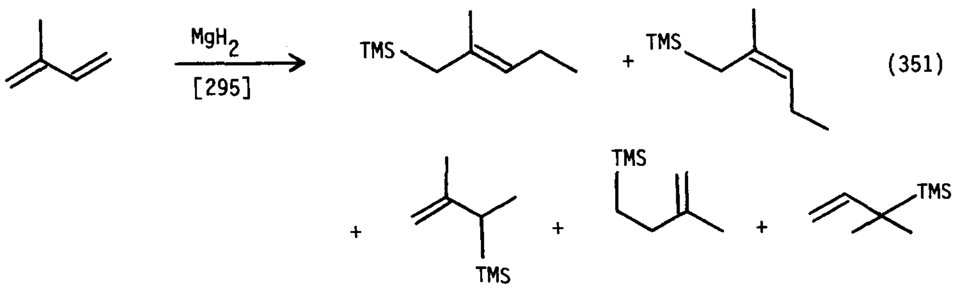


196

IX. ALLYLSILANES.

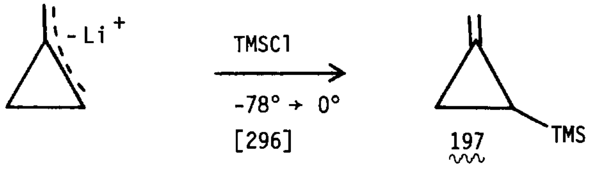
A. Preparation

The reaction of allylmetallic reagents with chlorosilanes provided the entry into several allylsilanes. Isoprene was reacted with magnesium hydride "in situ" and the resulting organomagnesium product treated with trimethylchlorosilane. This gave oligomers, four allylsilane isomers and one homoallylsilane. (Eqn. 351) Styrene was reacted in a similar manner.

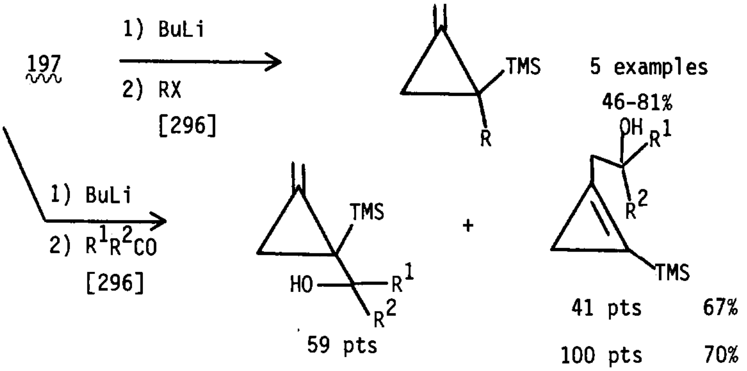


(351)

Methylenecyclopropane can be lithiated and silylated (Eqn. 352) The product, 2-(trimethylsilyl)methylenecyclopropane, can itself be lithiated and this species reacted with electrophiles. (Eqns. 353 and 354)



(352)



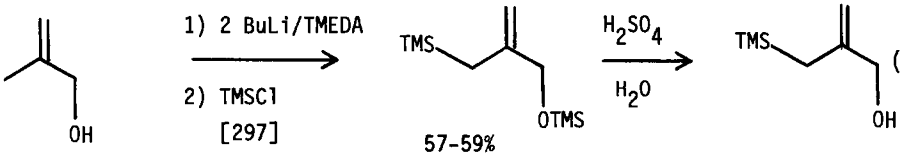
(353)

(354)

$R^1 = R^2 = Me$

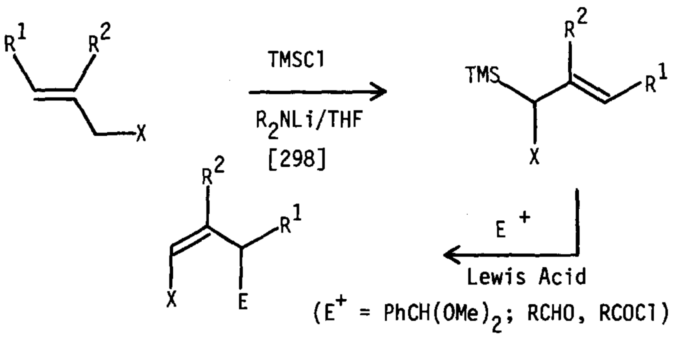
$R^1 = H; R^2 = Ph$

The dianion of 2-methyl-2-propen-1-ol doubly silylates. Hydrolysis of the OTMS group gives 2-(trimethylsilyl)-2-propen-1-ol. (Eqn. 355)



(355)

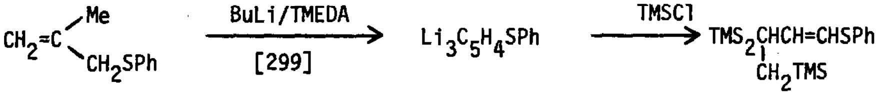
Allyl chlorides and bromides can be converted to allylsilanes in an "in situ" procedure. (Eqn. 356) These were used in allylation reactions. (Eqn. 357)



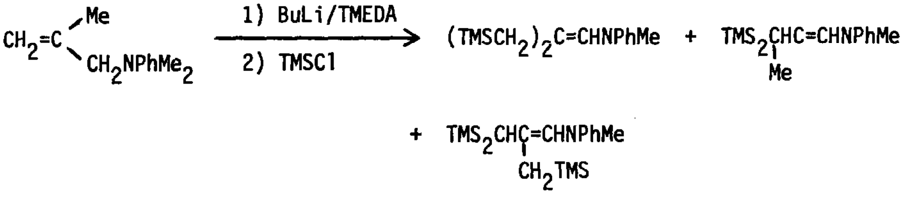
(356)

(357)

Phenylmethallyl sulfide can be deprotonated and silylated (Eqn. 358) as can phenylmethylmethallyl amine (Eqn. 359).



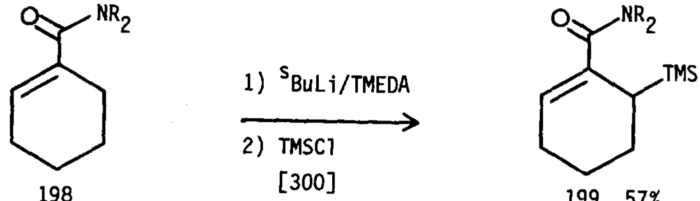
$$CH_2{=}C\begin{smallmatrix}Me\\CH_2SPh\end{smallmatrix} \xrightarrow[\text{[299]}]{\text{BuLi/TMEDA}} Li_3C_5H_4SPh \xrightarrow{\text{TMSCl}} TMS_2\underset{CH_2TMS}{C}HCH{=}CHSPh \qquad (358)$$



$$CH_2{=}C\begin{smallmatrix}Me\\CH_2NPhMe_2\end{smallmatrix} \xrightarrow[\text{2) TMSCl}]{\text{1) BuLi/TMEDA}} (TMSCH_2)_2C{=}CHNPhMe + TMS_2\underset{Me}{C}HC{=}CHNPhMe \qquad (359)$$

$$+ \; TMS_2CH\underset{CH_2TMS}{C}{=}CHNPhMe$$

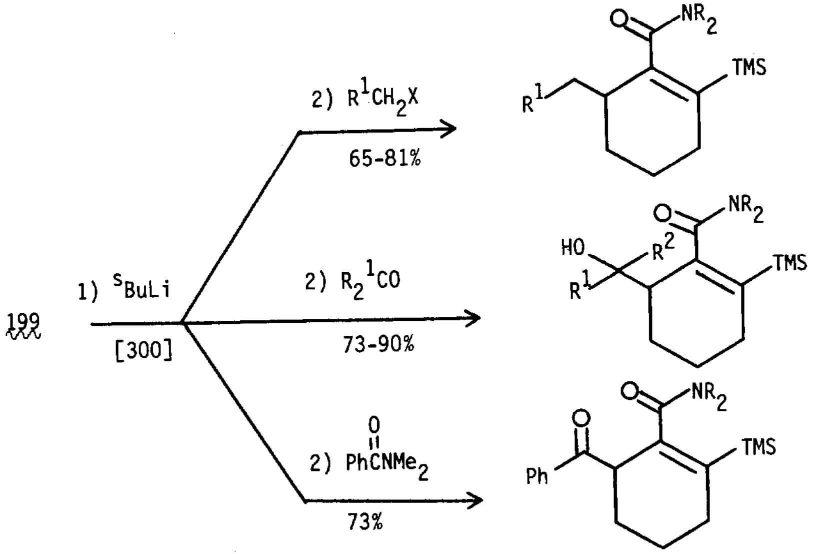
Lithiation-silylation of **198** gave **199** (Eqn. 360), which could also be lithiated and reacted with electrophiles. (Eqns. 360-364)



198
(R = iPr)

199 57%

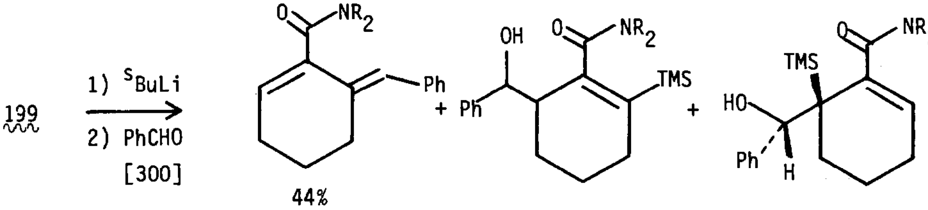
(360)



(361)

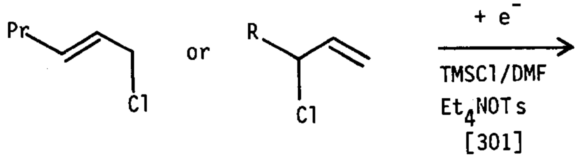
(362)

(363)

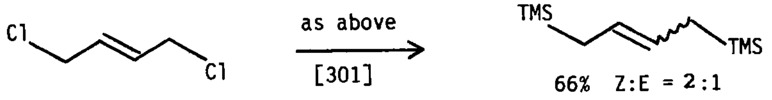


(364)

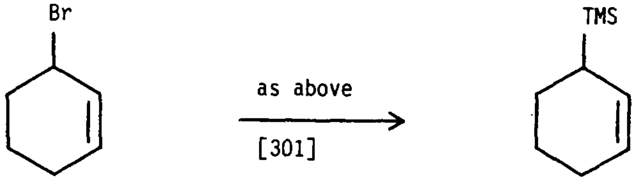
Allyl chlorides were reduced electrochemically in the presence of trimethylchlorosilane to give allylsilanes. (Eqns. 365-367)



(365)

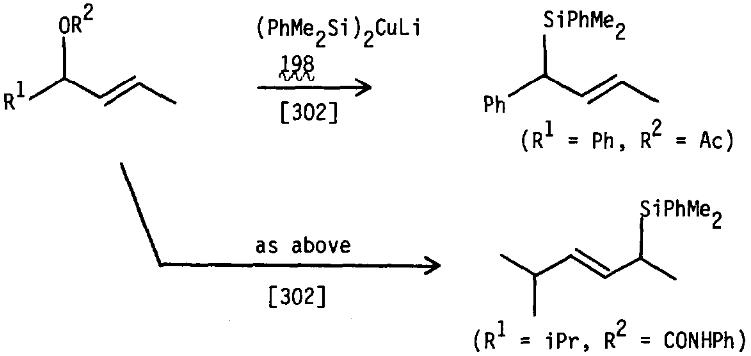


(366)



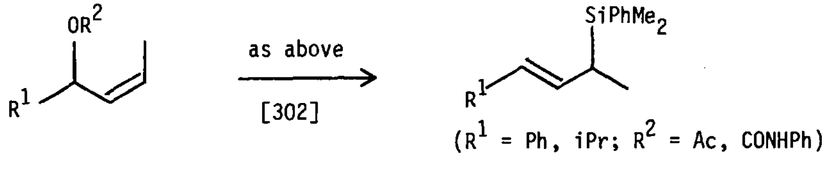
(367)

The addition of lithium disilylcuprates **199a** to allyl acetates and related systems gives allylsilanes. (Eqns. 368-373) The regiochemistry of the product depends on the starting material. Further examples are shown in equations 374-376. Allylsilanes were also prepared by the reaction of **199a** with α,β -unsaturated esters and then reduction-elimination. (Eqns. 377 and 378)

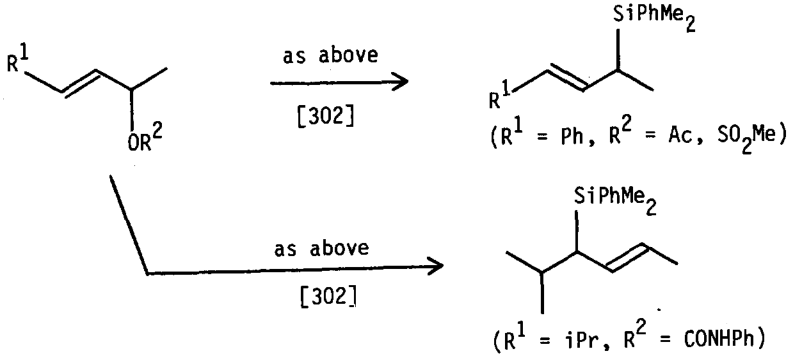


(368)

(369)

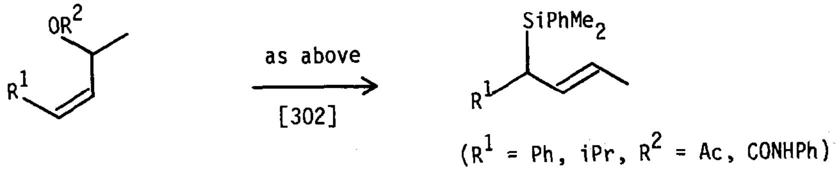


(370)

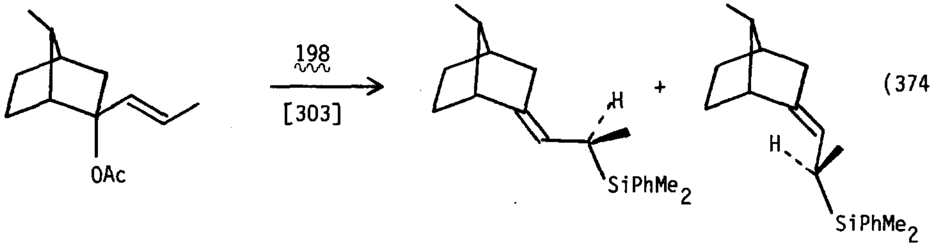


(371)

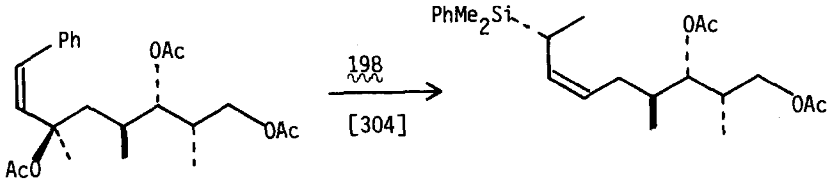
(372)



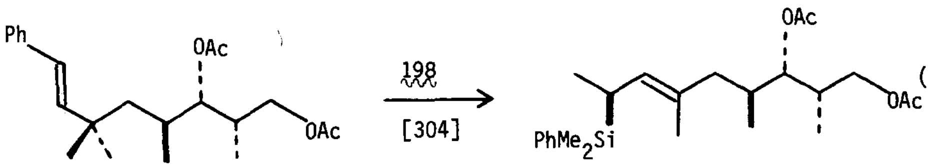
(373)



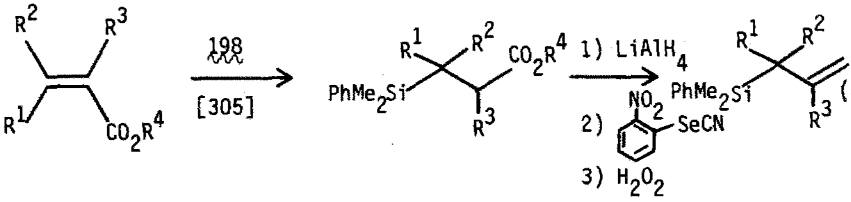
(374)



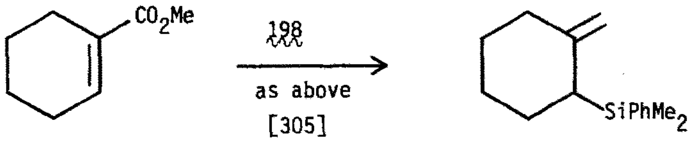
(375)



(376)

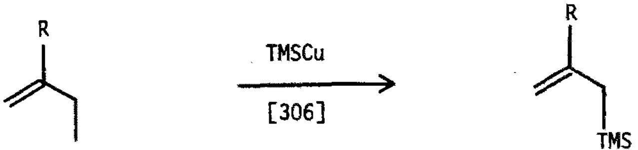


(377



(378)

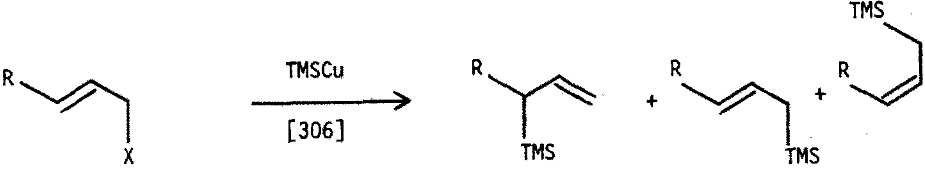
The reaction of trimethylsilyllithium and trimethylsilylcopper with allyl halides, tosylates or mesylates was studied as entries into allylsilanes. Examples are shown below. (Eqns. 379-383)



(379)

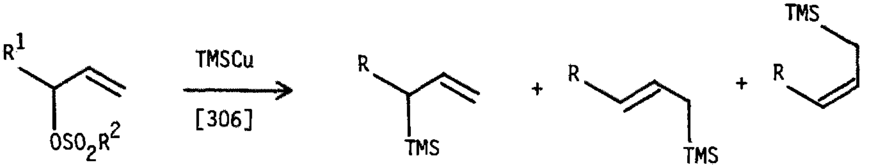
R = H, Br, Cl; X = Br, Cl

4 examples 45-90%
(TMSLi/HMPA gave 0-7%)



(380)

major product

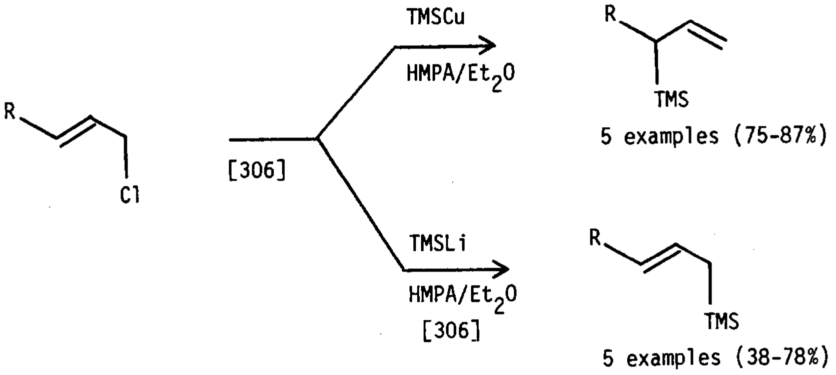


(381)

R^1 = n-alkyl, c-C_6H_{11}
R^2 = Me, p-MeC_6H_4

major product
R^1 = cC_6H_{11}

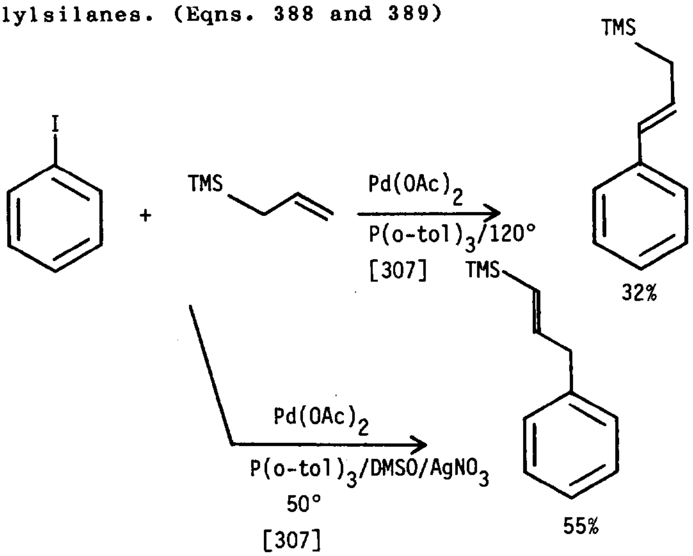
major product
R^1 = n-alkyl



(382)

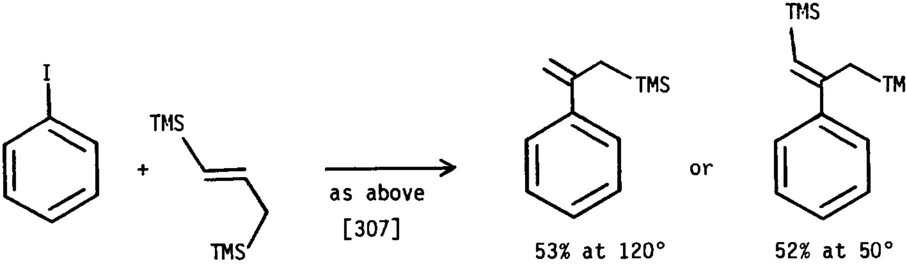
(383)

Allylsilanes can be cross-coupled to aryl iodides to give new allylsilanes. (Eqns. 384-387) Vinylsilanes can also be produced under similar conditions. (Eqn. 386) The metathesis of allylsilanes containing aromatic substitutents gives new allylsilanes. (Eqns. 388 and 389)

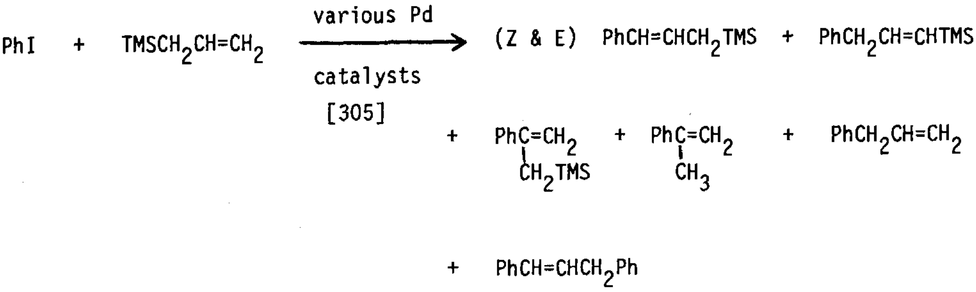


(384)

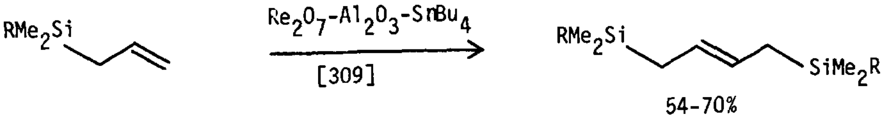
(385)



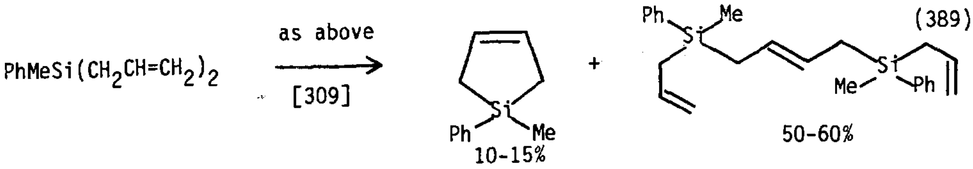
(386)



$$PhI + TMSCH_2CH{=}CH_2 \xrightarrow[\text{catalysts [305]}]{\text{various Pd}} (Z\ \&\ E)\ PhCH{=}CHCH_2TMS + PhCH_2CH{=}CHTMS + \underset{CH_2TMS}{PhC{=}CH_2} + \underset{CH_3}{PhC{=}CH_2} + PhCH_2CH{=}CH_2 + PhCH{=}CHCH_2Ph \quad (387)$$



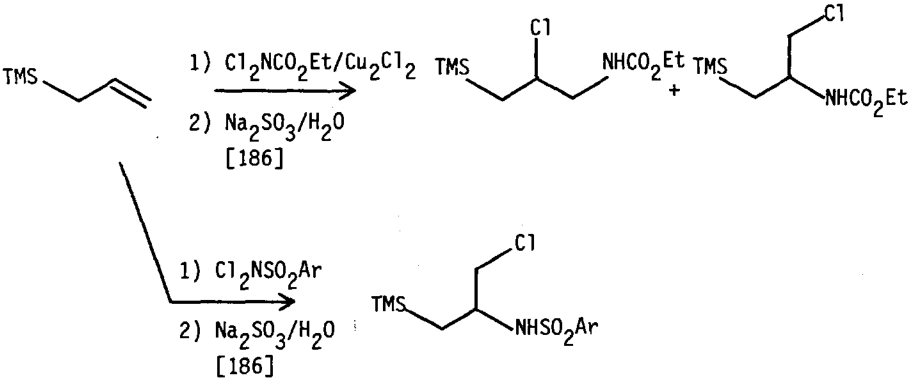
(388)



(389)

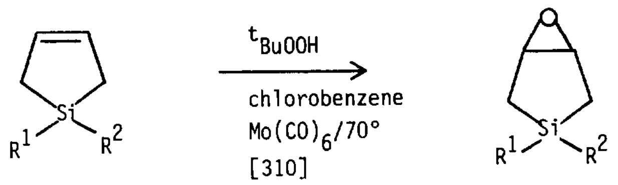
B. Reactions.

Two addition reactions to allylsilanes are reported here. The addition of the N-Cl bond was studied. (Eqns. 390 and 391) the epoxidation of 1-silacyclopent-3-enes was reported. (Eqn. 392)



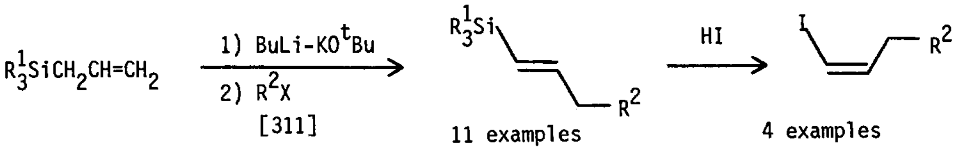
(390)

(391)



(392)

Anions of allylsilanes provided interesting and useful products as shown in the examples below. Allyltrimethylsilane itself provides vinylsilanes with the butyllithium-potassium-tert-butoxide reagent. These were converted to vinyl iodides. (Eqn. 393) The titanated reagent of **199a** reacts with aldehydes to give the Peterson olefination product. (Eqn. 394) Lithiation of **201** produces a reagent that gives mostly γ-attack with benzaldehyde, but α-attack and therefore Peterson olefination when titanated first. (Eqn. 396) These Peterson olefination products give enones upon hydrolysis.

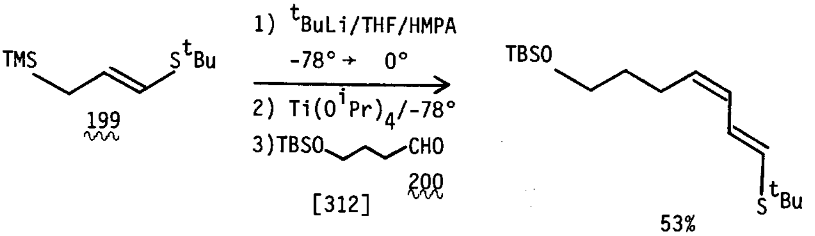


(393)

11 examples

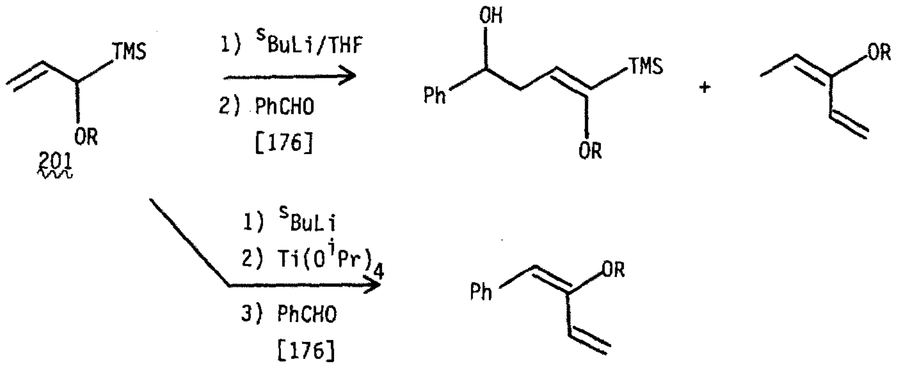
4 examples
83 - 96%

R^1	γ:α ratio
Me	4:1 → 9:1
Et	16:1 → 22:1
Pr	36:1 → 41:1
Ph	16:1 where R^2 = Pr



(394)

53%

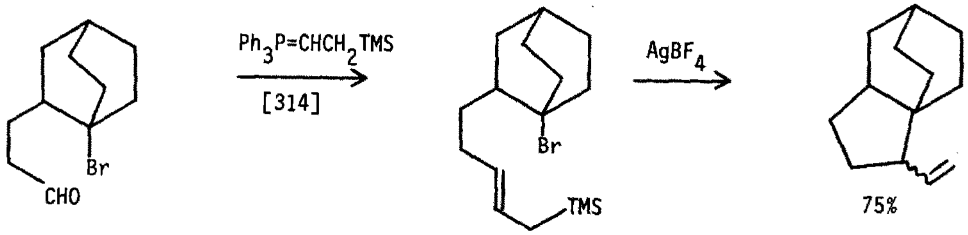


(395)

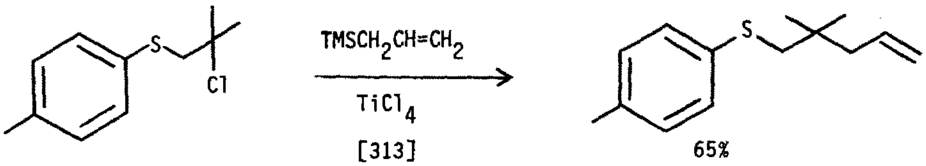
(396)

R = EE 83% (14 other examples 0-96%)

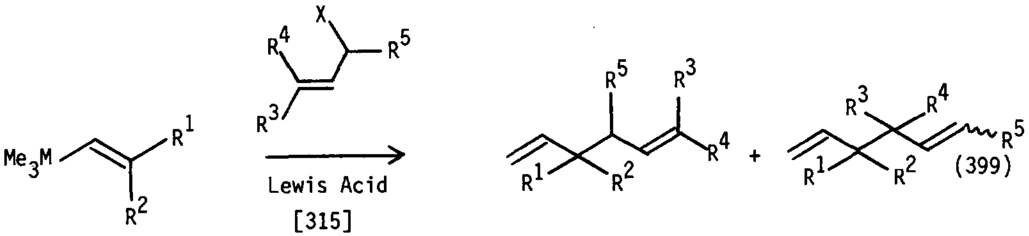
Electrophilic allylations employing allylsilanes continued to be an active area of research as well as applications. The allylation of tertiary halides was reported by two groups. (Eqns. 397 and 398) The synthesis of 1,5-hexadienes via allylsilane allylation of allyl halides and ethers was accomplished according to the general equation 399. Specific examples are given in equations 400 and 401. Allyltrimethyltin also was used successfully in these allylations.



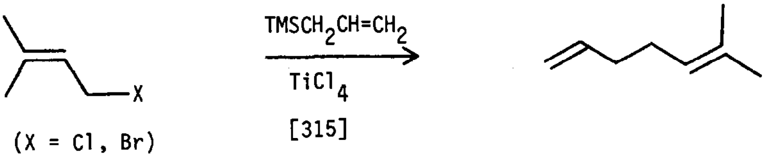
(398



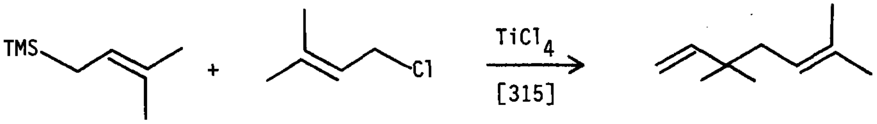
(397)



(399)

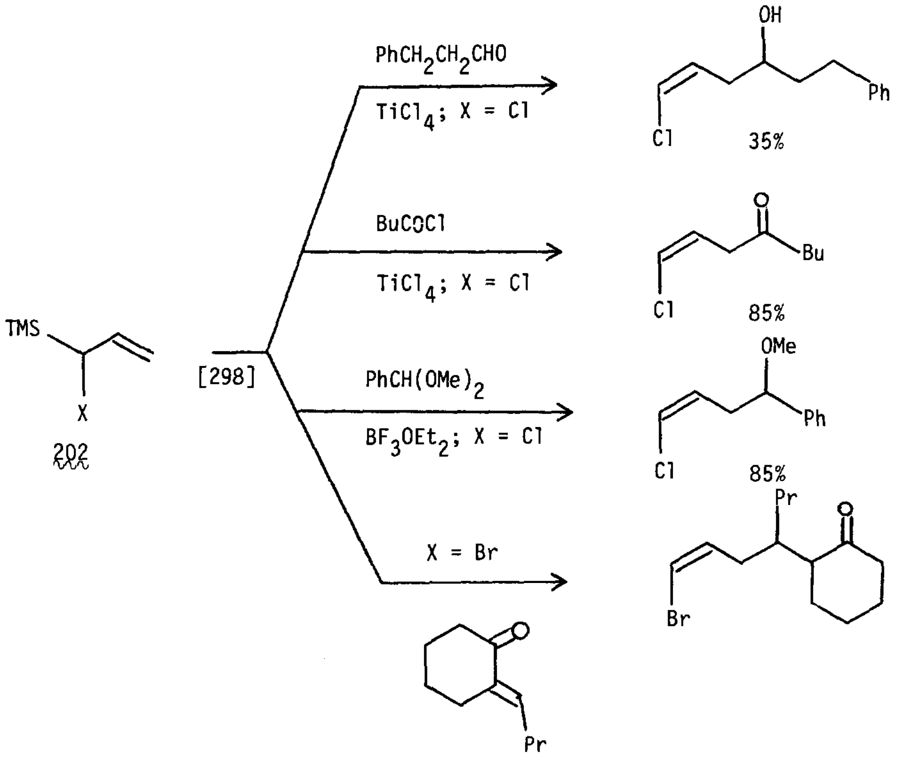


(400)



(401)

The allylation of aldehydes under Lewis acid catalysis was reported. The reactions of the α-functionalized allylsilanes **202** with aldehydes, (Eqn. 402) acid chlorides (Eqn. 403), acetals (Eqn. 404) and enones (Eqn. 405) were carried out. α-Benzyloxy aldehydes were allylated stereospecifically in the presence of gaseous boron fluoride. (Eqn. 406) The aldehyde **203** was allylated to give predominantly the erythro isomer **204**. (Eqn. 407) The allylation of aldehydes with dialkoxytitanium dichlorides were shown to give homoallylic ethers. (Eqn. 408) Good to excellent diastereoselectivity in the allylation of aldehydes was accomplished in this process using the chiral dialkyoxytitanium dichloride catalyst formed from two equivalents of (S) lithium 1-phenylethoxide and titanium tetrachloride. (Eqn. 409) Optically active (S) **205** was converted to optically active **206** as shown with a key step being the intramolecular allylation of the aldehyde. (Eqn. 410)

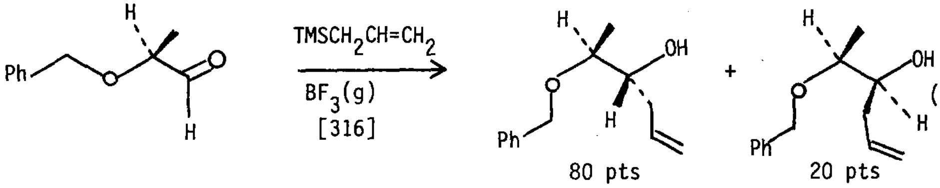


(402)

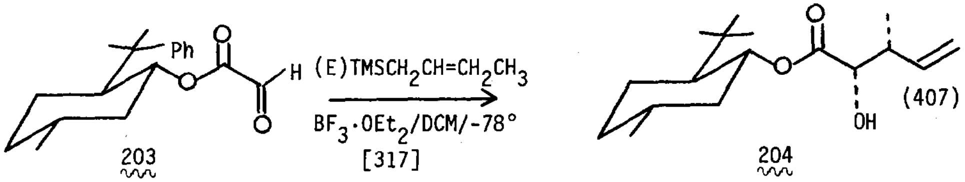
(403)

(404)

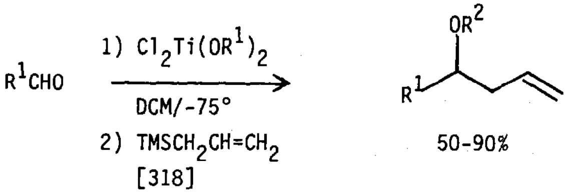
(405)



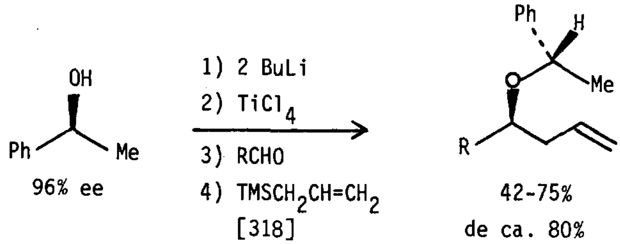
(406)



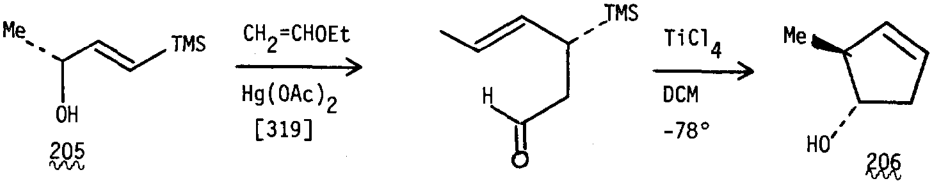
(407)



(408)

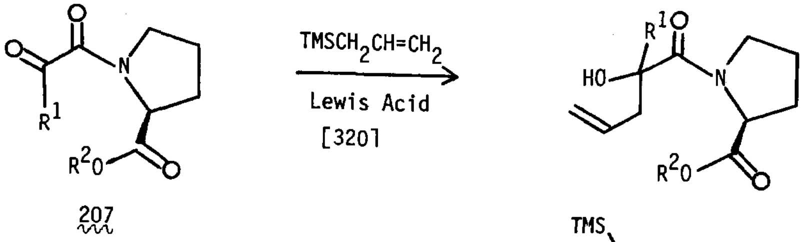


(409)

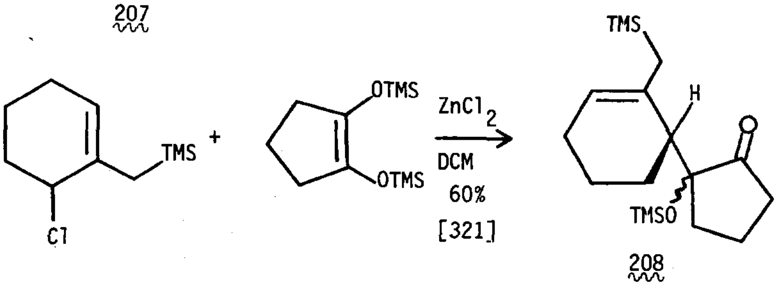


(410)

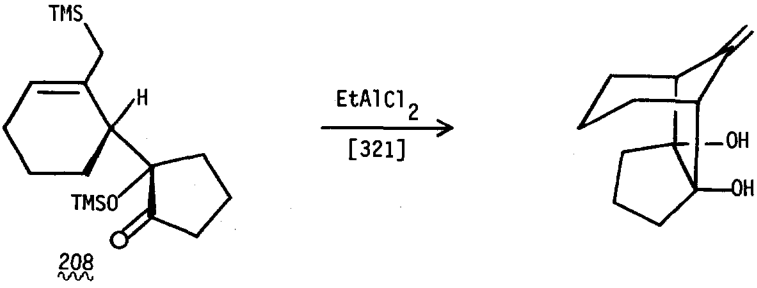
Two ketones were allylated. Thus, ketone **207** was allylated in poor to excellent yield and poor to excellent diastereoselectivity. (Eqn. 411) The intramolecular allylation of **208** provided an entry into the bicyclo[5.3.1]undecyl system of taxanes. (Eqns. 412-414)



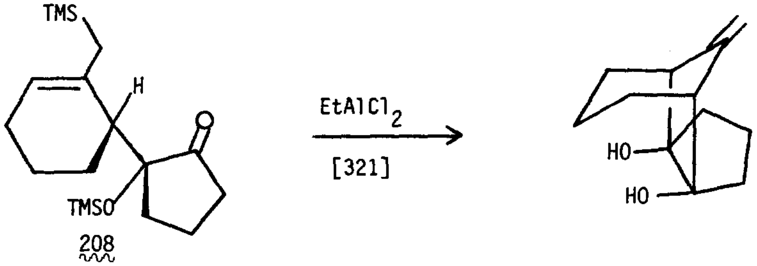
(411)



(412)

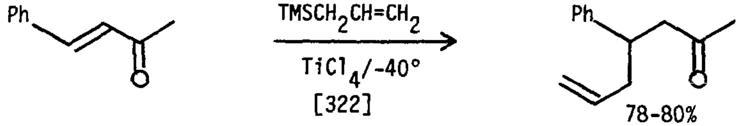


(413)



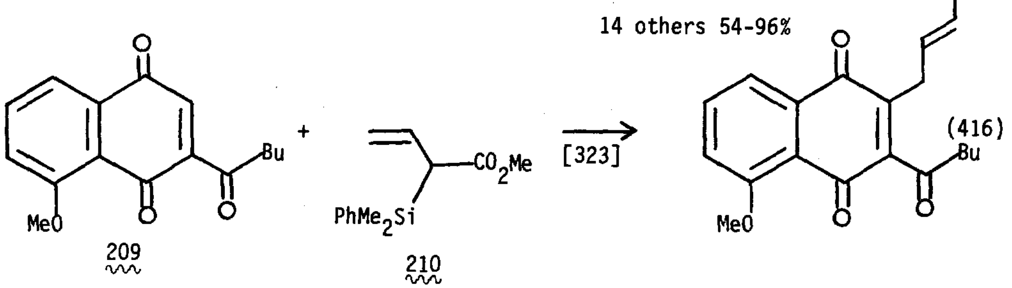
(414)

The conjugate allylation of α, β-unsaturated ketones was reported. A general procedure was published. (Eqn. 415) the naphthoquinone **209** reacted nicely with **210**. (Eqn. 416) The α-methylenecyclopentanone **211** was allylated with **212**. (Eqn. 417) An intramolecular allylation of dienone **213** gave nootkanone in 65 percent yield. (Eqn. 418)

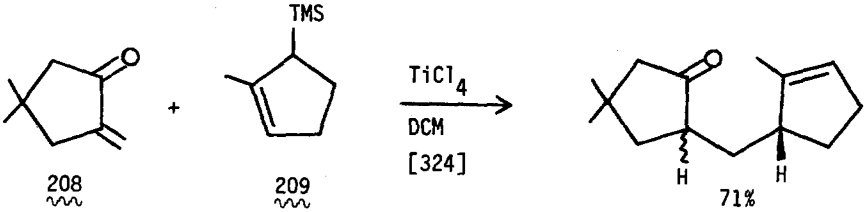


(415)

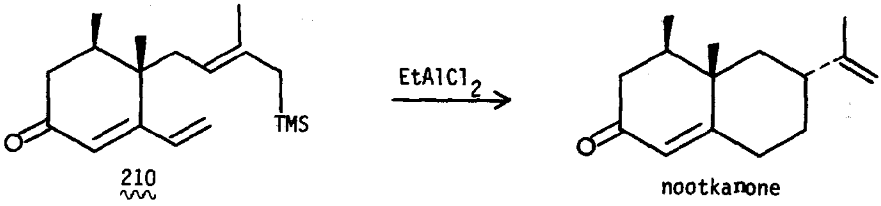
14 others 54-96%



(416)

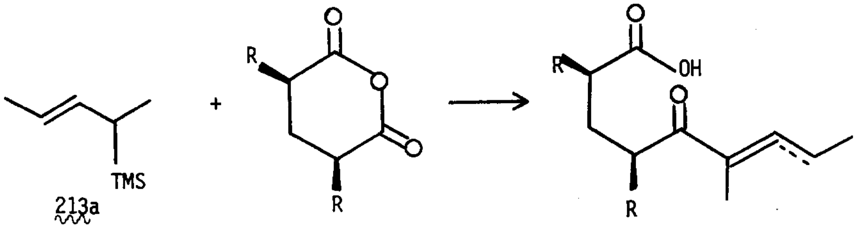


(417)

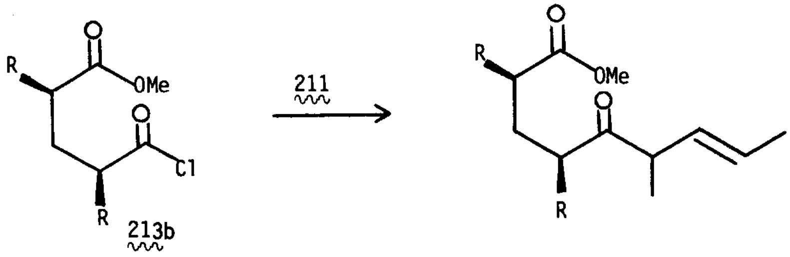


(418)

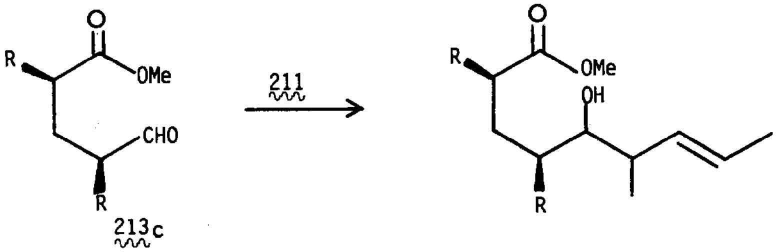
Derivatives of glutaric anhydride were selectively allylated with allylsilane **213a**. The anhydride itself gives δ-keto acids with some conjugation. (Eqn. 419) Acid chloride **213b** gives no conjugation of the product (Eqn. 420) and the aldehyde **213c** gives the δ-hydroxy ester. (Eqn. 421)



(419)

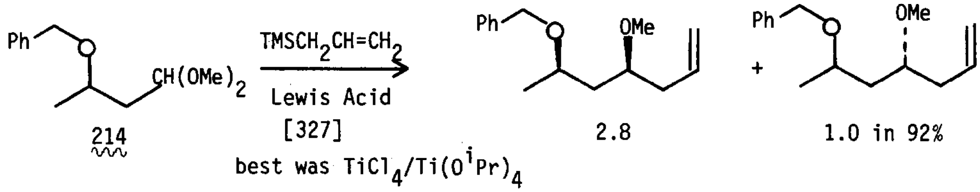


(420)



(421)

Acetals were also allylated, primarily with stereoselectivity in mind. α-Benzyloxy acetal **214** gave only a slight predominance of the syn (erythro) over the anti (threo) product under a variety of conditions. (Eqn. 422) The α-methyl system **215** gave a maximum of 3.5 erythro to threo product ratio. (Eqn. 423) Extremely high stereoselectivity was found in the allylation of the chiral acetals **216**. (Eqn. 424) The process ultimately provides homoallylic alcohols of high optical purity. (Eqn. 425) A more elaborate example as part of a synthesis aimed at calcitriol lactone is shown in equation 426. In a related reaction ethoxy amides **217** allylate intramolecularly to give indolizidines (n = 1) and quinolizidines (n = 2) in excellent yield. (Eqn. 427) (see Eqn. 459 for a similar reaction)



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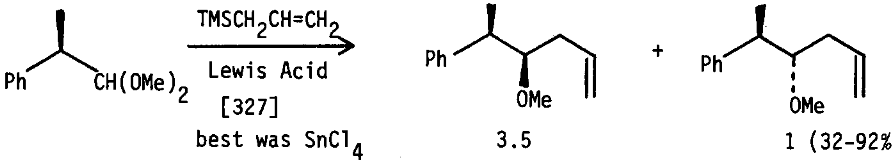
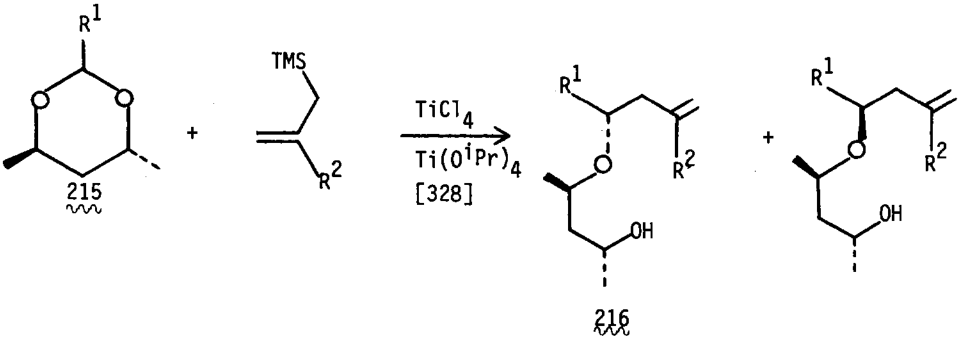
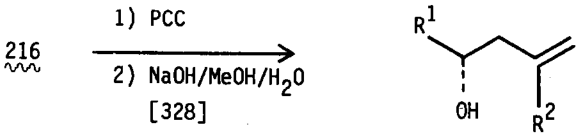


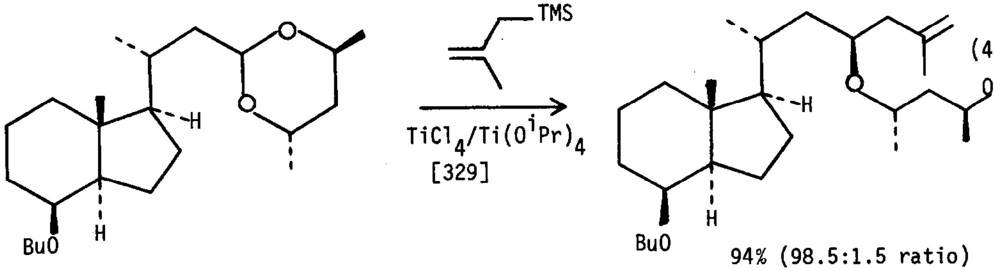
(423)



(424)

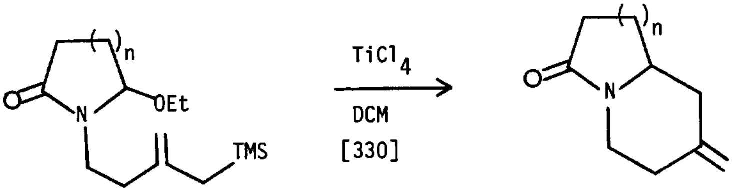


(425)



94% (98.5:1.5 ratio)

(426)

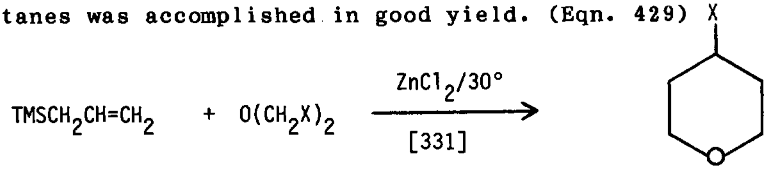


217
n = 1, 2

n = 1 70%
n = 2 94%

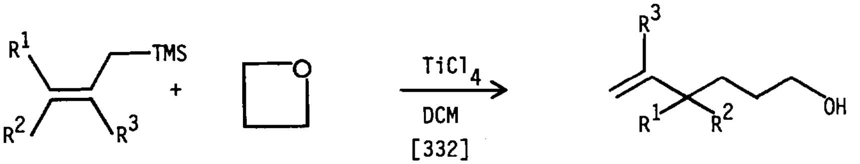
(427)

Allylations of bis-halomethyl ethers to give 4-halopyrans, albeit in low yield were reported. (Eqn. 428) The allylation of oxetanes was accomplished in good yield. (Eqn. 429)



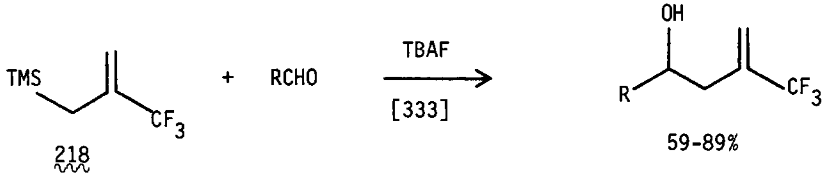
X = Cl (20%); Br (26%)

(428)



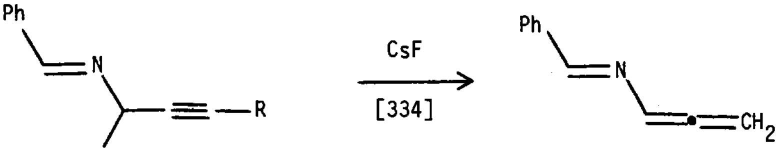
(429)

Fluorinated allyl compounds were prepared via the fluoride-induced condensation of aldehydes and **218**. (Eqn. 430) Allylsilanes **219**, **220** and **221** protodesilylated with π-bond transposition under the influence of cesium fluoride providing a route into 2-aza-1,3-dienes. (Eqns. 431 and 432) Under similar conditions in the presence of allyl or benzyl bromide alkylation takes place without π-bond transposition, however. (Eqns. 433 and 434)



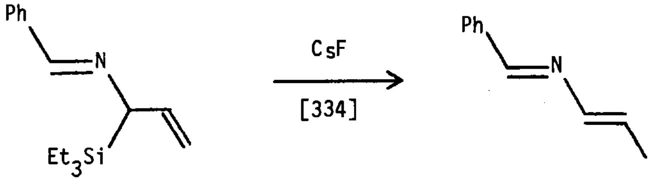
218

(430)



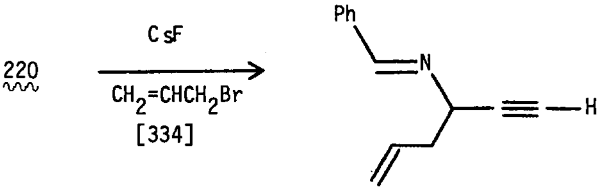
219 R = TMS; 220 R = H

(431)

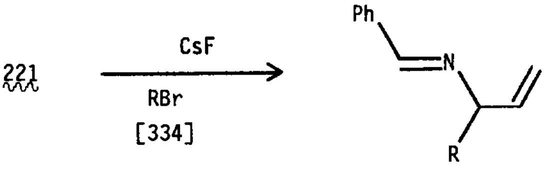


221

(432)



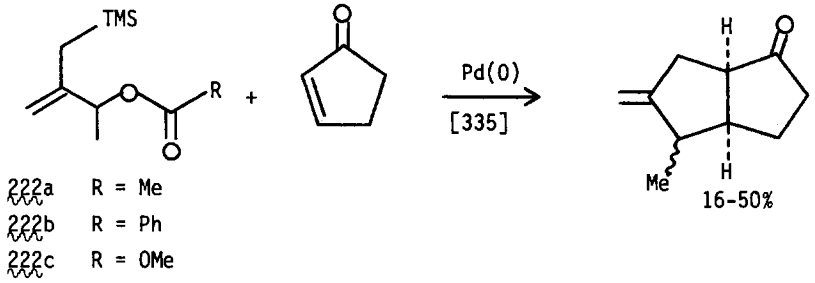
(433)



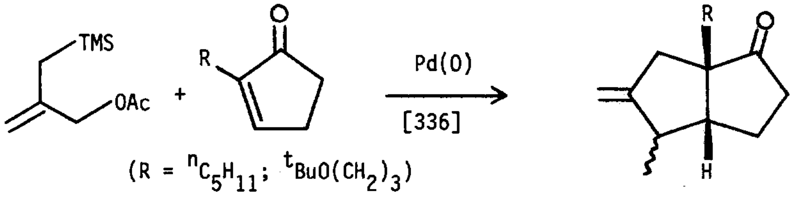
R = allyl, benzyl

(434)

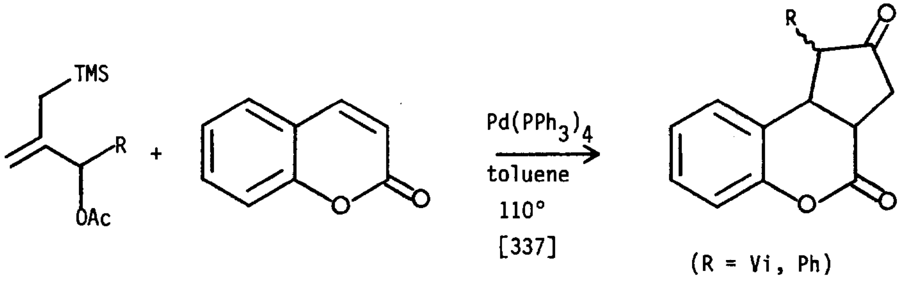
The allylsilanes **222** were used to generate trimethylene palladium species for 3 + 2 cycloadditions to cyclopentenones. (Eqn. 435) In a similar reaction **223** was cyclized with substituted cyclopentenones. (Eqn. 436) An example of a similar reaction is shown. (Eqn. 437)



(435)

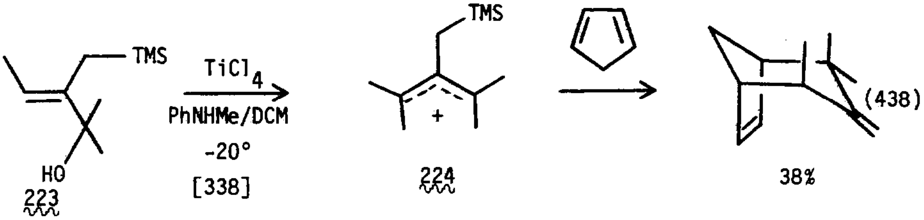


(436)

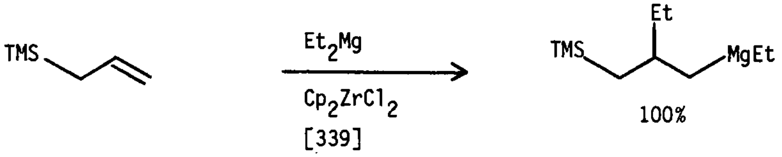


(437)

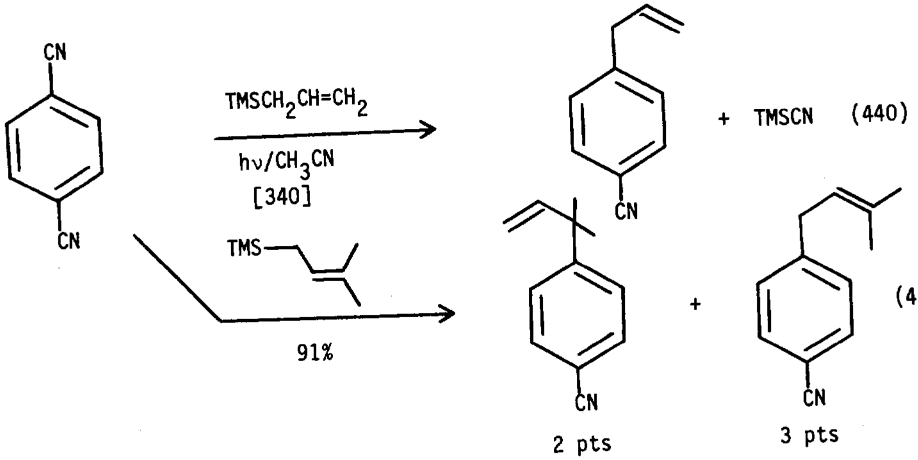
A variety of other reactions, more difficult to classify, were reported. Allylsilane **223** gave the allyl cation **224**, which will lose a proton or can add to cyclopentadiene. (Eqn. 438)



Ethylmagnesium bromide was added to allyltrimethylsilane. (Eqn. 439) The monoallylation of p-dicyanobenzene with allylsilanes was presented. The reaction is not regiospecific, however. (Eqns. 440 and 441) The o-dicyanobenzene also monoallylated. (Eqn. 442)

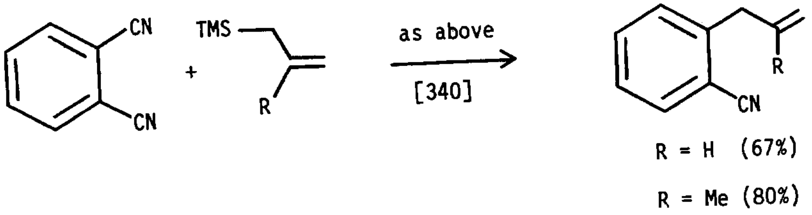


(439)



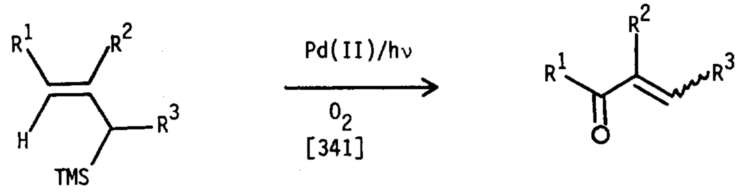
(440)

(441)

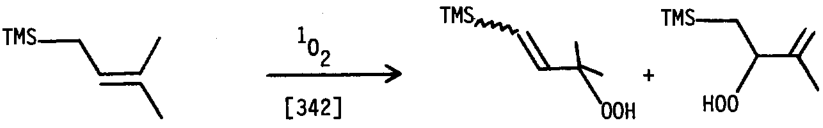


(442)

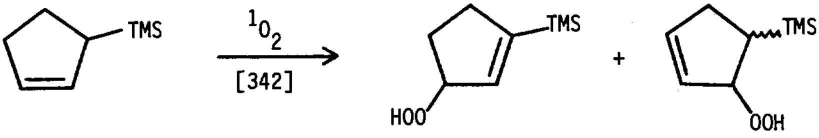
The palladium (II) catalyzed photochemical oxidation of allylsilanes provides enones. (Eqn. 443) The reaction of allylsilanes with singlet oxygen proceeds at the C-H and not the C-Si bond. Some examples are given. Other similar reactions were also reported. (Eqns. 444-446) Allylsilane **225** added tert-butyl hydroperoxide to give **226**. (Eqn. 447)



(443)



(444)



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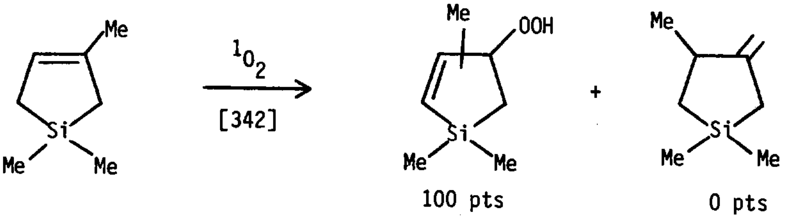

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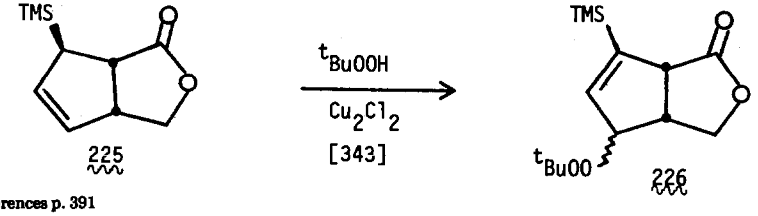
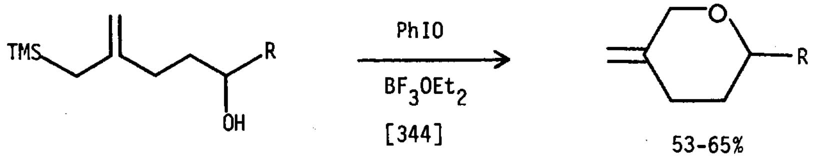


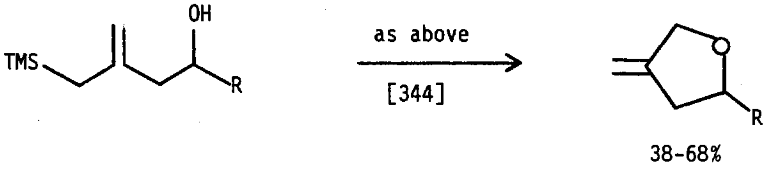
225 **226**

(447)

Hydroxy allylsilanes were cyclized intramolecularly with iodine (III) and boron fluoride etherate. (Eqns. 448 and 449) Thallium (III) and alcohols react with allylsilanes to give allyl ethers. (Eqns. 450 and 451) The reaction can be done intramolecularly as well. (Eqn. 452) Trimethylsilylcyclopentadiene reacts with sulfoxides in the presence of acetic anhydride to give **227**. (Eqn. 453) Diallylsilane **228** reacts under free radical conditions to give **229**. (Eqn. 454) Low pressure pyrolysis of dimethyldiallylsilane gives three isomers of the starting diallylsilane and the products shown. (Eqn. 455) the Arrhenius parameters are reported for the reaction.



(448)



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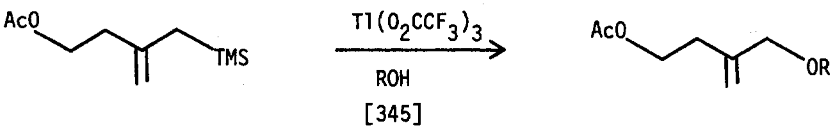

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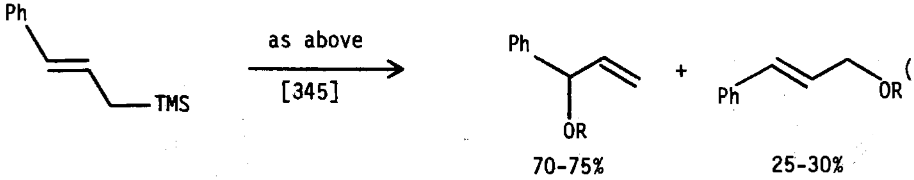
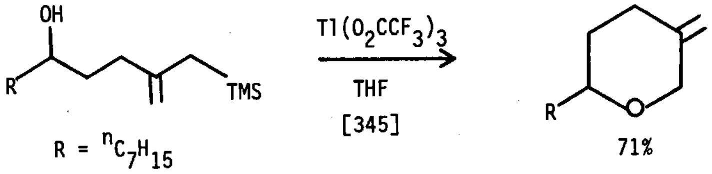
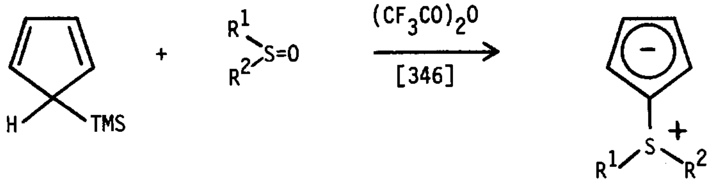


(451)

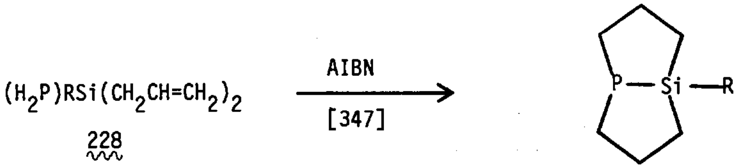


(452)



(453)

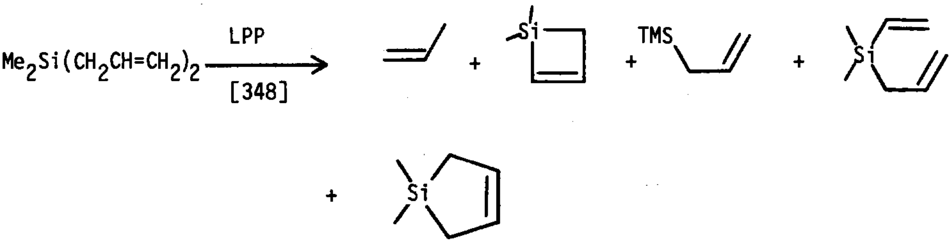
227



228

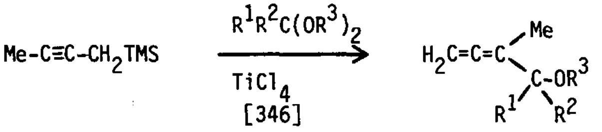
229

(454)



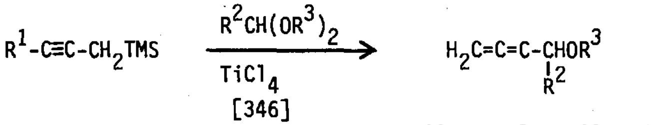
(455)

Two electrophilic reactions of propargylsilanes related to those of the allylsilanes are also noted here. 1-Trimethylsilyl-2-butyne and related compounds react with acetals and ketals to give allenyl ethers regiospecifically. (Eqns. 456 and 457) The propargylsilanes **230** cyclize via an "in situ" generated N-acyliminium ion. (Eqn. 458) The corresponding allylsilanes reacted as well. (Eqn. 459) (see Eqn. 427 for a similar reaction)



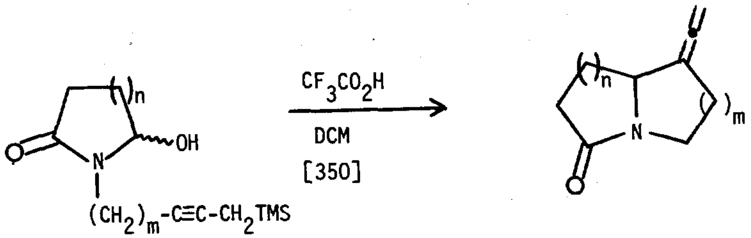
8 examples 32-92%

(456)



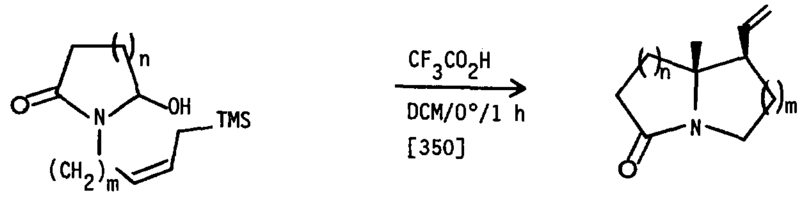
20 examples 20-90%

(457)



230
(n = 1, 2; m = 2, 3)

(458)

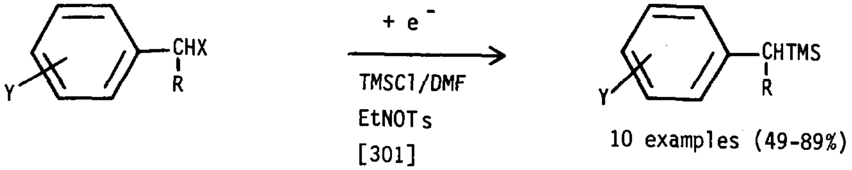


(n = 1, 2; m = 2, 3)

(459)

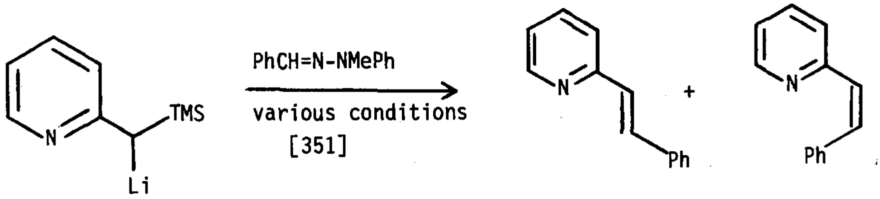
X. BENZYLSILANES

Benzylsilanes were prepared by the electrochemical reduction of benzyl halides in the presence of trimethylchlorosilane. (Eqn. 460)



(460)

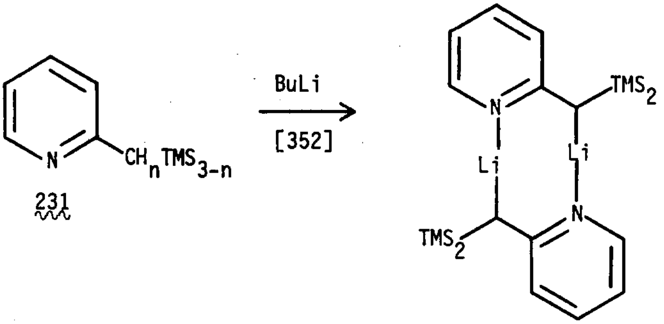
Deprotonation of benzylsilanes was used in a synthesis of stilbazoles. (Eqn. 461) A variety of conditions were employed for this reaction.



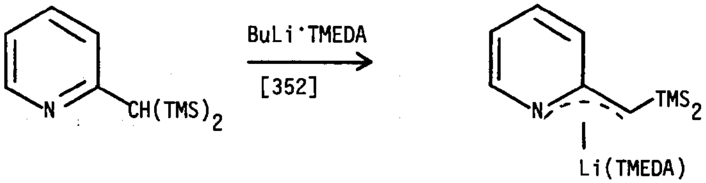
(461)

no additive	100% (E)	34% yield
18-C-6	100% (E)	74%
12-C-4	100% (E)	97%
triglyme	100% (E)	85%
[2.1.1]-CRPO	100% (Z)	22%
" reflux	92% (Z)	94%

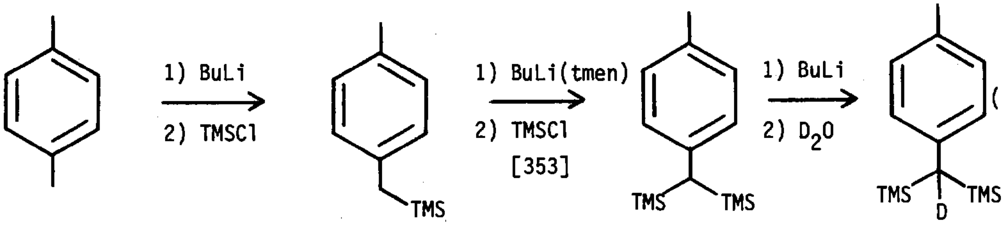
The lithiation of **231** led to the interesting 3-azallyl structures as determined by x-ray. (Eqns. 462 and 463) The lithiation-silylation of p-xylene and the lithiation-silylation of the products leads to the the products shown. (Eqn. 464) The crystal structure of **232** was determined. [353]



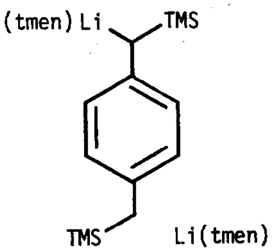
(462)



(463)

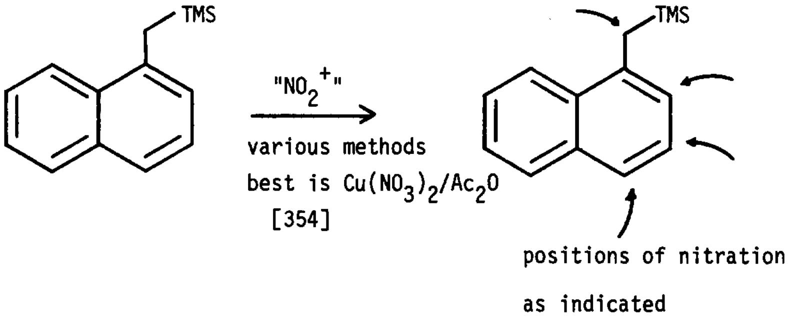


(46



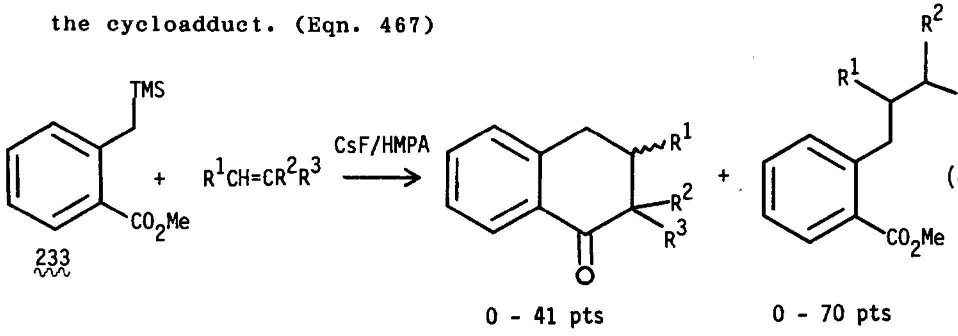
231

The electrophilic nitration of 1-trimethylsilylmethylnaphthalene gives considerable cleavage of the benzyl-silicon bond. Only below 0° can ring nitration products be obtained. The ring nitration occurs at carbons 2, 3 and 4. (Eqn. 465)



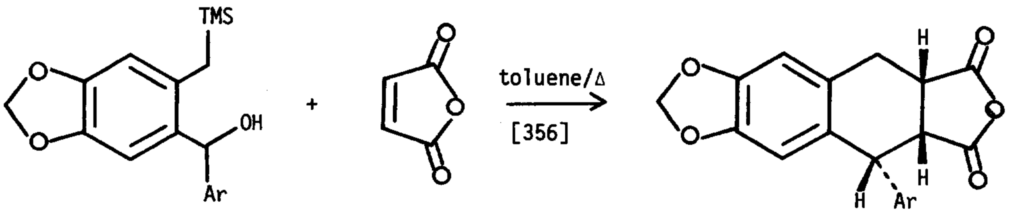
(465)

The reaction of benzylsilanes containing a leaving group on an ortho benzylic position serves as four carbon units in electrophilic reactions. Thus, ester **233** reacts with fluoride ion in the presence of good dienophiles to give α-tetralone derivatives. (Eqn. 466) The acyclic reaction also occurs. Benzylsilane **227** reacts thermally with maleic anhydride to give the cycloadduct. (Eqn. 467)



(466)

R^1, R^2 and R^3 combinations of H, Me, CO_2Me; cyclopentenone and cyclohexenone



(467)

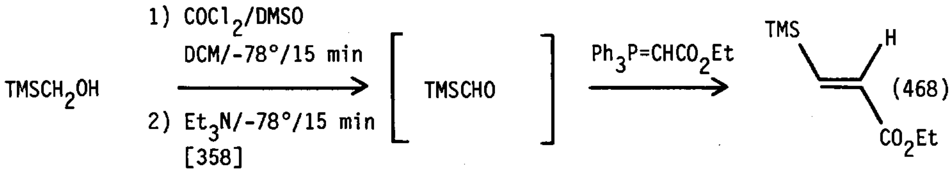
(Ar = 3,4,5-trimethoxyphenyl)

The alkaline cleavage of m-chlorobenzyldimethylmethoxysilane occurs rapidly. This is attributed to the formation of $ArMe_2SiO^-$. [357]

XI. α-FUNCTIONAL ORGANOSILANES

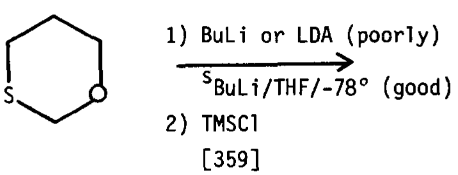
A. Preparation

A Swern oxidation of trimethylsilylmethanol provides formyltrimethylsilane at -78°. Although it cannot be isolated it can be reacted with a Wittig reagent as shown. (Eqn. 468)

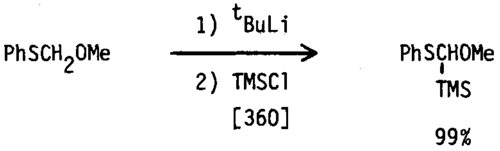


(468)

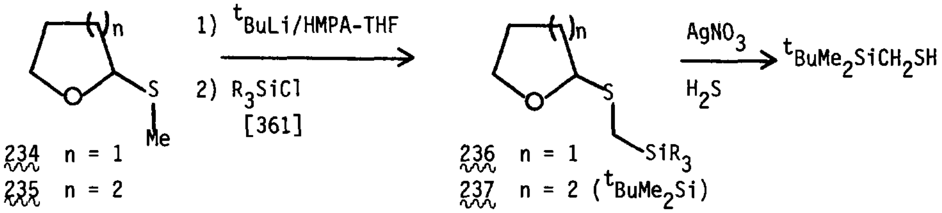
The silylation of α-heterosubstituted lithium reagents provided entries into a number of α-functional organosilanes. Several examples follow. Lithiation-silylation of 1,3-oxathianes proceeds in excellent yield. (Eqn. 469) α-Methoxythioanisole undergoes an analogous sequence in even better yield. (Eqn. 470) Deprotonation of (2-tetrahydrofuranyl)- and (2-tetrahydropyranyl)thiomethane occurs at the methyl group with silylation giving the corresponding trimethylsilylmethyl derivative. Silver promoted solvolysis gives the silylmethane thiol. The process can be repeated to provide bis- or tris-silylated systems without problem. (Eqns. 471-474) The "in situ" reaction of diiodomethane, phenyllithium and triphenylchloro- or triphenylbromosilane produces the corresponding iodomethyltriphenylsilane in reasonable yield. (Eqn. 475) Diiodomethyllithium reacts to give the diiodomethylsilane. (Eqn. 476) Deprotonation-silylation of allyl carbamate **238** gives the α-carbamoylsilane **239** as the predominant product. (Eqn. 477)



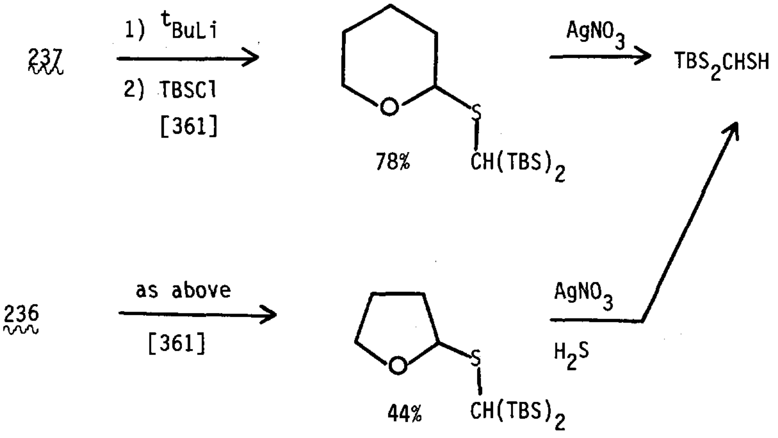
(469)



(470)

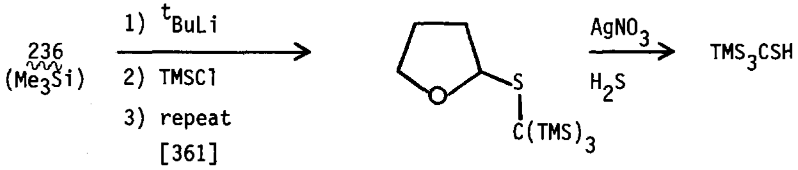


(471)



(472)

(473)



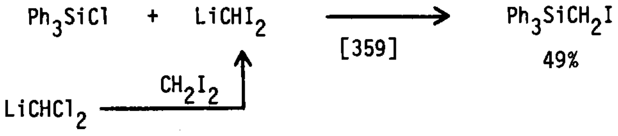
(474)

$$\underset{(X = Cl,\ Br)}{Ph_3SiX} \xrightarrow[-110^\circ \quad RT]{CH_2I_2/PhLi} Ph_3SiCH_2I \qquad (475)$$

[359]

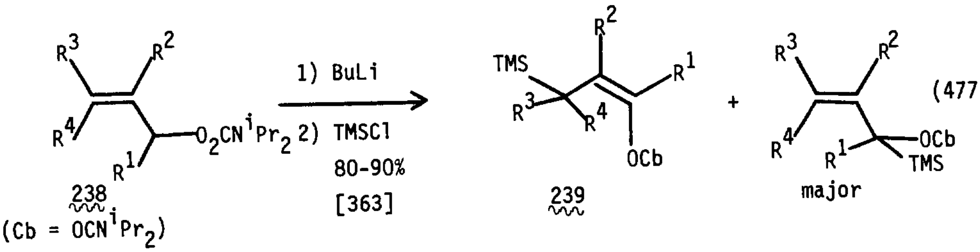
from X = Cl 35%

from X = Br 55%



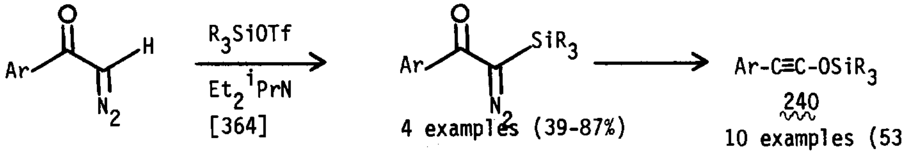
$$Ph_3SiCl + LiCHI_2 \xrightarrow[{[359]}]{} Ph_3SiCH_2I \;\; 49\% \qquad (476)$$

$$LiCHCl_2 \xrightarrow{CH_2I_2} LiCHI_2$$



(477)

The reaction of diazoacetophenones with trialkylsilyl triflates in the presence of a hindered amine gives the diazosilyl compound in good yield. These thermally convert to the aryl trialkylsilyloxy acetylenes. (Eqn. 478) A thermal rearrangement to the silyl enol ether followed by nitrogen extrusion and aryl migration was proposed to account for the product. (Eqn. 479)



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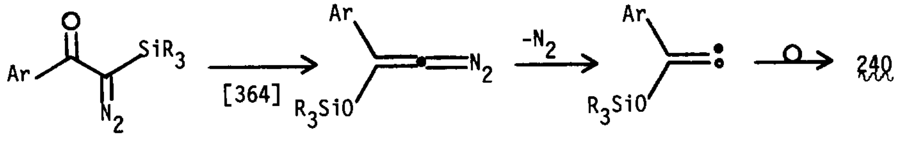


(479)

$R_3Si = Et_3Si;\ {}^tBuMe_2Si;\ {}^iPr_3Si$

The conversion of one α-functional group to another either via substitution as seen in equations 480 and 481 or by chemical modification as seen in equations 482-486 was used to prepare α-functional organosilicons.

$$(MeO)_3SiCH_2Cl \xrightarrow[\text{DMF}]{\text{ROM}} (MeO)_3SiCH_2OR \tag{480}$$

$$\text{80-90°} \quad [365] \qquad \text{80-100\%}$$

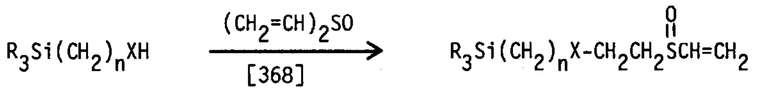
R = aryl, alkyl

$$TMSCH_2Cl + HN_3 \text{ or } NaN_3 \xrightarrow[{[366]}]{} TMSCH_2N_3 \tag{481}$$

$$\text{with } NaN_3 \ 95\%$$

$$O[SiMe_2CH_2OH]_2 + BuOCH{=}CH_2 \xrightarrow[\text{95-100°}]{Hg(OAc)_2} O[SiMe_2CH_2OCH{=}CH_2]_2 \tag{482}$$

$$[367]$$



$$R_3Si(CH_2)_nXH \xrightarrow[{[368]}]{(CH_2{=}CH)_2SO} R_3Si(CH_2)_nX\text{-}CH_2CH_2\overset{O}{\overset{\|}{S}}CH{=}CH_2 \tag{483}$$

R = Me, Et; n = 1-3; X = S 71-77%

R = Me, Et; n = 1-3; X = O 55-61%

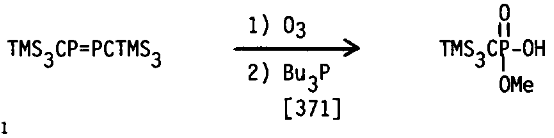
$$R_3Si(CH_2)_nSH \xrightarrow[{[369]}]{(Et_3M)_2Hg} R_3Si(CH_2)_nSMEt_3 \tag{484}$$

$$80\text{-}94\%$$

R = MeO; n = 1,2; M = Si, Ge

R = Me, n = 3; M = Si

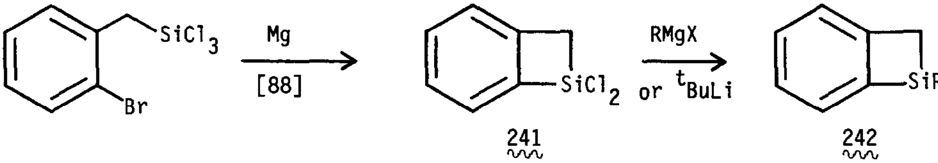
$$TMS_2CHPHGeCl_3 \xrightarrow[{[370]}]{DBU(xs)} TMS_2CHPH_2 + (TMS_2CHPH)_2 \tag{485}$$



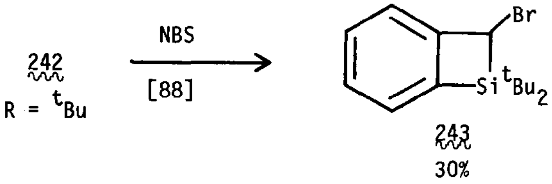
$$TMS_3CP{=}PCTMS_3 \xrightarrow[\text{2) } Bu_3P]{\text{1) } O_3} TMS_3C\underset{OMe}{\underset{|}{\overset{O}{\overset{\|}{P}}}}\text{-}OH \tag{486}$$

$$[371]$$

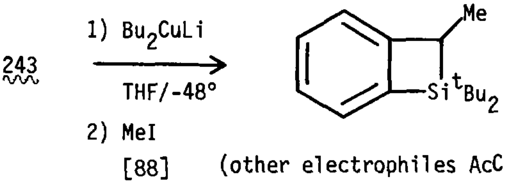
Benzosilacyclobutane **241** was prepared as shown. (Eqn. 487) The di-tert-butyl compound was selectively monobrominated (Eqn. 488) and this material treated with lithium dibutylcuprate and alkylated. (Eqn. 489) Hydrolysis in the presence of silver ion gives an insertion product (Eqn. 490) whereas methanolysis gives simple substitution. (Eqn. 491)



(487)

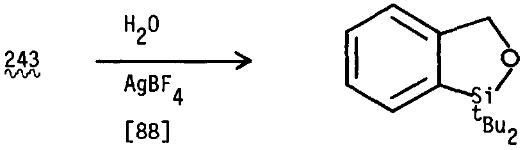


(488)

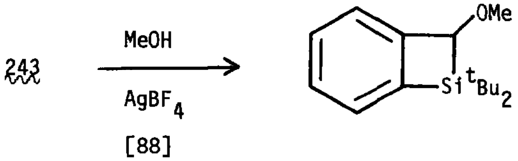


(489)

(other electrophiles AcCl, allylbromides PhCHO)

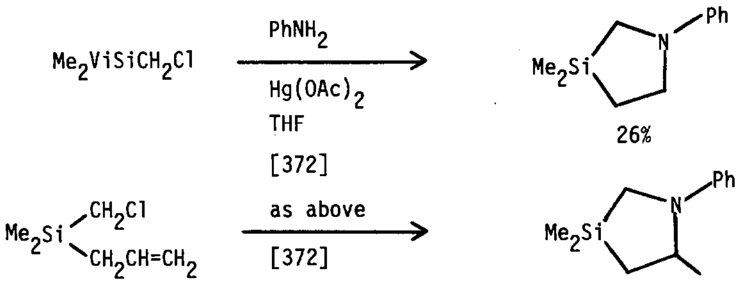


(490)



(491)

Chloromethyldimethylvinylsilane undergoes aminomercuration to give 1-aza-3-silacyclopentanes. (Eqn. 492) The allylsilane gives a similar reaction. (Eqn. 493)

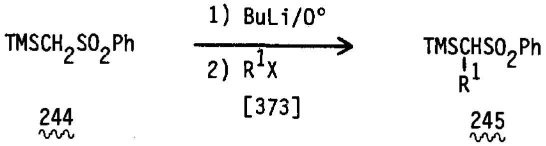


(492)

(493)

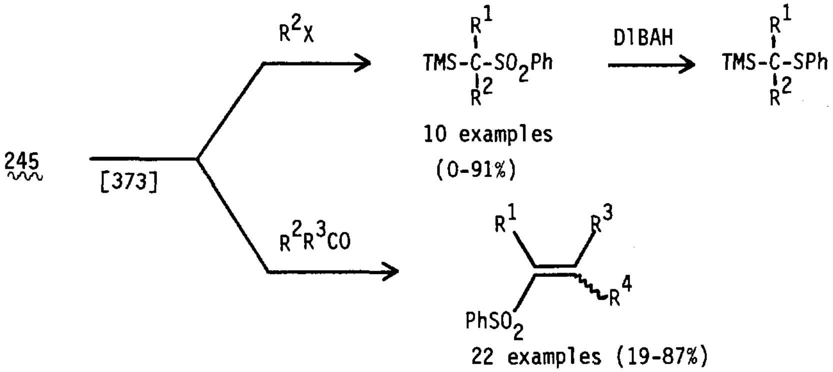
B. Reactions.

Several useful transformations again appeared wherein α-silyl organometallic reagents are employed. Those that also contain an additional functional group are particularly useful. Several examples of this are given. (see Eqns. 472-474 for other examples) α-Silyl sulfones were lithiated and alkylated.(Eqn. 494) These can be lithiated and alkylated a second time (Eqn. 495) or lithiated and treated with ketones to give vinylsulfones (Eqn. 496). It was further found that trimethylsilylmethyl phenyl sulfone can be dilithiated to give **246** (Eqn. 497), which can be derivatized in a variety of ways. (Eqns. 498-502) Several functionalized α-silyllithium reagents, prepared via lithiation-silylation of CH_2XY, were reacted with methoxycyclopropenylium triflates to give substituted triafulvenes. (Eqn. 503) 2-(Trimethylsilyl)-1,3-oxathianyllithium was reacted with several electrophiles, some of which are shown. (Eqn. 504) In a like manner **248** was lithiated and reacted with ketones and aldehydes. (Eqns. 505 and 506)



$$\underset{244}{\mathrm{TMSCH_2SO_2Ph}} \xrightarrow[\text{2) } R^1X \text{ [373]}]{\text{1) BuLi/0°}} \underset{245}{\mathrm{TMS}\underset{R^1}{\mathrm{C}}\mathrm{HSO_2Ph}}$$

(494)

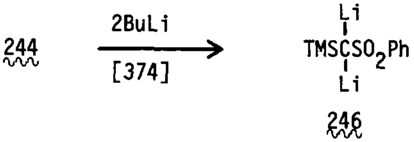


10 examples (0-91%)

22 examples (19-87%)

(495)

(496)



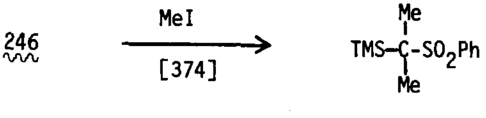
$$244 \xrightarrow[\text{[374]}]{\text{2BuLi}} \underset{246}{\mathrm{TMS}\overset{Li}{\underset{Li}{\mathrm{C}}}\mathrm{SO_2Ph}}$$

(497)

$$246 \xrightarrow[\text{[374]}]{\mathrm{DCl/D_2O}} \mathrm{TMSCO_2SOPh}$$

95%

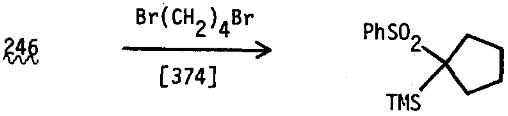
(498)



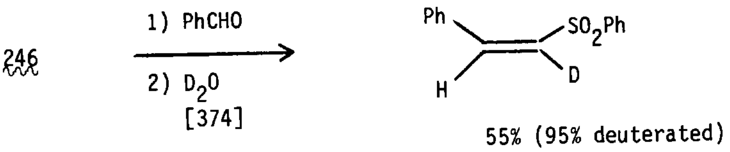
$$246 \xrightarrow[\text{[374]}]{\text{MeI}} \mathrm{TMS\text{-}}\overset{Me}{\underset{Me}{\mathrm{C}}}\mathrm{\text{-}SO_2Ph}$$

86%

(499)



(500)



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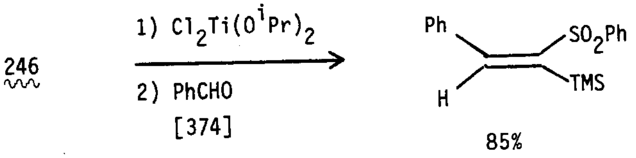

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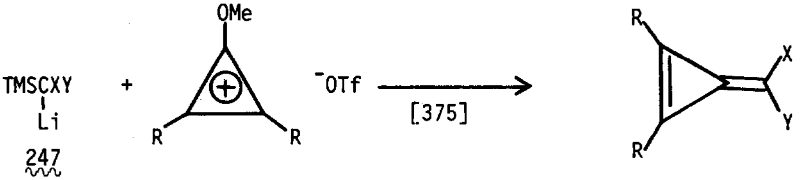
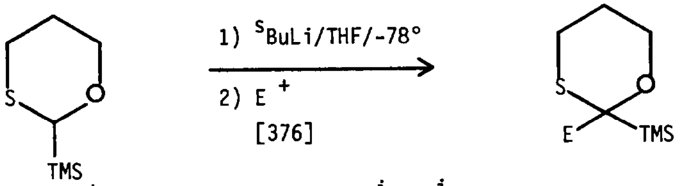


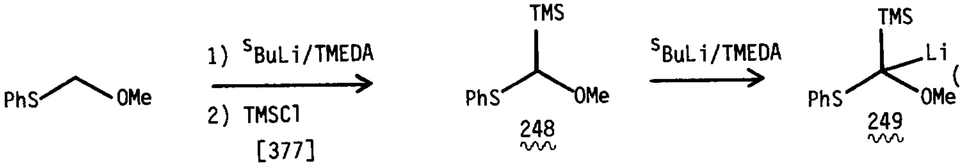
(503)

(X,Y = $S(CH_2)_3S$; $PhSO_2$, TMS; $p\text{-}MeC_6H_4SO_2$, SMe; $Ph_2P(O)$, TMS)

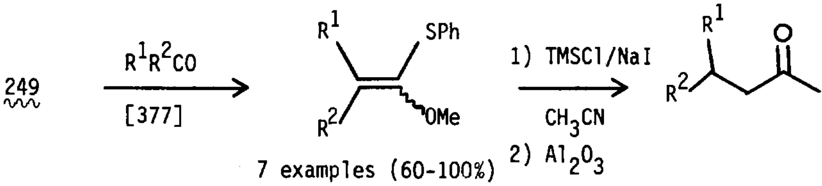


(504)

(E^+ = RI with R = Me, Et, ^iPr, ^iBu; PhCHO; Me_2S_2; cyclohexanone; cinnamaldehyde; benzonitrile)

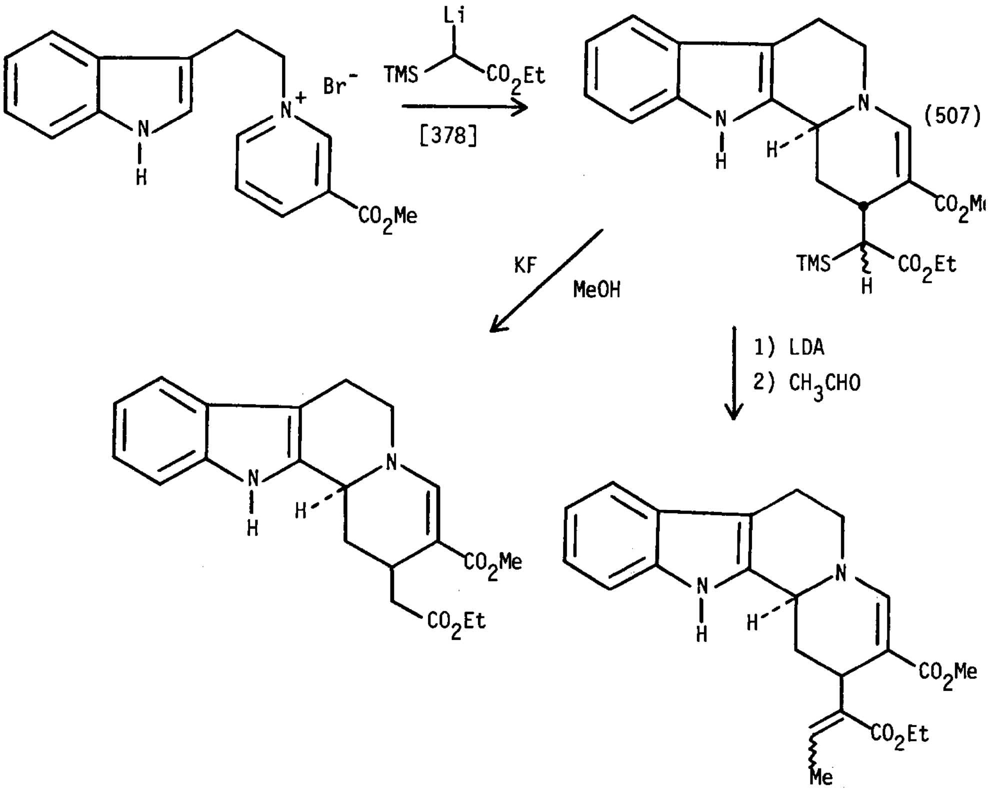


(505)



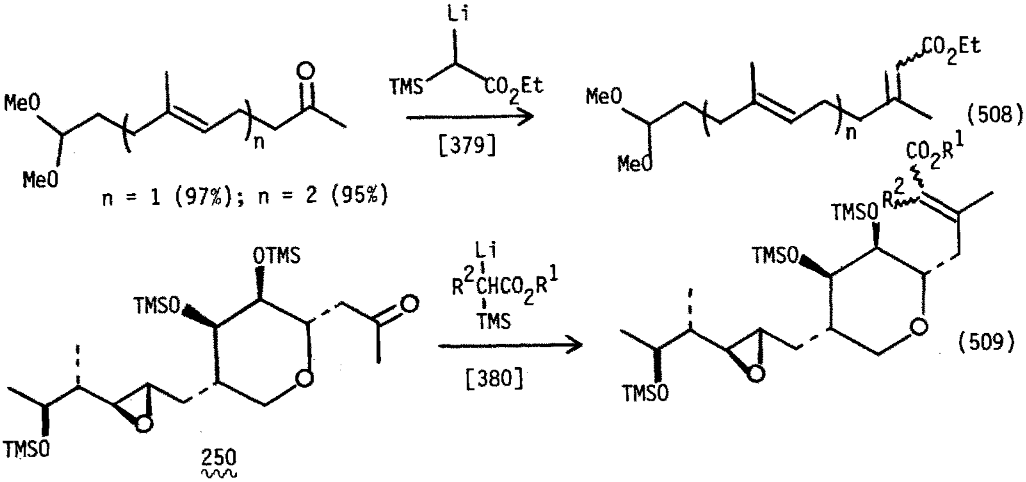
(506)

Several applications of α-silyl ester enolates, readily formed from the α-silyl ester and a strong, hindered base appeared. Thus, α-silyl ester enolates were employed twice in a synthetic approach to the indole alkaloid vallesiachotamine. The first reaction was addition to a nicotinium salt. The resulting α-silyl ester was then deprotonated and condensed with acetaldehyde. (Eqn. 507)



(507)

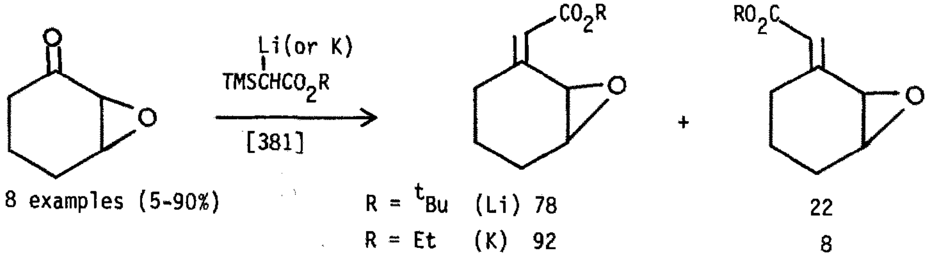
Ethyl (trimethylsilyl)lithioacetate was employed in the preparation of geranylgeraniol and farnesol. (Eqn. 508) 2-Substituted monic acid esters were prepared via the reaction of α-silyl enolates and ketone **250**. Phosphonate ester anions did not react with **250**. (Eqn. 509) 2,3-Epoxycyclohexanone reacts with α-silyl ester enolates much more stereoselectively then it does with phosphonate ester anions. (Eqn. 510)



(508)

(509)

250



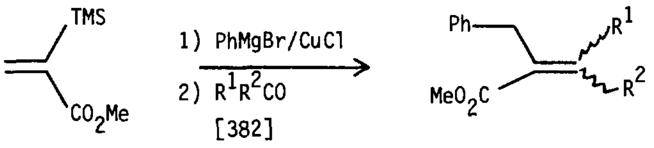
(510)

8 examples (5-90%)

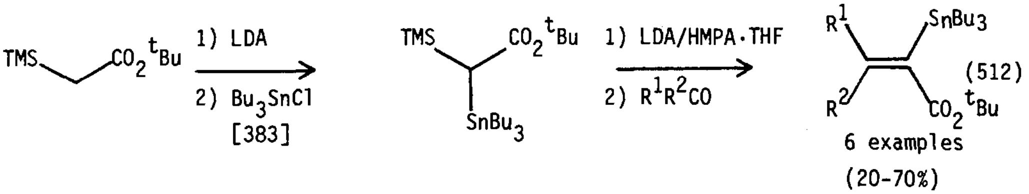
R = ^{t}Bu (Li) 78 22

R = Et (K) 92 8

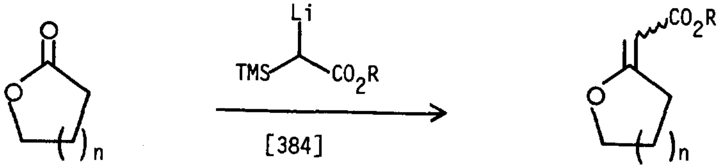
In further extensions of these reagents methyl α-trimethylsilylacrylate can be reacted with Grignard or lithium reagents in the presence of Cu(I) to give 1,4 addition and an α-silyl ester enolate. Subsequent trapping of the enolate with aldehydes or ketones provides mono-, di- or trisubstituted acrylates in good to excellent overall yield. (Eqn. 511) Tert-butyl trimethylsilylacetate can be stannylated. Deprotonation followed by reaction with ketones or aldehydes gives the α-stannyl α,β-unsaturated esters. (Eqn. 512) α-Silyl ester enolates were reacted with γ,δ and ε-lactones to give (Z)- and (E)-tetrahydrofurylidene acetates with the (Z) isomer generally predominating. (Eqns. 513 and 514) The lithium enolate of methyl α,α-bis(trimethylsilyl)acetate was employed in a highly enantioselective preparation of methyl jasmonate. (Eqn. 515)



(511)

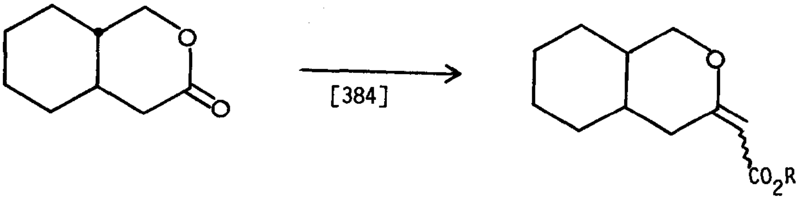


(512)

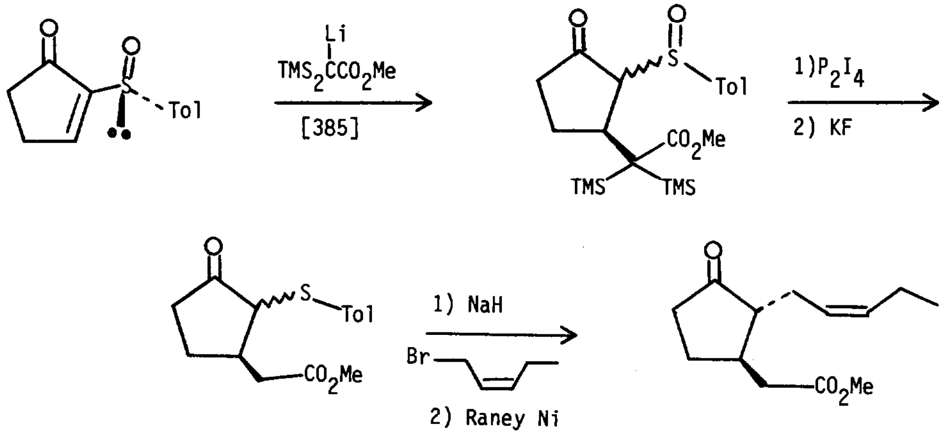


R = Me, ^{t}Bu; n = 1-3; 6 examples 20-70%)

(513)

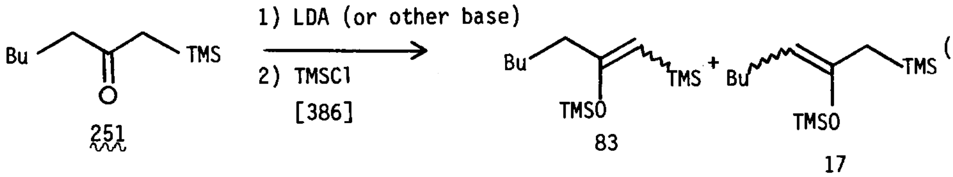


(514)



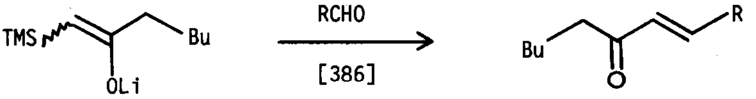
(515)

In related reactions ketone **251** was subjected to deprotonation-silylation to determine the regioselectivity of the deprotonation, with tert-butyllithium and 1-(trimethylsilyl)-hexyllithium) giving the highest selectivity. (Eqn. 516) The thusly generated α-silyl ketone enolate was reacted with aldehydes to give enones. (Eqn. 517) The α-trimethylsilyl anion **252** serves to introduce the isopropenyl functionality after suitable further manipulation. (Eqn. 518) Metalated α-silyl nitriles react with aldehydes to give α,β-unsaturated nitriles with reasonably good stereoselectivity in favor of the (Z) isomer. (Eqn. 519) Vinylsulfides are the products when **236** is lithiated and then reacted with ketones or aldehydes. (Eqn. 520)



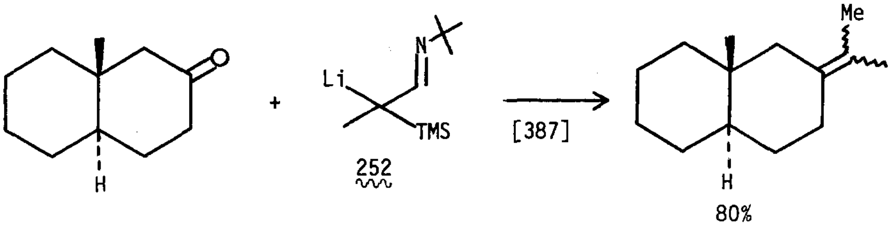
251

(516)

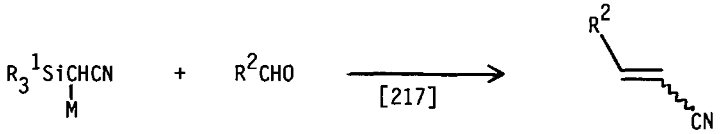


5 examples (75-91%)

(517)

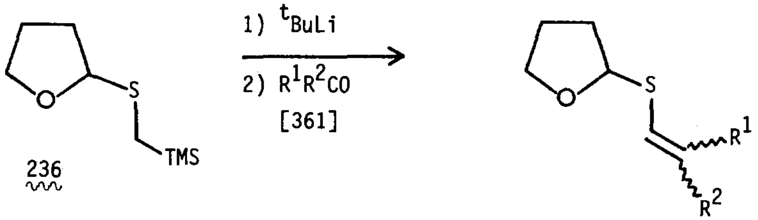


(518)



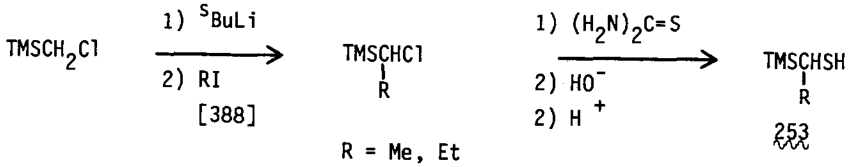
(519)

(M = Li; Ti; B; Mg; $R_1{}^3Si$ = Me_3Si; Ph_3Si; ${}^tBuMe_2Si$)



(520)

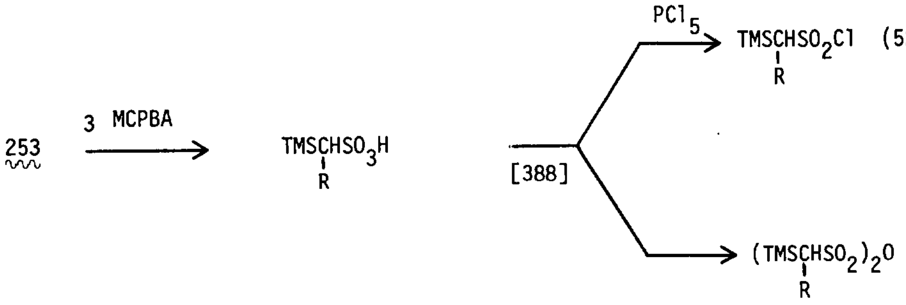
α-Silylchloromethyllithium reagents were prepared and reacted. Thus, a Magnus approach was used to prepare substituted α-chlorosilanes, which could then be converted to various α-thio species. (Eqn. 521-523)) The bis-methylene phosphoranes **254** were prepared as shown. (Eqn. 524) The analogous bis(methylene)-arsirane was formed in the same manner. It cyclized to the arsirane **255** (Eqn. 525) The Magnus reagent was used on 2,2-dimethylcyclohexanone. (Eqn. 526)



$$TMSCH_2Cl \xrightarrow[2)\ RI\ [388]]{1)\ {}^sBuLi} \underset{R}{TMSCHCl} \xrightarrow[2)\ HO^-\ \ 2)\ H^+]{1)\ (H_2N)_2C{=}S} \underset{R}{TMSCHSH} \quad (521)$$

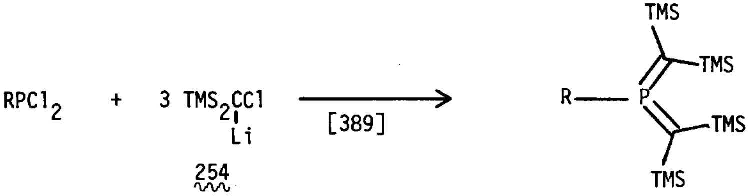
R = Me, Et

253

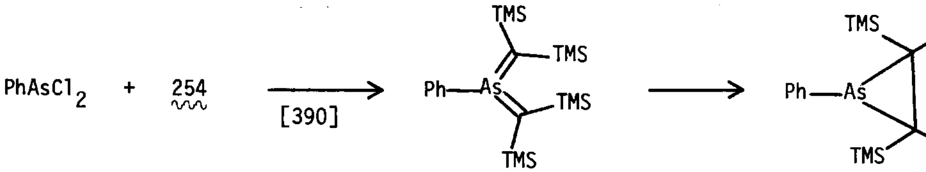


(522)

(523)

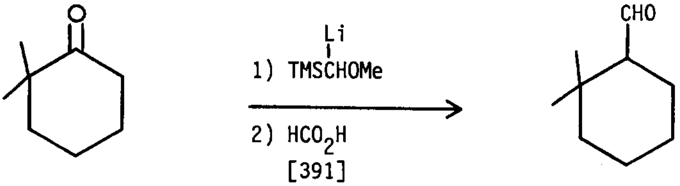


(524)



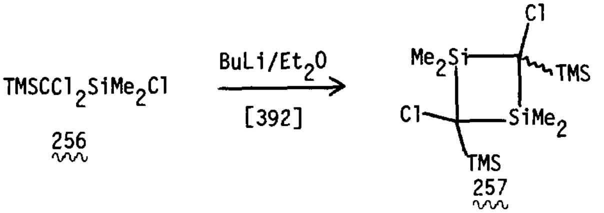
(525)

255

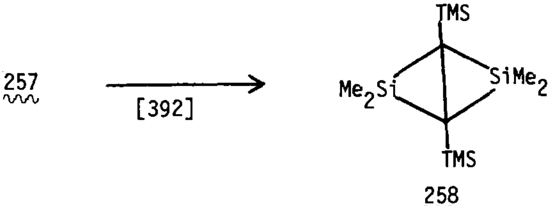


(526)

The reactions of **256** with butyllithium in ether provided cis and trans 1,3-disilacyclobutanes in addition to reduced material. (Eqn. 527) These disilacyclobutanes gave the disilabicyclobutane **258** upon treatment with butyllithium in THF showing that they lie on the pathway to **258** in the reaction of **256** with butyllithium in THF. (Eqns. 528 and 529) Other reactions were studied, a selected sampling of which shown. (Eqns. 530 and 531)

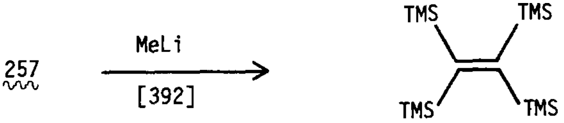


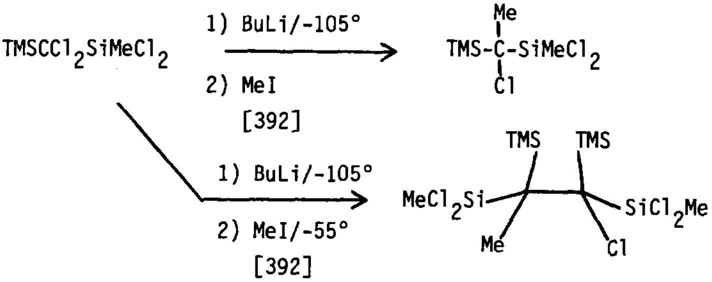
(527)



(528)

$$256 \xrightarrow[\text{[392]}]{\text{BuLi/THF}} 258 \qquad (529)$$





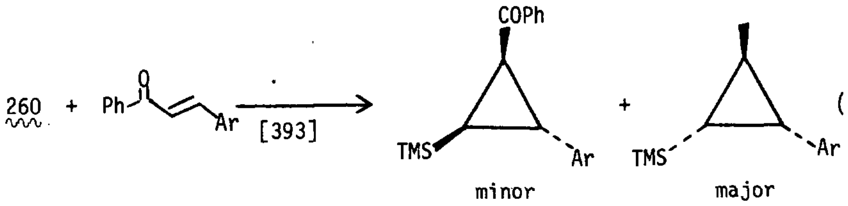
(530)

(531)

The α-silyl arsonium ylide was prepared (Eqn. 532) and reacted with enones to give cyclopropanation. (Eqn. 533)

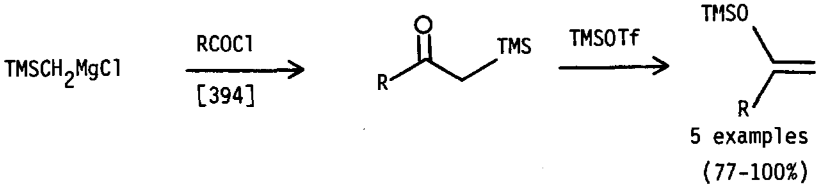
$$\overset{+}{Ph_3AsCH_2^-} \xrightarrow[\text{[393]}]{\text{TMSCl}} \overset{Cl^-}{\overset{+}{Ph_3AsCH_2TMS}} \xrightarrow{\text{NaBPh}_4} \underset{259}{\overset{+BPh_4^-}{Ph_3As\text{-}CH_2TMS}}$$

$$259 \xrightarrow[\text{PhLi}]{} \underset{260}{Ph_3As^+\text{-}\overset{-}{C}HTMS} \qquad (532)$$



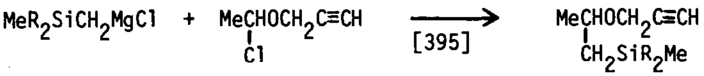
(533)

Reactions of trimethylsilylmethylmagnesium reagents were reported. The reaction with acid chlorides gives the B-keto silanes in excellent yield. These are precursors to regiospecifically generated kinetic enol silyl ethers. (Eqn. 534) The reaction with α-chloro propargyl ethers gives α-silylmethyl propargyl ethers. (Eqn. 535) Isopropoxydimethylsilylmethylmagnesium chloride reacts with aldehydes to give the expected β-hydroxysilane. The presence of the isopropoxy ligand on silicon, however, allows oxidation to the diol. (Eqn. 536) A similar hydroxymethylation was carried out with the allyl system **261** on enones to give 4-hydroxy ketones. (Eqns. 537 and 538) Replacement of the magnesium with titanium gives the β-hydroxysilanes upon treatment with benzaldehyde, although in low yield. (Eqn. 539) Bis(trimethylsilyl)methylmagnesium chloride reacts with dichloromesitylphosphine to give compound **263**, which can be eliminated to **264**. (Eqn. 540) Some reactions of **263** and **264** were reported.



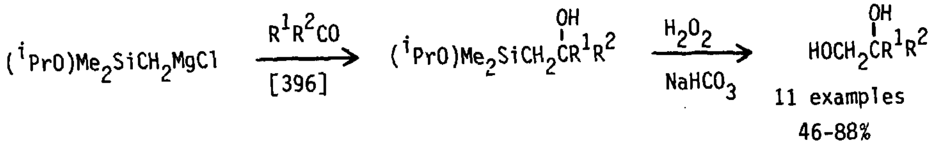
(534)

5 examples
(77-100%)



$$\mathrm{MeR_2SiCH_2MgCl} + \underset{\mathrm{Cl}}{\mathrm{MeCHOCH_2C{\equiv}CH}} \xrightarrow[{[395]}]{} \underset{\mathrm{CH_2SiR_2Me}}{\mathrm{MeCHOCH_2C{\equiv}CH}} \qquad (535)$$

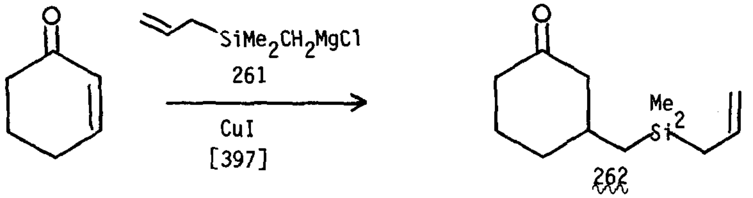
R = Me 61%
R = Et 56%



$$(^{i}PrO)Me_2SiCH_2MgCl \xrightarrow[\text{[396]}]{R^1R^2CO} (^{i}PrO)Me_2SiCH_2\overset{OH}{\overset{|}{C}}R^1R^2 \xrightarrow[NaHCO_3]{H_2O_2} HOCH_2\overset{OH}{\overset{|}{C}}R^1R^2$$

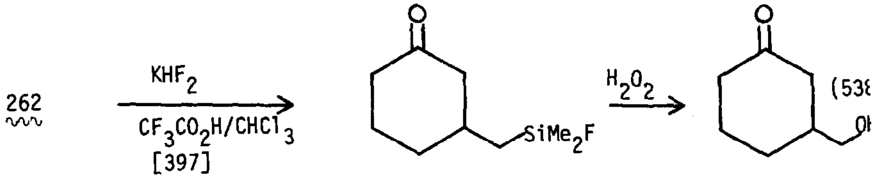
11 examples
46-88%

(536)

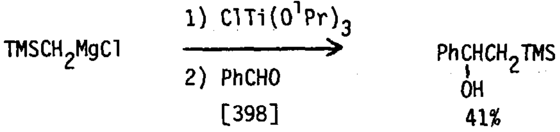


262

(537)



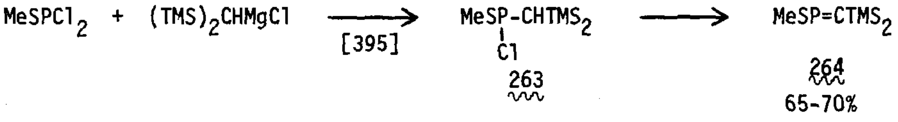
(53



$$TMSCH_2MgCl \xrightarrow[\text{2) PhCHO [398]}]{\text{1) } ClTi(O^{i}Pr)_3} Ph\underset{OH}{\underset{|}{C}}HCH_2TMS$$

41%

(539)

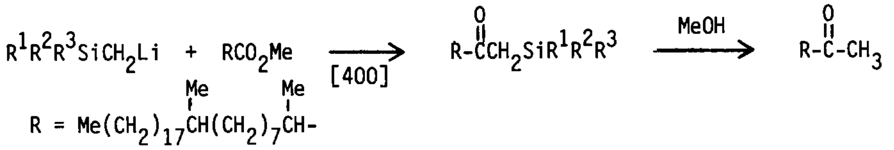


$$MeSPCl_2 + (TMS)_2CHMgCl \xrightarrow[\text{[395]}]{} \underset{\underset{\sim}{263}}{MeS\underset{Cl}{\underset{|}{P}}-CHTMS_2} \longrightarrow \underset{\underset{\sim}{264}}{MeSP{=}CTMS_2}$$

65-70%

(540)

Silylmethyllithium reagents react with esters to give β-ketosilanes and, after protonolysis, methyl ketones. (Eqn. 541)



$$R^1R^2R^3SiCH_2Li + RCO_2Me \xrightarrow[\text{[400]}]{} R\text{-}\overset{O}{\overset{\|}{C}}CH_2SiR^1R^2R^3 \xrightarrow{MeOH} R\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 \quad (541)$$

$$R = Me(CH_2)_{17}\overset{Me}{\overset{|}{C}H}(CH_2)_7\overset{Me}{\overset{|}{C}H}\text{-}$$

α-Silyldilithiomethanes were prepared via reaction of the appropriate dichlorides and lithium vapor. (Eqns. 542 and 543)

$$TMS_2CCl_2 \xrightarrow[\text{[401]}]{\text{Li (vapor)}} TMS_2CLi_2 \xrightarrow{D_2O} \underset{26\%}{TMS_2CD_2} \qquad (542)$$

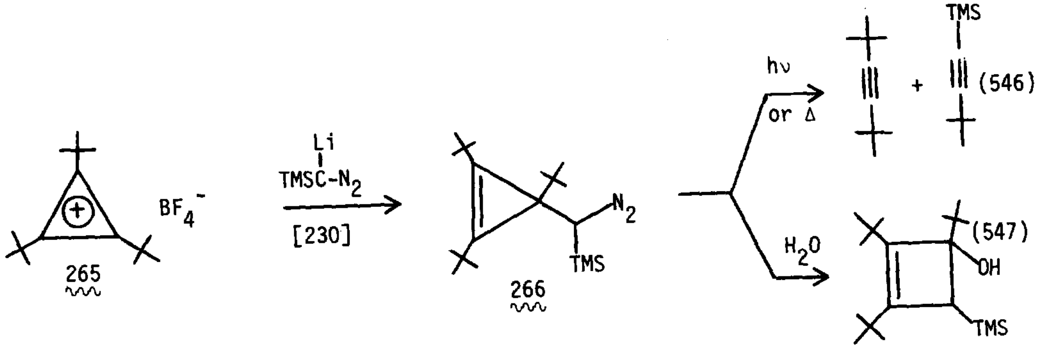
$$TMSCHCl_2 \xrightarrow[\text{2) } D_2O \text{ [401]}]{\text{1) Li (vapor)}} \underset{11\%}{TMSCHD_2} \qquad (543)$$

Trisilylmethyllithium reagents were used to prepare trisilylmethylboranes. (Eqns. 544 and 545)

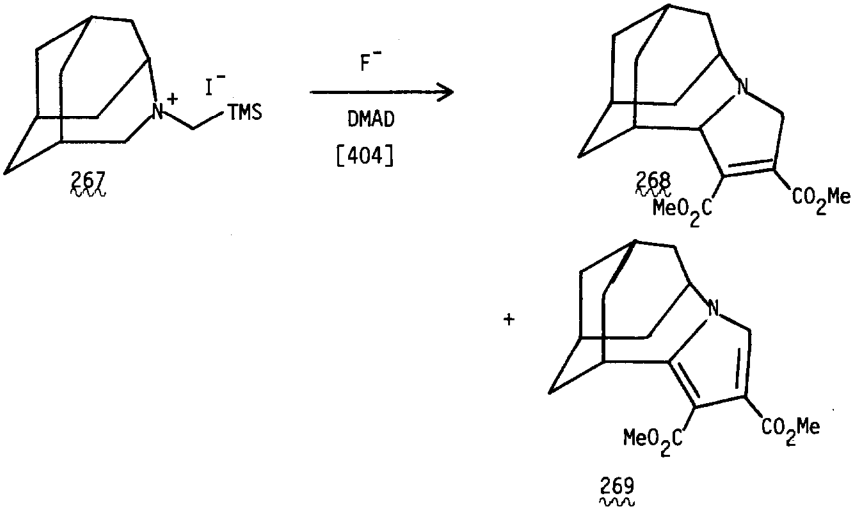
$$TMS_3CLi + Ph_2BBr \xrightarrow[\text{[402]}]{\text{THF/benzene}} \underset{\text{x-ray structure}}{TMS_3CBPh_2} \qquad (544)$$

$$(PhMe_2Si)_3CLi + BF_3OEt_2 \xrightarrow[\text{[403]}]{} (PhMe_2Si)_3CBF_2 \qquad (545)$$

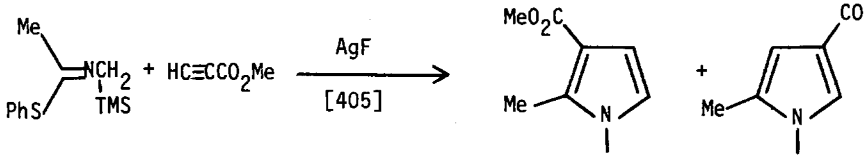
Trimethylsilyldiazomethyllithium reacts with **265** to give **266** which undergoes the reactions shown. (Eqns. 546 and 547)



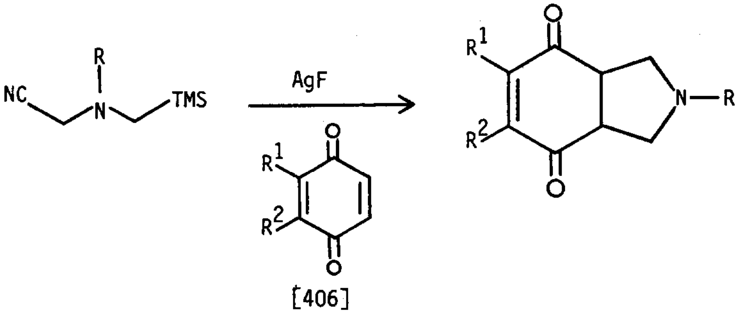
Treatment of α-trimethylsilyl iminium salts (or their precursors) continued to provide excellent entries into nitrile ylides for [3 + 2] cycloadditions. The aza-homoadamantane **267** reacts with dimethylacetylene dicarboxylate in the presence of fluoride ion to give pyrroles **268** and **269**. (Eqn. 548) α-silyl imines containing an α' leaving group also provide nitrile ylides upon treatment with fluoride ion. Examples are shown in equations 549 and 550).α-Silyl imines were shown to give nitrile ylide derived products when reacted with dipolarophiles in the presence of butyl halides or butyl tosylate. (Eqn. 551) The silylated carbodiimide reacts with fluoride ion in the presence of aldehydes to give oxazolidines. (Eqn. 552)



(548)



(549)



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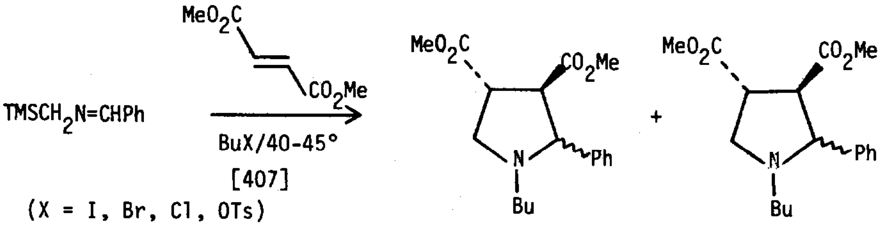

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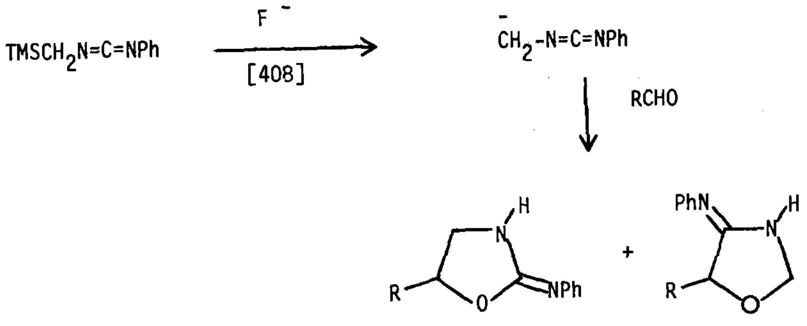
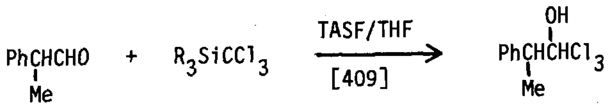

(552)

38-88% ca 1:1 mixtures

Other fluoride-induced reactions of α-functional organosilanes were reported. Trichloromethylsilane reacts with TASF in the presence of aldehydes to give the products of trichloromethyl anion addition. (Eqn. 553) Other systems react similarly as shown. (Eqns. 554-557) Chloromethyltrimethylsilane and difluoromethylphenyldimethylsilane failed to react.

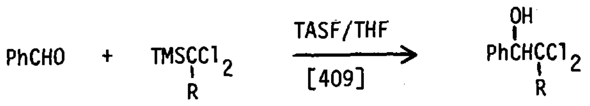


$$\underset{\displaystyle Me}{PhCHCHO} + R_3SiCCl_3 \xrightarrow[\text{[409]}]{\text{TASF/THF}} \underset{\displaystyle Me}{PhCH\overset{\displaystyle OH}{C}HCCl_3} \qquad (554)$$

erythro:threo ca. 88:12

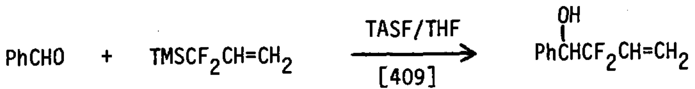
$R_3Si = Me_3Si$ (2 other examples 75-79%)

R_3Si also $PhMe_2Si$ and $^tBuMe_2Si$



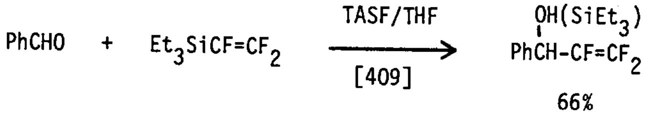
$$PhCHO + TMS\underset{\displaystyle R}{C}Cl_2 \xrightarrow[\text{[409]}]{\text{TASF/THF}} Ph\overset{\displaystyle OH}{C}H\underset{\displaystyle R}{C}Cl_2 \qquad (555)$$

R = H (74%); R = Me (97%)



$$PhCHO + TMSCF_2CH=CH_2 \xrightarrow[\text{[409]}]{\text{TASF/THF}} Ph\overset{\displaystyle OH}{C}HCF_2CH=CH_2 \qquad (556)$$

58%

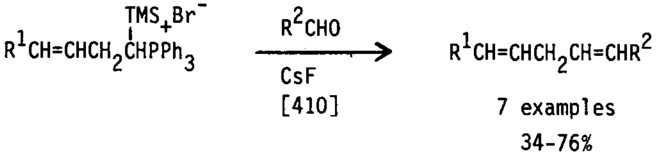


$$\mathrm{PhCHO} + \mathrm{Et_3SiCF{=}CF_2} \xrightarrow[\text{[409]}]{\text{TASF/THF}} \mathrm{Ph\overset{OH(SiEt_3)}{C}H{-}CF{=}CF_2} \qquad (557)$$

66%

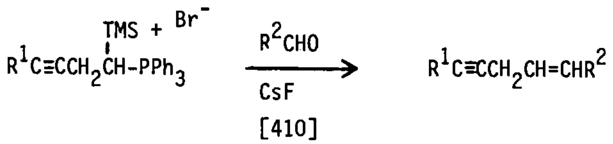
(other systems that were used are $\mathrm{Et_3SiCCl{=}CF_2}$, $\mathrm{Et_3SiCF{=}CFSEt}$, $\mathrm{Et_3SiCF{=}CHF}$ and $\mathrm{Et_3SiCF{=}CF^tBu}$ 38-84%)

α-Trimethylsilyl phosphonium salts were prepared and used as precursors to phosporus ylides. (Eqns. 558 and 559)



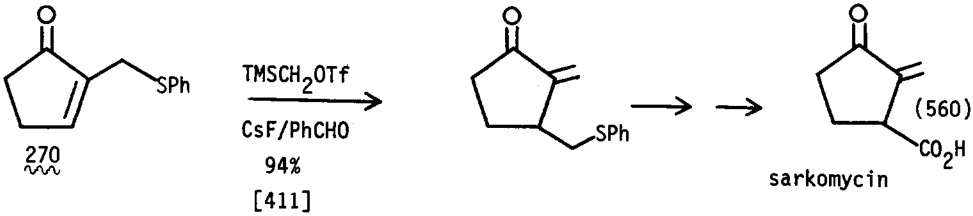
$$\mathrm{R^1CH{=}CHCH_2\overset{TMS\ \ Br^-}{C}H\overset{+}{P}Ph_3} \xrightarrow[\text{CsF [410]}]{\mathrm{R^2CHO}} \mathrm{R^1CH{=}CHCH_2CH{=}CHR^2} \qquad (558)$$

7 examples 34-76%

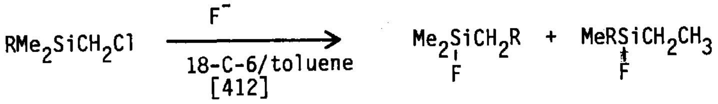


$$\mathrm{R^1C{\equiv}CCH_2\overset{TMS\ +\ Br^-}{C}H{-}PPh_3} \xrightarrow[\text{CsF [410]}]{\mathrm{R^2CHO}} \mathrm{R^1C{\equiv}CCH_2CH{=}CHR^2} \qquad (559)$$

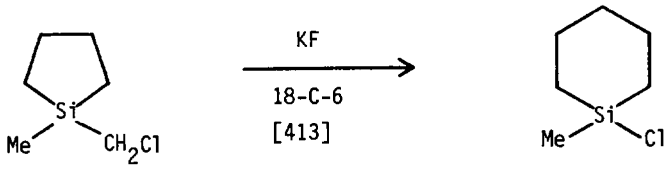
Treatment of **270** with trimethylsilylmethyl triflate, cesium fluoride and benzaldehyde results in the "in situ" preparation of the sulfonium methylide and [3.3] sigmatropic rearrangement. The product of the transformation was used to prepare sarkomycin. (Eqn. 560)



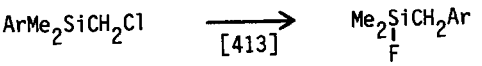
The fluoride-induced rearrangements of chloromethylsilanes were studied. Potassium or cesium fluoride solubilized with crown ethers was an excellent fluoride source for the reaction. The migratory aptitude of various R groups on silicon was studied. (Eqn. 561) The cyclic system **258** was also reacted. (Eqn. 562) A Hammett plot on the reaction **259** was carried out. (Eqn. 563)



$$RMe_2SiCH_2Cl \xrightarrow[\text{18-C-6/toluene} \atop [412]]{F^-} Me_2\underset{F}{Si}CH_2R + MeR\underset{F}{Si}CH_2CH_3 \qquad (561)$$

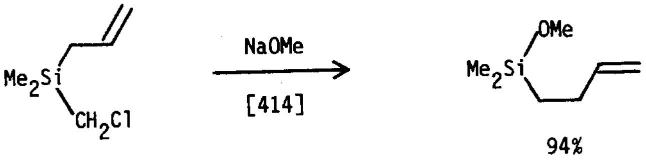


(562)

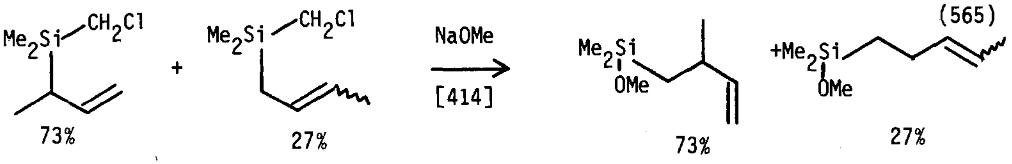


$$ArMe_2SiCH_2Cl \xrightarrow[{[413]}]{} Me_2\underset{F}{Si}CH_2Ar + \text{other products} \qquad (563)$$

Chloromethylallylsilanes react with methoxide ion to give migration of the allyl group. The migration occurs without double bond transposition. (Eqns. 564 and 565) Vinylsilanes also react, but the principle pathway is direct substitution. (Eqn. 566)

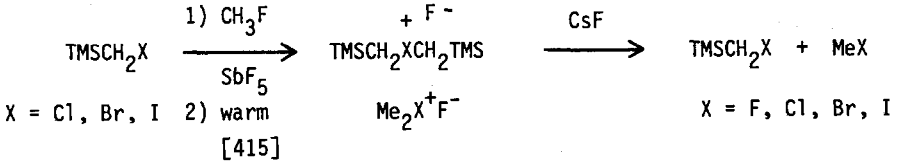


(564)


(565)


(566)

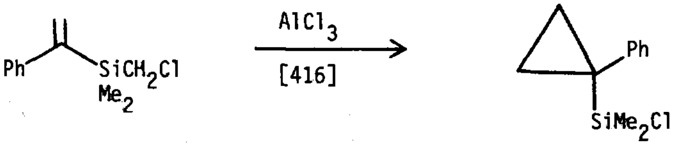
An attempt to prepare alkylhalonium methylides via the reaction of fluoride ion with trimethylsilylmethylhalonium salts failed. (Eqn. 567)

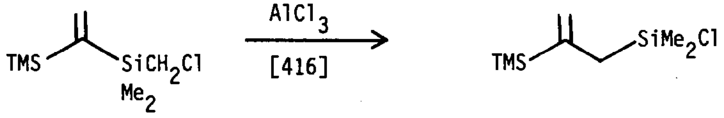


$$\underset{X = Cl,\ Br,\ I}{TMSCH_2X} \xrightarrow[SbF_5 \quad 2)\ \text{warm} \quad [415]]{1)\ CH_3F} \underset{Me_2X^+F^-}{\overset{+\ F^-}{TMSCH_2XCH_2TMS}} \xrightarrow{CsF} \underset{X = F,\ Cl,\ Br,\ I}{TMSCH_2X + MeX}$$

(567)

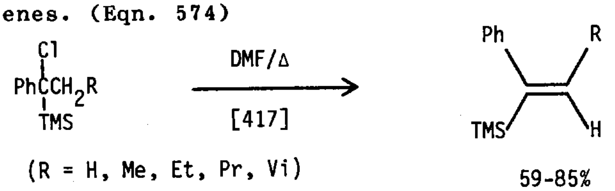
The aluminium chloride catalyzed reaction of chloromethylvinylsilanes was carried out. Allylsilanes and cyclopropylsilanes are the principle products. Silacyclopropylcarbinyl- and cyclopropylsilylenium cations are proposed as intermediates. (Examples are shown. (Eqns. 568 and 569)


(568)



(569)

Other reactions of α-functional organosilanes were reported. α-Chlorobenzylsilanes undergo thermal elimination of HCl to give (E) vinylsilanes in good yield. (Eqn. 570) Chloromethylsilanes react with bis(triethylsilyl) (or germyl) mercury to give the α-silyl mercury compounds. (Eqn. 571) α,α-Dichlorosilanes react with hexamethyldisilane in the presence of Pd(0) to give vinylsilanes. (Eqn. 572) The α-acetoxysilane **271** reacts with malonic esters in the presence of molybdenum hexacarbonyl to give **272**. (Eqn. 573) These allysilanes react with aryl acetals to give dienes. (Eqn. 574)

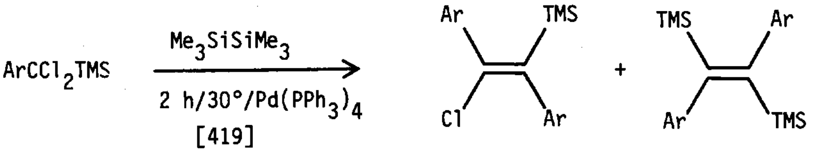


(570)

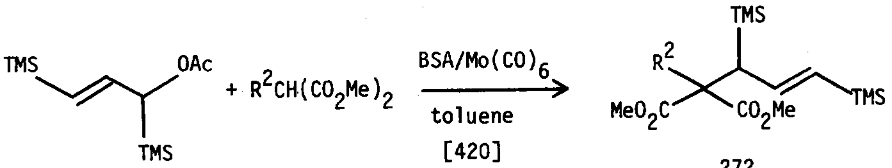
$$ClCH_2SiMe_{3-n}R_n \quad + \quad (Et_3M)_2Hg \xrightarrow[{[414]}]{} (R_nMe_{3-n}MCH_2)_2Hg \qquad (571)$$

M = Si, Ge

79.4-95.2%



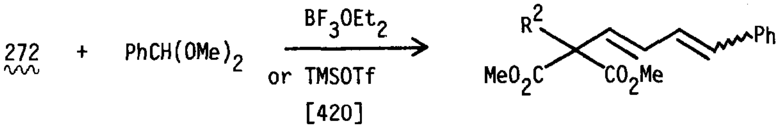
(572)



(573)

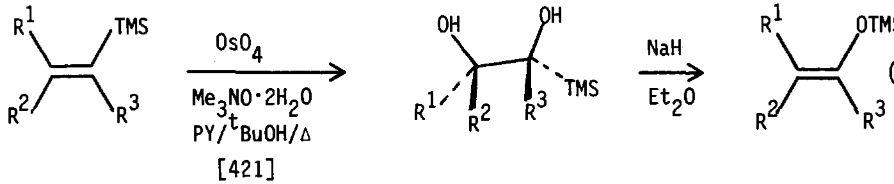
271

272

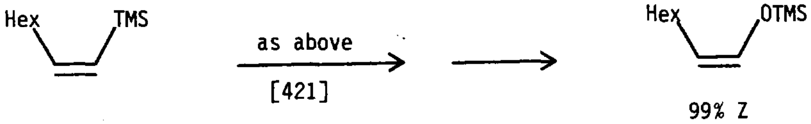


(574)

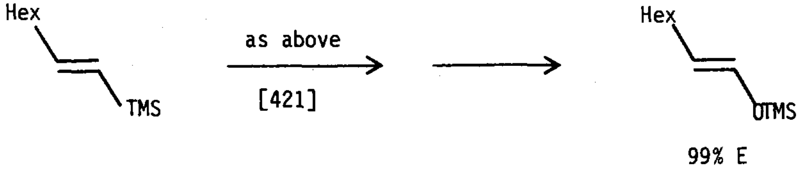
α, β-Dihydroxysilanes, prepared stereospecifically via hydroxylation of vinylsilanes, react with sodium hydride in ether to give enol silyl ethers regio- and stereospecifically. (Eqns. 575-577)



(575)

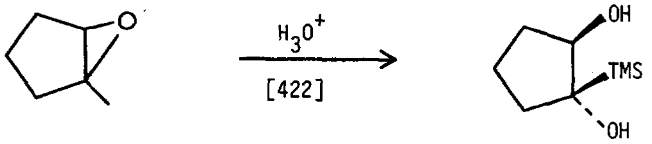


(576)

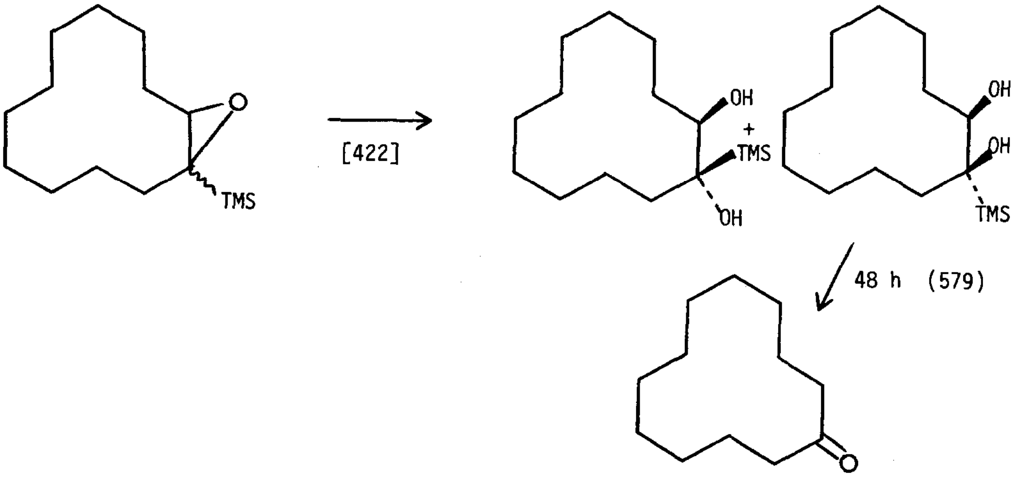


(577)

The effect of ring size on the acid-catalyzed hydrolysis of cyclic α,β-epoxsilanes was studied. The smaller rings give only cis-β-hydroxysilanes, which are stable to acid, (Eqn. 578) whereas the larger rings such as cyclododecyl give some trans-p-hydroxysilanes which hydrolyze in acid. (Eqn. 579)

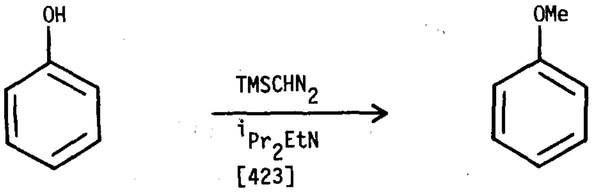


(578)

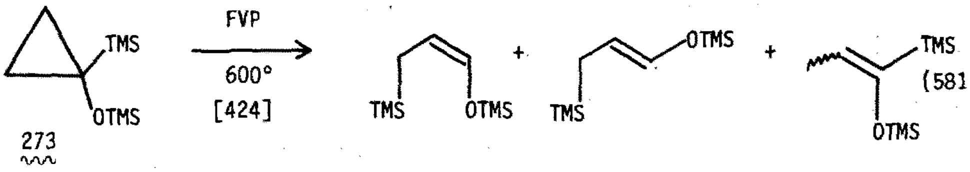


(579)

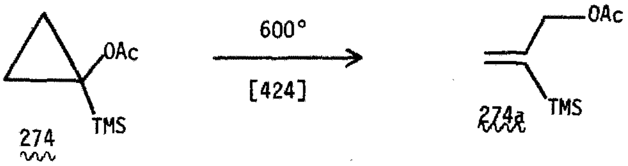
Trimethylsilyldiazomethane reacts with phenols to give anisoles. (Eqn. 580) The flash vacuum pyrolysis of **273** gives enol silyl ethers. (Eqn. 581) The acetate **274** gives **274a**. (Eqn. 582) Trimethylsilylmethyl azide was used to generate $CH_2{=}N^-$ in a flowing afterglow apparatus. (Eqn. 583)



(580)



(581)

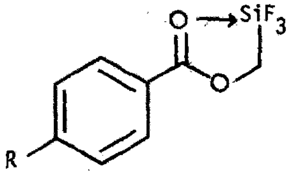


(582)

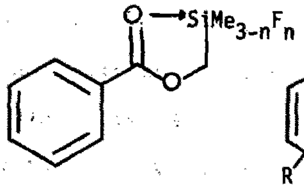
$$\mathrm{TMSCH_2N_3} \xrightarrow[\text{[421]}]{^{-}\mathrm{NH_2}} \mathrm{CH_2{=}N^-} \qquad (583)$$

C. Other Studies

The IR and Raman spectra of $\mathrm{ClCH_2Me_nSiCl_{3-n}}$ (n=0-2) were studied. [422] The trifluorosilylmethyl benzoates **275** - **278** were studied by IR (**275**, **276**, **277**). Their rotational isomerism (**278**) and insecticidal and nematocidal properties were also studied.(**277**) [427, 428, 429, 430]



275



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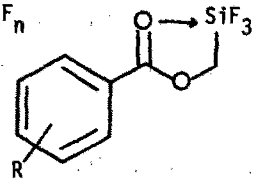

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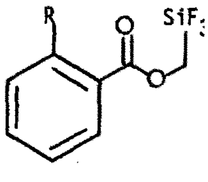
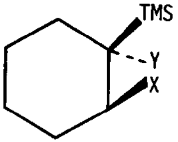


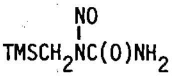
278

The conformations of fourteen different trans-1,2-disubstituted trimethylsilylcyclohexanes **279** were studied. Those that can form an intramolecular hydrogen bond do so placing the trimethylsilyl group axial. When this is not possible the trimethylsilyl group is equatorial. [431]



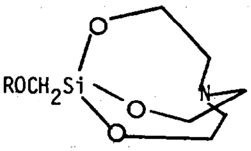
279

The mutagenicity and cytotoxicity as well as the hydrolysis of **280** have been studied. [432]] The toxicity and bactericidal activity of **281** have been studied. [433]



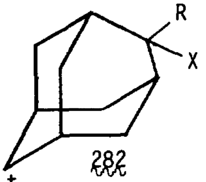
$TMSCH_2N(NO)C(O)NH_2$

280



281 (14 examples)

Theoretical studies on the effect of a silyl group on an α-carbonium ion [434, 435] and a β-silyl carbonium ion [435] have been carried out. The α-silyl carbonium ions are predicted to be somewhat less stable than their alkyl counterparts, but more stable than the hydrogen compounds. The stabilization of β-silyl cations is large. The solvolysis of **282** showed the following relative rates - ^{t}Bu>TMS~Me>H. [434]



282

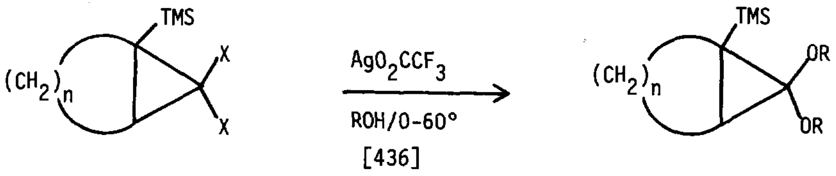
R = TMS; H; ^{t}Bu; H

X = p-NO_2-$C_6H_4CO_2$-

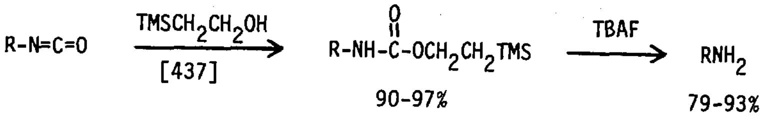
XII. β-FUNCTIONAL ORGANOSILANES

A. Preparation

Gem dihalocyclopropylsilanes were converted to the ketals as shown. (Eqn. 584) Silylethyl carbamates were prepared and treated with fluoride ion to give amines. (Eqn. 585)

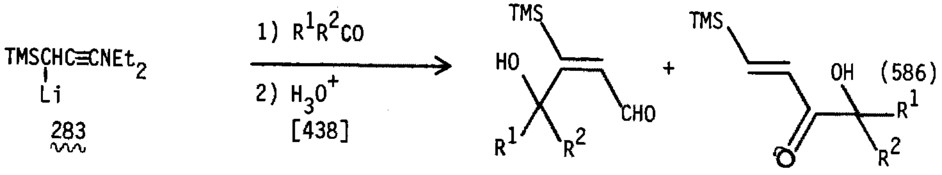


(584)



$$\text{R-N=C=O} \xrightarrow[\text{[437]}]{\text{TMSCH}_2\text{CH}_2\text{OH}} \underset{90\text{-}97\%}{\text{R-NH-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-OCH}_2\text{CH}_2\text{TMS}} \xrightarrow{\text{TBAF}} \underset{79\text{-}93\%}{\text{RNH}_2} \qquad (585)$$

Lithium reagent **283** reacts with aldehydes and ketones to give predominantly α-attack. (Eqn. 586)



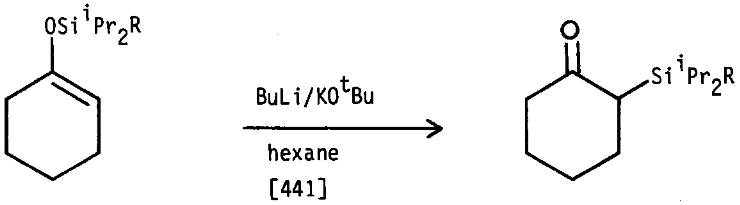
Several preparations of α-silyl carbonyl systems appeared. (Ethoxycarbonyl)carbene was inserted into the Si-H bond to give α-silyl esters. (Eqn. 587) Treatment of dimethylketene acetal with trialkylsilyl iodide gives the α-silyl ester. (Eqn. 588) Deprotonation of triisopropylsilyl or diisopropylmethylsilyl enol ethers results in β-ketosilanes via an O→C rearrangement. (Eqns. 589-591) 1-Tri-n-propylsilylethanol is oxidized to the aldehyde, which undergoes thermal rearrangement. (Eqn. 592) Formylation of **284** gives **285**. (Eqn. 593) O-Silylated oximes can be deprotonated whereupon the silicon migrates to carbon to give the α-silyl oxime. This is thermally converted to the original O-silylated isomer. (Eqn. 594)

$$R^1\text{-}C\equiv C\text{-}SiMe_nH_{3-n} \xrightarrow[\Delta \text{ or cat}/\Delta \text{ [439]}]{N_2CHCO_2R^2} R^1\text{-}C\equiv C\text{-}SiMe_nH_{2-n}CH_2CO_2R^2 \qquad (587)$$

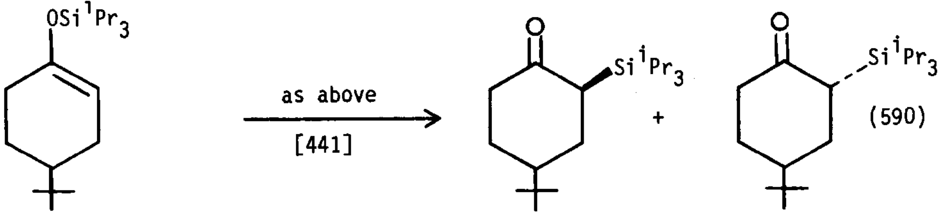
R^1 = Me, Bu, ${}^tBu$, Ph, $MeOCH_2$, $TMSCH_2$; R^2 = Me, Et; n = 0-2

$$CH_2{=}C(OMe)_2 \xrightarrow[\text{[440]}]{R_3SiI} R_3SiCH_2CO_2Me \qquad (588)$$

R = Me, Et 98%



(589)



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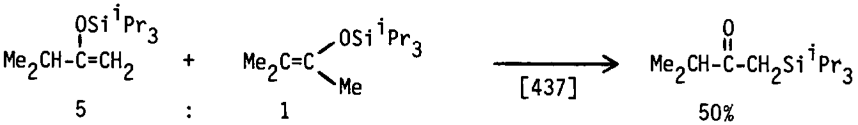
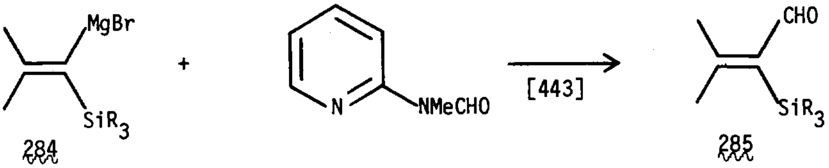


$$\underset{5}{Me_2CH-\overset{OSi^iPr_3}{C}=CH_2} \; + \; \underset{1}{Me_2C=C(OSi^iPr_3)Me} \xrightarrow{[437]} \underset{50\%}{Me_2CH-\overset{O}{\overset{\|}{C}}-CH_2Si^iPr_3} \quad (591)$$

5 : 1

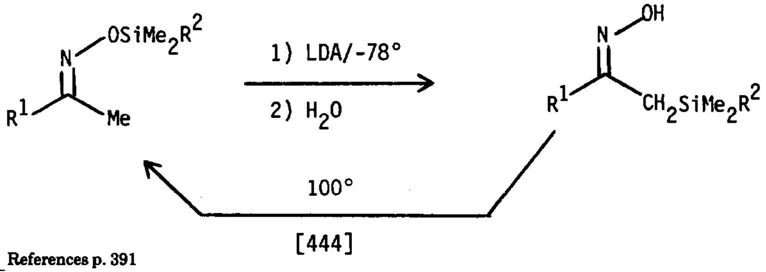
$$Pr_3SiCH_2CH_2OH \xrightarrow[{[442]}]{NCS} Pr_3SiCH_2CHO \longrightarrow CH_2=CHOSiPr_3 \quad (592)$$



284

285

(593)

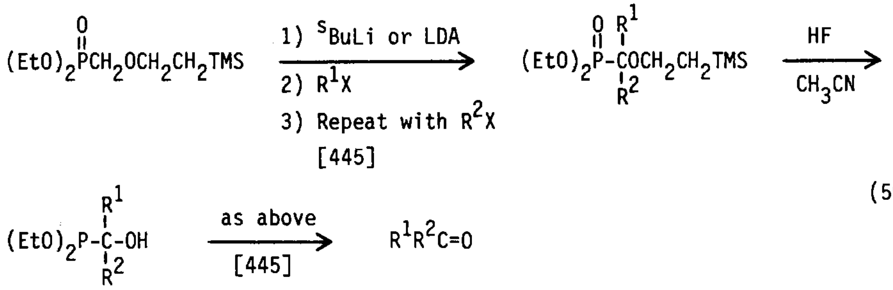


(594)

B. Reactions

The elimination of β-functional organosilanes to give olefins was reported. Deprotection of β-trimethylsilylethanol derivatives provided mild entries into α-hydroxyphosphonates and thus ketones (Eqn. 595) and β-lactams (Eqn. 596).

Cis-epoxysilanes were converted to (Z) or (E) enamines via elimination of the β-hydroxysilanes produced by amine opening of the epoxide. (Eqns. 597 and 598) β- Silyl sulfones can be eliminated with fluoride ion. (Equ. 599) The β-trifluoroacetoxysilane **287** gave methylenecyclobutane, but all attempts to use this strategy in preparing **298** or **299** failed. (Eqns. 600-604)



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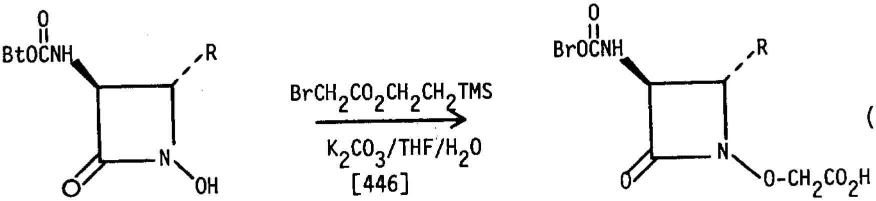

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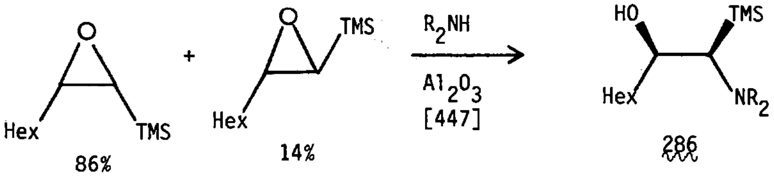

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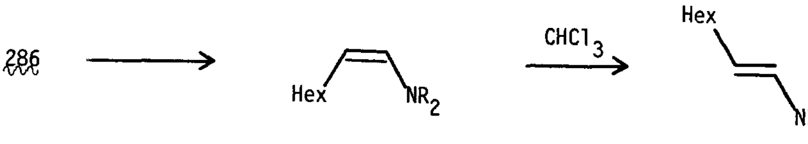
(597)



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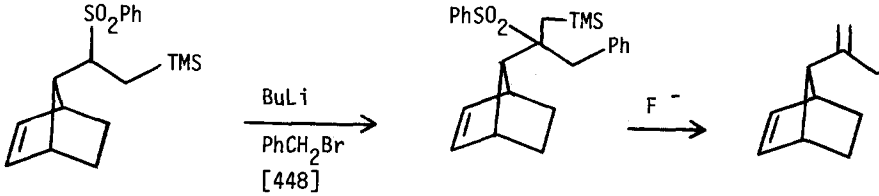

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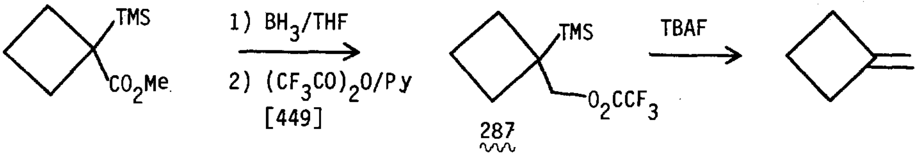
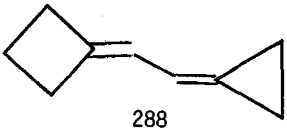


(600)



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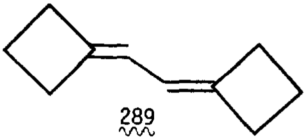

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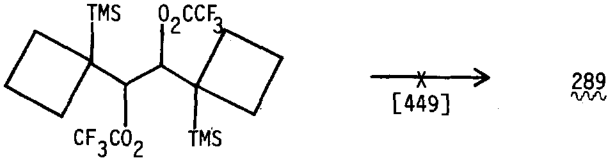

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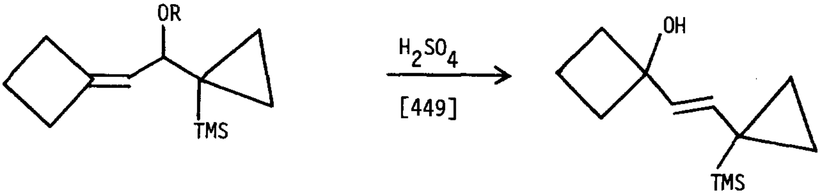
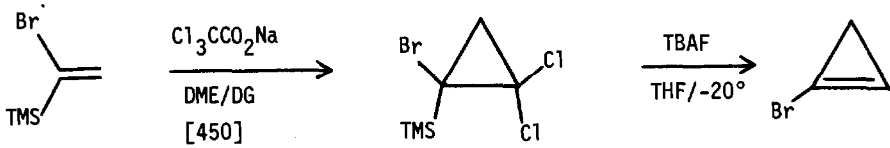


(602)

$$R = Ac \longrightarrow \underset{\sim\sim}{278} \qquad (603)$$

$$OR = Cl \longrightarrow \underset{\sim\sim}{278} \qquad (604)$$

The above results notwithstanding, some high energy double bonds were prepared by β-eliminations involving silicon. 1-Bromo-2-chlorocyclopropane was prepared by fluoride-induced loss of TMSCl. (Eqn. 605) Pyridine-borabenzene and pyridine-boranaphthalene were prepared by β-elimination of TMSOMe and TMSCl, respectively. (Eqns. 606 and 607) Methanethial (sulfine) and alkanethial S,S-dioxides were prepared by fluoride-induced elimination. These were trapped with cyclopentadiene. (Eqns. 608 and 609)



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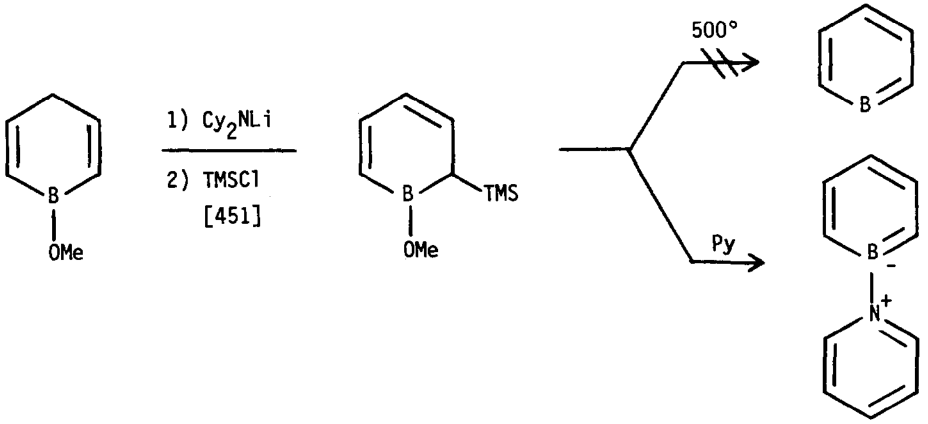

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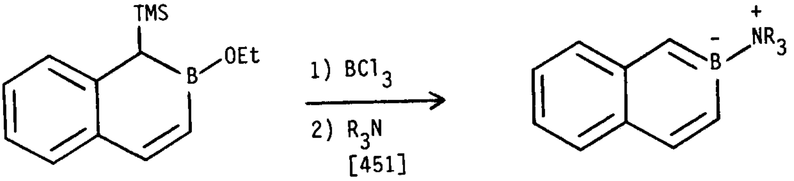

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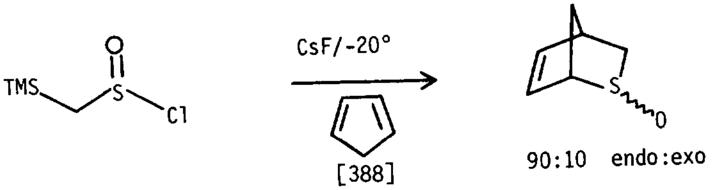

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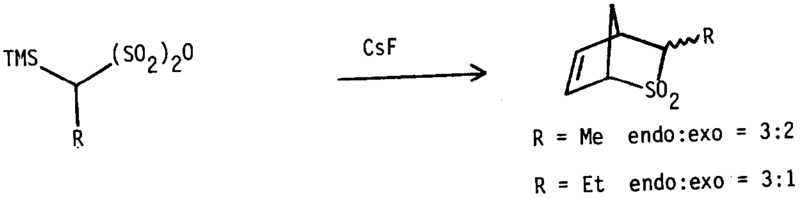
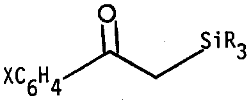


(609)

Several reactions of α-silyl carbonyl systems were reported. The hydrolysis of **290** in H_2O/THF and base catalyzed was studied kinetically. Structures **291** and **292** fit the data for each reaction, respectively.



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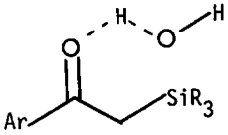

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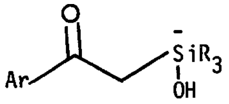
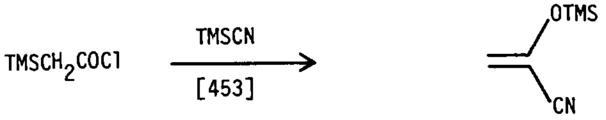


292

Trimethylsilylacetyl chloride reacts with trimethylsilyl cyanide to give the α-cyano enol silyl ether. (Eqn. 610) This same reagent adds nicely to trimethylsilylcyclopropanone. (Eqn. 611) β-Ketosilanes were shown to add to aldehydes under Lewis acid catalysis. (Eqn. 612) The bulky trimethylsilyl group allows enolate formation on the opposite side, which coupled with facile desilylation during workup results in a regioselective cross aldol reaction. (Eqn. 603) α-Silyl-α-stannyl ester **293** reacts with acetyl chloride to give enone **294**. (Eqn. 604) The reaction of fluoride ion with β-ketosilanes in the presence of an electrophile gives α-substituted ketones. (Eqns. 615 and 616)



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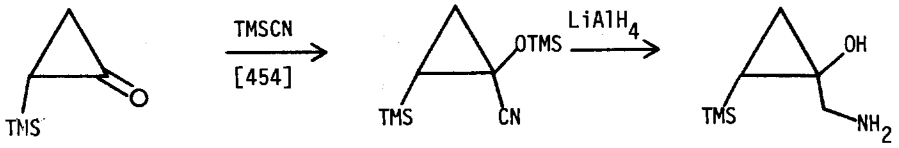

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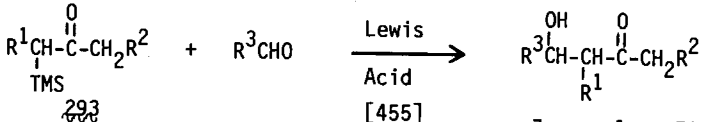


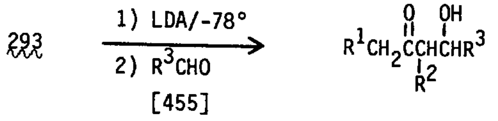
$$R^1\underset{\underset{TMS}{|}}{C}H-\overset{\overset{O}{\|}}{C}-CH_2R^2 + R^3CHO \xrightarrow[\text{Acid}]{\text{Lewis}} R^3\overset{\overset{OH}{|}}{C}H-\underset{\underset{R^1}{|}}{C}H-\overset{\overset{O}{\|}}{C}-CH_2R^2$$

293 [455]

7 examples 73-87%

Lewis acid = $TiCl_4$, $SnCl_4$, BF_3OEt_2(best) threo:erythro ∿ 30:70

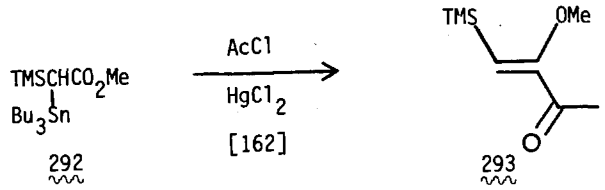
(612)



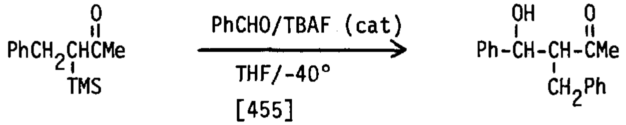
$$\mathbf{293} \xrightarrow[\text{2) } R^3CHO]{\text{1) LDA/-78°}} R^1CH_2\overset{\overset{O}{\|}}{C}\underset{\underset{R^2}{|}}{C}H\overset{\overset{OH}{|}}{C}HR^3$$

[455]

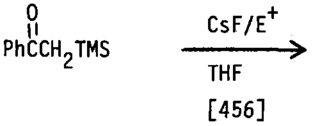
(613)



(614)


$$\underset{\text{TMS}}{\mathrm{PhCH_2CH}}\overset{\text{O}}{\overset{\|}{\text{C}}}\mathrm{Me}\xrightarrow[\text{THF}/-40^\circ\ [455]]{\text{PhCHO/TBAF (cat)}}\mathrm{Ph\text{-}\overset{OH}{CH}\text{-}\underset{CH_2Ph}{CH}\text{-}\overset{O}{\overset{\|}{C}}Me}$$

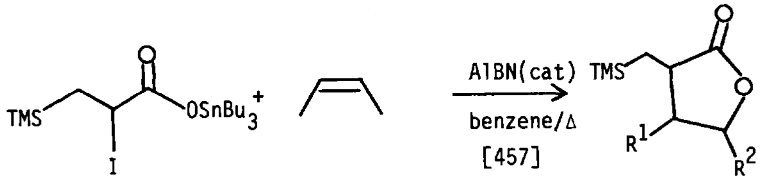
(615)


$$\mathrm{Ph\overset{O}{\overset{\|}{C}}CH_2TMS}\xrightarrow[\text{THF}\ [456]]{\text{CsF/E}^+}$$

(616)

E^+ = PhCHO; Cyclohexenone (1, 4); $PhCH_2Br$; allyl bromide; PhC(O)TMS;

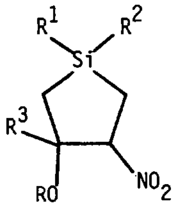
The β-iodosilane **296** photochemically adds to olefins to give β-lactones **297**. (Eqn. 617)



(617)

C. Other Studies

Low temperature ^{1}H NMR spectra of **297** showed them to have cis and trans isomers and be in a half-chair conformation. [458] A comparison of the crystal and molecular structures of **298** and **299** showed them to have almost identical arrangements. [459]



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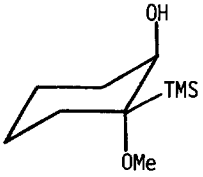

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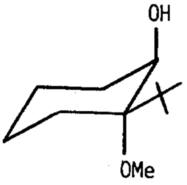
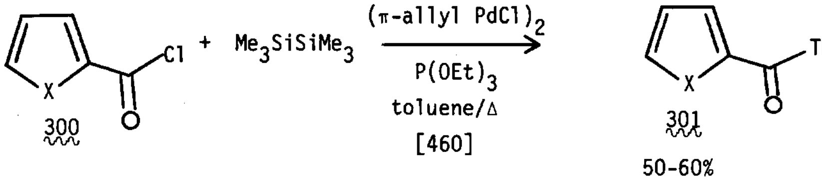


299

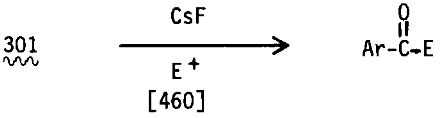
XIII. MISCELLANEOUS FUNCTIONAL ORGANOSILANES

A. Acylsilanes

The reaction of acid chlorides **300** with hexamethyldisilane in the presence of a palladium catalyst gives acylsilanes. (Eqn. 618) These react with certain electrophiles in the presence of fluoride ion. (Eqn. 619)



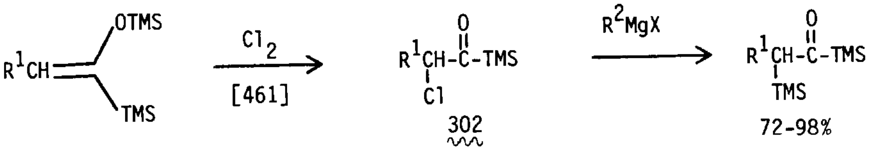
(618)



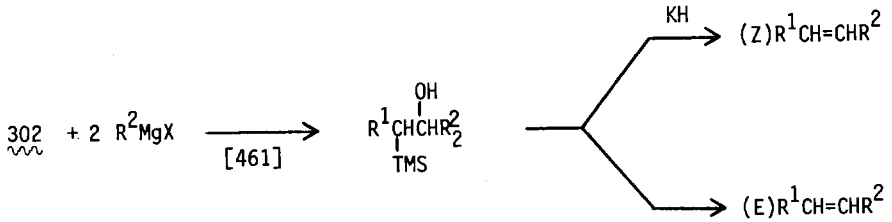
$$301 \xrightarrow[E^+ \;\; [460]]{\text{CsF}} \text{Ar}-\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{E} \qquad (619)$$

α-Chloroacylsilanes, prepared from enol silyl ethers of acylsilanes, react with one equivalent of a Grignard reagent to give β-ketosilanes. (Eqn. 620) The reaction with two equivalents of a Grignard reagent that contains α-hydrogens gives reduction of the β-ketosilane to the β-hydroxysilane which can be eliminated (syn or anti) to (Z)- or (E)- olefins with high stereoselectivity. (Eqn. 621 and 622)

The reaction of acylsilanes with vinylmagnesium bromide gives a homoenolate ion **303**, which in the presence of trimethylsilylethynyl copper (I), conjugate adds to enones. (Eqns. 623 and 624) α,β-Unsaturated esters also add this reagent. (Eqn. 625) Vinyllithium gives a similar reaction, although the homoenolate ion formation is slower in this ${}^{t}BuMe_2Si$ case. (Eqn. 626)

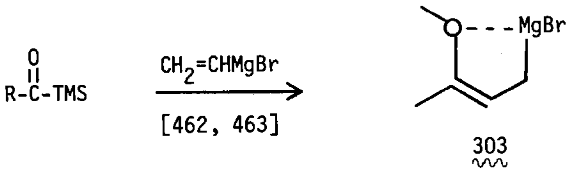


(620)

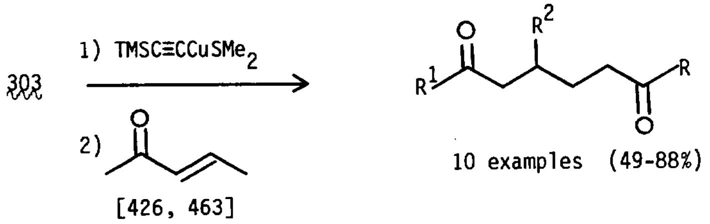


(621)

(622)



(623)



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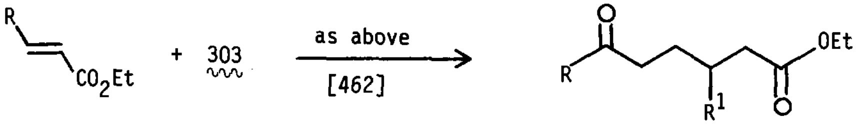

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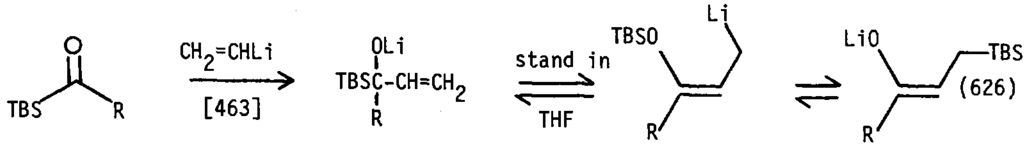
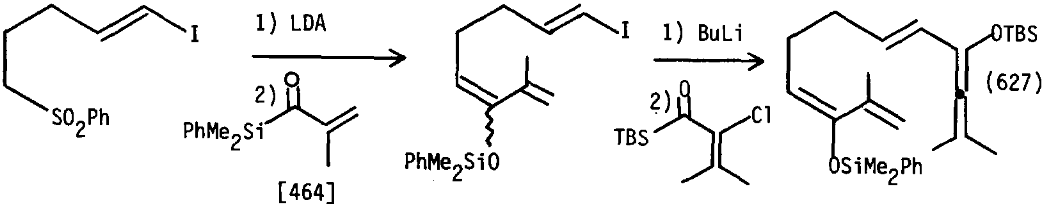


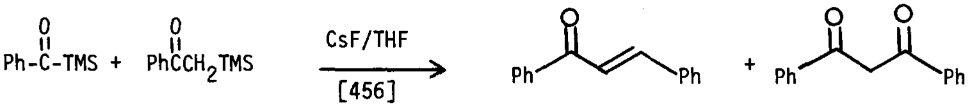
(626)

Acylsilanes were employed in the key steps for the preparation of vinyl allenes for intramolecular cycloadditions leading to eudesmane sesquiterpenes and eremophilane. (Eqn. 627)



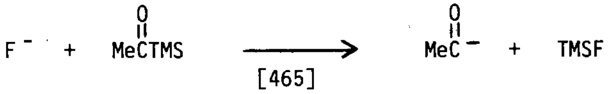
(627)

Acylsilanes were reacted with β-ketosilanes in the presence of fluoride ion. (Eqn. 628)

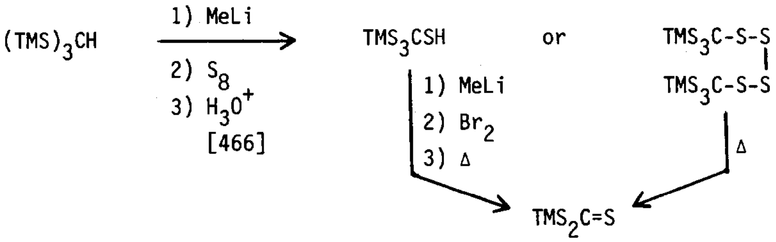


(628)

The interaction of fluoride ion and acyltrimethylsilane in the flowing afterglow apparatus provides the acyl anion, which was then studied. (Eqn. 629) Bis(trimethylsilyl)thioketone, **304** was prepared as shown. (Eqn. 630)



$$F^- + \mathrm{Me}\overset{O}{\overset{\|}{C}}\mathrm{TMS} \xrightarrow[{[465]}]{} \mathrm{Me}\overset{O}{\overset{\|}{C}}{}^- + \mathrm{TMSF} \qquad (629)$$

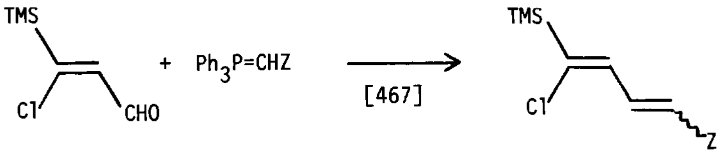


304

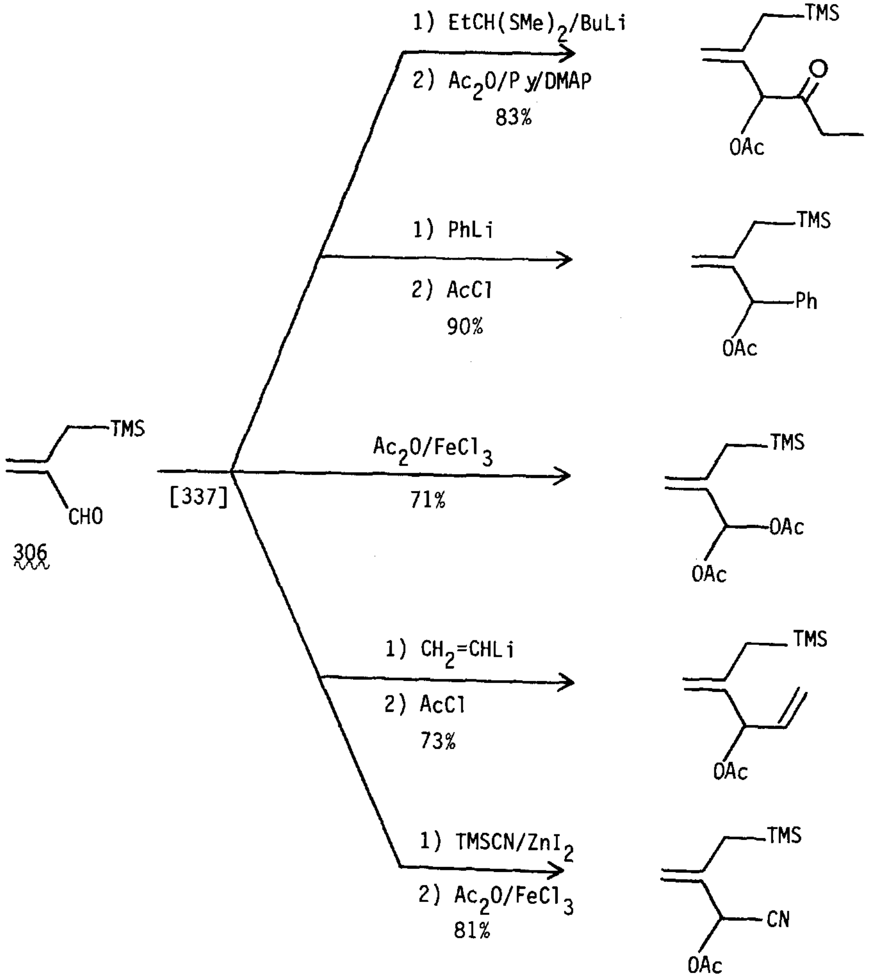
(630)

B. γ-Functional Organosilanes

Aldehyde **305** gives dienes upon treatment with Wittig reagents. (Eqn. 631) Aldehyde **306** is the starting point for the preparation of a variety of γ-functional organosilanes as shown. (Eqns. 632-636). Some similar aldehydes to **306** were used in diastereoselective cross aldol reactions. (Eqns. 637-640)



(631)



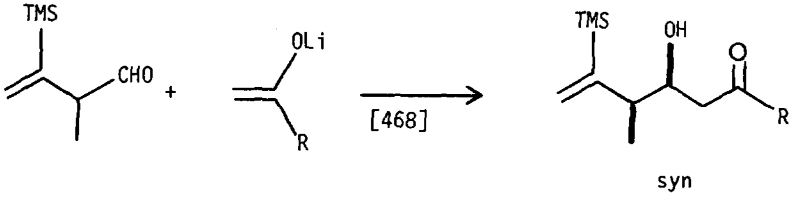
(632)

(633)

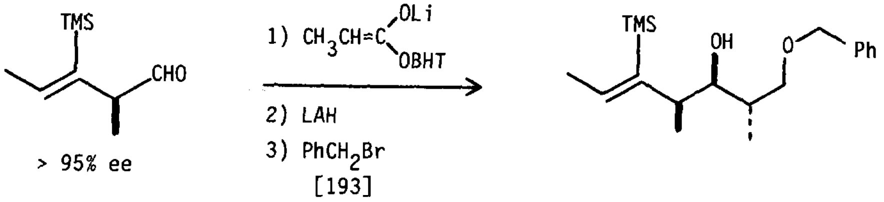
(634)

(635)

(636)



+ anti (637)



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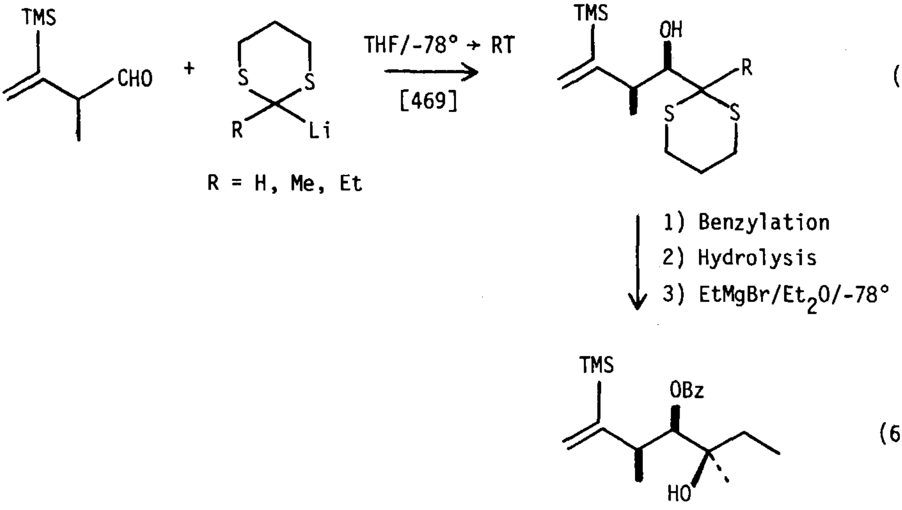
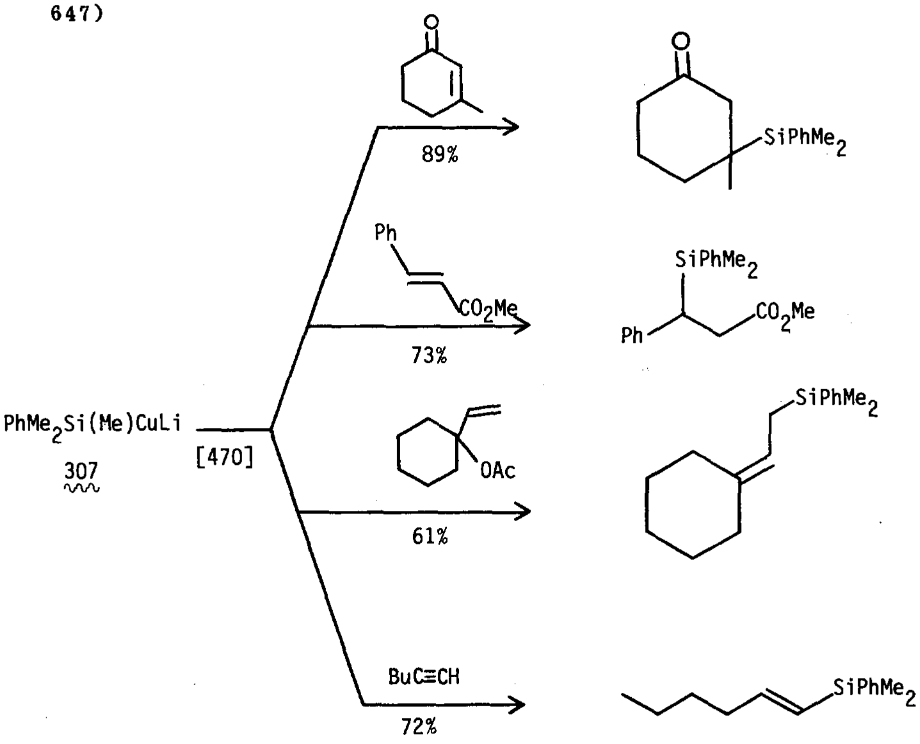


(639)

(640)

Silylcuprate reagent **307** undergoes Michael additions. (Eqns. 641 and 642) The trimethylsilyl reagent **308** Michael adds as well. (Eqns. 645 and 646) Both reagents add to acetylenes (Eqns. 644 and 648) and react with allyl acetates. (Eqns. 643 and 647)



(641)

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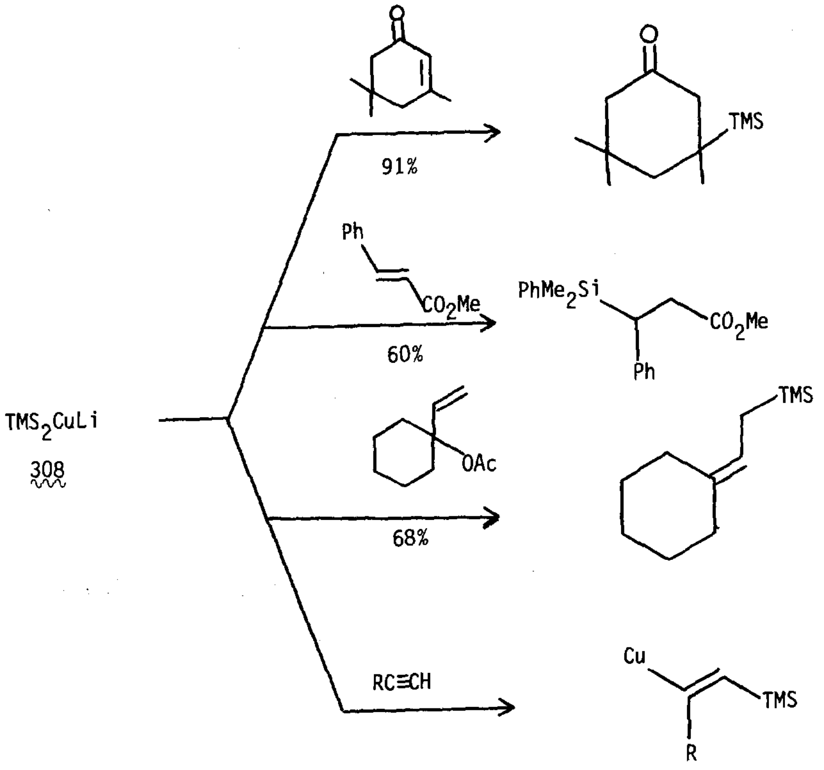


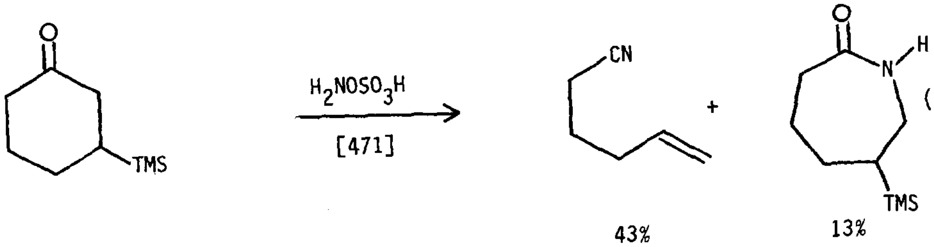
(645)

(646)

(647)

(648)

Cyclic β-silyl ketones undergo a silicon-directed Beckmann fragmentation. (Eqns. 649-651)



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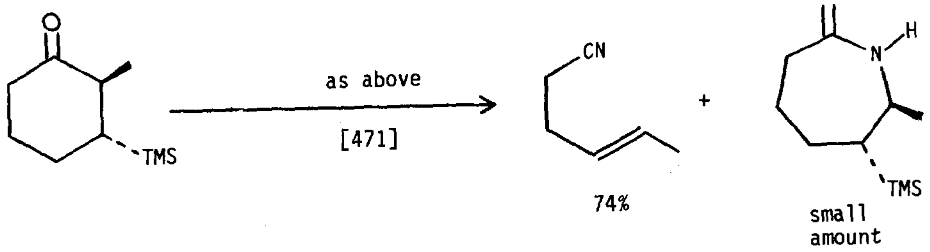

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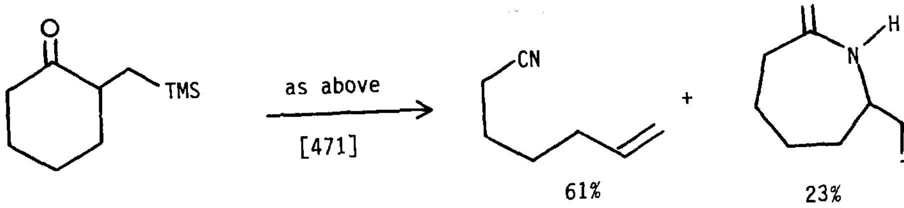
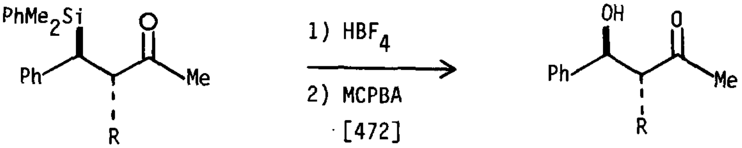


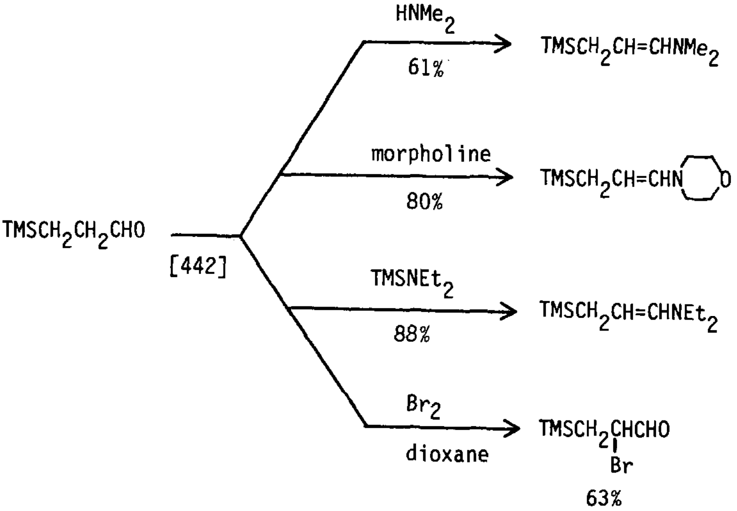
(651)

Acyclic β-silyl ketones and esters, from $(PhMe_2Si)_2CuLi$ and enones, were oxidized to β-hydroxy ketones and esters. (Eqn. 652)



(652)

β-Trimethylsilylpropionaldehyde underwent some standard aldehyde reactions without silicon involvement. (Eqns. 653-656)



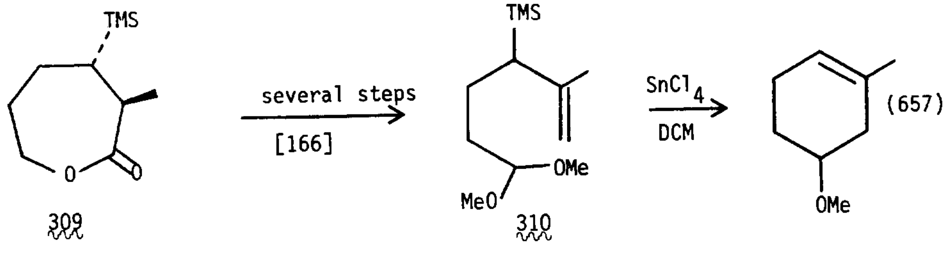
(653)

(654)

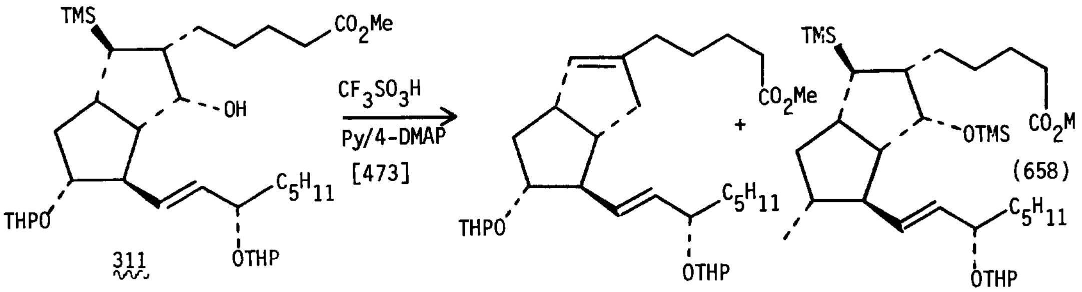
(655)

(656)

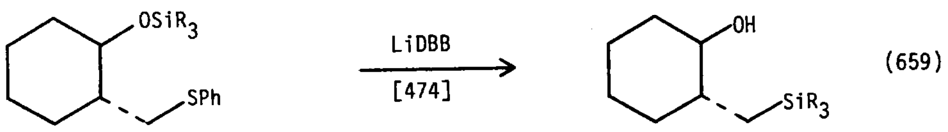
β-Trimethylsilyl lactone **309** was converted in several standard steps to allylsilane **310**, which was cyclized. (Eqn. 657)



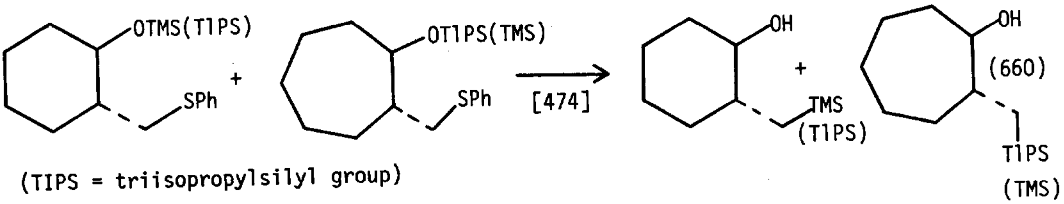
Rearrangement to a β-silyl cation followed by elimination is seen when γ-hydroxysilane **311** is treated with acid. (Eqn. 658)



γ-Silyl alcohols result when γ-silyloxy-alkyl-phenyl thio ethers are treated with lithium di-tert-butylbiphenyl (LIDBB). The rearrangement is intramolecular as shown by crossover experiments. (Eqns. 659 - 661) The bis-trimethylsilyl system **312** gives **313**.

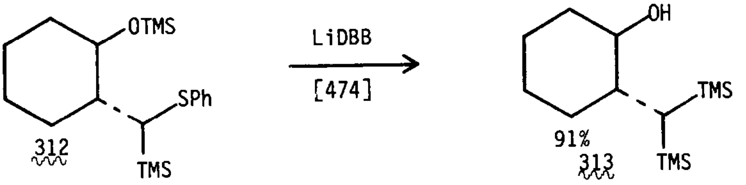


LiDBB = Lithium di-tert-butylbiphenyl



(TIPS = triisopropylsilyl group)

(660)



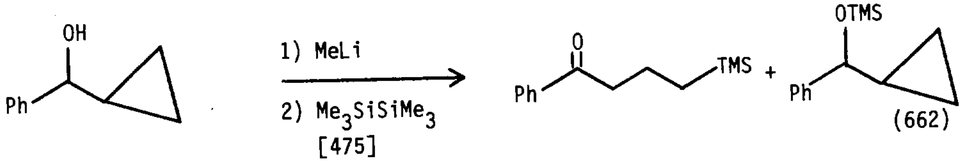
312

313

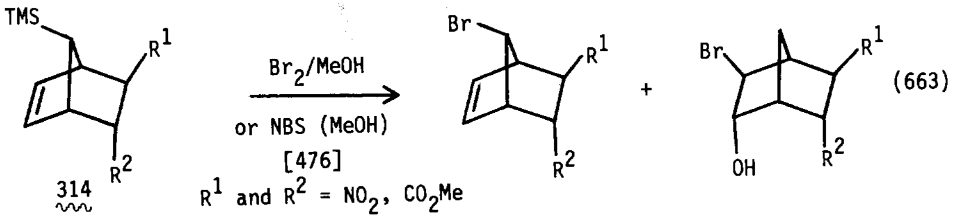
(661)

C. Other Functional Organosilanes

Cyclopropylphenylcarbinol reacts with methyllithium in the presence of hexamethyldisilane to give the δ-ketosilane. The mechanism was studied. (Eqn. 662) Syn-7-trimethylsilyl norbornenes **314** and **315** react with bromine or NBS to give only minor amounts of a silicon-assisted Wagner-Meerwein rearrangement for **314** but as a major pathway for **315**. (Eqns. 663 and 664)



(662)



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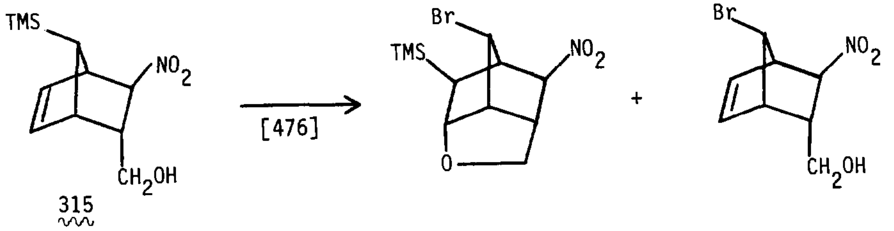
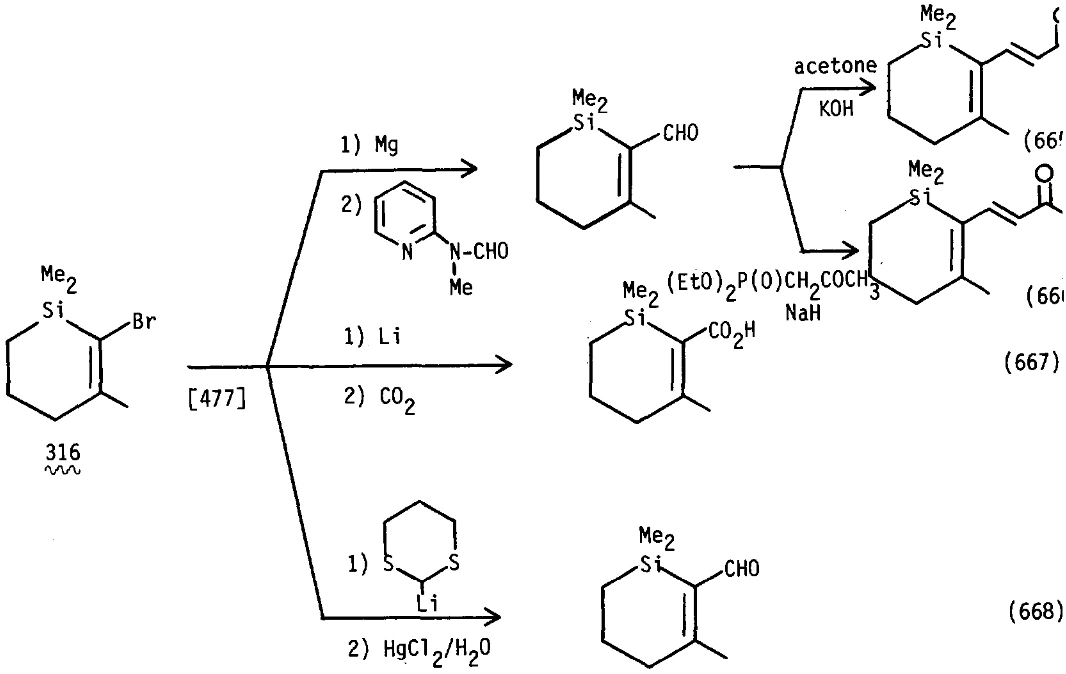
(663)



(664)

Some transformations of silane **316** (Eqns. 665-668) and also **317** (Eqns. 669-671) are given.



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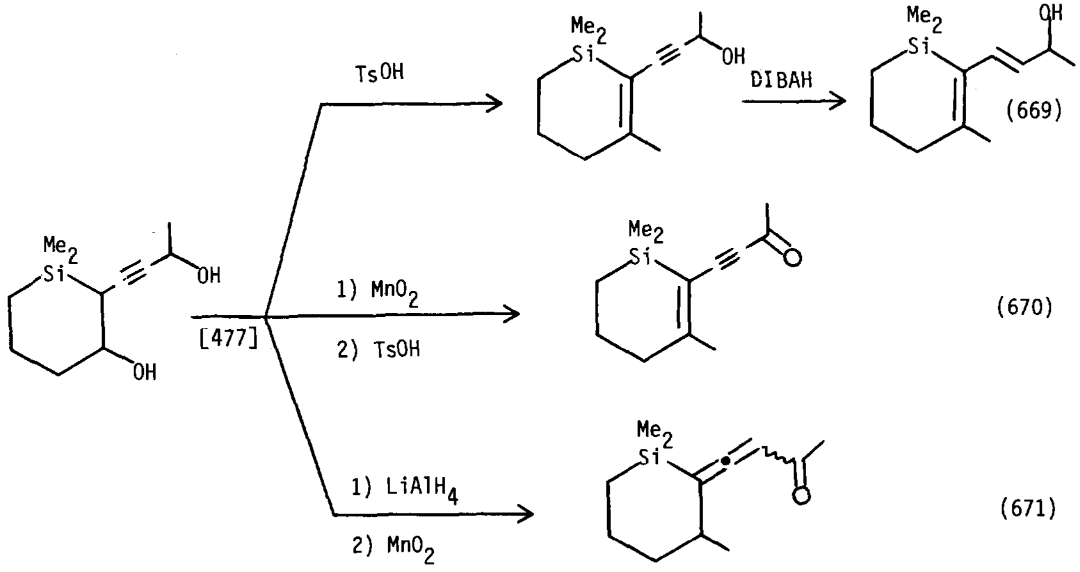

(669)

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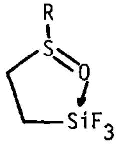
(671)

The kinetics of the reaction of γ-aminosilanes with benzylchloride were studied. [478] α-Silylaryl ureas were studied as possible anticancer drugs. [479] The β-silyl sulfoxide **316** shows nonequivalence of the fluorines in the ^{19}F NMR spectrum. [480]



316

XIV. REACTIVE SPECIES

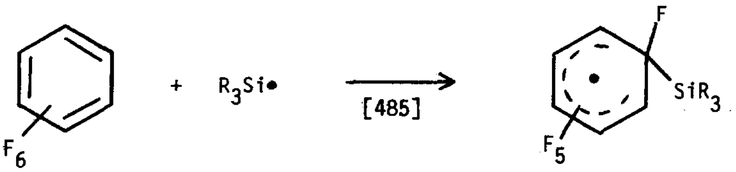
A. Radicals

Ab initio molecular orbital calculations have been carried out on the trimethylsilyl radical and other similar species. The CH_3 rotation is found to be about 14 kJ mol^{-1} and the radical is pyramidal with an out-of-plane angle of 14.6^{o}. [481] A linear correlation was found to exist between the ^{29}Si coupling constant in silyl radicals (R_3Si) and the Si-H coupling constant in the corresponding silane (R_3SiH). [482] An electron spin resonance study of triisopropyl- and tri-tert-butylsilyl radicals has been reported. The results are interpreted in terms of conformational effects. [483]

It was found that the triethylsilyl radical abstracts a chlorine atom from tetrachloroethylene. (Eqn. 672) The reaction has been studied mechanistically.

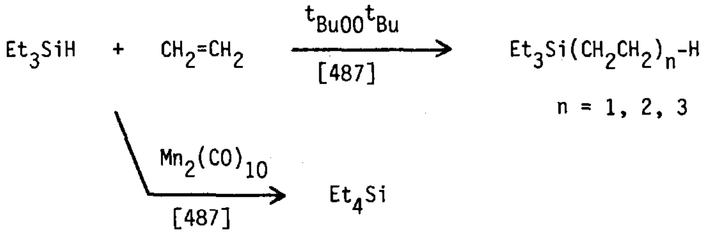
$$Cl_2C{=}CCl_2 \quad + \quad Et_3SiH \xrightarrow[\text{or radiolysis}\atop\text{[484]}]{h\nu} Et_3SiCl \quad + \quad Cl_2C{=}CHCl \qquad (672)$$

Hexafluorocyclohexadienyl radicals have been generated by the addition of silyl radicals to hexafluorobenzene. (Eqn. 673)



(673)

The photolysis of carbon tetrachloride in the presence of several different organosilanes results in a chain reaction. The kinetic parameters have been determined. [486] The generation of the triethylsilyl radical in the presence of ethylene gives telomerization of ethylene. Using dimanganese decacarbonyl as the initiator gives only tetraethylsilane. (Eqns. 674 and 675)

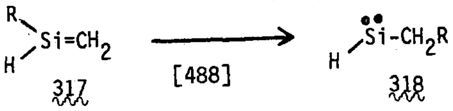


$$Et_3SiH + CH_2{=}CH_2 \xrightarrow[{[487]}]{{}^tBuOO{}^tBu} Et_3Si(CH_2CH_2)_n\text{-}H \qquad n = 1, 2, 3 \qquad (674)$$

$$\xrightarrow[{[487]}]{Mn_2(CO)_{10}} Et_4Si \qquad (675)$$

B. Silylenes

The barrier heights and transition states of silylenes have been looked at via ab initio calculations. It was calculated that for a 1,2 methyl shift (**317** → **318** R=Me) and a 1,2 hydrogen shift (**317** → **318** R=H) are too high, being some 40-55 kcal mol^{-1}, to occur at room temperature. The 1,2 silyl shift is also too high at 32.0 kcal mol^{-1}. (Eqn. 676)



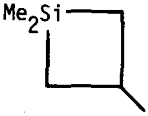
(676)

R = H, Me, H_3Si

Ab initio calculations on various silylenes indicate that the first transition of the visible spectrum is due to an n(Si) → 3p(Si) transition. [489] MCSCF and MRCI studies indicate that the ^1A silylene to disilene dimerization gives ground state disilene via the least motion path as we;; as tje non-least-motion path. Ground state methylene and excited state silylene give ground state silaethene via the least-motion pathway. [490]

Rate constants have been determined for the reaction of dichlorosilylene with some olefins and acetylenes. The rate-structure correlations follow an electrophilic trend. [491]

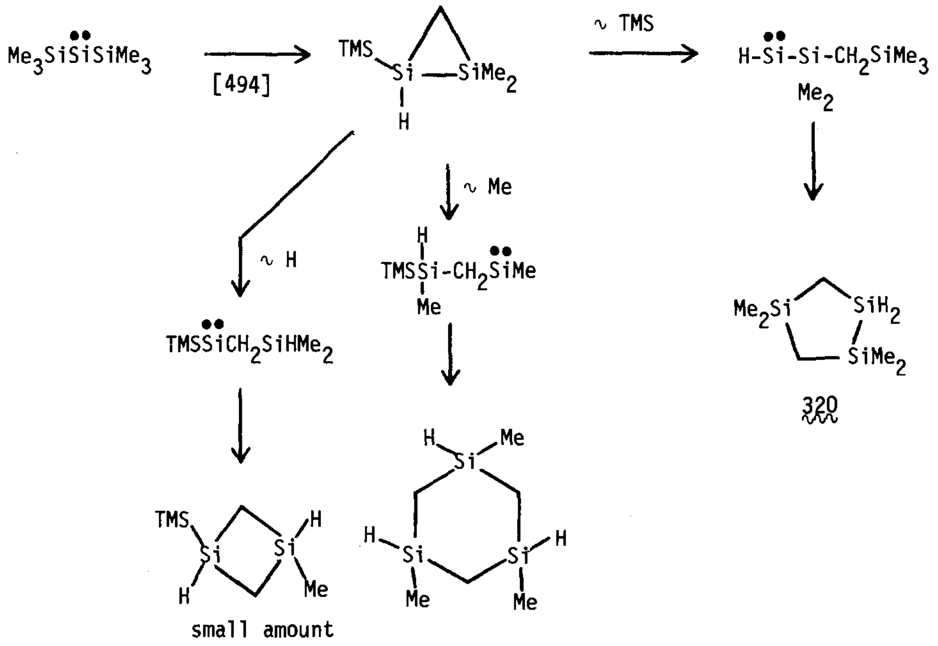
Adding xenon to the reaction mixture of the photolysis of **319** in benzene led to more extrusion of dimethylsilylene. [492]



319

The two primary decomposition pathways of ethylsilane are extrusion of H_2 to form EtSiH and of H_2 to form MeCH=SiH. The kinetics of the process was studied. [493]

A trimethylsilyl shift has been proposed as being the key in the formation of **320** from bis(trimethylsilyl)silylene. (Eqn. 677)

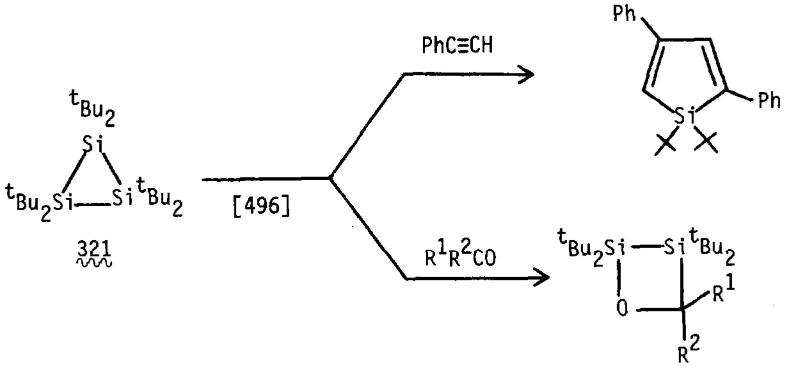


(677)

Dimethylsilylene also has been generated from dimethylsilyldiazide. (Eqn. 677a) The visible spectrum shows an absorbance at between 430 and 470 nm depending on the matrix isolation medium.

$$Me_2Si(N_3)_2 \xrightarrow[\text{matrix}\ [495]]{h\nu} Me_2Si: \underset{h\nu}{\overset{vis}{\rightleftharpoons}} MeHSi{=}CH_2 \qquad (677a)$$

Di-tert-butylsilylene also has been prepared and trapped as shown. (Eqns. 678 and 679)



321

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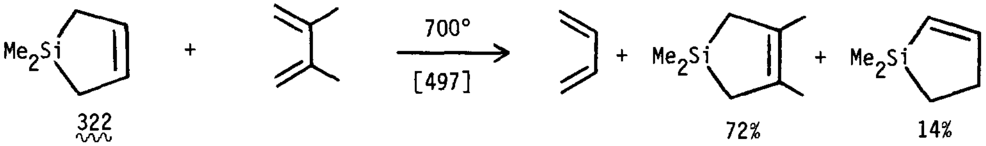
(679)

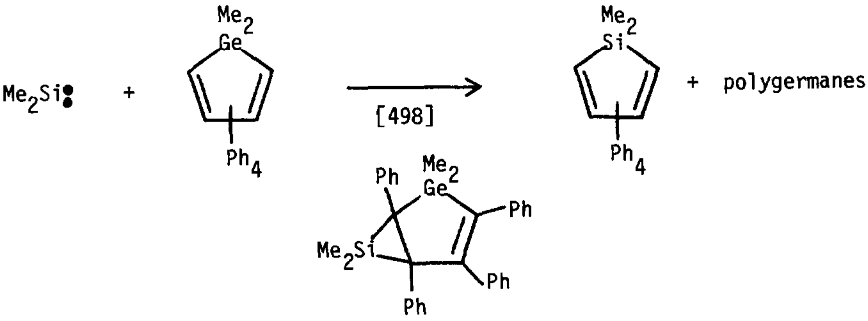
Dimethylsilylene has been shown to arise from pyrolysis of **322** as shown by trapping experiments. It was concluded that the Me_2Si: extrusion is not concerted. (Eqn. 680)



322

(68

Photolytically generated Me_2Si: exchanges with Me_2Ge: in 1-germacyclopentadiene. Intermediate **323** is proposed. (Eqn. 681)



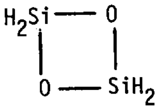
(681)

323

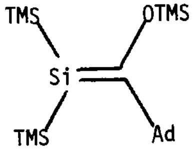
C. Silenes

An improved algorithm for the determination of an intrinsic reaction coordinate was applied to the rotation from a planar to a twisted structure for silene. The results of a rotational barrier of 37 kcal mol^{-1} agree well with experimental estimates. [499] An ab initio study of the reaction of silene with formaldehyde shows the reaction to be exothermic by approximately 30 kcal mol^{-1} with the intermediate at least 50 kcal mol^{-1} more stable than reactants or products. If, however, cyclodisiloxane **324** is taken as the product then it is 25 kcal mol^{-1} more stable than the intermediate. [550] Ab initio calculations show that the Si=C bond length of **325** is electronically elongated, with an electronically unperturbed bond length of ca. 1.70 pm. [501]

The pyrolysis of 1,1-dimethyl-1-sila-2-cyclobutene and dimethyldiallylsilane are both proposed as proceeding through **326**. [502]



324



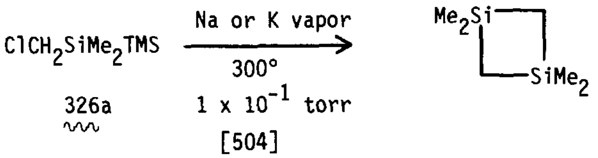
325

$Me_2Si=CH-CH=CH_2$

326

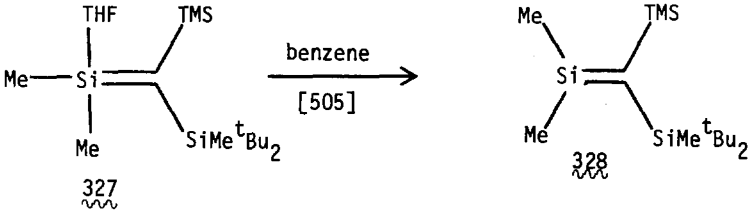
Mass spectral studies on a series of silacyclobutanes were used to determine the ΔH of the silacyclobutane to silene and ethylene reaction. [503]

The reaction of sodium or potassium vapors with **326a** produced 1,1-dimethylsilene. (Eqn. 682)



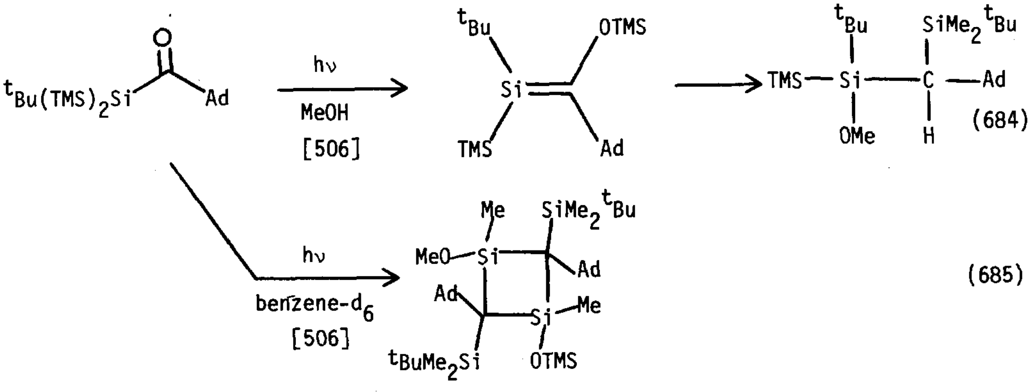
(682)

The THF complexed silene **327** when treated with benzene gives the THF free **328** whose structure was determined. The measured Si=C bond length of 1.702 pm is very close to the calculated value. (Eqn. 683)



(683)

Photolysis of **329** gives **330**, which adds methanol to give two diastereomers. (Eqn. 684) Photolysis in benzene leads to the head-to-tail dimer **331**. (Eqn. 685) A "working hypothesis" mechanism involving a silene to silylene rearrangement was put forth.

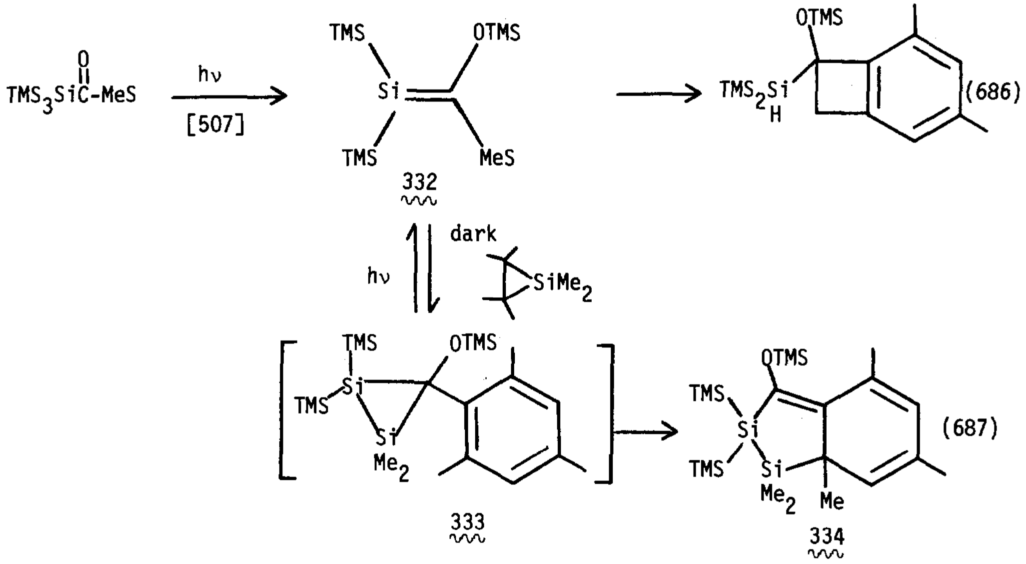


(684)

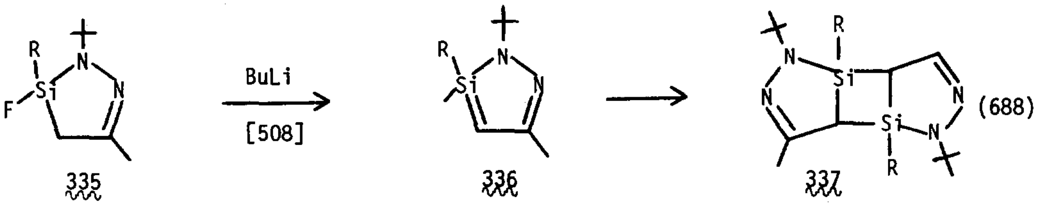
(685)

x-ray structure

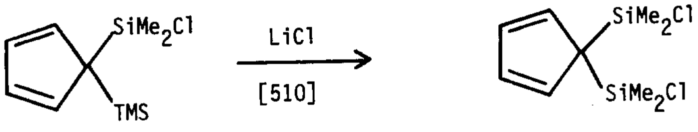
Silene **332** reacts with a silacyclopropane to give **334** via a disilacyclopropane **333**. (Eqn. 687) In the absence of substrate insertion occurs. (Eqn. 686)



Fluorosilane **335** was reacted with butyllithium to give dimer **337** via silene **336**. (Eqn. 688)



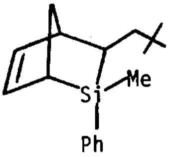
The reaction of (chlorodimethylsilyl)cyclopentadiene with tert-butyllithium or the Wittig reagent proceeds through silenoids. [5-9] In a related study it was found that lithium chloride desilylates **338**. This only occurs when the other silicon contains a chlorine substituent. (Eqn. 689)



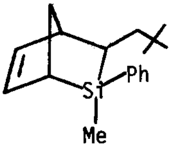
338

(689)

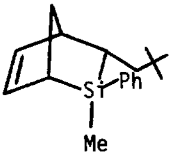
Thermal generation and trapping of **341** and **342**, from **339** and **340**, respectively, gives the same products. It is concluded that the silenes are configurationally unstable at those temperatures. [511]



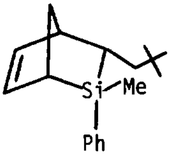
339a



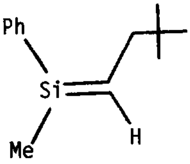
339b



340a



340b



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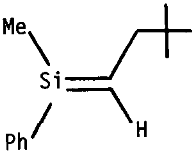
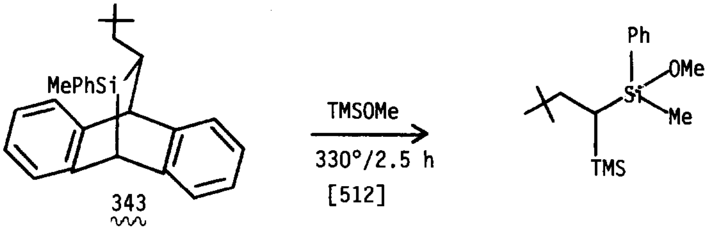


342

The addition of TMSOMe to silenes was determined to be stereospecific. In the key experiment precursor **343** generated a silene which was trapped to give a single diastereomeric product (98%), which was tentatively assigned the (R,S)(S,R) structure. (Eqn. 690) Iminomethylenephosphine **344** was added to **344a** to give **344b**. (Eqn. 691)



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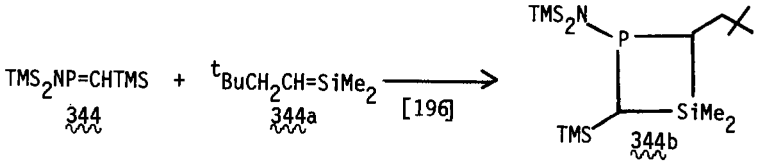


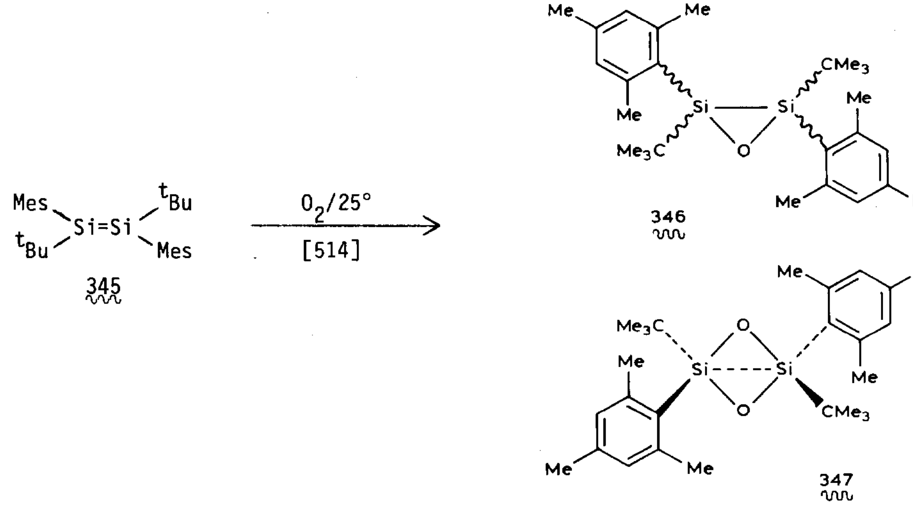
(691)

D. Disilenes

Using frontier-orbital theory and ab initio calculations it was concluded that disilene would act as an electron donor in [4+2] cycloadditions and would react with 1,3-butadiene and electron poor dienes. [513]

Treatment of **345** with molecular oxygen at 25°C gives **346**, but at -78°C gives the dioxetane **347**. (Eqns. 692 and 693) Both can be converted to **348**. (Eqns. 694 and 695) Tetramesityldisilene **349** and its tert-butyl derivative **350** react with elemental sulfur to give **351** and **352**, respectively. (Eqn. 696) An x-ray structure determination of **351** shows it to be nearly planar with a rather long 2.289 pm Si-Si bond. [515]

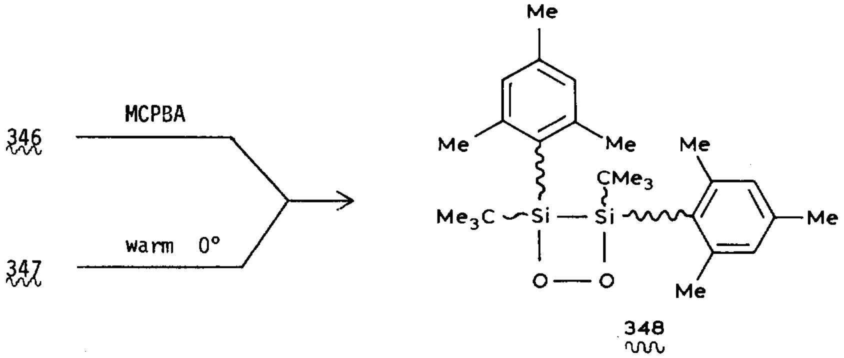
The kinetics of the cis-trans isomerization of disilenes was studied for **353** and **354**. For **353** the first order half-life at 25°C is ca. 3220 (± 200) hours and for **354** it is 42 (± 2) h. The activation energies are 31.3 (± 3.7) kcal mol^{-1} for **353** and 25.4 (± 2.2) kcal mol^{-1} for **354**. [516]



(692)

$$345 \xrightarrow{O_2/-78°} 347$$

(693)



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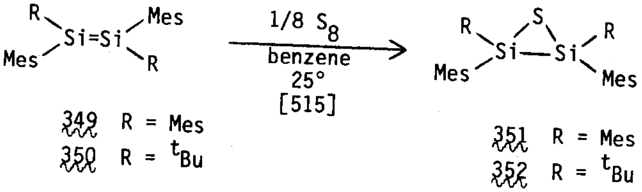

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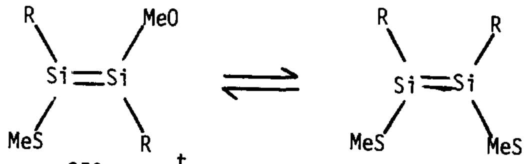
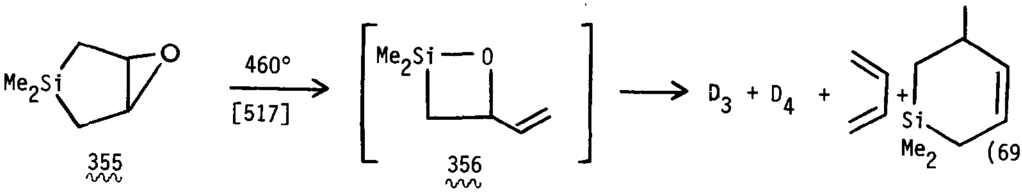


353 R = ^{t}Bu

354 R = TMS_2N

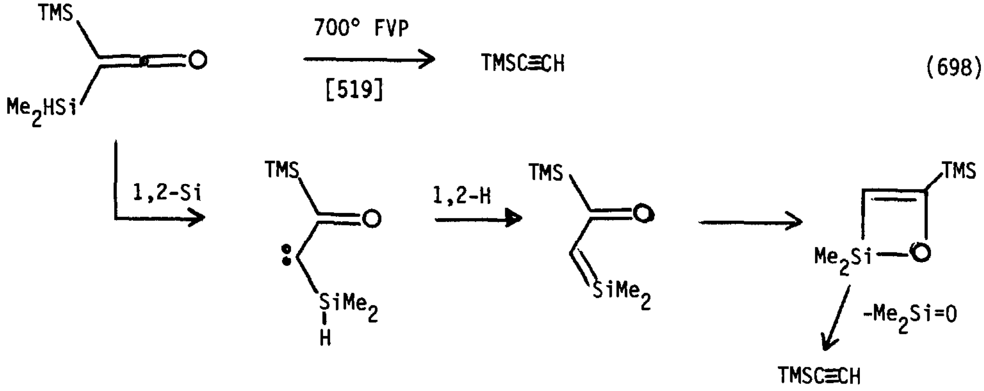
E. Silanones

Thermal decomposition of **355** produces dimethylsilanone and 1,3-butadiene. The kinetics of the reaction in terms of the production of 1,3-butadiene have been studied. The silaoxetane intermediate **356** is proposed. (Eqn. 697) Using **355** as the source of dimethylsilanone the kinetics of some gas phase reactions of dimethylsilanone have been studied. Comparisons of its reactivity are made to that of 1,1-dimethylsilane. [518]

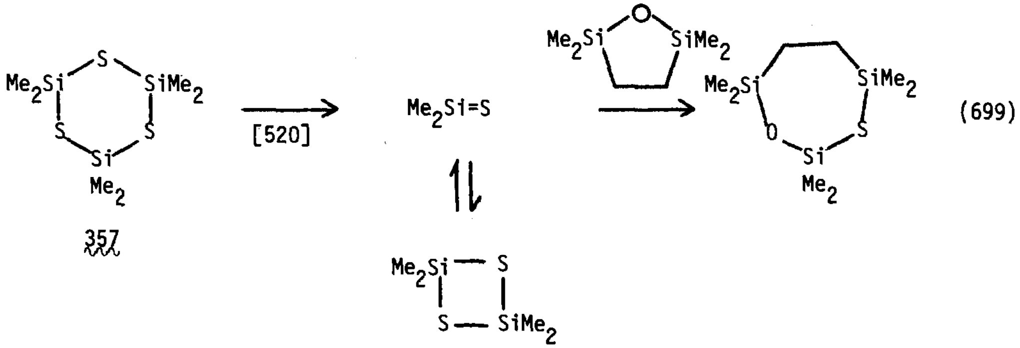


(697)

(Hydridosilyl)ketenes were shown to thermally extrude dimethylsilanone in a retro-Wolff rearrangement. (Eqn. 698) The mechanism proposed is that shown in equation 698.


(698)

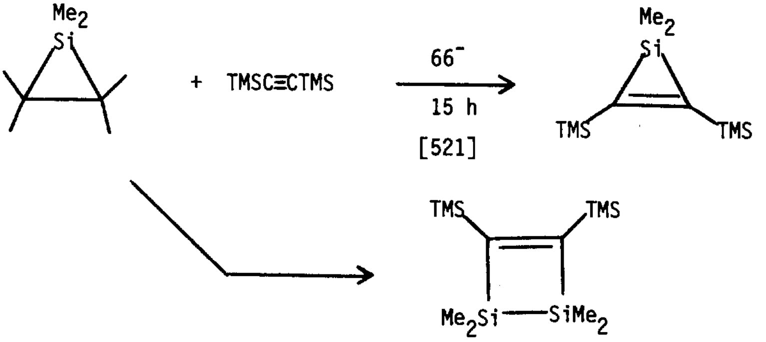
Pyrolysis of **357** gives products from dimethylsilanthione. (Eqn. 699)


357

(699)

F. Silacyclopropanes

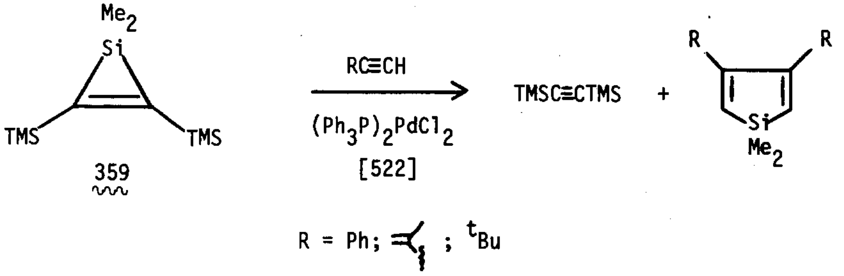
Compound **358** thermally extrudes dimethylsilylene, which can add to silylacetylenes to give silacyclopropenes. (Eqn. 700) With an excess of **358** 1,2-disilacyclobutanes are isolated. (Eqn. 701)



(700)

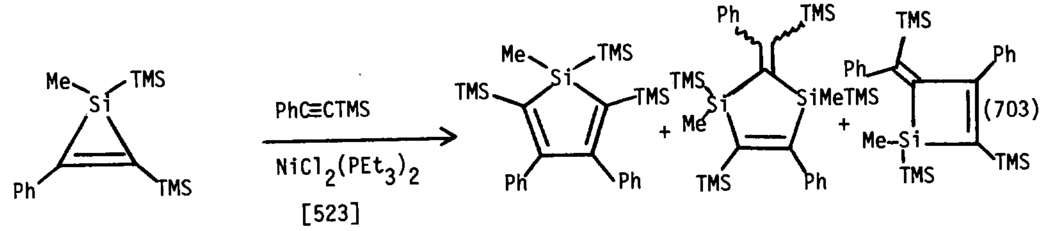
(701)

The silacyclopropene **359** reacts with acetylenes in the presence of Pd(II) to give silacyclopentadienes. (Eqn. 702) Other silacyclopropenes or their precursors have been reacted with acetylenes in the presence of Ni(II). (Eqn. 703)



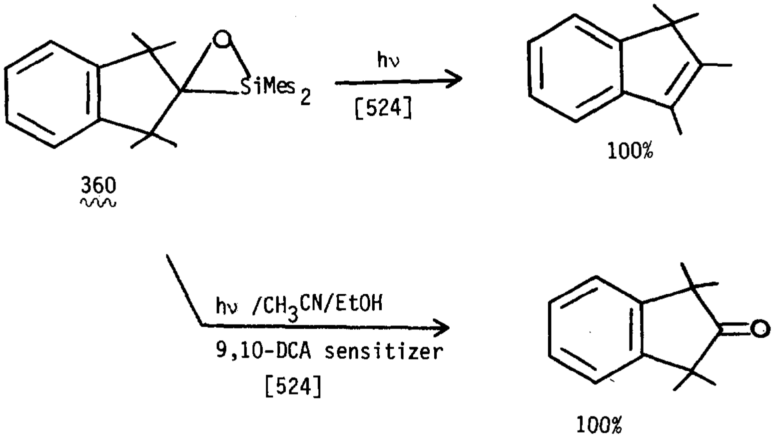
359

(702)



(703)

The photolysis or electrolysis of silaoxirane **360** extrudes dimesitylsilanone and gives indenes. (Eqn. 704) Photolysis in the presence of 9,10-dicycanoanthracene, however, gives indanone **361**. (Eqn. 705)



360

(704)

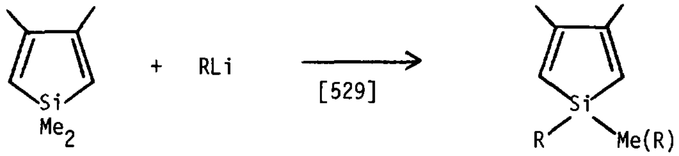
(705)

G. Other

Model SCF calculations have been made on the chlorosilane anion radical. [525] The esr spectra for anion radicals of alkylcyclotetra- and alkylcyclopentasilanes have been measured. [526] The anion radicals of three different disilenes **362** have been prepared and studied by esr. [527]

Ab initio SCF calculations have been carried out on the $CSiF_2$ structures. [528]

Silole **363** reacts with lithium reagents to give new siloles or, in the case of tert-butyllithium, the isomer **364**. (Eqn. 706)

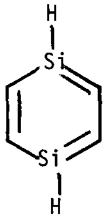


363 364 (706)

The generation of Me_3Si^+ from the reaction of Me_3SiOR and $^+Si^3H_3$ was studied. [530]

Ab initio calculations on disilabenzenes show the 1,4 isomer **365** to be the least stable and the 1,3 isomer **366** to be the most delocalized. [351]

Silabenzenes and silafulvenes account for many of the products of the decomposition of compounds **367** - **371**. [532]



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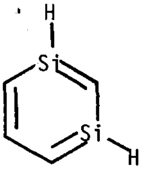

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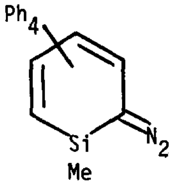

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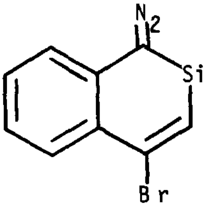

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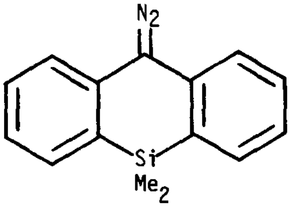

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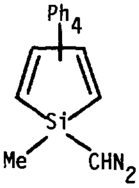

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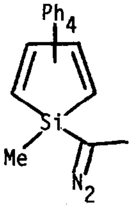

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